School of Molecular and Life Sciences

## Improving the Robustness of Ionic Liquid-based Electrochemical Gas Sensors

Simon Karl Heinrich Doblinger

0000-0002-6245-6121

This thesis is presented for the Degree of

**Doctor of Philosophy** 

of

**Curtin University** 

July 2021

## Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Date:

## Abstract

The reliable sensing of hazardous gases is still a major research focus in industry as well as academia since we are surrounded by gases in everyday life and lots of applications involve the release of a range of different gases to the environment. Commercially available electrochemical gas sensors have been developed and typically perform well in ambient conditions. However, in extreme conditions, *i.e.* at high or low temperatures (i.e. well below -20 °C and higher than 50 °C) and pressures (well below atmospheric conditions), aqueous-based electrolytes can evaporate or freeze, which can significantly shorten the lifetime of the sensing device (which can be, depending on the analyte, between 1 year to 10 years). Replacing the electrolyte with room temperature ionic liquids (RTILs), that have lower melting points and significantly lower vapor pressures than water, can result in more robust gas sensing devices. The electrochemical responses of various gaseous analytes in ionic liquids under ideal laboratory conditions have been studied previously by other researchers. However, the influence of external factors such as temperature and pressure changes as well as fluctuations in the humidity are much less investigated. This important behavior should be understood before applying room temperature ionic liquids as new electrolyte materials in electrochemical gas sensing devices.

This thesis provides a first step towards investigating the influence of varying humidity levels on the electrochemical sensing of oxygen and ammonia gas. In the first chapter, the choice of the RTIL cation and anion combination is shown to be crucial for oxygen sensing in humid environments, because absorbed water from the humid gas stream changes the electrochemical redox mechanism *via* follow-up reactions with the electrogenerated superoxide. It is shown that the ionic liquid structuring at the electrode/electrolyte interface can prevent the reaction of superoxide with water, however, the interfacial RTIL structure becomes weaker at higher humidity levels. A drastic dependence on the RTIL cation is observed. For ammonia oxidation, the presence of water does not affect the electrochemical reaction mechanism, but an obvious change in the transport properties and a narrowing of the electrochemical window is observed. Even so-called "hydrophobic" RTILs, typically with wide electrochemical windows, have significantly narrower windows in the presence of humidity, which partially superimposes with the ammonia oxidation currents at high

humidities. The addition of non-ionic polymers to the ionic liquid electrolyte to form so-called "gel-polymer electrolytes" showed some promising results in preventing the reaction between water and the superoxide radical for hydrophilic ionic liquids, but no obvious improvements were obtained for already hydrophobic RTILs.

Other important criteria for electrochemical gas sensors are high selectivity towards certain gases and good sensitivity. In the second chapter, the possibility to chemically functionalize ionic liquid ions with certain chemical moieties to either increase or decrease the interaction with certain gaseous analytes is attempted. RTILs based on the imidazolium cation were functionalized with polar groups and gas solubility values for hydrogen, oxygen and sulfur dioxide were measured. Polar functionalities in the RTIL did not result in a chemical binding of sulfur dioxide, instead all gases were reversibly physically dissolved, and the gas solubility appeared to be mainly dependent on the molar volume of the RTIL. The sensitivity of an electrochemical sensor can depend on the type of electrode material and its geometry. In this thesis, better electrochemical responses were obtained for the detection of low parts-per-million concentrations of sulfur dioxide via cyclic voltammetry on platinum compared to gold electrodes. A comparison between microarray and macro-disk electrodes resulted in good sensitivities for electrodes with both geometries, however, continuous monitoring of sulfur dioxide via long-term chronoamperometry resulted in the formation of sulfur deposits in the microarrays, hence passivating the electrode surface. A similar result was obtained for custom made micro-pillar interdigitated electrodes. In the latter study, the relatively high viscosity of RTILs (and significantly higher response times compared to aqueous-based electrolytes) was attempted to be overcome by employing a custom-made micro-pillar electrode design that uses capillary force to obtain a uniform thin layer of ionic liquid (~30 µm) above the electrode. This gave a fast response time for sulfur dioxide detection and appears to be promising for future investigations where fast response times to toxic gas leaks are required.

In the final chapter, poly(ionic liquid) (PIL) membranes were applied as a non-flowing electrolyte on thin-film electrodes. Preliminary studies revealed promising electrochemical responses for oxygen, ammonia and sulfur dioxide gas without any change in the cyclic voltammetry shape and no reduced electrochemical windows in comparison with pure ionic liquids. The increased viscosity of the PIL membranes

results in slower diffusion of the analyte and hence lower current responses. However, cleaner blank responses in the absence of an analyte resulted in lower limits of detection, which makes these electrolytes promising materials for the application in commercial gas sensors for the trace detection of toxic gases.

In summary, the results from this thesis provide fundamental knowledge that suggests that RTILs could indeed replace conventional electrolyte/solvent systems for electrochemical gas sensing. However, humidity in real world environments can significantly impact the electrochemical response and therefore several correction parameters would have to be introduced within the sensor device to account for this.

# Acknowledgements

First and foremost, I would like to express my gratitude to both my supervisors, Assoc. Prof. Debbie Silvester-Dean and Prof. Andrew Lowe for their guidance during my PhD. I would like to thank Assoc. Prof. Debbie Silvester-Dean for taking me on as an international PhD student to work on her Future Fellowship project and Curtin University for the Curtin International Postgraduate Research Scholarship. I would also like to thank Prof. Andrew Lowe for his expertise and help in polymer chemistry. Huge thanks are due to Prof. Margarida Costa Gomes and Prof. Agílio Pádua and their research group in Lyon for hosting me in their lab and teaching me lots of new things. I want to acknowledge Prof. David Mecerreyes and Dr. Lilian Tomé for the collaboration on the poly(ionic liquids) and Dr. Eva Alvarez de Eulate and her research group in Adelaide for the collaboration on custom-made electrodes.

I wish to acknowledge Ching, Chappy and the technicians for their expertise and advice in terms of the gas mixing setup and also for solving technical, software and computer problems during the last three years. I would like to thank Dr. Tom Becker for teaching me how to use his AFM instruments.

I would like to thank current and past students in the Electrochemistry and Sensors group at Curtin. I'm also grateful for the support of Juni, Ben, Johannes, Terence, Bren and Peter who all helped me out when I made my first steps as novice in electrochemistry. Some of the work presented in here would have not been possible without the help of Zoe and Taylor, who both had to deal with me during their research stays. Also, a huge thanks to Cathy who provided an office basketball hoop to improve my skills while procrastinating.

I would like to take the opportunity and thank Anna, Chiara, Laura, Shifaza, Federica, Matt and Pete for the regular coffee breaks and who all made it easy for me to adjust at Curtin University after moving halfway around the world to Australia. Huge thanks are also due for Karina, Manu, Andrew, Matt and lots of other friends who made it an awesome time in Perth away from the laboratory.

I feel very fortunate to have a family who supported me throughout my undergraduate studies, the tough year before moving to Australia and then during the PhD.

I would also like to thank everyone who I missed mentioning here who helped and supported me the last years in Perth.

# Copyright Statement

I have obtained permission from the copyright owners to use any third-party copyright material reproduced in the thesis (e.g. questionnaires, artwork, unpublished letters), or to use any of my own published work (e.g. journal articles) in which the copyright is held by another party (e.g. publisher, co-author).

Signature:

Date:

# Table of Contents

Abs	stract	•••••		11
Ack	nowl	edg	gements	<i>v</i>
Сор	oyrigh	t St	tatement	VII
Tab	ole of	Cor	ntents	VIII
1.	Bacl	kgr	round	1
1	.1.	Ga	as Sensors	1
	1.1.1		Different Methods	2
	1.1.2	•	Electrochemical Gas Sensors	3
	1.1.3	•	Challenges of Commercial Gas Sensors	6
1	2.	lor	nic Liquid-based Electrolytes	7
	1.2.1	•	Room Temperature Ionic Liquids	9
	1.	2.1.	.1. Classification	11
	1.	2.1.	.2. Physicochemical Properties	11
		1.2	2.1.2.1. Viscosity	12
		1.2	2.1.2.2. Hygroscopy	13
		1.2	2.1.2.3. Conductivity	14
		1.2	2.1.2.4. Electrochemical Window	15
		1.2	2.1.2.5. Thermal and Chemical Stability	16
		1.2	2.1.2.6. Tunability	17
		1.2	2.1.2.7. Gas Solubility	18
	1.	2.1.	.3. Structuring of Ionic Liquids (Bulk vs. Surface)	19
	1.	2.1.	.4. Electrochemistry	20
	1.2.2	•	Gel-Polymer Electrolytes	21
	1.2.3	•	Poly(Ionic Liquids)	22
1	.3.	Ele	ectrochemical Oxidation-Reduction Reactions of Gases	23
	1.3.1	•	Oxygen	23
	1.3.2	•	Ammonia	24
	1.3.3	•	Sulfur Dioxide	26
1	.4.	Ch	naracterization Methods	28
	1.4.1	•	Introduction to Electrochemistry	
	1.	4.1.	.1. Electrical Double Layer	28

	1.2.    Faradaic and Non-Faradaic Processes    30
1.4.	1.3. Mass Transport
1.4.	1.4. Electrochemical Setup
1.4.	1.5. Electrochemical Techniques
1	.4.1.5.1. Cyclic Voltammetry
1	.4.1.5.2. Chronoamperometry
1.4.2.	Atomic Force Microscopy
1.4.3.	Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy
1.5. <i>A</i>	ims of Thesis40
1.6. F	eferences42
2. Exper	imental Chapter59
2.1. 0	hemicals and Materials59
2.2. E	lectrochemical Experiments59
2.3.	as-mixing Setup60
2.4.	as Solubility Measurements61
2.5. F	eferences64
3. The E	ffect of Humidity on RTIL-based Gas Sensors65
3.1. E	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under
3.1. E Humidifi	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under ed Conditions
<b>3.1.</b> E Humidifi 3.1.1.	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under ed Conditions
<b>3.1.</b> E Humidifi 3.1.1. 3.1.2.	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under ed Conditions
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> </ul>	iffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> </ul>	iffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> </ul>	Introduction       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> </ul>	Introduction       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> </ul>	Introduction       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       76
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.</li> </ul>	iffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75         3.1.       Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.</li> <li>3.1.</li> </ul>	iffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75         3.1.       Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         .1.3.1.1.       Anion Effect       77
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.3.</li> <li>3.1.3</li> <li>3.1.33.</li> <li>3.1.33.<th>ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75         3.1.       Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         3.1.1.       Anion Effect       77         1.3.1.2.       Effect of Cation with Hydrophobic Anion, [NTf2]<sup>-</sup>       79</th></li></ul>	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75         3.1.       Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         3.1.1.       Anion Effect       77         1.3.1.2.       Effect of Cation with Hydrophobic Anion, [NTf2] <sup>-</sup> 79
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.3.</li> <li>3.1.3</li> <li>3.1.4</li> <li>3.1.5</li> <li>3.1.5</li></ul>	Affect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1. Chemical Reagents       71         2.2. Electrochemical Experiments       72         2.3. AFM Measurements       75         2.4. Computational Estimation of Ion Dimensions and Water-affinity       75         3.1. Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         3.1.1. Anion Effect       77         1.3.1.2. Effect of Cation with Hydrophobic Anion, [NTf <sub>2</sub> ] <sup>-</sup> 79         1.3.1.3. Effect of Cation with a Highly Hydrophobic Anion, [FAP] <sup>-</sup> 82
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.</li> <li>3.1.3.</li> <li>3.1.4.</li> </ul>	ffect of Ionic Liquid Structure on the Oxygen Reduction Reaction under         ed Conditions       66         Introduction       68         Experimental       71         2.1. Chemical Reagents       71         2.2. Electrochemical Experiments       72         2.3. AFM Measurements       75         2.4. Computational Estimation of Ion Dimensions and Water-affinity       75         3.1. Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         3.1.1. Anion Effect       77         1.3.1.2. Effect of Cation with Hydrophobic Anion, [NTf <sub>2</sub> ] <sup>-</sup> 79         1.3.1.3. Effect of Cation with a Highly Hydrophobic Anion, [FAP] <sup>-</sup> 82         3.2. Physical Characteristics of the Ionic Liquid Electrical Double Layer on a Pt-TFE.83
<ul> <li><b>3.1.</b> E</li> <li>Humidifi</li> <li>3.1.1.</li> <li>3.1.2.</li> <li>3.1.</li> </ul>	Introduction       66         Introduction       68         Experimental       71         2.1.       Chemical Reagents       71         2.2.       Electrochemical Experiments       72         2.3.       AFM Measurements       75         2.4.       Computational Estimation of Ion Dimensions and Water-affinity       75         3.1.       Cyclic Voltammetry of RTILs in Dry vs. Wet Environments       76         3.1.1.       Anion Effect       77         1.3.1.2.       Effect of Cation with Hydrophobic Anion, [NTf2] <sup>*</sup> 79         1.3.1.3.       Effect of Cation with a Highly Hydrophobic Anion, [FAP] <sup>*</sup> 82         3.2.       Physical Characteristics of the Ionic Liquid Electrical Double Layer on a Pt-TFE.83       1.3.2.1.

	3.1.4.	Conclusions	88
	3.1.5.	References	90
	3.1.6.	Supporting Information	95
3.	2. E <sup>.</sup>	ffect of Humidity and Impurities on the Electrochemical Window o	of Ionic
Lic	quids aı	nd Its Implications for Electroanalysis	104
	3.2.1.	Introduction	106
	3.2.2.	Experimental	108
	3.2.2	.1. Chemical Reagents	108
	3.2.2	.2. Electrochemical Experiments	109
	3.2.3.	Results and Discussion	110
	3.2.3	1. Effect of Humidity on the Electrochemical Window of RTILs	110
	3.2.3	2.2. Electrochemistry of Dissolved Species at Different RH% in [C4mpyri	r][NTf <sub>2</sub> ] 119
	3	2.3.2.1. Decamethylferrocene (DmFc)	119
	3	2.3.2.2. Ammonia Gas	
	3.2.4.	Conclusions	124
	3.2.5.	References	125
	3.2.6.	Supporting Information	131
3.3	3. E <sup>.</sup>	ffect of Humidity on Gel-Polymer Electrolytes	136
	3.3.1.	Introduction	136
	3.3.2.	Experimental	137
	3.3.2	.1. Chemical Reagents	137
	3.3.2	.2. Preparation of Gel-Polymer Electrolytes	
	3.3.2	.3. Electrochemical Experiments	
	3.3.2 3.3.3.	.3. Electrochemical Experiments Results and Discussion	
	3.3.2 3.3.3. 3.3.3	3.       Electrochemical Experiments         Results and Discussion        1.       Influence of Molecular Weight of Polymer	
	3.3.2 3.3.3. 3.3.3 3.3.3	.3.       Electrochemical Experiments         Results and Discussion         .1.       Influence of Molecular Weight of Polymer         .2.       Influence of Polymer	
	3.3.2 3.3.3. 3.3.3 3.3.3 3.3.4.	<ul> <li>Electrochemical Experiments</li></ul>	137 138 138 139 141 143
	3.3.2 3.3.3. 3.3.3 3.3.3 3.3.4. 3.3.5.	<ul> <li>Electrochemical Experiments</li></ul>	137 138 138 139 141 143 145
4.	3.3.2 3.3.3. 3.3.3 3.3.4 3.3.5. <i>Impro</i>	Electrochemical Experiments     Results and Discussion     Influence of Molecular Weight of Polymer     Influence of Polymer     Conclusions     References     Ving the Selectivity and Sensitivity of RTIL-based Gas Sensors	
<i>4.</i>	3.3.2 3.3.3. 3.3.3 3.3.4 3.3.5. <i>Impro</i> 1. F		
<i>4.</i> 4.:	3.3.2 3.3.3. 3.3.3 3.3.4. 3.3.5. <i>Impro</i> 1. Fi	<ul> <li>Electrochemical Experiments</li></ul>	
<i>4.</i> 4.: Ga	3.3.2 3.3.3. 3.3.3 3.3.4. 3.3.5. <i>Impro</i> 1. Fr as Sense 4.1.1.	<ul> <li>Electrochemical Experiments</li></ul>	
<i>4.</i> 4.: Ga	3.3.2 3.3.3 3.3.3 3.3.4 3.3.5. <i>Impro</i> 1. Fr as Sense 4.1.1. 4.1.2.	<ul> <li>Electrochemical Experiments</li></ul>	
<i>4.</i> 4.: Ga	3.3.2 3.3.3 3.3.3 3.3.4 3.3.5. <i>Impro</i> 1. For as Senso 4.1.1. 4.1.2. 4.1.2	<ul> <li>2.3. Electrochemical Experiments</li></ul>	
<i>4.</i> 4.∶ Ga	3.3.2 3.3.3. 3.3.3 3.3.4. 3.3.5. <i>Impro</i> 1. For as Senso 4.1.1. 4.1.2. 4.1.2. 4.1.2	<ul> <li>Electrochemical Experiments</li></ul>	

4.1.3	3. R	esults and Discussion	154
4	.1.3.1	Density and Viscosity	154
4	.1.3.2	Gas Solubilities	157
4.1.4	4. C	onclusions	
4.1.5	5. R	eferences	164
4.1.6	6. S	upporting Information	
4.2.	Det	ection of Sulfur Dioxide at Low Parts-per-million Concentration	ns using Low-
cost Pl	lanar	Electrodes with Ionic Liquid Electrolytes	186
4.2.2	1. Ir	ntroduction	
4.2.2	2. E	xperimental	
4	.2.2.1	Chemical Reagents	
4	.2.2.2	Electrochemical Experiments	
4	.2.2.3	Electrode Imaging	
4.2.3	3. R	esults and Discussion	
4	.2.3.1	Reduction of $SO_2$ on Macro Thin-film Electrodes	
4	.2.3.2	Reduction of $SO_2$ on Platinum Microarray Thin-film Electrodes	
4	.2.3.3	Sulfur Deposition After SO <sub>2</sub> Reduction Experiments	
4	.2.3.4	Detection of Low Parts-per-million Concentrations of SO <sub>2</sub>	201
4.2.4	4. C	onclusions	204
4.2.5	5. R	eferences	206
4.2.6	6. S	upporting Information	210
4.3.	Inte	rdigitated Array Microelectrodes for Gas Sensing	215
4.3.2	1. Ir	ntroduction	215
4.3.2	2. E	xperimental	216
4	.3.2.1	Chemical Reagents	216
4	.3.2.2	Electrode Fabrication and Imaging	217
4	.3.2.3	Electrochemical Experiments	218
4	.3.2.4	Electrode Imaging	219
4.3.3	3. R	esults and Discussion	219
4.3.4	4. C	onclusions	223
4.3.5	5. R	eferences	224
5. Poly	y(Ion	ic Liquids) For Electrochemical Gas Sensing	225
5.1.	Intr	oduction	226
5.2.	Exp	erimental	228
5.2	1. C	hemical Reagents	
5.2.2	2. P	IL/IL Membrane Preparation	

5.2.3	. Electrochemical Experiments	
5.3.	Results and Discussion	229
5.3.1	. Electrochemical Window of Membranes	
5.3.2	Oxygen	
5.3.3	. Sulfur Dioxide	
5.3.4	Ammonia	234
5.3.5	. Humidified Oxygen Gas	
5.4.	Conclusions	237
5.5.	References	220
		238
5.6.	Supporting Information	238
5.6. 6. Cond	Supporting Information	238 242 243
5.6. 6. Cond 6.1.	Supporting Information	238 242 243 243
5.6. 6. Cond 6.1. 6.2.	Supporting Information Clusions and Future Outlook Conclusions Future Outlook	238 242 243 243 243

# 1. Background

### 1.1. Gas Sensors

The human population all over the world is surrounded by gases, toxic ones like ammonia (NH<sub>3</sub>) or nitrogen oxides (NO<sub>x</sub>) but also vital ones such as oxygen (O<sub>2</sub>). The continuous and reliable monitoring of these gas concentrations is crucial to avoid harmful effects on the environment and human health. Nitrogen dioxide (NO<sub>2</sub>) can severely influence human health at concentrations as low as 0.3 parts-per-million (ppm).<sup>1</sup> Sulfur emissions are known contributors to air pollution and therefore contribute to climate change.<sup>2</sup> Air is composed of around 20.9 vol.% of oxygen gas, the ideal content required for the respiratory processes of most living organisms. However, at enriched or depleted concentrations of oxygen, the atmosphere can be hazardous (Table 1.1).

Atmospheric O <sub>2</sub> concentration / vol.%	Effects
25+	Spontaneous combustion of <i>e.g.</i> clothing
23.5+	Serious fire danger
20.9	Oxygen concentration of air
19.5	Minimum 'Safe Level'
16	Increased breathing and pulse rate, loss of coordination, impaired thinking and attention
14	Fatigue, faulty coordination, impaired judgement
12	Nausea, vomiting, disturbed respiration with possible permanent heart damage
< 10	Nausea, vomiting, inability to move and loss of consciousness followed by death
< 6	Convulsive movements, respiration stops and later heart action ceases, death in minutes
< 4	Unconsciousness after one or two breaths, death

Table 1.1. Oxygen concentrations according to the occupational health exposure standards.<sup>3</sup>

Gas sensor research is therefore a highly relevant topic in academia as well as in industry. Much research still focuses on improving certain properties such as obtaining lower detection limits and a higher sensor robustness. Other important criteria are long-term stability, low power consumption and miniaturization. The following two sections summarize general detection methods used in commercially available gas sensors, followed by a more detailed discussion of electrochemical methods and challenges of the different devices based on electrochemistry.

#### 1.1.1. Different Methods

Commercially available gas sensors are based on different measurement techniques, all having their advantages and disadvantages. A short summary of some of the methods will be discussed here, but further, more detailed information can be found in a detailed review by Liu *et al.*<sup>4</sup>

Only a few commercial gas sensors are based on acoustic methods, where the speed of sound or attenuation, *i.e.* energy loss of an acoustic wave travelling through a media<sup>5</sup>, is measured. Generally, the travel time of sound over a certain distance is determined and compared to a reference gas. Small differences in the travel time can then be used to determine the gas concentration.<sup>6</sup> Alternatively, the attenuation can be determined for the detection of specific gases such as oxygen<sup>7</sup> or methane, carbon dioxide or ethylene.<sup>8</sup> A major drawback of this method is the high power consumption as well as variations of environmental impacts, such as change of humidity, on the setup.

Due to its high costs and challenges for miniaturization, a method with less attention for commercial applications is gas chromatography (GC). In academia settings, GC is a well-established and widely used characterization technique due to its high sensitivity and selectivity as well as excellent separation performance.<sup>9</sup> The method is based on using a carrier gas (mobile phase) to transport the analyte through a column (stationary phase) where specific chemical and physical interactions of the sample molecules with the column results in a separation. The outlet of the column is connected to a detector, where the identity and concentration of analyte species are determined.<sup>10</sup>

More common sensing devices are based on calorimetric methods, *i.e.* a technique based on changes in the resistance of ceramics inside the sensor device in the presence of target gases. This allows the determination of combustion enthalpies or thermal conductivities of gases. The superior detection range and the lower limit of detection (LOD) values that can be achieved (as low as parts-per-thousand, ppt), makes this method suitable for industrial use. In catalytic conductivity sensors, the analyte gas is combusted at high temperatures on a ceramic that is modified with a catalyst.<sup>11</sup> The

heat produced (specific to the analyte gas and related to the specific combustion enthalpy), causes a change in the resistance of a reference coil, which is used to determine the chemical species and its concentration. In thermal conductivity sensors, the thermal conductivity of gases is used to identify them.<sup>12</sup> Here, the reference coil in a gas chamber is heated to a certain temperature. After introducing the target gas, the resistance of the coil changes due to the thermal conductivity of the surrounding gas. The drawback is that both methods exhibit high power consumption and the possibility of exploding.

Another commonly used technique in commercial sensors is based on optical methods.<sup>13-14</sup> This is due to significantly higher sensor lifetimes in combination with good selectivity and sensitivity and fast response times. There are several different techniques, but all of them are based on absorption spectrometry where the Beer-Lambert law<sup>15</sup> gives a direct relationship between analyte concentration and absorbance of photons at a specific wavelength. In the sensor, infrared (IR)-sources emit radiation into a gas chamber filled with the analyte. After the specific absorption of radiation by the target gas, the absorbed wavelength is determined by the inbuilt IR detector. A huge advantage of this technique is the possibility of miniaturization which is difficult to achieve for the previously discussed methods.

Most commercially available sensors are, however, based on various electrochemical measurement techniques, which will be discussed in the following section.

#### **1.1.2. Electrochemical Gas Sensors**

Electrochemical gas sensors are generally divided in three types: *potentiometric*, *conductometric* and *amperometric*.

In conductometric sensors, the change of the conductivity of the electrode in the presence of the target analyte is measured. Metal oxide semiconductors such as TiO<sub>2</sub>, SnO<sub>2</sub> or ZnO<sub>2</sub> that can electrochemically react with the target analyte are usually applied.<sup>16</sup> Adsorption or redox reactions of the analyte with the semiconductor surface results in an electronic change of the surface, causing a change in the resistivity of the material. This sensing technique is a highly sensitive and low cost method, however, the most promising and highly sensitive SnO<sub>2</sub>-based materials require high temperatures during sensing, which is still a huge drawback.<sup>16</sup>

In potentiometry, a potential change between a reference and a working electrode that are in contact with an electrolyte/solvent system, is used to identify the target analyte.<sup>17</sup> The general principle follows the Nernstian electrochemical cell (see equation 1.1).<sup>18-19</sup> In the case of two compartments separated by a frit with different oxygen partial pressures ( $p''_{0_2}$  and  $p'_{0_2}$ ), the open circuit potential (OCP) between the two electrodes is given by the Nernst equation<sup>18</sup>:

$$OCP = C + \frac{RT}{4F} \ln \left(\frac{p_{0_2}'}{p_{0_2}'}\right)$$
 1.1

where *C* is a constant, *R* is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), *T* the respective temperature and *F* the Faraday constant (96485 C mol<sup>-1</sup>). The main advantage of this technique is the wide concentration range of the analyte that can be detected; however, the whole setup must be in thermal and chemical equilibrium which results in prolonged response times.



Figure 1.1. Commercially available amperometric gas sensor design.

In amperometry, the current produced by applying a constant (or varying) potential, is related to the concentration of the analyte. The first amperometric gas sensor was the Clark sensor for continuous oxygen monitoring in blood, established by Leland Clark in 1953.<sup>20</sup> Generally, an amperometric gas sensor (see Figure 1.1) is composed of three electrodes immersed in an electrolyte/solvent. Additionally, the device is covered with a gas permeable membrane to allow the gas to diffuse into the electrolyte/solvent and prevent the evaporation of the liquid phase. The biasing of the working electrode causes an electron transfer reaction that oxidizes or reduces the target gas; the resulting current gives an indication of the analyte concentration. The applied potential at which the reaction is initiated can be used to identify the chemical species. Commercially

available gas sensors from companies such as Delphian (for hydrogen sulfide, carbon monoxide or sulfur dioxide), SGX Sensortech (for various gases, such as ammonia, carbon monoxide, oxygen) and MSA Safety (for gases such as oxygen, sulfur dioxide, nitrogen dioxide or carbon monoxide) are still based on the Clark-type and are used with aqueous-based electrolytes.<sup>21</sup> Commercially available hydrogen sulfide sensors for example have a similar design as the Clark-type oxygen sensor with an aqueous sulfuric acid electrolyte. This sensing device consumes water while detecting the gas electrochemically, however, the reaction at the counter electrode regenerates water by reducing oxygen which means that it is a so called non-consuming electrochemical sensing device. This device applicability is limited by the presence of oxygen. At high temperatures for an extended period of time, water can evaporate from any aqueousbased sensor causing a non-recoverable damage of the device.<sup>22</sup> Hence, the reactions at the working electrode as well as the counter electrode and the electrolyte are crucial for an electrochemical sensing device. Therefore, research in replacing aqueous-based electrolytes in gas sensing devices with more robust alternatives (such as non-volatile electrolytes that are not degrading and show good electrochemical responses) is of interest.

In 1999, Thomas Welton highlighted the use of room temperature ionic liquids as solvents for synthesis and catalysis.<sup>23</sup> Since then, several researchers started to replace conventional electrolyte/solvent systems with ionic liquid electrolytes in amperometric gas sensing devices.<sup>24-26</sup> Some characteristics of ionic liquids, such as low volatility, tunability of the cation and anion structures, polarity and viscosity made researchers propose to replace the gas permeable membrane and improve the robustness of the sensors, *i.e.* applying gas sensor devices at extremely high or low temperatures where aqueous electrolytes cannot be used. The high costs of ionic liquids can be overcome by changing the gas sensor design, where volumes of less than 10  $\mu$ L are required (see Figure 1.2). The hygroscopicity of ionic liquids influences the absorption of water or how to calibrate for this has to be performed; part of this will be covered in this thesis.



Figure 1.2. Sketch of the thin-film electrode (TFE) and the gas sensing setup used in previous research.<sup>27-29</sup>

#### 1.1.3. Challenges of Commercial Gas Sensors

The last two sections introduced various different gas sensing techniques, all of them with their advantages and drawbacks summarized in Table 1.2. As can be seen in the table, apart from acoustic sensing, all methods show good selectivity and sensitivity, but only electrochemical methods make it possible to produce miniaturized sensor devices at low cost and with long lifetimes. Amperometric sensors conform to most of the requirements for commercial devices. The only drawback is their robustness, *i.e.* currently available sensors require a gas permeable membrane to reduce the evaporation of the aqueous electrolyte, and even then, it cannot be prevented completely. The temperature at which these sensors can be operated is usually limited to -40 to +50 °C for an extended period of time.<sup>22</sup> Additionally, the relatively slow diffusion of the target gas through the membrane also increases the response time of the device. At temperatures well below 273 K, conventional aqueous electrolytes tend to solidify, making them not applicable for use in these types of sensors. Room temperature ionic liquids (RTILs) are being employed to overcome most of these problems, however they have additional drawbacks which must be accounted for. The fluidity of RTILs as well as their hygroscopic nature, are the two main drawbacks. Apart from that, the altered sensor design requires the partitioning of the gas into the viscous RTIL followed by the diffusion towards the electrode, whereas in a commercial design, the gas diffuses through a porous membrane directly to the

connected working electrode. Another major parameter is the selectivity towards certain analytes which is obtained in commercial sensing devices by the addition of filters that trap analytes that cause a false reading<sup>22</sup>, RTILs could be an alternative to replace these filters due to specific analyte gas-ionic liquid interactions (see 1.2.1.2.7).

Method	Selectivity and sensitivity	Low costs	Miniaturization	Long lifetime	Robustness
Acoustic	×	×	×	$\checkmark$	×
Gas Chromatography	$\checkmark$	×	×	$\checkmark$	$\checkmark$
Calorimetry	$\checkmark$	$\checkmark$	$\checkmark$	×	×
Optical	$\checkmark$	x	×	$\checkmark$	$\checkmark$
Conductometric	$\checkmark$	<b>√/</b> ×	$\checkmark$	×	×
Amperometric	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	×
Potentiometric	$\checkmark$	$\checkmark$	×	×	×

Table 1.2. Characterization of important gas sensor parameters for different gas sensing methods.<sup>4</sup>

### **1.2.** Ionic Liquid-based Electrolytes

Ionic liquids (ILs) are widely defined as salts with melting points (mp) below 100 °C. The first IL reported in 1888 by S. Gabriel and J. Weiner was ethanolammonium nitrate with a melting point of 52 – 55 °C.<sup>30</sup> A conventional salt such as sodium chloride has a melting point of 801 °C. Replacing the sodium cation with 1-butyl-3-methylimidazolium decreases the mp to approximately 70 °C which is already by definition an ionic liquid. Exchanging the chloride anion by bis(trifluoromethyl-sulfonyl)imide ([NTf<sub>2</sub>]<sup>-</sup>) further decreases the melting point to well below room temperature resulting in a so-called room temperature ionic liquid (RTIL). The loss of symmetry and weakening of intermolecular forces causes a significant drop in the melting point.

The story of true room temperature ionic liquids, *i.e.* salts that are liquid at room temperature, began in 1914 with Paul Walden who was searching for molten salts that were in a liquid state at temperatures where no special equipment was necessary to study chemical properties like conductivity and the molecular size.<sup>31</sup> He discovered that ethylammonium nitrate, abbreviated as [EtNH<sub>3</sub>][NO<sub>3</sub>], melts at 12 °C, this is nowadays referred to as the first real room temperature ionic liquid. However, no research was focused on this type of material for nearly 40 years until Hurley and Weir

recognized the benefits for electrodeposition applications by dissolving inorganic salts in 1-alkylpyridinium halides.<sup>32</sup> They established a binary phase diagram for 1ethylpyridinium bromide and aluminum chloride mixtures and discovered that a 2:1 molar ratio was liquid at room temperature. From then on, more and more researchers focused on ionic liquids and in the 1980s, the research topic began to broaden. In the early 1980s, 1-3-dialkylimidazolium cations with improved transport properties in terms of conductivity and viscosity, were introduced by Wilkes et al.<sup>33</sup> Up until now, imidazolium-based RTILs are the most popular cations. In 1996, a significant improvement towards air and moisture-stable RTILs was made by the introduction of  $[NTf_2]^-$  as an anion by Bonhote *et al.*<sup>34</sup>, which also allowed a broadening of the range of cations such as ammonium<sup>35</sup> and phosphonium<sup>36</sup> cations, applied in RTILs. In 2001, Jim Davies introduced the term 'task specific ionic liquids' (TSILs) which have moieties in the chemical structure that allow specific interactions with substrates.<sup>37</sup> Various combinations of cations and anions were then used by researchers that were targeted towards their research focus. Research into ionic liquids is still a major focus in chemistry with approximately 3500 new research papers per year (2020) and there are still several properties that are continuing to be understood on a molecular level. Also, their promising benefits means RTILs have been attempted to be introduced into commercial applications.<sup>38</sup> Baden Aniline and Soda Factory (BASF) solved a separation problem in the synthesis of alkoxyphenylphosphanes by applying ionic liquids, the so-called BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) process.39

In electrochemistry, ionic liquid electrolytes are considered as infinitely concentrated, *i.e.* solvent free, ionic solutions which is in contrast to traditional electrolyte/water systems that are considered as dissociated ions solvated by water.

#### **1.2.1. Room Temperature Ionic Liquids**



Figure 1.3. Chemical structures of room temperature ionic liquid cations and anions commonly used in electrochemical gas sensing applications, where n and x represent the number of carbon atoms in the alkyl chain.

Room temperature ionic liquids are salts composed of bulky organic cations, e.g. alkylimidazolium, alkylpyridinium or tetralkylammonium and tetraalkylphosphonium ions and mainly inorganic anions, such as halides, tetrafluoroborate, bis(trifluoromethylsulfonyl)imide or tris(perfluoroalkyl)trifluorophosphate (Figure 1.3). The size and asymmetry in at least one of the ions, in combination with weaker ion-ion interaction forces, results in low melting points and therefore they exist in a liquid state at ambient temperatures. This is in contrast to typical organic and inorganic salts, such as sodium chloride, that form crystal-like structures due to their small size and the strong ionic intermolecular forces.40-41

The liquid nature of RTILs allows their application as replacement solvents in different fields. They are good solvents with broad solubility characteristics that can dissolve starting materials in organic synthesis applications<sup>42</sup>, they can be applied in extraction purposes<sup>43</sup> or for dissolving gases<sup>44</sup>. Also, ionic liquids can be used in industry as

lubricants<sup>45-46</sup>, electrolytes in batteries<sup>47</sup> or in fuel cells<sup>48</sup>. The ability to dissolve various chemicals, *i.e.* polar and non-polar/hydrophilic and hydrophobic molecules, just by changing the cation or anion structure, in combination with their low volatility, makes them a useful solvent for the synthesis of new chemicals.

Abbreviation	IUPAC name	Sum formula	<i>M</i> <sub>w</sub> / g mol <sup>-1</sup>
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_8H_{11}F_6N_3O_4S_2$	391.31
[C <sub>2</sub> mim][FAP]	1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	$C_{12}H_{11}F_{18}N_2P$	556.17
[C <sub>4</sub> mim][BF <sub>4</sub> ]	1-butyl-3-methylimidazolium tetrafluoroborate	$C_8H_{15}BF_4N_2$	226.02
[C <sub>4</sub> mim][PF <sub>6</sub> ]	1-butyl-3-methylimidazolium hexafluorophosphate	$C_8H_{15}F_6N_2P$	284.18
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{10}H_{15}F_6N_3O_4S_2\\$	419.37
[C4mim][FAP]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	$C_{14}H_{15}F_{18}N_2P$	584.23
[C <sub>6</sub> mim][NTf <sub>2</sub> ]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{12}H_{19}F_6N_3O_4S_2\\$	447.42
[C <sub>6</sub> mim][FAP]	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	$C_{16}H_{19}F_{18}N_2P$	612.28
[C <sub>4</sub> py][NTf <sub>2</sub> ]	1-butylpyridinium bis(trifluoromethylsulfonyl)imide	$C_{11}H_{14}F_6N_2O_4S_2\\$	416.36
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonium)imide	$C_{11}H_{20}F_6N_2O_4S_2\\$	422.41
[C <sub>4</sub> mpyrr][FAP]	1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	$C_{15}H_{20}F_{18}NP$	587.27
[S <sub>2,2,1</sub> ][NTf <sub>2</sub> ]	diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide	$C_7H_{13}F_6NO_4S_3$	385.37
$[N_{4,1,1,1}][NTf_2]$	butyltrimethylammonium bis(trifluoromethylsulfonyl)imide	$C_{9}H_{18}F_{6}N_{2}O_{4}S_{2}$	396.37
$[P_{14,6,6,6}][NTf_2]$	trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	$C_{34}H_{68}F_6NO_4PS_2$	763.24
[P <sub>14,6,6,6</sub> ][FAP]	trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate	$C_{38}H_{68}F_{18}P_2$	928.10

Table 1.3. Abbreviations, IUPAC names and molecular weights  $(M_w)$  of commercially available RTILs used throughout this thesis.

The high cost of these solvents can be overcome by the possibility of recycling of the ionic liquids, therefore they are often referred to as 'green solvents'.<sup>49</sup> Their good solubility properties, however, come along with the challenge of obtaining high purity electrolytes where it is known that small levels of impurities can have a significant

effect on electrochemical responses.<sup>50</sup> More ionic liquid properties that are important for their use as electrolytes will be discussed in detail in the following sections.

#### 1.2.1.1. Classification

Various room temperature ionic liquids exist, classified according to their chemical structures, and therefore abbreviations rather than their full chemical names are typically used (Table 1.3 and Table 1.4). Multiple abbreviations for the same chemical structure are established by different researchers, *e.g.* 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is abbreviated as [C<sub>2</sub>mim][NTf<sub>2</sub>], [Emim][NTf<sub>2</sub>], [C<sub>2</sub>mim][TFSI], [Emim][TFSI], [C<sub>2</sub>C<sub>1</sub>im][NTf<sub>2</sub>] or [C<sub>2</sub>C<sub>1</sub>im][TFSI]. Table 1.3 and Table 1.4 summarize the full chemical names, abbreviations, and molecular masses of RTILs used throughout this thesis. In addition, RTILs are generally subdivided into protic (proton-donating group) and aprotic (non-proton-donating group) ionic liquids.<sup>51</sup> In this thesis, mainly aprotic RTILs were investigated because the presence of labile protons can result both in the degradation of the electrolyte via electron transfer reactions, or in a change of the electrochemical response of target analytes which makes them less applicable in analytical chemistry.

Abbreviation	IUPAC name	Sum formula	$M_{\rm w}$ / g mol <sup>-1</sup>
	1-(2-hydroxyethyl)-3-		
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	methylimidazolium	$C_8H_8F_6N_4O_4S_2\\$	407.31
	bis(trifluoromethylsulfonyl)imide		
[CCNmim][NITf]	1-methylnitrile-3-methylimidazolium	CHENOS	402.20
	bis(trifluoromethylsulfonyl)imide	$C_8\Pi_{11}\Gamma_6 N_3 O_5 S_2$	402.29
	2-(3-methylimidazolyl-1-yl)-ethoxy-4-		
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	oxobutanoic acid	$C_{12}H_{15}F_6N_3O_8S_2\\$	507.38
	bis(trifluoromethylsulfonyl)imide		
[CD an aming][NItf]	1-methylbenzyl-3-methylimidazolium	CHENOS	167 11
	bis(trifluoromethylsulfonyl)imide	$C_{14}\Pi_{15}\Gamma_{6}\Pi_{3}O_{4}S_{2}$	40/.41
	heptyltriethylammonium	CHENOS	100 52
[1N7,2,2,2][1N112]	bis(trifluoromethylsulfonyl)imide	$C_{15}\Pi_{30}\Gamma_6N_2O_4S_2$	480.53

Table 1.4. Abbreviations, IUPAC names and molecular weights of synthesized RTILs used in this thesis.

#### **1.2.1.2.** Physicochemical Properties

The promising properties of RTILs to be used as electrolytes in electrochemical gas sensors are discussed in the next sections. Additionally, advantages and disadvantages to aqueous-based systems will be described. Table 1.5 summarizes some physicochemical properties of a few ionic liquids, and for more data, Zhang *et al.* published a database on these properties of 588 RTILs composed of 276 different cations and 55 anions, extracted from 109 literature sources.<sup>52</sup>

DTH	Viscosity /	Conductivity /	Density /	Melting point /
KIIL	mPa s	S m <sup>-1</sup>	kg m <sup>3</sup>	K
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	$32.5 \pm 0.6^{53}$	$0.95\pm 0.02^{54}$	$1518 \pm 2^{53}$	$252\pm4^{55}$
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	$52\pm2^{56}$	$0.39\pm 0.04^{57}$	$1436\pm2^{56}$	$267\pm4^{55}$
[C <sub>6</sub> mim][NTf <sub>2</sub> ]	$70.1 \pm 0.1^{58}$	$0.218 \pm 0.004^{59}$	$1372 \pm 1^{57}$	$269\pm3^{60}$
[C <sub>7</sub> mim][NTf <sub>2</sub> ]	$81\pm4^{61}$		$1344\pm8^{55}$	$280\pm4^{55}$
[C <sub>2</sub> mim][BF <sub>4</sub> ]	$38.8 \pm 0.4^{62}$	$1.55\pm 0.02^{63}$	$1283\pm1^{62}$	$288\pm1^{64}$
[C <sub>2</sub> mim][PF <sub>6</sub> ]		$0.49 \pm 0.01^{65}$		$331\pm4^{55}$
[C <sub>4</sub> mim][PF <sub>6</sub> ]	$257\pm14^{66}$	$0.15\pm 0.02^{67}$	$1363\pm2^{68}$	$283\pm2^{69}$
[C <sub>4</sub> mim][FAP]	$78\pm1^{70}$		$1624\pm5^{70}$	
$[N_{4,1,1,1}][NTf_2]$	$98 \pm 10^{71}$	$0.15\pm0.02^{71}$	$1393 \pm 2^{72}$	$292\pm6^{71}$
$[N_{6,1,1,1}][NTf_2]$	$153\pm17^{73}$	$0.043 \pm 0.004^{73}$	$1311 \pm 26^{74}$	$305\pm1^{75}$
$[N_{8,2,2,2}][NTf_2]$	$239\pm7^{76}$	$0.062\pm0.003^{76}$	$1249.2\pm0.3^{77}$	$287\pm4^{78}$
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	$86\pm17^{79}$	$0.277\pm0.004^{80}$	$1395 \pm 2^{81} \\$	$258\pm6^{71}$
[C <sub>4</sub> mpyrr][FAP]	$272\pm14^{82}$		$1583 \pm 1^{83}$	$277\pm2^{82}$
$[P_{2,2,2,5}][NTf_2]$	$86.3 \pm 0.2^{84}$	$0.165\pm0.003^{84}$	$1303\pm2^{84}$	
[P <sub>14,6,6,6</sub> ][DCA]	$439\pm13^{85}$		$899\pm1^{85}$	
$[P_{14,6,6,6}][NTf_2]$	$337\pm12^{85}$		$1066 \pm 1^{85}$	
$[P_{14,6,6,6}][FAP]$	$347\pm12^{81}$		$1183.3\pm 0.8^{86}$	
$[S_{2,2,1}][NTf_2]$	$40.7\pm 0.7^{87}$	$0.69\pm0.01^{87}$	$1501 \pm 3^{87}$	$256.4 \pm 0.4^{88}$

Table 1.5. Physicochemical properties of RTILs commonly used for electrochemical gas sensing applications at 298 K.

#### 1.2.1.2.1. Viscosity

RTILs are entirely composed of cations and anions. Due to the strong van-der-Waals (vdW) forces, ion-ion interactions and hydrogen bonding, more energy is necessary for the movement of the ions. Viscosities in RTILs have been studied in detail by several groups<sup>89-90</sup> and values as low as 30 mPa s at 293 K are reported for [C<sub>2</sub>mim][NTf<sub>2</sub>]. In contrast, [P<sub>14,6,6,6</sub>][FAP], an ionic liquid with strong vdW interactions due to the long alkyl chains and strong hydrogen bonds caused by the fluoride ligands in the anion, has a viscosity of approximately 472 mPa s at 293 K.<sup>91</sup> Jiang *et al.* summarized the measured viscosities of 268 ionic liquids from 215

literature references and introduced corrections for water and halide residuals.<sup>90</sup> In summary, these impurities have a significant effect on the recorded viscosity which has to be taken into account during fundamental studies of thermodynamical properties. The viscosity typically follows the Vogel-Fulcher-Tammann (VFT) equation<sup>92</sup>:

$$\eta = \eta_0 \cdot e^{\frac{B}{T - T_{\rm VF}}}$$
 1.2

where  $\eta$  and T are the experimentally determined viscosity and temperature respectively,  $\eta_0$  and B are temperature dependent variables and  $T_{\rm VF}$  is a temperature that is approximately 50 K below the glass transition temperature of the ionic liquid.

For the use of solvents as electrolytes in electrochemical sensing applications, the viscosity is a crucial characteristic to ensure that analytes such as gases diffuse fast enough through the system. Slow diffusion rates increase the response time, which is an important factor for gas sensors in terms of detecting a gas leak. The dynamic viscosity of water at 298 K is 0.89 mPa s<sup>93</sup>, which is approximately 30 times lower than for [C<sub>2</sub>mim][NTf<sub>2</sub>]. The addition of co-solvents such as typical organic solvents, or even water, can overcome this issue but this can result in a limited operation in extreme conditions because of the volatile solvent.

#### **1.2.1.2.2.** Hygroscopy

The ionic nature of RTILs makes them highly hygroscopic. Some ionic liquids, such as those with imidazolium cations with short alkyl chains paired with halide anions, are fully miscible with water, whereas others, like [C<sub>4</sub>mim][NTf<sub>2</sub>], can absorb up to 3,280 ppm of water after equilibration.<sup>69</sup> Cations and anions of RTILs are quite bulky and therefore the solvation is sterically hindered. Hence, the absorption of water which solvates the ions, is a property that must be considered when using ionic liquids of different hydrophilicity. A general rule is that the larger the cations and anions are, the lower the water uptake.<sup>94</sup> The polarity of ionic liquids can be adjusted by increasing the alkyl chain length in the cation, *e.g.* in imidazolium-, ammonium- or phosphonium-based ILs. Substitution of the hydrogen atoms by fluorine atoms reduces the water uptake as well. O'Mahony *et al.* studied the water content in commercial RTILs at atmospheric conditions and concluded that the anions are more crucial for the overall water uptake.<sup>95</sup> Perfluorinated and bulky anions such as [FAP]<sup>-</sup>- or [NTf<sub>2</sub>]<sup>-</sup> in ionic

liquids have a lower water content than halide-based ones. This was supported in a computational study where the water content in ionic liquids was predicted by applying the conductor-like screening model for real solvents (COSMO-RS) by Zhou *et al.*<sup>96</sup> The presence of water can have beneficial effects like reduced viscosity and increased conductivity, however the presence of moisture can also have a significant influence on the electrochemical mechanisms of an analyte as well.

#### 1.2.1.2.3. Conductivity

The ionic conductivity is a function of the temperature and size as well as the mobility of ions in liquid media. In the case of non-conductive liquid media like water or organic solvents, salts are added in certain concentrations to increase the ionic conductivity. In the case of ultrapure water, the conductivity can be increased from 5.5 µS m<sup>-1</sup> to values around 1.3 S m<sup>-1</sup> by adding 0.1 M KCl as supporting electrolyte.<sup>97</sup> Commercial gas sensors usually contain a H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> electrolyte mixture with conductivities from 2.1 S m<sup>-1</sup> to approximately 8.0 S m<sup>-1</sup> for 0.025 M and 0.1 M H<sub>2</sub>SO<sub>4</sub>, respectively.<sup>98</sup> In aqueous electrolytes, the ions are solvated by the water molecules. The conductivities of RTILs are, however, more comparable to organic solvents like acetonitrile with 0.1 M of supporting electrolytes such as tetra-nbutylammonium perchlorate. In contrast to conventional organic solvents, RTILs are composed of cations and anions only and therefore act as both, the solvent and electrolyte. As previously discussed, the viscosity of ionic liquids is significantly higher than aqueous solutions which results in lower ionic mobility and therefore also lower conductivity values, usually in the range of 45 mS m<sup>-1</sup> for [C<sub>4</sub>mim][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>]<sup>34</sup> to 1.4 S m<sup>-1</sup> for  $[C_2 mim][BF_4]^{99}$ . An increase in the cation size or the presence of hydrogen bonding in ionic liquids, like in  $[PF_6]$ , comes along with a decrease in mobility and therefore also conductivity.<sup>100</sup> A temperature increase causes an increased mobility of ions and also influences the conductivity according to the Vogel-Fulcher-Tammann (VFT) law for conductivity<sup>101</sup>:

$$\kappa = A \cdot T^{-\frac{1}{2}} \cdot e^{-B(T-T_0)}$$
 1.3

where  $\kappa$  is the ionic conductivity, A, B and  $T_0$  are constants and T is temperature in K. The addition of co-solvents decreases the viscosity and therefore increases the mobility of ions. However, in contrast to electrolyte/organic solvent mixtures where the solvent is the main component, only approximately 15% of acetonitrile is necessary to increase the conductivity of imidazolium-based ionic liquids by a factor of 50.<sup>102</sup>

#### **1.2.1.2.4.** Electrochemical Window

The electrochemical window (EW) of a solvent is used as an indication for the electrochemical stability and it is also known as operating range, defined by the oxidation and reduction potential of the supporting electrolyte or the solvent. Therefore, it also limits the applicability of the electrolyte system for detecting certain analytes that are oxidized or reduced outside of this range. The H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> solvent system, a typical electrolyte/solvent combination in commercial gas sensors, has an EW of less than 2 V.<sup>103</sup> The application for certain analytes is therefore limited by the oxidation of water and the reduction of protons to hydrogen gas. In the case of RTILs, the oxidation limit is determined by the stability of the anion and the cathodic limit by the stability of the cation. It must be noted that EWs of RTILs are highly dependent on the electrode material. Zhao and Bond reported an electrode dependence of the EW for ionic liquids, which has to be taken into account.<sup>104</sup> A general trend is that on glassy carbon electrodes, a much wider electrochemical window is usually observed for protic as well as aprotic RTILs. Whereas noble metal electrodes such as platinum or gold have a smaller overpotential for the reduction of protons or impurities like water.<sup>105</sup> Suarez et al. concluded identical behavior after investigating the electrochemical window of two different ionic liquids on four electrode materials, *i.e.* tungsten, vitreous carbon, platinum and gold.<sup>106</sup> De Vos et al. discussed the electrochemical degradation mechanism of various RTIL cations and anions in their review, highlighting that the presence of water changes the mechanism significantly.<sup>107</sup> O'Mahony et al. established a stability trend for typical anions and the common  $[C_4 mim]^+$  cation that follows:  $[NTf_2]^- \approx [FAP]^- > [PF_6]^- \approx [BF_4]^- > halides.$ <sup>95</sup> For the cations with the same anion  $[NTf_2]^-$ , the trend follows pyrrolidinium  $\approx$  phosphonium  $\approx$  ammonium > imidazolium, with no crucial difference between cyclic and non-cyclic ammonium cations, as also concluded by Lane et al.<sup>108</sup> Electrochemical windows in dry conditions of between 3 - 7 V can be observed depending on the cation and anion combination, with a maximum of 7 V for  $[N_{6,2,2,2}]$  [FAP] reported by Howlett *et al.*<sup>109-</sup> <sup>110</sup> These values can alter in the presence of co-solvents or impurities. Variations in the reported EWs are not only due to a different purity level of the sample or different electrode materials, but also due to altering current cut-offs, *i.e.* the current of the

respective cathodic and anodic potential limit or different scan rates. Usually, current density cut-offs between 0.1 to a few mA cm<sup>-2</sup> are used.

O'Mahony *et al.* reported the EW changes in several vacuum-dried, atmospheric and wet ionic liquids at different temperatures on a platinum electrode and concluded that the more hydrophobic ionic liquids repel water more effectively (see Table 1.6).<sup>95</sup>

Table 1.6. Electrochemical window of nine room temperature ionic liquids on a platinum micro-disk electrode at a current density cut-off of 1 mA cm<sup>-2</sup> in vacuum-dried, atmospheric and wet conditions at 298 K reported by O'Mahony et al.<sup>95</sup>

	Electro	Electrochemical Window / V			
RTIL	vacuum-dried	atmospheric	wet		
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	4.2	2.8	2.6		
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	4.3	2.9	2.8		
[C <sub>4</sub> mim][PF <sub>6</sub> ]	4.8	3.9	2.6		
[C <sub>4</sub> mim][BF <sub>4</sub> ]	4.6	2.4	2.0		
[C4mim][OTf]	4.2	3.3	2.7		
[C <sub>4</sub> mim][I]	2.0	1.9	1.6		
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	4.2	3.0	2.0		
$[N_{6,2,2,2}][NTf_2]$	4.7	2.3	2.2		
$[P_{14,6,6,6}][NTf_2]$	5.2	3.2	1.8		

#### **1.2.1.2.5.** Thermal and Chemical Stability

Aqueous electrolyte systems are limited to a narrow operation temperature range, *i.e.* at very low temperatures, the system can solidify, and at elevated temperatures, the liquid can evaporate. RTILs, on the other hand, have a broad temperature range where they do not show any sign of decomposition. The solidification temperature depends on the ionic liquid structure and can be as low as 192 K for  $[C_4mim][BF4]^{111}$  and as high as 398 K for  $[C_1mim][AlCl4]^{112}$  (which is still considered as ionic liquid, but there are examples with significantly higher melting points which are by definition no ionic liquids anymore). The decomposition temperature (note: ionic liquids normally do not show a significant evaporation before decomposition) can be several 100 K higher than water, *e.g.*  $[C_4mim][NTf_2]$  decomposes at 723 K.<sup>69</sup> Maton *et al.* performed a thorough analysis of the decomposition mechanism of several RTILs and the effect of the ion structures on the thermal stability.<sup>113</sup> The decomposition mechanism can follow nucleophilic substitutions<sup>114</sup>, eliminations or dealkylations<sup>115</sup> depending on the cation

and anion structure. Generally, imidazolium cations are more thermally stable than tetraalkylammonium or tetraalkylphosphonium cations in a series of [NTf<sub>2</sub>]<sup>-</sup>based RTILs. The stability of the formed carbon radicals increases slightly with the number of carbons in the chain, hence short chained ionic liquids show a higher thermal stability. Replacing the alkyl chains with more stable aryl substitutes further enhances the thermal stability as shown by Davis et al for perarylphosphonium-based ionic liquids.<sup>116</sup> The presence of basic anions, such as halides, reduces the thermal stability significantly due to the possible alkyl chain cleavage. The thermal stability of RTILs follows the series<sup>117</sup>:

$$[PF_6]^- > [NTf_2]^- > [CF_3SO_3]^- > [BF_4]^- >> [I]^-, [Br]^-, [CI]^-$$

Also, the chemical stability of RTILs must be considered. Good solubility behavior is observed, and at ambient concentrations, the non-reactivity of most of the ionic liquid cations and anions is confirmed.<sup>113</sup> However, in the case of the solubilization of carbon dioxide gas in  $[C_2mim][OAc]$ , a study by Yokozeki *et al.*<sup>118</sup> showed a reversible chemical reaction between the gas and the RTIL ions.<sup>119</sup> The basicity of the acetate anion can cause a deprotonation of the hydrogen on the C<sub>2</sub> position of the imidazolium cation, resulting in chemical binding of the CO<sub>2</sub>. For electrochemical purposes, the chemical stability of the electrolyte is of special interest. The reduction or oxidation of analytes can result in the formation of highly reactive species such as radicals that can cause decomposition of the ionic liquid, *e.g.* the reduction of oxygen gas results in the formation of the highly reactive superoxide radicals, which can sometimes react with the ionic liquid.

#### 1.2.1.2.6. Tunability

RTILs are described as 'designer solvents' because of the tunability of their characteristics by simply changing their cation and anion combination. The change from an ionic liquid with a halide anion to one with [FAP]<sup>-</sup> significantly increases the hydrophobicity. Ionic liquids can be easily tailored to have particular properties in terms of hydrophobicity, viscosity or conductivity. Further options are to mix two or more ionic liquids or to chemically modify the cation or anion to get so-called task-specific ionic liquids.<sup>120</sup> Kermanioryani *et al.* attached functional groups, *i.e.* phenyl or benzyl, into the alkyl side chain of an imidazolium-based ionic liquid to increase the interactions with the analyte, methylene blue.<sup>121</sup> Several examples of this approach

can be found in the literature to improve the solubility of analytes. It is of special interest for analytical sensing applications to reduce the limit of detection for certain highly toxic compounds such as gaseous  $SO_2$  or  $H_2S$ , but also for solids such as explosives or drugs. A more detailed discussion on the tunability of ionic liquids towards gaseous analytes will be given in the next section.

#### 1.2.1.2.7. Gas Solubility

The promising solubility properties of RTILs require a fundamental study of the solubility mechanisms. Gas solubility data is very important for assessing chemical processes like gas separations for the removing of certain gaseous molecules<sup>122-123</sup>, gas-liquid reactions for reaction optimization<sup>124-125</sup> or gas sensing in sensors<sup>24, 126</sup>, and a broad database has been established over the last two decades. A lot of work has been reported on the solubility of non-polar gases such as nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>) and hydrogen (H<sub>2</sub>) as well as polar gases like carbon dioxide (CO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) in RTILs with regards to the identification of the structure relation between gas solubility and ionic liquid structure. Shiflett et al. discussed the different experimental methods commonly used to determine the gas solubility.<sup>127</sup> The methods are mainly subdivided into analytical, *i.e.* chromatographic and spectroscopic, and physical methods, such as gravimetric and synthetic. The different methods have advantages and drawbacks but nevertheless, the accuracy of the data requires a fully characterized ionic liquid phase in terms of purity and water content, as well as the gaseous analyte, and proper error analysis of the method to validate the measured data. The gas solubility is usually reported as mole fraction of gas ( $x_{gas}$ , equation 1.4) or as the Henry's law constant ( $K_{\rm H}$ , equation 1.5), defined as follows:

$$x_{\text{gas}} = \frac{n_{\text{gas}}^{\text{liq}}}{n_{\text{gas}}^{\text{liq}} + n_{\text{IL}}^{\text{liq}}}$$
 1.4

$$K_{\rm H} = \lim_{x_{\rm gas} \to 0} \frac{f_{\rm gas}(p, T, x_{\rm gas})}{x_{\rm gas}} \cong \frac{\varphi_{\rm gas}(p_{\rm eq}, T_{\rm eq})p_{\rm eq}}{x_{\rm gas}}$$
 1.5

Where  $n_{gas}^{liq}$  is the amount of gas in mole in the liquid phase,  $n_{IL}^{liq}$  is the amount of ionic liquid in mole in the liquid phase,  $f_{gas}$  is the fugacity of the gas and  $\varphi_{gas}$  the fugacity coefficient. T and T<sub>eq</sub> are temperature and temperature at the equilibrium, respectively, and p and p<sub>eq</sub> are pressure and pressure at the equilibrium.

The mole fraction solubilities reported by Jacquemin et al.<sup>128</sup> range from around 10<sup>-4</sup> for non-polar gases such as hydrogen to more than 0.015 for polar ones such as CO<sub>2</sub>, for [C<sub>4</sub>mim][BF<sub>4</sub>] at room temperature and a partial pressure of 0.1 MPa. Higher mole fraction solubilities are usually reported for SO<sub>2</sub> in RTILs, e.g. by Huang et al.<sup>129</sup> reported a value of 0.6 at room temperature at 1 bar in [C<sub>4</sub>mim][OAc]. However, huge variations, *i.e.* up to 100%, have been reported, particularly for hydrogen, oxygen and nitrogen, by different groups and measured with varying methods.<sup>44</sup> The endless combinations of ionic liquid cations and anions resulted in a focus towards less expensive computational predictions of solubility data compared to a more time consuming experimental approach. The relationship between ionic liquid and gas structure is therefore of major interest. The solubility is defined as either physical, *i.e.* only via van-der-Waals forces, electrostatic interactions or hydrogen bonding, or chemical in the case of a chemical bond between ionic liquid and gas. Non-polar gases are purely physically dissolved in the ionic liquid. However, at low temperatures and pressures, the presence of basic anions such as acetate can cause a dominant chemical binding of carbon dioxide, as has been demonstrated by Yokozeki et al.<sup>118</sup> CO<sub>2</sub> solubilities in RTILs have been a hot topic over the last decades, especially the CO<sub>2</sub> removal from flue gas and waste gas streams to reduce the CO<sub>2</sub> emissions. However, the removal of SO<sub>2</sub> from industrial flue gas is drawing more and more attention nowadays. Due to the high toxicity of sulfur dioxide, special precautions must be taken while handling this gas, and a reliable detection of low concentrations of SO<sub>2</sub> is required, which will be discussed in more detail in chapter 4.

#### **1.2.1.3.** Structuring of Ionic Liquids (Bulk vs. Surface)

In early times, room temperature ionic liquids were considered to be highly concentrated salt solutions showing structural characteristics similar to homogeneous, molecular liquids.<sup>130</sup> However, modern studies reveal a more complex dynamic, physical and chemical behavior. The presence of polar and non-polar moieties in the ionic liquid cation and anion structures causes an ordering, which can cover a range from small ion clusters<sup>131</sup> to self-assembled bicontinuous nanostructures, first reported by Schröder *et al.*<sup>132</sup> Canongia Lopes *et al.*<sup>133</sup> simulated the bulk structure of a set of [C<sub>n</sub>mim][PF<sub>6</sub>] ionic liquids with n = 2 - 12 and illustrated nano segregation into polar and non-polar domains. Snapshots of equilibrated states visually show that dominant polar regions are replaced by more and more extended non-polar domains with

increasing alkyl chain lengths in the imidazolium cation. The presence of the two domains lead to excellent solvent properties for a broad range of chemicals, *i.e.* polar as well as non-polar molecules. Nevertheless, the bulk structure is highly dependent on external factors like temperature and pressure, which influences the dynamics of the ionic liquid phase. Wang predicted structure variations in the presence of an externally applied electric field.<sup>134</sup> The reorganization of the ionic liquid structure in the electrical field is of special interest for electrochemical applications.<sup>135</sup> For supercapacitors, the ion density in the first layer as well as the length of the alkyl chains of imidazolium-based ionic liquids is an important parameter of the differential capacity of RTILs.<sup>136</sup> In battery research, an insulating solid electrolyte interphase is beneficial due to the stabilization of charged electrodes.<sup>137-138</sup> For electrochemical sensing applications, less research has been conducted so far but it is known that the structuring can have an effect on the sensitivity and selectivity of the device.<sup>139</sup> Hence, the interfacial structures of ionic liquids must be considered. The structure of RTILs close to an electrified solid, *i.e.* an electrode, has been studied by several research groups applying different methods (illustrated in Figure 1.4). Atomic force microscopy (AFM)<sup>140-141</sup>, surface force apparatus (SFA)<sup>142</sup> neutron reflectometry<sup>143</sup>, sum frequency generation vibrational spectroscopes (SFG-VS)<sup>144</sup> and surface-enhanced infrared absorption spectroscopes (SEIRAS)<sup>145</sup> were used for experimental characterizations of the solid-liquid electrical double layer (EDL) as well as theoretical approaches summarized by Fedorov and Kornyshev in their detailed review.<sup>146</sup>



*Figure 1.4. Expected electrical double layer (EDL) in dry and impurity free room temperature ionic liquids* 

#### 1.2.1.4. Electrochemistry

Electrochemical measurements in room temperature ionic liquids often differ from measurements in conventional electrolyte/solvent systems in terms of mass transport

and diffusion of an analyte and electrical double layer formation. The structure is important because the electron transfer is happening there.

A comparison of the diffusional transport of N,N,N',N'-tetramethylphenylenediamine in acetonitrile and RTILs revealed that ionic liquids can be treated in a similar manner as organic solvents, however, diffusion coefficients of neutral and ionic species are significantly lower due to higher viscosities.<sup>147</sup> Electron spin resonance (ESR) experiments to study rotational diffusion of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) in various RTILs showed that rotational and translational diffusion is dependent on the structure of the ionic liquids.<sup>148</sup> RTILs with an extensive lipophilic moiety, *i.e.* several long alkyl chains such as in [P<sub>14,6,6,6</sub>]<sup>+</sup>, can exhibit significantly different diffusion properties compared to ionic liquids with smaller cations such as [C<sub>2</sub>mim]<sup>+</sup>. Evans *et al.* reported differences in the diffusion coefficient of oxygen and the reduced superoxide radical of a factor of 10 for the reduction of oxygen gas in a series of RTILs.<sup>149</sup> Therefore, a broad variety of RTIL cation and anion combinations results in changing properties which therefore has to be considered for electrochemical applications.

The electrical double layer structure of aqueous electrolyte/solvent systems will be discussed in section 1.4.1.1. The Stern diffuse double layer model is not applicable for RTILs because of the absence of solvent molecules that solvate the ions. Instead, the EDL is composed of multi-layers of alternating cations and anions as shown for molten salts.<sup>150</sup> Nevertheless, the high capacitance and great stability allows their use in electrochemical double-layer capacitors.<sup>151-152</sup>

#### **1.2.2. Gel-Polymer Electrolytes**

Commercially available electrochemical gas sensors usually employ a gas-permeable membrane to avoid the evaporation of the electrolyte, but also to keep the liquid contained in the reservoir.<sup>26, 153</sup> RTILs exhibit higher viscosities, therefore the flow is significantly reduced, however, extreme agitation or changing orientations of planar sensors, such as upside down, are not practical for a 'membrane free' sensor. Therefore, researchers investigated the gelification of pure ionic liquids by the addition of polymers. These materials are known as gel-polymer electrolytes (GPEs).<sup>154-155</sup> The addition of lithium salts to these materials is often required to overcome the reduced intrinsic conductivity, especially in battery research.<sup>156-158</sup> GPEs have also found

application in several other fields like solar cells<sup>159</sup>, fuel cells<sup>160</sup> and gas sensors<sup>29, 161-162</sup>. The gelification of the ionic liquid electrolyte with poly(methyl methacrylate) (PMMA) makes it possible to use gas sensors in different orientations without any change in the electrochemical response as shown by Lee *et al.*<sup>29</sup> Amanchukwu *et al.* previously showed that not all polymers are stable in the presence of superoxide, which is electrochemically formed when oxygen is reduced.<sup>163</sup> Partially halogenated polymers such as poly(vinyl chloride) (PVC) or poly(vinylidene difluoride-co-hexafluoro-propylene) (PVDF-HFP) and poly(acrylonitrile) (PAN) are known to chemically degrade, whereas PMMA or poly(tetrafluoroethylene) (PTFE) are stable against a nucleophilic attack from superoxide. Various polymer and ionic liquid combinations can be studied and optimized for different applications. In addition, mixing commercially available polymers is a low-cost method to increase the robustness of the electrolyte material and make a material that does not flow. The mixing of RTILs with polymers is, however, limited by the interactions between the two compounds; unfavorable interactions could lead to a phase separation.

#### **1.2.3.** Poly(Ionic Liquids)

A newer and less investigated approach to increase the robustness of RTIL-based electrolytes is to polymerize either the ionic liquid cation or the anion to get so-called poly(ionic liquids) (also known as polymerized ionic liquids) (PILs) (not to be mistaken with protic ionic liquids with the same abbreviation). These materials drew more and more attention from the early 2000s onwards when Ohno's group reported various polymerized ionic liquid monomers.<sup>164-169</sup> Several types of PILs exist nowadays, with polycations<sup>166</sup> and polyanions<sup>165</sup>, in addition to copolymerized<sup>165</sup> and poly(zwitterionic)<sup>166</sup> ones. The ionic conductivity is improved compared to GPEs due to partly mobile counter ions, but lowered considerably compared to pure RTILs.<sup>169</sup> The PILs reported up until now are mainly solid with only a few showing liquid/fluidic behavior at ambient temperature. A huge advantage of PILs is their relatively easy purification, which is very challenging for neat RTILs due to their good solubilization properties and liquid nature. Precipitation from a solution or freeze-drying are well established methods for the purification of polymers; these methods can be also applied for PILs. Tang et al. reported in 2005 the significantly improved CO<sub>2</sub> absorption capacity of PILs compared to neat ILs.<sup>170</sup> Bara et al. confirmed a further improvement of CO<sub>2</sub> permeability and selectivity with increasing N-alkyl substituents
or incorporating a polar moiety into the cation structure.<sup>171</sup> PIL-based gas separation and sorption is still a strong research focus. Further applications of PIL materials are as highly selective gas chromatography stationary phases<sup>172</sup>, matrices for enzyme immobilisation<sup>173-174</sup> and catalysts<sup>175-176</sup>. Additionally, PILs have been also incorporated in sensing devices for gases<sup>177-178</sup>, biomolecules<sup>179-181</sup>, pH<sup>182</sup> and ions<sup>183-<sup>184</sup>. A recent study by Wang *et al.* showed the implementation of PIL nanofibrous membranes into real-life wearable electronics.<sup>185</sup></sup>

# 1.3. Electrochemical Oxidation-Reduction Reactions of Gases

Most of the work in this thesis involves the electrochemical oxidation/reduction of various gases in room temperature ionic liquids (RTILs). The following sections will therefore summarize the electrochemical mechanisms of the chosen gases in conventional as well as in RTIL electrolytes in dry environments.

espective standard potentials. <sup>24,222</sup>			
Electrolyte	Oxygen reduction reaction	Standard potential / V vs	
		NHE	
Acidic protic	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70	
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76	
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	
Basic protic	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.07	
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.87	
	$0_2+2H_20+4e^-\rightarrow 40H^-$	0.40	
Aprotic	$O_2 + e^- \rightarrow O_2^{\bullet -}$	Electrolyte dependent	
	$O_2^{\bullet-} + e^- \rightarrow O_2^{2-}$	Electrolyte dependent	

1.3.1. Oxygen

*Table 1.7. Oxygen reduction reaction in acidic protic, basic protic and aprotic electrolytes and respective standard potentials.*<sup>18, 186</sup>

Oxygen (O<sub>2</sub>) gas is a crucial part of everyday life and is required for biological respiration or in fuel cells for energy conversion. The reliable monitoring of oxygen concentrations is therefore an important requirement in health and safety. The Clark oxygen electrode developed by Leland Clark in 1953 is the first electrochemical sensor

for continuous oxygen sensing.<sup>20</sup> The whole setup is based on an aqueous electrolyte where oxygen can be reduced according to two pathways, either a 2-e<sup>-</sup> or a 4-e<sup>-</sup> reduction reaction. The exact mechanism and standard potential depend on the pH of the electrolyte (see Table 1.7). In the absence of protons, *i.e.* in aprotic solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), a 1-e<sup>-</sup> reduction to the superoxide radical  $(O_2^{\bullet-})$  is observed.<sup>187</sup> Various researchers have studied the kinetics of the oxygen reduction reaction (ORR) in aqueous media<sup>188-190</sup> and the influence of the electrode material<sup>191-192</sup> is still an important research focus, especially for an improved electron transfer efficiency, e.g. in fuel cells for energy production.<sup>193</sup> Most commercially available RTILs are also considered as aprotic electrolytes, and the electrochemical ORR responses have been therefore well studied by several groups.<sup>24,</sup> <sup>194-195</sup> However, the hygroscopic nature of RTILs results in the absorption of water molecules, whose presence can change the ORR mechanism from a 1-e<sup>-</sup> to a 2-e<sup>-</sup> or 4e<sup>-</sup> mechanism, as has been shown by Yuan et al.<sup>196</sup> who compared the response of dry and wet RTILs. A more detailed study with different water contents and various ionic liquids will be discussed later in the results section 3.1.

#### 1.3.2. Ammonia

Ammonia (NH<sub>3</sub>) is a colorless gas with a pungent odor and is a common chemical used in the production of important products such as fertilizers for agriculture, in the form of ammonium nitrate, and also in cleaning products as ammonium hydroxide, or as a cooling utility in refrigeration systems. One of the most commonly employed methods to synthesize ammonia gas is the Haber-Bosch process where nitrogen and hydrogen gas are combined at high pressure and high temperature in the presence of a catalyst.<sup>197</sup> Evidently, ammonia is very well present in our society and has many associated health risks and dangers. Ammonia is considered to be extremely hazardous due to its flammable nature and caustic properties, as well as its ability to cause neurotoxicity and metabotoxicity.<sup>198</sup> Recent studies have shown that exposure to a concentration of 25 ppm should be limited to a maximum of 10 hours.<sup>199</sup> Therefore, the reliable detection of ammonia gas, especially at low concentrations but also in extreme conditions such as high humidity levels or high temperatures, is critical to avoid accidents like explosions<sup>200</sup>, to detect air pollution from vehicles<sup>201</sup> as well as being an indication for diseases in medicine<sup>202</sup>. Müller and Spitzer (1905) studied and proposed the mechanism of the ammonia oxidation reaction (AOR) on a platinum electrode in basic aqueous media (equation  $1.6 - 1.8)^{203}$ :

$$NH_3 + 3OH^- \rightarrow \frac{1}{2}N_2 + 3H_2O + 3e^-$$
 1.6

$$NH_3 + 70H^- \rightarrow NO_2^- + 5H_2O + 6e^-$$
 1.7

$$NH_3 + 90H^- \rightarrow NO_3^- + 6H_2O + 8e^-$$
 1.8

Gerischer and Maurer (1970) performed analytical investigations of the products and proposed a more detailed mechanism.<sup>204</sup> The oxidation of NH<sub>3</sub> occurs by the reaction of adsorbed OH<sup>-</sup> radicals at the platinum surface to form NH<sub>x</sub> (x = 1 or 2) radicals and N<sub>2</sub>H<sub>y</sub> (y = 2 or 4) intermediates. Further oxidation results in the formation of nitrogen gas. The chemisorption of by-products on the platinum electrode results in an irreversible passivation.

A few studies about the ammonia oxidation on platinum or glassy carbon in nonaqueous media, such as acetonitrile<sup>205</sup>, dimethyl sulfoxide and also RTILs, have been reported so far.<sup>206-209</sup> A cyclic voltammetry study by Buzzeo *et al.* has revealed a large oxidative wave corresponding to the mechanism in equation 1.9.<sup>207</sup> The deprotonation of the electrogenerated ammonium (NH<sub>4</sub><sup>+</sup>) ion to ammonia gas and protons (equation 1.10), leads to a reductive wave assigned to the formation of hydrogen gas (equation 1.12). An additional oxidation wave is assigned to the bulk oxidation of hydrogen gas (equation 1.13) as confirmed by Ji *et al.* who also confirmed that a pre-reduction wave, only observed in RTILs, is caused by the solvation of the protons by the RTIL anions, *A*<sup>•</sup> (equation 1.11).<sup>208</sup>

$$4NH_3 \rightarrow \frac{1}{2}N_2 + 3NH_4^+ + 3e^-$$
 1.9

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \tag{1.10}$$

$$H^+ \cdots A^- + e^- \rightarrow \frac{1}{2}H_2 \tag{1.11}$$

$$H^+ + e^- \to \frac{1}{2}H_2$$
 1.12

$$H_2 \rightarrow 2H^+ + 2e^- \qquad 1.13$$

25

#### **1.3.3. Sulfur Dioxide**

Sulfur dioxide (SO<sub>2</sub>) is an invisible gas with a sharp smell that is hazardous to humans as well as nature even at very low parts-per-million (ppm) concentrations.<sup>2, 210</sup> SO<sub>2</sub> is a background environmental gas that can cause acidic rain in the presence of moisture and result in damage to building materials such as limestone. Sulfur dioxide is a byproduct in petroleum refineries and is a severe threat for air quality. Upon inhalation, it can result in respiratory problems and at higher concentrations it can be deadly.<sup>211</sup> Hawai'i Volcanoes National Park created a SO<sub>2</sub> air pollution advisory program outlining how the air quality influences human health (see Table 1.8). The National Institute for Occupational Safety and Health (NIOSH) defined a concentration of 100 ppm as hazardous to life and defined the permissible exposure limit (PEL) as 2 ppm averaged over a 10-hour work shift of 5 days and a maximum of 5 ppm during any 15-minute work period.

nups.//www.nps.gov/subjects/utr/numunneutin-sutjur.numt).		
Air quality index	Effects	
Good	No cautionary statement	
(0 – 0.1 ppm)		
Moderate	Reduce prolonged/heavy exertion outdoors	
(0.1 – 0.2 ppm)	for sensitive people	
Unhealthy for sensitive groups	Reduce prolonged/heavy exertion outdoors	
(0.2 – 1.0 ppm)	for people with lung disease/asthma	
Unhealthy	Avoid all exertion outdoors for people with lung disease/asthma	
(1.0 – 3.0 ppm)	Reduce prolonged/heavy exertion outdoors for everyone else	
Very unhealthy	Avoid all outdoor exertion for people with lung disease/asthma	
(3.0 – 5.0 ppm)	Reduce prolonged/heavy exertion outdoors for everyone else	
Hazardous	Avoid all outdoor exertion for everyone	
(>5.0 ppm)	Leave area if directed by Civil Defense	

Table 1.8. Air quality index and effects of different concentrations of sulfur dioxide in air (taken from https://www.nps.gov/subjects/air/humanhealth-sulfur.html).

The mechanism for the electrochemical SO<sub>2</sub> oxidation in aqueous media was first studied by Seo and Sawyer in 1963<sup>212</sup>, and it was extensively studied by Appleby and Pichon in 1979<sup>213</sup> and afterwards by several other researchers<sup>214-216</sup> for hydrogen production (patented later on as Westinghouse Process<sup>217</sup>). Various articles about the mechanism<sup>213</sup>, the influence of the electrocatalytic surface<sup>218</sup>, temperature dependence<sup>213</sup> and SO<sub>2</sub> concentrations<sup>213</sup> can be found in the literature.

The electrochemical reduction of aqueous SO<sub>2</sub> was only observed in acidic media (equations 1.14 and 1.15), while in basic or neutral media, no reduction signal is observed.<sup>219-221</sup> The mechanism on a dropping mercury electrode is a 2-e<sup>-</sup> reduction that is pH dependent<sup>221</sup>:

$$SO_2 + 2H^+ + 2e^- \rightleftharpoons H_2SO_2 \qquad 1.14$$

$$2H_2SO_2 \rightarrow S + SO_2 + 2H_2O$$
 1.15

The second step is slow at pH values above 1, which can lead to the formation of dithionite ions  $(S_2O_4^{2-})$  via chemical reactions. The reduction of dithionite to thiosulfate results in a small additional reduction wave.<sup>221</sup>

The reduction mechanism was also studied in non-aqueous media, *i.e.* dimethylformamide (DMF), on various electrodes using different electrolytes.<sup>222-225</sup> A one electron reduction mechanism, followed by a dimerization reaction is suggested (equations 1.16 and 1.17).

$$SO_2 + e^- \rightleftharpoons SO_2^{\bullet-}$$
 1.16

$$2SO_2^{\bullet-} \rightleftharpoons S_2O_4^{2-} \qquad 1.17$$

Barrosse-Antle *et al.* studied the reduction mechanism of high concentrations of  $SO_2$  by cyclic voltammetry in several RTILs. One cathodic wave was observed according to equation 1.16. Several anodic waves were assigned to solvated and non-solvated radicals and dimers; the solvation occurs due to the interaction of the acidic C<sub>2</sub> proton of the imidazolium cation.<sup>226</sup>

A patent for an amperometric gas sensor applying ionic liquids as electrolyte for the detection of SO<sub>2</sub> has been presented by Eckardt and Warratz.<sup>227</sup>

### **1.4.** Characterization Methods

The following sections give a brief theoretical overview about the characterization techniques used in this thesis. A more detailed description can be found in standard textbooks.<sup>18-19</sup>

#### **1.4.1. Introduction to Electrochemistry**

Electrochemistry is an interdisciplinary field between chemistry and physics where an electric potential is applied to an electrode that is in contact with an ionic conductor (electrolyte) to enforce electrochemical reactions at the electrode surface resulting in the detection of currents.<sup>18</sup> Dynamic electrochemistry is normally used to extract thermodynamic as well as kinetic quantities happening during an electrochemical experiment.<sup>19</sup> In this thesis, dynamic electrochemistry is applied to study electrochemical responses of certain gases in room temperature ionic liquid-based electrolytes. The other branch, equilibrium electrochemistry, studies electrochemical processes after the establishment of an equilibrium. In dynamic electrochemistry, a clear equilibrium is not obtained and the response after applying a constant or varying potential or current is measured. The respective responses that are obtained are then used to get insight into the electron transfer processes happening in the electrochemical cell. To understand and interpret the outcomes, some basic concepts of electrochemistry must be introduced. The following section introduces the experimental setup as well as important concepts such as the electrical double layer (EDL), Faradaic and non-Faradaic processes and mass transport that are important to understand the experiments in this thesis. The theory behind the two main electrochemical techniques used in the results chapters are also introduced, *i.e.* cyclic voltammetry (CV) and chronoamperometry (CA).

#### **1.4.1.1.** Electrical Double Layer

In an electrochemical cell, the electrode is in contact with the electrolyte/solvent system. The application of a positive or negative potential at the electrode results in a surface charge and an electric field decaying towards the bulk solution. The adsorption of counterions from the electrolyte/solvent system to screen the surface charge causes the formation of an electrical double layer (EDL). This EDL was first described by Hermann von Helmholtz<sup>228</sup> in 1853 and later improved by introducing a diffuse model by Louis Georges Gouy<sup>229</sup> and David Leonard Chapman<sup>230</sup> to the so-called 'Gouy-

Chapman model'. However, both models do not represent a highly charged EDL correctly. In 1924, Otto Stern<sup>231</sup> suggested the combination of the Helmholtz model and the Gouy-Chapman model. The widely accepted Stern model describes the EDL as containing strongly adsorbed counterions (Helmholtz model) in combination with a diffuse layer (Gouy-Chapman model). The Stern model (see Figure 1.5) considers that the smallest distance between the electrode and counterion is on the order of the ion size; this plane is defined as the outer Helmholtz plane (OHP). However, ions are treated as point charges which is a limitation of this model. The potential changes linearly within the strongly adsorbed ion layer and decays exponentially through the diffuse layer to the bulk solution, where a negligible potential is observed. The Stern model considers the solvation of the ions by solvent molecules, whereas for room temperature ionic liquids (RTILs) that are only composed of cations and anions, no solvation is possible and therefore the Stern model has not to be proven valid yet. At a charged electrode, the formation of dense RTIL cation and anion layers to form the EDL has been previously studied using theory by several groups.<sup>232-235</sup> Experimental methods such as atomic force microscopy (AFM)<sup>140-141</sup>, neutron reflectometry<sup>143</sup> or surface-enhanced infrared absorption spectroscopy (SEIRAS)<sup>145</sup> have been applied to study the EDL as well. A more detailed discussion on this can be found in section 1.3.1.3.



Distance from electrode

Figure 1.5. Sketch of the Stern model of the electrical double layer in conventional electrolytes. For simplicity, solvent molecules are not illustrated, and solvation of the cations and anions is illustrated as fading color.

#### 1.4.1.2. Faradaic and Non-Faradaic Processes

The application of a potential at the electrode generates a current that can be measured, resulting from a combination of Faradaic and non-Faradaic processes happening at the electrode/solution interface. These processes are named after Michael Faraday, one of the most important experimental scientists in the history of electrochemistry.<sup>236</sup> In 1952, Grahame defined a Faradaic process as a transfer of charged particles from the electrode to the electrolyte, meaning that applying a constant potential results in a constant current over time and a constant electrode composition.<sup>237</sup> The electron transfer from the electrode to the electrolyte or vice versa causes the occurrence of a reduction or oxidation process, respectively. The charge detected per mole of electrons passed through the electrode was defined by M. Faraday as Faraday's constant (96485 C mol<sup>-1</sup>). In contrast, at potentials where redox reactions are thermodynamically and kinetically unfavorable, adsorption or desorption processes can still occur at the electrode resulting in current responses. In these so-called non-Faradaic (or capacitive) processes, no electron transfer occurs across the electrode/electrolyte interface, but the charge is progressively stored at the electrode resulting in a change of the electrode/electrolyte interphase with time; therefore, these processes are dependent on both, the surface area of the electrode and the electrolyte composition. Both Faradaic and non-Faradaic processes can occur simultaneously and ideally, experimental conditions are optimized to minimize or determine the exact non-Faradaic contribution. The Faradaic currents are then used for analytical analysis as well as determining physical parameters, such as the diffusion coefficient or the bulk concentration.

#### 1.4.1.3. Mass Transport

The transport of electrochemically active species from the electrolyte bulk phase towards the electrode surface can occur via a combination of three different processes, *i.e.* convection, migration, and diffusion.

Convection is defined as the transfer of heat by the movement of material itself, in this case molecules, caused by thermal or concentration gradients in a solution. Convection can be also introduced by external factors such as stirring and pumping. The contribution from convection to the mass transport for the experiments performed in this thesis is assumed to be negligible.

Migration is defined as the movement of charged species due to the presence of an electric field. The contribution from migration to the overall mass transport is dependent on the ion charge and its concentration, as well as the electric field applied. In electrochemistry, the application of a potential at the electrode results in an electric field extending out towards the bulk solution, therefore migration is a crucial process. In conventional electrolyte/solvent systems, the concentration of an inert background electrolyte is usually high enough to reduce the effect of the analyte on the formation of an electric field out towards the bulk solution. For RTILs that purely consist of cations and anions, however, the high concentration of ions can have a larger effect on the migration of analytes. Due to the fact that overscreening and crowding can occur with RTILs, a net electric field can be present.<sup>234</sup>

Diffusion is defined as the movement of species from a high concentration region to a lower concentration region due to the presence of a concentration gradient. In electrochemistry, the conversion of one electrochemical species to another at the electrode establishes a concentration gradient that results in the diffusion of analyte species towards the electrode to balance the gradient. The flux of molecules due to a concentration gradient follows Fick's first  $law^{238}$  which includes a term for the diffusion coefficient, *D*, of the chemical species. In more viscous RTILs, significantly smaller diffusion coefficients are observed, in contrast to conventional electrolyte/solvent systems, where the diffusion of most of the analytes is significantly higher. Additionally, the difference in diffusion coefficient of charged and uncharged species is much more pronounced.<sup>239</sup>

#### 1.4.1.4. Electrochemical Setup

An electrochemical cell typically consists of three electrodes, *i.e.* a working electrode (WE), reference electrode (RE) and counter (or auxiliary) electrode (CE), which are connected via the electrolyte/solvent system. The electrochemical redox processes occur at the WE and the CE, and the potential of the WE is measured relative to the reference electrode potential, which is usually a commercially available Ag/AgCl electrode in aqueous solutions (see Figure 1.6). Common working electrode materials applied in electrochemical cells are platinum, gold, and glassy carbon, and for counter electrodes, platinum mesh, carbon rods or silver wires (typically in the shape of a coil to increase the surface area) are used. For room temperature ionic liquids, attempts have been made to develop stable reference electrodes, although no commercial REs

are established yet. Therefore, quasi-reference electrodes with an unstable reference potential, such as Ag or Pt wires, are usually applied. Wandt et al.<sup>240</sup> investigated a lithium iron phosphate reference electrode and Huber et al.<sup>241</sup> studied a Ag/Ag<sup>+</sup> micro reference electrode for electrochemical measurements in ionic liquids. However, these may be difficult to apply in all situations. As an alternative, internal references such as ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) or cobaltocene/cobaltocenium (Cc/Cc<sup>+</sup>) can be used to determine the exact reference potential. However, the requirement to dissolve ferrocene or cobaltocene in RTILs can affect the electrochemical response of the analyte by either electrochemical reactions or by changing the diffusion behavior as shown by Torriero et al.<sup>242</sup> The counter electrode is usually chosen so that the surface area is large, the choice of the material, *i.e.* Pt, Au or any other metal, is however less crucial, as long as the current flow at the working electrode is not restricted and the metal is conductive. The choice of the WE material is an important factor that must be considered before starting an electrochemical sensing experiment. Common working electrode materials applied in electrochemical cells are platinum, gold and glassy carbon, but not every analyte is electrochemically active on every surface, e.g. Tanner et al.<sup>243</sup> showed that for the reduction of carbon dioxide (CO<sub>2</sub>) in RTILs, only on gold and silver an obvious CO<sub>2</sub> reduction signal could be observed, with no response on platinum and glassy carbon. Other studies have shown that certain materials can act as catalysts to either detect an analyte at lower potentials or improve the sensitivity for the redox processes. Examples include metallophtalocyanine for nitric oxide (NO) sensing<sup>244</sup>, nickel phosphide nanosheets for non-enzymatic hydrogen peroxide ( $H_2O_2$ ) sensing<sup>245</sup> or porphyrin functionalized graphene for explosives sensing<sup>246</sup>.



Figure 1.6. Sketch of a conventional three-electrode setup composed of a working electrode (WE), counter electrode (CE) and reference electrode (RE) in a conventional electrolyte/solvent system.

In this thesis, various types of commercially available (MicruX Technologies, Oviedo, Spain), small ( $6 \text{ mm} \times 10 \text{ mm}$ ) and planar electrodes (see Figure 1.7) are used to study the electrochemical behavior of different gases. They are composed of three platinum electrodes or three gold electrodes, where the working electrode has different geometries. The metals are deposited on a glass substrate and protected with a SU-8 resin layer, giving the working electrode certain patterns (see Figure 1.7). Generally, they are divided into macro- and micro-disk electrodes, defined by the size of the working electrode. The diffusion pattern of analytes towards the electrode surface is defined by the WE dimension, where radial diffusion is dominant at micro electrodes and planar diffusion at macro electrodes. In this thesis, two out of three types of commercially available thin-film electrodes (TFEs) were used for electrochemical gas sensing experiments. TFEs have a 1 mm working electrode diameter and are considered as 'macro' electrodes with a dominant planar diffusion behavior (see Figure 1.7 top).<sup>105</sup> Microarray thin-film electrodes (MATFEs) have 91 recessed micro electrodes (10 µm diameter per micro electrode) and the diffusion behavior is mainly radial, with a small contribution of a planar diffusion inside the recession (see Figure 1.7 bottom).<sup>247-248</sup> Interdigitated array thin-film electrodes (IDAs) where two WE electrodes are interlocked like fingers (various number of pairs with adjustable electrode/gap widths) show a combination of planar and radial diffusion behavior (hemicylindrical).<sup>249</sup> It should be noted that in more viscous electrolytes, these diffusion trends could be different.



Figure 1.7. Sketch of the electrodes used for the gas sensing experiments in this thesis and comparison of diffusion patterns towards thin-film electrodes (TFEs), interdigitated array electrodes (IDAs) and microarray thin-film electrodes (MATFEs).

#### **1.4.1.5.** Electrochemical Techniques

The electrochemical techniques applied to study the electrochemical sensing of gaseous analytes in this thesis are explained in the following two sections. In cyclic voltammetry, the current is measured as a function of the applied potential, in contrast to chronoamperometry where the current is measured as a function of time at a fixed applied potential.

#### 1.4.1.5.1. Cyclic Voltammetry

In cyclic voltammetry (CV), the applied potential is swept linearly from a start potential ( $E_1$ ) to an end potential ( $E_2$ ) and reversed back to  $E_1$  while the current is recorded. The measured current vs. applied potential results in a voltammogram where the shape is a function of several factors such as concentration of analyte, size and geometry of the working electrode, mass transport, electrochemical redox mechanism of the analyte, diffusion coefficient of the analyte and scan rate, *i.e.* how fast the potential changes over time.<sup>250</sup>



Figure 1.8. Cyclic voltammetry peak shapes for a (a) reversible, (b) quasi-reversible and (c) irreversible electrochemical reaction on a macro-disk electrode.

The voltammogram usually starts at a potential where no electrochemical process and therefore no current occurs. As the potential is changing, electrons are transferred to or from the electrode and a current change is detected. The current increases until the rate of the electron transfer is limited by the diffusion of the analyte, resulting in a peak current ( $i_P$ ) for macro-disk electrodes. A further change of the applied potential results in a drop in current due to the increasing diffusion layer thickness and therefore a reduced rate of diffusion of the analyte from the bulk to the electrode. When the potential scan is reversed, the electrogenerated species is converted back to the initial analyte for reversible electrochemical reactions, where similar processes occur as previously discussed.

In the case of a fully reversible electrochemical mechanism (Figure 1.8a) with fast electron transfer kinetics, the voltammogram shows a peak-shaped behavior in the forward and the reverse scan with a peak-to-peak separation of 57/*n* mV at 298K (*n* is the number of electrons). A chemically irreversible process (Figure 1.8c), *i.e.* where the electrochemically produced species is chemically reacting (EC mechanism), only gives one peak in the forward scan and no peak-like response in the backward scan. In intermediate cases, the reaction is defined as electrochemically quasi-reversible (Figure 1.8b), where one peak is observed in the forward and one peak in the backward scan.

For a fully reversible process, the Randles-Sevcik equation (equation 1.18) gives the relationship between peak current ( $i_P$ ) and electrode area (A), diffusion coefficient (D) of the analyte as well as concentration of the analyte in the bulk phase ( $c_{bulk}$ ), scan rate (v) and number of electrons for the electrochemical process (n).<sup>251</sup> Also in the equation are Faraday's constant (F), the universal gas constant (R) and the temperature (T).

$$i_P = 0.4463 \cdot n \cdot F \cdot A \cdot c_{bulk} \cdot \left(\frac{nF\nu D}{RT}\right)^{\frac{1}{2}}$$
 1.18

A study of the change in peak current with scan rate can give information about processes occurring at the electrode as well as enabling the extraction of variables in the Randles-Sevcik equation. For quasi-reversible processes, this equation is not valid because the slower electron transfer kinetics also affect the peak current.

For electrochemically irreversible reactions with very slow kinetics, the peak current is given according to the following equation<sup>18</sup>:

$$i_P = 0.4958 \cdot F \cdot A \cdot c_{bulk} \cdot \left(\frac{\alpha F \nu D}{RT}\right)^{\frac{1}{2}}$$
 1.19

where  $\alpha$  is the charge transfer coefficient, a factor that signifies the fraction of the interfacial potential that drives the reaction at an electrode/electrolyte interface.<sup>252</sup>

For micro electrodes, such as MATFEs, the voltammogram usually shows a current plateau  $(i_S^{Ox})$  instead of a peak-like behavior as previously discussed for macro electrodes (Figure 1.9). The change from a dominant planar diffusion to radial

diffusion results in faster replenishment of the analyte due to a higher mass transport rate from the bulk to the electrode interface.<sup>250</sup>



Figure 1.9. Cyclic voltammetry response for an electrochemical reaction on a micro electrode.

It is noted that these equations were established for conventional electrolyte/solvent systems, however, room temperature ionic liquids (RTILs) often exhibit different physicochemical properties such as significantly higher viscosity values and therefore result in different transport properties. Evans *et al.* showed that the diffusion coefficients of oxygen and the reduced superoxide radical are a factor of 10 and 100, respectively, lower than in conventional solvent systems.<sup>149</sup>

#### 1.4.1.5.2. Chronoamperometry

In contrast to cyclic voltammetry where the potential is gradually changed with time, in chronoamperometry, the potential is stepped from a potential  $E_1$  where no electrochemical process happens and therefore no current is detected to a potential  $E_2$ where the analyte is either oxidized or reduced (Figure 1.10a). The current is measured as a function of time (Figure 1.10b). Short-term biasing (several seconds) of the electrode is mainly used for electroanalysis whereas long-term chronoamperometry (LTCA), where the electrode is constantly biased for several minutes to hours, is performed to check the stability of the setup and for continuous monitoring. LTCA is a harsh method which purposely can change the electrode surface and the analyte concentration. This can result in instabilities in the current response; therefore, this method is mainly used for stability tests of sensing devices. Depending on the electrode device, the Shoup and Szabo (equation 1.20)<sup>18, 253</sup> expression for microelectrodes, or the Cottrell equation (equation 1.22)<sup>18</sup> for macroelectrodes can be used to fit the chronoamperometric transients vs. time plots (Figure 1.10b) and to extract unknown variables.

$$i = 4 \cdot n \cdot F \cdot c_{\text{bulk}} \cdot D \cdot r_{\text{e}} \cdot f(\mathbf{t})$$
 1.20

Where f(t) is a dimensionless function according to:

$$f(t) = 0.7854 + 0.8863 \cdot t^{-\frac{1}{2}} + 0.2146 \cdot e^{-0.7823 \cdot t^{-\frac{1}{2}}}$$
 1.21

$$i = \frac{n \cdot F \cdot D^{\frac{1}{2}} \cdot A \cdot c_{bulk}}{\pi^{\frac{1}{2}} \cdot t^{\frac{1}{2}}}$$
 1.22

With the electrode radius ( $r_e$ ) and geometric surface area (A), diffusion coefficient (D) of the analyte as well as concentration of the analyte in the bulk phase ( $c_{bulk}$ ), number of electrons for the electrochemical process (n) and Faraday's constant (F).

This technique is usually not used to gain information about the kinetics of the electrochemical processes happening at the electrode because a potential  $E_2$ , higher than the standard potential of the electrochemical oxidation or reduction of the analyte, is usually applied.

As previously mentioned for cyclic voltammetry, the use of RTILs in chronoamperometry can also result in unexpected results, which will be discussed in the results chapters in this thesis.



Figure 1.10. (a) time (t) vs. potential (E) and (b) electrochemical current response (i) for a chronoamperometry experiment on a macro-disk electrode (red) and micro-disk electrode (black).

#### **1.4.2.** Atomic Force Microscopy

In 1986, atomic force microscopy (AFM), which is a high-resolution scanning probe microscopy technique, was invented by Binnig, Quate and Gerber.<sup>254</sup> In AFM, a mechanical tip scans over a sample surface, allowing vertical resolutions lower than 1 nm. Various surface properties such as the topography, electrical conductivity, friction, surface potential or adhesion can be measured. An atomic force microscope (see Figure 1.11) is composed of a cantilever with a sharp tip, a laser beam focused on the backside of the cantilever and reflected onto a photodiode, a light microscope and a piezo scanner that allows the precise movement of the sample. A control unit, connecting the photodiode and the piezo scanner, monitors and controls the cantilever continuously such that the laser spot is kept at the same position on the photodiode. An alternative type of AFM fixes the sample, and the cantilever is connected to the piezo scanner. Different modes are applied, depending on the information of interest, which can be found in standard literature about AFM.<sup>255</sup> In this thesis, force distance curves were measured to gain information about ionic liquid ordering at an electrified surface.



Figure 1.11. Schematic of an atomic force microscope consisting of a light microscope, a laser diode, a photodiode, a cantilever, a piezo scanner, and a control unit interfaced to a computer and an example of a force distance curve.

A complete force distance curve has an approach and retract curve. The cantilever moves towards the surface and the vertical laser deflection is recorded as a function of the z-piezo movement. At a certain distance, the so-called 'snap in' region, the cantilever tip is attracted to the surface, further approaching of the tip results in a bending of the cantilever and a steep increase in the deflection, which can be converted into a force according to Hooke's law<sup>256</sup> after calibration of the cantilever. After reaching the maximum force, the tip is slowly retracted from the surface. Due to an adhesion process, the tip may stick to the surface until the adhesion force is overcome. In this thesis, approach curves of a cantilever tip towards an electrode surface that is covered with ionic liquids, are measured. RTILs form cation and anion layers in the presence of an electric field, therefore several 'snap in' regions can be detected when the cantilever approaches and breaks through a layer.

## **1.4.3. Scanning Electron Microscopy and Energy-dispersive X**ray Spectroscopy

Scanning electron microscopy (SEM) is a characterization method that can be used to create an image by scanning a focused electron beam over a surface.<sup>257</sup> In 1937, SEM was developed by Manfred von Ardenne when the limited resolution of light microscopes became a problem.<sup>258</sup> The scanning electron microscope is based on an electron beam that is focused under vacuum onto a sample by several optical devices, *i.e.* lenses and apertures (see Figure 1.12). The interaction of the electrons with the sample results in the release of various signals that are used to obtain information about the topography and composition. Various detectors collect Auger, secondary and backscattered electrons as well as X-rays, which is usually referred to as energy dispersive X-ray spectroscopy (EDS). Transmitted and scattered electrons are used for morphological studies, which is part of transmission electron microscopy (TEM). SEM is often paired with EDS, where SEM is used to visualize the topography and EDS is used to obtain a semi-quantitative elemental composition of the sample.<sup>259</sup>

The interaction volume of the electron beam with the sample depends on the acceleration voltage of the electrons. A higher electron energy results in more information about the sample, however, it can result in melting and therefore a degradation of the specimen. The interaction of the electron beam with the electrons of the sample results in their elevation to an excited state. The return to their ground state results in the emission of X-rays, which is specific for the elements in the sample.

In this thesis, SEM is used to analyze the topography of poly(ionic liquid)/ionic liquid membranes. Additionally, EDS is used to analyze electrode surfaces after gas sensing experiments for analyzing surface modification.



Figure 1.12. Schematic of a scanning electron microscope consisting of an electron beam, an anode, two apertures, a condenser and objective lens, scan coils, a vacuum pump and a secondary electron, backscattered electron, and X-ray detector (left) and the signals that are obtained when an electron beam interacts with a sample (right).

### 1.5. Aims of Thesis

One research focus of this thesis is to determine the influence of non-ideal laboratory, *i.e.* humidified, conditions on the electrochemical gas sensing of toxic and non-toxic gases in room temperature ionic liquids. This starts with the comparison of two chosen analyte gases, *i.e.* oxygen and ammonia, where it has been shown in literature that the presence of water in humidified conditions causes a change of the electrochemical mechanism for oxygen, but not for ammonia gas. Additionally, the effect of the presence of water on the electrochemical window as a function of the ionic liquid structure will be analyzed. The studies will be performed in different room temperature ionic liquids with various cation and anion structures.

Further investigations in increasing the selectivity and sensitivity of gas sensors that will improve the ability to sense gases at concentrations below the permissible exposure limit will be conducted. Ionic liquids with various functional groups in their structures will be synthesized and the gas solubility of oxygen, hydrogen and sulfur dioxide will be measured to determine whether the gas selectivity of the electrolyte can be adjusted by changing the chemical structure of the ionic liquid. Also, various different electrodes, *i.e.* different electrode materials (platinum and gold) as well as

geometries (macro-, microarray- and interdigitated-electrodes), will be studied to further increase the gas sensing sensitivity of sulfur dioxide.

Another major aim will be to overcome the flowing nature of the ionic liquids. The sensing experiments in this thesis will be performed on planar and commercially available thin-film electrodes, however, this can be only done in an upright electrode orientation, because the liquid could easily flow off the electrode. Increasing the robustness of these type of planar devices will be attempted by the implementation of poly(ionic liquids) as electrolytes.

### 1.6. References

1. Bauer, M. A.; Utell, M. J.; Morrow, P. E.; Speers, D. M.; Gibb, F. R., Inhalation of 0.30 ppm Nitrogen Dioxide Potentiates Exercise-induced Bronchospasm in Asthmatics. *Am. Rev. Respir. Dis.* **1986**, *134*, 1203-1208.

2. Carmichael, G. R.; Streets, D. G.; Calori, G.; Amann, M.; Jacobsen, M. Z.; Hansen, J.; Ueda, H., Changing Trends in Sulfur Emissions in Asia: Implications for Acid Deposition, Air Pollution, and Climate. *Environ. Sci. Technol.* **2002**, *36*, 4707-4713.

3. McManus, N.; CIH; ROH; CSP, Oxygen: Health Effects and Regulatory Limits Part I: Physiological and Toxicological Effects of Oxygen Deficiency and Enrichment. **2009**.

4. Liu, X.; Cheng, S.; Liu, H.; Hu, S.; Zhang, D.; Ning, H., A Survey on Gas Sensing Technology. *Sensors* **2012**, *12*, 9635-9665.

5. Schmerr, L.; Song, J.-S., *Ultrasonic nondestructive evaluation systems*; Springer, 2007.

6. Changping, Z.; Minglei, S.; Yongfu, L.; Hongping, Z., Micro-concentration Detector for SF<sub>6</sub> Based on CPLD. *Chin. J. Sci. Instrum.* **2005**, *26*.

7. Toda, H.; Kobayakawa, T., High-speed gas concentration measurement using ultrasound. *Sens. Actuator A Phys.* **2008**, *144*, 1-6.

8. Petculescu, A.; Hall, B.; Fraenzle, R.; Phillips, S.; Lueptow, R. M., A prototype acoustic gas sensor based on attenuation. *J. Acoust. Soc. Am.* **2006**, *120*, 1779-1782.

9. Kim, K.-H., Performance characterization of the GC/PFPD for H<sub>2</sub>S, CH<sub>3</sub>SH, DMS, and DMDS in air. *Atmos. Environ.* **2005**, *39*, 2235-2242.

10. McNair, H. M.; Miller, J. M.; Snow, N. H., *Basic gas chromatography*; John Wiley & Sons, 2019.

11. Kulinyi, S.; Brandszájsz, D.; Amine, H.; Ádám, M.; Fürjes, P.; Bársony, I.; Dücső, C., Olfactory detection of methane, propane, butane and hexane using conventional transmitter norms. *Sens. Actuator B Chem.* **2005**, *111-112*, 286-292.

12. Tardy, P.; Coulon, J.-R.; Lucat, C.; Menil, F., Dynamic thermal conductivity sensor for gas detection. *Sens. Actuator B Chem.* **2004**, *98*, 63-68.

13. Baetz, W.; Kroll, A.; Bonow, G. In *Mobile robots with active IR-optical sensing for remote gas detection and source localization*, 2009 IEEE International Conference on Robotics and Automation, 12-17 May 2009; 2009; pp 2773-2778.

14. Chang, Y.; Hasan, D.; Dong, B.; Wei, J.; Ma, Y.; Zhou, G.; Ang, K. W.; Lee, C., All-Dielectric Surface-Enhanced Infrared Absorption-Based Gas Sensor Using Guided Resonance. *ACS Appl. Mater. Interfaces* **2018**, *10*, 38272-38279.

15. Ingle, J. D., Jr.; Crouch, S. R., *Spectrochemical analysis*; Prentice Hall College Book Division: United States, 1988.

16. Wang, C.; Yin, L.; Zhang, L.; Xiang, D.; Gao, R., Metal Oxide Gas Sensors: Sensitivity and Influencing Factors. *Sensors* **2010**, *10*, 2088-2106.

17. Wiemhöfer, H.-D.; Göpel, W., Fundamentals and principles of potentiometric gas sensors based upon solid electrolytes. *Sens. Actuator B Chem.* **1991**, *4*, 365-372.

18. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications, 2nd Edition*; John Wiley & Sons, Incorporated, 2000.

19. Fisher, A. C., *Electrode dynamics*; Oxford University Press: Oxford, New York, 1996; Vol. Oxford chemistry primers.

20. Clark, J. L. C.; Wolf, R.; Granger, D.; Taylor, Z., Continuous recording of blood oxygen tensions by polarography. *J. Appl. Physiol.* **1953**, *6*, 189-193.

21. Stetter, J. R.; Li, J., Amperometric Gas Sensors - A Review. *Chem. Rev.* 2008, *108*, 352-366.

22. Henderson, R. E., Measuring Hydrogen Sulfide. Industrial Safety & Hygiene News: 2011.

23. Welton, T., Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071-2084.

24. Buzzeo, M. C.; Hardacre, C.; Compton, R. G., Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.* **2004**, *76*, 4583-4588.

25. Giovanelli, D.; Buzzeo, M. C.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Determination of ammonia based on the electro-oxidation of hydroquinone in dimethylformamide or in the room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Talanta* **2004**, *62*, 904-911.

26. Silvester, D. S., Recent advances in the use of ionic liquids for electrochemical sensing. *Analyst* **2011**, *136*, 4871-4882.

27. Lee, J.; Hussain, G.; López-Salas, N.; MacFarlane, D. R.; Silvester, D. S., Thin films of poly(vinylidene fluoride-co-hexafluoropropylene)-ionic liquid mixtures as amperometric gas sensing materials for oxygen and ammonia. *Analyst* **2020**, *145*, 1915-1924.

28. Hussain, G.; Aldous, L.; Silvester, D. S., Preparation of platinum-based 'cauliflower microarrays' for enhanced ammonia gas sensing. *Anal. Chim. Acta* **2019**, *1048*, 12-21.

29. Lee, J.; Du Plessis, G.; Arrigan, D. W. M.; Silvester, D. S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Anal. Methods* **2015**, *7*, 7327-7335.

30. Gabriel, S.; Weiner, J., Ueber einige Abkoemmlinge des Propylamins. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 2669 - 2679.

31. Walden, P., Ueber die Molekulargroesse und elektrische Leitfaehigkeit einiger geschmolzener Salze. *Bulletin de l'Academie Imperiale des Sciences de St.-Petersbourg* 1914, 8, 405-422.

32. Hurley, F. H.; Weir, T. P., Electrodeposition of metals from fused quaternary ammonium salts. *J. Electrochem. Soc.* **1951**, *98*, 203-206.

33. Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L., Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. *Inorg. Chem.* **1982**, *21*, 1263-1264.

34. Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Graetzel, M., Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168-1178.

35. Sun, J.; MacFarlane, D. R.; Forsyth, M., Synthesis and properties of ambient temperature molten salts based on the quaternary ammonium ion. *Ionics* **1997**, *3*, 356-362.

36. Fraser, K. J.; MacFarlane, D. R., Phosphonium-Based Ionic Liquids: An Overview. *Aust. J. Chem.* **2009**, *62*, 309-321.

37. Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. J. H.; Rogers, R. D., Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. *Chem. Commun.* **2001**, *1*, 135-136.

38. Rogers, R. D.; Seddon, K. R., Ionic Liquids--Solvents of the Future? *Science* **2003**, *302*, 792-793.

39. Volland, M.; Seitz, V.; Maase, M.; Flores, M.; Papp, R.; Massonne, K.; Stegmann, V.; Halbritter, K.; Noe, R.; Bartsch, M.; Siegel, W.; Becker, M.; Huttenloch, O. Method for the separation of acids from chemical reaction mixtures by means of ionic liquids. 2003.

40. Zheng, W.; Mohammed, A.; Hines, L. G.; Xiao, D.; Martinez, O. J.; Bartsch, R. A.; Simon, S. L.; Russina, O.; Triolo, A.; Quitevis, E. L., Effect of Cation Symmetry on the Morphology and Physicochemical Properties of Imidazolium Ionic Liquids. *J. Phys. Chem. B* **2011**, *115*, 6572-6584.

41. Malvaldi, M.; Chiappe, C., From molten salts to ionic liquids: effect of ion asymmetry and charge distribution. *J. Phys.: Condens. Matter* **2008**, *20*, 035108.

42. Wasserscheid, P.; Welton, T., *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2002.

43. Dietz, M. L., Ionic Liquids as Extraction Solvents: Where do We Stand? *Sep. Sci. Technol.* **2006**, *41*, 2047-2063.

44. Lei, Z.; Dai, C.; Chen, B., Gas Solubility in Ionic Liquids. *Chem. Rev.* **2014**, *114*, 1289-1326.

45. Jimenez, A.-E.; Bermudez, M.-D., Ionic liquids as lubricants for steelaluminum contacts at low and elevated temperatures. *Tribol. Lett.* **2007**, *26*, 53-60.

46. Stolte, S.; Steudte, S.; Areitioaurtena, O.; Pagano, F.; Thoemi, J.; Stepnowski, P.; Igartua, A., Ionic liquids as lubricants or lubrication additives: An ecotoxicity and biodegradability assessment. *Chemosphere* **2012**, *89*, 1135-1141.

47. Lewandowski, A.; Swiderska-Mocek, A., Ionic liquids as electrolytes for Liion batteries—An overview of electrochemical studies. *J. Power Sources* **2009**, *194*, 601-609.

48. Nakamoto, H.; Watanabe, M., Brønsted acid-base ionic liquids for fuel cell electrolytes. *Chem. Commun.* **2007**, *24*, 2539-2541.

49. Mallakpour, S.; Dinari, M., Ionic Liquids as Green Solvents: Progress and Prospects. In *Green Solvents II: Properties and Applications of Ionic Liquids*, Mohammad, A.; Inamuddin, D., Eds. Springer Netherlands: Dordrecht, 2012; pp 1-32.
50. Barrosse-Antle, L. E.; Bond, A. M.; Compton, R. G.; O'Mahony, A. M.; Rogers, E. I.; Silvester, D. S., Voltammetry in Room Temperature Ionic Liquids: Comparisons and Contrasts with Conventional Electrochemical Solvents. *Chemistry – An Asian Journal* 2010, *5*, 202-230.

51. Parker, A. J., The effects of solvation on the properties of anions in dipolar aprotic solvents. *Q. Rev., Chem. Soc.* **1962**, *16*, 163-187.

52. Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X., Physical Properties of Ionic Liquids: Database and Evaluation. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475-1517.

53. Anwar, N.; Riyazuddeen; Yasmeen, S., Volumetric, compressibility and viscosity studies of binary mixtures of [EMIM][NTf<sub>2</sub>] with ethylacetate/methanol at (298.15–323.15) K. *J. Mol. Liq.* **2016**, *224*, 189-200.

54. Bansal, S.; Kaur, N.; Chaudhary, G. R.; Mehta, S. K.; Ahluwalia, A. S., Physiochemical Properties of New Formulations of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide with Tritons. *J. Chem. Eng. Data* **2014**, *59*, 3988-3999.

55. Dzyuba, S. V.; Bartsch, R. A., Influence of Structural Variations in 1-Alkyl(aralkyl)-3-Methylimidazolium Hexafluorophosphates and Bis(trifluoromethyl-sulfonyl)imides on Physical Properties of the Ionic Liquids. *ChemPhysChem* **2002**, *3*, 161-166.

56. Andanson, J. M.; Meng, X.; Traïkia, M.; Husson, P., Quantification of the impact of water as an impurity on standard physico-chemical properties of ionic liquids. *J. Chem. Thermodynamics* **2016**, *94*, 169-176.

57. Kanakubo, M.; Harris, K. R.; Tsuchihashi, N.; Ibuki, K.; Ueno, M., Temperature and Pressure Dependence of the Electrical Conductivity of 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide. *J. Chem. Eng. Data* **2015**, *60*, 1495-1503.

58. Widegren, J. A.; Magee, J. W., Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* **2007**, *52*, 2331-2338.

59. Nazet, A.; Sokolov, S.; Sonnleitner, T.; Makino, T.; Kanakubo, M.; Buchner, R., Densities, Viscosities, and Conductivities of the Imidazolium Ionic Liquids [Emim][Ac], [Emim][FAP], [Bmim][BETI], [Bmim][FSI], [Hmim][TFSI], and [Omim][TFSI]. *J. Chem. Eng. Data* **2015**, *60*, 2400-2411.

60. Gómez, E.; Calvar, N.; Domínguez, Á.; A. Macedo, E., Thermal Analysis and Heat Capacities of 1-Alkyl-3-methylimidazolium Ionic Liquids with  $NTf_2^-$ , TFO<sup>-</sup>, and DCA<sup>-</sup> Anions. *Ind. Eng. Chem. Res.* **2013**, *52*, 2103-2110.

61. Tariq, M.; Carvalho, P. J.; Coutinho, J. A. P.; Marrucho, I. M.; Canongia Lopes, J. N.; Rebelo, L. P. N., Viscosity of  $(C_2-C_{14})$  1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids in an extended temperature range. *Fluid Phase Equilib.* **2011**, *301*, 22-32.

62. Neves, C. M. S. S.; Kurnia, K. A.; Coutinho, J. A. P.; Marrucho, I. M.; Canongia Lopes, J. N.; Freire, M. G.; Rebelo, L. P. N., Systematic Study of the Thermophysical Properties of Imidazolium-Based Ionic Liquids with Cyano-Functionalized Anions. *J. Phys. Chem. B* **2013**, *117*, 10271-10283.

63. Stoppa, A.; Hunger, J.; Buchner, R., Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, *54*, 472-479.

64. Noda, A.; Hayamizu, K.; Watanabe, M., Pulsed-Gradient Spin–Echo <sup>1</sup>H and <sup>19</sup>F NMR Ionic Diffusion Coefficient, Viscosity, and Ionic Conductivity of Non-Chloroaluminate Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2001**, *105*, 4603-4610.

65. Vila, J.; Fernández-Castro, B.; Rilo, E.; Carrete, J.; Domínguez-Pérez, M.; Rodríguez, J. R.; García, M.; Varela, L. M.; Cabeza, O., Liquid–solid–liquid phase transition hysteresis loops in the ionic conductivity of ten imidazolium-based ionic liquids. *Fluid Phase Equilib.* **2012**, *320*, 1-10.

66. Páez, M. S.; Vega, Y. A.; Romero, C. M., Effect of temperature on the viscosities and the volumetric properties of the binary mixtures of the ionic liquids [bmim][PF<sub>6</sub>] and [bmim][CF<sub>3</sub>SO<sub>3</sub>]. *J. Mol. Liq.* **2017**, *243*, 78-84.

67. Widegren, J. A.; Saurer, E. M.; Marsh, K. N.; Magee, J. W., Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. *J. Chem. Thermodynamics* **2005**, *37*, 569-575.

68. Tariq, M.; Forte, P. A. S.; Costa Gomes, M. F.; Canongia Lopes, J. N.; Rebelo, L. P. N., Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: Effect of temperature, alkyl chain length, and anion. *J. Chem. Thermodynamics* **2009**, *41*, 790-798.

69. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D., Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation *Green Chem.* **2001**, *3*, 156-164.

70. Safarov, J.; Lesch, F.; Suleymanli, K.; Aliyev, A.; Shahverdiyev, A.; Hassel, E.; Abdulagatov, I., Viscosity, Density, Heat Capacity, Speed of Sound and Other Derived Properties of 1-Butyl-3-Methylimidazolium tris(Pentafluoroethyl) Trifluorophosphate over a Wide Range of Temperature and at Atmospheric Pressure. *J. Chem. Eng. Data* **2017**, *62*, 3620-3631.

71. Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M., How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593-19600.

72. Santos, Â. F. S.; Moita, M.-L. C. J.; Silva, J. F. C. C.; Lampreia, I. M. S., Volumetric and sound speed study of ammonium-based ionic liquid mixtures with ethanol. *J. Chem. Thermodynamics* **2017**, *104*, 118-127.

73. Sun, J.; Forsyth, M.; MacFarlane, D. R., Room-Temperature Molten Salts Based on the Quaternary Ammonium Ion. *J. Phys. Chem. B* **1998**, *102*, 8858-8864.

74. Kilaru, P.; Baker, G. A.; Scovazzo, P., Density and Surface Tension Measurements of Imidazolium-, Quaternary Phosphonium-, and Ammonium-Based Room-Temperature Ionic Liquids: Data and Correlations. *J. Chem. Eng. Data* **2007**, *52*, 2306-2314.

75. Le, M. L. P.; Tran, N. A.; Ngo, H. P. K.; Nguyen, T. G.; Tran, V. M., Liquid Electrolytes Based on Ionic Liquids for Lithium-Ion Batteries. *J. Solution Chem.* **2015**, *44*, 2332-2343.

76. Machanová, K.; Boisset, A.; Sedláková, Z.; Anouti, M.; Bendová, M.; Jacquemin, J., Thermophysical Properties of Ammonium-Based

Bis{(trifluoromethyl)sulfonyl}imide Ionic Liquids: Volumetric and Transport Properties. J. Chem. Eng. Data 2012, 57, 2227-2235.

77. Machanová, K.; Troncoso, J.; Jacquemin, J.; Bendová, M., Excess molar volumes and excess molar enthalpies in binary systems N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imide+methanol. *Fluid Phase Equilib.* **2014**, *363*, 156-166.

78. MacFarlane, D. R.; Meakin, P.; Amini, N.; Forsyth, M., Structural studies of ambient temperature plastic crystal ion conductors. *J. Phys. Condens. Matter* **2001**, *13*, 8257-8267.

79. Seki, S.; Serizawa, N.; Ono, S.; Takei, K.; Hayamizu, K.; Tsuzuki, S.; Umebayashi, Y., Densities, Viscosities, and Refractive Indices of Binary Room-Temperature Ionic Liquids with Common Cations/Anions. *J. Chem. Eng. Data* **2019**, *64*, 433-441.

80. Vranes, M.; Dozic, S.; Djeric, V.; Gadzuric, S., Physicochemical Characterization of 1-Butyl-3-methylimidazolium and 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2012**, *57*, 1072-1077.

81. Gaciño, F. M.; Regueira, T.; Lugo, L.; Comuñas, M. J. P.; Fernández, J., Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 4984-4999.

82. Fletcher, S. I.; Sillars, F. B.; Hudson, N. E.; Hall, P. J., Physical Properties of Selected Ionic Liquids for Use as Electrolytes and Other Industrial Applications. *J. Chem. Eng. Data* **2010**, *55*, 778-782.

83. Domańska, U.; Lukoshko, E. V.; Królikowski, M., Phase behaviour of ionic liquid 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate with alcohols, water and aromatic hydrocarbons. *Fluid Phase Equilib.* **2013**, *345*, 18-22.

84. Harris, K. R.; Kanakubo, M.; Kodama, D.; Makino, T.; Mizuguchi, Y.; Watanabe, M.; Watanabe, T., Temperature and Density Dependence of the Transport Properties of the Ionic Liquid Triethylpentylphosphonium Bis(trifluoromethanesulfonyl)amide, [P<sub>222,5</sub>][Tf<sub>2</sub>N]. *J. Chem. Eng. Data* **2018**, *63*, 2015-2027.

85. Neves, C. M. S. S.; Carvalho, P. J.; Freire, M. G.; Coutinho, J. A. P., Thermophysical properties of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids. *J. Chem. Thermodynamics* **2011**, *43*, 948-957.

86. Gaciño, F. M.; Regueira, T.; Bolotov, A. V.; Sharipov, A.; Lugo, L.; Comuñas,
M. J. P.; Fernández, J., Volumetric behaviour of six ionic liquids from T=(278 to 398)K and up to 120MPa. *J. Chem. Thermodynamics* 2016, *93*, 24-33.

87. Nazet, A.; Sokolov, S.; Sonnleitner, T.; Friesen, S.; Buchner, R., ;, Densities, Refractive Indices, Viscosities, and Conductivities of Non-Imidazolium Ionic Liquids [Et<sub>3</sub>S][TFSI], [Et<sub>2</sub>MeS][TFSI], [BuPy][TFSI],[N<sub>8881</sub>][TFA], and [P<sub>14</sub>][DCA]. *J. Chem. Eng. Data* **2017**, *62*, 2549-2561.

88. Domańska, U.; Królikowski, M.; Zawadzki, M.; Wróblewska, A., Phase equilibrium investigation with ionic liquids and selectivity in separation of 2-phenylethanol from water. *J. Chem. Thermodynamics* **2016**, *102*, 357-366.

89. Paduszynski, K.; Domanska, U., Viscosity of Ionic Liquids: An Extensive Database and a New Group Contribution Model Based on a Feed-Forward Artificial Neural Network. *J. Chem. Inf. Model.* **2014**, *54*, 1311-1324.

90. Jiang, S.; Hu, Y.; Wang, Y.; Wang, X., Viscosity of Typical Room-Temperature Ionic Liquids: A Critical Review. *J. Phys. Chem. Ref. Data* **2019**, *48*.

91. Gacino, F. M.; Regueira, T.; Lugo, L.; Comunas, M. J. P.; Fernandez, J., Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 4984-4999.

92. Harris, K. R.; Woolf, L. A.; Kanakubo, M., Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777-1782.

93. Korson, L.; Drost-Hansen, W.; Millero, F. J., Viscosity of water at various temperatures. *J. Phys. Chem.* **1969**, *73*, 34-39.

94. Maiti, A.; Kumar, A.; Rogers, R. D., Water-clustering in hygroscopic ionic liquids—an implicit solvent analysis. *Phys. Chem. Chem. Phys.* 2012, *14*, 5139-5146.
95. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* 2008, *53*, 2884-2891.

96. Zhou, T.; Chen, L.; Ye, Y.; Chen, L.; Qi, Z.; Freund, H.; Sundmacher, K., An Overview of Mutual Solubility of Ionic Liquids and Water Predicted by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 6256-6264.

97. Lide, D. R., *CRC Handbook of Chemistry and Physics*: Boca Raton, FL, 2004.
98. Golnabi, H.; Matloob, M. R.; Bahar, M.; Sharifian, M., Investigation of electrical conductivity of different water liquids and electrolyte solutions. *Iran. Phys. J.* 2009, *3*, 24-28.

99. Noda, A.; Hayamizu, K.; Watanabe, M., Pulsed-Gradient Spin–Echo <sup>1</sup>H and <sup>19</sup>F NMR Ionic Diffusion Coefficient, Viscosity, and Ionic Conductivity of Non-Chloroaluminate Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2001**, *105*, 4603-4610.

100. Miran, M. S.; Kinoshita, H.; Yasuda, T.; Susan, M. A. B. H.; Watanabe, M., Hydrogen bonds in protic ionic liquids and their correlation with physicochemical properties. *Chem. Commun.* **2011**, *47*, 12676-12678.

101. MacFarlane, D. R.; Sun, J.; Golding, J.; Meakin, P.; Forsyth, M., High conductivity molten salts based on the imide ion. *Electrochim. Acta* **2000**, *45*, 1271-1278.

102. Chaban, V. V.; Voroshylova, I. V.; Kalugin, O. N.; Prezhdo, O. V., Acetonitrile Boosts Conductivity of Imidazolium Ionic Liquids. *J. Phys. Chem. B* **2012**, *116*, 7719-7727.

103. Polcari, D.; Dauphin-Ducharme, P.; Mauzeroll, J., Scanning Electrochemical Microscopy: A Comprehensive Review of Experimental Parameters from 1989 to 2015. *Chem. Rev.* **2016**, *116*, 13234-13278.

104. Zhao, C.; Burrell, G.; Torriero, A. A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R.; Bond, A. M., Electrochemistry of Room Temperature Protic Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 6923-6936.

105. Bard, A. J.; Faulkner, L. R., *Electrochemical methods : fundamentals and applications*; Wiley: New York, 1980.

106. Suarez, P. A. Z.; Selbach, V. M.; Dullius, J. E. L.; Einloft, S.; Piatnicki, C. M. S.; Azambuja, D. S.; de Souza, R. F.; Dupont, J., Enlarged electrochemical window in dialkyl-imidazolium cation based room-temperature air and water-stable molten salts. *Electrochim. Acta* **1997**, *42*, 2533-2535.

107. De Vos, N.; Maton, C.; Stevens, C. V., Electrochemical Stability of Ionic Liquids: General Influences and Degradation Mechanisms. *ChemElectroChem* **2014**, *1*, 1258-1270.

108. Lane, G. H., Electrochemical reduction mechanisms and stabilities of some cation types used in ionic liquids and other organic salts. *Electrochim. Acta* **2012**, *83*, 513-528.

109. Howlett, P. C.; Izgorodina, E. I.; Forsyth, M.; MacFarlane, D. R., Electrochemistry at negative potentials in bis (trifluoromethanesulfonyl) amide ionic liquids. *Z. Phys. Chem.* **2006**, *220*, 1483-1498.

110. Ignat'ev, N. V.; Welz-Biermann, U.; Kucheryna, A.; Bissky, G.; Willner, H., New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions. *J. Fluor. Chem.* **2005**, *126*, 1150-1159.

111. Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J., Synthesis and physical-chemical properties of ionic liquids based on 1-n-butyl-3-methylimidazolium cation. *J. Chim. Phys.* **1998**, *95*, 1626-1639.

112. Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L., Properties of 1,3dialkylimidazolium chloride-aluminum chloride ionic liquids. 2. Phase transitions, densities, electrical conductivities, and viscosities. *J. Phys. Chem.* **1984**, *88*, 2614-2621.

113. Maton, C.; De Vos, N.; Stevens, C. V., Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools. *Chem. Soc. Rev.* **2013**, *42*, 5963-5977. 114. Chan, B. K. M.; Chang, N.; Grimmett, M. R., The synthesis and thermolysis of imidazole quaternary salts. *Aust. J. Chem.* **1977**, *9*, 2005-2013.

115. Chowdhury, A.; Thynell, S. T., Confined rapid thermolysis/FTIR/ToF studies of imidazolium-based ionic liquids. *Thermochim. Acta* **2006**, *443*, 159-172.

116. Soltani, M.; McGeehee, J. L.; Stenson, A. C.; O'Brien, R. A.; Duranty, E. R.; Salter, E. A.; Wierzbicki, A.; Glover, T. G.; Davis, J. H., Ionic liquids of superior thermal stability. Validation of  $PPh_4^+$  as an organic cation of impressive thermodynamic durability. *RSC Adv.* **2020**, *10*, 20521-20528.

117. Chen, Y.; Mu, T., Thermal Stability of Ionic Liquids. In *Encyclopedia of Ionic Liquids*, Zhang, S., Ed. Springer Singapore: Singapore, 2019; pp 1-13.

118. Yokozeki, A.; Shiflett, M. B.; Junk, C. P.; Grieco, L. M.; Foo, T., Physical and Chemical Absorptions of Carbon Dioxide in Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2008**, *51*, 16654-16663.

119. Stevanovic, S.; Podgorsek, A.; Padua, A. A. H.; Costa Gomes, M. F., Effect of Water on the Carbon Dioxide Absorption by 1-Alkyl-3-methylimidazolium Acetate Ionic Liquids. *J. Phys. Chem. B* **2012**, *116*, 14416-14425.

120. Giernoth, R., Task-Specific Ionic Liquids. Angew. Chem. Int. Ed. 2010, 49, 2834-2839.

121. Kermanioryani, M.; Abdul Mutalib, M. I.; Gonfa, G.; El-Harbawi, M.; Mazlan, F. A.; Lethesh, K. C.; Leveque, J.-M., Using tunability of ionic liquids to remove methylene blue from aqueous solution. *J. Environ. Chem. Eng.* **2016**, *4*, 2327-2332.

122. Sasikumar, B.; Arthanareeswaran, G.; Ismail, A. F., Recent progress in ionic liquid membranes for gas separation. *J. Mol. Liq.* **2018**, *266*, 330-341.

123. Cserjési, P.; Nemestóthy, N.; Bélafi-Bakó, K., Gas separation properties of supported liquid membranes prepared with unconventional ionic liquids. *J. Membr. Sci.* **2010**, *349*, 6-11.

124. Wasserscheid, P.; Keim, W., Ionic Liquids-New "Solutions" for Transition Metal Catalysis. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789.

125. Haumann, M.; Riisager, A., Hydroformylation in Room Temperature Ionic Liquids (RTILs): Catalyst and Process Developments. *Chem. Rev.* **2008**, *108*, 1474-1497.

126. Gębicki, J.; Kloskowski, A.; Chrzanowski, W.; Stepnowski, P.; Namiesnik, J., Application of Ionic Liquids in Amperometric Gas Sensors. *Crit. Rev. Anal. Chem.* **2016**, *46*, 122-138.

127. Shiflett, M. B.; Maginn, E. J., The Solubility of Gases in Ionic Liquids. *AlChE J.* **2017**, *63*, 4722-4737.

128. Jacquemin, J.; Costa Gomes, M. F.; Husson, P.; Majer, V., Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283K and 343K and at pressures close to atmospheric. *J. Chem. Thermodyn.* **2006**, *38*, 490-502.

129. Huang, J.; Riisager, A.; Berg, R. W.; Fehrmann, R., Tuning ionic liquids for high gas solubility and reversible gas sorption. *J. Mol. Catal. A Chem.* **2008**, *279*, 170-176.

130. Bernal, J. D., The structure of liquids. *Proc. R. Soc. London, Ser. A* **1964**, *280*, 299-322.

131. Weingärtner, H.; Merkel, T.; Käshammer, S.; Schröer, W.; Wiegand, S., The Effect of Short-Range Hydrogen-Bonded Interactions on the Nature of the Critical Point of Ionic Fluids. Part I: General Properties of the New System Ethylammonium Nitrate+n-Octanol with an Upper Consolute Point Near Room Temperature. *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 970-975.

132. Schroeder U., W. J. D., Compton R. G., Marken F., Suarez P. A. Z., Consorti C. S., de Souza R. F., Dupon J., Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphaye ionic liquids. *New J. Chem* **2000**, *24*, 1009-1015.

133. Canongia Lopes, J. N. A.; Padua, A. A. H., Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330-3335.

134. Wang, Y., Disordering and Reordering of Ionic Liquids under an External Electric Field. *J. Phys. Chem. B* **2009**, *113*, 11058-11060.

135. Xie, G.; Luo, J.; Guo, D.; Liu, S., Nanoconfined ionic liquids under electric fields *Appl. Phys. Lett.* **2010**, *96*, 043112.

136. Dong, Y., Effect of alkyl chain length on interfacial structure of imidazoliumbased tetrafluoroborate ionic liquids on Au(100) electrodes. *Mater. Res. Express* **2020**, 7, 075010.

137. Wang, Z.; Sun, Y.; Mao, Y.; Zhang, F.; Zheng, L.; Fu, D.; Shen, Y.; Hu, J.; Dong, H.; Xu, J.; Wu, X., Highly concentrated dual-anion electrolyte for non-flammable high-voltage Li-metal batteries. *Energy Storage Mater.* 2020, *30*, 228-237.
138. Sun, H.; Zhu, G.; Zhu, Y.; Lin, M.-C.; Chen, H.; Li, Y.-Y.; Hung, W. H.; Zhou, B.; Wang, X.; Bai, Y.; Gu, M.; Huang, C.-L.; Tai, H.-C.; Xu, X.; Angell, M.; Shyue, J.-J.; Dai, H., High-Safety and High-Energy-Density Lithium Metal Batteries in a Novel Ionic-Liquid Electrolyte. *Adv. Mater.* 2020, *32*, 2001741.

139. Rehman, A.; Zeng, X., Interfacial composition, structure, and properties of ionic liquids and conductive polymers for the construction of chemical sensors and biosensors: a perspective. *Curr. Opin. Electrochem.* **2020**, *23*, 47-56.

140. Li, H.; Endres, F.; Atkin, R., Effect of alkyl chain length and anion species on the interfacial nanostructure of ionic liquids at the Au(111)-ionic liquid interface as a function of potential. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14624-14633.

141. Hayes, R.; Borisenko, N.; Tam, M. K.; Howlett, P. C.; Endres, F.; Atkin, R., Double Layer Structure of Ionic Liquids at the Au(111) Electrode Interface: An Atomic Force Microscopy Investigation. *J. Phys. Chem. C* **2011**, *115*, 6855-6863.

142. Perkin, S., Ionic liquids in confined geometries. *Phys. Chem. Chem. Phys.* 2012, *14*, 5052-5062.

143. Lauw, Y.; Rodopoulos, T.; Gross, M.; Nelson, A.; Gardner, R.; Horne, D., Electrochemical cell for neutron reflectometry studies of the structure of ionic liquids at electrified interface. *Rev. Sci. Instrum.* **2010**, *81*, 074101.

144. Rivera-Rubero, S.; Baldelli, S., Surface Spectroscopy of Room-Temperature Ionic Liquids on a Platinum Electrode: A Sum Frequency Generation Study. *J. Phys. Chem. B* **2004**, *108*, 15133-15140.

145. Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T., Interfacial Structure at the quaternary Ammonium-Based Ionic Liquid/Gold Electrode Interface Probed by Surface-Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior. *J. Phys. Chem. C* **2017**, *121*, 1658-1666.

146. Fedorov, M. V.; Konrnyshev, A. A., Ionic Liquids at Electrified Interfaces. *Chem. Rev.* **2014**, *114*, 2978-3036.

147. Evans, R. G.; Klymenko, O. V.; Price, P. D.; Davies, S. G.; Hardacre, C.; Compton, R. G., A Comparative Electrochemical Study of Diffusion in Room Temperature Ionic Liquid Solvents versus Acetonitrile. *ChemPhysChem* **2005**, *6*, 526-533.

148. Evans, R. G.; Wain, A. J.; Hardacre, C.; Compton, R. G., An Electrochemical and ESR Spectroscopic Study on the Molecular Dynamics of TEMPO in Room Temperature Ionic Liquid Solvents. *ChemPhysChem* **2005**, *6*, 1035-1039.

149. Evans, R. G.; Klymenko, O. V.; Saddoughi, S. A.; Hardacre, C.; Compton, R.G., Electroreduction of Oxygen in a Series of Room Temperature Ionic Liquids

Composed of Group 15-Centered Cations and Anions. J. Phys. Chem. B 2004, 108, 7878-7886.

150. Graves, A. D.; Inman, D., The electrical double layer in molten salts: Part 2. The double-layer capacitance. *J. Electroanal. Chem.* **1970**, *25*, 357-372.

151. Lewandowski, A.; Galiński, M., Carbon–ionic liquid double-layer capacitors. *J. Phys. Chem. Solids* **2004**, *65*, 281-286.

152. Nanjundiah, C.; McDevitt, S. F.; Koch, V. R., Differential Capacitance Measurements in Solvent-Free Ionic Liquids at Hg and C Interfaces. *J. Electrochem. Soc.* **1997**, *144*, 3392-3397.

153. Wang, Z.; Lin, P.; Baker, G. A.; Stetter, J.; Zeng, X., Ionic Liquids as Electrolytes for the Development of a Robust Amperometric Oxygen Sensor. *Anal. Chem.* **2011**, *83*, 7066-7073.

154. Li, Z.; Jiang, J.; Lei, G.; Gao, D., Gel polymer electrolyte prepared by in situ polymerization of MMA monomers in room temperature ionic liquid. *Polym. Adv. Technol.* **2006**, *17*, 604-607.

155. Ramesh, S.; Liew, C.-W.; Ramesh, K., Evaluation and investigation on the effect of ionic liquid onto PMMA-PVC gel polymer blend electrolytes. *J. Non-Cryst. Solids* **2011**, *357*, 2132-2138.

156. Song, J. Y.; Wang, Y. Y.; Wan, C. C., Review of gel-type polymer electrolytes for lithium-ion batteries. *J. Power Sources* **1999**, *77*, 183-197.

157. Bohnke, O.; Frand, G.; Rezrazi, M.; Rousselot, C.; Truche, C., Fast ion transport in new lithium electrolytes gelled with PMMA. 1. Influence of polymer concentration. *Solid State Ion.* **1993**, *66*, 97-104.

158. Feuillade, G.; Perche, P., Ion-conductive macromolecular gels and membranes for solid lithium cells. *J. Appl. Electrochem.* **1975**, *5*, 63-69.

159. Singh, P. K.; Kim, K.-W.; Park, N.-G.; Rhee, H.-W., Mesoporous nanocrystalline TiO<sub>2</sub> electrode with ionic liquid-based solid polymer electrolyte for dye-sensitized solar cell application. *Synth. Met.* **2008**, *158*, 590-593.

160. Fernicola, A.; Panero, S.; Scrosati, B.; Tamada, M.; Ohno, H., New Types of Brönsted Acid–Base Ionic Liquids-Based Membranes for Applications in PEMFCs. *ChemPhysChem* **2007**, *8*, 1103-1107.

161. Nádherná, M.; Opekar, F.; Reiter, J., Ionic liquid–polymer electrolyte for amperometric solid-state NO<sub>2</sub> sensor. *Electrochim. Acta* **2011**, *56*, 5650-5655.

162. Fort, A.; Lotti, C.; Mugnaini, M.; Palombari, R.; Rocchi, S.; Vignoli, V., A two electrode C–NiO Nafion amperometric sensor for NO<sub>2</sub> detection. *Microelectron. J.* **2009**, *40*, 1308-1312.

163. Amanchukwu C.V., H. J. R., Shao-Horn Y., Hammond P. T., Understanding the Chemical Stability of Polymer for Lithium-Air Batteries. *Chem. Mater.* **2015**, *27*, 550-561.

164. Hirao, M.; Ito, K.; Ohno, H., Preparation and polymerization of new organic molten salts; N-alkylimidazolium salt derivatives. *Electrochim. Acta* **2000**, *45*, 1291-1294.

165. Yoshizawa, M.; Ogihara, W.; Ohno, H., Novel polymer electrolytes prepared by copolymerization of ionic liquid monomers. *Polym. Adv. Technol.* **2002**, *13*, 589-594.

166. Yoshizawa, M.; Hirao, M.; Ito-Akita, K.; Ohno, H., Ion conduction in zwitterionic-type molten salts and their polymers. *J. Mater. Chem.* **2001**, *11*, 1057-1062.

167. Ogihara, W.; Washiro, S.; Nakajima, H.; Ohno, H., Effect of cation structure on the electrochemical and thermal properties of ion conductive polymers obtained from polymerizable ionic liquids. *Electrochim. Acta* **2006**, *51*, 2614-2619.

168. Nakajima, H.; Ohno, H., Preparation of thermally stable polymer electrolytes from imidazolium-type ionic liquid derivatives. *Polymer* **2005**, *46*, 11499-11504.

169. Ohno, H., Design of Ion Conductive Polymers Based on Ionic Liquids. *Macromol. Symp.* 2007, 249-250, 551-556.

170. Tang, J.; Sun, W.; Tang, H.; Radosz, M.; Shen, Y., Enhanced CO<sub>2</sub> absorption of poly(ionic liquid)s. *Macromolecules* **2005**, *38*, 2037-2039.

171. Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D., Improving CO<sub>2</sub> permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid. *Polym. Adv. Technol.* **2008**, *19*, 1415-1420.

172. Zhao, Q.; Anderson, J. L., Highly selective GC stationary phases consisting of binary mixtures of polymeric ionic liquids. *J. Sep. Sci.* **2010**, *33*, 79-87.

173. López, M. S. P.; Mecerreyes, D.; López-Cabarcos, E.; López-Ruiz, B., Amperometric glucose biosensor based on polymerized ionic liquid microparticles. *Biosens. Bioelectron.* **2006**, *21*, 2320-2328.

174. Zhang, Q.; Lv, X.; Qiao, Y.; Zhang, L.; Liu, D.-L.; Zhang, W.; Han, G.-X.; Song, X.-M., Direct Electrochemistry and Electrocatalysis of Hemoglobin Immobilized in a Polymeric Ionic Liquid Film. *Electroanalysis* 2010, *22*, 1000-1004.
175. Döbbelin, M.; Jovanovski, V.; Llarena, I.; Claros Marfil, L. J.; Cabañero, G.; Rodriguez, J.; Mecerreyes, D., Synthesis of paramagnetic polymers using ionic liquid chemistry. *Polym. Chem.* 2011, *2*, 1275-1278.

176. Kim, D. W.; Chi, D. Y., Polymer-Supported Ionic Liquids: Imidazolium Salts as Catalysts for Nucleophilic Substitution Reactions Including Fluorinations. *Angew. Chem. Int. Ed.* **2004**, *43*, 483-485.

177. Li, Y.; Li, G.; Wang, X.; Zhu, Z.; Ma, H.; Zhang, T.; Jin, J., Poly(ionic liquid)-wrapped single-walled carbon nanotubes for sub-ppb detection of CO<sub>2</sub>. *Chem. Commun.* **2012**, *48*, 8222-8224.

178. Willa, C.; Yuan, J.; Niederberger, M.; Koziej, D., When Nanoparticles Meet Poly(Ionic Liquid)s: Chemoresistive CO<sub>2</sub> Sensing at Room Temperature. *Adv. Funct. Mater.* **2015**, *25*, 2537-2542.

179. Zhang, Q.; Wu, S.; Zhang, L.; Lu, J.; Verproot, F.; Liu, Y.; Xing, Z.; Li, J.; Song, X.-M., Fabrication of polymeric ionic liquid/graphene nanocomposite for glucose oxidase immobilization and direct electrochemistry. *Biosens. Bioelectron.* **2011**, *26*, 2632-2637.

180. Lee, S.; Ringstrand, B. S.; Stone, D. A.; Firestone, M. A., Electrochemical Activity of Glucose Oxidase on a Poly(ionic liquid)–Au Nanoparticle Composite. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2311-2317.

181. Mao, H.; Liang, J.; Zhang, H.; Pei, Q.; Liu, D.; Wu, S.; Zhang, Y.; Song, X.-M., Poly(ionic liquids) functionalized polypyrrole/graphene oxide nanosheets for electrochemical sensor to detect dopamine in the presence of ascorbic acid. *Biosens. Bioelectron.* **2015**, *70*, 289-298.

182. Zhao, Q.; Yin, M.; Zhang, A. P.; Prescher, S.; Antonietti, M.; Yuan, J., Hierarchically Structured Nanoporous Poly(Ionic Liquid) Membranes: Facile Preparation and Application in Fiber-Optic pH Sensing. *J. Am. Chem. Soc.* **2013**, *135*, 5549-5552.

183. Hu, X.; Huang, J.; Zhang, W.; Li, M.; Tao, C.; Li, G., Photonic Ionic Liquids Polymer for Naked-Eye Detection of Anions. *Adv. Mater.* **2008**, *20*, 4074-4078.

184. Huang, J.; Tao, C.; An, Q.; Zhang, W.; Wu, Y.; Li, X.; Shen, D.; Li, G., 3D-ordered macroporous poly(ionic liquid) films as multifunctional materials. *Chem. Commun.* **2010**, *46*, 967-969.

185. Wang, Z.; Si, Y.; Zhao, C.; Yu, D.; Wang, W.; Sun, G., Flexible and Washable Poly(Ionic Liquid) Nanofibrous Membrane with Moisture Proof Pressure Sensing for Real-Life Wearable Electronics. *ACS Appl. Mater. Interfaces* 2019, *11*, 27200-27209.
186. Yeager, E., Dioxygen electrocatalysis: mechanisms in relation to catalyst structure. *J. Mol. Catal.* 1986, *38*, 5-25.

187. Song, C.; Zhang, J., Electrocatalytic Oxygen Reduction Reaction. In *PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and Applications*, Zhang, J., Ed. Springer London: London, 2008; pp 89-134.

188. Parthasarathy, A.; Srinivasan, S.; Appleby, A. J.; Martin, C., Temperature dependence of the electrode kinetics of oxygen reduction at the platinum/Nafion interface - A microelectrode investigation. *J. Electrochem. Soc.* 1992, *139*, 2530-2537.
189. Antoine, O.; Bultel, Y.; Durand, R., Oxygen reduction reaction kinetics and mechanism on platinum nanoparticles inside Nafion®. *J. Electroanal. Chem.* 2001, *499*, 85-94.

190. Shih, Y.-H.; Sagar, G. V.; Lin, S. D., Effect of Electrode Pt Loading on the Oxygen Reduction Reaction Evaluated by Rotating Disk Electrode and Its Implication on the Reaction Kinetics. *J. Phys. Chem. C* **2008**, *112*, 123-130.

191. Meng, H.; Shen, P. K., Tungsten Carbide Nanocrystal Promoted Pt/C Electrocatalysts for Oxygen Reduction. J. Phys. Chem. B 2005, 109, 22705-22709.

192. Stassi, A.; D'urso, C.; Baglio, V.; Di Blasi, A.; Antonucci, V.; Arico, A. S.; Castro Luna, A. M.; Bonesi, A.; Triaca, W. E., Electrocatalytic behaviour for oxygen reduction reaction of small nanostructured crystalline bimetallic Pt–M supported catalysts. *J. Appl. Electrochem.* **2006**, *36*, 1143-1149.

193. González-Huerta, R. G.; Chávez-Carvayar, J. A.; Solorza-Feria, O., Electrocatalysis of oxygen reduction on carbon supported Ru-based catalysts in a polymer electrolyte fuel cell. *J. Power Sources* **2006**, *153*, 11-17.

194. Barnes, A. S.; Rogers, E. I.; Streeter, I.; Aldous, L.; Hardacre, C.; Wildgoose, G. G.; Compton, R. G., Unusual Voltammetry of the Reduction of O<sub>2</sub> in

 $[C_4 dmim][N(Tf)_2]$  Reveals a Strong Interaction of  $O_2^{-}$  with the  $[C_4 dmim]^+$  Cation. J. *Phys. Chem. C* **2008**, *112*, 13709-13715.

195. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Tan, X. M., Electrochemical reduction of dioxygen in Bis(trifluoromethylsulfonyl)imide based ionic liquids. *J. Electroanal. Chem.* **2011**, *657*, 150-157.

196. Yuan, X.-Z.; Alzate, V.; Xie, Z.; Ivey, D. G.; Qu, W., Oxygen Reduction Reaction in 1-Butyl-1-methyl-pyrrolidinium Bis(trifluoromethanesulfonyl)imide: Addition of Water as a Proton Species. *J. Electrochem. Soc.* **2014**, *161*, A451-A457.

197. Haber, F.; van Oordt, G., Ueber die Bildung von Ammoniak aus den Elementen. Z. Anorg. Chem. 1905, 44, 341-378.

198. Norenberg, M. D.; Rama Rao, K. V.; Jayakumar, A. R., Ammonia Neurotoxicity and the Mitochondrial Permeability Transition. *J. Bioenerg. Biomembr.* **2004**, *36*, 303-307.

199. Kristensen, H. H.; Wathes, C. M., Ammonia and poultry welfare: a review. *World's Poultry Science Journal* **2000**, *56*, 235-245.

200. Husain, D.; Norrish, R. G. W., The explosive oxidation of ammonia and hydrazine studied by kinetic spectroscopy. *Proc. R. Soc. Lond. A* **1962**, *273*, 145-164. 201. Karlsson, H. L., Ammonia, nitrous oxide and hydrogen cyanide emissions from five passenger vehicles. *Sci. Total Environ.* **2004**, *334-335*, 125-132.

202. Narasimhan, L. R.; Goodman, W.; N.;, P. C. K., Correlation of breath ammonia with blood urea nitrogen and creatinine during hemodialysis. *PNAS* **2001**, *98*, 4617-4621.

203. Müller, E.; Spitzer, F., Über die Elektrolytische Oxydation des Ammoniaks und Ihre Abhängigkeit vom Anodenmaterial. *Z. Elektrochem. Angew. Physik. Chem.* **1905**, *11*, 917-931.

204. Gerischer, H.; Mauerer, A., Untersuchungen Zur anodischen Oxidation von Ammoniak an Platin-Elektroden. *J. Electroanal. Chem. Interf. Electrochem.* **1970**, *25*, 421-433.

205. Schiffer, Z.; Lazouski, N.; Corbin, N.; Manthiram, K. In *Rate-Determining Step and Mechanistic Understanding of Electrochemical Ammonia Oxidation in a Non-Aqueous Electrolyte*, 2019 North American Catalysis Society Meeting, NAM: 2019.

206. Barnes, K. K.; Mann, C. K., Electrochemical oxidation of primary aliphatic amines. J. Org. Chem. **1967**, *32*, 1474-1479.

207. Buzzeo, M. C.; Giovanelli, D.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Elucidation of the Electrochemical Oxidation Pathway of Ammonia in Dimethylformamide and the Room Temperature Ionic Liquid, 1-Ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide. *Electroanalysis* **2004**, *16*, 888-896.

208. Ji, X.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Mechanistic Studies of the Electro-oxidation Pathway of Ammonia in Several Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 9562-9572.

209. Ji, X.; Banks, C. E.; Compton, R. G., The Direct Electrochemical Oxidation of Ammonia in Propylene Carbonate: A Generic Approach to Amperometric Gas Sensors. *Electroanalysis* **2006**, *18*, 449-455.

210. National Park Service, U. S. D. o. t. I. Sulphur Dioxide Effects on Health. (accessed 16. September 2020).

211. Khan, R. R.; Siddiqui, M. J. A., Review on effects of Particulates; Sulfur Dioxide and Nitrogen Dioxide on Human Health. *Int. Res. J. Environment Sci.* **2014**, *3*, 70-73.

212. Seo, E. T.; Sawyer, D. T., Determination of sulfur dioxide in solution by anodic voltammetry and by u.v. spectrophotometry. *J. Electroanal. Chem.* **1964**, *7*, 184-189.

213. Appleby, A. J.; Pichon, B., The mechanism of the electrochemical oxidation of sulfur dioxide in sulfuric acid solutions. *J. Electroanal. Chem.* **1979**, *95*, 59-71.

214. Kohler, H.; Piron, D. L.; Bélanger, G., A Linear Sweep Voltammetry Theory for Irreversible Electrode Reactions with an Order of One or Higher: I. Mathematical Formulation. *J. Electrochem. Soc.* **1987**, *134*, 120.

215. Lu, P. W. T.; Ammon, R. L., An investigation of electrode materials for the anodic oxidation of sulfur dioxide in concentrated sulfuric acid. *J. Electrochm. Soc.* **1980**, *127*, 2610.

216. Piron, D. L.; Kohler, H.; Masse, N., A Linear Sweep Voltammetry Theory for Irreversible Electrode Reactions with an Order of One or Higher: II. Experimental Results. *J. Electrochem. Soc.* **1991**, *138*, 445.

217. Brecher, L. E.; Spewock, S.; Warde, C. J., The Westinghouse Sulfur Cycle for the thermochemical decomposition of water. *Int. J. Hydrog. Energy* **1977**, *2*, 7-15.

218. Wiesener, K., The electrochemical oxidation of sulphur dioxide at porous catalysed carbon electrodes in sulphuric acid. *Electrochim. Acta* **1973**, *18*, 185-189.

219. Gosman, B., Polarographic studies with the dropping mercury kathode. Part X. The reduction of sulphurus acid. *Collect. Czech. Chem. Commun.* **1930**, *2*, 185-197.

220. Kolthoff, I. M.; Miller, C. S., The reduction of sulfurous acid (sulfur dioxide) at the dropping mercury electrode. *J. Am. Chem. Soc.* **1941**, *63*, 2818-2821.

221. Jacobsen, E.; Sawyer, D. T., Electrochemical reduction of sulfur dioxide at a mercury electrode. *J. Electroanal. Chem.* **1967**, *15*, 181-192.

222. Rinker, R. G.; Lynn, S., The formation of the  $S_2O_4^-$  free radical in dimethylformamide. *J. Phys. Chem.* **1968**, *72*, 4706-4707.

223. Bonnaterre, R.; Cauquis, G., Dimerisation consecutive a un transfert monoelectronique: II. Réduction électrochimique du bioxyde de soufre dans le diméthylsulfoxyde. *J. Electroanal. Chem.* **1971**, *32*, 215-223.

224. Martin, R. P.; Sawyer, D. T., Electrochemical reduction of sulfur dioxide in dimethylformamide. *Inorg. Chem.* **1972**, *11*, 2644-2647.

225. Magno, F.; Mazzocchin, G. A.; Bontempelli, G., Voltammetric behaviour of sulphur dioxide at a platinum electrode in dimethylformamide. *J. Electroanal. Chem.* **1974**, *57*, 89-96.

226. Barrosse-Antle, L. E.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Electroreduction of Sulfur Dioxide in Some Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2008**, *112*, 3398-3404.

227. Eckardt, R.; Warratz, R. Electrochemical gas sensor with an ionic liquid electrolyte system including at least one monoalkylammonium, dialkylammonium, or trialkylammonium cation 2011.

228. Helmholtz, H., Ueber einige Gesetze der Vertheilung elektrischer Ströme in körperlichen Leitern mit Anwendung auf die thierisch-elektrischen Versuche. *Ann. Phys.* **1853**, *165*, 211-233.

229. Gouy, M., Sur la constitution de la charge électrique à la surface d'un électrolyte. J. Phys. Theor. Appl. 1910, 9, 457-468.

230. Chapman, D. L., LI. A contribution to the theory of electrocapillarity. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1913**, *25*, 475-481.

231. Stern, O., Zur Theorie der Elektrolytischen Doppelschicht. Z. Elektrochem. 1924, 30, 508-516.

232. Kornyshev, A. A., Double-Layer in Ionic Liquids: Paradigm Change? J. Phys. Chem. B 2007, 111, 5545-5557.

233. Graves, A. D.; Inman, D., The electrical double layer in molten salts: Part 2. The double-layer capacitance. *J. Electroanal. Chem. Interf. Electrochem.* **1970**, *25*, 357-372.

234. Bazant, M. Z.; Storey, B. D.; Kornyshev, A. A., Double layer in ionic liquids: overscreening versus crowding. *Physical review letters* **2011**, *106*, 046102.

235. Yan, J.-W.; Tian, Z.-Q.; Mao, B.-W., Molecular-level understanding of electric double layer in ionic liquids. *Curr. Opin. Electrochem.* **2017**, *4*, 105-111.

236. Faraday, M., Experimental researches in electricity. *Philos. Trans. R. Soc. Lond.* 1832, 122, 125-162.

237. Grahame, D. C., Mathematical theory of the faradaic admittance. J. electrochem. Soc. 1952, 99, 370-385.

238. Fick, A., Über Diffusion. Ann. Phys. 1855, 170, 59-86.

239. Schröder U., W. J. D., Compton R. G., Marken F., Suarez P. A. Z., Consorti C. S., de Souza R. F., Dupon J., Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphaye ionic liquids. *New J. Chem.* **2000**, *24*, 1009-1015.

240. Wandt, J.; Lee, J.; Arrigan, D.; Silvester, D. S., A lithium iron phosphate reference electrode for ionic liquid electrolytes. *Electrochem. Commun.* **2018**, *93*, 148-151.

241. Huber, B.; Roling, B., Development of a Ag/Ag<sup>+</sup> micro-reference electrode for electrochemical measurements in ionic liquids. *Electrochim. Acta* **2011**, *56*, 6569-6572.

242. Torriero, A. A. J.; Sunarso, J.; Howlett, P. C., Critical evaluation of reference systems for voltammetric measurements in ionic liquids. *Electrochim. Acta* **2012**, *82*, 60-68.

243. Tanner, E. E. L.; Batchelor-McAuley, C.; Compton, R. G., Carbon Dioxide Reduction in Room-Temperature Ionic Liquids: The Effect of the Choice of Electrode Material, Cation, and Anion. *J. Phys. Chem. C* **2016**, *120*, 26442-26447.

244. Brown, M. D.; Schoenfisch, M. H., Catalytic selectivity of metallophthalocyanines for electrochemical nitric oxide sensing. *Electrochim. Acta* **2018**, *273*, 98-104.

245. Xiong, X.; You, C.; Cao, X.; Pang, L.; Kong, R.; Sun, X., Ni<sub>2</sub>P nanosheets array as a novel electrochemical catalyst electrode for non-enzymatic H<sub>2</sub>O<sub>2</sub> sensing. *Electrochim. Acta* **2017**, *253*, 517-521.

246. Guo, C. X.; Lei, Y.; Li, C. M., Porphyrin Functionalized Graphene for Sensitive Electrochemical Detection of Ultratrace Explosives. *Electroanalysis* 2011, *23*, 885-893.

247. Arrigan, D. W. M., Nanoelectrodes, nanoelectrode arrays and their applications. *Analyst* **2004**, *129*, 1157-1165.

248. Guo, J.; Lindner, E., Cyclic Voltammograms at Coplanar and Shallow Recessed Microdisk Electrode Arrays: Guidelines for Design and Experiment. *Anal. Chem.* **2009**, *81*, 130-138.

249. Le Drogoff, B.; El Khakani, M. A.; Silva, P. R. M.; Chaker, M.; Vijh, A. K., Effect of the Microelectrode Geometry on the Diffusion Behavior and the Electroanalytical Performance of Hg-Electroplated Iridium Microelectrode Arrays Intended for the Detection of Heavy Metal Traces. *Electroanalysis* **2001**, *13*, 1491-1496.

250. Compton, R. G.; Banks, C. E., *Understanding voltammetry*; World Scientific, 2018.

251. Randles, J. E. B., A cathode ray polarograph. Part II.—The current-voltage curves. *Trans. Faraday Soc.* **1948**, *44*, 327-338.

252. Guidelli, R.; Compton, R. G.; Feliu, J. M.; Gileadi, E.; Lipkowski, J.; Schmickler, W.; Trasatti, S., Defining the transfer coefficient in electrochemistry: An assessment (IUPAC Technical Report). *Pure Appl. Chem.* **2014**, *86*, 245.

253. Shoup, D.; Szabo, A., Chronoamperometric current at finite disk electrodes. *J. Electroanal. Chem. Interf. Electrochem.* **1982**, *140*, 237-245.

254. Binnig, G.; Quate, C. F.; Gerber, C., Atomic Force Microscope. *Physical review letters* **1986**, *56*, 930-933.

255. Meyer, E., Atomic force microscopy. Prog. Surf. Sci. 1992, 41, 3-49.

256. Hooke, R., *De Potentia Restitutiva, or of Spring. Explaining the Power of Springing Bodies* Printed for J. Martyn: London, 1678.

257. Reimer, L., Electron Scattering and Diffusion. In *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*, Springer Berlin Heidelberg: Berlin, Heidelberg, 1998; pp 57-134.

258. von Ardenne, M., On the history of scanning electron microscopy, of the electron microprobe, and of early contributions to transmission electron microscopy. In *"The Beginnings of Electron Microscopy"*, Academic Press Orlando: 1985; pp 1-21.

259. Goldstein, J. I.; Newbury, D. E.; Michael, J. R.; Ritchie, N. W. M.; Scott, J. H. J.; Joy, D. C., *Scanning electron microscopy and X-ray microanalysis*; Springer, 2017.
## 2. Experimental Chapter

This chapter summarizes general experimental setups and techniques used in this thesis that are not specifically explained in the respective chapters. Chemicals or techniques for individual studies will be described in the relevant chapters.

## 2.1. Chemicals and Materials

All chemicals, room temperature ionic liquids and gases used for this thesis will be specified in the experimental section of the respective chapter.

## 2.2. Electrochemical Experiments

All experiments were performed with a PGSTAT101 Autolab potentiostat (Metrohm Autolab, Gladesville, NSW, Australia) interfaced to a computer with NOVA 1.11 software. The electrochemical cell was housed inside an aluminum Faraday cage to reduce electromagnetic interferences. The working electrode (WE), counter electrode (CE) and reference electrode (RE) of the macro thin-film electrodes (TFEs) (ED-SE1, MicruX Technologies, Oviedo, Spain) are composed of either platinum (Pt) or gold (Au) deposited on a Pyrex substrate, with a WE disk diameter of 1 mm.

The platinum microarray thin-film electrodes (MATFEs) (ED-mSE-10-Pt, MicruX Technologies, Oviedo, Spain) were also employed as sensing devices. For MATFEs, the 1 mm diameter Pt disk is covered with a layer of SU-8 resin, into which 91 microholes ( $\mu$ -holes) of 10  $\mu$ m diameter were made to create 91 recessed micro-disk electrodes. The center-to-center distance between each  $\mu$ -hole is 100  $\pm$  1  $\mu$ m and the SU-8 layer has a depth of 3.5  $\pm$  1.0  $\mu$ m, according to the manufacturer.

The interdigitated platinum micro-pillar electrodes were fabricated at the South Australian node of the Australian National Fabrication Facility (ANFF-SA) by the research team led by Dr. Eva Alvarez de Eulate from University of South Australia. The glass substrate contains 40 pairs of interdigitated platinum electrode fingers with a width of 10  $\mu$ m, a length of 5,000  $\mu$ m and a 50  $\mu$ m gap between the fingers. The SU-8 micro-pillars in the gaps have a height of 30  $\mu$ m and a diameter of 30  $\mu$ m. One set of the electrode fingers was used as a working electrode the second set as the counter electrode. A silver wire, acting as reference electrode, was placed in contact with the RTIL in the reservoir area.

An electrode adapter supplied by MicruX (for the commercially available electrodes), or soldered wires (for the fabricated electrodes) were employed to connect the electrodes to the potentiostat. The Pt-WE electrode was usually electrochemically activated prior to each experiment by cyclic voltammetry (CV) cycling (~ 100 times) at 1 V s<sup>-1</sup> in nitrogen purged 0.5 M H<sub>2</sub>SO<sub>4</sub> (aq) between -0.75 V and +0.70 V. For the Au-WE, CV cycles between -1.2 V and 1.1 V were performed. For all experiments, a step potential of 2.5 mV has been used. The activated electrodes were then rinsed twice with ultrapure water and acetone before drying under a nitrogen stream. Please refer to the respective chapter for the exact activation procedure.

A chosen volume of the ionic liquid (see respective experimental part for the exact volumes) was drop-cast to cover all three electrodes. For all measurements on the commercially available MicruX electrodes, the integrated CE and RE, *i.e.* Pt or Au, were used. A silver wire was used as a RE for the Pt-µ-pillar IDA electrodes. The prepared electrode was then inserted into the glass T-cell supported by a silicon-bung. The whole cell was then thoroughly purged with nitrogen to remove dissolved gases and impurities (such as oxygen and carbon dioxide) and monitored electrochemically until a constant blank CV was obtained. Two electrochemical techniques, *i.e.* cyclic voltammetry (CV) and chronoamperometry (CA), were applied to perform the electrochemical experiments. More detailed explanations about the sensing of analytes under humidified conditions and introducing different concentrations of an analyte, are discussed in the following sections.

## 2.3. Gas-mixing Setup

The gas-mixing setup used in this thesis to obtain different analyte concentrations in the gas phase is illustrated in Figure 2.1. The supplier, purity level and concentration of the gas cylinders are specified in the respective experimental part of each chapter.

The gas cylinders were equipped with a pressure regulator which is specific to the analyte gas. Poly(tetrafluoroethylene) (PTFE) tubing equipped with Swagelok fittings were used to connect the gas cylinder to a flowmeter (FC1 or FC2). Two separate gas lines were then connected to a Swagelok T-joint to achieve homogenous mixing of the two gases. The relative flow rates, set at the flow meter, were used to calculate the gas concentration in the gas stream in volume percentage (vol.%). The gas line was connected to the glass T-cell equipped with the gas sensing device via Swagelok

fitting. Additionally, the gas outlet of the T-cell was connected to another PTFE tubing to ensure the safe release of the gas mixture in the fume cupboard. Overall flowrates were kept constant throughout an experiment and are specified in the experimental parts.



Figure 2.1. Gas mixing setup used throughout the experiments for this thesis.

## 2.4. Gas Solubility Measurements

The experimental setup used for the measurement of gas solubilities is based on an isochoric saturation technique previously applied and described by various researchers.<sup>1-3</sup> In this method, an accurately determined quantity of a certain gas is brought into contact with a precisely determined volume of the ionic liquid. After reaching equilibrium at a certain temperature, the pressure above the ionic liquid phase is directly related to the gas solubility in the ionic liquid. The gas solubility is calculated from pressure-temperature (*pT*) measurements at various temperatures.

The apparatus (see Figure 2.2) is composed of an equilibrium cell (EC) with a magnetic stir bar for the ionic liquid, a manometer (M) and a gas bulb (GB) inside a temperature controlled ( $\pm 0.01$  K) thermostatic bath (TB). Additionally, the cell has two valves (V1 and V2) to separate certain compartments and is connected to a vacuum pump (VP), a vacuum gauge (VG), a cold trap (TP) and the respective gas cylinder.

Before the gas solubility evaluation, the precise calibration of the volume of the gas bulb ( $V_{GB}$ ) at two temperatures to consider the thermal expansion of the Pyrex glass as

well as the temperature dependent density of the ionic liquid ( $\rho_{RTIL}$ ) by density measurements, must be conducted. Firstly, the GB is filled with the respective gas, the exact quantity of the gas is determined by measuring the gas pressure at a constant temperature with the thermally equilibrated manometer. After closing V2, a certain amount of ionic liquid is introduced into the EC. The precise mass is determined gravimetrically. The ionic liquid is degassed for several hours at a constant temperature before V1 is closed and V2 opened to bring the gas in contact with the liquid phase. The overall volume ( $V_{tot}$ ) of the part that is inside the TB and segregated by V1 was previously determined *via* gas expansion experiments. The pressures and temperatures are recorded as a function of time until constant values are observed, indicating thermodynamic equilibrium. A temperature dependent gas solubility value can be obtained by changing the temperature of the thermostatic bath and repeating the previous steps.



Figure 2.2. Schematic of the experimental apparatus consisting of a vacuum pump (VP), a cold trap (TP), a vacuum gauge (VG), a thermostatic bath (TB), a precise manometer (M), an equilibrium cell (EC) with a stir bar, a gas bulb (GB), valves (V1 and V2) and connectors (C1 and C2) and the flow chart of the experimental procedure.

The gas content in the ionic liquid,  $n_2^{liq}$ , is calculated by the difference of two *pVT* measurements – one when the bulb is filled with gas and the other when the vapor-liquid equilibrium is attained:

$$n_{2}^{liq} = \frac{p_{ini}V_{GB}}{[Z_{2}(p_{ini}, T_{ini})RT_{ini}]} - \frac{p_{eq}(V_{tot} - V_{liq})}{[Z_{2}(p_{eq}, T_{eq})RT_{eq}]}$$
2.1

with  $p_{ini}$  and  $T_{ini}$  as initial pressure and temperature respectively and  $p_{eq}$  and  $T_{eq}$  after reaching the equilibrium, R the universal gas constant and  $Z_2$  the compressibility factor of the respective pure gas given as:

$$Z_2 = 1 + \frac{p}{RT} \cdot B \tag{2.2}$$

where *B* is the second virial coefficient for the pure gas, usually taken from books by Dymonds.<sup>4-5</sup>

The gas solubility can be expressed in various forms, such as mole fraction  $x_2$  (eq. 2.3) or as Henry's law constant  $K_H$  (eq. 2.4):

$$x_2 = \frac{n_2^{liq}}{n_2^{liq} + n_1^{liq}}$$
 2.3

$$K_{\rm H} = \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\varphi_2(p_{eq}, T_{eq})p_{eq}}{x_2}$$
 2.4

where  $n_1^{liq}$  is the quantity of ionic liquid in the liquid phase,  $n_2^{liq}$  is the quantity of gas in the liquid phase,  $f_2$  is the fugacity of the solute and  $\varphi_2$  the fugacity coefficient. T and p are the temperature and pressure and T<sub>eq</sub> and p<sub>eq</sub>, the temperature and pressure at the equilibrium.

## 2.5. References

1. Husson-Borg, P.; Majer, V.; Costa Gomes, M. F., Solubilities of Oxygen and Carbon Dioxide in Butyl Methyl Imidazolium Tetrafluoroborate as a Function of Temperature and at Pressures Close to Atmospheric Pressure. *J. Chem. Eng. Data* **2003**, *48*, 480-485.

2. Jacquemin, J.; Costa Gomes, M. F.; Husson, P.; Majer, V., Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283K and 343K and at pressures close to atmospheric. *J. Chem. Thermodyn.* **2006**, *38*, 490-502.

3. Shiflett, M. B.; Maginn, E. J., The Solubility of Gases in Ionic Liquids. *AlChE J.* **2017**, *63*, 4722-4737.

4. Dymond, J. D.; Marsh, K. N.; Wilhoit, R. C., *Virial Coefficients of Pure Gases and Mixtures*; Springer-Verlag Berlin Heidelberg, 2003.

5. Dymond, J. H.; Smith, E. B., *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon: Oxford, 1980.

## **3.** The Effect of Humidity on RTILbased Gas Sensors

Room temperature ionic liquids are known to be highly hygroscopic, which results in a change of their physicochemical properties. The electrochemical redox mechanism of various gases has already been studied in dry RTILs in detail, however, for the application of RTIL-based gas sensors in real world environment, the impact of humidity on the sensing must be understood. This chapter is divided in three subchapters that address the impact of humidity on sensing responses.

The first part discusses how the mechanism of the oxygen reduction reaction in RTILs changes at different humidity levels and shows that the choice of RTIL cation and anion can significantly change this behavior. This study leads to the second chapter where the influence of water on the electrochemical window of RTILs is investigated. The effect on ammonia oxidation, a mechanism that does not change in the presence of water, is then studied.

In the last section, an attempt to overcome the significant influence of water on the oxygen reduction mechanism is made, by mixing the RTIL with commercially available polymers to create so-called gel-polymer electrolytes (GPEs).

## 3.1. Effect of Ionic Liquid Structure on the Oxygen Reduction Reaction under Humidified Conditions

This chapter has been published in the following peer-reviewed journal:

Doblinger, S., Lee, J., Silvester, D. S., Effect of Ionic Liquid Structure on the Oxygen Reduction Reaction Under Humidified Conditions. *J. Phys. Chem. C* 2019, *123*, 10727-10737.

The abstract has been removed from this chapter and the supporting information has been included after the references. Figure and table captions as well as equation numbers have been changed. A few changes of the formatting have been made.

#### **Author Contribution:**

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 85%/100%

Acquisition of Data and Method: 75%/100%

Data Conditioning and Manipulation: 70%/100%

Analysis and Statistical Method: 70%/100%

Interpretation and Discussion: 70%/100%

Final Approval: 60%/100%

Signature:

Simon Doblinger

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 10%/100%

Acquisition of Data and Method: 25%/100%

**Data Conditioning and Manipulation: 30%/100%** 

Analysis and Statistical Method: 30%/100%

#### Interpretation and Discussion: 20%/100%

Final Approval: 20%/100%

Signature: \_\_\_\_\_

Junqiao Lee

I, as co-author, endorse that the contributions indicated below are appropriate.

Conception and Design: 5%/100%

Acquisition of Data and Method: 0%/100%

Data Conditioning and Manipulation: 0%/100%

Analysis and Statistical Method: 0%/100%

Interpretation and Discussion: 10%/100%

Final Approval: 20%/100%

Signature:

Debbie S. Silvester

#### **3.1.1. Introduction**

The reliable monitoring of gases under extreme conditions is an important criteria for sensors in industry, and is especially important for health and safety requirements.<sup>1</sup> Commercially available sensors usually consist of a three-electrode setup, with an aqueous-based electrolyte (usually water/H<sub>2</sub>SO<sub>4</sub>), and a gas permeable membrane that prevents solvent evaporation at high temperatures.<sup>2</sup> However, this membrane also reduces the diffusion rate of gases towards the electrode.<sup>3</sup> An alternative, proposed by Buzzeo *et al.*, is the use of room temperature ionic liquids (RTILs) as a non-volatile electrolyte, which removes the need for a membrane layer.<sup>4</sup>

RTILs are composed of cations and anions that are liquid at room temperature due to asymmetry in at least one of the ions<sup>5</sup> and weaker ion-ion interaction forces.<sup>6</sup> RTILs are increasingly used in synthesis,<sup>7</sup> as well as in electrochemistry applications,<sup>8-11</sup> due to their promising characteristics, such as negligible volatility, high stability up to certain temperatures without decomposition, and high conductivity.<sup>12</sup> Due to their intrinsic conductivity, they have been extensively explored as alternative electrolyte materials.<sup>13</sup> The wide electrochemical windows (ca. 4-6 V)<sup>14</sup> of these solvents make them suitable candidates for electrochemical sensing applications; with the detection of gaseous analytes like hydrogen, oxygen or ammonia already reported in the literature.<sup>15</sup> However, the hygroscopic nature of RTILs is an issue for their use in practical environments that currently hinders their implementation in commercial membrane-free sensors. The tendency for RTILs to absorb moisture can lead to instability and unreliability in the measurements when the gas-sensor is subjected to real-atmospheres with changing humidity levels.<sup>16-18</sup> It is hence clear that water is a significant impurity in RTIL-based gas sensors that need to be investigated; this can be indirectly monitored by studying the oxygen reduction reaction (ORR).

The ORR has been widely reported in aprotic RTILs for the purposes of oxygen gas detection.<sup>4, 8, 19-20</sup> Katayama *et al.* published an almost reversible redox couple in ammonium-based ionic liquids with a peak current density ratio of 0.97.<sup>21</sup> It has also been shown that the reduction of oxygen can undergo different mechanistic pathways, depending on the presence and concentration of protic species such as water (which provides H<sup>+</sup>), which could cause a shift from a 1-e<sup>-</sup> (equation 3.1) to a 2-e<sup>-</sup> (equation 3.2) or even a 4-e<sup>-</sup> (equation 3.3) reduction reaction.<sup>22-24</sup> This significantly complicates the reliable calibration of a sensor when exposed to different humidity levels, since

water can act as an effective proton source,<sup>25</sup> opening up electrochemical reaction pathways that are dependent upon the concentration of water.

$$0_2 + e^- \to 0_2^{-\bullet} \tag{3.1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 3.2

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 3.3

Therefore, several groups (including ours), have used hydrophobic RTILs,<sup>26-28</sup> or mixed the electrolyte with a hydrophobic polymer to reduce the water uptake.<sup>29-30</sup> However, this did not eliminate the water absorption problem entirely.

When examining the impact of absorbed moisture on the electrochemical processes at the electrode-RTIL interface, the structure of the RTIL at the interface must be taken into account.<sup>17</sup> Research performed by other groups has shown that as with conventional solvents, ionic liquids form electrical double layers (EDLs) at the electrode/solution interface.<sup>31-32</sup> The EDL structure at the electrode interface could have a severe impact on the transport of analytes such as gases or moisture towards the surface, which is required to induce an electrochemical reaction. Several methods including atomic force microscopy (AFM),<sup>33-34</sup> surface force apparatus (SFA),<sup>35</sup> neutron reflectometry,<sup>36</sup> sum frequency generation vibrational spectroscopy (SFG-VS)<sup>37</sup> and surface-enhanced infrared absorption spectroscopy (SEIRAS)<sup>38</sup> have been used to try to elucidate this behavior. For RTILs, the thickness and number of layers at the electrode is strongly dependent on the charge density at the surface and the nature of the cation and anion. Depending on the cation and anion structure, the EDL that is formed when a potential is applied can be either more or less pronounced.<sup>34, 39-41</sup> Single as well as ion-pair layers have been detected at the interface using AFM.<sup>33, 42</sup> With regards to layer thickness, theoretical simulations of these EDL structures are in good accordance with experimental data.<sup>43</sup> It is already well known that when the electrode is highly charged, more than one cation or anion layer can be formed near the electrode<sup>44</sup> which means that either the cation-analyte or anion-analyte interactions may influence the concentration profile of various dissolved species. Hence, knowledge of the EDL structure is crucial to explain changes in the response in electrochemical experiments. However, the structuring of RTILs on surfaces in the presence of other species (e.g. oxygen or water) is not very well understood.

Computational studies have been carried out to investigate the influence of adsorption of water<sup>45</sup> or ferrocene<sup>46</sup> in RTILs. However, despite the extensive literature published on the structure of the EDL of RTILs, experimental studies on the influence of species, such as absorbed gases or water, are still lacking.<sup>23</sup> Characteristics of the RTIL, such as the charge carrying atom, as well as the alkyl chain length, number, and position(s) on both the cation and the anion, appear to be key determining factors of water sorption properties of RTILs. COSMO-RS predictions have shown that there is a strong interaction between water and ionic liquid anion in the bulk phase.<sup>47</sup> This means that for different RTILs that have the same anion, the mutual solubility of water only varies slightly, while for RTILs with same cation and different anions, the effect is more pronounced.<sup>47</sup> It should also be noted that the bulk-phase behavior of water in RTILs can be very different to the behavior near a charged electrode surface. For example, Bi et al.<sup>48</sup> showed that the electrosorption of water on electrodes in humid, hydrophobic ILs was higher than in hydrophilic RTILs even though the bulk phase solubility of water showed the opposite trend. Therefore, the effect of water on electrode processes may be different to the trends expected based on the hydrophobicity/hydrophilicity of the RTILs.

In this work, we demonstrate the influence of the RTIL structure at the EDL – varying both the cation and the anion – and show its effect on the ORR in humidified environments using cyclic voltammetry (CV). Six different cation types (imidazolium-, pyrrolidinium-, pyridinium-, ammonium-, sulfonium- and phosphonium-) with different alkyl chain lengths and several different anions are analyzed. Atomic force microscopy (AFM) is then performed under unbiased and biased conditions to provide insights into the impact of water on the EDL structure of RTILs on a charged surface, and to give an explanation for the electrochemistry results.

#### 3.1.2. Experimental

#### 3.1.2.1. Chemical Reagents



Figure 3.1. Chemical structures and abbreviations of the room temperature ionic liquid cations and anions used in this study.

All RTILs were obtained at the highest purities possible. Diethylmethylsulfonium 99%, IoLiTec-Ionic Liquids bis(trifluoromethylsulfonyl)imide ([S<sub>2,2,1</sub>][NTf<sub>2</sub>], Technologies GmbH, Heilbronn, butyltrimethylammonium Germany), bis(trifluoromethylsulfonyl)imide ([N<sub>4,1,1</sub>][NTf<sub>2</sub>], 99.5%, IoLiTec), butylpyridinium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>py][NTf<sub>2</sub>], 99%. IoLiTec), trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate  $([P_{14,6,6,6}]][FAP], >98\%$ , Merck Pty. Ltd. Kilsyth, Victoria, Australia), butylmethylpyrrolidinium bis(trifluoromethylsulfonium)imide ([C4mpyrr][NTf2], 99.5%, IoLiTec), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  $([C_2mim][NTf_2],$ 99.5%, 1-ethyl-3-methylimidazolium IoLiTec), tris(pentafluoroethyl)trifluorophosphate ([C<sub>2</sub>mim][FAP], for synthesis >98%, Merck),

1-butyl-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C<sub>4</sub>mim][FAP], high purity >99%, Merck), 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim][BF4], 99%, IoLiTec), 1butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>], high purity >99%, tris(pentafluoroethyl)trifluorophosphate Merck). 1-hexyl-3-methylimidazolium  $([C_6mim][FAP],$ high purity, Merck) were used as received. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P<sub>14,6,6,6</sub>] [[NTf<sub>2</sub>]) was kindly donated by the group of Professor Chris Hardacre (now at the University of Manchester, UK) when he was located at Queens University Belfast, UK. 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>6</sub>mim] [NTf<sub>2</sub>], 99%, IoLiTec) was kindly donated by Professor Rob Atkin (University of Western Australia). The RTIL heptyltriethylammonium bis(trifluoromethylsulfonyl)imide  $([N_{2,2,2,7}][NTf_2])$  was synthesized according to standard literature procedures<sup>49</sup> (see electronic supplementary information (ESI) Figure S3.8 for the NMR data). The chemical structures of the ionic liquid cations and anions used in this study are summarized in Figure 3.1. Ultrapure water with a resistivity of 18.2 M $\Omega$  cm prepared by a Milli-Q laboratory water purification system (Millipore Pty Ltd., North Ryde, NSW, Australia) was used for humidifying the oxygen gas stream. Acetone (CHROMASOLV®, for HPLC, ≥99.0%, Sigma-Aldrich) and ferrocene (98%, Sigma-Aldrich) were used as received. A 1 M stock solution of H<sub>2</sub>SO<sub>4</sub>(aq) (prepared with ultrapure water from a 95-98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for the activation of the thin-film electrodes. High purity oxygen gas (>99.5%) and high purity nitrogen gas (99.99%) cylinders were purchased from BOC Gases (Welshpool, WA, Australia).

#### **3.1.2.2.** Electrochemical Experiments

CV measurements were performed with a PGSTAT101 Autolab potentiostat (Metrohm Autolab, Gladesville, NSW, Australia) interfaced to a computer with NOVA 1.11 software. The electrochemical cell was housed in an aluminum Faraday cage to reduce electromagnetic interferences. The working electrode (WE), counter electrode (CE) and reference electrode (RE) of the thin-film electrodes (TFEs) (ED-SE1 Pt, MicruX Technologies, Oviedo, Spain) are composed of platinum (Pt) deposited on a Pyrex substrate, with a WE diameter of 1 mm. Wires were soldered

onto the connecting pads of the chip. The WE was electrochemically activated prior to each experiment by CV cycling (> 300 times) at 1 Vs<sup>-1</sup> in nitrogen purged 1 M H<sub>2</sub>SO<sub>4</sub> (aq) between -0.75 and +0.7 V. The activated chips were then rinsed twice with ultrapure water and acetone before drying under a nitrogen stream. To account for the unstable Pt quasi-RE on the TFE, modification of the RE with lithium iron phosphate (LFP) (previously developed by our group<sup>50</sup>) was attempted. However, the interaction of superoxide with the LFP material led to a change in ORR peak shape and current over consecutive scans, making measurements unreliable. Therefore, to investigate the influence of humidity on CV peak potentials for selected RTILs, ferrocene was added in-situ, and potentials were shifted such that the midpoint of the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was at 0 V.

Seven  $\mu$ L of the ionic liquid was drop-cast to cover all three electrodes on the TFE and purged for at least 45 min in a high purity nitrogen stream at a flow rate of 500 mL min<sup>-1</sup> to remove dissolved gases and impurities such as oxygen and carbon dioxide. The relatively high volume of electrolyte on the small chip (compared to our previous experiments) ensures that the electrogenerated products from each scan can be effectively diluted, so that their accumulation is negligible. For all oxygen measurements, the integrated CE and WE were used. After purging the electrolyte with nitrogen gas for at least 45 min, oxygen was introduced into one arm of a modified glass T-cell.<sup>51</sup> The oxygen line was additionally connected to a humidity generator (Owlstone Humidity Generator OHG-4, Owlstone, Cambridge, UK) that separates the gas flow into 'dry' and 'wet' streams by bubbling the gas through a container of 400 mL of ultrapure water at a flow rate of 500 mL min<sup>-1</sup>. Adjusting the dry to wet flow ratio results in different humidity levels and the measured dew point (*T*<sub>d</sub>) was converted to obtain the relative humidity percentage (RH%), using equation 3.4<sup>52</sup>:

$$RH\% = 100\% * 10^{m\left(\frac{T_d}{T_d + T_n} - \frac{T_{amb}}{T_{amb} + T_n}\right)}$$
 3.4

with the constants m = 7.59 and  $T_n = 240.73$  °C, the ambient temperature  $T_{amb}$  and the dew point  $T_d$  in °C (Humidity Conversion Formulas, Vaisala).<sup>53</sup> The dew point was measured at a location close to the electrochemical cell to ensure that the actual humidity introduced into the T-cell is not affected by condensation or adsorption along the tubing (see Figure 3.2).



Figure 3.2. Schematic of the gas humidifying system used for voltammetric measurements on thin-film electrodes (TFEs).

Since the humidity generator is not able to detect humidity levels lower than 1 RH%, measurements were conducted at a starting humidity level of ~1 RH%. It is also known in the literature that even with prolonged vacuum purging, a significant amount of water is retained (in the  $\sim 10 - 100$  ppm range)<sup>54</sup> in the RTIL. An equilibration time of 45 min was employed before performing CV scans at each humidity level to ensure that the gas was fully saturated, particularly into the most viscous ionic liquid. Repeated CV scans for O<sub>2</sub> reduction were carried out under constant humidity conditions to identify the duration for a stable peak current to be achieved (see Figure S3.10 to Figure S3.13 in the supporting information). 45 mins was found to be more than sufficient for equilibrium to be attained across all RTILs and humidities. Hence, before the commencement of experiments, the RTILs were also first purged under N<sub>2</sub> gas for more than 45 mins. It is noted that water uptake times of up to 180 min were observed for RTILs at different humidity environments,55 but that study employed a larger volume of ionic liquid and used a static set-up, in contrast to the large surfaceto-volume (seven microliter RTIL droplet spread out over a thin-film electrode) and the constant flow system used in our experiments.

All experiments were carried out at least in triplicate and all data points were used to establish the trendline that was fitted by a logistic regression analysis. In order to remove the contributions caused by different solubilities and diffusion coefficients in the RTILs, the currents were normalized, where the measured currents at different humidities were divided by those measured at 1 RH%.

#### 3.1.2.3. AFM Measurements

Atomic force microscopy (AFM) experiments were carried out with a Bruker Dimension Icon interfaced to a computer with NanoScope 9.4 software in contact mode using activated Pt TFEs. Force curves were collected continuously with a scan rate of 0.16 Hz while the ramp size was between 100 and 160 nm. A silicone barrier (Selleys Silicone Sealant, Padstow, NSW, Australia) was constructed around the electrode cell to confine the ionic liquid during the AFM measurements. All experiments were performed with a silicon nitride AFM tip (SNL-10, spring constant 0.35 Nm<sup>-1</sup>). The tips were carefully cleaned in sulfuric acid (1 M) for 60 s, washed with ultrapure water and acetone, and finally dried under a nitrogen stream. Measurements were conducted on an uncharged and a negatively charged electrode surface under mildly humidified conditions (ca. 40 RH%). When the electrode was negatively polarized, rapid formation and growth of H<sub>2</sub> bubbles were observed at < -1 V in [C<sub>2</sub>mim] [NTf<sub>2</sub>] (see supporting information for a detailed discussion). Hence, a less negative biasing potential of -0.8 V was chosen for the studies. Due to the roughness of the electrode surface (see Figure S3.15 in the supporting information), flat areas of the electrode surface were used for the AFM measurements.

## 3.1.2.4. Computational Estimation of Ion Dimensions and Wateraffinity

The structure of several RTIL cations and the  $[NTf_2]^-$  anion was computationally optimized (Spartan '14, Wavefunction, Inc., California, USA) with a semi-empirical approach, using the parameterized model number 3 (PM3) method for single isolated ions in vacuum. For the cations with significant degree of freedom (*e.g.*  $[N_{4,1,1,1}]^+$  and  $[P_{14,6,6,6}]^+$ ) the alkyl chains were pre-oriented before the structures were minimized. The dimensions were estimated from the optimized structures based on their expected orientations. Re-positioning of the RTIL side-chains, due to interactions with the electrode surface (unbiased/negatively-biased), and neighboring species (*e.g.* cation, anion, water) can affect the layer thickness created by the cations/anions. It is noted that the computationally obtained values are simply to aid with the analysis of AFM force-curve measurements; a more thorough computational investigation of layer thicknesses is beyond the scope of this work. The value estimated for  $[C_2mim]^+$  agrees well with literature.<sup>56</sup> The computationally estimated orthogonal dimensions, corresponding space-filling (CPK) volumes for each of the ions and the water molecule, as well as their solvation energies (SEs) are summarized in Table S3.1. The CPK volumes follow the trend:

$$\begin{split} & [P_{14,6,6,6}]^+ >>> [N_{7,2,2,2}]^+ > [FAP]^- > [C_6 mim]^+ > [C_4 mpyrr]^+ > [C_4 mim]^+ \\ & \approx [C_4 py]^+ > [NTf_2]^- \approx [N_{4,1,1,1}]^+ > [C_2 mim]^+ \approx [S_{2,2,1}]^+ >> [PF_6]^- > [BF_4]^- \qquad 3.5 \\ & > H_2 O \end{split}$$

The PM3 calculated SEs of selected single isolated RTIL molecules are also listed in Table S3.1 to provide the local affinity of each ion towards surrounding water molecules; the greater the SE value, the more hydrophobic the molecule is likely to be. It is noted that these values are relevant on the inter-molecular scale but may or may not apply for the bulk RTIL as they do not account for RTIL-RTIL and bulk interactions, and hence may not coincide with bulk properties of hygroscopicity and hydrophobicity. The SEs (listed in Table S3.1) follow the trend:

$$\begin{split} & [P_{14,6,6,6}]^+ >>> [FAP]^- > [C_6 mim]^+ > [N_{7,2,2,2}]^+ > [C_4 mim]^+ > [C_2 mim]^+ \approx \\ & [C_4 mpyrr]^+ \approx [C_4 py]^+ > [N_{4,1,1,1}]^+ > [S_{2,2,1}]^+ >> [NTf_2]^- >> [PF_6]^- >> H_2O \qquad 3.6 \\ & > [BF_4]^- \end{split}$$

#### 3.1.3. Results and Discussion

#### 3.1.3.1. Cyclic Voltammetry of RTILs in Dry vs. Wet Environments

CV was carried out in different RTILs under a pure oxygen atmosphere at a range of humidity levels from < 1 RH% up to ~95 RH%. Representative cyclic voltammograms in  $[N_{4,1,1,1}][NTf_2]$  at four different humidity levels are presented in Figure 3.3. A reversible one-electron reduction to superoxide (see equation 3.1) was observed in a dry environment (<1 RH%, black line). The CV shape is typical for an electrochemically quasi-reversible process, which is well reported for the oxygen/superoxide redox couple in RTILs.<sup>16</sup> At increased humidity levels, the reductive peak current becomes larger and the reduction process became more irreversible, resulting in a decreased superoxide oxidation peak. Ferrocene was added to the solution as an internal reference due to significant potential shifting occurring at the Pt quasi-RE in the presence of the humidified gas. The voltammograms were shifted so that the midpoint of the ferrocene/ferrocenium redox process was at 0 V, and a substantial shift (~600 mV) of the ORR potential, from ca. -1.3 V (*vs.* Fc/Fc<sup>+</sup>) at < 1 RH% (dry) to ca. -0.7 V at 95 RH% (wet) was observed. This is likely due to the

increased presence of proton-donors that catalyze the reduction reaction (see equations 3.2 and 3.3), which is further supported by the significant increase in the ORR peak current. From < 1 RH% to 55 RH%, a current increase of approximately 2.5 times (from -6  $\mu$ A to -15  $\mu$ A) was observed, indicating a mix of 2- and 4-electron processes, which is supported by the absence of the superoxide oxidation peak. At 95 RH%, the current increased by a factor of three (to ca. -19  $\mu$ A), which suggests closer to a 4-electron process is dominating (equation 3.3). A change in the oxygen diffusion coefficient as the result of viscosity changes in the water-saturated RTIL may also contribute to the increased currents, but a detailed study of this effect is well beyond the scope of this work.

In contrast with  $[N_{4,1,1,1}][NTf_2]$ , the peak position *vs*. the Pt quasi-RE in  $[P_{14,6,6,6}][FAP]$  was substantially less affected by humidity (see supporting information Figure S3.9 b), and the ORR peak current only showed a ~20% increase, likely owing to the much higher hydrophobicity of the  $[P_{14,6,6,6}]^+$  cation compared to  $[N_{4,1,1,1}]^+$  (see trend in equation 3.6).



Figure 3.3.Cyclic voltammograms at 100 mV s<sup>-1</sup>, in  $[N_{4,1,1,1}][NTf_2]$  on a Pt TFE, with 7 mM ferrocene as internal reference in an O<sub>2</sub>-saturated flow with RH% of < 1 RH% (black), 13 RH% (green), 55 RH% (blue) and approximately 95 RH% (red).

3.1.3.1.1. Anion Effect

The type of anion is known to have a significant impact on the hygroscopic behavior of RTILs.<sup>54, 57</sup> The bulk solubility of water in ionic liquids containing the  $[FAP]^-$  anion is much lower compared to  $[NTf_2]^-$ ,  $[PF_6]^-$ , or  $[BF_4]^-$  – see trend in equation 3.6, and also in reference [57]. It was previously shown that electro-absorption of water in the

EDL is more pronounced for hydrophilic anions at negative potentials.<sup>58</sup> In an ionic liquid, absorbed water molecules are known to preferentially interact with the anion.<sup>6, 47, 58-59</sup> Hence, it is important to investigate how different anionic species may affect the ORR reaction at different humidity levels. Figure 3.4 shows the normalized ORR current as a function of increasing humidity levels in four different [C<sub>4</sub>mim]<sup>+</sup>-based RTILs. The current is mostly unaffected at low humidity levels (< 15 RH%) suggesting that the cation is the determining factor at low humidity levels. This is consistent with AFM<sup>32-33, 39, 60</sup> and SEIRAS<sup>38</sup> studies, where it is well known that the innermost layer at a negatively biased surface is mainly composed by cations. The normalized ORR current then begins to increase above 15 RH%. The current at high humidity levels (> 95 RH%) follows the trend:

$$[FAP]^{-} < [NTf_2]^{-} < [PF_6]^{-} < [BF_4]^{-}$$
 3.7

which is consistent with the computationally predicted molecular-hydrophobicity and volume trends for individual anionic molecules (see trends 3.5 and 3.6), and by COSMO-RS calculations<sup>47</sup> from a separate study.

For the  $[BF_4]^-$  RTIL, there is a lower than expected current trend between 20 and 80 RH%. It was suspected that this may be due to insufficient equilibration time. However, waiting 130 min instead of 45 min before recording the first scan did not affect the current response (see supporting information Figure S3.10). Instead, repeated CV scanning caused an increase in the current, suggesting a possible side-reaction and build-up of electrogenerated products contributing to the current. This is not surprising considering that  $[BF_4]^-$ , as well as  $[PF_6]^-$ , can undergo hydrolysis.<sup>61</sup> At 90 RH%, the electrogenerated products are likely saturated at the EDL from the initial scan; consecutive scans at this humidity level can cause severe changes in the ORR current due chemical reactions with previously electrogenerated species, such as H<sub>2</sub>O<sub>2</sub>. Overall, the results in Figure 3.4 suggest that bulky, hydrolytically stable and hydrophobic anions such as  $[FAP]^-$  are recommended for applications where a stable ORR response in humidified environments is required, *e.g.* for oxygen sensing.



Figure 3.4. Effect of humidified environments on the normalized current for oxygen reduction in  $[C_4mim][BF_4]$  (•),  $[C_4mim][PF_6]$  (•),  $[C_4mim][NTf_2]$  (•) and  $[C_4mim][FAP]$  (•) with increasing relative humidity percentages (RH%). CVs (at 100 mV s<sup>-1</sup>) were obtained on Pt-TFEs, with each scan was taken after 45 min equilibration time. All experiments were performed at least in triplicate and the trendlines were fitted by a logistic regression analysis.

#### 3.1.3.1.2. Effect of Cation with Hydrophobic Anion, [NTf<sub>2</sub>]<sup>-</sup>

A negatively polarized electrode during oxygen reduction voltammetry implies that the EDL structure at the electrode-RTIL interface will be dominated by the RTIL cation. In contrast with anions, cations generally only have a slight influence on the solubility of water in RTILs.<sup>45, 47</sup> Properties such as the molecular affinity to water (predicted by SE values), coupled with cation size (based on CPK volumes) – which may sterically hinder the adsorption of other species at the electrode surface (see Table S3.1 in the supporting information) – need to be considered. In this study, only RTILs displaying quasi-reversible ORRs were included, *i.e.* the pyridinium ionic liquid was omitted due to an irreversible ORR process (see supporting information, Figure S3.14). The presence of an obvious superoxide oxidation peak for the remaining RTILs implies that any impurities in the RTILs (*e.g.* left over from the synthesis procedure) are minimal, and do not affect the electrochemical processes occurring during the oxygen reduction reaction.

Figure 3.5 presents normalized ORR peak currents vs. humidity for eight different RTILs sharing the same (moderately hydrophobic)  $[NTf_2]^-$  anion. Compared to the previous study of different anions (section 3.1.3.1.1), the type of cation appears to have a more significant influence on the ORR current at lower humidity levels (*i.e.* < 40 RH%). There is a clear difference between the humidity level at which the ORR current starts to sharply increase – referred to as the "onset-humidity" – typically occurring at below 30 RH%, and follows the trend:

$$[P_{14,6,6,6}]^{+} > [C_{6}mim]^{+} > [C_{4}mim]^{+} \approx [N_{7,2,2,2}]^{+} \approx [N_{4,1,1,1}]^{+} >> [C_{4}mpyrr]^{+} \\ \approx [S_{2,2,1}]^{+} >> [C_{2}mim]^{+}$$
3.8

This is in contrast with the different anions discussed in section 3.1.3.1.1, where the onset-humidity appears to be almost unaffected by the type of cation present. Significant variability in the data points towards higher humidity levels prevents a confident evaluation of the 95 RH% current trends, although it is clear that the ORR current in the  $[P_{14,6,6,6}]^+$  RTIL is much less affected by water compared to the other cations. The variability in current could be due several factors including increased follow-up chemical reactions and even bubble formation at the electrode-RTIL interface due to water-splitting reactions (see Figure S3.18 in the supporting information).

Zhong *et al.*<sup>60</sup> reported that at low water contents, a stable structuring of the RTIL at the electrode exists and is dominated by the cation. At increasing humidity levels, water molecules begin to disrupt and weaken the structuring of the RTILs at an electrode. Hence, the intermediate RH% trends are dominated by the tendency of the EDL structure to be affected by the presence of water. The trends at high RH% are thus a better reflection of the bulk hydrophobicity of the RTILs.



Figure 3.5. Effect of humidified environments on the normalized current for oxygen reduction in  $[C_{2mim}][NTf_2]$  ( $\bullet$ ),  $[S_{2,2,1}][NTf_2]$  (-),  $[C_{4mpyrr}][NTf_2]$  ( $\bullet$ ),  $[C_{4mim}][NTf_2]$  ( $\bullet$ ),  $[N_{4,1,1,1}][NTf_2]$  ( $\checkmark$ ),  $[N_{7,2,2,2}][NTf_2]$  (+),  $[C_{6mim}][NTf_2]$  ( $\bigcirc$ ) and  $[P_{14,6,6,6}][NTf_2]$  (1) with increasing relative humidity percentage (RH%). CVs at 100 mV s<sup>-1</sup> were carried out on Pt-TFEs and each scan was taken after 45 min equilibration time. The scans were taken at 100 mV s<sup>-1</sup> and with a step potential of -2.5 mV. The trendlines were fitted by a logistic regression analysis.

Between the three imidazolium-based RTILs, the trends are in order of increasing alkyl chain length, as expected in terms of increased cation hydrophobicity. The ORR in [C<sub>2</sub>mim][NTf<sub>2</sub>] appears to be the most affected by the presence of moisture at extremely low humidity levels, where a sharp ORR current increase from 0 to 3 RH% is present. This is in contrast with the other RTILs where a relatively more stable region of low ORR current vs. humidity is present. The significant dependency of the onset-humidity on the type of cations is a factor to be considered when designing humidity sensors where sensitivity within a particular humidity range is desired; or for the case of an oxygen sensor, where sensitivity to moisture should be avoided. Surface spectroscopy measurements<sup>37</sup> have shown that imidazolium cations with small alkyl chains (e.g.  $[C_2mim]^+$ ) tend to align with the aromatic ring structure flat against platinum surfaces. Applying a negative potential stabilizes this conformation, while increasing the alkyl chain length causes a tilting of the planar structure. However, it is surprising that there is a substantial difference in the ORR CV current response behavior between  $[C_2 mim]^+$  (black squares),  $[C_4 mim]^+$  (red circles) and  $[C_6 mim]^+$ (purple hollow circles). Nevertheless, the longer alkyl chains of  $[C_4 mim]^+$  and  $[C_6 mim]^+$  allow the formation of a more hydrophobic innermost layer that prevents accumulation of water near the electrode.

Interestingly, the two ammonium ionic liquids, [N<sub>4,1,1,1</sub>][NTf<sub>2</sub>] and [N<sub>7,2,2,2</sub>][NTf<sub>2</sub>], with significantly different cation alkyl chain lengths, produced similar ORR-current behavior in Figure 3.5. A layer of ammonium cations will form at a negatively charged surface. At sufficiently high negative surface polarization, the positively charged nitrogen group will be pulled towards the negative surface charge, inducing a reorientation of the short alkyl chains. Ultimately, this results in a dense structure of cations at the electrode interface, where longer alkyl groups are expected to point away from the charged surface, orientating in the most stable energetic state to maximize interaction with the anion layer above. However, the three shorter alkyl chains of the ammonium RTILs studied are too short and less flexible to effectively cover the electrode surface area between repelling cations, and do not form a highly dense hydrophobic layer at the electrode surface. Furthermore, the positively charged nitrogen atom is less shielded by the shorter alkyl chains. This can allow water molecules to interact via the electronegative oxygen, and with the two aligning

hydrogens more strongly attracted to the negatively polarized surface. However, in the case of  $[P_{14,6,6,6}][NTf_2]$ , the reorientation of the four long alkyl chains forms a dense hydrophobic layer that prevents the absorption of water in the EDL close to the electrode surface. Hence it is recommended for bulky and highly hydrophobic cations (*e.g.*  $[P_{14,6,6,6}]^+$ ) to be employed for stable responses with less interaction from water.

## 3.1.3.1.3. Effect of Cation with a Highly Hydrophobic Anion, [FAP]<sup>-</sup>

Figure 3.6 shows ORR peak currents *vs*. humidity for different RTILs with the most hydrophobic  $[FAP]^-$  anion used in this study, and different cations, namely  $[P_{14,6,6,6}][FAP]$ ,  $[C_2mim][FAP]$ ,  $[C_4mim][FAP]$ , and  $[C_6mim][FAP]$ . As expected, normalized currents at > 30 RH% for the  $[FAP]^-$ -based RTILs are lower than the corresponding  $[NTf_2]^-$ -based RTILs (Figure 3.5), because of the higher hydrophobicity of  $[FAP]^-$ . Additionally, the  $[FAP]^-$  anion has an onset-humidity of 10 RH% for  $[C_2mim][FAP]$  (Figure 3.6) which is a significant improvement compared to  $[C_2mim][NTf_2]$  (Figure 3.5). The onset-humidity follows the trend:



Figure 3.6. Effect of humidified environments on the normalized current for oxygen reduction of  $[C_{2mim}][FAP]$  (•),  $[C_{4mim}][FAP]$  (•),  $[C_{6mim}][FAP]$  (•) and  $[P_{14,6,6,6}][FAP]$  (•) with increasing relative humidity percentages (RH%). CVs were carried out on Pt-TFEs. Each scan was taken after 45 min equilibration time and all experiments were performed at least in triplicate. The scans were taken at 100 mV s<sup>-1</sup> and with a step potential of -2.5 mV. The trendlines were fitted by a logistic regression analysis.

Interestingly, the onset-humidity trend for the three imidazolium cations with the  $[FAP]^-$  anion is not as expected and is different to that observed for  $[NTf_2]^-$ . It is not entirely obvious as to why it is the case for the  $[FAP]^-$ -based RTILs, but this unusual

behavior is consistent with a previous AFM study under dry conditions that revealed differences in the packing density of the three imidazolium ionic liquid cations that did not follow the expected trend based of increasing alkyl chain length.<sup>33</sup>

# 3.1.3.2. Physical Characteristics of the Ionic Liquid Electrical Double Layer on a Pt-TFE

Fedorov and Kornyshev's<sup>62</sup> study of the ionic liquid (IL) EDL at the electrified solid-IL interfaces reveals a "generally more complicated than expected" structure, due to the tendency of ILs to self-assemble. Previous work suggests an EDL structure that is comparable to aqueous electrolytes, consisting of an adsorbed ion layer succeeded by an electrostatically bound diffuse layer.<sup>63-65</sup> However, it was found from AFM studies that a multilayer of both single and cation-anion pair layers can form at the interface, and the number of layers increased and were more tightly organized at higher potentials.<sup>34, 66</sup> Here, three RTILs:  $[C_{2}mim][NTf_{2}]$ ,  $[N_{4,1,1,1}][NTf_{2}]$ , and  $[P_{14,6,6,6}][NTf_{2}]$ were selected to perform AFM force curve measurements under humidified conditions at ca. 40 RH% (Figure 3.7), and will be contrasted with the CV results in the previous sections. These RTILs represent three distinct behaviors observed in the electrochemical studies above: (case 1)  $[C_{2}mim][NTf_{2}]$  shows a significant change in ORR current at low humidities, (case 2)  $[N_{4,1,1,1}][NTf_{2}]$  gives a stable ORR current at low RH%, and (case 3)  $[P_{14,6,6,6}][NTf_{2}]$  where the ORR current remains stable up to high moisture contents.

The electrode was held at the open circuit potential (OCP) and biased at -0.8 V (*vs.* the quasi-Pt-RE) to compare the effect of a negative surface biasing during ORR on the EDL. Several force-distance curves were collected and one representative curve per sample and condition is used for the discussion. It is noted that the studies were conducted on rough platinum thin-film electrodes which complicates the interpretation of results but were performed to represent the real conditions used for electrochemical sensing. Three overlayed force-distance curves per sample can be found in the ESI (Figure S3.17) to show the reproducibility at different areas on the electrode. We note that the layering of RTILs such as  $[C_2mim][NTf_2]$ ,<sup>55</sup>  $[C_4mpyrr][NTf_2]^{60}$  or ammonium RTILs<sup>38</sup> on a flat electrode under 'dry' conditions has been previously reported, but these conclusions may not be valid for a significantly rougher surface.



Figure 3.7 Representative force vs. distance curves for a silicon nitride cantilever approaching a Pt-TFE surface at the OCP (grey) and -0.8 V (vs. pseudo Pt RE) (orange) in (A) [C<sub>2</sub>mim][NTf<sub>2</sub>], in (B)  $[N_{4,1,1,1}][NTf_2]$  and in (C)  $[P_{14,6,6,6}][NTf_2]$  in 40 RH% (in air). An overlay of three force-curves for each experimental case can be found in the supporting information (Figure S3.17).

#### **3.1.3.2.1.** General Trends in AFM Force-curves

Overall, the force-curves in Figure 3.7 for both charged and uncharged surfaces show step-like features, superimposed on a broad curve with the force gradually increasing towards 0 nm separation. The broad curve is related to the compression of stable EDL structures by the tip as well as the interaction of the tip with the rough electrode surface. The steps correspond to tip-interaction with structured layers of molecules (*e.g.* cations, anions, water, etc.) orientated and assembled over the electrode surface. Subtle step-features are also present in between the more pronounced ones, which are attributed to either different conformations of ions, the presence of interstitial water or may be caused by roughness of the electrode surface. In the following discussions, the more pronounced layers will be referred to as layers 1, 2, 3, etc., with layer 1 being the surface-adsorbed innermost ion layer.

The thickness of the EDL can be observed by the occurrence of a 'snap-on' event. This is defined as the distance at which the descending tip experiences the first significant attractive force towards the diffuse layer and is observed as an abrupt drop in the measured force coinciding with the start of the compression behavior. Within the EDL, the pronounced layer-thicknesses can be estimated by measuring the width between

each step of the force-curves and are expected to be a function of the ion or ion-pair sizes. The force required for the AFM tip to puncture through a layer is referred to as the "push-through" force. Zhong *et al.*<sup>60</sup> reported that the EDL of [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] is structurally weakened in the presence of water, even at very low water contents around 66 ppm. Based on the results shown in Figure 3.5, [C<sub>2</sub>mim][NTf<sub>2</sub>], [S<sub>2,2,1</sub>][NTf<sub>2</sub>] and [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] show an early onset humidity, meaning that there is a significant amount of water present in the EDL even at low humidity levels. This is in contrast to the research reported by Cheng et al., where AFM studies were carried out in dry and humidified [C<sub>2</sub>mim][NTf<sub>2</sub>] on mica surfaces, with a silica-terminated silicon AFM tip (of 5-10 nm radius).<sup>55</sup> The steps appeared more pronounced under humidified conditions (43 RH%), and a negligible compression behavior was observed. This is probably because of the atomically smooth and uniform surface of Mica as well as the fact that water is required to charge the Mica surface. The uniformly charged and smooth surface of Mica allows highly ordered establishment of the first layer, which can then allow more ordered subsequent layers to form, whereas more disordered and less defined structures are expected on the rougher Pt-TFE surface used in our study (see discussions in supporting information).

Also, an interface-selective vibrational spectroscopy study on the behavior of ammonium ILs at Au interfaces showed that alkyl chains form a loose structure that reaches into the anion layer, resulting in a more interdigitated structure rather than a clearly separated alternating cation/anion layer.<sup>38</sup> This behavior could further add to the contribution of the superimposed compression-like feature, especially for the longer chain RTILs (*e.g.* [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>]). For this work, we have chosen to examine the EDL on the non-ideal Pt-TFE (also used for the CV experiments) since this is a more typical representation of an electrode surface found in real sensors.

#### **3.1.3.2.2.** Comparison of the EDL of Individual RTILs

To aid with the discussion, estimations of the layer thicknesses were obtained from computationally optimized molecular structures of each ion, as shown in Figure S3.20 in the supporting information. Orientations of the ions were based on suggestions from other research.<sup>37-38</sup>. Since only the first few layers are expected to have a strong influence on the electrochemistry at the Pt-RTIL interface, they will be focused on in the following sections.

#### Case 1: Unbiased electrode (at OCP)

In  $[C_2mim][NTf_2]$  and  $[N_{4,1,1,1}][NTf_2]$  several pronounced layers (Figure 3.7A and B grey arrows) are visible in the force-curves. However, in  $[P_{14,6,6,6}][NTf_2]$  no pronounced layers are discernible. During tip-engagement, the initial interaction with the EDL is with the diffuse layer, which typically occurs at a separation between 3.5 and 4.5 nm. For  $[C_2mim][NTf_2]$  the initial "snap-on" behavior occurs from ca. 4.5 nm to ca. 3.8 nm, which could indicate a higher degree of water-incorporation into the EDL structure compared to the bulk RTIL.

In [C<sub>2</sub>mim][NTf<sub>2</sub>], layer thicknesses are approximately 0.3 nm (layer 1), 0.63 nm (layer 2), and ~0.51 nm each for layers 3, 4 and 5. [C<sub>2</sub>mim]<sup>+</sup> is known to rest relatively flat and well-ordered on the surface.<sup>37</sup> The stability of this orientation will determine the effectiveness of the cation to block moisture adsorption at the electrode surface. Comparing the layer thicknesses with Figure 3.7, it can be assumed that the innermost layer almost equals the size of a cation ( $\approx$ 0.25 nm), followed by an anion layer ( $\approx$ 0.6 nm), as expected. Further layers are significantly thicker (around 0.5 nm) that would match a water + cation layer, or an anion layer. So the layer thickness suggests water incorporation between the ion layers, which was also concluded by Zhong *et al.* for [C<sub>4</sub>mpyrr][NTf<sub>2</sub>].<sup>60</sup>

 $[N_{4,1,1,1}][NTf_2]$  has approximately the following layer thicknesses: 0.5 nm (layer 1), 1.1 nm (layer 2), and the subsequent three layers are ca. 0.7–0.9 nm thick. Again, it can be assumed based on previous research that the innermost layer is formed by cations, followed by an anion layer. However, in this case no separate cation and anion layers can be detected and therefore it cannot be determined whether there is water incorporation or simply a less well separated cation–anion layer due to the presence of the longer alkyl chain. It may even be possible that the innermost layer is formed of a cation bilayer followed by the expected cation-anion double layers as predicted by Kornyshev *et al.* for 'tricky quaternary structures in combination with more compact anions'.<sup>67</sup> Examining the structure of  $[N_{4,1,1,1}]^+$ , the three short methyl groups (believed to be facing the electrode surface) would not be effective at shielding the localized positive charge on the nitrogen atom, allowing interaction with the water molecules and preventing adsorption on the Pt-surface. The absence of a 'snap-on' behavior, indicates that there is insignificant water incorporation within the EDL of this RTIL, and is consistent with the results in Figure 3.5. However it can be seen that the innermost layer is thicker for  $[N_{4,1,1,1}]^+$  compared to  $[C_2mim]^+$ .

In contrast,  $[P_{14,6,6,6}][NTf_2]$  does not form very prominent layers. Most force curves in this RTIL were dominated by a very obvious compression-like behavior without obvious structuring. These features could be associated with conformational changes of the long (14-carbon) alkyl chains coupled with re-organization of anions sandwiched between the cation layers that are held in an interdigitated pattern. Like with  $[N_{4,1,1,1}][NTf_2]$ , no initial "snap-on" behavior was present in  $[P_{14,6,6,6}][NTf_2]$ , which suggests an insignificant amount of water-incorporation into the EDL, consistent with the electrochemistry results. In summary, even on the rough Pt surface, ionic liquid structuring in the EDL can be observed in humid environments for the smaller cations, but no conclusions can be drawn for the larger phosphonium one – characterization on a flat electrode or SEIRAS measurements are required to determine whether structuring is present or not.

#### Case 2: Biased Pt electrode (at -0.8 V)

At a negatively biased Pt surface, the force-curves for  $[C_2mim][NTf_2]$  and  $[N_{4,1,1,1}][NTf_2]$  (Figure 3.7A and B, orange) reveal greater forces on the cantilever below a separation of ~1.5 nm compared to the unbiased case. In general, higher forces are required to push through the innermost layers which are composed of more ordered cations that are attracted more strongly to the negatively charged surface, as previously reported by Rivera-Rubero *et al.*<sup>37</sup> However, for  $[P_{14,6,6,6}][NTf_2]$ , the long hydrophobic alkyl chains are able to significantly shield the influence of the surface electric field, thus reducing the stabilizing effect of a negative potential bias and therefore no obvious changes in the structuring can be seen. Our experimental results agree well with a molecular dynamics simulation study,<sup>48</sup> and also support the CV observations for the  $[P_{14,6,6,6}]^+$ -based RTILs in Figure 3.5 and Figure 3.6.

Under negative potential biasing and above a separation of 0.5 nm, less pronounced steps are observed in humidified  $[C_2mim][NTf_2]$  (Figure 3.7A orange) as a result of water molecules competing for space with ions in the layers and therefore weakening the layering compared to the unbiased surface (Figure 3.7A grey) or dry environment.<sup>34, 60, 66</sup> In contrast, a higher number of pronounced layers are observed on the charged Pt electrode in  $[N_{4,1,1,1}][NTf_2]$ , which may hint at less disruption from

an increased number of water molecules incorporating in the EDL and competing for space with the RTIL ions under humidified conditions. For  $[P_{14,6,6,6}][NTf_2]$ , the much longer alkyl group of the cation prevents condensed and stable structures from forming but shielding of the positive charge coupled with the high hydrophobicity inhibits the incorporation of polar water molecules into the EDL. Furthermore, at distances > 1.5 nm, the layers remain relatively unaffected by negative biasing, which further substantiates this interpretation. In conclusion, potential biasing results in an increased force required to push through the innermost layers, and for the small RTIL cations, obvious structural layers begin to vanish due to the competition between water and IL ions.

#### 3.1.4. Conclusions

The ORR mechanism was studied by CV on Pt-TFEs in several different RTILs under humidified conditions. Peak potentials and currents were found to vary with humidity levels, showing a gradual shift in the reduction mechanism with increasing humidity (from < 1 to 95 RH%). The degree by which a given RTIL is susceptible to humidity changes was found to be a function of ion size, structure, and water affinity. Generally speaking, the cation influences the ORR current at humidity levels below 40 RH% due to the more pronounced structuring of the ions near the negatively charged electrode, while the anion has a more significant impact on the ORR reaction above 65 RH% where water molecules begin to disintegrate the EDL structures. AFM force-curve results indicated that water is present at the electrode-RTIL interface in [C<sub>2</sub>mim][NTf<sub>2</sub>] and [N<sub>4,1,1,1</sub>][NTf<sub>2</sub>], but is not detected in the hydrophobic RTIL [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>], which agrees well with the CV results. A much greater level of water incorporation in [C<sub>2</sub>mim][NTf<sub>2</sub>] was detected, which explains why the ORR current in this RTIL was highly affected by the presence of moisture even at extremely low humidity levels (e.g. < 5 RH%). The innermost EDL layers are stabilized at the negatively polarized electrode, and the water layer near the electrode-RTIL interface becomes more apparent in [C<sub>2</sub>mim][NTf<sub>2</sub>] and [N<sub>4,1,1,1</sub>][NTf<sub>2</sub>] due to the presence of ions and/or water molecules whereas the outer layers vanish due to the water incorporation. However, in [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>], the longer alkyl chain of the cation reduces the layering effect of the negative surface bias, and even at an electrode bias of -0.8 V, no indication of a waterlayer at the electrode-RTIL interface was observed. These results suggest that for applications where a stable ORR current response is necessary, the use of highly

hydrophobic and large RTIL cations and anions (*e.g.*  $[P_{14,6,6,6}]^+$  and  $[FAP]^-$ ) is recommended. Alternatively, if a large change with humidity is desired (*e.g.* for humidity sensors), the choice of hydrophilic ionic liquids could be favorably exploited.

### 3.1.5. References

1. Stetter, J. R.; Li, J., Amperometric Gas Sensors - A Review. *Chem. Rev.* 2008, 108, 352-366.

2. Xiong, L.; Compton, R. G., Amperometric Gas Detection: A Review. *Int. J. Electrochem. Sci.* **2014**, *9*, 7152-7181.

3. Freeman, B. D., Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes. *Macromolecules* **1999**, *32*, 375-380.

4. Buzzeo, M. C.; Hardacre, C.; Compton, R. G., Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.* **2004**, *76*, 4583-4588.

5. Malvaldi, M.; Chiappe, C., From molten salts to ionic liquids: effect of ion asymmetry and charge distribution. *J. Phys.: Condens. Matter* **2008**, *20*, 035108.

6. Freire, M. G.; Santos, L. M. N. B. F.; Fernandes, A. M.; Coutinho, J. A. P.; Marrucho, I. M., An overview of the mutual solubilities of water-imidazolium-based ionic liquid systems. *Fluid Ph. Equilibria* **2007**, *261*, 449-454.

7. Welton, T., Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chemical Reviews* **1999**, *99*, 2071-2084.

8. Buzzeo, M. C.; Evans, R. G.; Compton, R. G., Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry—A Review. *ChemPhysChem* **2004**, *5*, 1106-1120.

9. Shiddiky, M. J. A.; Torriero, A. A. J., Application of ionic liquids in electrochemical sensing systems. *Biosens Bioelectron* **2011**, *26*, 1775-1787.

Shvedene, N. V.; Chernyshov, D. V.; Pletnev, I. V., Ionic liquids in electrochemical sensors. *Russian Journal of General Chemistry* 2008, *78*, 2507-2520.
 Silvester, D. S., Recent advances in the use of ionic liquids for electrochemical sensing. *Analyst* 2011, *136*, 4871-4882.

12. Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R., Room temperature ionic liquids and their mixtures- A Review. *Fluid Phase Equilib.* **2004**, *219*, 93-98.

13. Barrosse-Antle, L. E.; Bond, A. M.; Compton, R. G.; O'Mahony, A. M.; Rogers, E. I.; Silvester, D. S., Voltammetry in Room Temperature Ionic Liquids: Comparisons and Contrasts with Conventional Electrochemical Solvents. *Chemistry – An Asian Journal* **2010**, *5*, 202-230.

14. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X., Investigating the electrochemical windows of ionic liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106-112.

15. Rehman, A.; Zeng, X., Methods and approaches of utilizing ionic liquids as gas sensing materials. *RSC Adv.* **2015**, *5*, 58371 - 58392.

16. Khan, A.; Gunawan, C. A.; Zhao, C., Oxygen Reduction Reaction in Ionic Liquids: Fundamentals and Applications in Energy and Sensors. *ACS Sustain. Chem. Eng.* **2017**, *5*, 3698-3715.

17. Chi, X.; Tang, Y.; Zeng, X., Electrode Reactions Coupled with Chemical Reactions of Oxygen, Water and Acetaldehyde in an Ionic Liquid: New Approaches for Sensing Volatile Organic Compounds. *Electrochim. Acta* **2016**, *216*, 171-180.

18. Lee, J.; Silvester, D. S., Electrochemical Detection of Explosive Compounds in an Ionic Liquid in Mixed Environments: Influence of Oxygen, Moisture, and Other Nitroaromatics on the Sensing Response. *Aust. J. Chem.* **2018**, *72*, 122-129.

19. Barnes, A. S.; Rogers, E. I.; Streeter, I.; Aldous, L.; Hardacre, C.; Wildgoose, G. G.; Compton, R. G., Unusual Voltammetry of the Reduction of  $O_2$  in  $[C_4dmim][N(Tf)_2]$  Reveals a Strong Interaction of  $O_2^{\bullet-}$  with the  $[C_4dmim]^+$  Cation. *J. Phys. Chem. C* **2008**, *112*, 13709-13715.

20. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Tan, X. M., Electrochemical reduction of dioxygen in Bis(trifluoromethylsulfonyl)imide based ionic liquids. *J. Electroanal. Chem.* **2011**, *657*, 150-157.

21. Katayama, Y.; Onodera, H.; Yamagata, M.; Miura, T., Electrochemical reduction of oxygen in some hydrophobic room-temperature molten systems. *J. Electrochem. Soc.* **2004**, *151*, A59-A63.

22. Switzer, E. E.; Zeller, R.; Chen, Q.; Sieradzki, K.; Buttry, D. A.; Friesen, C., Oxygen Reduction Reaction in Ionic Liquids: The Addition of Protic Species. *J. Phys. Chem. C* **2013**, *117*, 8683-8690.

23. Zhang, D.; Okajima, T.; Matsumoto, F.; Ohsaka, T., Electroreduction of Dioxygen in 1-n-Alkyl-3-methylimidazolium Tetrafluoroborate Room-Temperature Ionic Liquids. *J. Electrochem. Soc.* **2004**, *151*, D31-D37.

24. Yuan, X.-Z.; Alzate, V.; Xie, Z.; Ivey, D. G.; Qu, W., Oxygen Reduction Reaction in 1-Butyl-1-methyl-pyrrolidinium Bis(trifluoromethanesulfonyl)imide: Addition of Water as a Proton Species. *J. Electrochem. Soc.* **2014**, *161*, A451-A457.

25. Xiong, L.; Barnes, E. O.; Compton, R. G., Amperometric detection of oxygen under humid conditions: The use of a chemically reactive room temperature ionic liquid to 'trap' superoxide ions and ensure a simple one electron reduction. *Sens. Actuators B* **2014**, *200*, 157-166.

26. Tian, S.; Hou, Y.; Wu, W.; Ren, S.; Qian, J., Hydrophobic task-specific ionic liquids: Synthesis, properties and application for the capture of SO<sub>2</sub>. *J. Hazard. Mat.* **2014**, *278*, 409-416.

27. Fukay, Y.; Ohno, H., Hydrophobic and polar ionic liquids. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4066-4072.

28. Messadi, A.; Mohamadou, A.; Boudesocque, S.; Dupont, L.; Fricoteaux, P.; Nguyen-Van-Nhien, A.; Courty, M., Syntheses and characterisation of hydrophobic ionic liquids containing trialkyl(2-ethoxy-2-oxoethyl)ammonium or N-(1-methylpyrrolidyl-2-ethoxy-2-oxoethyl)ammonium cations. *J. Mol. Liq.* **2013**, *184*, 68-72.

29. Fuller, J.; Breda, A. C.; Carlin, R. T., Ionic liquid-polymer gel electrolytes from hydrophilic and hydrophobic ionic liquids. *J. Electroanal. Chem.* **1998**, *459*, 29-34.

30. Guan, J.; Li, Y.; Li, J., Stretchable Ionic-Liquid-Based Gel Polymer Electrolytes for Lithium-Ion Batteries. *Ind. Eng. Chem. Res.* **2017**, *56*, 12456-12463.

31. Ruzanov, A.; Lembinen, M.; Jakovits, P.; Srirama, S. N.; Voroshylova, I. V.; Cordeiro, M. N. D. S.; Pereira, C. M.; Rossmeisl, J.; Ivaništšev, V. B., On the thickness of the double layer in ionic liquids. *Phys. Chem. Chem. Phys.* **2018**, *20*, 10275-10285.

32. Hayes, R.; Warr, G. G.; Atkin, R., Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* 2015, *115*, 6357-6426.

33. Li, H.; Endres, F.; Atkin, R., Effect of alkyl chain length and anion species on the interfacial nanostructure of ionic liquids at the Au(111)-ionic liquid interface as a function of potential. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14624-14633.

34. Hayes, R.; Borisenko, N.; Tam, M. K.; Howlett, P. C.; Endres, F.; Atkin, R., Double Layer Structure of Ionic Liquids at the Au(111) Electrode Interface: An Atomic Force Microscopy Investigation. *J. Phys. Chem. C* **2011**, *115*, 6855-6863.

35. Perkin, S., Ionic liquids in confined geometries. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5052-5062.

36. Lauw, Y.; Rodopoulos, T.; Gross, M.; Nelson, A.; Gardner, R.; Horne, D., Electrochemical cell for neutron reflectometry studies of the structure of ionic liquids at electrified interface. *Rev. Sci. Instrum.* **2010**, *81*, 074101.

37. Rivera-Rubero, S.; Baldelli, S., Surface Spectroscopy of Room-Temperature Ionic Liquids on a Platinum Electrode: A Sum Frequency Generation Study. *J. Phys. Chem. B* **2004**, *108*, 15133-15140.

38. Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T., Interfacial Structure at the quaternary Ammonium-Based Ionic Liquid/Gold Electrode Interface Probed by Surface-Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior. *J. Phys. Chem. C* **2017**, *121*, 1658-1666.

39. Hoth, J.; Hausen, F.; Mueser, M. H.; Bennewitz, R., Force microscopy of layering and friction in an ionic liquid. *J. Phys. Condens. Matter* **2014**, *26*, 284110.

40. McLean, B.; Li, H.; Stefanovic, R.; Wood, R. J.; Webber, G. B.; Ueno, K.; Watanabe, M.; Warr, G. G.; Page, A.; Atkin, R., Nanostructure of [Li(G4)] TFSI and [Li(G4)] NO<sub>3</sub> solvate ionic liquids at HOPG and Au(111) electrode interfaces as a function of potential. *Phys. Chem. Chem. Phys.* **2015**, *17*, 325-333.

41. Zhong, Y.-X.; Yan, J.-W.; Li, M.-G.; Zhang, X.; He, D.-W.; Mao, B.-W., Resolving Fine Structures of the Electric Double Layer of Electrochemical Interfaces in Ionic Liquids with an AFM Tip Modification Strategy. *J. Am. Chem. Soc.* **2015**, *136*, 14682-14685.

42. Carstens, T.; Hayes, R.; El Abedin, S. Z.; Corr, B.; Webber, G. B.; Borisenko, N.; Atkin, R.; Endres, F., In situ STM, AFM and DTS study of the interface 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate/Au(111). *Electrochim. Acta* **2012**, *82*, 48-59.

43. Ivanistsev, V.; O'Connor, S.; Fedorov, M. V., Poly(a)morphic portrait of the electrical double layer ionic liquids. *Electrochem. Commun.* **2014**, *48*, 61-64.

44. Fedorov, M. V.; Kornyshev, A. A., Towards understanding the structure and capacitance of electrical double layer in ionic liquids. *Electrochim. Acta* **2008**, *53*, 6835-6840.

45. Feng, G.; Jiang, X.; Qiao, R.; Kornyshev, A. A., Water in Ionic Liquids at Electrified Interfaces: The Anatomy of Electrosorption. *ACS Nano* **2014**, *8*, 11685-11694.

46. Nikitina, V. A.; Kislenko, S. A.; Nazmutdinov, R. R.; Bronshtein, M. D.; Tsirlina, G. A., Ferrocene/Ferrocenium Redox Couple at Au(111)/Ionic Liquid and

Au(111)/Acetonitrile Interfaces: A Molecular-Level View at the Elementary Act. J. Phys. Chem. C 2014, 118, 6151-6164.

47. Zhou, T.; Chen, L.; Ye, Y.; Chen, L.; Qi, Z.; Freund, H.; Sundmacher, K., An Overview of Mutual Solubility of Ionic Liquids and Water Predicted by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 6256-6264.

48. Bi, S.; Wang, R.; Liu, S.; Yan, J.; Mao, B.; Kornyshev, A. A.; Feng, G., Minimizing the electrosorption of water from humid ionic liquids on electrodes. *Nat. Commun.* **2018**, *9*, 5222.

49. Sun, J.; MacFarlane, D. R.; Forsyth, M., Synthesis and Properties of Ambient Temperature Molten Salts Based on the Quaternary Ammonium Ion. *Ionics* **1997**, *3*, 356-362.

50. Wandt, J.; Lee, J.; Arrigan, D.; Silvester, D. S., A lithium iron phosphate reference electrode for ionic liquid electrolytes. *Electrochem. Commun.* **2018**, *93*, 148-151.

51. Lee, J.; Du Plessis, G.; Arrigan, D. W. M.; Silvester, D. S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Anal. Methods* **2015**, *7*, 7327-7335.

52. Wagner, W.; Pruss, A., The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387535.

53. Oyi, V. Humidity Conversion Formulas; B210973EN-F; 2013.

54. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 2884-2891.

55. Cheng, H. W.; Dienemann, J. N.; Stock, P.; Merola, C.; Chen, Y. J.; Valtiner, M., The Effect of Water and Confinement on Self-Assembly of Imidazolium Based Ionic Liquids at Mica Interfaces. *Sci. Rep.* **2016**, *6*, 30058.

56. Cheng, H.-W.; Stock, P.; Moeremans, B.; Baimpos, T.; Banquy, X.; Renner, F. U.; Valtiner, M., Characterizing the Influence of Water on Charging and Layering at Electrified Ionic-Liquid/Solid Interfaces. *Adv. Mater. Interfaces* **2015**, *2*, 1500159.

57. Ignat'ev, N. V.; Welz-Biermann, U.; Kucheryna, A.; Bissky, G.; Willner, H., New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions. *J. Fluor. Chem.* **2005**, *126*, 1150-1159.

58. Budkov, Y. A.; Kolesnikov, A. L.; Goodwin, Z. A. H.; Kiselev, M. G.; Kornyshev, A. A., Theory of electrosorption of water from ionic liquids. *Electrochim. Acta* **2018**, *284*, 346-354.

59. Khan, I.; Kurnia, K. A.; Mutelet, F.; Pinho, S. P.; Coutinho, J. A. P., Probing the Interactions between Ionic Liquids and Water: Experimental and Quantum Chemical Approach. *J. Phys. Chem. B* **2014**, *118*, 1848-1860.

60. Zhong, Y.; Yan, J.; Li, M.; Chen, L.; Mao, B., The Electric Double Layer in an Ionic liquid Incorporated with Water Molecules: Atomic Force Microscopy Force Curve Study. *ChemElectroChem* **2016**, *3*, 2221-2226.

61. Freire, M. G.; Neves, C. M. S. S.; Marrucho, I. M.; Coutinho, J. A. P.; Fernandes, A. M., Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A* **2010**, *114*, 3744-3749.

62. Fedorov, M. V.; Konrnyshev, A. A., Ionic Liquids at Electrified Interfaces. *A. Chem. Rev.* **2014**, *114*, 2978-3036.

63. Feng, G.; Zhang, J. S.; Qiao, R., Microstructure and Capacitance of the Electrical Double Layers at the Interface of Ionic Liquids and Planar Electrodes. *J. Phys. Chem. C* **2009**, *113*, 4549-4559.

64. Lockett, V.; Horne, M.; Sedev, R.; Rodopoulos, T.; Ralston, J., Differential capacitance of the double layer at the electrode/ionic liquids interface. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12499-12512.

65. Lockett, V.; Sedev, R.; Harmer, S.; Ralston, J.; Horne, M.; Rodopoulos, T., Orientation and mutual location of ions at the surface of ionic liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13816-13827.

66. Hayes, R. Structure in Ionic Liquids. The University of Newcastle, Australia, 2014.

67. Kornyshev, A. A., Double-Layer in Ionic Liquids: Paradigm Change? J. Phys. Chem. B 2007, 111, 5545-5557.
#### **3.1.6.** Supporting Information



*Figure S3.8. Chemical structure and* <sup>1</sup>*H-NMR signals of the synthesized RTIL* [*N*<sub>7,2,2,2</sub>][*NT*<sub>f2</sub>].

Nuclear magnetic resonance spectra were recorded using a Bruker Avance 400 spectrometer (400 MHz for <sup>1</sup>H-NMR).

<sup>1</sup>H-NMR (δ / ppm, acetone-*d*<sub>6</sub>): 0.89 (3H, m), 1.32 (4H, m), 1.42 (13H, m), 1.85 (2H, m), 3.45 (2H, m), 3.53 (6H, q).



Figure S3.9. ORR CVs of (a)  $[C_{4}mim][BF_{4}]$  and (b)  $[P_{14,6,6,6}][FAP]$  at different humidities. CVs were measured every 45 min with a scan rate of 100 mV s<sup>-1</sup>, a step potential of -2.5 mV and an oxygen concentration of 100 vol.%.



Figure S3.10. Normalized current as a function of exposure time for the ionic liquid [C<sub>4</sub>mim][BF<sub>4</sub>] at RH% values of 10% ( $\bullet$ ), 60% ( $\bullet$ ), 60% with a longer waiting time ( $\blacktriangle$ ) and 90% ( $\bigtriangledown$ ).



Figure S3.11. Normalized current as a function of exposure time for the ionic liquid  $[P_{14,6,6,6}][FAP]$  at RH% values of 10% ( $\blacksquare$ ), 50% ( $\bullet$ ) and 90% ( $\blacktriangle$ ).



Figure S3.12. Normalized current as a function of exposure time for the ionic liquid  $[C_{2mim}][NTf_{2}]$  at RH% values of 10% ( $\blacksquare$ ), 55% ( $\bullet$ ) and 90% ( $\blacktriangle$ ).



Figure S3.13. Normalized current as a function of exposure time for the ionic liquid  $[C_4 mim][PF_6]$  at RH% values of 10% ( $\blacksquare$ ), 50% ( $\bullet$ ) and 90% ( $\blacktriangle$ ).



Figure S3.14. (a) CVs and (b) normalized current vs. applied humidity for the ORR in the RTIL  $[C_{4}py][NTf_{2}]$ . CVs were measured every 45 min at a scan rate of 100 mV s<sup>-1</sup> and a step potential of -2.5 mV and an oxygen concentration of 100 vol.%. Current was normalized according to the peak current of the lowest humidity level.

An AFM map of a bare Pt-TFE surface is shown in Figure S3.15. The surface statistics were analyzed using the software Gwyddion 2.49 (<u>http://gwyddion.net/</u>), giving an average height of 4.1 nm and a mean-square roughness of 1.2 nm. These values are larger than the sub-nm EDL structures that are being probed. The step-like structures can be attributed to the AFM-tip interacting with the EDL established on the electrode, with superimposed compression-like features from the diffuse layer established from the surrounding troughs and valleys, illustrated in Figure S3.16.



Figure S3.15. Three-dimensional AFM map of an activated bare Pt-TFE surface in air obtained by contact-mode technique. Note: The Z-axis is not on the same scale as the X-Y plane, making the protrusion of surface features more exaggerated.



Figure S3.16. Illustration of how the electrical double layer of the RTIL may vary on an uneven surface, such as the Pt thin-film electrode used in the experiments.

Table S3.1. Cartesian (x, y, and z) dimensions of each ionic species from PM3 computationally optimized structures (shown in Figure S3.20) with the x-axis aligned with the widest length, as well as the corresponding (CPK model) volumes.

RTIL ion	<i>x  </i> nm	<i>y</i> / nm	<i>z  </i> nm	Volume / nm <sup>3</sup>	Solvation
					Energy <sub>(aq)</sub> , SE* /
					kJ mol <sup>-1</sup>
$[C_2 mim]^+$	0.69	0.50	0.26	0.137	-189
$[C_4mim]^+$	-	-	-	0.173	-185
$[C_6mim]^+$	-	-	-	0.208	-173
$[C_4py]^+$	-	-	-	0.171	-191
$[C_4mpyrr]^+$	-	-	-	0.185	-190
$[N_{4,1,1,1}]^+$	0.73	0.43	0.36	0.159	-200
$[N_{7,2,2,2}]^+$	-	-	-	0.266	-177
$[P_{14,6,6,6}]^+$	1.98	1.04	0.73	0.630	32
$[S_{2,2,1}]^+$	-	-	-	0.131	-204
$[NTf_2]^-$	0.81	0.39	0.31	0.160	-222
$[PF_6]^-$	-	-	-	0.073	-244
[FAP] <sup>-</sup>	-	-	-	0.247	-169
$[BF_4]^-$	-	-	-	0.053	-268
$H_2O$	0.16	-	-	0.019	-259

\* The lower the SE values, the greater the affinity towards the surrounding polar molecules (*e.g.* water). Note: All values are based on a single ionic molecule in vacuum.

NOTE: Due to air exposure, an oxide layer is expected to form on the surface of the silicon nitride AFM-tip, which can react with moisture to form a layer of hydrophilic hydroxyl groups when immersed in the humidified RTIL. A hydrophilic interface will thus impart a small attractive force on the engaging AFM-tip.



Figure S3.17. Three overlayed force-distance curves for the RTILs  $[P_{14,6,6,6}][NTF_2]$  (top),  $[N_{4,1,1,1}][NTf_2]$  (middle) and  $[C_{2}mim][NTf_2]$  (bottom) at the OCP (left) and a bias potential of -0.8 V (right).

Before proceeding with the force curve measurements, the sample was mapped, and a suitable flat spot was chosen. At least 500 and up to over 1,000 force curves were collected for each RTIL, with the Pt-TFE substrate unbiased at OCP, and then biased at -0.8 V. The raw data was batch-processed with the help of a code (programmed inhouse) to extract useful data, to assist with the identification and selection of force curves that show distinct EDL features, as well as to automate the conversion into force-separation plots. The best ca. 20 short-listed force-curves were then selected for analysis. The rough electrode surface made averaging the force curves difficult, therefore a representative "best" force curve for each RTIL and biasing condition is

presented, with an overlay of three force-distance curves shown in Figure S3.17. The approach of the AFM tip disturbs the surface structure, therefore low scan rates as well as high ramp sizes were chosen to allow time for reorganization of ions in the EDL.



H<sub>2</sub> bubble formation at the RTIL-Pt interface under negative bias:

Figure S3.18. Generation of  $H_2$  bubbles during AFM measurements in the RTIL [ $C_2mim$ ][NT $f_2$ ] at an applied potential of -0.8 V (vs. pseudo Pt) as a function of time: (A) 0 s, (B) 150 s, (C) 300 s, (D) 500 s, (E) 750 s, (F) 2,000 s, (G) 3,500 s and (H) 4500 s. The cantilever dimension (from tip to edge of the photo) is 100  $\mu$ m.



Figure S3.19. Absence of  $H_2$  bubble generation during AFM measurements in the RTIL [ $P_{14,6,6,6}$ ][NTf<sub>2</sub>] at an applied potential of -0.8 V (vs. pseudo Pt) as a function of time (A) 0 s, (B) 100 s, (C) 250 s, (D) 500 s, (E) 750 s, (F) 1,500 s, (G) 2,500 s and (H) 4,000 s. The cantilever dimension (from tip to edge of the photo) is 100  $\mu$ m.

It was observed that at sufficiently high negative biasing (> -1 V), rapid formation of  $H_2$  bubbles on the Pt surface appear in [C<sub>2</sub>mim][NTf<sub>2</sub>] due to the reduction of water. Hence, a biasing of -0.8 V was used, to reduce the rate of  $H_2$  bubble formation at the electrode-RTIL interface. Optical images from the AFM instrument showing the bubble growth and build-up over time can be found in Figure S3.18, where visible  $H_2$  bubbles are generated after ca. 300 s. In contrast, no observable bubbles were formed in  $[P_{14,6,6,6}][NTf_2]$  at WE potentials from -0.8 V and even down to -2.5 V after 30 min of constant biasing (see Figure S3.19). This observation agrees with the CV (Figure 3.5) and AFM results (Figure 3.7) in the main text. Significant O<sub>2</sub> bubble formation was also observed under an anodic bias at +1 V in  $[C_2mim][NTf_2]$  (not shown).

The bubbles can "block" the accessible electrode surface and hinder the progress of the ORR. High instability in the CV peak currents is apparent from the  $I_{norm}$  vs. humidity plots in Figures 4 to 6 of the main text, especially approaching higher humidity levels. [P<sub>14,6,6,6</sub>]<sup>+</sup>-based RTILs exhibit significantly less instability in the measured peak currents (Figure 3.5 and Figure 3.6 of the main text). The gradual build-up and growth of the interfacial bubbles could lead to extreme instability during constant biasing conditions (*e.g.* amperometric monitoring of O<sub>2</sub>). This highlights the importance of the choice of electrode material in RTIL-based experiments or for applications carried out under humid conditions. The use of an electrode material (*e.g.* gold, silver, or glassy carbon) that does not have a significant growth of H<sub>2</sub> bubbles *e.g.* at biasing times < 300 s). It is believed that during repeated tip-surface engagement, the tip was occasionally able to displace any formed micro-bubbles, thus allowing the RTIL EDL to re-form and be probed on the next tip-engagement.

Estimation of cation and anion dimensions from computationally optimized molecular structures.



Figure S3.20. Computationally optimized (PM3) structures of cations  $[C_{2mim}]^+$ ,  $[N_{4,1,1,1}]^+$ , and  $[P_{14,6,6,6}]^+$ , and the anion  $[NTf_2]^-$ -based on assumed orientations and conformations suggested in other work.<sup>1-2</sup> Distances that are assumed to be significant to the double-layers formed are estimated as indicated.

### References

1. Rivera-Rubero, S.; Baldelli, S., Surface Spectroscopy of Room-Temperature Ionic Liquids on a Platinum Electrode: A Sum Frequency Generation Study. *J. Phys. Chem. B* **2004**, *108*, 15133-15140.

2. Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T., Interfacial Structure at the quaternary Ammonium-Based Ionic Liquid/Gold Electrode Interface Probed by Surface-Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior. *J. Phys. Chem. C* **2017**, *121*, 1658-1666.

### 3.2. Effect of Humidity and Impurities on the Electrochemical Window of Ionic Liquids and Its Implications for Electroanalysis

This chapter has been published in the following peer-reviewed journal:

Doblinger, S., Donati, T. J., Silvester, D. S., Effect of Humidity and Impurities on the Electrochemical Window of Ionic Liquids and Its Implications for Electrocatalysis. *J. Phys. Chem. C* **2020**, *124*, 20309-20319.

The abstract has been removed for this chapter and the supporting information has been included after the references. Figure and table captions as well as equation numbers have been changed. A few changes to the formatting have been made.

#### **Author Contributions:**

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 80%/100%

Acquisition of Data and Method: 80%/100%

**Data Conditioning and Manipulation:** 90%/100%

Analysis and Statistical Method: 85%/100%

Interpretation and Discussion: 70%/100%

Final Approval: 70%/100%

Signature:

Simon Doblinger

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 0%/100%

Acquisition of Data and Method: 20%/100%

**Data Conditioning and Manipulation:** 10%/100%

Analysis and Statistical Method: 15%/100% Interpretation and Discussion: 10%/100% Final Approval: 10%/100%

Signature: \_\_\_\_\_

Taylor J. Donati

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design: 20%/100%** 

Acquisition of Data and Method: 0%/100%

Data Conditioning and Manipulation: 0%/100%

Analysis and Statistical Method: 0%/100%

**Interpretation and Discussion:** 20%/100%

Final Approval: 20%/100%

Signature: \_\_\_\_\_

Debbie S. Silvester

#### **3.2.1.** Introduction

Room temperature ionic liquids (RTILs) are employed in various research fields as replacements for conventional solvents due to their promising characteristics like low volatility, intrinsic conductivity, good solubilization properties, high chemical and physical stability, in combination with broad electrochemical windows.<sup>1-2</sup> Their application as electrolytes in batteries<sup>3</sup> and fuel cells<sup>4</sup>, as solvents in organic synthesis<sup>5</sup> or as lubricants<sup>6-7</sup> is an active research topic nowadays. RTILs are liquid at 25 °C due to the combination of asymmetrical cations and anions that cause reduced ion-ion interactions and lower melting points than traditional salts.<sup>5, 8</sup> However, the ionic nature results in a highly hygroscopic characteristic, the strength of which depends upon the exact cation-anion combination. COSMO-RS calculations<sup>9</sup> as well as experimental studies<sup>10-11</sup> have shown that the solubility of water is highly dependent on the ionic liquid anion-water interactions in the bulk phase, with a trend of increasing hydrophilicity from  $[FAP]^- < [NTf_2]^- < [PF_6]^- < [BF_4]^- < [halides]^-$ . The physicochemical properties are highly dependent on the water content and the influence on properties like density and viscosity has been studied by several groups.<sup>12-</sup> <sup>13</sup> However, an in-depth understanding of what occurs at a molecular level is still not fully present. In addition to their hygroscopic nature, a challenge faced when using RTILs is the difficulty of purification after synthesis; due to their good solubilization properties, as well as high boiling points, simple distillation or extraction steps are less successful. A review by Barrosse-Antle et al.14 discussed the effect of different impurities such as water, halides, gases and trace synthetic impurities on the cyclic voltammetry response of the ionic liquid. It is noted that cyclic voltammetry is a highly sensitive electrochemical method for observing even low concentrations of redox active molecules.

The use of RTILs for electrochemical sensing applications has been the research focus of several groups.<sup>15-24</sup> The voltammetric responses of various gases in RTILs including oxygen<sup>25-26</sup>, nitrogen dioxide<sup>27</sup>, ammonia gas<sup>28</sup> and hydrogen sulfide<sup>29</sup> have been studied mostly in ideal 'dry' conditions with only one analyte present. However, the presence of water, in the case of a sensor exposed to an open environment with a broad range of humidity conditions, or other impurities, in enclosed systems like batteries, has a significant influence. Liu *et al.*<sup>30</sup> studied the effect of water on electrochemical oxygen sensing in 'dry' and 'wet' [C4mim][BF4] on a planar microsensor device,

showing a drastic influence of water on the redox potential and the current of the oxygen reduction reaction (ORR), and good stability for the water-free and watersaturated electrolyte. We previously demonstrated the effect of the RTIL structure on the ORR in various RTILs<sup>31</sup>, where it is known that in dry conditions, a reversible oneelectron reduction to superoxide is observed.<sup>32</sup> The presence of moisture, however, changes the mechanism to an irreversible two- or even four-electron process, depending on the concentration of water.<sup>33-35</sup> At low relative humidity (RH) levels, the ionic liquid cation structure significantly alters the availability of water within the electrical double layer to react with the electrogenerated superoxide radical, whereas the anion mainly affects the response at high moisture contents where the electrolyte behaves more like the ionic liquid 'bulk'.<sup>31</sup> This is because RTILs form structures at electrified interfaces<sup>36-38</sup>, where at low relative humidities, the alkyl chains of the cations can form a compact hydrophobic layer, effectively preventing the accumulation of water at the electrode. At high humidity levels, a weakening of the structuring and a dramatic change of the ORR mechanism, is observed. For the oxygen reduction reaction, where the electrochemical mechanism changes at different moisture contents, this effect can be suppressed or enhanced by changing the cation and anion combination of the ionic liquid.<sup>31</sup>

O'Mahony *et al.*<sup>11</sup> investigated the effect of water on the electrochemical window and the potential limits of 12 RTILs in 'dried', 'ambient' and 'water saturated' systems at three temperatures, *i.e.* 298 K, 318 K and 338 K. Their study clearly showed a drastic reduction in the electrochemical window from vacuum-dried to water saturated conditions, *e.g.* for  $[C_{2}mim][NTf_{2}]$ , the window was reduced from 4.2 V (vacuum-dried) to 2.8 V in atmospheric conditions, using a cut-off current density of 1 mA cm<sup>-2</sup>.<sup>11</sup> The variation in water content due to the identity of the anion was also discussed, indicating the same trend as stated above. Schröder *et al.*<sup>39</sup> investigated the absorption of water from a water-saturated argon gas stream into ionic liquids. It was concluded that the presence of water reduces the viscosity of the RTIL, and the rate of diffusion of dissolved ionic and non-ionic species is affected differently in 'wet' RTILs due to the nanostructuring of polar and non-polar regions. We note that the impact of a controlled relative humidity level on the electrochemical window has not been studied in detail so far. Therefore, in this work we have studied this effect using cyclic voltammetry for nine commercially available RTILs with various cations and anions,

by controlling the humidity of the gas phase above the ionic liquid. Additionally, we have investigated the effect of changing transport properties like viscosity and the reduced electrochemical window of the water-saturated ionic liquids on the voltammetric response of two model analytes, decamethylferrocene (DmFc) and ammonia (NH<sub>3</sub>) gas. The anodic and cathodic limits of the electrochemical window are determined in dry conditions by the oxidation and reduction of the ionic liquid cation and anion, respectively. The introduction of water via a gas stream of a controlled relative humidity level eventually results in the two limits being defined by the electrochemical window of water.

#### **3.2.2.** Experimental

#### 3.2.2.1. Chemical Reagents

All RTILs were obtained at the highest purities possible from commercial suppliers. Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide ([S<sub>2,2,1</sub>][NTf<sub>2</sub>], 99%, Technologies IoLiTec-Ionic Liquids GmbH, Heilbronn, Germany), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N<sub>4,1,1</sub>][NTf<sub>2</sub>], 99.5%, IoLiTec), butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide  $([C_4mpyrr][NTf_2],$ 99.5%, IoLiTec). butylmethylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([C4mpyrr][FAP], high purity >99%, Merck Kilsyth, Ltd. Victoria, Australia), 1-ethyl-3-methylimidazolium Pty. bis(trifluoromethylsulfonyl)imide ([C2mim][NTf2], 99.5%, IoLiTec), 1-butyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec), 1-butyl-3-methylimidazolium tetrafluoroborate ([C<sub>4</sub>mim][BF<sub>4</sub>], 99%, IoLiTec), 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>], high >99%. Merck). 1-butyl-3-methylimidazolium purity tris(pentafluoroethyl)trifluorophosphate ([C<sub>4</sub>mim][FAP], high purity >99%, Merck) were used as received. Ultrapure water with a resistivity of 18.2 M $\Omega$  cm prepared by a Milli-Q laboratory water purification system (Millipore Pty Ltd., North Ryde, NSW, Australia) was used for humidifying the nitrogen gas stream. Acetone HPLC, ≥99.0%, (CHROMASOLV®, for Sigma-Aldrich) and bis(pentamethylcyclopentadienyl)iron(II) (DmFc, 97%, Sigma-Aldrich) were used as received. A saturated DmFc solution in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] was prepared by dissolving 5 mg of the solid in 0.5 mL of ionic liquid. An aliquot of 1  $\mu$ L of the supernatant was then used for the electrochemical experiment. A 0.5 M stock solution of  $H_2SO_4$  (aq) 108

(prepared with ultrapure water from a 95-98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for the activation of the platinum thin-film electrodes (Pt-TFEs). An ammonia gas cylinder (1000 ppm in nitrogen) was purchased from CAC Gases (NSW, Australia) and a high purity nitrogen gas cylinder (99.99%, grade 4) was purchased from Coregas (NSW, Australia).

#### **3.2.2.2.** Electrochemical Experiments

Cyclic voltammetry (CV) measurements were performed with a PGSTAT101 Autolab potentiostat (Metrohm, Gladesville, NSW, Australia) interfaced to a computer with NOVA 1.11 software. The electrochemical cell was housed in an aluminum Faraday cage to reduce electromagnetic interferences. The working electrode (WE), counter electrode (CE) and reference electrode (RE) of the thin-film electrodes (TFEs) (ED-SE1 Pt, MicruX Technologies, Oviedo, Spain) are composed of platinum (Pt) deposited on a Pyrex substrate, with a WE disk diameter of 1 mm (area ~0.785 mm<sup>2</sup>). Wires were soldered onto the connecting pads of the chip. The WE was electrochemically activated prior to each experiment by CV cycling ( $\approx$  100 times) at 1 V s<sup>-1</sup> in nitrogen purged 0.5 M H<sub>2</sub>SO<sub>4</sub> (aq) between -0.75 V and +0.70 V. The activated chips were then rinsed twice with ultrapure water and acetone before drying under a nitrogen stream. Previous investigations<sup>40-41</sup> have shown an excellent reproducibility (within ~2–5%) for electrochemical responses on these TFEs.

1  $\mu$ L of the electrolyte was drop-cast to cover all three electrodes on the TFE and purged for approximately 30 min in a high purity nitrogen stream at a flow rate of 500 mL min<sup>-1</sup> until a constant blank CV was measured. This was done to remove dissolved gases such as oxygen and carbon dioxide. The low volume of electrolyte required to cover all electrodes on the planar device ensures that the equilibration time is relatively fast. For all measurements, the integrated Pt-CE, Pt-WE and Pt-RE were used. After achieving a constant blank, humidified nitrogen gas at a flow rate of 500 mL min<sup>-1</sup> was introduced into one arm of a modified glass T-cell<sup>42</sup> for the potential window and DmFc experiments. For the NH<sub>3</sub> experiments, dry ammonia gas with a flow rate on 125 mL min<sup>-1</sup> was introduced. To introduce environments with different humidities, the dry carrier nitrogen gas line was additionally connected to a humidity generator (Owlstone Humidity Generator OHG-4, Owlstone, Cambridge, UK) that separates the gas flow into 'dry' and 'wet' streams by bubbling the gas through a container of 400 mL of ultrapure water at a flow rate of 500 mL min<sup>-1</sup>. The detailed experimental set-up is shown in our previous work.<sup>31</sup>

Since the humidity sensor is not able to measure humidity levels lower than 1 RH%, measurements were conducted at a starting humidity level of ~1 RH%. It has been reported in the literature that even with prolonged vacuum purging, a significant amount of water is retained (in the  $\sim 10 - 100$  ppm range<sup>11</sup>) in the RTIL. An equilibration time of 20 min was employed before performing CV scans at each humidity level to ensure that the gas was fully saturated, particularly in the most viscous ionic liquid. A second CV scan for NH<sub>3</sub> detection was carried out after further 20 min under constant humidity conditions to ensure full equilibration. 20 mins was found to be more than sufficient for equilibrium to be attained across all RTILs and humidities. It is noted that water uptake times of up to 180 min were observed for RTILs at different humidity environments,<sup>43</sup> but that study employed a larger volume of ionic liquid and used a static set-up, in contrast to the large surface-to-volume (one microliter RTIL droplet spread out over a thin-film electrode) and the constant flow system used in our experiments.

#### 3.2.3. Results and Discussion

The effect of increasing moisture contents on the electrochemical window (EW) of nine commercially available room temperature ionic liquids (RTILs) with different cations and anions has been studied via cyclic voltammetry (CV), showing how water reduced the electrochemical window (EW) and promoted the observation of dissolved impurities already present in the ionic liquids. We also demonstrate how the presence of moisture in  $[C_4mpyrr][NTf_2]$  affected the voltammetry of two dissolved species (decamethylferrocene (DmFc) and ammonia (NH<sub>3</sub>)), whose electrochemical reaction mechanisms are known to be unaffected by follow-up reactions in the presence of water.

# 3.2.3.1. Effect of Humidity on the Electrochemical Window of RTILs

The impact of impurities and moisture on the electrochemical window (EW) of nine different ionic liquids has been examined by analyzing the cyclic voltammetry response on a platinum thin-film electrode (Pt-TFE) at a scan rate of 100 mV s<sup>-1</sup>. Electrochemical windows of various ionic liquids have been widely reported by

several research groups with typical cut-off current densities higher than 0.5 mA cm<sup>-2</sup>.<sup>11, 39, 44-45</sup> However, most researchers do not show a close-up of the lower current region, where often it is observed to have some noticeable redox features (based on our observations), in contrast to conventional solvent/electrolyte systems that show featureless voltammetry. Even at the highest purity level offered by commercial suppliers, RTILs contain some impurities, and they often vary from batch to batch for the same RTIL. Therefore, we determined the electrochemical window of several commercially available RTILs with different cations and anions under 'dry' conditions (at a relative humidity level below 1%) using a cut-off current of 15 µA (~1.9 mA cm<sup>-2</sup> current density) (blue) as well as 1.5  $\mu$ A (~0.19 mA cm<sup>-2</sup> current density) (red) (Figure 3.21). As can be seen for the higher cut-off current, most CVs appear to be relatively flat resulting in wide electrochemical windows between 4.3 and 6.5 V, which are comparable to those reported previously by other research groups for 'dry' RTILs.<sup>11, 14, 45-48</sup> Due to the use of a platinum pseudo reference electrode, anodic and cathodic potential limits between different ionic liquids cannot be directly compared, although the absolute potential windows should not be affected by the unstable reference. We note that the RTILs used in our study were not vacuum dried, only thoroughly purged in a nitrogen stream with a controlled humidity level of <1 RH%.

Comparing ionic liquids with the same anion, *i.e.*  $[NTf_2]^-$ , and different cations (see Figure 3.21a, b, d, e and g), the trend of the widest electrochemical window, and therefore electrochemically more stable ionic liquid, is as follows:  $[C_2mim]^+ < [C_4mim]^+ < [S_{2,2,1}]^+ < [N_{4,1,1,1}]^+ \approx [C_4mpyrr]^+$ . Consistent with other reports<sup>49</sup>, imidazolium-based cations are more easily reduced compared to single centered cations like pyrrolidinium or ammonium, and the longer the alkyl chain in the RTIL, the higher the electrochemical stability. The trend for electrolytes with the same cation, *i.e.*  $[C_4mim]^+$ , and different anions (see Figure 3.21c, e, f and i) is:  $[BF_4]^- < [PF_6]^- \approx [NTf_2]^- < [FAP]^-$ . This is in contrast to the trend of increasing stability from  $[NTf_2]^- < [BF_4]^- < [PF_6]^- \approx [BF_4]^- < [PF_6]^-$  established via computational calculations by Kazemiabnavi *et al.*<sup>50</sup> In our experiments, a controlled humidity level of <1 RH% and no vacuum drying of the RTILs means that traces of water are introduced into in the electrolyte, which we believe is enough to cause a reduced EW for the two more hydrophilic samples, *i.e.*  $[C_4mim][BF_4]$  and  $[C_4mim][PF_6]$ . The electrochemically most stable RTIL out of the

ones studied, is therefore [C<sub>4</sub>mpyrr][FAP] - a combination of the most stable cation and most stable anion - with a potential window of 6.5 V.

The purity of ionic liquids is a major concern for their applications in several fields, e.g. the presence of ions like lithium, sodium or potassium cations results in an increase in the density and viscosity, therefore changing the transport properties of the ionic liquid.<sup>51</sup> De Giorgio et al.<sup>52</sup> have shown that traces of lithium ions in ionic liquids cause a decrease in the oxygen reduction current due to the formation of insoluble lithium-oxygen species blocking the electrode, which presents a major drawback for lithium-air batteries employing ionic liquids. Often, precursors can be left over from the RTIL synthesis, and give voltammetric responses in the blank signal which can be problematic for sensing of analytes at extremely low concentrations. We chose a cutoff current of 1.5  $\mu$ A because this is a typical current response for gases (e.g. for 20 vol.% of oxygen on these TFEs), therefore the CV scan was reversed at  $+/-1.5 \mu A$ to determine the EWs (see narrower dashed lines in Figure 3.21 and solid black line in Figure 3.22). As can be seen, the electrochemical windows are significantly smaller, *i.e.* approximately 1 V smaller for most of the electrolytes. It can be observed that the single centered cations,  $[S_{2,2,1}]^+$ ,  $[N_{4,1,1,1}]^+$  and  $[C_4mpyrr]^+$  typically show pronounced redox processes in that current range that reduce the EW significantly, especially in case of the sulfonium-based RTIL where the window is reduced by 1.5 V, compared to a reduction of <1 V for imidazolium-based ionic liquids.

Figure 3.22 shows the close-up CV scans of the full electrochemical window of all nine commercially available RTILs as the relative humidity level is gradually increased from <1 RH% to >95 RH% on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup>, with a cut-off current of +/- 1.5  $\mu$ A to minimize the electrolyte decomposition and build-up of side products. The close-up scans clearly illustrate that some commercially available RTILs with reported purities of 99.5%, such as [C<sub>2</sub>mim][NTf<sub>2</sub>] (Figure 3.22b) and [N<sub>4,1,1</sub>][NTf<sub>2</sub>] (Figure 3.22d), still contain redox active impurities in the available EW. Also [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] (Figure 3.22g) shows large quasi-reversible voltammetric responses close to both the cathodic, as well as the anodic, limit of the scanned window.



Figure 3.21. Electrochemical window and chemical structures of a)  $[S_{2,2,1}][NTf_2]$ , b)  $[C_{2mim}][NTf_2]$ , c)  $[C_4mim][BF_4]$ , d)  $[N_{4,1,1,1}][NTf_2]$ , e)  $[C_4mim][NTf_2]$ , f)  $[C_4mim][PF_6]$ , g)  $[C_4mpyrr][NTf_2]$ , h)  $[C_4mpyrr][FAP]$  and i)  $[C_4mim][FAP]$  on a platinum thin-film electrode at <1 RH%. The red dashed lines represent a cut-off current of 1.5  $\mu$ A and the blue dashed line shows a cut-off current of 15  $\mu$ A. All scans were taken at 100 mV s<sup>-1</sup>. The black arrows indicate the start potential and the scan direction.

As can be seen in Figure 3.22, most of the imidazolium-based ionic liquids (Figure 3.22b, c, e and f) show the same prominent impurity peak between -0.4 V and -0.8 V, which becomes slightly more pronounced with increasing relative humidity level. The potential of the impurity signal stays relatively constant, even as the electrochemical window decreases, indicating that the redox mechanism does not change in the presence of water, in contrast to what is known for the oxygen reduction mechanism in humidified conditions.<sup>31</sup> Similar behavior is observed for the ammonium RTIL in Figure 3.22d. As mentioned, the purification of ionic liquids is quite challenging due to their good solubilization properties and low vapor pressures. Residues from the synthesis are therefore most likely causing voltammetric responses, *e.g.* imidazole is known to be a common impurity in commercially synthesized ILs.<sup>53</sup> Attempts to identify these impurities are not successful as their concentration is below the detection limit of typical analytical methods, *e.g.* via NMR, and suppliers do not include all

information on impurities. However, from our extensive experience, electrochemistry is very sensitive to these impurities, as demonstrated in Figure 3.22.



Figure 3.22. Effect of increasing relative humidity (RH%) on the electrochemical window of the RTILs a)  $[S_{2,2,1}][NTf_2]$ , b)  $[C_{2mim}][NTf_2]$ , c)  $[C_{4mim}][BF_4]$ , d)  $[N_{4,1,1,1}][NTf_2]$ , e)  $[C_{4mim}][NTf_2]$ , f)  $[C_{4mim}][PF_6]$ , g)  $[C_{4mpyrr}][NTf_2]$ , h)  $[C_{4mpyrr}][FAP]$  and i)  $[C_{4mim}][FAP]$  on a platinum thin-film electrode at a scan rate of 100 mV s<sup>-1</sup>. The black arrows indicate the start potential and the scan direction.

As mentioned above, the controlled humidity environment above the liquid phase causes absorption of water into the ionic liquid, resulting in a reduced viscosity which causes an increased diffusion coefficient of dissolved species like impurities or analytes and also the possibility of a proton-coupled redox pathway for the impurity signals.<sup>39</sup> The more pronounced voltammetric response is therefore explained by a higher diffusion coefficient; this effect will be discussed in more detail in section 3.2.3.2.1 using the intentionally dissolved species decamethylferrocene (DmFc), where the electrochemical behavior is quite well known.

Table 3.2 summarizes the total electrochemical window (EW<sub>total</sub>) of all nine RTILs at a cut-off current of 15  $\mu$ A (at <1 RH%), 1.5  $\mu$ A (at <1 RH%) and 1.5  $\mu$ A (at >95 RH%). Table S3.3 in the supporting information also summarizes the anodic and cathodic limits of the EWs. It is noted that these experiments were performed with a

platinum pseudo-reference electrode that is built into the TFE devices. The potential of Pt references are likely to be unstable, especially upon the introduction of different gases.<sup>54</sup> Therefore, the absolute anodic and cathodic limits of the electrochemical window cannot be used for comparison of different RTILs. However, the total EW values can be used for comparison between the different RTILs.

Table 3.2. Total electrochemical windows of nine RTILs at cut-off currents of 15  $\mu$ A (~1.9 mA cm<sup>-2</sup> current density) at <1 RH%, 1.5  $\mu$ A (~0.19 mA cm<sup>-2</sup> current density) at <1 RH% and 1.5  $\mu$ A at >95 RH%.

	$I_{\rm cutoff} = 15 \ \mu {\rm A},$	$I_{\rm cutoff} = 1.5 \ \mu {\rm A},$	$I_{\rm cutoff} = 1.5 \ \mu {\rm A},$
	<1 RH%	<1 RH%	>95 RH%
RTIL	$\mathbf{E}\mathbf{W}_{total}$ / $\mathbf{V}$	EW <sub>total</sub> / V	$\mathbf{E}\mathbf{W}_{total}$ / $\mathbf{V}$
$[S_{2,2,1}][NTf_2]$	5.0	3.5	2.1
$[N_{4,1,1,1}][NTf_2]$	5.9	4.1	2.3
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	5.9	5.6	2.3
[C4mpyrr][FAP]	6.5	5.4	2.6
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	4.3	3.6	2.0
[C <sub>4</sub> mim][BF <sub>4</sub> ]	4.4	3.5	1.8
[C <sub>4</sub> mim][PF <sub>6</sub> ]	4.8	3.6	2.1
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	4.7	3.8	2.2
[C4mim][FAP]	5.2	4.5	2.6

Under 'dry' conditions (<1 RH%), the limits of the EW are determined by the oxidation of the ionic liquid anion and the reduction of the ionic liquid cation; the exact electrochemical degradation mechanisms have been described in a detailed review by De Vos *et al.*<sup>55</sup> Whereas under humidified conditions (>95 RH%), all ionic liquids show approximately the same operation range due to the fact that the limits are now determined by the oxidation and reduction of water. Figure S3.28 in the supporting information shows that scanning over a much wider potential range results in a plateau current where water has been electrolyzed. However, consecutive scans bring about a color change of the RTIL from colorless to brown as a result in the build-up of by-products due to degradation of the RTIL; a more detailed discussion can be found in the supporting information. The studied ionic liquids were not vacuum dried due to the planar electrode set-up, but were thoroughly purged for an extended time in dry

nitrogen (<1 RH%), before the experiment and therefore EW values somewhere between the 'vacuum-dried' and 'atmospheric' values reported by O'Mahony *et al.*<sup>11</sup> are expected. Comparing the 'vacuum-dried' values at current densities of 1 mA cm<sup>-2</sup> with our values at currents of 15  $\mu$ A at <1 RH% (which equals 1.9 mA cm<sup>-2</sup> considering our geometric working electrode area of 0.785 mm<sup>2</sup>), similar values are observed. The 'wet' values reported by O'Mahony *et al.*<sup>11</sup> are between 1.6 V for [C<sub>4</sub>mim][I] to 2.9 V for [C<sub>4</sub>dmim][NTf<sub>2</sub>], which is in the same range as our reported values at >95 RH% (between 1.8 V for [C<sub>4</sub>mim][BF<sub>4</sub>] and 2.6 V for the two [FAP]<sup>-</sup>-based RTILs). The fact that the electrochemical windows in highly humidified conditions are quite similar for all RTILs (1.8 – 2.6 V) leads us to conclude that the window is determined by mainly water. The electrolyte can therefore be described as 'water-in-RTIL' at low humidities and 'RTIL-in-water' at very high relative humidities.<sup>56</sup>



Figure 3.23. Plot of electrochemical window at cut-off currents of +/- 1.5  $\mu$ A versus relative humidity level (RH%) for RTILs with the same cation (a) and the same anion (b).

As previously discussed, the presence of synthetic impurities can reduce the EW. For  $[C_4mpyrr][NTf_2]$ , the change is quite small (0.3 V), whereas the presence of redox active compounds in  $[N_{4,1,1,1}][NTf_2]$  causes a reduction of 1.8 V. It is also shown in Figure 3.22 that the presence of water causes further limitations to the electrochemical window. Figure 3.23 shows the cathodic and anodic electrochemical window values at a cut-off current of 1.5  $\mu$ A as a function of the relative humidity (RH) for a range of RTILs with the same cation,  $[C_4mim]^+$ , (Figure 3.23a) and a range of RTILs with the same cation,  $[C_4mim]^+$ , (Figure 3.23a) and a range of RTILs with the same anion,  $[NTf_2]^-$ , (Figure 3.23b). For both cases, similar trends are observed, independent of the cation and anion combination. More hydrophilic RTILs like  $[C_4mim][BF_4]$  and  $[C_4mim][PF_6]$  initially have a smaller EW than the more hydrophobic  $[C_4mim][FAP]$  in dry conditions, but the effect of water under saturated

conditions is mostly the same (Figure 3.23a). For the same anion (Figure 3.23b), only [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] showed a sharp decline at the cathodic limit of the electrochemical window before levelling off. Apart from that, the presence of water typically causes a linear reduction of the EW with increasing relative humidity.

Various literature articles have shown the formation of well-defined interfacial structures of RTILs at charged interfaces<sup>36, 57</sup>, which has been investigated using different experimental methods, including atomic force microscopy (AFM)<sup>38, 58</sup>, surface-enhanced infrared absorption spectroscopy (SEIRAS)<sup>59</sup> and sum frequency generation vibrational spectroscopy (SFG-VS)<sup>60</sup>. These studies reveal that the electrical double layer (EDL) is formed by well-defined alternating cation and anion layers close to the charged surface that become less ordered and more similar to the RTIL bulk structure further away from the electrode. The presence of water causes a weakening of the dense layer, but the exact mechanism and the dependence of the RTIL structure is yet to be investigated. Reid *et al.*<sup>61</sup> showed that water can fully dissociate or form aggregates in the RTIL bulk phase depending on the cation and anion hydrophilicity and on the concentration of dissolved water. Feng et al.<sup>62</sup> studied the electrosorption of water at electrified interfaces via molecular dynamics simulations, revealing that water accumulates at nanometer distances from charged surfaces in humidified imidazolium-based ionic liquids. Water molecules easily fill the voids between the electrode surface and the bulky ionic liquids resulting in a layer of water that is more pronounced close to a positively charged electrode, where the RTIL anions are the counterions.<sup>62</sup> This can be also seen in our results in Figure 3.23, where at positive potentials, the electrochemical window limit is already significantly reduced at low humidity levels. A similar trend in the electrochemical window change of the nine RTILs with different hydrophilicities as a function of humidity level (Figure 3.23), supports the predictions by Feng *et al.*<sup>62</sup>, where a low humidity level in controlled gas environments introduces water that accumulates close to the electrode and therefore determines the width of the electrochemical window.

Our previous study<sup>31</sup> on the oxygen reduction reaction as a function of different humidity levels showed that the electrochemical mechanism, which is highly sensitive to traces of water, is not the same for RTILs with different hydrophilicities. We concluded that up to a reasonably high humidity level (~70 RH%), a certain degree of ionic liquid structures is still present but are significantly weakened (depending on the

chemical structure of the RTIL) at electrified interfaces, preventing the accumulation of water. Increasing the water content further causes a complete disruption of the dense structure at the electrified surface. Long alkyl chains and large relative sizes of polar and non-polar moieties in the chemical structure can result in hydrophobic pockets formed by non-polar groups in the RTIL structure, especially in the presence of water as has been discussed by Hayes *et al.*<sup>36</sup> However, this behavior is still not fully understood yet and requires further investigation using both, computational and experimental methods.

Based on this knowledge and our results in water saturated conditions, we suggest a simplified model of the interface between a charged electrode and an ionic liquid in both 'dry' and 'wet' conditions, as shown in Figure 3.24. For simplicity, only the case of a negatively charged electrode is illustrated. In 'dry' RTILs, the electrode charge is balanced by dense alternating cation-anion layers (Figure 3.24a). In the presence of water, it is likely that partially solvated RTIL ions balance the electrode charge (Figure 3.24b). Instead of a layer of pure water close to the electrode, solvated cations introduce sufficient water to the electrode to reduce the electrochemical window. For a large hydrophobic moiety in the side chain of the cation, small and non-polar molecules can become dissolved in these pockets and are protected from the surrounding water but are still close enough to the electrode to be electrochemically reduced or oxidized. We suggest that the electrolyte composition inside the electrical double layer changes from 'water-in-RTIL'- to 'RTIL-in-water' behavior from 'dry' to 'humidified' conditions (see Figure 3.24), i.e. comparable to a conventional electrolyte/solvent system.<sup>63</sup> In hydrophobic RTILs such as [C<sub>4</sub>mpyrr][NTf<sub>2</sub>], the bulk-phase water content in a water-saturated sample is around 1.1 wt.%<sup>11</sup>, which does not seem to be significant. However, on a molecular level, the molar concentration of water is significantly higher than the weight-per-volume concentration, resulting in an approximate ratio of 1:4 for water:RTIL ions. The operating range of the electrolyte is therefore determined by water electrolysis at higher humidity levels, and not by the RTIL oxidation and reduction. It is also important to mention that the bulk and interfacial solubility of water in ionic liquids is probably very different, but this has not been studied in detail yet. This requires further studies to determine the exact mechanism of the change between the two extremes (Figure 3.24) in water-controlled environments, as well as the influence of the RTIL structure.



Figure 3.24. Schematic illustration of the suggested structures of room temperature ionic liquids at a negatively charged surface in dry (a) and highly humidified conditions (b).<sup>64</sup> The ionic liquid ions are shown in orange (cation) and blue (anion) and the water is shown in red (oxygen) and grey (hydrogen).

# 3.2.3.2. Electrochemistry of Dissolved Species at Different RH% in [C4mpyrr][NTf2]

Ionic liquids are considered to be hygroscopic, and the extent of water uptake depends on their cation and anion structure.<sup>65</sup> This means that the application of room temperature ionic liquids in real-world environments where moisture is present, requires fundamental understanding of the impact of water on the physicochemical properties. Several researchers have studied the impact of water on the physicochemical properties such as density and viscosity of the RTIL bulk phase by adding certain contents of water to the RTILs.<sup>12-13</sup> The impact of relative humidity on the electrochemical window (EW) of RTILs<sup>11</sup> and on the voltammetry of dissolved species in RTILs<sup>39</sup> has also been previously discussed.<sup>11</sup> Yaghini et al.<sup>66</sup> studied the effect of water on transport properties such as self-diffusivity and conductivity for imidazolium-based ionic liquids, concluding that water enhances the mobility of ionic species, and the extent at which the diffusion of the cations and anions is influenced, depends on their molecular structure. For hydrophobic, water immiscible ILs, cations and anions are equally affected.<sup>66</sup> Therefore, we have chosen to study the change in the voltammetric response of two dissolved species that are not expected to participate in follow-up chemical reactions with water, *i.e.* decamethylferrocene (DmFc) and ammonia (NH<sub>3</sub>), in an environment with controlled relative humidity levels.

#### **3.2.3.2.1. Decamethylferrocene (DmFc)**

Decamethylferrocene is a well-studied internal reference that is stable in the presence of water, showing a one electron redox mechanism in RTILs according to equation 3.10.<sup>67</sup> DmFc has been shown to be a superior redox standard compared to ferrocene in various organic solvents due to a less solvent dependent redox potential.<sup>67-68</sup> Therefore, DmFc has been used as a model probe to study the effect of water on the diffusion behavior in the ionic liquid [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] by cyclic voltammetry (CV).

$$DmFc \Rightarrow DmFc^+ + e^-$$
 3.10

Figure 3.25 shows the voltammograms at a scan rate of 100 mV s<sup>-1</sup> of the oxidation of DmFc and subsequent reduction of decamethylferrocenium (DmFc<sup>+</sup>) (according to equation 3.10) in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] as a function of different humidity levels, with the normalized change of the current shown in the inset. Successive CV scans at the same humidity level resulted in identical responses, confirming that the response is stable with CV scanning and there is no electrode fouling occurring. The voltammetric response for DmFc in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] is chemically reversible with a peak-to-peak separation of  $\Delta E_p = 63.5 \pm 2$  mV for all humidity levels.

As can be seen in Figure 3.25, increasing the humidity level results in an increased oxidation peak current up to approximately 70 RH% (orange line); further increase of the water content in the gas stream results in a less severe but still noticeable current change. An increase in current of approximately 35% from 'dry' (<1 RH%) to 'wet' (>95 RH%) conditions was observed in [C4mpyrr][NTf2]. In contrast, Schröder et al.<sup>39</sup> studied the impact of water absorbed into the ionic liquid from a controlled gas flow on the diffusion coefficient of redox systems in ionic liquids with more hydrophilic anions, including [C<sub>4</sub>mim][BF<sub>4</sub>] and [C<sub>4</sub>mim][PF<sub>6</sub>]. Their study revealed an increase of the diffusion coefficient of the neutral N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) by a factor of two at a water content of approximately 5 wt.%, and a one order of magnitude increase for the ionic methyl viologen (MV<sup>2+</sup>), showing that the effect of water on the diffusion coefficient for neutral and ionic species are not affected in the same way. It is therefore reasonable to expect a smaller impact on transport properties due to a lower water concentration in more hydrophobic ionic liquids, like [C<sub>4</sub>mpyrr][NTf<sub>2</sub>]. In the case of DmFc, the redox signal occurs well away from the edge of the electrochemical window or the location of impurity peaks, so the narrowing potential limits shown earlier in Figure 3.22 are not expected to affect the currents. A 35% increase in current is therefore likely caused by a reduction in viscosity and increase in diffusion coefficient of DmFc as water is added to the RTIL.



Figure 3.25 Cyclic voltammetry response of decamethylferrocene (saturated concentration) in  $[C_{4}mpyrr][NTf_2]$  as function of different relative humidity levels (RH%) on a platinum thin-film electrode at a scan rate of 100 mV s<sup>-1</sup>. The inset plot shows the normalized current ( $I_{norm}$ ) as a function of the relative humidity, where the oxidation peak currents were normalized to the current recorded at the driest condition, i.e. <1 RH%.

#### 3.2.3.2.2. Ammonia Gas

Ammonia (NH<sub>3</sub>) was chosen because its oxidation mechanism is not expected to be affected by water in terms of follow-up reactions, but the oxidation potential is closer to the edge of the electrochemical window<sup>69</sup> and therefore, might be more affected by the reduced EW. The mechanism of ammonia oxidation in RTILs and aprotic solvents such as acetonitrile, is believed to follow equations 3.11 - 3.13.<sup>70-72</sup>

$$4 \operatorname{NH}_3(g) \to 3 \operatorname{NH}_4^+ + \frac{1}{2} \operatorname{N}_2(g) + 3 e^-$$
 3.11

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$
 3.12

$$\mathrm{H}^+ + e^- \to \frac{1}{2} \mathrm{H}_2 \tag{3.13}$$

In an extension of the mechanism, Buzzeo *et al.*<sup>70</sup> also showed that RTIL anions can bind to the electrogenerated proton. In our experiments, ammonia gas (200 ppm) was introduced into the glass cell with 1  $\mu$ L of [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-TFE. The full redox response at <1 RH% (see supporting information Figure S3.29) shows the same features as previously reported in dry conditions<sup>70</sup>, *i.e.* a single oxidation peak followed by two reduction processes and an additional oxidation of adsorbed hydrogen gas. According to the mechanism, the addition of water (or protons) should not have a significant effect on the oxidation reaction in terms of follow-up chemistry. For simplicity, only linear sweep voltammetry (LSV) for the ammonia oxidation is further shown.

Figure 3.26 shows the LSV response for the oxidation of 200 ppm  $NH_3$  gas as a function of increasing relative humidity level. The response in the absence of ammonia at <1 RH% (dashed line) shows no voltammetric features. Changing the humidity level results in a systematic increase in the current response for the oxidation process. Additionally, a shift in the oxidation potential from approximately 0.85 V to around 0.45 V can be seen which is most likely caused by the unstable reference potential (as described before). The onset of the electrochemical window is obvious for the scan at 78 RH% (olive line) and very obvious for >95 RH% (navy line) in Figure 3.22g.

For DmFc (section 3.2.3.2.1), an approximate 35% increase in current over the whole humidity range was observed. The DmFc/DmFc<sup>+</sup> redox process occurs at potentials around 0 V (vs. the integrated Pt-RE), far away from the onset of the electrochemical window. However, the ammonia oxidation signal occurs at ~0.85 V vs. Pt at <1 RH%, significantly closer to the anodic limit of the EW. Therefore, the introduction of water causes both a reduced viscosity of the solvent (hence an increased NH<sub>3</sub> diffusion coefficient) and also a shift in the onset of the anodic limit of the electrochemical window which, according to Table S3.3, reduces by approximately 1.6 V form 'dry' to 'wet' [C<sub>4</sub>mpyrr][NTf<sub>2</sub>]. The peak current for ammonia oxidation approximately doubles, which is significantly higher than the 35% increase for DmFc, likely due to the greater contribution from the reduction in the EW. Shiddiky et al.<sup>73</sup> previously reported the "nonadditivity" of faradaic currents in ionic liquids when two electrochemically active analytes (ferrocene and cobaltocenium) are present in the same solution, resulting in a different current response with an alteration in the capacitive currents. This non-conventional behavior may be important to consider in our work because water as an impurity could also cause a faradaic current contribution to the DmFc response.

Ammonia oxidation was further studied in ionic liquids with different cations and anions, and the results are shown in full in the supporting information (Figure S3.30 and Figure S3.31). In general, all ionic liquids show the same behavior as for [C<sub>4</sub>mpyrr][NTf<sub>2</sub>], showing a shift of the NH<sub>3</sub> oxidation potential and a gradual increase

of the oxidation peak current. Due to different ammonia gas solubilities in the ionic liquids, the peak currents were normalized to the response at the driest condition.



Figure 3.26. Linear sweep voltammetry for the oxidation of 200 ppm of ammonia gas in  $[C_4mpyrr][NTf_2]$  on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different relative humidity levels (RH%). Dashed line represents the blank in the absence of ammonia gas at <1 RH%.

Figure 3.27 shows the normalized ammonia oxidation current  $(I_{norm})$  as a function of the relative humidity level (from <1 RH% to >95 RH%) for four RTILs with different hydrophilicities. Some additional RTILs were not included, *i.e.* [C<sub>4</sub>mim][BF<sub>4</sub>] and [C<sub>4</sub>mim][PF<sub>6</sub>], for the reasons discussed in more detail in the supporting information. All RTILs show a similar trend: a gradual increase of the normalized current by approximately 100% with increasing humidity. These ionic liquids cover a range of relatively hydrophilic electrolytes like [C<sub>2</sub>mim][NTf<sub>2</sub>] and [S<sub>2,2,1</sub>][NTf<sub>2</sub>] to more hydrophobic ones like  $[N_{4,1,1,1}][NTf_2]$ , hence the water uptake is not expected to be identical. No drastic effect of the cation could be seen (in contrast to our previous study for humidified oxygen experiments<sup>31</sup>), supporting the assumption that the ammonia oxidation reaction mechanism remains the same. In the case of a change of the redox mechanism of NH<sub>3</sub> gas in the presence of water, much more dramatic trends of Inorm vs. RH% would be observed. Therefore, for the oxidation of ammonia gas in humidified conditions, the choice of the ionic liquid is less important than for oxygen.<sup>31</sup> The change in current response for ammonia oxidation as the humidity level is increased is a combination of increased diffusion coefficients caused by decreased solvent viscosity, in addition to the narrowing electrochemical window that contributes to the current at the same potential as the ammonia oxidation process.



Figure 3.27. Normalized ammonia oxidation current as a function of different relative humidity level (RH%) for four ionic liquids. Currents were normalized to the oxidation current at the lowest humidity level for easy comparison between different electrolytes.

#### **3.2.4.** Conclusions

In dry conditions, the nine RTILs in this study have relatively large available electrochemical windows of 4.3 - 6.5 V. These become systematically reduced as the humidity of the environment is increased, until eventually reaching electrochemical windows mostly defined by water oxidation and reduction (1.8 - 2.6 V). This behavior supports the suggestion of a different structure of the electrical double layer for RTILs at charged electrodes in 'dry' and 'humidified' conditions. Electroactive intrinsic dissolved impurities were also present in the lower current range chosen for this study, also becoming more obvious with humidity. For two intentionally dissolved species whose mechanisms are not affected by follow-up reactions with water, one that occurs in the middle of the electrochemical window (DmFc) showed current increase caused by a reduced viscosity (higher diffusion coefficient). The other one (ammonia) that occurs closer to the potential limit of the electrochemical window is affected by both the change of transport properties and the reduction of the electrochemical window. This is an important observation that should be considered for electrochemical applications, when RTILs are exposed to an 'open' environment where the absorption of water not only affects the transport properties, but also the electrochemical operating range.

#### **3.2.5. References**

1. Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R., Room temperature ionic liquids and their mixtures- A Review. *Fluid Phase Equilibr*. **2004**, *219*, 93-98.

2. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X., Investigating the electrochemical windows of ionic liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106-112.

3. Lewandowski, A.; Swiderska-Mocek, A., Ionic liquids as electrolytes for Liion batteries—An overview of electrochemical studies. *J. Power Sources* **2009**, *194*, 601-609.

4. Nakamoto, H.; Watanabe, M., Brønsted acid–base ionic liquids for fuel cell electrolytes. *Chem. Commun.* **2007**, *24*, 2539-2541.

5. Malvaldi, M.; Chiappe, C., From molten salts to ionic liquids: effect of ion asymmetry and charge distribution. *J. Phys.: Condens. Matter* **2008**, *20*, 035108.

6. Jimenez, A.-E.; Bermudez, M.-D., Ionic liquids as lubricants for steelaluminum contacts at low and elevated temperatures. *Tribol. Lett.* **2007**, *26*, 53-60.

7. Stolte, S.; Steudte, S.; Areitioaurtena, O.; Pagano, F.; Thoemi, J.; Stepnowski, P.; Igartua, A., Ionic liquids as lubricants or lubrication additives: An ecotoxicity and biodegradability assessment. *Chemosphere* **2012**, *89*, 1135-1141.

8. Buzzeo, M. C.; Evans, R. G.; Compton, R. G., Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry-A Review. *Chem. Phys. Chem.* **2004**, *5*, 1106-1120.

9. Zhou, T.; Chen, L.; Ye, Y.; Chen, L.; Qi, Z.; Freund, H.; Sundmacher, K., An Overview of Mutual Solubility of Ionic Liquids and Water Predicted by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 6256-6264.

10. Wippermann, K.; Giffin, J.; Korte, C., In Situ Determination of the Water Content of Ionic Liquids. *J. Electrochem. Soc.* **2018**, *165*, H263-H270.

11. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 2884-2891.

12. Rodriguez, H.; Brennecke, J. F., Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145-2155.

13. Widegren, J. A.; Magee, J. W., Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* **2007**, *52*, 2331-2338.

14. Barrosse-Antle, L. E.; Bond, A. M.; Compton, R. G.; O'Mahony, A. M.; Rogers, E. I.; Silvester, D. S., Voltammetry in Room Temperature Ionic Liquids: Comparisons and Contrasts with Conventional Electrochemical Solvents. *Chem. Asian J.* **2010**, *5*, 202-230.

15. Buzzeo, M. C.; Hardacre, C.; Compton, R. G., Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.* **2004**, *76*, 4583-4588.

16. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Tan, X. M., Electrochemical reduction of dioxygen in Bis(trifluoromethylsulfonyl)imide based ionic liquids. *J. Electroanal. Chem.* **2011**, *657*, 150-157.

17. Barnes, A. S.; Rogers, E. I.; Streeter, I.; Aldous, L.; Hardacre, C.; Wildgoose, G. G.; Compton, R. G., Unusual Voltammetry of the Reduction of  $O_2$  in  $[C_4dmim][N(Tf)_2]$  Reveals a Strong Interaction of  $O_2^{\bullet-}$  with the  $[C_4dmim]^+$  Cation. J. *Phys. Chem. C* **2008**, *112*, 13709-13715.

18. Wan, H.; Yin, H.; Lin, L.; Zeng, X.; Mason, A. J., Miniaturized planar room temperature ionic liquid electrochemical gas sensor for rapid multiple gas pollutants monitoring. *Sens. Actuators B Chem.* **2018**, *255*, 638-646.

19. Silvester, D. S., Recent advances in the use of ionic liquids for electrochemical sensing. *Analyst* **2011**, *136*, 4871-4882.

20. Gębicki, J.; Kloskowski, A.; Chrzanowski, W.; Stepnowski, P.; Namiesnik, J., Application of Ionic Liquids in Amperometric Gas Sensors. *Crit. Rev. Anal. Chem.* **2016**, *46*, 122-138.

21. Zhao, C.; Gunawan, C.; Ge, M.; Gondosiswanto, R.; Aldous, L., Recent advantages in ionic liquid-based gas sensors. In *Analytical Applications of Ionic Liquids*, 2016; pp 287-338.

22. Carter, M. T.; Stetter, J. R.; Findlay, M. W.; Patel, V., Rational Design of Amperometric Gas Sensors with Ionic Liquid Electrolytes. *ECS Trans.* **2014**, *64*, 95-103.

23. Rehman, A.; Zeng, X., Methods and approaches of utilizing ionic liquids as gas sensing materials. *RSC Adv.* **2015**, *5*, 58371-58392.

24. Silvester, D. S., New innovations in ionic liquid–based miniaturised amperometric gas sensors. *Curr. Opin. Electrochem.* **2019**, *15*, 7-17.

25. Huang, X.-J.; Aldous, L.; O'Mahony, A. M.; del Campo, F. J.; Compton, R. G., Toward Membrane-Free Amperometric Gas Sensors: A Microelectrode Array Approach. *Anal. Chem.* **2010**, *82*, 5238-5245.

26. Hu, C.; Bai, X.; Wang, Y.; Jin, W.; Zhang, X.; Hu, S., Inkjet Printing of Nanoporous Gold Electrode Arrays on Cellulose Membranes for High-Sensitive Paper-Like Electrochemical Oxygen Sensors Using Ionic Liquid Electrolytes. *Anal. Chem.* **2012**, *84*, 3745-3750.

27. Kubersky, P.; Altsmid, J.; Hamacek, A.; Nespurek, S.; Zmeskal, O., An Electrochemical NO<sub>2</sub> Sensor Based on Ionic Liquid: Influence of the Morphology of the Polymer Electrolyte on Sensor Sensitivity. *Sensors* **2015**, *15*, 28421-28434.

28. Murugappan, K.; Lee, J.; Silvester, D. S., Comparative study of screen printed electrodes for ammonia gas sensing in ionic liquids. *Electrochem. Commun.* **2011**, *13*, 1435-1438.

29. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., The Electrochemical Reduction of Hydrogen Sulfide on Platinum in Several Room Temperature Ionic Liquids. *J. Phys. Chem. C* **2008**, *112*, 7725-7730.

30. Liu, X.; Chen, X.; Xu, Y.; Chen, T.; Zeng, X., Effects of water on ionic liquid electrochemical microsensor for oxygen sensing. *Sens. Actuators B Chem.* **2019**, *285*, 350-357.

31. Doblinger, S.; Lee, J.; Silvester, D. S., Effect of Ionic Liquid Structure on the Oxygen Reduction Reaction Under Humidified Conditions. *J. Phys. Chem. C* **2019**, *123*, 10727-10737.

32. AlNashef, I. M.; Leonard, M. L.; Kittle, M. C.; Matthews, M. A.; Weidner, J. W., Electrochemical Generation of Superoxide in Room-Temperature Ionic Liquids. *Electrochem. Solid-State Lett.* **2001**, *4*, D16-D18.

33. Yuan, X.-Z.; Alzate, V.; Xie, Z.; Ivey, D. G.; Qu, W., Oxygen Reduction Reaction in 1-Butyl-1-methyl-pyrrolidinium Bis(trifluoromethanesulfonyl)imide: Addition of Water as a Proton Species. *J. Electrochem. Soc.* **2014**, *161*, A451-A457.

34. Switzer, E. E.; Zeller, R.; Chen, Q.; Sieradzki, K.; Buttry, D. A.; Friesen, C., Oxygen Reduction Reaction in Ionic Liquids: The Addition of Protic Species. *J. Phys. Chem. C* **2013**, *117*, 8683-8690.

35. Zhang, D.; Okajima, T.; Matsumoto, F.; Ohsaka, T., Electroreduction of Dioxygen in 1-n-Alkyl-3-methylimidazolium Tetrafluoroborate Room-Temperature Ionic Liquids. *J. Electrochem. Soc.* **2004**, *151*, D31-D37.

36. Hayes, R.; Warr, G. G.; Atkin, R., Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* **2015**, *115*, 6357-6426.

37. Zhong, Y.-X.; Yan, J.-W.; Li, M.-G.; Zhang, X.; He, D.-W.; Mao, B.-W., Resolving Fine Structures of the Electric Double Layer of Electrochemical Interfaces in Ionic Liquids with an AFM Tip Modification Strategy. *J. Am. Chem. Soc.* **2015**, *136*, 14682-14685.

38. Hayes, R.; Borisenko, N.; Tam, M. K.; Howlett, P. C.; Endres, F.; Atkin, R., Double Layer Structure of Ionic Liquids at the Au(111) Electrode Interface: An Atomic Force Microscopy Investigation. *J. Phys. Chem. C* **2011**, *115*, 6855-6863.

39. Schröder U., W. J. D., Compton R. G., Marken F., Suarez P. A. Z., Consorti C. S., de Souza R. F., Dupon J., Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphaye ionic liquids. *New J. Chem.* **2000**, *24*, 1009-1015.

40. Doblinger, S.; Lee, J.; Gurnah, Z.; Silvester, D. S., Detection of sulfur dioxide at low parts-per-million concentrations using low-cost planar electrodes with ionic liquid electrolytes. *Anal. Chim. Acta* **2020**, *1124*, 156-165.

41. Hussain, G.; Silvester, D. S., Detection of sub-ppm Concentrations of Ammonia in an Ionic Liquid: Enhanced Current Density Using "Filled"Recessed Microarrays. *Anal. Chem.* **2016**, *88*, 12453-12460.

42. Lee, J.; Du Plessis, G.; Arrigan, D. W. M.; Silvester, D. S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Anal. Methods* **2015**, *7*, 7327-7335.

43. Cheng, H. W.; Dienemann, J. N.; Stock, P.; Merola, C.; Chen, Y. J.; Valtiner, M., The Effect of Water and Confinement on Self-Assembly of Imidazolium Based Ionic Liquids at Mica Interfaces. *Sci. Rep.* **2016**, *6*, 30058.

44. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X., Investigating the electrochemical windows of ionic liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106-112.

45. Evans, R. G.; Klymenko, O. V.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Oxidation of N,N,N',N'-tetraalkyl-para-phenylenediamines in a series of room temperature ionic liquids incorporating the bis(trifluoromethylsulfonyl)imide anion. *J. Electroanal. Chem.* **2003**, *556*, 179-188.

46. Ignat'ev, N. V.; Welz-Biermann, U.; Kucheryna, A.; Bissky, G.; Willner, H., New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions. *J. Fluor. Chem.* **2005**, *126*, 1150-1159.

47. MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M., Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases. *J. Phys. Chem. B* **1999**, *103*, 4164-4170.

48. Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M., Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168-1178.

49. Lane, G. H., Electrochemical reduction mechanisms and stabilities of some cation types used in ionic liquids and other organic salts. *Electrochim. Acta* **2012**, *83*, 513-528.

50. Kazemiabnavi, S.; Zhang, Z.; Thornton, K.; Banerjee, S., Electrochemical Stability Window of Imidazolium-Based Ionic Liquids as Electrolytes for Lithium Batteries. *J. Phys. Chem. B* **2016**, *120*, 5691-5702.

51. Tong, J.; Wu, S.; von Solms, N.; Liang, X.; Huo, F.; Zhou, Q.; He, H.; Zhang, S., The Effect of Concentration of Lithium Salt on the Structural and Transport Properties of Ionic Liquid-Based Electrolytes. *Front Chem* **2020**, *7*, 945.

52. De Giorgio, F.; Soavi, F.; Mastragostino, M., Effect of lithium ions on oxygen reduction in ionic liquid-based electrolytes. *Electrochem. Commun.* **2011**, *13*, 1090-1093.

53. Holbrey, J. D.; Seddon, K. R.; Wareing, R., A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. *Green Chem.* **2001**, *3*, 33-36.

54. Wandt, J.; Lee, J.; Arrigan, D.; Silvester, D. S., A lithium iron phosphate reference electrode for ionic liquid electrolytes. *Electrochem. Commun.* **2018**, *93*, 148-151.

55. De Vos, N.; Maton, C.; Stevens, C. V., Electrochemical Stability of Ionic Liquids: General Influences and Degradation Mechanisms. *ChemElectroChem* **2014**, *1*, 1258-1270.

56. Stettner, T.; Gehrke, S.; Ray, P.; Kirchner, B.; Balducci, A., Water in Protic Ionic Liquids: Properties and Use of a New Class of Electrolytes for Energy-Storage Devices. *ChemSusChem* **2019**, *12*, 3827-3836.

57. Rodenbücher, C.; Wippermann, K.; Korte, C., Atomic Force Spectroscopy on Ionic Liquids. *Appl. Sci.* **2019**, *9*, 2207.

58. Li, H.; Endres, F.; Atkin, R., Effect of alkyl chain length and anion species on the interfacial nanostructure of ionic liquids at the Au(111)-ionic liquid interface as a function of potential. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14624-14633.

59. Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T., Interfacial Structure at the quaternary Ammonium-Based Ionic Liquid/Gold Electrode Interface

Probed by Surface-Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior. J. Phys. Chem. C 2017, 121, 1658-1666.

60. Rivera-Rubero, S.; Baldelli, S., Surface Spectroscopy of Room-Temperature Ionic Liquids on a Platinum Electrode: A Sum Frequency Generation Study. *J. Phys. Chem. B* **2004**, *108*, 15133-15140.

61. Reid, J. E. S. J.; Walker, A. J.; Shimizu, S., Residual water in ionic liquids: clustered or dissociated? *Phys. Chem. Chem. Phys.* **2015**, *17*, 14710-14718.

62. Feng, G.; Jiang, X.; Qiao, R.; Kornyshev, A. A., Water in Ionic Liquids at Electrified Interfaces: The Anatomy of Electrosorption. *ACS Nano* **2014**, *8*, 11685-11694.

63. Bard, A. J.; Faulkner, L. R., *Electrochemical methods : fundamentals and applications*; Wiley: New York, 1980.

64. Zhong, Y.; Yan, J.; Li, M.; Chen, L.; Mao, B., The Electric Double Layer in an Ionic Liquid Incorporated with Water Molecules: Atomic Force Microscopy Force Curve Study. *ChemElectroChem* **2016**, *3*, 2221-2226.

65. Tran, C. D.; De Paoli Lacerda, S. H.; Oliveira, D., Absorption of water by room-temperature ionic liquids: effect of anions on concentration and state of water. *Applied spectroscopy* **2003**, *57*, 152-7.

66. Yaghini, N.; Nordstierna, L.; Martinelli, A., Effect of water on the transport properties of protic and aprotic imidazolium ionic liquids – an analysis of self-diffusivity, conductivity, and proton exchange mechanism. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9266-9275.

67. Torriero, A. A. J., Characterization of decamethylferrocene and ferrocene in ionic liquids: argon and vacuum effect on their electrochemical properties. *Electrochim. Acta* **2014**, *137*, 235-244.

68. Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L., The Decamethylferrocenium/Decamethylferrocene Redox Couple: A Superior Redox Standard to the Ferrocenium/Ferrocene Redox Couple for Studying Solvent Effects on the Thermodynamics of Electron Transfer. *J. Phys. Chem. B* **1999**,

103, 6713-6722.

69. Hussain, G.; Silvester, D. S., Detection of sub-ppm Concentrations of Ammonia in an Ionic Liquid: Enhanced Current Density Using "Filled" Recessed Microarrays. *Anal. Chem.* **2016**, *88*, 12453-12460.

70. Buzzeo, M. C.; Giovanelli, D.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Elucidation of the Electrochemical Oxidation Pathway of Ammonia in Dimethylformamide and the Room Temperature Ionic Liquid, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Electroanalysis* **2004**, *16*, 888-896.

71. Ji, X.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Mechanistic Studies of the Electro-oxidation Pathway of Ammonia in Several Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 9562-9572.

72. Schiffer, Z.; Lazouski, N.; Corbin, N.; Manthiram, K. In *Rate-Determining Step and Mechanistic Understanding of Electrochemical Ammonia Oxidation in a* 

*Non-Aqueous Electrolyte*, 2019 North American Catalysis Society Meeting, NAM: 2019.

73. Shiddiky, M. J. A.; Torriero, A. A. J.; Zhao, C.; Burgar, I.; Kennedy, G.; Bond, A. M., Nonadditivity of Faradaic Currents and Modification of Capacitance Currents in the Voltammetry of Mixtures of Ferrocene and the Cobaltocenium Cation in Protic and Aprotic Ionic Liquids. *J. Am. Chem. Soc.* **2009**, *131*, 7976-7989.
### 3.2.6. Supporting Information

Table S3.3. Anodic  $(EW_{pos})$  and cathodic  $(EW_{neg})$  potentials (vs. the integrated platinum pseudoreference electrode), as well as total electrochemical windows ( $E_{total}$ ) of nine RTILs at cut-off currents of 15  $\mu$ A at <1 RH%, 1.5  $\mu$ A at <1 RH% and 1.5  $\mu$ A at >95 RH%.

	$I_{\rm cutoff} = 15 \ \mu {\rm A},$		$I_{\rm cutoff} = 1.5 \ \mu {\rm A},$		$I_{\rm cutoff} = 1.5 \ \mu {\rm A},$				
	<1 RH%		<1 RH%			>95 RH%			
DTH	$\mathrm{EW}_{\mathrm{pos}}$	$\mathrm{EW}_{\mathrm{neg}}$	$\mathrm{EW}_{\mathrm{total}}$	$\mathrm{EW}_{\mathrm{pos}}$	$\mathrm{EW}_{\mathrm{neg}}$	$\mathrm{EW}_{\mathrm{total}}$	$\mathrm{EW}_{\mathrm{pos}}$	$\mathrm{EW}_{\mathrm{neg}}$	$\mathrm{EW}_{\mathrm{total}}$
KIIL	/ V	/ V	/ V	/ V	/ V	/ V	/ V	/ V	/ V
$[S_{2,2,1}][NTf_2]$	2.5	-2.5	5.0	1.2	-2.3	3.5	0.6	-1.5	2.1
$[N_{4,1,1,1}][NTf_2]$	2.7	-3.2	5.9	1.5	-2.6	4.1	0.5	-1.8	2.3
[C4mpyrr][NTf2]	2.8	-3.1	5.9	2.5	-3.1	5.6	0.9	-1.4	2.3
[C4mpyrr][FAP]	3.1	-3.4	6.5	2.3	-3.1	5.4	1.1	-1.5	2.6
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	2.2	-2.1	4.3	1.9	-1.7	3.6	0.9	-1.1	2.0
[C4mim][BF4]	2.9	-1.5	4.4	2.1	-1.4	3.5	1.0	-0.8	1.8
[C <sub>4</sub> mim][PF <sub>6</sub> ]	2.7	-2.1	4.8	2.1	-1.5	3.6	1.1	-1.0	2.1
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	2.3	-2.4	4.7	2.2	-1.6	3.8	1.0	-1.2	2.2
[C4mim][FAP]	3.1	-2.1	5.2	2.6	-1.9	4.5	1.1	-1.5	2.6



Figure S3.28. Cyclic voltammetry over a very wide potential range in (a)  $[C_4mpyrr][NTf_2]$  and (c)  $[C_4mim][BF_4]$  on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different relative humidity levels (RH%). Photos of the electrodes and the electrolytes after the experiment ((b) and (d)), after scanning the extended potential range at increased humidity levels.

All nine RTILs showed a similar trend of reduced electrochemical windows with increasing relative humidity, as shown in Figure 3.22 in the main text. To support the suggestion that the cathodic and anodic limits of the electrochemical window is determined by the water oxidation and reduction, further studies were performed. The

potentials were scanned to more positive and more negative values to see whether the current increases continuously, or if the current plateaus once the water has been electrolyzed.

Figure S3.28 shows CV over a wide potential range for [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] and [C<sub>4</sub>mim][BF<sub>4</sub>] on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different humidity levels and photos of the electrodes after the wide-scan experiment. For the more hydrophobic [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] (Figure S3.28a), the electrochemical window between 3 and -3.2 V was scanned in the 'dry' and the 'humidified' conditions. In contrast to the CV scans illustrated in Figure 3.22, the potential at which the scan was reversed, was kept constant for all cases and no cut-off current was applied. The inset shows a gradual increase of the CV response at the cathodic and anodic limit of the electrochemical window with increasing humidity level. At the maximum relative humidity (>95 RH%), the CV response at the negative potential became significantly noisier, which is most likely cause by the hydrogen bubble formation at the electrode. At these wide potential ranges, consecutive scanning also causes a degradation of the ionic liquid, illustrated by a color change from colorless to brown (see Figure S3.28b).

For  $[C_4mim][BF_4]$ , which is fully miscible with water, the same study was attempted. However, at only 6 RH%, one wide scan (red line in Figure S3.28c) resulted in the browning of the RTIL (Figure S3.28d), suggesting that at this humidity level, a large concentration of water is already present. It is therefore not advisable to scan very positive or very negative potentials if water is present in the RTIL, due to the build-up of unwanted electrogenerated products. It is known that the tetrafluoroborate anion is not electrochemically stable in the presence of water and ionic liquids based on this anion are highly hygroscopic.<sup>1</sup> This suggests that the electrochemical window of completely dry  $[BF_4]$ -based RTILs should be significantly larger (as predicted by computational calculations<sup>2</sup>), however the high water contents (and lower current cutoffs) result in smaller experimentally measured EWs.



Figure S3.29. Cyclic voltammetry response for the oxidation of 200 ppm of ammonia gas in  $[C_4mpyrr][NTf_2]$  on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different relative humidity levels (RH%). The dashed line represents the blank in the absence of ammonia gas at <1 RH%.



Figure S3.30. Linear sweep voltammetry for the oxidation of 200 ppm of ammonia gas in a)  $[C_{2}mim][NTf_{2}]$ , b)  $[S_{2,2,1}][NTf_{2}]$ , c)  $[C_{4}mpyrr][NTf_{2}]$  and d)  $[N_{4,1,1,1}][NTf_{2}]$  on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different humidity levels (RH%). The dashed line represents the scan in the absence of ammonia gas at <1 RH%.



Figure S3.31. Linear sweep voltammetry for the oxidation of 200 ppm of ammonia gas in a)  $[C_4 mim][BF_4]$  and b)  $[C_4 mim][PF_6]$  on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> at different humidity levels (RH%). The dashed line represents the blank in the absence of ammonia gas.

 $[BF_4]^-$  and  $[PF_6]^-$  anions are known to be hydrolytically unstable, and typically, ionic liquids containing these anions are highly hygroscopic.<sup>1</sup> Dry  $[C_4mim][BF_4]$  forms strong cation-anion networks, however, in the presence of water, these networks change due to strong hydrogen bond interactions between the tetrahedral  $[BF_4]^-$  and the pseudo-tetrahedral water network.<sup>3</sup> Therefore, at high humidity levels, the water content is so high that water-anion interactions dominate over ionic liquid cation-anion interactions, where the electrolyte composition is believed to change from 'water-in-RTIL'-like to 'RTIL-in-water'. LSV for ammonia oxidation at different humidities in  $[C_4mim][BF_4]$  is shown in Figure S3.31a. A large increase in current is observed (approximately 6 times) from 'dry' (<1 RH%) to 'humidified' (>95 RH%) conditions. It is noted that this RTIL is the only one in the study that is fully miscible with water, so it is likely a very large amount of water present<sup>4</sup>, and the effect of water on the RTIL may be much more complicated than simply a change in the transport properties.

For ammonia oxidation in [C<sub>4</sub>mim][PF<sub>6</sub>], the current was observed to reduce on successive scans, even at low humidity levels (see Figure S3.31b), which means that accurate currents cannot be recorded. Unusual behavior for ammonia oxidation in this RTIL has been reported previously.<sup>5</sup> Because of the unstable currents for ammonia oxidation in this RTIL, this data was not included in the discussion in the main manuscript.

# References

1. Freire, M. G.; Neves, C. M. S. S.; Marrucho, I. M.; Coutinho, J. A. P.; Fernandes, A. M., Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A* **2010**, *114*, 3744-3749.

2. Kazemiabnavi, S.; Zhang, Z.; Thornton, K.; Banerjee, S., Electrochemical Stability Window of Imidazolium-Based Ionic Liquids as Electrolytes for Lithium Batteries. *J. Phys. Chem. B* **2016**, *120*, 5691-5702.

3. Schröder, C.; Rudas, T.; Neumayr, G.; Benker, S.; Steinhauser, O., On the collective network of ionic liquid/water mixtures. I. Orientational structure. *J. Chem. Phys* **2007**, *127*, 234503.

4. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 2884-2891.

5. Ji, X.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Mechanistic Studies of the Electro-oxidation Pathway of Ammonia in Several Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 9562-9572.

## **3.3.** Effect of Humidity on Gel-Polymer Electrolytes

### 3.3.1. Introduction

Chapter 3.1 has revealed that the RTIL structure at the electrode/ionic liquid interface has a significant effect on the electrochemical response obtained for the oxygen reduction reaction at different humidity level. Various research groups attempted different methods to prevent water from accumulating in the RTIL, such as modifying the ionic liquid structures with alkyl chains<sup>1-2</sup>, attaching fluorine moieties in the cation/anion structure<sup>3</sup> or adding hydrophobic polymers<sup>4-5</sup>. Lee *et al.* mixed RTILs with poly(methyl methacrylate) (PMMA) to successfully show a less severe effect from water on the ORR.<sup>6</sup> Additionally, this also led to a gel-like material – a so-called gel-polymer electrolyte (GPE) – that overcame the flowing nature of the electrolyte, meaning that the planar gas sensing device could be operated in various orientations without any leakage. 50 wt.% of polymer was required to create a stable non-flowing gel, which simultaneously came along with a significantly higher viscosity and lower conductivity of the electrolyte. However, the investigation did not study a broad humidity range, only dry, ambient, and wet conditions.

The motivation in this thesis is to study these GPEs in more detail, by employing various molar masses of the polymer as well as different polymer species in combination with different RTIL structures. In this chapter, non-ionic polymers will be added to neat RTILs to obtain GPEs, to study whether adding polymers can prevent water from reacting with the electrogenerated superoxide species. Because of the low cost and wide availability of the polymers, this could give access to a less expensive alternative to pure RTIL electrolytes. In this section, a series of polymers with different hydrophilic/hydrophobic characteristics and different molar masses were mixed with three chosen RTILs. The RTILs were those that showed a massive change of the ORR current at low humidities, a small change at intermediate humidities and a stable ORR current even at high humidities (see chapter 3.1.). It was also investigated whether these electrolyte systems showed reversible responses in the voltammetry.

This study is preliminary work and due to time constraints, no in depth characterization of the results was performed. Further studies are required.

### **3.3.2.** Experimental

### 3.3.2.1. Chemical Reagents

The RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec-Ionic Liquids Technologies GmbH, Heilbronn, Germany), was used as received. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P<sub>14,6,6,6</sub>][[NTf<sub>2</sub>]) was kindly donated by the group of Professor Chris Hardacre (now at the University of Manchester, UK) when he was located at Queens University Belfast, UK. The RTIL heptyltriethylammonium bis(trifluoromethylsulfonyl)imide ([N<sub>2,2,2,7</sub>][NTf<sub>2</sub>]) was synthesized according to standard literature procedures.<sup>7</sup> The polymers poly(methyl methacrylate) (average M<sub>w</sub> = 15,000, Sigma Aldrich), poly(methyl methacrylate) (average  $M_w = 120,000$ , Sigma Aldrich), poly(methyl methacrylate) (average  $M_w = 350,000$ , Sigma Aldrich), poly(ethyl methacrylate) (average M<sub>w</sub> = 850,000, Sigma Aldrich) and poly(butyl methacrylate) (average  $M_w = 337,000$ , Sigma Aldrich) were used as received. Ultrapure water with a resistivity of 18.2 M $\Omega$  cm prepared by a Milli-Q laboratory water purification system (Millipore Pty Ltd., North Ryde, NSW, Australia) was used for humidifying the oxygen gas stream. Acetone (CHROMASOLV®, for HPLC,  $\geq$ 99.0%, Sigma-Aldrich) and tetrahydrofuran ( $\geq$ 99.0%, Sigma Aldrich) were used as received. A 1 M stock solution of  $H_2SO_4$  (aq) (prepared with ultrapure water from a 95-98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for the activation of the thin-film electrodes. High purity oxygen gas (>99.5%) and high purity nitrogen gas (99.99%) cylinders were purchased from BOC Gases (Welshpool, WA, Australia).

### **3.3.2.2.** Preparation of Gel-Polymer Electrolytes

Different mixtures of polymers and ionic liquids were prepared according to the following procedure (see Table 3.4). The polymer was dissolved in the respective amount of THF in a glass vial by heating and ultra-sonication until it was a homogenous solution. Afterwards the required amount of RTIL was added. The volume of THF was adjusted to reduce the viscosity so that the GPEs could be pipetted easily. The concentration of the polymer was approximately 25 wt.% for samples with  $[C_{2}mim][NTf_{2}]$  and  $[N_{7,2,2,2}][NTf_{2}]$  and 10 wt.% for samples with the RTIL

 $[P_{14,6,6,6}]$ [NTf<sub>2</sub>]. The volumes of GPE mixture that were pipetted onto the electrode were adjusted so that the volume of the THF-free electrolyte was around 7  $\mu$ L.

Sampla	<i>m</i> Polymer /	<i>m</i> rtil /	[Polymer] /	m <sub>THF</sub> /	[GPE] /
Sample	mg	mg	wt.%	mg	wt.%
25PMMA120/75C2mim	50.5	151.8	25	750.3	21
25PMMA350/75C2mim	50.3	151.5	25	741.0	21
25PMMA15/75C2mim	51.6	150.7	26	347.5	37
25PEMA/75C2mim	51.3	156.7	25	702.1	23
25PBMA/75C2mim	52.1	153.8	25	317.9	39
25PMMA15/75N7,2,2,2	52.6	152.2	26	325.2	39
25PEMA/75N7,2,2,2	52.7	150.3	26	495.0	29
25PBMA/75N7,2,2,2	49.6	152.1	25	319.6	39
10PMMA15/90P14,6,6,6	21.8	185.8	11	148.8	58
10PEMA/90P14,6,6,6	19.9	182.0	10	357.3	36
10PBMA/90P14,6,6,6	22.3	188.8	11	323.3	40

Table 3.4. Sample name, mass of polymer ( $m_{polymer}$ ), mass of RTIL ( $m_{RTHL}$ ), polymer concentration in the solvent free sample ([Polymer]), mass of the casting solvent ( $m_{THF}$ ) and concentration of GPE in the sample ([GPE]).

### **3.3.2.3.** Electrochemical Experiments

CV measurements were performed, and electrodes were prepared as previously explained in section 3.1.2.2. The required volume of the GPE mixtures was drop-cast to cover all three electrodes on the TFE (working electrode disc diameter of 1 mm<sup>2</sup>) and purged overnight under a nitrogen stream to remove dissolved gases, impurities such as oxygen and carbon dioxide and THF.

### 3.3.3. Results and Discussion

Gel-polymer electrolytes composed of commercially available polymers, *i.e.* poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate (PEMA) and poly(butyl methacrylate) (PBMA) and different ionic liquids, *i.e.* [C<sub>2</sub>mim][NTF<sub>2</sub>], [N<sub>7,2,2,2</sub>][NTf<sub>2</sub>] and [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>] were used as electrolytes to study the effect on the oxygen reduction reaction in humidified conditions. The impact of molecular weight as well as the nature of the polymer was investigated. The improvements as well as the drawbacks compared using pure ionic liquids will be discussed.

### 3.3.3.1. Influence of Molecular Weight of Polymer

Several gel-polymer electrolytes composed of 25 wt.% of PMMA with three different average molecular weights, *i.e.* 15,000, 120,000 and 350,000 g mol<sup>-1</sup>, and 75 wt.% of  $[C_2mim][NTf_2]$  were prepared. The influence of the polymer molecular weight of the polymer on the response of the electrochemical oxygen reduction reaction in humidified conditions was studied.

As has been concluded from several researchers in the field of polymer science, the physical properties of polymers such as their fatigue, endurance or tensile strength, depends on the molecular weight (M<sub>W</sub>) as well as on the molecular weight distribution (MWD).<sup>8</sup> In case of using polymers as a scaffold for neat ionic liquids in electrolytes, several characteristics have to be fulfilled. First, the scaffold is required to be electrochemically stable and should not affect the redox mechanism. Second, the scaffold must also provide a stable and homogeneous electrolyte composition for sensing applications with reproducible responses.

Figure 3.32 shows the current, normalized to the response at a relative humidity level of less than 1 RH%, as a function of relative humidities from <1 RH% to >95 RH% for the three different GPE compositions. Also included is the line of best fit for the neat [C<sub>2</sub>mim][NTf<sub>2</sub>] ionic liquid taken from the study described in chapter 3.1 (dashed line), where a huge current change at low humidities was observed, reaching a normalized current plateau of approximately 4 from 12 to 95 RH%.

All samples containing PMMA showed significant improvement compared to the neat ionic liquid at low relative humidity levels. The electrolyte composed of the polymer with the lowest molecular weight, *i.e.* 15,000 g mol<sup>-1</sup> shows a superior performance compared to all other samples. The maximum current change at the highest RH% is approximately 2 which is only 25% of the current change of the neat  $[C_2mim][NTf_2]$ electrolyte. In comparison, the polymer with an intermediate molecular weight of 120,000 does in general show also an improvement compared to the neat IL, but the maximum change in the normalized current is still around 3. No improvement for the 350,000 g mol<sup>-1</sup> sample could be observed at high moisture contents. The prepared samples did not show obvious phase separation, however, the normalized current response at varying humidity levels is different, suggesting a crucial difference in the ability to repel water from the electrode surface and therefore from reacting with the reduced superoxide radical.



Figure 3.32. Effect of different molecular weights of PMMA in the GPE composed of 25 wt.% PMMA/75 wt.% C<sub>2</sub>mim NTf<sub>2</sub> on the normalized ORR current in humidified conditions.

All systems were prepared and characterized at least in triplicate, and it is noted that there are higher variations for samples with higher molecular weights (data not shown). The electrolytes were drop casted after dilution using THF as casting solvent and sometimes the electrochemical response was very resistive depending on how the film dried. In those cases, the gel was removed, then the electrode was freshly activated and newly prepared. It is assumed that during the evaporation of the casting solvent, mainly polymer molecules precipitate from the liquid phase. Passivation of the working electrode is a clear indication that the GPEs are not homogeneous on a microscopic scale.

Another observation was a significantly different cyclic voltammetry shape for the oxygen reduction reaction. The GPE composed of the low molecular weight PMMA showed a quasi-reversible CV, where only a very small oxidation current was obtained (green CV in Figure 3.33). In contrast, the other two GPEs showed a more comparable response to the neat [C<sub>2</sub>mim][NTf<sub>2</sub>] (see Figure 3.33). The peak current responses decrease with increasing molecular weight of the polymer which can be attributed to a change in the viscosity and therefore the diffusion coefficient of the gas. However, due to the absence of the reverse peak for the GPE composed of low molecular weight PMMA, the results in Figure 3.32 must be interpreted carefully. The absence of the reverse peak implies that the electrogenerated superoxide radical already reacts in the electrolyte even in the absence of water, so the change of the normalized peak current

is not caused by the reaction of water with superoxide. It is suggested that the change of the diffusion behavior due to a lower viscosity is a possible explanation.



Figure 3.33. Cyclic voltammetry response for the electrochemical reduction of 100 vol.% of oxygen in  $[C_{2mim}][NTf_2]$ , and GPEs composed of 75 wt.%  $[C_{2mim}][NTf_2]$  and 25 wt.% of PMMA ( $M_w = 15,000$ ), PMMA ( $M_w = 120,000$ ) or PMMA ( $M_w = 350,000$ ).

### 3.3.3.2. Influence of Polymer

The previous section has shown that the molecular weight of the polymer contributes to the current response significantly. GPEs composed of low molecular weight PMMA showed superior improvement towards preventing the reaction of superoxide with water for the whole humidity range, however, no reversible ORR response was obtained. It was attempted to increase the hydrophobicity of the polymer, by using polymers with longer alkyl chains compared to the methyl chain in PMMA. It is noted that polymer with intermediate to high molecular weight of PEMA and PBMA were used for preliminary tests only. Figure 3.34 shows the normalized oxygen reduction current fit for the neat [C<sub>2</sub>mim][NTf<sub>2</sub>], the fit for the GPE composed of the low molecular weight PMMA (taken from Figure 3.32) and [C<sub>2</sub>mim][NTf<sub>2</sub>] mixed with high molecular weight samples of PMMA, PEMA (ethyl chain) and PBMA (butyl chain). The trend of a less normalized current change with increasing humidity between the different polymer species is expected due to the increased hydrophobicity of the longer chained polymers. At 95 RH%, the current changed by a factor of 4 for PMMA, approximately 3 for PEMA and 2.5 for PBMA.

As discussed in chapter 3.1, the current change at high humidity levels is determined by the hydrophobicity of the electrolyte; more hydrophobic ILs show a smaller current change than more hydrophilic ILs. At lower RH%, the RTIL interfacial structures at the electrode surface can prevent the superoxide reaction with water. In a series of imidazolium-based RTILs with different alkyl chain lengths, no current change up to 15 RH% was observed for  $[C_4mim]^+$  and  $[C_6mim]^+$  in contrast to  $[C_2mim]^+$ . It has been suggested that the alkyl chains of the cations can form a hydrophobic layer close to the electrode where water is not reacting with the electrogenerated superoxide.



Figure 3.34. Effect of different high molecular weight methacrylates, i.e. PMMA, PEMA, PBMA, in the GPE composed of 25 wt.% polymer/75 wt.% C<sub>2</sub>mim NTf<sub>2</sub> on the normalized ORR current in humidified conditions. Also included is the low MW PMMA fit from Figure 3.32 (green dashed line).

It appears that PEMA and PBMA have a similar effect on the current response, where the alkyl chains of the polymers enhance the hydrophobic nature, or at least form hydrophobic regions within the electrolyte, where water can be separated from the superoxide radical and therefore no chemical reaction between the two species occurs. However, the results obtained from these GPEs are not as promising as GPEs composed of low molecular weight PMMA, where it is noted that no reversible cyclic voltammetry shape for the oxygen reduction reaction had been observed.

GPEs with the previously mentioned polymers, and different  $[N_{7,2,2,2}][NTf_2]$  and  $[P_{14,6,6,6}][NTf_2]$  were investigated as well. Figure 3.35 shows the change of the normalized current as a function of the humidity level up to 50 RH% for GPEs composed of low molecular weight PMMA, PEMA ( $M_W = 850,000$ ) or PBMA ( $M_W = 337,000$ ) with  $[N_{7,2,2,2}][NTf_2]$  or  $[P_{14,6,6,6}][NTf_2]$ , respectively. All GPE compositions showed a single reduction wave in a dry gas environment, however, at increased humidity level, the peak merged with the onset of the electrochemical window and no peak current could be extracted. The limited data obtained does not suggest any reduced impact of the presence of water on the ORR for  $[N_{7,2,2,2}][NTf_2]$ . In fact for  $[P_{14,6,6,6}][NTf_2]$ , a significant normalized current change for the GPE in contrast to the

neat IL, which means that the addition of the polymer altered the RTIL structuring at the electrode that ended up allowing the reaction of water with superoxide.

Overall, it shows that adding a hydrophobic polymer to a RTIL does not necessarily make the electrolyte more water repellent. The approach is promising for more hydrophilic RTILs, such as [C<sub>2</sub>mim][NTf<sub>2</sub>], an RTIL that was not able to prevent the superoxide reaction with water even at low humidity levels. However, for the more hydrophobic RTILs, *i.e.* [N<sub>7,2,2,2</sub>][NTf<sub>2</sub>] and [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>], no obvious improvement compared to the neat RTIL could be observed.



Figure 3.35. Effect of different high molecular weight methacrylates, i.e. PEMA, PBMA, PMMA in the GPE composed of 25 wt.% polymer/75 wt.% IL on the normalized ORR current in humidified conditions. Left with [N<sub>7,2,2,2</sub>][NTf<sub>2</sub>] and right [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>].

### 3.3.4. Conclusions

Commercially available, non-ionic polymers were added to ionic liquids to obtain gelpolymer electrolytes for electrochemical gas sensing in humidified conditions. Preliminary studies on the effect of different molecular weights and polymers on the oxygen reduction reaction response were investigated via cyclic voltammetry. GPEs composed of low molecular weight PMMA showed no reversible electrochemical response and promisingly, the influence of water on the ORR current was minimal. Higher molecular weight PMMA showed good reversibility in dry gas conditions with a lower degree of change of the normalized ORR current compared to neat [C<sub>2</sub>mim][NTf<sub>2</sub>]. High molecular weight polymers with longer alkyl chains, like PEMA and PBMA, combined with [C<sub>2</sub>mim][NTf<sub>2</sub>] showed promising responses in terms of prevention of the reaction of water with the superoxide radical. However, the GPEs containing [N<sub>7,2,2,2</sub>][NTf<sub>2</sub>] or [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>] showed a more severe current change, even more significant than the pure RTIL. It is therefore assumed that the combination of polymer and RTIL must be fully optimized before GPEs can be applied further for humid gas sensing applications. This requires further, more detailed investigations.

# **3.3.5. References**

1. Giernoth, R., Task-Specific Ionic Liquids. Angew. Chem. Int. Ed. 2010, 49, 2834-2839.

2. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

3. Xue, H.; Verma, R.; Shreeve, J. M., Review of ionic liquids with fluorinecontaining anions. *J. Fluor. Chem.* **2006**, *127*, 159-176.

4. Guan, J.; Li, Y.; Li, J., Stretchable Ionic-Liquid-Based Gel Polymer Electrolytes for Lithium-Ion Batteries. *Ind. Eng. Chem. Res.* **2017**, *56*, 12456-12463.

5. Fuller, J.; Breda, A. C.; Carlin, R. T., Ionic liquid-polymer gel electrolytes from hydrophilic and hydrophobic ionic liquids. *J. Electroanal. Chem.* **1998**, *459*, 29-34.

6. Lee, J.; Silvester, D. S., Low-cost microarray thin-film electrodes with ionic liquid gel-polymer electrolytes for miniaturised oxygen sensing. *Analyst* **2016**, *141*, 3705-3713.

7. Sun, J.; MacFarlane, D. R.; Forsyth, M., Synthesis and Properties of Ambient Temperature Molten Salts Based on the Quaternary Ammonium Ion. *Ionics* **1997**, *3*, 356-362.

8. Nunes, R. W.; Martin, J. R.; Johnson, Influence of molecular weight and molecular weight distribution on mechanical properties of polymers. *Polym. Eng. Sci.* **1982**, *22*, 205-228.

# 4. Improving the Selectivity and Sensitivity of RTIL-based Gas Sensors

A robust electrochemical gas sensor should show high sensitivity and good selectivity towards the gas in a real-world environment. This chapter is divided in three sub chapters: one is focused on selectivity and the other two are focused on sensitivity.

A significant advantage of using RTILs is the possibility to chemically modify the structure and therefore make these electrolytes "task specific" or more selective towards certain gases. The first part of this chapter studies the effect of various functional groups attached to the RTIL cation on the solubility of oxygen (O<sub>2</sub>), hydrogen (H<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) gases. Based on these results, relationships between the gas solubility of polar and non-polar gases and the chemical structure of RTILs are made.

The second part focuses on the electrochemical reduction of sulfur dioxide, a gas that has a permissible exposure limit (PEL) of 2 ppm. Various electrode materials, geometries and electrochemical techniques were investigated and optimized to achieve a reliable and stable detection limit of low parts-per-million concentrations of SO<sub>2</sub>.

The third part investigates specially manufactured electrodes that form thin RTIL layers for fast response times for sulfur dioxide sensing.

# 4.1. Functionalized Imidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids for Gas Sensors: Solubility of H<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub>

This chapter has been published in the following peer-reviewed journal:

<u>Doblinger, S.</u>, Silvester, D. S., Costa Gomes, M. Functionalized Imidazolium Bis(trifluormethylsulfonyl)imide Ionic Liquids for Gas Sensors: Solubility of H<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub>. *Fluid Ph. Equilibria* **2021**, *549*, 113211.

The abstract has been removed in this chapter and the supporting information has been included after the references. Figure and table captions as well as equation numbers have been changed. A few changes have been made.

### Author Contributions:

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 70%/100%

Acquisition of Data and Method: 90%/100%

Data Conditioning and Manipulation: 85%/100%

Analysis and Statistical Method: 80%/100%

**Interpretation and Discussion:** 60%/100%

Final Approval: 60%/100%

Signature:

Simon Doblinger

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 0%/100%

Acquisition of Data and Method: 0%/100%

Data Conditioning and Manipulation: 0%/100% Analysis and Statistical Method: 0%/100% Interpretation and Discussion: 10%/100% Final Approval: 10%/100%

Signature:

Debbie S. Silvester

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 30%/100%

Acquisition of Data and Method: 10%/100%

**Data Conditioning and Manipulation:** 15%/100%

Analysis and Statistical Method: 20%/100%

**Interpretation and Discussion:** 30%/100%

Final Approval: 30%/100%

Signature:

Margarida Costa Gomes

### **4.1.1. Introduction**

The need for highly sensitive and robust gas sensors is a main research focus in the area of gas monitoring for environmental, industrial and health purposes. A broad variety of systems are available, however the requirements of low cost, small and mobile sensors that have high robustness in extreme conditions are not often fulfilled. Room temperature ionic liquids (RTILs) are drawing more and more attention for application as electrolytes in gas sensors<sup>1</sup> due to their unique characteristics like low volatility, high conductivity, large electrochemical window, good solvent properties as well as high chemical and thermal stability.<sup>2</sup> It has been shown that the high thermal stability up to approximately 350 °C of certain ionic liquids makes it possible to detect volatile organic compounds (VOCs) up to 200 °C.<sup>3</sup> By far, the most attractive property of RTILs is the possibility of tuning their properties by appropriately combining cations and anions or by introducing chemical functionalities in their structures.<sup>4</sup> This allows the adjustment of the physicochemical properties towards certain requirements such as low or high viscosities, high gas absorption or increased selectivity towards certain analytes. This concept is present in the preparation of task-specific ionic liquids (TSILs) initially prepared to increase the selectivity in gas absorption and improve sensitivity towards trace analyte capture and detection.

Bates and co-workers introduced the idea of TSIL with an amine-functionalized imidazolium-based IL with increased carbon dioxide capacity due to the reversible formation of a carbamate.<sup>5</sup> To avoid the increase of the viscosity of the RTIL solution after the gas absorption, further developments have been proposed by Gurkan *et al.*<sup>6</sup> who designed ionic liquids based on suitably substituted aprotic heterocyclic anions capable of selectively and reversely absorbing carbon dioxide while maintaining the liquid fluidity. Polymerized ionic liquids (PILs) and amino-acid-based polymerized ionic liquids (AAPILs) have also been used for enhanced carbon dioxide sorption.<sup>7</sup> In the case of sulfur dioxide (SO<sub>2</sub>), little research has been performed so far compared to CO<sub>2</sub> especially with regards to SO<sub>2</sub>/O<sub>2</sub> or SO<sub>2</sub>/H<sub>2</sub> separation in mixed gas streams. Anderson *et al.*<sup>8</sup> measured Henry constants,  $K_{\rm H}$ , for sulfur dioxide and carbon dioxide in two commercially available ionic liquids based on the [NTf<sub>2</sub>]<sup>-</sup> anion. They showed a significantly higher  $K_{\rm H}$  and therefore lower solubility at 25 °C for CO<sub>2</sub> (around 32 bar) compared to SO<sub>2</sub> (approximately 1.6 bar) for both RTILs, explained by a pure physical absorption mechanism. Shiflett *et al.*<sup>9</sup> studied SO<sub>2</sub> absorption in imidazolium-

based ionic liquids with different anions and suggested a chemical absorption mechanism. Yuan *et al.*<sup>10</sup> studied the impact of the chemical modification of ammonium ionic liquids with hydroxyl groups and measured high, reversible SO<sub>2</sub> capacities explained by the reaction of the gas at the –NH group in the hydroxyl ammonium cation to form N–S bonds. Under vacuum conditions or at elevated temperatures, this reaction can be reversed to release SO<sub>2</sub>, which makes these RTILs reusable. Jin *et al.*<sup>11</sup> compared SO<sub>2</sub> absorptions in conventional 1-butyl-3-methylimidazolium tetrafluoroborate, [C<sub>4</sub>mim][BF<sub>4</sub>], and hexafluorophosphate, [C<sub>4</sub>mim][PF<sub>6</sub>], and in the TSILs 1,1,3,3-tetramethylguanidinium lactate and monoethanolaminium lactate, and concluded that both ILs can absorb SO<sub>2</sub> effectively at high partial pressures, but only TSILs exhibit high sulfur dioxide capacities at low partial pressures of SO<sub>2</sub>. A comparison of solubility isotherms revealed that the proposed TSILs absorb SO<sub>2</sub> chemically as well as physically in contrast to a pure physical absorption mechanism in RTILs.

Several researchers have measured the solubilities of non-polar and small gases like hydrogen and oxygen in commercially available RTILs such as [C<sub>4</sub>mim][BF<sub>4</sub>], [C<sub>4</sub>mim][PF<sub>6</sub>] or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>4</sub>mim][NTf<sub>2</sub>]. For O<sub>2</sub>, some work showed no change in the solubility with temperature<sup>12</sup> whereas others noted increasing solubility with increased temperature<sup>13</sup>, not coherent with the common exothermal gas dissolution observed in RTILs.<sup>14-16</sup> Even if for hydrogen, an 'inverse' temperature effect, *i.e.* hydrogen solubility increases with increasing temperature in [C<sub>4</sub>mim][PF<sub>6</sub>]<sup>16</sup> and [C<sub>4</sub>mim][NTf<sub>2</sub>]<sup>17</sup> has been reported, the temperature has only a small influence on the solubility of light, nonpolar gases in RTILs, supported by the enthalpy of solvation ( $\Delta_{solv}H^{\infty}$ ) values being only slightly negative. The mole fraction solubility of light gases in RTILs are in general 1–2 orders of magnitude lower than that of CO<sub>2</sub>.<sup>18</sup>

It has been first established by Anthony *et al.*<sup>14</sup> that dissolved gases mainly interact with the anion of the RTILs. More recently, it is assumed that gas solvation mechanisms are more complex and, depending on the structure of the RTIL, might be controlled by functionalization of the cations as clearly seen when the cation side chains are fluorinated.<sup>19-20</sup> Blesic *et al.*<sup>21</sup> studied also the phase behavior of mixtures of ionic liquids and fluorinated and non-fluorinated benzenes, observing that the competition of the solute interaction with the polar and non-polar nanoregions determines the solubility in this case. When the solubility of gases is not controlled by

specific interactions with RTIL ions, it increases with the size and flexibility of the ions or, in other words, when the molar volume ( $V_m$ ) of the RTIL increases.<sup>22</sup> However, for gases that have strong interactions with ionic liquids, the segregation of the liquid into polar and non-polar regions has to be taken into account.<sup>23</sup> Therefore, modification of the domain in which the analyte is mainly distributed is one way to increase the solubility of different gases, *i.e.* CO<sub>2</sub> and SO<sub>2</sub> in the polar region and H<sub>2</sub> and O<sub>2</sub> in the non-polar domain of the RTIL.

This work focusses on chemically modifying imidazolium cations by functionalizing with different moieties and quantify how they influence the absorption and selectivity of different gases namely  $SO_2/H_2$  and  $SO_2/O_2$ . The anion was kept identical, *i.e.* bis(trifluoromethylsulfonyl)imide,  $[NTf_2]^-$ , and the alkyl side-chains in the imidazolium cations were functionalized to change the non-polar nanoregion probably affecting the gas solubilities of analytes that dissolve in the non-polar regions.

Based on these results obtained herein, the developed systems could be used as electrolytes to study their suitability for electrochemical gas sensing experiments. Several researchers showed that ionic liquids form alternating cation- and anion-rich layers next to a charged surface, with a thickness that depends on the applied potential. <sup>24-27</sup> For electrochemical sensing applications, analytes can be either locally retained from or accumulated in the electrical double layer by choosing an appropriate cation and anion combination that more effectively solubilizes the analyte, or one that chemically binds the analyte reversibly to influence the diffusion towards or away from the electrode. If there is no chemical interaction between the gas and the ionic liquid, the application of an external electrical field can restructure the polar and non-polar ionic liquid domains to change the solubility of the gas.

In this paper, the experimentally measured solubilities of hydrogen, oxygen and sulfur dioxide in a series of functionalized and non-functionalized imidazolium-based ionic liquids with the  $[NTf_2]^-$  anion are reported at temperatures between 303 and 333 K using the well-established isochoric saturation method.<sup>28</sup> A set of functionalized ionic liquids was synthesized, and their densities and viscosities were determined in a temperature range of 293 to 353 K. Additionally, the selectivity is discussed based on the experimentally determined gas solubilities.

### 4.1.2. Experimental

### 4.1.2.1. Chemical Reagents

All commercially available RTILs were obtained at the highest purity level possible. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec) were used without further purification. 1-(2hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>OHmim] 1-methylnitrile-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  $[NTf_2]$ ), ([CCNmim][NTf<sub>2</sub>]), 2-(3-methylimidazolyl-1-yl)-ethoxy-4-oxobutanoic acid bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>succmim][NTf<sub>2</sub>]) and 1-methylbenzyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ([CBenzmim][NTf<sub>2</sub>]) were synthesized and characterized according to standard literature procedures (see details in the supporting information). The structures of the RTILs studied are shown in Figure 4.1. All RTILs were dried overnight at 60 °C under reduced pressure to remove traces of water as well as dissolved gases before experiments.

Oxygen 5.0 (99.999% pure) was purchased from Messer, nitrogen 5.0 (99.999% pure) and hydrogen 5.0 (99.999%) were purchased from Linde Gas and sulfur dioxide 4.0 (99.99%) was purchased from Air Liquide. All gases were used as supplied without further purification.

### 4.1.2.2. Density and Viscosity Measurements

Densities were measured at atmospheric pressure and within a temperature range from 293 to 353 K with a U-shaped vibration-tube densimeter (Anton Paar, model DMA<sup>TM</sup> 5000 M). The temperatures were kept constant within 0.001 K and measured with an accuracy of 0.01 K. The precision was determined as 10<sup>-5</sup> g cm<sup>-3</sup>. The densimeter was calibrated before the measurements with air and the Anton Paar certified ultra-pure water. The measured values were corrected for viscosity using the inbuilt full range viscosity correction option from Anton Paar.

Dynamic viscosities were measured with a rolling ball viscosimeter (Anton Paar, Lovis 2000 ME) within a temperature range from 293 to 353 K. The temperatures were controlled within 0.005 K. The experiments were performed with a capillary tube (1.59 mm diameter) and a steel ball. Calibration experiments were performed as a function of temperature and angle with appropriate standard viscosity oils from

Paragon Sci. The overall uncertainty was estimated as 0.5%. Samples were dried overnight at 333 K under reduced pressure before measurements were performed.



Figure 4.1. Chemical structures and abbreviations of the commercial and synthesized ionic liquid cations and the anion,  $[NTf_2]^-$ , used in this work.

### 4.1.2.3. Gas Absorption Measurements

Gas absorption was measured with an in-house built apparatus which is based on an isochoric saturation method as described elsewhere in more detail.<sup>28</sup>

A precisely calibrated bulb with volume  $V_{\text{GB}}$  is filled with the respective gas at a known pressure and constant temperature thus allowing the calculation of the quantity of gas in the equilibration cell. After bringing the gas in contact with the dried and degassed ionic liquid, the constant temperature and pressure above the liquid at the equilibrium can be used to calculate the solubility of the respective gas in the liquid phase. The quantity of ionic liquid present in the equilibrium cell,  $n_1$ , is determined gravimetrically with a precision of  $\pm 0.1$  mg. The volume occupied by the liquid solution,  $V_{\text{liq}}$ , is determined through the knowledge of the density of the pure ionic liquid, assuming that it does not change significantly upon the dissolution of the gas. The gas content in the ionic liquid,  $n_2^{\text{liq}}$ , is calculated by the difference of the two *pVT* measurements – one when bulb is filled with gas and the other when the vapor-liquid equilibrium is attained:

$$n_{2}^{liq} = \frac{p_{ini}V_{GB}}{[Z_{2}(p_{ini}, T_{ini})RT_{ini}]} - \frac{p_{eq}(V_{tot} - V_{liq})}{[Z_{2}(p_{eq}, T_{eq})RT_{eq}]}$$

$$4.1$$

with  $p_{ini}$  and  $T_{ini}$  as initial pressure and temperature respectively and  $p_{eq}$  and  $T_{eq}$  after reaching the equilibrium.  $V_{tot}$  is the total volume of the equilibration cell and  $Z_2$  is the compressibility factor of the respective pure gas. The gas solubility can be expressed as mole fraction  $x_2$  according to equation 4.2 or as Henry's law constant  $K_H$  (equation 4.3):

$$x_2 = \frac{n_2^{liq}}{n_2^{liq} + n_1^{liq}} \tag{4.2}$$

$$K_{\rm H} = \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\varphi_2(p_{eq}, T_{eq})p_{eq}}{x_2}$$
 4.3

where  $f_2$  is the fugacity of the solute and  $\varphi_2$  the fugacity coefficient.

For the calculation of the compressibility factor, the fit function for the second virial coefficient, *B*, of hydrogen from 273 to 400 K was taken from the compilation by Dymond and Smith<sup>29</sup> and for oxygen and sulfur dioxide from Dymond *et al.*<sup>30</sup> (see equations 4.4 to 4.6) for temperature ranges from 270 to 373 K and 270 to 470 K respectively.

$$B_{H_2} = -1.03725 \times 10^{-4} T^2 + 8.27777 \times 10^{-2} T - 8.36008 \times 10^{-1}$$

$$B_{O_2} = -4.64968 \times 10^{-4} T^2 + 4.92052 \times 10^{-2} T - 1.21657 \times 10^{+2}$$
4.5

 $B_{SO_2} = -8.26060 \times 10^{+9} T^3 - 4.97860 \times 10^{+6} T^2 - 2.3892 \times 10^{+2} T + 2.47940 \times 10^{+1}$  4.6

### 4.1.3. Results and Discussion

### 4.1.3.1. Density and Viscosity

The experimentally measured densities are listed in Table S4.7 and were fitted as a function of temperature according to the following equation (see Table 4.1):

$$\rho = \rho_0 - A \cdot T \tag{4.7}$$

The linear density dependence on temperature perfectly describes the experimental data.

Ionic Liquid	$ ho_{ heta}$ / kg m <sup>-3</sup>	<i>A</i> / 10 <sup>-4</sup> K
[CCNmim][NTf <sub>2</sub> ]	1899.7	696.27
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	1814.3	892.53
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	1866.9	980.36
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1717.3	405.52
[CBenzmim][NTf <sub>2</sub> ]	1727.3	871.57
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	1855.4	860.02

Table 4.1. Parameters of equation 4.7 used to fit the experimental density  $\rho$  as a function of the temperature in K.

The results were compared to the literature, when data were available, and the densities are in good agreement with reported values (see supporting information Figure S4.4 to Figure S4.7). For [C<sub>2</sub>mim][NTf<sub>2</sub>], a huge dataset of experimentally measured densities has already been reported. The deviation from most of the literature values is less than 0.1%. The negative deviation of 0.05% — *i.e.* lower experimental densities in our case — can be explained by the fact that other groups prepared the ionic liquids in their laboratory (at least the anion exchange steps) whereas the sample that was used for this study was obtained commercially with the highest purity available, *i.e.* 99.5%. Residues of the salts used for the anion exchange can cause a higher RTIL density. For [C<sub>4</sub>mim][NTf<sub>2</sub>], very good agreement with literature data was achieved. The datasets for which large deviations were found, were obtained for less pure salts or samples containing large amounts of water. For [CCNmim][NTf2] and [C2OHmim][NTf2] (two of the synthesized samples), only a limited number of density values are reported and significant differences in these values can be observed. In the case of synthesized ionic liquids, unreacted precursors can still be present after purification steps.<sup>31</sup> The densities measured herein (equation 4.7 and Table 4.1) were necessary for the calculation of the gas solubility.

Viscosity data (see Table S4.8) were fitted via the Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = \eta_0 \cdot e^{\frac{B}{T - T_{\rm VF}}} \tag{4.8}$$

where  $\eta$  and T are the experimentally determined viscosity and temperature values respectively,  $\eta_0$  and B are temperature dependent variables and  $T_{\rm VF}$  is a temperature that is approximately 50 K below the glass transition temperature of the substance.

Ionic Liquid	$\eta_0$ / mPa s	<i>B</i> / K	<i>T</i> <sub>VF</sub> / K
[CCNmim][NTf <sub>2</sub> ]	0.25	696.27	200.48
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	0.12	892.53	139.12
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	0.08	980.36	159.74
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	0.59	405.52	207.84
[CBenzmim][NTf <sub>2</sub> ]	0.13	871.57	147.11
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	0.15	860.02	186.67

Table 4.2. Parameters of equation 4.8 used to fit the experimental viscosity  $\eta$  as a function of the temperature in K.

Comparison of experimentally determined viscosities with previously published data are shown in the supporting information (Figure S4.4 to Figure S4.7). Positive and negative deviations of our data to that previously reported, indicates that our results do not present systematic errors. However, even if the viscosities of [C<sub>2</sub>mim][NTf<sub>2</sub>] and [C<sub>4</sub>mim][NTf<sub>2</sub>] are in good agreement with literature values (within 2%), the glass transition temperatures ( $T_g$ ) — which should be approximately 50 K above the  $T_{VF}$ values — are in accordance to published ones for the shorter alkyl side-chain ( $T_g$  = 195 K) but not for the cation with a longer chain ( $T_g$  = 186 K) see (Table 4.2).<sup>32</sup>

Table 4.3. Overview of experimentally measured densities  $\rho$  and viscosities  $\eta$  for the studied ionic liquids at 313.15 K.

Ionic Liquid	ho / g cm <sup>-3 a</sup>	η / mPa s <sup>b</sup>
[CCNmim][NTf <sub>2</sub> ]	1.59335	126.6
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	1.50276	20.2
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	1.56222	47.3
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1.42200	28.5
[CBenzmim][NTf <sub>2</sub> ]	1.44206	98.5
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	1.55439	138.1

 $^{a} \pm 10^{-5} \text{ g cm}^{-3}$   $^{b} \pm 0.5\%$ 

Table 4.3 summarizes the densities and viscosities at 313.15 K of the ionic liquids studied herein. In general, attaching more polar functional groups such as –OH, –CN or –COOH, increases the molecular weight as well as intermolecular forces like dipole-dipole interactions and hydrogen bonding. As can be seen in Table 4.3, increased densities are observed for functionalized imidazolium-based ionic liquids. The density at 313 K follows the order  $[C_4mim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Mim][NTf_2] < [C_2Mim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [C_$ 

Oliveira *et al.*<sup>33</sup> studied the effect of water on the two physical chemical properties of RTILs and concluded that the presence of water is more crucial for variations in the viscosity than those of the density, due to the fact that viscosity is highly dependent on intermolecular interactions. Generally, this could explain the higher variations between experimental and literature data in the case of viscosity. The study<sup>33</sup> also revealed that the relative density difference between 'water saturated' and 'dried' pyridinium-based ionic liquid is less than 1%. It is noted that the viscosity only affects the time to reach thermodynamical equilibrium, whereas the variation in density directly affects the determination of the gas solubility. Due to the fact that comparison of our data with literature data did not show significant differences, no further drying of the samples was performed before the measurements. For gas solubility determinations, the ionic liquid was degassed and kept under vacuum for several hours while the pressure was continuously measured to ensure that no volatile compounds were present in the cell before equilibration of the gas with the ionic liquid was performed.

#### 4.1.3.2. Gas Solubilities

Experimentally measured temperatures, T, and pressures, p, the measured mole fraction gas solubilities,  $x_2$ , calculated Henry's law constants,  $K_{\rm H}$ , mole fraction corrected for a partial pressure of 1 bar,  $x_2$  (1 bar), and molarity, c, are reported in the supporting information Table S4.9 to Table S4.11.

The precision (*u*) was calculated via error propagation for each measurement based on the uncertainty of the gravimetrically determined mass ( $\pm 0.001$  g) and the volume of the glass bulb cell, as well as the variation of the pressure (approximately  $\pm 0.02$  mbar) and temperature (approximately  $\pm 0.003$  K) measurements. The precision of the mole fraction solubility for all measurements is within  $\pm 2 \times 10^{-4}$  to  $\pm 4 \times 10^{-4}$  for all samples and temperatures which also indicates the limits for the gas solubility values with this kind of setup.

The gas solubilities for all studied gases decrease with increasing temperature and therefore, especially for the less soluble hydrogen and oxygen, the experimental data shows a much larger relative error for the higher temperatures studied here (*e.g.* a relative error of more than 100% is reported for the very low solubility of H<sub>2</sub> in  $[C_2mim][NTf_2]$  at 333.15 K). For SO<sub>2</sub>, the measured absorptions are several orders of magnitude higher, therefore the contribution of the precision of the experimental setup affects the overall error much less, the reported values are being affected with errors within 0.2%. The uncertainty introduced by the experimental method has to be taken into account for the following discussion and hence the gas absorptions at the lower temperatures (*i.e.* 313 K), with generally lower relative errors, were used for comparison between the solutes.

Table 4.4 lists the mole fraction solubility of the three gases, hydrogen, oxygen and sulfur dioxide, in the functionalized and non-functionalized imidazolium ionic liquids at 313 K. As can be seen, the solubilities of hydrogen and oxygen are approximately 2-3 orders of magnitude lower than for SO<sub>2</sub>, in general H<sub>2</sub> being slightly less soluble than O<sub>2</sub> in the RTILs studied.

The differences in solubility can be rationalized by the Hildebrandt solubility parameters,  $\delta$ , which take the cohesive energy density into account.<sup>34</sup> Hydrogen and oxygen are considered as non-polar gases with small solubility parameters, *e.g.* 5.08 MPa<sup>1/2</sup> for H<sub>2</sub> and 14.64 MPa<sup>1/2</sup> for O<sub>2</sub>.<sup>35</sup> For CO<sub>2</sub>, a value of 19.10 MPa<sup>1/2</sup> has been reported, and it can be assumed that SO<sub>2</sub>, which is also a polar and heavy gas, has an equally high  $\delta$  even in the absence of literature data. Solubility parameters for imidazolium-based RTILs were calculated by Bara *et al.*<sup>36</sup> based on a modified Kapustinskii equation<sup>37</sup>, they are between 38.4 MPa<sup>1/2</sup> for [C<sub>2</sub>mim][NTf<sub>2</sub>] and 50.9 MPa<sup>1/2</sup> for 1-ethyl-3-methylimidazolium dicyanamide, [C<sub>2</sub>mim][DCA]. According to the regular solution theory, gases with higher, *i.e.* more similar, solubility parameters to ionic liquids are more easily dissolved.

As can be seen in Figure 4.2, the trend of increasing gas solubility for all ionic liquids is  $H_2 < O_2 < SO_2$ , as predicted by the regular solution theory. Furthermore, the solubility of the non-polar gases mainly follows the trend of increasing molar volume,  $V_{\rm m}$ , of the ionic liquid, even if the errors for these low solubilities are significant (see Table S4.9 to Table S4.11). This means that the solubility is dominated by the free volume of the ionic liquid -i.e. non-specific interactions between the gas and the liquid. However, in the case of oxygen, it can be seen that non-functionalized ionic liquids show slightly higher oxygen solubilities when compared to the functionalized ones. As previously mentioned, the solubility of light gases is mainly defined as physical absorption in the non-polar region of the ionic liquid, therefore the solubility is assumed to decrease with the addition of more polar groups in the side-chain, keeping the molar volume,  $V_{\rm m}$ , the same. This effect can be seen for  $[C_2 \text{mim}][NTf_2]$  $(V_{\rm m} = 260.30 \text{ cm}^3 \text{ mol}^{-1})$  and  $[C_2OHmim][NTf_2] (V_{\rm m} = 260.72 \text{ cm}^3 \text{ mol}^{-1})$  where the synthesized sample shows smaller gas solubilities even if the molar volumes are approximately the same. This assumption can only be confirmed for oxygen as for hydrogen, the molar volume is more decisive taking into account that the relative error of the solubility data.

	<i>V</i> <sub>m</sub> /	<i>x</i> (H <sub>2</sub> ) /	x(O <sub>2</sub> ) /	x(SO <sub>2</sub> ) /
Ionic Liquid	cm <sup>3</sup> mol <sup>-1</sup>	10-4	10-4	10-4
[CCNmim][NTf <sub>2</sub> ]	252.48	4.7	9.3	2913
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	260.39	9.8	15	3727
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	260.72	7.3	13	3077
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	294.91	7.6	20	3017
[CBenzmim][NTf <sub>2</sub> ]	323.87	13	15	3626
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	326.42	19	26	4129

Table 4.4. Overview of molar volumes,  $V_m$ , calculated from the experimental densities of the RTILs and mole fraction gas solubilities, x, corrected for a 1 bar partial pressure of the gas in the studied ionic liquids at 313 K.

It has been reported that the ionic liquid anion-gas interaction is an important factor that contributes to the solubility of polar gases like  $CO_2$ , the cation having only a small effect.<sup>38-40</sup> Greater flexibility in the anion structure such as in the  $[NTf_2]^-$  anion, supports the presence of a larger free volume in the polar region of the RTIL where polar gases are absorbed.<sup>41-43</sup> As in our study the anion was kept the same for all

samples, the modifications on the cation are the reasons for the change in solubility. Table 4.4 shows that the solubilities are significantly higher for the more polar SO<sub>2</sub> by more than two orders of magnitude, in comparison to the non-polar gases. No evidence of a chemical absorption of SO<sub>2</sub> is found. Apart from [C<sub>2</sub>mim][NTf<sub>2</sub>], which has an unexpectedly high SO<sub>2</sub> solubility, ionic liquids with more polar functional groups in their side chain, such as –CN or –OH, give markedly lower mole fraction solubility values compared to less polar benzyl or alkyl side chains.

Both chemical and physisorption have been reported for SO<sub>2</sub> in RTILs, depending on the cation and anion.<sup>8, 18, 44</sup> Huang *et al.*<sup>45</sup> observed a purely physical absorption of SO<sub>2</sub> in several imidazolium and 1,1,3,3-tetramethylguanidinium-based ionic liquids with  $[BF_4]^-$  and  $[NTf_2]^-$  as anion. Anderson *et al.*<sup>8</sup> calculated the partial molar enthalpy and entropy of dissolution of SO<sub>2</sub> and CO<sub>2</sub> in  $[C_6mim][NTf_2]$  and reported a significantly stronger interaction between the solvent and solute (SO<sub>2</sub>) with an enthalpy of dissolution ( $\Delta_{solv}H^{\infty}$ ) value of approximately –20 kJ mol<sup>-1</sup> compared to –11 kJ mol<sup>-1</sup> for CO<sub>2</sub>. The entropic contribution ( $\Delta_{solv}S^{\infty}$ ) is also twice as high for SO<sub>2</sub>. These values suggest a purely physical absorption mechanism favored for sulfur dioxide compared with carbon dioxide.

Ionic Liquid	$\Delta_{ m solv}H^{\infty}$ / kJ mol <sup>-1</sup>	$\Delta_{solv}S^{\infty}$ / J mol <sup>-1</sup> K <sup>-1</sup>
[CCNmim][NTf <sub>2</sub> ]	$-20 \pm 2$	$-75 \pm 5$
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	$-20 \pm 2$	$-71 \pm 5$
[C <sub>2</sub> OHmim][NTf <sub>2</sub> ]	$-21 \pm 2$	$-75 \pm 5$
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	$-19\pm2$	$-70 \pm 5$
[CBenzmim][NTf <sub>2</sub> ]	$-20 \pm 2$	$-71 \pm 5$
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]	$-18 \pm 1$	$-65 \pm 4$

Table 4.5. Molar enthalpy of solvation  $(\Delta_{solv}H^{\infty})$  and molar entropy of solvation  $(\Delta_{solv}S^{\infty})$  of SO<sub>2</sub> at a pressure of 0.1 MPa in the six ionic liquids averaged over the temperature range from 304 to 333 K.

Table 4.5 shows the calculated molar enthalpy and entropy values of solvation for SO<sub>2</sub>, calculated from the experimental data for the synthesized and commercially available imidazolium-based ionic liquids. As can be seen,  $\Delta_{solv}H^{\infty}$  is within the experimental error (around -20 kJ mol<sup>-1</sup>) for all samples, which is the same as reported by Anderson *et al.*<sup>8</sup> for [C<sub>6</sub>mim][NTf<sub>2</sub>] and for physical absorption of CO<sub>2</sub> in [C<sub>4</sub>mim][TFA], by Carvalho *et al.*<sup>46</sup> Furthermore, similar molar entropy values for all ionic liquids

indicate that the effect of the solute in the structure of the liquid phase is similar for all gases, also pointing towards physical absorption of the gas.



Figure 4.2. Comparison of solubility of hydrogen, oxygen and sulfur dioxide in the studied RTILs corrected for a partial pressure of 1 bar at 313 K ( $x_2 \times 10^{-4}$ ). For simplification, only the abbreviation for the cation was used. SO<sub>2</sub> solubilities are significantly higher (as listed in Table 4) but are capped in this Figure at  $x(SO_2) = 40 \times 10^{-4}$ .

Based on the calculated molar enthalpies and entropies of dissolution, there is no indication of chemical binding of SO<sub>2</sub>, as has been confirmed previously for CO<sub>2</sub> by several groups<sup>46-49</sup> in the case of an ionic liquid anion, such as acetate, which is able to deprotonate an acidic hydrogen from the ionic liquid cation.<sup>49-50</sup> The bis(trifluoromethylsulfonyl)imide anion is known to be a weak base that cannot deprotonate the most acidic hydrogen atom from the imidazolium ring and thus not allowing the reaction with carbon dioxide or sulfur dioxide.

For applications where these ionic liquids are used in electrochemical gas sensors, the spontaneous, irreversible chemical binding of an analyte is undesirable. A chemically bound analyte could accumulate in the electrolyte and the establishment of a calibration curve over a broad concentration range would not be reliable. However, sensing of trace concentrations of toxic gases like SO<sub>2</sub> could be improved. The gas analyte should be absorbed reversibly, and the electrolyte must be electrochemically stable, preferably over a wide electrochemical window.

For gas sensors based on RTILs for use in real world environments, it is also desired to have a high selectivity towards certain gases that are toxic or dangerous at low concentrations. Therefore, the selectivities of  $SO_2/H_2$  and  $SO_2/O_2$  were calculated based on the molar fraction solubility of the respective gases and corrected for a partial

pressure of 1 bar at 313 K (see supporting information Table S4.9 – Table S4.11). Air is mainly composed of nitrogen which is electrochemically inert, and oxygen, which can be electrochemically reduced at similar potentials as SO<sub>2</sub>. Therefore, a high  $SO_2/O_2$  selectivity is desired for the sensing of low concentrations of sulfur dioxide.



Figure 4.3. Gas selectivities,  $SO_2/H_2$  and  $SO_2/O_2$ , calculated from the ratio of the mole fraction solubility at 313 K.

Figure 4.3 illustrates the SO<sub>2</sub>/H<sub>2</sub> and SO<sub>2</sub>/O<sub>2</sub> selectivities of the different ionic liquids at 313 K calculated from the experimental mole fractions ordered from the lowest  $V_m$ (left) to the highest (right). As can be seen, for the SO<sub>2</sub>/H<sub>2</sub> selectivity, high sulfur dioxide selectivities can be achieved in [CCNmim][NTf<sub>2</sub>] due to a low hydrogen and reasonably high SO<sub>2</sub> solubility. As previously discussed, hydrogen is mainly dissolved in the non-polar domains formed by the ionic liquid structure, whereas sulfur dioxide can act as a linker between the cation and the anion in certain RTILs, and so strongly interacts with the ring hydrogen atoms in the imidazolium cation<sup>51</sup>; therefore it is mainly present in the polar region of the ionic liquid structure. For the selectivity of sulfur dioxide and oxygen, the trends are not as obvious. In general, a similar trend as for hydrogen could be observed, however taking into account that relative error on the measured solubilities of the non-polar gases, it may be concluded that there is no significant improvement in the selectivity towards sulfur dioxide achieved by attaching polar functional groups to the side chain of the imidazolium cation.

### 4.1.4. Conclusions

The density, viscosity and gas solubilities of hydrogen, oxygen, and sulfur dioxide in a set of functionalized and non-functionalized imidazolium-based room temperature ionic liquids with the same bis(trifluoromethylsulfonyl)imide anion, are reported. In general, the trend of increasing solubility is  $H_2 < O_2 < SO_2$ , with the solubility values for oxygen approximately twice as high as for hydrogen. For SO<sub>2</sub>, the solubility is 2-3 orders of magnitude higher. No chemical binding of the gases was observed, confirmed by the calculation of the molar enthalpy and entropy of SO<sub>2</sub> solvation. The attachment of polar groups to the imidazolium side chain appears to have only minor effects on the solubility of sulfur dioxide, whereas the change of the molar volume  $V_m$ that occurs because of the functionalization explains the hydrogen solubility. For oxygen, a competing effect between improved solubility with increased  $V_m$  and decreased solubility with increased polarity in the side chain could be observed.

# 4.1.5. References

1. Silvester, D. S., New innovations in ionic liquid–based miniaturised amperometric gas sensors. *Curr. Opin. Electrochem.* **2019**, *15*, 7-17.

2. Wasserscheid, P.; Keim, W., Ionic Liquids-New "Solutions" for Transition Metal Catalysis. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789.

3. Rehman, A.; Zeng, X., Ionic Liquids as Green Solvents and Electrolytes for Robust Chemical Sensor Development. *Acc. Chem. Res.* **2012**, *45*, 1667-1677.

4. Sheridan, Q. R.; Schneider, W. F.; Maginn, E. J., Role of Molecular Modeling in the Development of CO<sub>2</sub>–Reactive Ionic Liquids. *Chem. Rev.* **2018**, *118*, 5242-5260.

5. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

6. Gurkan, B.; Goodrich, B. F.; Mindrup, E. M.; Ficke, L. E.; Massel, M.; Seo, S.; Senftle, T. P.; Wu, H.; Glaser, M. F.; Shah, J. K.; Maginn, E. J.; Brennecke, J. F.; Schneider, W. F., Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO<sub>2</sub> Capture. *J. Phys. Chem. Lett.* **2010**, *1*, 3494-3499.

7. Raja Shahrom, M. S.; Wilfred, C. D.; Taha, A. K. Z., CO<sub>2</sub> capture by task specific ionic liquids (TSILs) and polymerized ionic liquids (PILs and AAPILs). *J. Mol. Liq.* **2016**, *219*, 306-312.

8. Anderson, J. L.; Dixon, J. K.; Maginn, E. J.; Brennecke, J. F., Measurement of SO<sub>2</sub> Solubility in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 15059-15062.

9. Shiflett, M. B.; Yokozeki, A., Chemical Absorption of Sulfur Dioxide in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2010**, *49*, 1370-1377.

10. Yuan, X. L.; Zhang, S. J.; Lu, X. M., Hydroxyl Ammonium Ionic Liquids: Synthesis, Properties, and Solubility of SO<sub>2</sub>. *J. Chem. Eng. Data* **2007**, *52*, 596-599.

11. Jin, M.; Hou, Y.; Wu, W.; Ren, S.; Tian, S.; Xiao, L.; Lei, Z., Solubilities and Thermodynamic Properties of SO<sub>2</sub> in Ionic Liquids. *J. Phys. Chem. B* **2011**, *115*, 6585-6591.

12. Kumelan, J.; Kamps, A. P.-S.; Urukova, I.; Tuma, D.; Maurer, G., Solubility of oxygen in the ionic liquid [bmim][PF<sub>6</sub>]: Experimental and molecular simulation results. *J. Chem. Thermodynamics* **2005**, *37*, 595-602.

13. Anthony, J. L.; Maginn, E. J.; Brennecke, J. F., Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-n-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315-7320.

14. Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F., Anion Effects on Gas Solubility in Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6366-6374.

15. Anderson, J. L.; Dixon, J. K.; Brennecke, J. F., Solubility of CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1208-1216.

16. Jacquemin, J.; Husson, P.; Majer, V.; Costa Gomes, M. F., Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate. *Fluid Phase Equilib.* **2006**, *240*, 87-95.

17. Raeissi, S.; Peters, C. J., Understanding Temperature Dependency of Hydrogen Solubility in Ionic Liquids, Including Experimental Data in [bmim][Tf<sub>2</sub>N]. *J. AlChE J.* **2012**, *58*, 3553-3559.

18. Lei, Z.; Dai, C.; Chen, B., Gas Solubility in Ionic Liquids. *Chem. Rev.* **2014**, *114*, 1289-1326.

19. Almantariotis, D.; Gefflaut, T.; Pádua, A. A. H.; Coxam, J. Y.; Costa Gomes, M. F., Effect of Fluorination and Size of the Alkyl Side-Chain on the Solubility of Carbon Dioxide in 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide Ionic Liquids. *J. Phys. Chem. B* **2010**, *114*, 3608-3617.

20. Lepre, L. F.; Andre, D.; Denis-Quanquin, S.; Gautier, A.; Pádua, A. A. H.; Costa Gomes, M. F., Ionic Liquids Can Enable the Recycling of Fluorinated Greenhouse Gases. *ACS Sustainable Chem. Eng.* **2019**, *7*, 16900-16906.

21. Blesic, M.; Canongia Lopes, J. N.; Padua, A. A. H.; Shimizu, K.; Costa Gomes, M. F.; Rebelo, L. P. N., Phase Equilibria in Ionic Liquid–Aromatic Compound Mixtures, Including Benzene Fluorination Effects. *J. Phys. Chem. B* **2009**, *113*, 7631-7636.

22. Moura, L.; Santini, C. C.; Costa Gomes, M. F., Gaseous hydrocarbon separations using functionalized ionic liquids. *Oil & Gas Science and Technology* **2016**, *71*, 23.

23. Pádua, A. A. H.; Costa Gomes, M. F.; Canongia Lopes, J. N. A., Molecular Solutes in Ionic Liquids: A Structural Perspective. *Acc. Chem. Res.* **2007**, *40*, 1087-1096.

24. Li, H.; Endres, F.; Atkin, R., Effect of alkyl chain length and anion species on the interfacial nanostructure of ionic liquids at the Au(111)-ionic liquid interface as a function of potential. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14624-14633.

25. Hoth, J.; Hausen, F.; Mueser, M. H.; Bennewitz, R., Force microscopy of layering and friction in an ionic liquid. *J. Phys. Condens. Matter* **2014**, *26*, 284110.

26. Hayes, R.; Warr, G. G.; Atkin, R., Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* 2015, *115*, 6357-6426.

27. Nishi, N.; Minami, K.; Motobayashi, K.; Osawa, M.; Sakka, T., Interfacial Structure at the quaternary Ammonium-Based Ionic Liquid/Gold Electrode Interface Probed by Surface-Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior. *J. Phys. Chem. C* **2017**, *121*, 1658-1666.

28. Husson-Borg, P.; Majer, V.; Costa Gomes, M. F., Solubilities of Oxygen and Carbon Dioxide in Butyl Methyl Imidazolium Tetrafluoroborate as a Function of Temperature and at Pressures Close to Atmospheric Pressure. *J. Chem. Eng. Data* **2003**, *48*, 480-485.

29. Dymond, J. H.; Smith, E. B., *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon: Oxford, 1980.

30. Dymond, J. H.; Marsh, K. N.; Wilhoit, R. C.; Wong, K. C.; Frenkel, M. D., *Virial Coefficients of Pure Gases*, 2002; Vol. 21.

31. Holbrey, J. D.; Seddon, K. R.; Wareing, R., A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. *Green Chem.* **2001**, *3*, 33-36.

32. Dzyuba, S. V.; Bartsch, R. A., Influence of Structural Variations in1-Alkyl(aralkyl)-3-Methylimidazolium Hexafluorophosphates and Bis(trifluoromethyl-sulfonyl)imides on Physical Properties of the Ionic Liquids. *ChemPhysChem* **2002**, *3*, 161-166.

33. Oliveira, F. S.; Freire, M. G.; Carvalho, P. J.; Coutinho, J. A. P.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Marrucho, I. M., Structural and Positional Isomerism Influence in the Physical Properties of Pyridinium NTf<sub>2</sub>-Based Ionic Liquids: Pure and Water-Saturated Mixtures. *J. Chem. Eng. Data* **2010**, *55*, 4514-4520.

34. Hildebrand, J. H.; Scott, R. L., *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold Publishing Corporation: New York, USA, 1950.

35. Marcus, Y., Solubility Parameters of Permanent Gases. J. Chem. 2016, 2016, 4701919.

36. Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D., Guide to CO<sub>2</sub> Separations in Imidazolium-Based Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739-2751.

37. Camper, D.; Becker, C.; Koval, C.; Noble, R., Low Pressure Hydrocarbon Solubility in Room Temperature Ionic Liquids Containing Imidazolium Rings Interpreted Using Regular Solution Theory. *Ind. Eng. Chem. Res.* **2005**, *44*, 1928-1933.

38. Hu, Y.-F.; Liu, Z.-C.; Xu, C.-M.; Zhang, X.-M., The molecular characteristics dominating the solubility of gases in ionic liquids. *Chem. Soc. Rev.* **2011**, *40*, 3802-3823.

39. Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J., Why Is CO<sub>2</sub> So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300-5308.

40. Kazarian, S.; Briscoe, B. J.; Welton, T., Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO<sub>2</sub> dissolved in two ionic liquids at high pressures. *Chem. Commun.* **2000**, *20*, 2047-2048.

41. Castriota, M.; Caruso, T.; Agostino, R. G.; Cazzanelli, E.; Henderson, W. A.; Passerini, S., Raman Investigation of the Ionic Liquid N-Methyl-N-propylpyrrolidinium Bis(trifluoromethanesulfonyl)imide and Its Mixture with LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>. *J. Phys. Chem. A* **2005**, *109*, 92-96.

42. Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J., The imide ion: potential energy surface and geometries. *Electrochim. Acta* **1998**, *43*, 1375-1379.

43. Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Padua, A. A. H.; Sheppard, O.; Soper, A. K., Liquid Structure of the Ionic Liquid 1,3-Dimethylimidazolium Bis{(trifluoromethyl)sulfonyl}amide. *J. Phys. Chem. B* **2006**, *110*, 12055-12061.

44. Wu, W.; Han, B.; Gao, H.; Liu, Z.; Jiang, T.; Huang, J., Desulfurization of Flue
Gas: SO<sub>2</sub> Absorption by an Ionic Liquid. *Angew. Chem. Int. Ed.* 2004, *43*, 2415-2417.
45. Huang, J.; Riisager, A.; Wasserscheid, P.; Fehrmann, R., Reversible physical absorption of SO<sub>2</sub> by ionic liquids. *Chem. Commun.* 2006, *38*, 4027-4029.

46. Carvalho, P. J.; Álvarez, V. H.; Schröder, B.; Gil, A. M.; Marrucho, I. M.; Aznar, M.; Santos, L. M. N. B. F.; Coutinho, J. A. P., Specific Solvation Interactions
of CO<sub>2</sub> on Acetate and Trifluoroacetate Imidazolium Based Ionic Liquids at High Pressures. J. Phys. Chem. B 2009, 113, 6803-6812.

47. Cabaco, M. I.; Besnard, M.; Danten, Y.; Coutinho, J. A. P., Carbon Dioxide in 1-Butyl-3-methylimidazolium Acetate. I. Unusual Solubility Investigated by Raman Spectroscopy and DFT Calculations. *J. Phys. Chem. A* **2012**, *116*, 1605-1620.

48. Besnard, M.; Cabaco, M. I.; Chavez, F. V.; Pinaud, N.; Sebastiao, P. J.; Coutinho, J. A. P.; Danten, Y., On the spontaneous carboxylation of 1-butyl-3-methylimidazolium acetate by carbon dioxide. *Chem. Commun.* **2012**, *48*, 1245-1247.

49. Gurau, G.; Rodriguez, H.; Kelley, S. P.; Janiczek, P.; Kalb, R. S.; Rogers, R. D., Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angew. Chem. Int. Ed.* **2011**, *50*, 12024-12026.

50. Lepre, L. F.; Szala-Bilnik, J.; Pison, L.; Traïkia, M.; Pádua, A. A. H.; Ando, R. A.; Costa Gomes, M. F., Can the tricyanomethanide anion improve CO<sub>2</sub> absorption by acetate-based ionic liquids? *Phys. Chem. Chem. Phys.* **2017**, *19*, 12431-12440.

51. Firaha, D. S.; Kavalchuk, M.; Kirchner, B., SO<sub>2</sub> Solvation in the 1-Ethyl-3-Methylimidazolium Thiocyanate Ionic Liquid by Incorporation into the Extended Cation–Anion Network. *J. Solution Chem.* **2015**, *44*, 838-849.

#### 4.1.6. Supporting Information

#### **Synthesis of Task-specific Ionic Liquids:**

1. 1-methylnitrile-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [CCNmim][NTf<sub>2</sub>]

The compound was synthesized according to standard literature procedures.<sup>1</sup> 1methylnitrile-3-methylimidazoliumchloride was separated as a solid in good yield from a 1:1 mixture of 1-methylimidazole and chloroacetonitrile. The solution was stirred for 5 h at room temperature. The solid was recrystallized from acetonitrile/ethyl acetate.

For the anion exchange, 1-methylnitrile-3-methylimidazolium chloride was dissolved in water and an equimolar amount of  $\text{LiNTf}_2$  was added. After stirring for 2 h, the organic phase was separated and washed several times with water until the addition of AgNO<sub>3</sub> to the water phase did not from a precipitate. The liquid was dried under vacuum and characterized via NMR.



<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  8.59 (s, 1H), 7.52 (t, *J* = 1.9 Hz, 1H), 7.42 (t, *J* = 1.8 Hz, 1H), 5.20 (s, 2H), 3.85 (s, 3H). Signals at 2.14 ppm and 2.09 ppm are assigned to water and acetone respectively, which were removed during the drying step.



 $^{13}\text{C}$  NMR (101 MHz, CD\_3CN)  $\delta$  137.58, 125.22, 123.17, 122.13, 118.94, 37.80, 36.97.



<sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN) δ -80.19.

### 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>2</sub>OHmim][NTf<sub>2</sub>]

The compound was synthesized according to standard literature procedures.<sup>2</sup> 1methylimidazole and bromoethanol were mixed in acetonitrile and stirred for 2 d at 70 °C. After evaporation of the solvent, the resulting solid was recrystallized from ethyl acetate/methanol in a ratio of 2/1 (v/v).

For the anion exchange, 1-(2-hydroxyethyl)-3-methylimidazolium bromide was dissolved in water and an equimolar amount of LiNTf<sub>2</sub> was added. After stirring for 2 h, the product was extracted with dichloromethane and washed several times with water until the addition of AgNO<sub>3</sub> to the water phase did not from a precipitate. The solvent was evaporated, and the liquid was dried under vacuum and characterized via NMR.



<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  8.47 (s, 1H), 7.42 (t, J = 1.7 Hz, 1H), 7.36 (t, J = 1.7 Hz, 1H), 4.24 – 4.20 (m, 2H), 3.88 – 3.78 (m, 5H). Signal at 2.12 ppm is assigned acetone, which was removed during the drying step.



 $^{13}$ C NMR (101 MHz, CD<sub>3</sub>CN)  $\delta$  136.82, 123.99, 123.41, 60.30, 52.55, 36.47. Signals at 30.48 ppm and 207.08 ppm are assigned to acetone which was removed during the drying step.



 $^{19}\text{F}$  NMR (376 MHz, CD\_3CN)  $\delta$  -80.20.

1-methylbenzyl-3-methylimidazolium
 [CBenzmim][NTf<sub>2</sub>]

The compound was synthesized according to a slightly modified standard literature procedure.<sup>3</sup> 1-methylimidazole and 2-phenethylbromide were dissolved in toluene and stirred for 1 d at room temperature. After evaporation of the solvent, the resulting solid was washed with ethyl acetate.

For the anion exchange, 1-methylbenzyl-3-methylimidazolium bromide was dissolved in water and an equimolar amount of LiNTf<sub>2</sub> was added. After stirring for 2 h, the product was extracted with dichloromethane and washed several times with water until the addition of AgNO<sub>3</sub> to the water phase did not from a precipitate. The solvent was evaporated, and the liquid was dried under vacuum and characterized via NMR.



<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  8.24 (s, 1H), 7.36 – 7.25 (m, 5H), 7.20 – 7.15 (m, 2H), 4.37 (t, J = 7.2 Hz, 2H), 3.76 (s, 3H), 3.12 (t, J = 7.2 Hz, 2H). Signals at 2.15 ppm and 2.09 ppm are assigned to water and acetone respectively, which were removed during the drying step.



<sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN)  $\delta$  137.21, 136.39, 129.41, 129.30, 127.75, 124.20, 122.98, 122.14, 118.95, 51.22, 36.43, 36.37. Signals at 30.48 ppm and 207.08 ppm are assigned to acetone which was removed during the drying step.



 $^{19}\text{F}$  NMR (376 MHz, CD<sub>3</sub>CN)  $\delta$  -80.17.

4.2-(3-methylimidazolyl-1-yl)-ethoxy-4-oxobutanoicacidbis(trifluoromethylsulfonyl)imide [C2succmim][NTf2]

The compound was synthesized according to a slightly modified standard literature procedure.<sup>4</sup> 1-(2-hydroxyethyl)-3-methylimidazolium bromide and succinic anhydride were mixed in acetonitrile and stirred at 80 °C for 1 d. The product was washed several times with ethyl acetate and dried under vacuum.

For the anion exchange, 2-(3-methylimidazolyl-1-yl)-ethoxy-4-oxobutanoic acid bromide was dissolved in water and an equimolar amount of LiNTf<sub>2</sub> was added. After stirring for 2 h, the product was extracted with dichloromethane and washed several times with water until the addition of AgNO<sub>3</sub> to the water phase did not from a precipitate. The solvent was evaporated, and the liquid was dried under vacuum and characterized via NMR.



<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 8.69 (s, 1H), 7.46(t, 1H), 7.40 (t, 1H), 4.46 (m, 2H), 4.26 (t, 2H), 3.88 (t, 2H), 3.85 (s, 3H), 2.61 (m, 2H).



<sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O) δ 176.92, 174.29, 136.45, 136.35, 123.77, 123.61, 122.57, 122.44, 120.83, 117.65, 62.87, 59.75, 48.22, 35.67, 28.81.



 $^{19}\text{F}$  NMR (376 MHz, D2O)  $\delta$  -79.16.

		Purity	
Abbreviation	Source	(mole	Purification
		%)	
[C <sub>2</sub> mim]	IoL Too		
$[NTf_2]$	IOLITEC	99.5	purification
[C <sub>4</sub> mim]	IoL Too	No.	No further
[NTf <sub>2</sub> ]	Iolifec	99.5	purification
			Recrystallisation
[CCNmim]	C1	$> 00^{a}$	and thoroughly
bis(trifluoromethylsulfonyl)imide [NTf <sub>2</sub> ]		2 99 <sup>2</sup>	washing with
			water
			Recrystallisation
[C <sub>2</sub> OHmim]		> 003	and thoroughly
[NTf <sub>2</sub> ]	Synthesized	> 99"	washing with
			water
			Thoroughly
[CBenzmim]	<b>C</b> 1	> 003	washing with
[NTf <sub>2</sub> ]	Synthesized	> 99 <sup>a</sup>	ethyl acetate and
			water
			Thoroughly
[C2succmim] [NTf2]	Synthesized	> 99ª	washing with
			ethyl acetate and
			water
	Abbreviation [C2mim] [NTf2] [C4mim] [NTf2] [CCNmim] [NTf2] [C2OHmim] [NTf2] [CBenzmim] [NTf2] [CBenzmim] [NTf2] [C2succmim] [NTf2]	AbbreviationSource[C_2mim] [NTf2]IoLiTec[C_4mim] [NTf2]IoLiTec[CCNmim] [NTf2]Synthesized[C_2OHmim] [NTf2]Synthesized[CBenzmim] [NTf2]Synthesized[C2succmim] [NTf2]Synthesized	AbbreviationSourcePurity (mole $\%$ ) $[C_2mim]$ $[NTf_2]IoLiTec99.5[C_4mim][NTf_2]IoLiTec99.5[CCNmim][NTf_2]Synthesized>99a[C_2OHmim][NTf_2]Synthesized>99a[CBenzmim][NTf_2]Synthesized>99a[CBenzmim][NTf_2]Synthesized>99a[C_2sucemim][NTf_2]Synthesized>99a$

*Table S4.6. IUPAC name and abbreviation of ionic liquids used in this study, including supplier, purity level and purification if applicable.* 

<sup>a</sup> Estimated as no additional signals in NMR spectra and no precipitate for AgNO<sub>3</sub> test

[C <sub>2</sub> Suc	cmim][NTf <sub>2</sub> ]	[CBenzn	[CBenzmim][NTf <sub>2</sub> ]		im][NTf <sub>2</sub> ]
$T/{ m K}$ a	ho / g cm <sup>-3 b</sup>	<i>T /</i> K <sup>a</sup>	ho / g cm <sup>-3 b</sup>	<i>T /</i> K ª	ho / g cm <sup>-3 b</sup>
293.15	1.57406	293.15	1.46069	293.15	1.61341
298.15	1.56910	298.15	1.45599	298.15	1.60835
303.15	1.56416	303.15	1.45131	303.15	1.60330
308.15	1.55926	308.15	1.44667	308.15	1.59828
313.15	1.55439	313.15	1.44206	313.15	1.59335
323.15	1.54955	323.15	1.43293	323.15	1.58359
328.15	1.54476	328.15	1.42840	328.15	1.57872
333.15	1.53997	333.15	1.42388	333.15	1.57389
338.15	1.53522	338.15	1.41940	338.15	1.56908
343.16	1.53048	343.16	1.41493	343.16	1.56426
348.15	1.52575	348.15	1.41047	348.15	1.55945
353.15	1.52102	353.15	1.40602	353.15	1.55465
[C <sub>2</sub> OH	OHmim][NTf <sub>2</sub> ] [C <sub>2</sub> mim][NTf <sub>2</sub> ]		m][NTf <sub>2</sub> ]	2] [C <sub>4</sub> mim][NTf <sub>2</sub> ]	
$T/{ m K}$ a	ho / g cm <sup>-3 b</sup>	<i>T /</i> K <sup>a</sup>	ho / g cm <sup>-3 b</sup>	$T$ / K $^{a}$	ho / g cm <sup>-3 b</sup>
293.15	1.58193	293.15	1.52293	293.15	1.44112
298.15	1.57704	303.15	1.51280	303.15	1.43153
303.15	1.57207	313.15	1.50276	313.15	1.42200
308.15	1.56712	323.15	1.49279	323.15	1.41254
313.15	1.56222	333.15	1.48288	333.15	1.40316
323.15	1.55245	343.16	1.47304	343.15	1.39382
328.15	1.54761	353.15	1.46325	353.15	1.38454
333.15	1.54276				
338.15	1.53796				
343.16	1.53317				
348.15	1.52839				
353.15	1.52362				
$a \pm 0.01 \text{ K}$	$^{b} \pm 10^{-5} \text{ g cm}^{-3}$				

Table S4.7. Experimental densities ( $\rho$ ) of the studied ionic liquids as a function of temperature at atmospheric pressure.

[C <sub>2</sub> Suc	cmim][NTf <sub>2</sub> ]	[CBer	[CBenzmim][NTf <sub>2</sub> ]		nim][NTf <sub>2</sub> ]
<i>T /</i> K <sup>a</sup>	$\eta$ / mPa s <sup>b</sup>	$T/{ m K}$ a	$\eta$ / mPa s <sup>b</sup>	$T/{ m K}$ a	η / mPa s <sup>b</sup>
303.15	245.4	303.15	175.0	303.15	
308.15	182.7	308.15	129.7	308.15	169.4
313.15	138.1	313.15	98.5	313.15	126.6
323.15	81.9	323.15	58.5	323.15	73.3
328.15	65.8	328.15	47.2	328.15	58.6
333.15	54.0	333.15	38.7	333.15	47.7
338.15	44.8	338.15	32.2	338.15	39.5
343.16	37.6	343.16	27.1	343.16	33.2
348.15	32.0	348.15	23.1	348.15	28.2
353.15	27.5	353.15	19.9	353.15	24.2
[C <sub>2</sub> OH	[mim][NTf <sub>2</sub> ]	[C <sub>2</sub> ]	nim][NTf <sub>2</sub> ]	[C <sub>4</sub> m	im][NTf <sub>2</sub> ]
<i>T /</i> K <sup>a</sup>	η / mPa s <sup>b</sup>	$T /{ m K}$ a	η / mPa s <sup>ь</sup>	$T /{ m K}$ a	$\eta$ / mPa s <sup>b</sup>
293.15	127.3	293.15	39.1	293.15	68.8
298.15	95.8	303.15	27.4	303.15	41.1
303.15	74.1	313.15	20.2	313.15	28.5
308.15	58.6	323.15	15.0	323.15	20.0
313.15	47.3	333.15	11.9	333.15	15.1
323.15	31.1	343.16	9.5	343.15	11.8
328.15	26.2			353.15	9.4
333.15	22.4				
338.15	19.4				
343.16	16.9				
348.15	14.9				
353.15	13.2				
$a \pm 0.005 \text{ K}$	$^{b} \pm 0.5\%$				

Table S4.8. Experimental viscosities  $(\eta)$  of the studied ionic liquids as a function of temperature at atmospheric pressure.



Figure S4.4. Variation from the literature values of the density (left) and viscosity (right) of  $[C_{2mim}][NTf_2]$ . Fröba et al.<sup>5</sup>, Tariq et al.<sup>6</sup>, Seki et al.<sup>7</sup>, Watanabe et al.<sup>8</sup>, Seoane et al.<sup>9</sup>, Hofmann et al.<sup>10</sup> and Yadav et al.<sup>11</sup>.



Figure S4.5. Variation from the literature values of the density (left) and viscosity (right) of  $[C_4mim][NTf_2]$ . Kassim et al.<sup>12</sup>, Vranes et al.<sup>13</sup>, de Azevedo et al.<sup>14</sup>, Nieto de Castro et al.<sup>15</sup>, Tomida et al.<sup>16</sup>, Harris et al.<sup>17</sup> and Atilhan et al.<sup>18</sup>.



*Figure S4.6. Variation from the literature values of the density (left) and viscosity (right) of* [*CCNmim*][*NTf*<sub>2</sub>]. *Liu et al.*<sup>19</sup>.



Figure S4.7. Variation from the literature values of the density (left) and viscosity (right) of  $[C_2OHmim][NTf_2]$ . Liu et al.<sup>19</sup>, Sakhaeinia et al.<sup>20</sup>, Jin et al.<sup>21</sup>.

<i>T</i> / K <sup>a</sup>	<i>p</i> / 10 <sup>2</sup> Pa <sup>b</sup>	$x_2 / 10^{-4}$	<i>K</i> <sub>H</sub> / 10 <sup>5</sup>	$x_2 / 10^{-4}$	<i>c</i> / mM	u / %
	1	-	Pa	(1 bar)		
[C <sub>2</sub> mim][NTf <sub>2</sub> ]						
304.43	723.58	8.81	822	12.17	4.71	20.7
313.38	744.42	7.32	1018	9.83	3.78	22.6
323.33	767.61	4.43	1734	5.77	2.20	34.6
333.27	790.76	0.82	9697	1.03	0.39	193.5
[C <sub>4</sub> mim][NTf <sub>2</sub> ]						
304.43	653.05	5.39	1212	8.25	3.32	28.0
313.38	671.77	5.10	1318	7.59	3.04	26.9
323.32	692.58	3.83	1809	5.53	2.20	33.3
333.27	713.36	1.94	3677	2.72	1.08	67.6
[C2OHmim][NTf2]						
304.42	679.64	5.67	1200	8.33	3.22	17.2
313.35	698.91	5.07	1378	7.27	2.79	15.1
323.27	720.40	3.87	1864	5.37	2.05	18.3
333.18	741.82	2.65	2801	3.57	1.35	30.1
[CBenzmim][NTf <sub>2</sub> ]						
304.43	662.85	10.25	647	15.46	4.81	17.2
313.38	681.93	9.04	755	13.25	4.10	17.7
323.33	703.15	6.54	1076	9.30	2.85	22.7
333.27	724.41	2.67	2712	3.69	1.12	57.3
[CCNmim] [NTf <sub>2</sub> ]						
304.43	646.22	3.48	1855	5.39	2.15	52.7
313.38	664.73	3.15	2112	4.73	1.88	53.0
323.32	685.29	1.78	3861	2.59	1.02	87.3
333.26	705.86					
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]						
304.43	692.68	13.26	523	19.13	5.91	43.1
313.38	712.46	13.70	520	19.23	5.90	34.2
323.32	734.48	10.47	702	14.24	4.34	37.8
333.27	756.52	4.39	1723	5.80	1.76	86.0
indicates va	lues below the	detection lin	nit <sup>a</sup> ±0	.003 K	$^{b} \pm 2$ Pa	

Table S4.9. Experimental results for the solubility of  $H_2$  in the studied ionic liquids at different temperature, T, expressed as mole fraction,  $x_2$ , both at experimental equilibrium pressure, p, as well as corrected for 1 bar, Henry's law constant,  $K_H$ , molarity, c, in mM and the uncertainty, u, in %.

<i>T</i> / K <sup>a</sup>	<i>p</i> / 10 <sup>2</sup> Pa <sup>b</sup>	$x_2 / 10^{-4}$	<i>K</i> <sub>H</sub> / 10 <sup>5</sup> Ра	x <sub>2</sub> / 10 <sup>-4</sup> (1 bar)	<i>c</i> / mM	u / %
[C <sub>2</sub> mim][NTf <sub>2</sub> ]						
304.44	706.03	11.76	600	16.67	6.45	15.2
313.39	726.34	10.86	669	14.95	5.75	14.9
323.33	748.90	9.03	829	12.06	4.61	16.7
333.27	771.48	5.90	1308	7.65	2.90	24.2
[C <sub>4</sub> mim][NTf <sub>2</sub> ]						,
304.44	690.77	14.45	478	20.93	8.44	10.9
313.38	710.63	13.86	513	19.51	7.83	10.4
323.33	732.76	11.84	619	16.16	6.45	11.2
333.27	754.91	8.66	872	11.47	4.55	15.8
[C2OHmim][NTf2]						
303.44	640.33	8.53	751	13.32	5.15	14.7
313.38	660.78	8.59	769	13.00	4.99	13.1
323.32	681.23	7.90	862	11.60	4.42	13.3
333.26	701.69	6.48	1083	9.24	3.50	16.6
[CBenzmim][NTf <sub>2</sub> ]						
303.44	639.03	9.80	652	15.34	4.77	13.4
313.38	659.47	9.70	680	14.71	4.55	13.0
323.32	679.83	9.47	717	13.94	4.28	12.5
333.27	700.21	8.38	836	11.97	3.65	14.5
[CCNmim][NTf <sub>2</sub> ]						
303.44	637.91	5.82	1095	9.13	3.64	32.1
313.38	658.24	6.09	1081	9.25	3.67	28.8
323.32	678.61	4.95	1371	7.30	2.87	31.6
333.26	699.01	2.35	2968	3.37	1.32	68.3
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]						
304.43	654.60	13.21	495	20.19	6.23	29.2
304.44	644.14	13.50	477	20.96	6.47	28.2
313.39	673.19	17.43	386	25.89	7.95	23.9
313.39	662.49	15.82	419	23.88	7.33	26.0
323.34	694.01	14.84	467	21.39	6.53	23.4
333.28	714.85	9.34	765	13.07	3.96	38.3

Table S4.10. Experimental results for the solubility of  $O_2$  in the studied ionic liquids at different temperature, *T*, expressed as mole fraction,  $x_2$ , both at experimental equilibrium pressure, *p*, as well as corrected for 1 bar, Henry's law constant, *K*<sub>H</sub>, molarity, *c*, in mM and the uncertainty, *u*, in %.

 $^{a}\pm0.003~K \qquad ^{b}\pm2~Pa$ 

<b>T</b> / <b>L</b> / a	n / 10 <sup>2</sup> Do b	x. / 10-4	<i>K</i> <sub>H</sub> / 10 <sup>5</sup>	$x_2 / 10^{-4}$	a / M	u / %
<i>I</i> / <b>N</b> <sup></sup>	<i>p</i> / 10 <sup>-</sup> ra *	$x_2 / 10^{-2}$	Pa	(1 bar)	c / mivi	
[C <sub>2</sub> mim][NTf <sub>2</sub> ]						
304.42	411.21	1880.8	2.17	4603.6	3295.5	0.1
313.35	454.05	1681.5	2.68	3727.2	2281.9	0.1
323.26	500.17	1471.4	3.38	2960.5	1604.5	0.1
333.18	544.24	1277.4	4.23	2361.6	1171.8	0.1
[C <sub>4</sub> mim][NTf <sub>2</sub> ]						
304.42	456.80	1673.2	2.71	3689.5	1994.0	0.1
313.34	505.62	1514.3	3.32	3016.5	1464.6	0.1
323.27	560.29	1339.1	4.15	2407.0	1067.8	0.1
333.19	612.62	1177.9	5.17	1936.1	803.4	0.1
[C2OHmim][NTf2]						
304.42	501.41	1914.5	2.60	3848.6	2412.8	0.1
313.35	552.60	1687.2	3.25	3077.3	1704.9	0.1
323.26	606.56	1453.7	4.14	2415.1	1213.7	0.1
333.19	656.83	1245.8	5.23	1910.9	894.8	0.1
[CBenzmim][NTf <sub>2</sub> ]						
304.41	549.09	2442.5	2.23	4487.0	2526.9	0.1
313.35	601.39	2162.3	2.76	3626.3	1756.5	0.1
323.27	655.94	1875.0	3.47	2882.3	1242.4	0.1
333.19	706.63	1617.7	4.33	2307.7	914.6	0.1
[CCNmim][NTf <sub>2</sub> ]						
304.42	611.84	2196.1	2.76	3624.2	2263.6	0.2
313.35	655.27	1891.4	3.43	2913.4	1628.2	0.2
323.27	700.02	1590.2	4.36	2291.8	1170.4	0.2
333.19	740.66	1339.2	5.48	1823.4	872.4	0.2
[C <sub>2</sub> Succmim][NTf <sub>2</sub> ]						
304.41	635.81	3181.2	1.99	5016.8	3101.2	0.2
313.34	673.77	2774.9	2.42	4129.4	2154.8	0.2
323.27	712.78	2366.8	3.00	3329.1	1519.4	0.2
333.19	748.29	2023.8	3.69	2711.3	1125.5	0.3
$a \pm 0.003 \text{ K}$ b $\pm$	= 2 Pa					

Table S4.11. Experimental results for the solubility of SO<sub>2</sub> in the studied ionic liquids at different temperature, T, expressed as mole fraction,  $x_2$ , both at experimental equilibrium pressure, p, as well as corrected for 1 bar, Henry's law constant,  $K_{H,}$ , molarity, c, in mM and the uncertainty, u, in %.

## References

1. Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J., Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality. *Inorg. Chem.* **2004**, *43*, 2197-2205.

2. Tsurumaki, A.; Ohno, H., Dissolution of oligo(tetrafluoroethylene) and preparation of poly(tetrafluoroethylene)-based composites by using fluorinated ionic liquids. *Chem. Commun.* **2018**, *54*, 409-412.

3. Cvjetko, M.; Vorkapic-Furac, J.; Znidarsic-Plazl, P., Isoamyl acetate synthesis in imidazolium-based ionic liquids using packed bed enzyme microreactor. *Process Biochem.* **2012**, *47*, 1344-1350.

4. de Souza Ramos, T. J.; Berton, G. H.; Cassol, T. M.; Alves Junior, S., Carboxyl-functionalized ionic liquids: synthesis, characterization and synergy with rare-earth ions. *J. Mater. Chem. C* **2018**, *6*, 6270-6279.

5. Froeba, A. P.; Kremer, H.; Leipertz, A., Density, Refractive Index, Interfacial Tension, and Viscosity of Ionic Liquids [EMIM][EtSO<sub>4</sub>], [EMIM][NTf<sub>2</sub>], [EMIM][N(CN)<sub>2</sub>], and [OMA][NTf<sub>2</sub>] in Dependence on Temperature at Atmospheric Pressure. *J. Phys. Chem. B* **2008**, *112*, 12420-12430.

6. Tariq, M.; Serro, A. P.; Mata, J. L.; Saramago, B.; Esperanca, J. M. S. S.; Canongia Lopes, J. N.; Rebelo, L. P. N., High-temperature surface tension and density measurements of 1-alkyl-3-methylimidazolium bistriflamide ionic liquids. *Fluid Phase Equilib.* **2010**, *294*, 131-138.

7. Seki, S.; Tsuzuki, S.; Hayamizu, K.; Umebayashi, Y.; Serizawa, N.; Takei, K.; Miyashiro, H., Comprehensive Refractive Index Property for Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2211-2216.

8. Watanabe, M.; Kodama, D.; Makino, T.; Kanakubo, M., CO<sub>2</sub> absorption properties of imidazolium based ionic liquids using a magnetic suspension balance. *Fluid Phase Equilib.* **2016**, *420*, 44-49.

9. Seoane, R. G.; Corderi, S.; Gomez, E.; Calvar, N.; Gonzalez, E. j.; Macedo, E. A.; Dominguez, A., Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 2492-2504.

10. Hofmann, A.; Migeot, M.; Hanemann, T., Investigation of Binary Mixtures Containing 1-Ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)azanide and Ethylene Carbonate. *J. Chem. Eng. Data* **2016**, *61*, 114-123.

11. Yadav, A.; Guha, A.; Pandey, A.; Pal, M.; Trivedi, S.; Pandey, S., Densities and dynamic viscosities of ionic liquids having 1-butyl-3-methylimidazolium cation with different anions and bis(trifluoromethylsulfonyl)imide anion with different cations in the temperature range (283.15 to 363.15) K. *J. Chem. Thermodynamics* **2018**, *116*, 67-75.

12. Kassim, M. A.; Sairi, N. A.; Yusoff, R.; Ramalingam, A.; Alias, Y.; Aroua, M. K., Experimental densities and viscosities of binary mixture of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or glycerol with sulfolane and their molecular interaction by COSMO-RS. *Thermochim. Acta* **2016**, *639*, 130-147.

13. Vranes, M.; Dozic, S.; Djeric, V.; Gadzuric, S., Physicochemical Characterization of 1-Butyl-3-methylimidazolium and 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2012**, *57*, 1072-1077.

14. de Azevedo, R. G.; Esperanca, J. M. S. S.; Najdanovic-Visak, V.; Visak, Z. P.; Guedes, H. J. R.; Nunes da Ponte, M.; Rebelo, L. P. N., Thermophysical and Thermodynamic Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate over an Extended Pressure Range. *J. Chem. Eng. Data* **2005**, *50*, 997-1008.

15. Nieto de Castro, C. A.; Langa, E.; Morais, A. L.; Matos Lopes, M. L.; Lourenco, M. J. V.; Santos, F. J. V.; Santos, M. S. C. S.; Canongia Lopes, J. N.; Veiga, H. I. M.; Macatrao, M.; Esperanca, J. M. S. S.; Marques, C. S.; Rebelo, L. P. N.; Afonso, C. A. M., Studies on the density, heat capacity, surface tension and infinite dilution diffusion with the ionic liquids [C<sub>4</sub>mim][NTf<sub>2</sub>], [C<sub>4</sub>mim][dca], [C<sub>2</sub>mim][EtOSO<sub>3</sub>] and [Aliquat][dca]. *Fluid Phase Equilib.* **2010**, *294*, 157-179.

16. Tomida, D.; Kanno, S.; Qiao, K.; Yokoyama, C., Viscosities at pressures up to 20 MPa and thermal conductivities at 0.1 MPa of 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amides. *High Temp.-High Press.* **2016**, *46*, 231-245.

17. Harris, K. R.; Kanakubo, M.; Woolf, L. A., Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2007**, *52*, 1080-1085.

18. Atilhan, M.; Jacquemin, J.; Rooney, D.; Khraisheh, M.; Aparicio, S., Viscous Behavior of Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.* **2013**, *52*, 16774-16785.

19. Liu, Q.-S.; Liu, J.; Liu, X.-X.; Zhang, S.-T., Density, dynamic viscosity, and electrical conductivity of two hydrophobic functionalized ionic liquids. *J. Chem. Thermodynamics* **2015**, *90*, 39-45.

20. Sakhaeinia, H.; Jalili, A. H.; Taghikhani, V.; Safekordi, A. A., Solubility of H<sub>2</sub>S in Ionic Liquids 1-Ethyl-3-methylimidazolium Hexafluorophosphate ([emim][PF<sub>6</sub>]) and 1-Ethyl-3-methylimidazolium Bis(trifluoromethyl)sulfonylimide ([emim][Tf<sub>2</sub>N]). *J. Chem. Eng. Data* **2010**, *55*, 5839-5845.

21. Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M., Physical Properties of Ionic Liquids Consisting of the 1-Butyl-3-Methylimidazolium Cation with Various Anions and the Bis(trifluoromethylsulfonyl)imide Anion with Various Cations. *J. Phys. Chem. B* 2008, *112*, 81-92.

## 4.2. Detection of Sulfur Dioxide at Low Parts-permillion Concentrations using Low-cost Planar Electrodes with Ionic Liquid Electrolytes

This chapter has been published in the following peer-reviewed journal:

Doblinger, S., Lee. J., Gurnah, Z., Silvester, D. S., Detection of sulfur dioxide at low parts-per-million concentrations using low-cost planar electrodes with ionic liquid electrolytes. *Anal. Chim. Acta* **2020**, *1124*, 156-165.

The abstract has been removed in this chapter and the supporting information has been included after the references. Figure and table captions as well as equation numbers have been changed. A few changes to the formatting have been made.

#### **Author Contributions:**

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 70%/100%

Acquisition of Data and Method: 70%/100%

Data Conditioning and Manipulation: 75%/100%

Analysis and Statistical Method: 80%/100%

Interpretation and Discussion: 70%/100%

Final Approval: 60%/100%

Signature:

Simon Doblinger

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 20%/100%

Acquisition of Data and Method: 15%/100%

**Data Conditioning and Manipulation:** 20%/100%

Analysis and Statistical Method: 15%/100% Interpretation and Discussion: 25%/100% Final Approval: 20%/100%

Signature: \_\_\_\_\_

Junqiao Lee

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design: 0%/100%** 

Acquisition of Data and Method: 15%/100%

**Data Conditioning and Manipulation: 5%/100%** 

Analysis and Statistical Method: 5%/100%

**Interpretation and Discussion:** 5%/100%

Final Approval: 0%/100%

Signature: \_\_\_\_\_

Zoe Gurnah

I, as co-author, endorse that the contributions indicated below are appropriate.

**Conception and Design:** 10%/100%

Acquisition of Data and Method: 0%/100%

Data Conditioning and Manipulation: 0%/100%

Analysis and Statistical Method: 0%/100%

**Interpretation and Discussion:** 0%/100%

Final Approval: 20%/100%

Signature: \_\_\_\_\_

Debbie S. Silvester

#### 4.2.1. Introduction

The reliable monitoring of air quality is a major focus of gas sensing research, especially due to the fact that some gases, even at low parts-per-million (ppm) concentrations, can cause harmful effects on nature and humans.<sup>1-2</sup> One of the background environmental gases is sulfur dioxide (SO<sub>2</sub>), an invisible gas with a sharp smell that, in the presence of moisture, can cause acidic rain and damage to building materials such as limestone. SO<sub>2</sub> is a typical by-product in petroleum refineries or fossil fuel burning power plants. It is known that SO<sub>2</sub> is a severe threat towards air quality and health<sup>2</sup>, therefore the release of the gas needs to be strictly regulated. It causes respiratory problems upon inhalation and at higher concentrations it can be deadly.<sup>3</sup> The National Institute for Occupational Safety and Health (NIOSH) defined a concentration of 100 ppm as dangerous to life, and stated that the recommended permissible exposure limit (PEL) is 2 ppm averaged over a 10-hour work shift of 5 days per week, and a maximum of 5 ppm during any 15-minute work period. The effects on health are felt quickly – usually within 15 minutes – so a fast responding sensor for low ppm concentrations is essential.

Generally, gas sensors based on optical<sup>4</sup>, gas chromatographic<sup>5</sup> or electrochemical<sup>6</sup> techniques have been studied extensively. Electrochemical techniques give access to low energy consuming devices with good sensitivity and selectivity in combination with good repeatability and low concentration detection.<sup>7</sup> Much research has been focused on electrochemical SO<sub>2</sub> sensors for industrial usage.<sup>8-9</sup> The electroanalysis of sulfites (including SO<sub>2</sub>) using low-cost devices has recently been the focus of various research papers.<sup>10-13</sup> One type of electrochemical sensor is an amperometric gas sensor, containing three electrodes in contact with a liquid electrolyte; there are several amperometric sensors available commercially for SO<sub>2</sub> detection.<sup>14</sup> However, the drawback of these sensors, which are typically based on aqueous electrolytes, is their short lifetime in extreme conditions such as high temperatures, causing evaporation of the solvent. Therefore, research has been focused towards replacing conventional solvents with room temperature ionic liquids (RTILs) in amperometric gas sensor devices.<sup>15</sup> RTILs are a class of non-volatile, chemically and thermally stable electrolytes with high conductivity and wide electrochemical windows.<sup>15-18</sup> They typically consist of bulky cations and anions that result in melting points well below 100 °C and most commonly below room temperature and are highly tunable.<sup>19-20</sup> A

variety of gases, including  $O_2^{21-22}$  and toxic gases such as  $NO_2^{23}$  or  $H_2S^{24}$ , have already been studied in RTILs. Hussain *et al.* for example showed that sub-parts-permillion (sub-ppm) concentration detection of ammonia gas in room temperature ionic liquids is possible with low-cost thin-film electrodes (TFEs) or microarray thin-film electrodes (MATFEs).<sup>25</sup>

The electrochemical reduction mechanism of sulfur dioxide at saturated concentrations has been studied in different ionic liquids on a platinum micro-disk electrode (10  $\mu$ m diameter) by Barrosse-Antle *et al.*<sup>26</sup>, and is believed to proceed by the following reactions:

$$SO_2 + e^- \rightarrow SO_2^{\bullet-}$$
 4.9

$$SO_2^{\bullet-} \leftarrow SO_2 + e^-$$
 4.10

$$SO_2^{\bullet^-} \cdots \text{ solvent} \rightleftharpoons SO_2 + e^-$$
 4.11

$$2 \operatorname{SO}_2^{\bullet-} \rightleftharpoons \operatorname{S}_2 \operatorname{O}_4^{2^-}$$
 4.12

 $S_2 O_4^{2^-} \rightleftharpoons 2 SO_2 + 2 e^-$  4.13

$$S_2 O_4^{2^-} \cdots \text{ solvent } \rightleftharpoons 2 SO_2 + 2 e^-$$
 4.14

It was suggested (also by other groups)<sup>27-29</sup> that the mechanism follows a one-electron reduction of SO<sub>2</sub> to the SO<sub>2</sub><sup> $\bullet$ </sup> radical anion (equation 4.9). There are two to four oxidative back peaks consistently reported, but their assignment is however still inconsistent in literature. Therefore, Barrosse-Antle et al. performed a more detailed mechanistic study where it was proposed that the two main oxidation peaks are caused by the oxidation of non-solvated (equation 4.10) and solvated  $SO_2^{\bullet}$  (equation 4.11), and the other two were from dimers formed after dimerization of the radicals (equation 4.12), *i.e.* the non-solvated and solvated dimerized dithionite,  $S_2O_4^{2-}$  (equation 4.13) and 4.14).<sup>26</sup> Choi et al. investigated the stabilizing effect of the acidic proton of the imidazolium ring which could cause the separation of the oxidative back peaks into solvated and non-solvated processes.<sup>30</sup> Huang et al. also established a calibration curve between 2 and 100% of SO<sub>2</sub> in [C<sub>4</sub>mim][PF<sub>6</sub>] that resulted in a curved relationship due to a significant increase in the diffusion coefficient with increasing sulfur dioxide concentration.<sup>31</sup> The increased diffusion coefficients could be due to the fact that SO<sub>2</sub> solubilities are extremely high and the gas acts as a lubricant in conventional ionic liquids, as concluded by Ren et al.32

In this study, we investigate the electrochemical SO<sub>2</sub> response on thin-film electrodes for the first time. Six diverse RTILs and different thin-film electrodes will demonstrate that the ionic liquid structure as well as the choice of the electrode surface has a great influence on the electrochemical sensing behavior. We also show the sustained detection of sulfur dioxide at the permissible exposure limit (PEL) of 2 ppm by employing these miniaturized, low-cost and commercially available electrode devices using very small RTIL volumes. Based on our results, the next step towards commercial SO<sub>2</sub> sensors based on room temperature ionic liquid electrolytes for detection of low ppm concentrations in real world environments may be realized.

#### 4.2.2. Experimental

#### 4.2.2.1. Chemical Reagents

All RTILs were purchased at the highest purity possible. Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide ([S<sub>2,2,1</sub>][NTf<sub>2</sub>], 99%, IoLiTec-Ionic Liquids GmbH, Technologies Heilbronn, Germany), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C4mpyrr][NTf2], 99.5%, IoLiTec), 1-ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>], 99.5%. IoLiTec), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec), 1-butyl-3-methylimidazolium tetrafluoroborate 99%. ([C<sub>4</sub>mim][BF<sub>4</sub>], IoLiTec), 1-butyl-3-methylimidazolium and tris(pentafluoroethyl)trifluorophosphate ([C<sub>4</sub>mim][FAP], high purity >99%, Merck Pty. Ltd. Kilsyth, Victoria, Australia), were used as received. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P<sub>14,6,6,6</sub>][NTf<sub>2</sub>]) was kindly donated by the group of Professor Chris Hardacre, now at the University of Manchester, UK. The chemical structures of the ionic liquid cations and anions used in this study are shown in Figure 4.8. Acetone (CHROMASOLV®, for HPLC, ≥99.0%, Sigma-Aldrich) and acetonitrile (anhydrous, 99.8%, Sigma-Aldrich, Missouri, United States) were used as received. A 0.5 M stock solution of H<sub>2</sub>SO<sub>4</sub>(aq) (prepared with ultrapure water from a 95-98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for activation of the thin-film electrodes. Sulfur dioxide (509 ppm in nitrogen) and high purity nitrogen gas (>99.999%) were purchased from Coregas (NSW, Australia).



Figure 4.8. Room temperature ionic liquid cation and anion structures used for this study.

#### 4.2.2.2. Electrochemical Experiments

All experiments were performed with a PGSTAT101 Autolab potentiostat (Metrohm Autolab, Gladesville, NSW, Australia) interfaced to a computer with NOVA 1.11 software. The electrochemical cell was housed inside an aluminum Faraday cage to reduce electromagnetic interferences. The working electrode (WE), counter electrode (CE) and reference electrode (RE) of the macro thin-film electrodes (TFEs) (ED-SE1, MicruX Technologies, Oviedo, Spain) are composed of either platinum (Pt) or gold (Au) deposited on a Pyrex substrate, with a WE disk diameter of 1 mm. Furthermore, platinum microarray thin-film electrodes (MATFEs) (ED-mSE-10-Pt, MicruX Technologies, Oviedo, Spain) were also employed as sensing devices. For MATFEs, the 1 mm diameter Pt disk is covered with a layer of SU-8 resin, into which 91 microholes (µ-holes) of 10 µm diameter were made to create 91 recessed micro-disk electrodes. The center-to-center distance between each  $\mu$ -hole is  $100 \pm 1 \mu m$  and the SU-8 layer has a depth of  $3.5 \pm 1.0 \ \mu\text{m}$ , according to the manufacturer. Photos and images of the electrode devices are given in the supporting information in Figure S4.13a. An electrode adapter supplied by MicruX was employed to connect the electrodes to the potentiostat. The Pt-WE was electrochemically activated prior to each experiment by cyclic voltammetry (CV) cycling (~ 100 times) at 1 V s<sup>-1</sup> in nitrogen purged 0.5 M H<sub>2</sub>SO<sub>4</sub> (aq) between -0.75 V and +0.70 V. For the Au-WE, CV cycles between -1.2 V and 1.1 V were performed. The activated electrodes were then rinsed twice with ultrapure water and acetone before drying under a nitrogen stream. 0.5 µL of the ionic liquid was drop-cast to cover all three electrodes on the TFE or MATFE (see Figure S4.13b). The low volume of electrolyte on the small chip ensures relatively fast response times, whilst also keeping the cost of the sensor as low as possible, noting that RTILs themselves are relatively expensive if used in large quantities. For all measurements, the integrated CE and RE, i.e. Pt or Au, were used. The prepared electrode was then inserted into the glass T-cell supported by a silicon-bung, which is then purged with nitrogen for approximately 30 min to remove dissolved gases and impurities (such as oxygen and carbon dioxide) and monitored electrochemically until a constant blank CV was obtained, before commencing with the SO<sub>2</sub> experiments. To obtain different concentrations of SO<sub>2</sub>, the 509 ppm sulfur dioxide cylinder (nitrogen fill) was diluted with nitrogen using a gas mixing system, by adjusting relative flow rates, according to our previous work.<sup>33</sup> A sketch of the gas sensing set-up is shown in Figure S4.13c. For the sensing experiments at 1-10 ppm, the overall flow rate is increased to 1000 mL min<sup>-1</sup> to obtain the lowest concentrations in this study.

For long-term chronoamperometry (LTCA) experiments, the initial potential was held at 0 V for 5 s for stabilization, before stepping to a potential where diffusion-controlled SO<sub>2</sub> reduction occurs. The system is initially placed under nitrogen to record a stable blank transient, before the analyte gas is subsequently introduced at defined concentrations, *i.e.* either 2 ppm or different SO<sub>2</sub> concentrations from 1–10 ppm.

#### 4.2.2.3. Electrode Imaging

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Clara-FESEM, Tescan, Kohoutovic, Czech Republic) was used to analyze the working electrodes of Pt-TFEs and Pt-MATFEs after the SO<sub>2</sub> reduction experiments have been carried out, as well as on the control samples, which were prepared by subjecting to the same electrochemical parameters, but in the absence of SO<sub>2</sub> gas. The SEM/EDS measurements were all carried out using an accelerating voltage of 10 keV at a working distance of 15 mm.

The SEM/EDS samples were consistently prepared by either performing cyclic voltammetry calibration of SO<sub>2</sub> gas from 10 to 200 ppm on MATFEs or first performing two CV scans on freshly activated Pt-TFEs to verify the position of the SO<sub>2</sub> peak, before holding the potential at the SO<sub>2</sub> reduction overpotential for five minutes. The prepared electrodes were then gently soaked for 3 mins, consecutively in 3 separate vials containing clean acetonitrile, before drying under a gentle stream of dry air. The samples were then coated with ~3 nm of platinum via vapor deposition to prevent surface charging during imaging.

#### 4.2.3. Results and Discussion

#### 4.2.3.1. Reduction of SO<sub>2</sub> on Macro Thin-film Electrodes

In order to detect SO<sub>2</sub> gas favorably at low parts-per-million (ppm) concentrations, it is important to select the optimum ionic liquid structure and electrode device that gives stable and reproducible responses. Six common RTILs with different cations and anions were used to screen their suitability for detecting low ppm concentrations of the analyte. Plots of reduction peak current *vs*. the square root of scan rate were linear in all RTILs, suggesting that the process is diffusion controlled (plots not shown). Figure 4.9 shows typical cyclic voltammetry (CV) responses for the reduction of sulfur dioxide at a scan rate of 100 mV s<sup>-1</sup> in the six ionic liquids on a platinum macro thinfilm electrode (Pt-TFE). The measured currents were converted into current densities (*J*) using the geometrical surface area of the working disk (diameter of 1 mm) to easily compare with the response on microarrays (see section 4.2.3.2). Background subtracted calibration curves (shown as insets in Figure 4.9) were extracted from cyclic voltammetry measurements at concentrations of 10, 25, 50, 100, 150 and 200 ppm. Dashed lines represent the response in the absence of SO<sub>2</sub>.

As reported by other researchers on conventional disk electrodes, a single SO<sub>2</sub> reduction peak according to eq. 4.9 is observed in RTILs.<sup>27-29, 34-35</sup> However, the number and position of the reverse oxidation peaks are strongly dependent on the scan rate as well as the solvation of the reduced species, as reported by Barrosse-Antle *et al.*<sup>26</sup> In their study, electrochemical SO<sub>2</sub> reduction was examined in several saturated imidazolium-based ionic liquids (100% SO<sub>2</sub>), where it was revealed that four oxidative peaks can be observed in [C<sub>4</sub>mim][NO<sub>3</sub>] at a fast scan rate of 4 V s<sup>-1</sup>. A comparison between experimental and simulated cyclic voltammograms resulted in the assignment

of the first reverse peak to the oxidation of non-solvated  $SO_2^{\bullet}$  (eq. 4.10) followed by the oxidation of the solvated species (eq. 4.11). The acidic proton on the imidazolium cation was used as possible explanation for the solvation. Additional back-peaks belong to the oxidation of the dimer.



Figure 4.9. Cyclic voltammetry at a scan rate of  $100 \text{ mV s}^{-1}$  for electrochemical sulfur dioxide reduction at concentrations from 10 to 200 ppm in (a) [C<sub>2</sub>mim][NTf<sub>2</sub>], (b) [S<sub>2,2,1</sub>][NTf<sub>2</sub>], (c) [C<sub>4</sub>mim][NTf<sub>2</sub>], (d) [C<sub>4</sub>mpyrr][NTf<sub>2</sub>], (e) [C<sub>4</sub>mim][BF<sub>4</sub>] and (f) [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>] on a Pt-TFE (diameter 1 mm) with background subtracted calibration curves shown in the insets. The dashed line represents the response in the absence of SO<sub>2</sub>.

In the present work, much lower concentrations (parts-per-million) of sulfur dioxide are studied on macro thin-film electrodes, and several different RTIL cations are employed. As shown in Figure 4.9, one reduction wave was obtained in all RTILs, consistent with that by Barrosse-Antle *et al.*<sup>26</sup> In contrast to the previous study in saturated SO<sub>2</sub> electrolytes, no third or fourth oxidation peak was observed suggesting that the dimerized products are not present. This is not unexpected due to the much

lower concentrations studied in our work, leading to a lower rate of dimerization. In the imidazolium-based ionic liquids, the presence of two oxidation back-peaks can be seen. Whereas in the sulfonium-, pyrrolidinium- and phosphonium-based ones, either one or zero anodic waves are observed. This suggests that the cation has a very large effect on the voltammetric wave shapes, which is expected because the cation provides solvation of the negatively charged SO<sub>2</sub> radical ion. Out of the non-imidazolium-based cations, the peak-to-peak separation is largest in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] (Figure 4.9d) compared to [S<sub>2,2,1</sub>][NTf<sub>2</sub>] (Figure 4.9b), with no obvious oxidative peak in [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>] (Figure 4.9f). It is assumed that these single-centered cations are not able to solvate the radical anion effectively due to the absence of acidic protons and shielding of the cation by the hydrophobic alkyl chains.

It can also be seen in Figure 4.9 that a shift in the reduction potential occurs as the concentration is changed, especially in [C<sub>2</sub>mim][NTf<sub>2</sub>], which is the ionic liquid with the lowest viscosity (Table 4.12). For this study, the inbuilt reference electrode (RE) was used, however it has previously been demonstrated by Wandt *et al.* that the introduction of gas can cause a severe RE potential shift.<sup>36</sup> The reference potential can also be affected by the migration of electrogenerated species towards the platinum reference electrode, especially in a less viscous solvent. Out of the six different RTILs studied, the shift in SO<sub>2</sub> reduction potential was only significant in [C<sub>2</sub>mim][NTf<sub>2</sub>] (which has the lowest viscosity out of the different RITLs used).<sup>37</sup> Therefore, it is concluded [C<sub>2</sub>mim][NTf<sub>2</sub>] is not an ideal electrolyte for SO<sub>2</sub> detection on these electrode devices. In terms of the analytical response, almost all ionic liquids show an excellent linear relationship ( $R^2 \approx 0.999$ ) between current density and concentration. In contrast, Huang *et al.*<sup>31</sup> reported a curved like behavior, most likely caused by the high SO<sub>2</sub> solubility that can act as lubricant resulting in increased diffusion coefficients.

We also studied the use of gold thin-film electrodes in four of the RTILs to determine if Au shows an improved behavior compared to Pt (see cyclic voltammetry for 10 - 200 ppm SO<sub>2</sub> on gold electrodes in the supporting information Figure S4.14). Similar trends as on Pt can be observed with a single reduction peak and the reduction potential shifting in [C<sub>2</sub>mim][NTf<sub>2</sub>]. In terms of the oxidative back-peaks, the reverse peaks appear to be sharper and well defined on gold; specifically the imidazolium-based RTILs show a more pronounced first oxidation peak and for [C<sub>4</sub>mpyrr][NTf<sub>2</sub>], two oxidation waves are observed in contrast to a single one on platinum. However, the behavior in  $[P_{14,6,6,6}][NTf_2]$ , is much better on Pt compared to Au, where an obvious reduction peak is not observed on Au. Linear calibration curves were obtained for all samples on gold electrodes (Figure S4.14), with the exception of  $[P_{14,6,6,6}][NTf_2]$ . According to the literature<sup>38</sup>, the adsorption strength of SO<sub>2</sub> is markedly different between platinum and gold surfaces, which may affect the sensing response, especially in the presence of the large tetraalkylphosphonium cation.

In Table 4.12, the slopes of the calibration plots on the Pt-TFE and the Pt-MATFE (discussed in section 4.2.3.2), are summarized in order of increasing RTIL viscosity. The viscosities cover a broad range from 39.7 mPa s for  $[C_2mim][NTf_2]$  to 453.6 mPa s for  $[P_{14,6,6,6}][NTf_2]$ . The sensitivity – defined as the slope of the calibration curve – is the highest in  $[C_2mim][NTf_2]$ , approximately six times higher than the lowest sensitivity in  $[P_{14,6,6,6}][NTf_2]$ . The sensitivity decreases with increasing viscosity, suggesting that a lower viscosity of the electrolyte is desired for higher sensitivity detection of analytes. It should be noted that imidazolium-based RTILs can solvate the reduced superoxide radical, which is in contrast to the sulfonium-, ammonium- and phosphonium-based ionic liquids.

		Pt-TFE	Pt-MATFE
DTH	η /	slope /	slope /
KIIL	mPa s	mA m <sup>-2</sup> ppm <sup>-1</sup>	mA m <sup>-2</sup> ppm <sup>-1</sup>
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	39.7 <sup>39</sup>	6.0	7.3
$[S_{2,2,1}][NTf_2]$	$49.9^{40}$	4.6	10.1
[C <sub>4</sub> mim][NTf <sub>2</sub> ]]	$66.4^{41}$	2.7	4.6
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	98.7 <sup>42</sup>	2.9	7.7
[C4mim][BF4]	135.643	2.6	1.4
$[P_{14,6,6,6}][NTf_2]$	453.644	0.89	0.38

Table 4.12. Summary of viscosities ( $\eta$ ) at 293 K and sensitivities for 10 - 200 ppm SO<sub>2</sub> on a Pt-TFE and a Pt-MATFE in six different ionic liquids.

The lowest concentrations of sulfur dioxide detected in the existing literature are well below 10 ppm, but all employ modified electrodes at high temperatures, and different electrochemical techniques (*i.e.* not amperometric). Betty *et al.* reported the detection

of 1 ppm SO<sub>2</sub> at room temperature with synthesized SnO<sub>2</sub> nanoparticle films via DC conductance and AC impedance.<sup>45</sup> Zhou *et al.* were able to electrochemically detect 3 ppm of SO<sub>2</sub> on NiO-ZnO nanodisks at 240 °C.<sup>46</sup> And Liu *et al.* reported the detection of 0.5 ppm on Au-modified SnO<sub>2</sub> at 200 °C.<sup>47</sup> Based on our results, the combination of commercially available room temperature ionic liquids and low-cost Pt-TFEs are a good option for sensing low concentrations of SO<sub>2</sub> gas using amperometric techniques at ambient temperatures without high power consumption. The 10 ppm CV response is clearly distinguishable from the blank measurement and suggests that much lower analyte concentrations can be easily detected, as will be described in more detail later.

# 4.2.3.2. Reduction of SO<sub>2</sub> on Platinum Microarray Thin-film Electrodes

Microelectrodes give rise to higher current densities due to the dominance of radial diffusion. Although the overall current is lower at microelectrodes, this can be compensated for by including multiple electrodes in an array. Microarray thin-film electrodes (MATFEs) are commercially available, such as those from MicruX used in this study, which have a design with 91 recessed microelectrodes having 10 µm diameter. Hussain et al. already demonstrated the improved sensing behavior of MATFEs over macro thin-film electrodes (TFEs), resulting in the detection of subppm concentrations of ammonia gas.<sup>25</sup> We therefore studied SO<sub>2</sub> reduction on Pt-MATFEs to compare current densities and sensitivities with a view to detect ultra-low concentrations of the gas. Figure 4.10 shows typical cyclic voltammetry responses for the reduction of sulfur dioxide at a scan rate of 100 mV s<sup>-1</sup> in six ionic liquids on platinum microarray thin-film electrodes (Pt-MATFEs). The measured currents were converted into current densities (J) using the geometrical surface area of the working electrodes (10 µm diameter per electrode multiplied by 91 electrodes), for direct comparison with the macro TFEs. Background subtracted calibration plots are shown as insets and the dashed lines show the response in the absence of the analyte.

In contrast to the peak-shaped behavior observed on macro TFEs, MATFEs show steady state or slanted steady state behavior due to the microelectrode-like nature and dominance of radial diffusion. The slanted response is thought to be caused by background impurities in the RTILs that superimpose the steady state current as can be seen in the blank CVs (Figure 4.10). At such low gas concentrations, any small impurity peak can have a significant effect on the analyte current. This is especially

apparent in the imidazolium RTILs (Figure 4.10a, c and e), where it has been reported that impurities such as imidazole can be left over from the synthesis.<sup>48</sup> However, the response of 10 ppm SO<sub>2</sub> gas is still clearly distinguishable from the blank and a highly linear relationship ( $R^2 \approx 0.999$ ) between SO<sub>2</sub> concentration and *J* is observed in all electrolytes. As expected, the current densities are higher on microarray electrodes for most of the samples. Both, [S<sub>2,2,1</sub>][NTf<sub>2</sub>] as well as [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] give current densities more than twice as high on the MATFEs compared to macro TFEs. Whereas, for the two more viscous RTILs, *i.e.* [C<sub>4</sub>mim][BF<sub>4</sub>] and [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>], *J* is approximately half on the MATFE compared to the TFE. This could perhaps be the result of significant build up SO<sub>2</sub> reduction products, trapped in the micro-holes of the MATFEs (see discussion in section 4.2.3.3), or the fact that the current density in the MATFE configuration. It is also worth mentioning the flatter blank response in [S<sub>2,2,1</sub>][NTf<sub>2</sub>] and [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] in the potential range for SO<sub>2</sub> reduction, which is more ideal for sensing lower concentrations of the gas.

A comparison of the slopes (sensitivities) of the calibration plots of the macro TFEs and MATFEs is shown in Table 4.12, revealing significantly higher sensitivities (2.2 – 2.6 times) for the microarrays, with values of 10.1 and 7.7 mA m<sup>-2</sup> ppm<sup>-1</sup> for  $[S_{2,2,1}][NTf_2]$  and  $[C_4mpyrr][NTf_2]$ , respectively. The most viscous RTILs have the smallest slopes, and interestingly, they even show lower sensitivities on the microarray thin-film electrode compared to the macro TFE. The improvement in the sensitivity by more than a factor of two for the sulfonium- and the pyrrolidinium-based ionic liquids, in addition to their flatter blank response, appear to be good characteristics for further studies at ultra-low ppm concentrations of SO<sub>2</sub>.



Figure 4.10. Cyclic voltammetry at a scan rate of  $100 \text{ mV s}^{-1}$  for electrochemical sulfur dioxide reduction at concentrations between 10 and 200 ppm in (a) [ $C_2mim$ ][ $NTf_2$ ], (b) [ $S_{2,2,1}$ ][ $NTf_2$ ], (c) [ $C_4mim$ ][ $NTf_2$ ], (d) [ $C_4mpyrr$ ][ $NTf_2$ ], (e) [ $C_4mim$ ][ $BF_4$ ] and (f) [ $P_{14,6,6,6}$ ][ $NTf_2$ ] on a Pt-MATFE with background subtracted calibration curves shown in the insets. The dashed line represents the response in the absence of SO<sub>2</sub>.

#### 4.2.3.3. Sulfur Deposition After SO<sub>2</sub> Reduction Experiments

Figure 4.11a shows a scanning electron microscope (SEM) image of a micro-hole on a Pt-MATFE after cyclic voltammetry experiments from 10 to 200 ppm SO<sub>2</sub> were performed in  $[C_4mpyrr][NTf_2]$ . The particles deposited within the micro-hole were verified as sulfur (S) as shown in Figure 4.11b on the grey marked area (1). The blue area (2) was chosen on a cleaner area within the micro-hole showing a large Pt peak and a subtle sulfur peak, and finally (3) was measured on the surrounding SU-8 layer showing the absence of both Pt and S peaks. The silicon (Si) peak is from the underlying glass substrate of the Pt-MATFE due to penetration of the electron beam – which also makes the EDS measurement of thinner sulfur contaminants and particles more challenging (see Figure S4.16). Similar sulfur deposits were found in the microholes of Pt-MATFEs after SO<sub>2</sub> reduction in the RTIL  $[S_{2,2,1}][NTf_2]$  (results not shown). The electrochemical reduction of SO<sub>2</sub> in aqueous solutions produces sulfur according to the following mechanism<sup>38</sup>:

$$SO_2(aq) + 4 H^+ + 4 e^- \rightarrow S(s) + 2 H_2O$$
 4.15

To the best of our knowledge, the electrochemical reduction of  $SO_2$  to sulfur in aprotic ionic liquids has previously not been observed in the literature. However, it is well known that trace concentrations of water persist in ionic liquids even after purging under high vacuum.<sup>49-51</sup> This could cause the reaction in equation 4.15 to occur even in aprotic RTILs, resulting in the formation of sulfur particles on the platinum electrode surface.



Figure 4.11. (a) SEM image of a Pt-MATFE micro-hole after carrying out cyclic voltammetry calibration experiments in  $[C_{4}mpyrr][NTf_{2}]$  (as shown in Figure 4.10d). (b) EDS spectra measured on three different areas as marked in the SEM image in (a).

Long-term chronoamperometry (LTCA) experiments were carried out at a potential where diffusion-controlled SO<sub>2</sub> reduction occurs in the presence of 200 ppm SO<sub>2</sub> in  $[C_4mpyrr][NTf_2]$  and  $[C_4mim][NTf_2]$ , as well as in  $[C_4mim][FAP]$  (a non-sulfur containing ionic liquid) on macro-sized Pt-TFEs, where no micro-holes are present. All experiments show that the surface is populated with tiny particulates of sulfur deposits (see Figure S4.15a) after SO<sub>2</sub> reduction experiments. A few larger deposits were also observed near the edge of the macro working electrode of the Pt-TFE – likely due to higher flux at the edges, similar to the case of the MATFEs. However, carrying out the exact same LTCA measurements in the absence of SO<sub>2</sub> gas resulted in a clean

Pt-TFE surface as shown in Figure S4.15b, showing that it is the SO<sub>2</sub> reduction process that is responsible for the presence of the deposits.

It is known that the electrochemical oxidation performance of SO<sub>2</sub> on Pt electrodes in aqueous media is intrinsically linked to sulfur formation at the electrode surface at reducing potentials.<sup>38</sup> In other words, the presence of sulfur on the working electrode acts as a catalyst for SO<sub>2</sub> oxidation in aqueous solvents. However, the impact of sulfur deposits towards SO<sub>2</sub> reduction in aprotic RTILs has not yet been reported in the literature. To compare the impact of sulfur deposition on SO<sub>2</sub> reduction on both TFEs and MATFEs, and to investigate the suitability of our sensors for continuous monitoring of SO<sub>2</sub> gas (even with the possibility of electrode fouling), we proceeded with further amperometric studies on both TFEs and MATFEs in the two selected RTILs, [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] and [S<sub>2,2,1</sub>][NTf<sub>2</sub>]. To reduce the significance of sulfur build-up on the working electrode, as well as to study the low concentration analytical utility of these devices for SO<sub>2</sub> sensing, a lower SO<sub>2</sub> concentration range (1–10 ppm) was chosen, as discussed in the next section.

#### 4.2.3.4. Detection of Low Parts-per-million Concentrations of SO<sub>2</sub>

The permissible exposure limit (PEL) for sulfur dioxide gas is 2 ppm, averaged over a 10-hour working shift, according to the National Institute for Occupational Safety and Health (NIOSH). The reliable and fast detection of concentrations well below 10 ppm is therefore a focus in SO<sub>2</sub> sensing research to avoid harmful effects on human health. Due to the higher current density, Pt-MATFEs were initially selected as the most ideal surface to carry out low concentration detection of sulfur dioxide. The RTILs [S<sub>2,2,1</sub>][NTf<sub>2</sub>] and [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] were chosen because they showed the highest sensitivity in combination with very clean responses in the absence of SO<sub>2</sub> (see Figure 4.10). Additionally, the relatively low viscosities of these RTILs are a desired characteristic for faster response times.

Figure S4.17 and Figure S4.18 in the supporting information show CVs for 1 - 10 ppm SO<sub>2</sub> in [S<sub>2,2,1</sub>][NTf<sub>2</sub>] and [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on Pt-MATFEs, which were the most promising systems at higher concentrations. CV measurements showed a linear relationship ( $R^2 = 0.996$  and 0.999, respectively) between current density and concentration. However, long-term chronoamperometry (LTCA) revealed unstable currents during the continuous monitoring of SO<sub>2</sub>. A more detailed discussion can be

found in the supporting information. The instability is attributed to the electrode surface being fouled by sulfur deposits during the electrochemical reduction of  $SO_2$ , as discussed previously. Therefore, instead of acting as catalysts (as was the case for aqueous  $SO_2$  oxidation<sup>38</sup>), the sulfur deposits act as a passivate for the reduction process in RTILs. Furthermore, the recessed electrodes lead to accumulation of reduction products, which in turn could lead to complete sulfur passivation of the microelectrodes within the array. The harsh constant biasing LTCA technique is therefore not suitable for  $SO_2$  sensing on MATFEs that have recessed electrode designs.



Figure 4.12. (a) Cyclic voltammetry at a scan rate of 100 mV s<sup>-1</sup> for electrochemical SO<sub>2</sub> reduction at concentrations from 1 to 10 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-TFE with the background subtracted calibration curve including error bars from 3 independent experiments shown in the inset. The dashed line represents the blank scan in the absence of SO<sub>2</sub>. A total flow rate of 1000 mL min<sup>-1</sup> was employed. (b) Long-term chronoamperometry (LTCA) response for electrochemical sulfur dioxide reduction at concentrations from 1 to 10 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-TFE with the background subtracted calibration curve including error bars from 3 independent experiments shown in the inset. (c) Long-term chronoamperometry response for electrochemical sulfur dioxide reduction at concentrations from 1 to 10 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-TFE with the background subtracted calibration curve including error bars from 3 independent experiments shown in the inset. (c) Long-term chronoamperometry response for electrochemical sulfur dioxide reduction by a periodic introduction of 2 ppm SO<sub>2</sub> (response phase) followed by a period of N<sub>2</sub>-purging (recovery phase) in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-TFE, with a nitrogen flushing step employed between SO<sub>2</sub> additions.

In light of this, we employed mm-sized (macro) Pt-TFEs for low concentration (< 10 ppm) SO<sub>2</sub> sensing. Of the two RTILs,  $[C_4mpyrr][NTf_2]$  was singled out as it was substantially less impacted by the occurrence of sulfur deposition compared to  $[S_{2,2,1}][NTf_2]$ . Figure 4.12a shows the CV response of 1 – 10 ppm SO<sub>2</sub> in
$[C_4mpyrr][NTf_2]$  on a Pt-TFE, with the blank measurement in pure nitrogen shown as the dashed line. The inset shows a calibration plot of current density *vs*. concentration. The shapes of the CVs at these low concentrations appear similar to that obtained at the higher (10 – 200 ppm) concentration range (see Figure 4.9d). A good fit ( $R^2 =$ 0.998) was achieved for the calibration, however, the definition of peaks at lower concentrations is not as good as the higher concentrations, resulting in the calibration plot for CV measurements giving a limit of detection (based on three standard deviations of the line) of 1.5 ppm.

Long-term chronoamperometry (LTCA) was then performed to show if SO<sub>2</sub> can be continuously monitored at low concentrations. The potential was held at -1.5 V where sulfur dioxide is reduced, and the cell was placed under nitrogen to obtain a blank amperometric transient. SO<sub>2</sub> at different concentrations from 1 - 10 ppm was then introduced, and the plateau current obtained at each ppm level was used to establish a calibration curve. Figure 4.12b shows the LTCA response from 1 to 10 ppm of SO<sub>2</sub>, with the inset calibration plot showing a highly linear relationship between *J* and [SO<sub>2</sub>]. The limit of detection (LOD) was found to be 0.5 ppm for LTCA, compared to 1.5 ppm for CV, which suggests the preference of long-term chronoamperometry over cyclic voltammetry for reliably detecting very low SO<sub>2</sub> concentrations. This is consistent with our previous experiments for ammonia detection, which also showed that LTCA was the preferred technique compared to CV at sub-ppm concentrations.<sup>52</sup>

It was noticed that the plateau current on TFEs was constant for more than 180 s, suggesting good stability with minimal effects from electrode fouling. To determine if the sensor can reliably measure at concentrations close to the permissible exposure limit, repeated additions of 2 ppm SO<sub>2</sub> were performed. Figure 4.12c shows the amperometric response for periodic introductions of 2 ppm SO<sub>2</sub> (response phase) followed by a period of N<sub>2</sub>-purging (recovery phase) for four cycles. Reproducible responses and very little change in the plateau currents were observed. Table 4.13 summarizes the sensitivity (slopes) in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on the macro Pt-TFE obtained from the CV measurements for both concentration ranges, the sensitivity obtained from the LTCA calibration at 1 - 10 ppm of SO<sub>2</sub> and the *t*<sub>90</sub> response and *t*<sub>90</sub> recovery time (where *t*<sub>90</sub> is defined as the time taken to reach 90% of the steady-state current). As can be seen, the sensitivity using CV is highly consistent and within experimental error for both concentration ranges. The response and recovery times of 91 (± 8) s and

103 ( $\pm$  11) s respectively, are significantly higher compared to smaller, non-polar gases with lower solubilities, such as oxygen, which had a response time of approximately 20 s according to Huang *et al.*<sup>21</sup> Although a low volume of ionic liquid was used in our study (0.5 µL), it is expected that the response time could be further reduced with a thinner electrolyte layer. Based on these observations, we believe it should be even possible to reliably detect SO<sub>2</sub> at concentrations lower than 1 ppm. This is a significant outcome, since so far, the reliable detection of such low concentrations of sulfur dioxide has not been observed in room temperature in RTILs, especially with miniaturized, low-cost electrodes.

Table 4.13. Electrochemical data for the reduction of  $SO_2 (10 - 200 \text{ ppm})$  and (1 - 10 ppm) in the RTIL [C4mpyrr][NTf2], using cyclic voltammetry (CV) and long-term chronoamperometry (LTCA) on platinum thin-film electrodes (Pt-TFEs) including the slope of the calibration curves, and the t90 response and t90 recovery for 2 ppm additions using LTCA.

	CV		LTCA	LTCA for 2 ppm SO <sub>2</sub>		
RTIL	slope (10– 200 ppm) / mA m <sup>-2</sup> ppm <sup>-1</sup>	slope (1– 10 ppm) / mA m <sup>-2</sup> ppm <sup>-1</sup>	slope (1– 10 ppm) / mA m <sup>-2</sup> ppm <sup>-1</sup>	t90 response / s	<i>t</i> 90 recovery / s	
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	2.9 (±0.1)	3.0 (±0.1)	0.57 (±0.01)	91 (±8)	103 (±11)	

#### 4.2.4. Conclusions

The electrochemical reduction of sulfur dioxide has been studied in six different room temperature ionic liquids (RTILs) on two different electrode materials and using two different electrode geometries using cyclic voltammetry. Linear relationships between current density *vs*. SO<sub>2</sub> concentrations from 10 - 200 ppm were established for all systems with higher current densities on microarray electrodes compared to their macro counterparts, except in the two most viscous ionic liquids, [C<sub>4</sub>mim][BF<sub>4</sub>] and [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>]. It was concluded that platinum electrodes outperformed gold surfaces in all RTILs. The most promising ionic liquid – [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] – was then employed for further studies with a Pt-TFE and a Pt-MATFE for sensing experiments at low ppm SO<sub>2</sub> concentrations. Linear relationships between current density (*J*) and concentration were obtained for 1 - 10 ppm SO<sub>2</sub> using both cyclic voltammetry and long-term chronoamperometry. In the case of microarray electrodes, long-term stability and reproducibility was not ideal due to fouling of the electrode surface caused by sulfur

deposition in the micro-holes; this was verified with scanning electron microscopy in conjunction with energy dispersive spectroscopy. This is the believed to be the first observation of this phenomenon in aprotic RTILs. Sulfur deposition was not found to affect the amperometric sensing performance on the larger (macro) Pt-TFEs at ppm SO<sub>2</sub> concentrations. Therefore, we recommend the use of low-cost macro-sized thin-film electrodes (TFEs) for the reliable detection of sulfur dioxide in RTILs at concentrations close to, and lower than, the permissible exposure limit (PEL) of 2 ppm.

## 4.2.5. References

1. Bauer, M. A.; Utell, M. J.; Morrow, P. E.; Speers, D. M.; Gibb, F. R., Inhalation of 0.30 ppm Nitrogen Dioxide Potentiates Exercise-induced Bronchospasm in Asthmatics. *Am. Rev. Respir. Dis.* **1986**, *134*, 1203-1208.

2. Carmichael, G. R.; Streets, D. G.; Calori, G.; Amann, M.; Jacobsen, M. Z.; Hansen, J.; Ueda, H., Changing Trends in Sulfur Emissions in Asia: Implications for Acid Deposition, Air Pollution, and Climate. *Environ. Sci. Technol.* **2002**, *36*, 4707-4713.

3. Khan, R. R.; Siddiqui, M. J. A., Review on effects of Particulates; Sulfur Dioxide and Nitrogen Dioxide on Human Health. *Int. Res. J. Environment Sci.* **2014**, *3*, 70-73.

4. Levitsky, I. A., Porous Silicon Structures as Optical Gas Sensors. *Sensors* **2015**, *15*, 19968-19991.

5. Li, M.; Myers, E. B.; Tang, H. X.; Aldridge, S. J.; McCaig, H. C.; Whiting, J. J.; Simonson, R. J.; Lewis, N. S.; Roukes, M. L., Nanoelectromechanical Resonator Arrays for Ultrafast, Gas-Phase Chromatographic Chemical Analysis. *Nano Lett.* **2010**, *10*, 3899-3903.

6. Fergus, J. W., A review of electrolyte and electrode materials for high temperature electrochemical CO<sub>2</sub> and SO<sub>2</sub> gas sensors. *Sens. Actuators B* **2008**, *134*, 1034-1041.

7. Yunusa, Z.; Hamidon, M. N.; Kaiser, A.; Awang, Z., Gas Sensors: A Review. *Sens. Transducers* **2014**, *168*, 61-75.

8. Hodgson, A. W. E.; Jacquinot, P.; Hauser, P. C., Electrochemical Sensor for the Detection of SO<sub>2</sub> in the Low-ppb Range. *Anal. Chem.* **1999**, *71*, 2831-2837.

9. Skeaff, J. M.; Dubreuil, A. A., Electrochemical measurement of SO<sub>3</sub> -SO<sub>2</sub> in process gas streams. *Sens. Actuators B* **1993**, *10*, 161-168.

10. Bezerra Martins, A.; Lobato, A.; Tasić, N.; Perez-Sanz, F. J.; Vidinha, P.; Paixão, T. R. L. C.; Moreira Gonçalves, L., Laser-pyrolyzed electrochemical paperbased analytical sensor for sulphite analysis. *Electrochem. Commun.* **2019**, *107*, 106541.

11. Rocha, P.; Vilas-Boas, Â.; Fontes, N.; Geraldo, D.; Bento, F., Evaluation of Polyphenols in Wine by Voltammetric Techniques with Screen Printed Carbon Electrodes. *Electroanalysis* **2020**, *32*, 159-165.

12. Ramos, R. M.; Brandão, P. F.; Gonçalves, L. M.; Vyskočil, V.; Rodrigues, J. A., Electrochemical sensing of total sulphites in beer using non-modified screenprinted carbon electrodes. *J. Inst. Brew.* **2017**, *123*, 45-48.

13. Ramos, R. M.; Gonçalves, L. M.; Vyskočil, V.; Rodrigues, J. A., Free sulphite determination in wine using screen-printed carbon electrodes with prior gas-diffusion microextraction. *Electrochem. Commun.* **2016**, *63*, 52-55.

14. Xiong, L.; Compton, R. G., Amperometric Gas Detection: A Review. *Int. J. Electrochem. Sci.* **2014**, *9*, 7152-7181.

15. Buzzeo, M. C.; Hardacre, C.; Compton, R. G., Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.* **2004**, *76*, 4583-4588.

16. Rehman, A.; Zeng, X., Methods and approaches of utilizing ionic liquids as gas sensing materials. *RSC Adv.* **2015**, *5*, 58371 - 58392.

17. Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R., Room temperature ionic liquids and their mixtures- A Review. *Fluid Phase Equilib.* **2004**, *219*, 93-98.

18. Buzzeo, M. C.; Evans, R. G.; Compton, R. G., Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry-A Review. *Chem. Phys. Chem.* **2004**, *5*, 1106-1120.

19. Freire, M. G.; Santos, L. M. N. B. F.; Fernandes, A. M.; Coutinho, J. A. P.; Marrucho, I. M., An overview of the mutual solubilities of water-imidazolium-based ionic liquid systems. *Fluid Ph. Equilibria* **2007**, *261*, 449-454.

20. Malvaldi, M.; Chiappe, C., From molten salts to ionic liquids: effect of ion asymmetry and charge distribution. *J. Phys.: Condens. Matter* **2008**, *20*, 035108.

21. Huang, X.-J.; Aldous, L.; O'Mahony, A. M.; del Campo, F. J.; Compton, R. G., Toward Membrane-Free Amperometric Gas Sensors: A Microelectrode Array Approach. *Anal. Chem.* **2010**, *82*, 5238-5245.

22. Hu, C.; Bai, X.; Wang, Y.; Jin, W.; Zhang, X.; Hu, S., Inkjet Printing of Nanoporous Gold Electrode Arrays on Cellulose Membranes for High-Sensitive Paper-Like Electrochemical Oxygen Sensors Using Ionic Liquid Electrolytes. *Anal. Chem.* **2012**, *84*, 3745-3750.

23. Kubersky, P.; Altsmid, J.; Hamacek, A.; Nespurek, S.; Zmeskal, O., An Electrochemical NO<sub>2</sub> Sensor Based on Ionic Liquid: Influence of the Morphology of the Polymer Electrolyte on Sensor Sensitivity. *Sensors* **2015**, *15*, 28421-28434.

24. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., The Electrochemical Reduction of Hydrogen Sulfide on Platinum in Several Room Temperature Ionic Liquids. *J. Phys. Chem. C* **2008**, *112*, 7725-7730.

25. Hussain, G.; Silvester, D. S., Detection of sub-ppm Concentrations of Ammonia in an Ionic Liquid: Enhanced Current Density Using "Filled" Recessed Microarrays. *Anal. Chem.* **2016**, *88*, 12453-12460.

26. Barrosse-Antle, L. E.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Electroreduction of Sulfur Dioxide in Some Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2008**, *112*, 3398-3404.

27. Neta, P.; Huie, R. E.; Harriman, A., One-Electron-Transfer Reactions of the Couple SO<sub>2</sub>/SO<sub>2</sub><sup>-</sup> in Aqueous Solutions. Pulse Radiolytic and Cyclic Voltammetric Studies. *J. Phys. Chem.* **1987**, *91*, 1606-1611.

28. Potteau, E.; Levillain, E.; Lelieur, j.-P., Mechanism of the electrochemical reduction of sulfur dioxide in non-aqueous solvents. *J. Electroanal. Chem.* **1999**, *476*, 15-25.

29. Gardner, C. L.; Fouchard, D. T.; Fawcett, W. R., The Kinetics and Mechanism of the Electroreduction of Sulfur Dioxide in Nonaqueous Media: II . Effects of Electrolyte and Solvent on the Mechanism of Reduction. *J. Electrochem. Soc.* **1981**, *128*, 2345-2350.

30. Choi, D. S.; Kim, D. H.; Shin, U. S.; Deshmukh, R. R.; Lee, S.; Song, C. E., The dramatic acceleration effect of imidazolium ionic liquids on electron transfer reactions. *Chem. Commun.* **2007**, *33*, 3467-3469.

31. Huang, Q.; Hu, Y.; Wang, J.; Jiang, K.; Wu, T., The Principle of Detect SO<sub>2</sub> Concentration by Using the Electrochemical Method in Ionic Liquid *Wuhan Univ. J. Nat. Sci.* **2019**, *24*, 400-404.

32. Ren, S.; Hou, Y.; Wu, W.; Liu, Q.; Xiao, Y.; Chen, X., Properties of Ionic Liquids Absorbing SO<sub>2</sub> and the Mechanism of the Absorption. *J. Phys. Chem. B* **2010**, *114*, 2175-2179.

33. Lee, J.; Du Plessis, G.; Arrigan, D. W. M.; Silvester, D. S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Anal. Methods* **2015**, *7*, 7327-7335.

34. Martin, R. P.; Sawyer, D. T., Electrochemical Reduction of Sulfur Dioxide in Dimethylformamide. *Inorg. Chem.* **1972**, *11*, 2644-2647.

35. Jacobsen, E.; Sawyer, D. T., Electrochemical reduction of sulfur dioxide at a mercury electrode. *J. Electroanal. Chem.* **1967**, *15*, 181-192.

36. Wandt, J.; Lee, J.; Arrigan, D.; Silvester, D. S., A lithium iron phosphate reference electrode for ionic liquid electrolytes. *Electrochem. Commun.* **2018**, *93*, 148-151.

37. Lee, J.; Caporale, C.; McKinley, A.; Fuller, R.; Silvester, D. S., Electrochemical Properties of a Verdazyl Radical in Room Temperature Ionic Liquids. *Aust. J. Chem.* **2020**, *73*, 1001-1009.

38. O'Brien, J. A.; Hinkley, J. T.; Donne, S. W., Electrochemical Oxidation of Aqueous Sulfur Dioxide II. Comparative Studies on Platinum and Gold Electrodes. *The Electrochemical Society* **2012**, *159*, 585-593.

39.Tariq, M.; Carvalho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P.N.,Viscosityof(C2-C14)1-alkyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)amideionicliquidsinan extended temperature range.Fluid Phase Equilib. 2011, 301, 22-32.

40. Bhattacharjee, A.; Luis, A.; Santos, J. H.; Lopes-da-Silva, J. A.; G.;, F. M.; Carvalho, P. J.; Coutinho, J. A. P., Thermophysical properties of sulfonium- and ammonium-based ionic liquids. *Fluid Phase Equilib.* **2014**, *381*, 36-45.

41. Almeida, H. F. D.; Lopes, J. N. C.; Rebelo, L. P. N.; Coutinho, J. A. P.; Freire, M. G.; Marrucho, I. M., Densities and Viscosities of Mixtures of Two Ionic Liquids Containing a Common Cation. *J. Chem. Eng. Data* **2016**, *61*, 2828-2843.

42. Gacino, F. M.; Regueira, T.; Lugo, L.; Comunas, M. J. P.; Fernandez, J., Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 4984-4999.

43. Harris, K. R.; Kanakubo, M.; Woolf, L. A., Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate: Viscosity and Density Relationships in Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 2425-2430.

44. Neves, C. M. S. S.; Carvalho, P. J.; Freire, M. G.; Coutinho, J. A. P., Thermophysical properties of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids. *J. Chem. Thermodyn.* **2011**, *43*, 948-957. 45. Betty, C. A.; Choudhury, S., Charge carrier transport in nanocrystalline  $SnO_2$  thin film sensor and temperature dependence of toxic gas sensitivity. *Sens. Actuators B* **2016**, *237*, 787-794.

46. Zhou, Q.; Zeng, W.; Chen, W.; Xu, L.; Kumar, R.; Umar, A., High sensitive and low-concentration sulfur dioxide (SO<sub>2</sub>) gas sensor application of heterostructure NiO-ZnO nanodisks. *Sens. Actuators B* **2019**, *298*, 126870.

47. Liu, L.; Liu, S., Oxygen Vacancies as an Efficient Strategy for Promotion of Low Concentration SO<sub>2</sub> Gas Sensing: The Case of Au-Modified SnO<sub>2</sub>. *ACS Sustain. Chem. Eng.* **2018**, *6*, 13427-13434.

48. Holbrey, J. D.; Seddon, K. R.; Wareing, R., A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. *Green Chem.* **2001**, *3*, 33-36.

49. O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 2884-2891.

50. Köddermann, T.; Wertz, C.; Heintz, A.; Ludwig, R., The Association of Water in Ionic Liquids: A Reliable Measure of Polarity. *Angew. Chem., Int. Ed.* **2006**, *45*, 3697-3702.

51. Reid, J. E. S. J.; Walker, A. J.; Shimizu, S., Residual water in ionic liquids: clustered or dissociated? *Phys. Chem. Chem. Phys.* **2015**, *17*, 14710-14718.

52. Lee, J.; Hussain, G.; López-Salas, N.; MacFarlane, D. R.; Silvester, D. S., Thin films of poly(vinylidene fluoride-co-hexafluoropropylene)-ionic liquid mixtures as amperometric gas sensing materials for oxygen and ammonia. *Analyst* **2020**, *145*, 1915-1924.

## 4.2.6. Supporting Information



Figure S4.13. (a) Photograph of the commercial thin-film electrode used in this work, consisting of platinum working, reference and counter electrodes on a glass substrate. Images to the right are scanning electron microscopy (SEM) images of a thin-film working electrode (diameter 1 mm) and a thin-film microelectrode array electrode. The microarray is formed within a SU-8 polymer layer (ca. 3.5  $\mu$ m thick) to create 91 recessed micro-disk electrodes each with a diameter 10  $\mu$ m. (b) Illustration of the sensing mechanism. SO<sub>2</sub> gas is continuously flowed over the room temperature ionic liquid (RTIL) droplet which is on top of the three electrodes. After equilibration, the solvated SO<sub>2</sub> is reduced at the electrode and a current is produced. (c) Illustration of the gas sensing experimental set-up. The analyte gas (SO<sub>2</sub>) is diluted with nitrogen gas through a gas-mixing system to create different concentrations of SO<sub>2</sub> gas. This is passed through a sealed glass cell that contains the planar electrode device. The electrical contacts of the planar electrode are outside of the glass cell and are connected via soldered wires to the potentiostat.



Figure S4.14. Cyclic voltammetry at a scan rate of  $100 \text{ mV s}^{-1}$  for electrochemical sulfur dioxide reduction at concentrations from 10 to 200 ppm in (a) [C<sub>2</sub>mim][NTf<sub>2</sub>], (b) [C<sub>4</sub>mpyrr][NTf<sub>2</sub>], (c) [C<sub>4</sub>mim][BF<sub>4</sub>] and (d) [P<sub>14,6,6,6</sub>][NTf<sub>2</sub>] on a gold macro thin-film electrode (Au-TFE). The calibration curves – plot of peak current vs. concentration – are shown in the insets. The dashed line represents the blank scan in the absence of SO<sub>2</sub>. A constant total flow rate of 400 mL min<sup>-1</sup> was employed.



Figure S4.15. SEM images of platinum thin-film electrodes after conducting 5 mins of long-term chronoamperometry at -1.5 V in the RTIL  $[C_4mpyrr][NTf_2]$  (a) in the presence of 200 ppm SO<sub>2</sub> gas, and (b) in the absence of SO<sub>2</sub> gas (i.e. nitrogen purged environment). The inset to (a) shows one of the few sparsely distributed larger sulfur particles deposited at the edge of the working electrode disk. No deposits were observed in the absence of SO<sub>2</sub> gas.



Figure S4.16. EDS spectra from one of the particles in Figure S4.15 (a) fitted without sulfur, and (b) fitted with sulfur.

As shown in Figure S4.17a, cyclic voltammetry for SO<sub>2</sub> reduction in  $[S_{2,2,1}][NTf_2]$  on a Pt-MATFE, which was found to be the most promising combination for SO<sub>2</sub> reduction at higher concentrations (10 - 200 ppm) using cyclic voltammetry. In contrast to the steady state behavior at higher concentrations (Figure 4.10b in the main manuscript), a slanted behavior is observed at lower ppm concentrations, due to a larger relative contribution from the blank. A single oxidative back peak arises at approximately -0.4 V (*vs.* Pt) that was absent at high SO<sub>2</sub> concentrations. In order to test the ability to continuously monitor SO<sub>2</sub> gas, long-term chronoamperometry (LTCA) was performed. Sulfur dioxide was introduced while applying a constant potential at the sulfur dioxide reduction peak (see Figure S4.17b), revealing an unstable current response for repeated additions of 2 ppm SO<sub>2</sub>.

The same experiment in the second chosen RTIL ([C<sub>4</sub>mpyrr][NTf<sub>2</sub>]) gave much better CV responses (see Figure S4.18a). The steady state response for the lowest concentration (1 ppm) of SO<sub>2</sub> can be easily distinguished from the blank, and the calibration plot of current density *vs*. concentration is highly linear ( $R^2 > 0.99$ ). LTCA, however, showed decreasing current responses for successive additions at the same concentration (2 ppm) of analyte. Figure S4.18b (inset) shows the calibration graph obtained for 1 – 10 ppm SO<sub>2</sub> using LTCA. After the current reached a plateau following a concentration change, a gradual drop in current was observed over time, indicating the possibility of a fouled surface. A reproducibility test was performed by

introducing 2 ppm SO<sub>2</sub> repeatedly, with a nitrogen flushing step between each addition (see Figure S4.18c). A decrease in plateau current was observed upon successive additions. Due to the fact that these microarray thin-film electrodes consist of an array of recessed electrodes, the deposition of sulfur particles in the recessed holes (as discussed in the main paper) can passivate the electrodes and give rise to a smaller electrode surface area available for the electrochemical reduction process. After the electrode had been used for calibration experiments in Figure S4.18b, the current decreased even further (see Figure S4.18d), showing further passivation of the electrode over time. This suggests that continuous real-time SO<sub>2</sub> measurements on MATFEs may not be possible using this technique. However, a macro TFE shows a much less pronounced effect even when employing LTCA.

Therefore, we conclude that microarray electrodes are promising for the detection of low ppm concentrations of sulfur dioxide using cyclic voltammetry, whereas continuous real-time monitoring of the analyte using LTCA may not be possible due to the build-up of sulfur particles that result in electrode fouling. Macro TFEs, however, have a larger electrode surface area and are less affected in terms of electrode fouling due to the sulfur deposits, so LTCA is a viable method.



Figure S4.17. (a) Cyclic voltammetry at a scan rate of 100 mV s<sup>-1</sup> for electrochemical SO<sub>2</sub> reduction at concentrations from 1 to 10 ppm SO<sub>2</sub> in [S<sub>2,2,1</sub>][NTf<sub>2</sub>] on a Pt-MATFE. The calibration curve for current density (at -1.25 V) vs. SO<sub>2</sub> concentration is shown in the inset. The dashed line represents the blank response in the absence of SO<sub>2</sub>. A total flow rate of 1000 mL min<sup>-1</sup> was employed. (b) Long-term chronoamperometry response for electrochemical sulfur dioxide reduction at repeated additions of 2 ppm in [S<sub>2,2,1</sub>][NTf<sub>2</sub>] on a Pt-MATFE, with nitrogen flushing step performed between SO<sub>2</sub> additions.



Figure S4.18. (a) Cyclic voltammetry at a scan rate of 100 mV s<sup>-1</sup> for electrochemical SO<sub>2</sub> reduction at concentrations from 1 to 10 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-MATFE with the calibration curve shown in the inset. The dashed line represents the blank response in the absence of SO<sub>2</sub>. A total flow rate of 1000 mL min<sup>-1</sup> was employed. (b) Long-term chronoamperometry (LTCA) response for electrochemical sulfur dioxide reduction at concentrations from 1 to 10 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-MATFE with the calibration curve shown in the inset. (c) Long-term chronoamperometry response for electrochemical sulfur dioxide reduction at repeated additions of 2 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-MATFE, with a nitrogen flushing step performed between SO<sub>2</sub> additions. (d) LTCA response for electrochemical sulfur dioxide reduction at repeated additions of 2 ppm in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on a Pt-MATFE, with a nitrogen flushing step performed between SO<sub>2</sub> additions after a calibration experiment (shown in Figure S4.18b) was performed.

# 4.3. Interdigitated Array Microelectrodes for Gas Sensing

### 4.3.1. Introduction

In the previous chapters, it was shown that room temperature ionic liquids have specific advantages over aqueous-based electrolytes, *i.e.* wide electrochemical windows as well as good chemical and thermal stability in combination with good solubilization properties. In addition to the electrolyte, the electrode material and its geometry can have a crucial effect on the electrochemical response. This is especially true in the case of sulfur dioxide, where it was shown for microarray electrodes that sulfur deposits, formed by the electrochemical reduction of  $SO_2$  gas, can block the electrode.

However, the slower diffusion of the analyte in viscous RTILs can result in slow responses, and in many cases, a fast response is an important criterion for gas sensors. This slow response can be overcome by reducing the viscosity of the RTIL, for example by adding an organic solvent. However, the planar electrode devices used in this thesis can then not be applied in different orientations due to the flowing nature of the electrolyte. Different approaches have been proposed to overcome this problem. Gel-polymer electrolytes (GPEs), which are physical mixtures of ionic liquids with polymers have been examined for robust gas sensing. For GPEs, the addition of polymer increases the viscosity so that no flow occurs, while the RTIL provides the electrical conductivity required for the electrochemical sensing. Various polymers, e.g. cross-linked poly(ethylene glycol)methyl ether (PEG-MEMA)<sup>1-2</sup>, partially porous polyethylene<sup>3</sup>, poly(methyl methacrylate)<sup>4-5</sup>, or poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP)<sup>6</sup>, have been tested so far for gas sensing with RTILs. Good responses were observed for gaseous analytes and proof-of-concept studies on the applicability of the sensor in different orientations were reported.<sup>5</sup> However, the main challenges of introducing polymers are the very slow diffusion of the analyte, in addition to the possibility of the polymer reacting with the electrogenerated species as has been shown for PVDF-HFP reacting with superoxide.<sup>6</sup>

One way to overcome the challenge of slow gas diffusion is to reduce the thickness of the RTIL layer on the electrode. This can be achieved by reducing the RTIL volume that is drop-casted, or by employing external forces that spread the RTIL, *e.g.* by spin casting, or by forming microchannels, as was demonstrated by attaching 1-hexadecanethiol to gold electrode electrodes via gold-thiol chemistry resulting in fast response times for gases such as oxygen<sup>7</sup>, ammonia and hydrogen chloride<sup>8</sup>. However, this technique is limited to gold surfaces which is an electrode surface that is not suitable for all gaseous analytes (*e.g.* hydrogen) due to poor kinetics. Alternatively, electrodeposition of metals in the channels can be attempted.<sup>9</sup>

An alternative approach is proposed in this chapter, using microchannels to "wick" RTILs and create a thin layer of RTIL for fast gas sensing responses. The research group of Dr. Eva Alvarez de Eulate from University of South Australia fabricated custom-made interdigitated electrodes with micro-pillars in between the electrode arms (see Figure 4.19). The spread of the RTIL is therefore achieved by capillary force and the height of the pillars determines the thickness of the electrolyte layer as well as reducing the flow of the liquid. A small volume of the RTIL is loaded onto the reservoir area (see Figure 4.20a) and the spread of the RTIL over time can be observed visually over the whole electrode area (see Figure 4.20b-d).

## 4.3.2. Experimental

#### 4.3.2.1. Chemical Reagents

The temperature ionic liquid 1-butyl-1-methylpyrrolidinium room bis(trifluoromethylsulfonyl)imide ([C4mpyrr][NTf2], 99.5%, IoLiTec, Heilbronn, Germany) was used as received without further purification. Acetone (CHROMASOLV®, for HPLC, ≥99.0%, Sigma-Aldrich, Missouri, United States) and acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) were used to clean the electrodes. A 0.5 M H<sub>2</sub>SO<sub>4</sub> stock solution (prepared with ultrapure water with a resistivity of 18.2 MΩ cm, from a 95–98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for the electrode activation. Ammonia (48 ppm in nitrogen), sulfur dioxide (51 ppm in nitrogen) and high purity nitrogen (>99.99% purity) gas cylinders were purchased from Coregas (NSW, Australia).

#### 4.3.2.2. Electrode Fabrication and Imaging

The electrodes used for the electrochemical gas sensing experiments were prepared by the research group led by Dr. Eva Alvarez de Eulate at the University of South Australia in Adelaide according to the following procedure:



Figure 4.19. 45-degree SEM image of the platinum  $\mu$ -pillar interdigitated array electrode (Pt- $\mu$ -pillar IDA) taken by the team of Dr. Alvarez de Eulate. Scale bar = 10  $\mu$ m.

The wicking platinum micro-pillar interdigitated array electrodes (Pt-µ-pillar IDAs) were fabricated at the South Australia node of the Australian National Fabrication Facility (ANFF-SA) on smooth borosilicate glass substrates (BF4" round and 1.1 mm thick). First, approximately 100 nm of Cr was sputtered (HHV TF500) onto a borosilicate glass wafer followed by a AZ5214EAT resist deposition at 4000 rpm for 30 s (spin coater Delat 80 RC). The substrate was soft-baked for 60 s at 110 °C and exposed to a hard contact electrode mask using a constant dose of 50 mJ cm<sup>-2</sup> for patterning the AZ5214E layer. Reversal baked at 115 °C for 2 min on a hotplate and flood exposed at a constant dose of 400 mJ cm<sup>-2</sup> (use a blank glass mask) is required for reversal lithography. The substrate was then developed using AZ-726 developer for 60 s. Subsequently, 10 nm of Ti and 100 nm of Pt were sputtered on top of the patterned surface. The photoresist was removed using acetone and etching of the Cr with ceric ammonium nitrate which rendered the Pt interdigitated electrodes on the glass substrate. Once the electrodes were patterned, they were cleaned with acetone and isopropanol, a layer of SU8-10 was spin-coated at 1000 rpm for 30 s. The substrate was then soft baked for 2 min at 65 °C and 10 min at 95 °C. After aligning with a mask aligner (EVG 620) to the cross marks between the capillary, the 30  $\mu$ m in diameter micro-pillar mask is exposed to a hard contact at a constant dose of 10 mJ cm<sup>-2</sup>. Post exposure, the wafer was baked for 1 min at 65 °C and 1 min at 95 °C, and finally the SU8 pillars (see Figure 4.19) were developed using glycol methyl ether acetate (PGMEA) for 2 min with a final hard bake at 130 °C for 10 min.

#### 4.3.2.3. Electrochemical Experiments

A PGSTAT101 Autolab potentiostat (Metrohm, Gladesville, NSW, Australia) was interfaced to a computer with NOVA 1.11 software and used to perform all electrochemical experiments. The platinum micro-pillar interdigitated array electrodes (called Pt-µ-pillar IDAs hereafter) were activated in air plasma for 30 s to reduce the contact angle of the SU8 pillars to promote spontaneous spreading of the RTIL. The array consists of two Pt arms with 40 interdigitated fingers (width 10 µm and 5000 µm in length) defined by an SU-8 layer masking the remainder of the surface. One arm of the IDA was used as the working electrode (WE) with the other arm used as the counter electrode (CE). The electrochemical cell was housed inside an aluminum Faraday cage to reduce ambient electromagnetic interferences. For gas sensing, the Pt-µ-pillar IDAs were prepared with an external silver wire, acting as a pseudo-reference electrode (RE), attached to the surface. Prior to experiments, both fingers of the electrode were electrochemically activated by cyclic voltammetry (CV) in nitrogen-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> (aq) between -0.55 V and +1.0 V (vs. Ag) at 1 V s<sup>-1</sup> for >100 cycles. The activated electrodes were rinsed thoroughly with ultrapure water and acetone, before drying under a gentle stream of nitrogen. Approximately 1 µL of the RTIL [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] was loaded onto the reservoir area to connect to the external silver wire RE. The RTIL was allowed sufficient time to wick via capillary force to evenly cover the electrodes of the Pt-µ-pillar IDA device (see Figure 4.20).

The height of the micropillars (30  $\mu$ m) is believed to define the thickness of the RTIL layer. The prepared electrode was then inserted through the slit of a silicone-bung (made in-house) before being placed into a glass cell. The cell was then purged with nitrogen for *ca*. 30 min to remove dissolved gases and impurities in the RTIL, before commencing with the gas sensing experiments, consecutive CV scans (with 5 min wait times) were carried out until a constant blank CV was obtained. To obtain different concentrations of the analyte gases, the relative flow rates of nitrogen and ammonia or sulfur dioxide were adjusted. The total flow rate was kept constant at 500 mL min<sup>-1</sup>.



Figure 4.20. Microscope images of the Pt- $\mu$ -pillar IDA taken by the team of Dr. Alvarez de Eulate; (a) before the loading of the RTIL, and after 4, 6 and 15 s (b – d).

## 4.3.2.4. Electrode Imaging

The electrodes were analyzed with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Clara-FESEM, Tescan, Kohoutovic, Czech Republic) by the research group at the University of South Australia. The SEM/EDS measurements were all carried out using an accelerating voltage of 10 keV at a working distance of 10 mm. The samples were coated with approximately 3 nm of platinum via vapor deposition to prevent surface charging during the imaging. The EDS measurements were carried out with an accelerating voltage of 10 keV as well as analyzed using Aztec® 4.3 software (Oxford Instruments Nanotechnology Tools Limited, Tubney Woods, Abington, UK).

### 4.3.3. Results and Discussion

The electrochemical response of two analyte gases, ammonia and sulfur dioxide, has been studied on the fabricated Pt- $\mu$ -pillar IDA electrodes. Both analytes have been previously studied on macro thin-film electrodes (TFEs), where linear relationships between currents and concentrations were established.<sup>10-11</sup> Cyclic voltammetry responses of ammonia and sulfur dioxide gas for two concentration ranges, *i.e.* 1 - 10 ppm and 10 - 50 ppm, are shown in Figure 4.21. Clear redox responses were observed for both gases.



Figure 4.21. Cyclic voltammetry responses of the electrochemical oxidation of ammonia gas at (a) high (10-50 ppm) and (b) low (1-10 ppm) concentrations and of the electrochemical reduction of sulfur dioxide gas at (c) high and (d) low concentrations. Dashed line is the response in the absence of the analyte gas. The insets show the background corrected calibration graphs for current vs. concentration for ascending and descending runs, including a line of best fit.

Ammonia oxidation resulted in a steady state like CV shape, as expected for interdigitated electrodes, which is caused by the radial diffusion of the analyte in one dimension and linear diffusion in the other. Highly reproducible currents for the ascending and descending calibration runs were obtained at higher concentrations of the gas. Slightly higher currents were detected for the descending run at the lower concentration range. In contrast, sulfur dioxide did not show a steady state CV shape. Instead, CV peaks were obtained for both concentration ranges. For the calibration curves, the currents at 1.1 V for the oxidation of ammonia and at -1.2 V for the reduction of sulfur dioxide (see dashed lines in Figure 4.21) were used. A linear relationship between current and gas concentration was still obtained, despite more obvious differences in the current response between the ascending and descending runs. For both gases and both concentration ranges, good linearity between current responses and gas concentrations ( $R^2 >> 0.99$ ) were observed. LOD values of 0.28 ppm for ammonia and 0.25 ppm for sulfur dioxide were obtained, both well below the permissible exposure limit (PEL) of the gases (see Table 4.14).

Table 4.14. Summary of sensitivity, Pearson's correlation coefficient ( $R^2$ ), and limit of detection (LOD) obtained from the calibration experiments from the descending calibration curve at different concentration ranges on the Pt- $\mu$ -pillar IDA electrode.

Gas	Concentration range	Sensitivity	$R^2$	LOD*
NH <sub>3</sub>	High (10 – 50 ppm)	4.9 nA ppm <sup>-1</sup>	0.9972	2.41 ppm
$\mathrm{NH}_3$	Low (1 – 10 ppm)	6.4 nA ppm <sup>-1</sup>	0.9992	0.28 ppm
$SO_2$	High (10 – 50 ppm)	14.0 nA ppm <sup>-1</sup>	0.9983	1.99 ppm
$SO_2$	Low (1 – 10 ppm)	14.8 nA ppm <sup>-1</sup>	0.9994	0.25 ppm

\*LOD was calculated from three times the standard deviation of the line of best fit.



Figure 4.22. Chronoamperometric transients for the electrochemical oxidation of ammonia gas, carried out at +1.1 V, at (a) high (10 - 50 ppm) and (b) low (1 - 10 ppm) concentrations, and the electrochemical reduction of sulfur dioxide gas, carried out at -1.2 V, at (c) high and (d) low concentrations. Dashed line is the response in the absence of the analyte gas. The insets show the background corrected calibration graphs for current vs. concentration for the ascending and descending runs, including the lines of best fit.

Chronoamperometry (CA) experiments were examined as alternative to CV for possible continuous gas sensing. Figure 4.22 shows the chronoamperometric transients for ammonia oxidation and sulfur dioxide reduction for the two concentration ranges, *i.e.* 1 - 10 ppm and 10 - 50 ppm. As can be seen in Figure 4.22a and Figure 4.22b, excellent linear relationships between the transient current response and ammonia concentration were observed for both, the ascending and descending runs. The lowest concentration, *i.e.* 1 ppm of NH<sub>3</sub>, can be clearly differentiated from the blank response

which is also a good indication of a very low limit of detection. The transients for sulfur dioxide (Figure 4.22c and d) change linearly with a change in concentration, but a huge discrepancy in the current between the ascending and descending runs is observed. We have previously shown that sulfur deposits, that block the electrode, can be formed at the electrode of microarray electrodes and result in a decrease in current response (see chapter 4.2). Similar behavior is expected to cause the change in response for Pt- $\mu$ -pillar IDA electrodes, especially as small particles that block the electrode area contribute to a more significant change of the electrode area for smaller electrode sizes.

Long-term chronoamperometry (LTCA) has been attempted for both analyte gases to study the possibility for continuous real-time sensing. However, like the MATFE study in chapter 4.2, a successive decline of current was observed for sulfur dioxide. For ammonia (see Figure 4.23), a similar but less extreme, response decay as for sulfur dioxide was observed. In contrast to sulfur dioxide, ammonia oxidation should not form any solid particles that block the electrode, however, it has been shown that LTCA of ammonia oxidation on platinum electrodes results in electrode fouling<sup>12</sup>. The chronoamperometric transients recorded at 1 ppm of NH<sub>3</sub> gas have been used to calculate the response and recovery time, because it is expected that the thin RTIL film should reduce the response time significantly. Hussain et al. reported a response time of  $315 \pm 20$  s that has been observed for 1 ppm of ammonia gas on a platinum microarray electrode where the RTIL layer thickness of  $0.14 \pm 0.03$  mm was estimated.<sup>13</sup> For the Pt-µ-pillar IDA electrodes, the layer thickness is assumed to be determined by the 30 µm pillar height, *i.e.* the RTIL layer is approximately 5 times thinner. A response time of  $50 \pm 5$  s and a recovery time of  $104 \pm 10$  s was obtained. This is a promising outcome as it suggests that further decreasing of the pillar height could result in even faster response times. A fast response time is an important criterion for gas sensors, especially for toxic gases. However, this has to be appropriately balanced with a sufficient volume of ionic liquid, because electrogenerated product build-up can be more significant with a very thin layer.



Figure 4.23. Long-term chronoamperometry (LTCA) transient for ammonia oxidation calibration, carried out at +1.1 V with periodic introduction of varying concentrations of  $NH_3$  (response phase) and  $N_2$ -purging (recovery phase) in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] on the Pt- $\mu$ -pillar IDA at 10, 8, 6, 4, 2, 1 ppm NH<sub>3</sub> gas, descending followed by ascending concentrations. On the right-hand-side are the background subtracted calibration plots of the ammonia oxidation currents for the (blue) descending and (red) ascending sequence of concentrations, together with the linear regression lines.

## 4.3.4. Conclusions

The electrochemical gas sensing behavior of specially fabricated platinum micro-pillar interdigitated array electrodes has been investigated for ammonia oxidation and sulfur dioxide reduction. The micro pillars present between the electrode fingers resulted in the formation of a thin ionic liquid layer, where the RTIL was spread using capillary force. Electrochemical gas sensing of the two analyte gases, *i.e.* ammonia and sulfur dioxide, gave linear calibration curves for concentration ranges from 1 to 50 ppm via cyclic voltammetry with limits of detection of 0.28 ppm for NH<sub>3</sub> and 0.25 ppm for SO<sub>2</sub>, which are well below the respective permissible exposure limits. Chronoamperometry experiments showed a good linear relationship between current and gas concentration for both, the ascending and descending runs for ammonia. For sulfur dioxide, however, the currents were not reproducible on successive runs, which is most likely caused by sulfur deposits that block the electrode. Long-term chronoamperometry experiments indicated faster response times compared to commercially available MicruX electrodes for ammonia gas due to a thinner electrolyte layer.

The fabricated electrodes appear to be a promising prospect to reduce the response times of electrochemical gas sensors based on viscous ionic liquids. Further work to optimize the electrode materials for longer-term sensing for different gases should therefore be conducted but is out of the scope of this thesis.

## 4.3.5. References

1. Nádherná, M.; Opekar, F.; Reiter, J., Ionic liquid–polymer electrolyte for amperometric solid-state NO<sub>2</sub> sensor. *Electrochim. Acta* **2011**, *56*, 5650-5655.

2. Nádherná, M.; Opekar, F.; Reiter, J.; Štulík, K., A planar, solid-state amperometric sensor for nitrogen dioxide, employing an ionic liquid electrolyte contained in a polymeric matrix. *Sensor Actuat. B-Chem.* **2012**, *161*, 811-817.

3. Wang, R.; Okajima, T.; Kitamura, F.; Ohsaka, T., A Novel Amperometric O<sub>2</sub> Gas Sensor Based on Supported Room-Temperature Ionic Liquid Porous Polyethylene Membrane-Coated Electrodes. *Electroanalysis* **2004**, *16*, 66-72.

4. Lee, J.; Du Plessis, G.; Arrigan, D. W. M.; Silvester, D. S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Anal. Methods* **2015**, *7*, 7327-7335.

5. Lee, J.; Silvester, D. S., Low-cost microarray thin-film electrodes with ionic liquid gel-polymer electrolytes for miniaturised oxygen sensing. *Analyst* **2016**, *141*, 3705-3713.

6. Lee, J.; Hussain, G.; López-Salas, N.; MacFarlane, D. R.; Silvester, D. S., Thin films of poly(vinylidene fluoride-co-hexafluoropropylene)-ionic liquid mixtures as amperometric gas sensing materials for oxygen and ammonia. *Analyst* **2020**, *145*, 1915-1924.

7. Gunawan, C. A.; Ge, M.; Zhao, C., Robust and versatile ionic liquid microarrays achieved by microcontact printing. *Nat. Commun.* **2014**, *5*, 3744.

8. Ge, M.; Hussain, G.; Hibbert, D. B.; Silvester, D. S.; Zhao, C., Ionic Liquidbased Microchannels for Highly Sensitive and Fast Amperometric Detection of Toxic Gases. *Electroanalysis* **2019**, *31*, 66-74.

9. Hussain, G.; Ge, M.; Zhao, C.; Silvester, D. S., Fast responding hydrogen gas sensors using platinum nanoparticle modified microchannels and ionic liquids. *Anal. Chim. Acta* **2019**, *1072*, 35-45.

10. Doblinger, S.; Lee, J.; Gurnah, Z.; Silvester, D. S., Detection of sulfur dioxide at low parts-per-million concentrations using low-cost planar electrodes with ionic liquid electrolytes. *Anal. Chim. Acta* **2020**, *1124*, 156-165.

11. Hussain, G.; Silvester, D. S., Detection of sub-ppm Concentrations of Ammonia in an Ionic Liquid: Enhanced Current Density Using "Filled"Recessed Microarrays. *Anal. Chem.* **2016**, *88*, 12453-12460.

12. Murugappan, K.; Lee, J.; Silvester, D. S., Comparative study of screen printed electrodes for ammonia gas sensing in ionic liquids. *Electrochem. Commun.* **2011**, *13*, 1435-1438.

13. Hussain, G.; Aldous, L.; Silvester, D. S., Preparation of platinum-based 'cauliflower microarrays' for enhanced ammonia gas sensing. *Anal. Chim. Acta* **2019**, *1048*, 12-21.

# 5. Poly(Ionic Liquids) For Electrochemical Gas Sensing

The last two experimental chapters showed how the presence of water influences the electrochemical gas sensing responses in ionic liquids (chapter 3) and how the sensitivity and selectivity of these sensing devices can be improved (chapter 4). However, a main challenge of the gas sensing setup used throughout this research is that the RTIL is a liquid electrolyte that can flow off the planar electrode. As mentioned previously, this can be overcome by either increasing the viscosity of the RTIL by adding a polymer to create a 'gel' or by confining the electrolyte in a certain area.

This final chapter introduces poly(ionic liquids) as alternative electrolyte materials to the previously discussed gel-polymer electrolytes. Mixtures of ionic liquids with poly(ionic liquids) can result in free-standing and peelable membranes. These have been widely studied for gas separation applications, but their use as an electrolyte for amperometric gas sensing applications has not yet been investigated.

## 5.1. Introduction

Commercially available amperometric gas sensors are typically based on the historical Clark type design<sup>1</sup>, composed of two (or three) electrodes, connected with an electrolyte/solvent (usually H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O), and covered with a gas permeable membrane to both retain the solvent inside the sensor, and to impart some selectivity towards different gases like oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>) or ammonia (NH<sub>3</sub>). Their limitations include the evaporation/solidification of the solvent at extremely high or low temperatures, and the high response times caused by the slow diffusion of the analyte through the membrane. The use of room temperature ionic liquids (RTILs) however, can overcome these drawbacks. RTILs are often considered as replacements for conventional electrolyte/solvent systems due to their promising characteristics, such as high conductivity, wide electrochemical windows, good chemical and thermal stability and good solubilization properties.<sup>2-6</sup> They also exist in the liquid state over a broad temperature range and the vapor pressure at room temperature is very low (a few mPa<sup>7</sup> compared to 2620.2 Pa for water<sup>8</sup>), therefore the solvent does not evaporate and can be used in a 'membrane-free' design. However, apart from the high hygroscopicity caused by the ionic nature of RTILs, the flowing of the electrolyte prevents the application in robust commercially available sensors. They are required to be encapsulated due to leakage of the liquid, and the sensor may not be suitable to be used in different orientations.

Lee *et al.*<sup>9</sup> investigated the use of gel-polymer electrolytes (GPEs), which contain commercial polymers mixed with RTILs, for oxygen sensing with cheap planar electrodes. The addition of up to 50 wt.% of poly(methyl methacrylate) (PMMA) to pure [C<sub>2</sub>mim][NTf<sub>2</sub>] resulted in an electrolyte that did not flow but was conductive enough to still be used for oxygen sensing. This combination of a low-cost electrolyte and a low-cost planar electrode device could be used in various orientations and additionally water was successfully repelled from the system. The drawback is, however, lower conductivity values due to the reduced mobility of the ionic liquid cations and anions in the rigid polymer scaffold. Later on, Lee *et al.*<sup>10</sup> studied the suitability of thin films of poly(vinylidene fluoride-co-hexafluoropropylene)/ionic liquid GPEs for amperometric gas sensing of oxygen and ammonia. Highly reproducible currents and fast response times were obtained for both gases. However,

long-term experiments resulted in a staining of the electrolyte due to the suspected degradation of the polymer or build-up of reaction products.<sup>11</sup>

Poly(ionic liquid)s (PILs) are polyelectrolytes that combine the promising characteristics of neat ionic liquids (conductivity, chemical and thermal stability, tenability of the structure) and the physical stability of polymers<sup>12</sup>, and have drawn more and more attention in various fields. Qin et al.<sup>13</sup> showed the application of pyrrolidinium-based PIL membranes as eco-friendly and antibacterial materials in the healthcare sector. In materials science, PEDOT (poly(3,4-ethylenedioxythiophene) has several advantageous properties (high transparency, electrical conductivity, thermal stability) in various applications such as in antistatic coatings, photovoltaic cells, or organic light-emitting diodes (OLEDs). Hydrophobic PEDOT/PIL dispersions have been explored as superior and more stable alternatives to aqueous PEDOT/PSS (poly(styrene sulfonate sodium salt)), which degrade over time due to the presence of water and acidic PSS), in OLEDs.<sup>14-15</sup> PIL-based sensors for pH<sup>16</sup>, ions<sup>17-</sup> <sup>18</sup>, biomolecules<sup>19-21</sup> and gases<sup>22-23</sup> have been explored by different groups. Willa et al.<sup>22</sup> incorporated La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in PIL membranes to detect CO<sub>2</sub> by electrochemical impedance spectroscopy which resulted in good sensitivity in humid environments. Ji et al.<sup>23</sup> combined PILs with single walled carbon nanotubes for carbon dioxide sensing via impedance spectroscopy, which resulted in good selectivity. However, UV irradiation was required to desorb the gas for good reproducibility. No research has been focused on amperometric sensing methods so far. The most active research is performed as membranes for efficient gas sorption and separation<sup>24-26</sup> and as flexible electronics<sup>27</sup>. The most studied gas so far is carbon dioxide due to the high CO<sub>2</sub>-affinity of certain ionic liquids. Various methods for the synthesis of these membranes have been investigated so far, e.g. pure PIL membranes<sup>28-29</sup>, PIL copolymer membranes<sup>30</sup> and neat RTILs incorporated into the PIL structure<sup>31</sup>. Their application as robust electrolytes in amperometric sensors has not been explored in detail so far.

In this chapter, the applicability of PIL/IL membranes for electrochemical purposes was studied by gradually replacing the pure IL with poly(ionic liquids). The suitability of these new materials was assessed by examining the electrochemical window response and the redox behavior of different gases such as oxygen (O<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>). As mentioned previously, the electrochemical behavior of all analytes is already well-studied in neat RTILs by our group<sup>6, 32-33</sup> and by other researchers<sup>34-35</sup>.

## 5.2. Experimental

## 5.2.1. Chemical Reagents

The commercially available RTIL was obtained at the highest purity possible. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>], 99.5%, IoLiTec-Ionic Liquids Technologies GmbH, Heilbronn, Germany) was used as received. Poly(diallyl-1-dimethylammonium bis(trifluoromethylsulfonyl)imide was synthesized according to standard literature procedures<sup>36</sup> and kindly donated by Dr. Liliana Tomé (Universidade Nova de Lisboa, Portugal) and Prof. David Mecerreyes (Ikerbasque, Basque Foundation for Science, Spain). Acetone (CHROMASOLV®, for HPLC,  $\geq$ 99.0%, Sigma-Aldrich) was used as received. A 0.5 M stock solution of H<sub>2</sub>SO<sub>4</sub> (aq) (prepared with ultrapure water from a 95-98 wt.% H<sub>2</sub>SO<sub>4</sub> solution, Ajax Finechem, WA, Australia) was used for the activation of the thin-film electrodes. Sulfur dioxide (509 ppm in nitrogen), ammonia (969 ppm in nitrogen) and oxygen (high purity) were purchased from Coregas (NSW, Australia) and a high purity nitrogen gas (99.99%) cylinder was purchased from BOC Gases (Welshpool, WA, Australia).



Figure 5.1. PIL/IL membrane composed of poly(diallyl-1-dimethylammonium) bis(trifluoromethylsulfonyl)imide ([PolyDADMA][NTf2]) and [C2mim][NTf2] used as electrolyte for electrochemical sensing experiments.

## 5.2.2. PIL/IL Membrane Preparation

Different concentrations of the PIL/IL mixture were prepared according to Table S5.3. The PIL was first weighed in a glass vial and dissolved in the respective amount of acetone. The respective neat ionic liquid quantity was added, and the mixture was stirred overnight at room temperature at a rotation speed of 400 rpm. 19  $\mu$ L of the mixture was drop cast on the electrode and the casting solvent was left to evaporate

slowly at room temperature, by keeping it in a closed environment, resulting in a gelled membrane on the electrode.

## 5.2.3. Electrochemical Experiments

The thin-film electrodes (working electrode disc diameter of 1 mm<sup>2</sup>) were prepared according to the procedure outlined in section 2.2. The respective amount of neat ionic liquid (7  $\mu$ L) or PIL/IL mixture (19  $\mu$ L) was drop-cast to cover all three electrodes on the TFE, and the casting solvent was then evaporated slowly in a closed environment. Afterwards the cell was purged for approximately 30 min under a nitrogen stream at a flowrate of 500 mL min<sup>-1</sup> to remove dissolved gases and impurities such as oxygen and carbon dioxide. For gas sensing experiments, the removal of impurities was monitored by repeated CV scanning until a stable blank response was observed. For all measurements, the integrated CE and RE were used. After obtaining a constant blank, dry analyte gas was introduced into one arm of the T-cell. To obtain different concentrations of the analyte, the respective cylinder was diluted with dry nitrogen through a gas mixing system by adjusting the relative gas flow rates (as described previously). See section 3.1.2.2 for the experimental setup for the humidity study.

## 5.3. **Results and Discussion**

#### 5.3.1. Electrochemical Window of Membranes

A wide operation range is a promising characteristic for robust RTIL-based electrolytes for the detection of analytes in a wide potential range. The suitability of IL/PIL membranes as a highly robust electrolyte without the drawback of a reduced electrochemical window has therefore been studied on two common electrode materials, *i.e.* platinum and gold. It has been shown by some groups that for certain analytes, such as carbon dioxide<sup>37</sup>, platinum is electrochemically inactive, therefore, the applicability of these membranes on gold as an electrode material was also studied. The electrochemical window at a current cut-off of 10  $\mu$ A of three ionic liquid/poly(ionic liquid) (IL/PIL) membranes with weight ratios of 60/40, 40/60 and 20/80 was determined via cyclic voltammetry on a platinum thin-film electrode (Pt-TFE) as shown in Figure 5.2a, and a gold thin-film electrode (Au-TFE) as shown in Figure 5.2b at a scan rate of 100 mV s<sup>-1</sup>. For comparison, the response of pure [C<sub>2</sub>mim][NTf<sub>2</sub>] has been included and shown as a green line.

Significant impurity signals between -0.4 and -1.0 V are observed for pure  $[C_{2}mim][NTf_{2}]$  which were also seen in our previous study (see chapter 3.2). All commercially available imidazolium-based RTILs gave similar quasi-reversible signals that are most likely left over precursors from the synthesis.<sup>38</sup> It is obvious that adding more PIL to the neat  $[C_{2}mim][NTf_{2}]$  in the membranes results in smaller impurity responses, which is probably because the PIL is a solid and is easier to purify post-synthesis compared to the ionic liquid. A membrane composition as high as 80 wt.% PIL showed a slanted electrochemical response caused by large ohmic drop contributions at both the oxidation and reduction limits, as well as significant redox peaks within the scanned window, therefore this membrane was excluded for further studies.

It is assumed that the irreversible reduction of the cation results in the formation of electrogenerated products which cause significant signals in the CV responses. As can be seen in Figure 5.2a, the electrochemical window (EW) increases with higher polymer content on platinum electrodes. This is due to the PIL cation is composed of the electrochemically more stable pyrrolidinium compared to imidazolium. Sharply increasing currents at the oxidation and reduction limits were observed for the pure IL as well as for IL/PIL ratios of 40/60 and 60/40, which indicates that adding relatively large quantities of the polymer does not significantly alter the kinetics of the cation reduction and anion oxidation. On gold electrodes (Figure 5.2b), similar behavior as on Pt-TFEs were observed. However, the effect of wider EWs for higher polymer contents is less pronounced.



Figure 5.2. Cyclic voltammetry showing the electrochemical window of the pure IL and the IL/PIL membranes with the weight ratios of 60/40, 40/60 and 20/80 at a current cut-off of 10  $\mu$ A on a platinum thin-film electrode (a) and a gold thin-film electrode (b). All scans were recorded at 100 mV s<sup>-1</sup>. The black arrows indicate the start potential and scan direction.

In summary, adding PILs to create gelled membranes can not only improve the robustness of the electrolyte, but also give good electrochemical responses as long as the polymer content in the membrane is not too high. An additional benefit is that slightly wider EWs were observed on both electrode materials as well.

### 5.3.2. Oxygen

The electrochemical oxygen reduction reaction (ORR) in RTILs has been studied extensively by several groups<sup>4, 39-40</sup> and the mechanism in shown in section 1.3.1. Figure 5.3 shows the electrochemical response for the reduction of oxygen to superoxide at various concentrations  $(0 - 100 \text{ vol.}\% \text{ O}_2)$  in pure [C<sub>2</sub>mim][NTf<sub>2</sub>] and different ratios of [C<sub>2</sub>mim][NTf<sub>2</sub>] / PIL mixtures (*i.e.* 60/40 and 40/60 wt.%) on platinum thin-film electrodes (Pt-TFEs) at a scan rate of 100 mV s<sup>-1</sup>. Blank measurements in the absence of oxygen are shown as dashed lines. We attempted to also study the mixture with the ratio [C<sub>2</sub>mim][NTf<sub>2</sub>]/PIL (20/80 wt.%), however no clear peak response could be obtained for high oxygen concentrations; only the lower oxygen concentrations, *i.e.* 5 to 40 vol.% resulted in peak like behavior (see supporting information Figure S5.8). Generally, all three membrane compositions showed similar responses where the currents decrease gradually with increasing polymer content in the electrolyte but there is no obvious change in the peak shape observed. The most likely reasons for the lower currents with increasing polymer content are either the lower oxygen solubility in the PIL, or a significantly increased viscosity that results in the slower diffusion of oxygen.

Interestingly, the increasing polymer content results in improved blank responses. In the case of neat [C<sub>2</sub>mim][NTf<sub>2</sub>], a reduction process around the oxygen reduction potential is observed in the presence of non-electrochemically active nitrogen which is caused by impurities in the ionic liquid, *e.g.* imidazole is known to be a common impurity in commercially synthesized ILs.<sup>38</sup> The purification of RTILs is challenging due to the good solubilization properties, in combination with high boiling points, which means that simple distillation or extraction of impurities is often not successful. Solid polymers, however, can be easily separated from the liquid starting materials by precipitation and can be further purified by recrystallization.

Baseline subtracted calibration plots were established as shown in Figure 5.3d, and calibration equations show a highly linear relationship ( $R^2 > 0.999$ ) between the

reduction current *I* and the oxygen concentration (see Table 5.1). The sensitivities (the slope of the calibration line) were seen to decrease with increasing polymer content. However, the limit of detection (LOD) improves with higher PIL content, which is most likely due to a cleaner blank response in the absence of an analyte gas.



Figure 5.3. Cyclic voltammetry for electrochemical oxygen reduction at concentrations between 20 and 100 vol.% in (a) pure IL, (b) 60 wt.% IL / 40 wt.% PIL, (c) 40 wt.% IL / 60 wt.% PIL and (d) the respective baseline corrected calibration curves on a Pt-TFE. The dashed line represents the blank without  $O_2$  at a scan rate of 100 mV s<sup>-1</sup> and an overall flow rate of 500 mL min<sup>-1</sup>.

	Oxygen				Sulfur Dioxide			
Sample	<i>R</i> <sup>2</sup>	Sensitivity /mA vol.% <sup>-1</sup>	LOD <sup>a</sup> /vol.%	ΔE <sub>P</sub> /mV	<i>R</i> <sup>2</sup>	Sensitivity /mA ppm <sup>-1</sup>	LODª /ppm	ΔE <sub>P</sub> /mV
pure IL	0.9996	-57.3	2.9	369	0.9993	-3.8	23	137
60 wt.% IL / 40 wt.% PIL	0.9999	-30.0	1.6	286	0.9997	-2.0	14	142
40 wt.% IL / 60 wt.% PIL	0.9999	-17.8	1.3	286	0.9995	-1.1	19	134

Table 5.1. Summary of Pearson's correlation coefficient  $R^2$ , sensitivity, limit of detection (LOD), and peak-to-peak separation for the highest gas concentration  $\Delta E$  for the electrochemical oxygen reduction, and sulfur dioxide reduction in the previously specified electrolytes.

<sup>a</sup> LOD was calculated from three times the standard deviation of the line of best fit.

#### 5.3.3. Sulfur Dioxide

The voltammetric responses for the reduction of different concentrations of sulfur dioxide (25 to 500 ppm) in pure  $[C_2mim][NTf_2]$  and 60/40 and 40/60 membrane compositions on a Pt-TFE at a scan rate of 100 mV s<sup>-1</sup> are shown in Figure 5.4a – c. Dashed lines represent the response in the absence of the analyte. The corresponding calibration plots (baseline corrected) are shown in Figure 5.4d. The electrochemical mechanism of the reduction of sulfur dioxide has been studied by various researchers, previously<sup>33, 41-42</sup> and has been also discussed in section 1.3.3, but adding the polymer does not seem to change the mechanism, only the magnitude of the current responses.



Figure 5.4. Cyclic voltammetry for the electrochemical sulfur dioxide reduction at concentrations between 25 and 500 ppm in (a) pure IL, (b) 60 wt.% IL / 40 wt.% PIL, (c) 40 wt.% IL / 60 wt.% PIL and (d) the respective baseline corrected calibration curves on a Pt-TFE. The dashed line represents the blank scan without sulfur dioxide at a scan rate of 100 mV s<sup>-1</sup> and an overall flow rate of 500 mL min<sup>-1</sup>.

Generally, the SO<sub>2</sub> reduction peak shapes did not change significantly but the currents decreased with increasing polymer content, as previously shown for oxygen. Also, smaller voltammetric responses in the blank scans (in the absence of SO<sub>2</sub>) can be observed with increasing PIL content. This is significant as it enables the possibility to detect very low concentrations of a toxic analyte gas without any interference from impurity responses. Another promising observation in these experiments is the reduced reference potential shift which is a common occurrence for thin-film electrodes with a pseudo reference electrode. It is suggested that the higher viscosity of the gelled

membranes hinders the diffusion of electrogenerated species from the working electrode towards the reference electrode, altering the electrode surface.

The relationship between the current and the SO<sub>2</sub> concentration is highly linear ( $R^2 > 0.99$ ) for all samples (Table 5.1). Also, the LOD values are slightly lower in the presence of PILs which is an excellent outcome, despite the lower currents. It is noted that the limits of detection are relatively high compared to literature values; however, very low sulfur dioxide concentrations were not yet tested, so future studies using PILs will focus on the reliable detection of concentrations below 10 ppm.

## 5.3.4. Ammonia

The electrochemical ammonia (NH<sub>3</sub>) oxidation mechanism is well-studied in aprotic solvents by Schiffer *et al.*<sup>43</sup> and also as in RTILs by various researchers<sup>44-45</sup> as discussed in section 1.3.2. Therefore, the oxidation of 20 to 500 ppm ammonia gas was performed in the [C<sub>2</sub>mim][NTf<sub>2</sub>]/PIL membranes as well as in pure [C<sub>2</sub>mim][NTf<sub>2</sub>] for comparison. Figure 5.5 summarizes the cyclic voltammetry responses (a–c) on a Pt-TFE taken at a scan rate of 100 mV s<sup>-1</sup> and the respective background subtracted calibration curves in (d).



Figure 5.5. Cyclic voltammetry for electrochemical ammonia oxidation at concentrations between 20 and 500 ppm in (a) pure IL, (b) 60 wt.% IL / 40 wt.% PIL, (c) 40 wt.% IL / 60 wt.% PIL and (d) the respective baseline corrected calibration curves on a Pt-TFE. The dashed line represents the blank scan without ammonia at a scan rate of 100 mV s<sup>-1</sup> and an overall flow rate of 500 mL min<sup>-1</sup>.

	Ammonia				
Sample	<b>R</b> <sup>2</sup>	Sensitivity / mA ppm <sup>-1</sup>	LOD <sup>a</sup> / ppm		
pure IL	0.9960	1.15	54		
60 wt.% IL / 40 wt.% PIL	0.9955	0.68	57		
40 wt.% IL / 60 wt.% PIL	0.9970	0.50	47		

Table 5.2. Summary of Pearson's correlation coefficient  $R^2$ , sensitivity, and calculated limit of detection (LOD), for the electrochemical ammonia oxidation in the different electrolytes.

<sup>a</sup> LOD was calculated from three times the standard deviation of the line of best fit.

Generally, the peak shapes do not change significantly as more poly(ionic liquid) is added. However, the currents become lower for membranes with a higher polymer content. The relationship between the current and NH<sub>3</sub> concentration is highly linear  $(R^2 > 0.99)$  for all samples (see Table 5.2). Also, in contrast to the oxygen and sulfur dioxide experiments, no improvement of the blank CV could be observed because the positive potential region in pure [C<sub>2</sub>mim][NTf<sub>2</sub>] does not show voltammetric responses in the blank scan. The calculated LOD values for all three electrolytes are roughly similar. It is again noted that the limits of detection are relatively high compared to literature values; however lower ammonia concentrations were not yet tested, and this will be the focus of future studies.

## 5.3.5. Humidified Oxygen Gas

Chapter 3.1 of this thesis discussed the effect of water on the oxygen reduction reaction at different humidity level as a function changing the ionic liquid structure. This effect has been attempted to be overcome by adding commercially available polymers, such as PMMA, PEMA or PBMA, which in fact was possible, however, the results were not fully reproducible (see chapter 3.3). Because PIL-based electrolytes showed promising characteristics for electrochemical gas sensing, the humidity test was also performed with these materials. Figure 5.6 shows the cyclic voltammetry response for the electrochemical reduction of 100 vol.% oxygen gas at different humidity levels in the two PIL membranes on platinum thin-film electrodes. A reversible one-electron reduction in dry conditions was observed, as previously discussed. For both compositions, a similar change of the CV shape was obtained at around 18 RH%, where a transition from a single reduction peak to a merged double peak occurred. A further increase in the water content in the gas phase, resulted in a single reduction wave with a significantly more negative current, this is assumed to be due to a change in the mechanism to a 2-electron reduction process, supported by the absence of the superoxide oxidation peak.



Figure 5.6. Cyclic voltammetry response for the electrochemical reduction of 100 vol.% oxygen at different humidity levels in the electrolyte membranes composed of (a) 60 wt.% IL / 40 wt.% PIL and (b) 40 wt.% IL / 60 wt.% PIL on Pt TFEs.

The peak currents were normalized to the peak current at the driest condition and plotted against the relative humidity level (see Figure 5.7). Small current changes up to approximately 10 RH%, followed by a sigmoidal shape between 10 and 60 RH% and an almost plateau-like trend was obtained at high humidities. The results obtained for neat [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] showed similar behavior where a maximum current change of approximately 4 was observed. This suggests that the studied IL/PIL membranes do not show improved capacity to prevent the reaction of superoxide with water in humidified conditions. This could be because the poly(ionic liquid) is still highly charged and therefore attracts water molecules in a similar way as pure ionic liquids; a PIL species with longer alkyl chains or an extended lipophilic moiety in the polymer backbone is assumed to give more promising results.



Figure 5.7. Plot of the normalized cyclic voltammetry current for the electrochemical reduction of 100 vol.% oxygen at different humidity level, normalized to the current obtained at the driest condition in IL/PIL membranes with a composition of 60/40 and 40/60.

## 5.4. Conclusions

Poly(ionic liquid)-based membranes were investigated as robust, non-flowing electrolytes for electrochemical gas sensing on planar thin-film electrodes. Different ratios of polymer to neat ionic liquid content showed only a small influence on the initial electrochemical window, however, a high amount (80 wt.%) of PIL resulted in a change of the cyclic voltammetry shape after consecutive scans which indicates a composition change or high resistance. IL/PIL ratios of 40/60 and 60/40 were used as electrolytes for the electrochemical gas sensing of oxygen, ammonia, and sulfur dioxide. The cyclic voltammetry shapes did not change with increasing polymer content, suggesting the mechanism does not change. Significantly less features in the blank response with the PILs resulted in improved limits of detection, especially for oxygen gas. However, the ionic nature of the polymer meant that the gelled membranes could not prevent the absorption of water at most humidity levels.

The IL/PIL membranes used in this thesis appear to be highly promising alternatives as electrolytes on planar electrodes devices due to their non-flowing nature and featureless blank responses. The possibility to regulate the electrolyte thickness by adjustment of the drop casting mixture composition could result in a very fastresponding gas sensor. Further characterization of these membranes should therefore be conducted in the future, as they show excellent prospects for use in robust membrane-free gas sensing devices for a range of gases.

## 5.5. References

1. Clark, J. L. C.; Wolf, R.; Granger, D.; Taylor, Z., Continuous recording of blood oxygen tensions by polarography. *J. Appl. Physiol.* **1953**, *6*, 189-193.

2. Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R., Room temperature ionic liquids and their mixtures- A Review. *Fluid Phase Equilib.* **2004**, *219*, 93-98.

3. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Mei, T. X., Investigating the electrochemical windows of ionic liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106-112.

4. Buzzeo, M. C.; Hardacre, C.; Compton, R. G., Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.* **2004**, *76*, 4583-4588.

5. Buzzeo, M. C.; Evans, R. G.; Compton, R. G., Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry-A Review. *Chem. Phys. Chem.* **2004**, *5*, 1106-1120.

6. Silvester, D. S.; Compton, R. G., Electrochemistry in room temperature ionic liquids: A review and some possible applications. *Z. Phys. Chem.* **2006**, *220*, 1247-1274.

7. Chowdhury, A.; Thynell, S. T., Confined rapid thermolysis/FTIR/ToF studies of imidazolium-based ionic liquids. *Thermochim. Acta* **2006**, *443*, 159-172.

8. Ambrose, D.; Lawrenson, I. J., The vapour pressure of water. J. Chem. Thermodyn. 1972, 4, 755-761.

9. Lee, J.; Silvester, D. S., Low-cost microarray thin-film electrodes with ionic liquid gel-polymer electrolytes for miniaturised oxygen sensing. *Analyst* **2016**, *141*, 3705-3713.

10. Lee, J.; Hussain, G.; López-Salas, N.; MacFarlane, D. R.; Silvester, D. S., Thin films of poly (vinylidene fluoride-co-hexafluoropropylene)-ionic liquid mixtures as amperometric gas sensing materials for oxygen and ammonia. *Analyst* **2020**, *145*, 1915-1924.

11. Amanchukwu C.V., H. J. R., Shao-Horn Y., Hammond P. T., Understanding the Chemical Stability of Polymer for Lithium-Air Batteries. *Chem. Mater.* **2015**, *27*, 550-561.

12. Mecerreyes, D., Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog. Polym. Sci.* **2011**, *36*, 1629-1648.

13. Qin, J.; Guo, J.; Xu, Q.; Zheng, Z.; Mao, H.; Yan, F., Synthesis of Pyrrolidinium-Type Poly(ionic liquid) Membranes for Antibacterial Applications. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10504-10511.

14. Pozo-Gonzalo, C.; Marcilla, R.; Salsamendi, M.; Mecerreyes, D.; Pomposo, J. A.; Rodríguez, J.; Bolink, H. J., PEDOT:Poly(1-vinyl-3-ethylimidazolium) dispersions as alternative materials for optoelectronic devices. *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 3150-3154.

15. Kim, T. K.; Suh, M.; Kwon, S. J.; Lee, T. H.; Kim, J. E.; Lee, Y. J.; Kim, J. H.; Hong, M. P.; Suh, K. S., Poly(3,4-ethylenedioxythiophene) Derived from Poly(ionic liquid) for the Use as Hole-Injecting Material in Organic Light-Emitting Diodes. *Macromol. Rapid Commun.* **2009**, *30*, 1477-1482.
16. Zhao, Q.; Yin, M.; Zhang, A. P.; Prescher, S.; Antonietti, M.; Yuan, J., Hierarchically Structured Nanoporous Poly(Ionic Liquid) Membranes: Facile Preparation and Application in Fiber-Optic pH Sensing. *J. Am. Chem. Soc.* **2013**, *135*, 5549-5552.

17. Hu, X.; Huang, J.; Zhang, W.; Li, M.; Tao, C.; Li, G., Photonic Ionic Liquids Polymer for Naked-Eye Detection of Anions. *Adv. Mater.* **2008**, *20*, 4074-4078.

18. Huang, J.; Tao, C.; An, Q.; Zhang, W.; Wu, Y.; Li, X.; Shen, D.; Li, G., 3D-ordered macroporous poly(ionic liquid) films as multifunctional materials. *Chem. Commun.* **2010**, *46*, 967-969.

19. Mao, H.; Liang, J.; Zhang, H.; Pei, Q.; Liu, D.; Wu, S.; Zhang, Y.; Song, X.-M., Poly(ionic liquids) functionalized polypyrrole/graphene oxide nanosheets for electrochemical sensor to detect dopamine in the presence of ascorbic acid. *Biosens. Bioelectron.* **2015**, *70*, 289-298.

20. Zhang, Q.; Wu, S.; Zhang, L.; Lu, J.; Verproot, F.; Liu, Y.; Xing, Z.; Li, J.; Song, X.-M., Fabrication of polymeric ionic liquid/graphene nanocomposite for glucose oxidase immobilization and direct electrochemistry. *Biosens. Bioelectron.* **2011**, *26*, 2632-2637.

21. Lee, S.; Ringstrand, B. S.; Stone, D. A.; Firestone, M. A., Electrochemical Activity of Glucose Oxidase on a Poly(ionic liquid)–Au Nanoparticle Composite. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2311-2317.

22. Willa, C.; Yuan, J.; Niederberger, M.; Koziej, D., When Nanoparticles Meet Poly(Ionic Liquid)s: Chemoresistive CO<sub>2</sub> Sensing at Room Temperature. *Adv. Funct. Mater.* **2015**, *25*, 2537-2542.

23. Li, Y.; Li, G.; Wang, X.; Zhu, Z.; Ma, H.; Zhang, T.; Jin, J., Poly(ionic liquid)-wrapped single-walled carbon nanotubes for sub-ppb detection of CO<sub>2</sub>. *Chem. Commun.* **2012**, *48*, 8222-8224.

24. Tang, J.; Sun, W.; Tang, H.; Radosz, M.; Shen, Y., Enhanced CO<sub>2</sub> absorption of poly(ionic liquid)s. *Macromolecules* **2005**, *38*, 2037-2039.

25. Tang, J.; Shen, Y.; Radosz, M.; Sun, W., Isothermal Carbon Dioxide Sorption in Poly(ionic liquid)s. *Ind. Eng. Chem. Res.* **2009**, *48*, 9113-9118.

26. Mineo, P. G.; Livoti, L.; Giannetto, M.; Gulino, A.; Lo Schiavo, S.; Cardiano, P., Very fast CO<sub>2</sub> response and hydrophobic properties of novel poly(ionic liquid)s. *J. Mater. Chem.* **2009**, *19*, 8861-8870.

27. Wang, Z.; Si, Y.; Zhao, C.; Yu, D.; Wang, W.; Sun, G., Flexible and Washable Poly(Ionic Liquid) Nanofibrous Membrane with Moisture Proof Pressure Sensing for Real-Life Wearable Electronics. *ACS Appl. Mater. Interfaces* **2019**, *11*, 27200-27209.

28. Jeffrey Horne, W.; Andrews, M. A.; Shannon, M. S.; Terrill, K. L.; Moon, J. D.; Hayward, S. S.; Bara, J. E., Effect of branched and cycloalkyl functionalities on CO<sub>2</sub> separation performance of poly(IL) membranes. *Sep. Purif. Technol.* **2015**, *155*, 89-95.

29. Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D., Improving CO<sub>2</sub> permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid. *Polym. Adv. Technol.* **2008**, *19*, 1415-1420.

30. Hu, X.; Tang, J.; Blasig, A.; Shen, Y.; Radosz, M., CO<sub>2</sub> permeability, diffusivity and solubility in polyethylene glycol-grafted polyionic membranes and their CO<sub>2</sub> selectivity relative to methane and nitrogen. *J. Membr. Sci.* **2006**, *281*, 130-138.

31. Gouveia, A. S. L.; Ventaja, L.; Tomé, L. C.; Marrucho, I. M., Towards Biohydrogen Separation Using Poly(Ionic Liquid)/Ionic Liquid Composite Membranes. *Membranes* **2018**, *8*, 124.

32. Kang, C.; Lee, J.; Silvester, D. S., Electroreduction of 2,4,6-Trinitrotoluene in Room Temperature Ionic Liquids: Evidence of an EC2 Mechanism. *J. Phys. Chem. C* **2016**, *120*, 10997-11005.

33. Barrosse-Antle, L. E.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Electroreduction of Sulfur Dioxide in Some Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2008**, *112*, 3398-3404.

34. Nagy, L.; Gyetvai, G.; Kollár, L.; Nagy, G., Electrochemical behavior of ferrocene in ionic liquid media. *J. Biochem. Biophys. Methods* **2006**, *69*, 121-132.

35. Khan, A.; Lu, X.; Aldous, L.; Zhao, C., Oxygen Reduction Reaction in Room Temperature Protic Ionic Liquids. *J. Phys. Chem. C* **2013**, *117*, 18334-18342.

36. Pont, A.-L.; Marcilla, R.; De Meatza, I.; Grande, H.; Mecerreyes, D., Pyrrolidinium-based polymeric ionic liquids as mechanically and electrochemically stable polymer electrolytes. *Journal of Power Sources* **2009**, *188*, 558-563.

37. Tanner, E. E. L.; Batchelor-McAuley, C.; Compton, R. G., Carbon Dioxide Reduction in Room-Temperature Ionic Liquids: The Effect of the Choice of Electrode Material, Cation, and Anion. *J. Phys. Chem. C* **2016**, *120*, 26442-26447.

38. Holbrey, J. D.; Seddon, K. R.; Wareing, R., A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. *Green Chem.* **2001**, *3*, 33-36.

39. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M.; Tan, X. M., Electrochemical reduction of dioxygen in Bis(trifluoromethylsulfonyl)imide based ionic liquids. *J. Electroanal. Chem.* **2011**, *657*, 150-157.

40. Barnes, A. S.; Rogers, E. I.; Streeter, I.; Aldous, L.; Hardacre, C.; Wildgoose, G. G.; Compton, R. G., Unusual Voltammetry of the Reduction of  $O_2$  in  $[C_4dmim][N(Tf)_2]$  Reveals a Strong Interaction of  $O_2^{-}$  with the  $[C_4dmim]^+$  Cation. J. *Phys. Chem. C* **2008**, *112*, 13709-13715.

41. Potteau, E.; Levillain, E.; Lelieur, j.-P., Mechanism of the electrochemical reduction of sulfur dioxide in non-aqueous solvents. *J. Electroanal. Chem.* **1999**, *476*, 15-25.

42. Neta, P.; Huie, R. E.; Harriman, A., One-Electron-Transfer Reactions of the Couple SO<sub>2</sub>/SO<sub>2</sub><sup>-</sup> in Aqueous Solutions. Pulse Radiolytic and Cyclic Voltammetric Studies. *J. Phys. Chem.* **1987**, *91*, 1606-1611.

43. Schiffer, Z.; Lazouski, N.; Corbin, N.; Manthiram, K. In *Rate-Determining Step and Mechanistic Understanding of Electrochemical Ammonia Oxidation in a Non-Aqueous Electrolyte*, 2019 North American Catalysis Society Meeting, NAM: 2019.

44. Ji, X.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G., Mechanistic Studies of the Electro-oxidation Pathway of Ammonia in Several Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 9562-9572.

45. Buzzeo, M. C.; Giovanelli, D.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Elucidation of the Electrochemical Oxidation Pathway of Ammonia in Dimethylformamide and the Room Temperature Ionic Liquid, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Electroanalysis* **2004**, *16*, 888-896.

## 5.6. Supporting Information

Table S5.3. Masses of PIL, IL and acetone used for the preparation of the membrane. Calculated IL percentage in the membrane after evaporation of the casting solvent and IL/PIL content in the mixture.

Sample	m(PIL)	$m([C_2mim][NTf_2])$	<i>m</i> (acetone)	% IL	% IL/PIL
	/ <b>mg</b>	/ <b>mg</b>	/ <b>mg</b>	/ wt.%	/ wt.%
20 wt.% IL /	160.5	41.0	347.7	20.3	36.7
80 wt.% PIL					
40 wt.% IL /	120.7	80.7	355.1	40.1	36.2
60 wt.% PIL					
60 wt.% IL /	80.9	121.6	353.9	60.0	36.4
40 wt.% PIL					



Figure S5.8. Cyclic voltammetry response for the oxygen reduction reaction in the membrane composed of 20 wt.% IL / 80 wt.% PIL.



Figure S5.9. Plot of peak current (I) vs. square root of scan rate (v) for the electrochemical reduction of 100 vol.% oxygen in pure [ $C_{2}$ mim][ $NTf_{2}$ ] and IL/PIL membranes with weight ratios of 60/40 and 40/60 on platinum thin-film electrodes. Scans were taken at 2000, 1000, 750, 500, 250, 100, 50 and 10 mV s<sup>-1</sup>.

# 6. Conclusions and Future Outlook 6.1. Conclusions

The work reported in this thesis gives significant fundamental insights into the application of room temperature ionic liquids (RTILs) as electrolytes in electrochemical gas sensors for toxic gases such as sulfur dioxide or ammonia, and vital gases, such as oxygen. Investigations have been conducted to improve the robustness of the planar sensing devices so that they can be applied outside of ideal 'dry' laboratory conditions.

The influence of humidity on the electrochemical response was investigated for ammonia and oxygen gas as well as the electrochemical window, which was studied via cyclic voltammetry. The electrochemical oxygen reduction mechanism was found to be greatly affected by the presence of water. However, varying the ionic liquid cation and anion structures can alter the structure of the electrical double layer at the electrode and therefore prevent the reaction of the electrogenerated superoxide radical with water. For ammonia gas, the presence of water does not directly affect the electrochemical mechanism, however, water significantly changes the electrochemical window (operation range of the electrolyte). This resulted in a higher than expected current response which must be considered for the sensing of analytes in humid conditions, especially where the redox potential of the analyte is close to the limits of the electrochemical window. The addition of commercially available neutral polymers to ionic liquids showed a partial improvement in terms of blocking water, however, it also resulted in a large drop of conductivity and the observation of some nonhomogeneous electrolyte compositions and irreproducible electrochemical behavior.

The selectivity of gas sensors towards certain target gases can be influenced by the properties of the electrolyte. RTILs with various functional groups have been synthesized and the influence of the gas solubility of oxygen, hydrogen and sulfur dioxide has been studied. The increased polarity of the side chains in the ionic liquid cation was assumed to increase the gas solubility of the polar sulfur dioxide over non-polar gases, like oxygen or hydrogen. However, no significantly increased selectivity towards sulfur dioxide was observed for the synthesized RTILs, as all three gases were physically solubilized. Therefore, the gas solubilities increased with molar volume and

only a small contribution of the polar side groups were observed. The variation of the electrode material and geometry was studied to increase the selectivity of sulfur dioxide gas sensing devices. Platinum showed better electrochemical responses than gold on commercially available thin-film electrodes. Linear relationships between current response and gas concentration were obtained for macro-, microarray and interdigitated electrodes via cyclic voltammetry. However, a significant current decay over time has been observed for smaller electrode sizes, *i.e.* microarray and interdigitated electrodes, when continuous gas sensing has been attempted via long-term chronoamperometry. It has been shown that solid sulfur particles can form and block the electrode surface, which has a significantly more severe effect for smaller electrode sizes. An attempt to use capillary force to form a thin and uniform layer of ionic liquid to reduce the response time showed promising results for future electrode designs.

To overcome the flow of ionic liquids from planar electrode devices, freestanding poly(ionic liquid) (PIL) membranes have been investigated as alternative electrolytes. These membranes combine the characteristics of polymers, such as mechanical stability, with the physico-chemical characteristics of ionic liquids, like good electrochemical stability, wide electrochemical windows and good solubility properties. Preliminary investigations confirmed that a PIL content of 40 wt.% is enough to form freestanding and peelable membranes with an identical (or slightly larger) electrochemical window compared to pure RTILs. Linear calibration curves via cyclic voltammetry have been obtained for the three gases, oxygen, ammonia and sulfur dioxide, where decreased current responses and lower sensitivities were observed with increasing polymer content. In contrast, typical impurity signals that were observed in neat RTILs are significantly decreased which allows the easier identification of low currents in the negative potential window region.

### 6.2. Future Outlook

The work discussed in this thesis provides insights into the challenges and improvements of ionic liquid-based gas sensors for the application in real world environments.

Room temperature ionic liquids have been well studied in laboratory conditions, however, the performance in real-world environments with several varying conditions,

such as humidity, temperature and mixed gases, has not been studied so far. This thesis has shown that the presence of humidity can significantly alter the properties of RTILs. Future research in the calibration of ionic liquid-based gas sensors for different analytes must consider the change of the electrochemical responses in the presence of various humidity levels. For ammonia gas for example, the change in humidity mainly influences diffusion behavior as well as the electrochemical window, this can be easily adjusted for by a correction factor that considers the relative current change at different humidities for each gas concentration. This must be done for every gas and ionic liquid separately as the RTIL properties are highly structure dependent. For gases such as oxygen, where a change of the electrochemical mechanism is observed, further research is required to determine whether the build-up of by-products in the electrolyte causes a loss of the sensing capacity. Further research is required to analyze the influence of temperature or pressure on the current response, which could result in additional correction factors for the calibration curve.

Chapter 4 discussed some attempts to influence the sensitivity and selectivity of gas sensing devices. The modification of the ionic liquid structure to increase the selectivity towards certain gases did not show significantly improved behavior, however, this should be a focus point for future research, as this could result in highly selective electrolytes. Further functional groups such as amines, thiols or sulfates could be studied in future investigations. The physico-chemical as well as the electrochemical performance must be studied to evaluate whether these task specific analytes can actually be alternatives to commercially available ionic liquids. It has also been shown that the electrode material and geometry can greatly affect the electrochemical responses. Platinum has been shown to be a more ideal material over gold, so other, less expensive materials (like graphite or copper) could also be used to keep the electrode costs even lower. The comparison between macro, microarray and interdigitated electrodes revealed good sensitivities and responses via cyclic voltammetry for sulfur dioxide sensing. A continuous long-term detection of SO<sub>2</sub> via long-term chronoamperometry was not successful on platinum. However, a change of the electrode material where no sulfur deposits are formed, would be of benefit. In terms of shorter response times, the Pt-µ-pillar IDA electrodes showed highly promising results. The implementation of the capillary effect to macro sized electrodes could be a future research focus to exactly define the RTIL thickness on the electrode,

and it is predicted that a further decrease of the pillar height might give even shorter response times.

The planar and commercially available MicruX electrode devices are a good starting point for miniaturized gas sensors. Ionic liquids have shown promising characteristics for electrochemical applications in their pure state, however, this thesis also showed multiple drawbacks when the electrolyte is exposed to ambient conditions. The last experimental chapter has solved the problem of the limitations in the orientation, the sensing devices can be used. Poly(ionic liquid) membranes offered similar electrochemical properties to pure RTILs, but with the extra benefit of the increased mechanical stability, resulting in a more robust gas sensor device. Significantly more research is required to determine the long-term stability of these membranes. It must be also studied whether property trends established for neat RTILs, like gas solubilities, temperature and pressure stability and hygroscopicity, are also valid for PIL/IL membranes. In addition, so far only one membrane composition has been investigated, the incorporation of different ionic liquid structures into the membrane could further improve the robustness of the material.

With that said, the humidity studies and the research on the sensitivity and selectivity of these ionic liquid-based planar gas sensing devices give several insights into the fundamental aspects. However, for a more applied purpose, the research on PIL/IL membranes as electrolytes is more promising due to a significantly more robust gas sensor device. The fact that the electrolyte thickness can be adjusted by dilution of the PIL/IL/acetone mixture or alternatively by spin casting gives hope for very fast responding sensors. Additionally, these electrolyte membranes could be also applied for the sensing of analytes that are present in aqueous or non-aqueous solutions, where the analyte is extracted from the liquid phase into the membrane. After the extraction process, the setup can be used straight away for electrochemical sensing experiments without any additional preparation steps. This could result in easy-to-use sensing devices for onsite sensing.

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

# Appendix

### Effect of Ionic Liquid Structure on the Oxygen Reduction Reaction Under Humidified Conditions

Author: Simon Doblinger, Junqiao Lee, Debbie S. Silvester ACS Publications

Publication: The Journal of Physical Chemistry C Publisher: American Chemical Society Date: May 1, 2019

Copyright © 2019, American Chemical Society

#### PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

 Permission is granted for your request in both print and electronic formats, and translations.
 If figures and/or tables were requested, they may be adapted or used in part.
 Please print this page for your records and send a copy of it to your publisher/graduate school.
 Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {VER} American Chemical Society." Insert appropriate information in place of the capitalized words.
 One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any user, places cubmit a new request. uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

<u>BACK</u> 



**ACS** Publications Publication: The Journal of Physical Chemistry C Publisher: American Chemical Society Date: Sep 1, 2020

Copyright © 2020, American Chemical Society

### PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.

- Permission is granted for your request in both print and electronic formats, and translations.
 - If givers and/or tables were requested, they may be adapted or used in part.
 - Please print this page for your records and send a copy of it to your publisher/graduate school.
 - Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
 - One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any provide the top the superstance of the

uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

RUID PHASE EQUILIBRIA A ditistication and and Fund phase EQUILIBRIA	Functionalized Imidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids for Gas Sensors: Solubility of H2, O2 Author: S. Doblinger,D.S. Silvester,M. Costa Gomes Publication: Fluid Phase Equilibria Publisher: Elsevier Date: 1 December 2021 © 2021 Elsevier B.V. All rights reserved.
Journal Author Please note that, not required, but visit: https://www. BACK	Rights as the author of this Elsevier article, you retain the right to include it in a thesis or dissertation, provided it is not published commercially. Permission is please ensure that you reference the journal as the original source. For more information on this and on your other retained rights, please elsevier.com/about/our-business/policies/copyright#Author-rights CLOSE WINDOW
© 2021 Convertent All Bi	abre Berneried L. Constricts Claster Inc. L. Brivers et tempert. L. Terms and Conditions

Comments? We would like to hear from you. E-mail us at customercare@copyright.com

**CLOSE WINDOW** 

**CLOSE WINDOW** 

	Detection of sulfur dioxide at low parts-per-million concentrations using low-cost planar electrodes with ionic liquid electrolytes Author: Simon Doblinger,Junqiao Lee,Zoe Gurnah,Debbie S. Silvester Publication: Analytica Chimica Acta Publisher: Elsevier Date: 8 August 2020
Journal Author Please note that, a not required, but	Rights Is the author of this Elsevier article, you retain the right to include it in a thesis or dissertation, provided it is not published commercially. Permission is please ensure that you reference the journal as the original source. For more information on this and on your other retained rights, please

CLOSE WINDOW