Effect of Humidity and Impurities on the Electrochemical Window of Ionic Liquids and its Implications for Electroanalysis

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Abstract

Replacing conventional aqueous-based electrolytes with room temperature ionic liquids (RTILs) for electrochemical applications is a major research focus. However, in applications where RTILs are exposed to real-world environments, their hygroscopic nature affects their promising physicochemical properties, such as broad electrochemical windows (EWs) and high chemical stability. In this study, the electrochemical windows of nine commercially available RTILs have been determined on platinum thin-film electrodes in 'dry' conditions (4.3 – 6.5 V) via cyclic voltammetry, and a systematic study over a wide humidity range (relative humidity (RH) between <1 to >95%) has been carried out. A significant reduction in the EW occurs even at low moisture contents (<10 RH%), which is especially evident for the most electrochemically stable ions in the study (i.e. $[C_4mpyrr]^+$, $[FAP]^-$ and $[NTf_2]^-$). At saturated water levels, the electrochemical windows come close to that of water (approximately 2 V) regardless of the cation or anion structure, where the electrolyte behaviour changes from 'water-in-RTIL' to 'RTIL-in-water'. Additionally, the appearance of redox peaks from dissolved impurities inherent to the RTIL becomes more obvious with increasing water content. The effect of moisture on the electrochemical response of two model species where the presence of water does not alter the electrochemical mechanism, i.e. decamethylferrocene and ammonia, was also studied. For ammonia, the increase in current is not only caused by a change in the transport properties of the electrolyte (lower viscosity), but also by the shift in the anodic limit of the electrochemical window. This is believed to be the most detailed study of the effect of water on RTILs over a wide humidity range, and emphasises the importance of understanding the effect on voltammetric responses of dissolved species in RTILs under different environmental conditions.

Keywords

Room temperature ionic liquids; electrochemical window; humidity; water; thin-film electrodes; cyclic voltammetry; decamethylferrocene; ammonia

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 solubilisation properties, high chemical and thermal stability, in combination with broad electrochemical windows.[1-2] Their application as electrolytes in batteries[3] and fuel cells[4], as solvents in organic synthesis[5] or as lubricants[6-7] 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.[5, 8] However, their ionic nature results in a highly hygroscopic characteristic, the strength of which depends upon the exact cation-anion combination. COSMO-RS calculations[9] as well as experimental studies[10-11] 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.[12-13] 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 solubilisation 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.[15-24] The voltammetric responses of various gases in RTILs including oxygen[25-26], nitrogen dioxide[27], ammonia gas[28] and hydrogen sulfide[29] 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.[30] studied the effect of water on electrochemical oxygen sensing in ‘dry’ and ‘wet’ $[C_4mim][BF_4]$ 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 water-saturated electrolyte. We previously demonstrated the effect of the RTIL structure on the ORR in various RTILs[31], where it is known that in dry conditions, a reversible one-electron reduction to superoxide is observed.[32] The presence of moisture, however, changes the mechanism to an irreversible two- or even four-electron process, depending on the amount of water.[33-35] At low relative humidity (RH) levels, the ionic liquid cation structure significantly alters the availability of water within the electric 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’.[31] This is because RTILs form structures at electrified interfaces[36-38], 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 supressed or enhanced by changing the cation and anion combination of the ionic liquid.[31]

O'Mahony et al.[11] 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_2mim][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^{-2}.[11] 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.[39] 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 nonpolar 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_3) 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.

2. Experimental

2.1. Chemical reagents

All RTILs were obtained at the highest purities possible from commercial suppliers. Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide ([$S_{2,2,1}$][NTf_2], 99%, IoLiTec-Ionic Liquids Technologies GmbH, Heilbronn, Germany), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([$N_{4,1,1,1}$][NTf_2], 99.5%, IoLiTec), butylmethylpyrrolidinium bis(trifluoromethylsulfonium)imide ([C_4mpyrr][NTf_2], 99.5%, IoLiTec), butylmethylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([C_4mpyrr][FAP], high purity >99%, Merck Pty. Ltd. Kilsyth, Victoria, Australia), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim][NTf_2], 99.5%, IoLiTec), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][NTf_2], 99.5%, IoLiTec), 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4], 99%, IoLiTec), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6], high purity >99%, Merck), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C_4mim][FAP], high purity >99%, Merck) were used as received. Ultrapure water with a resistivity of 18.2 MΩ 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 (CHROMASOLV®, for HPLC, ≥99.0 %, Sigma-Aldrich) and bis(pentamethylcyclopentadienyl)iron(II) (DmFc, 97%, Sigma-Aldrich) were used as received. A saturated DmFc solution in [C_4mpyrr][NTf_2] was prepared by dissolving 5 mg of the solid in 0.5 mL of ionic liquid. An aliquot of 1 µL of the supernatant was then used for the electrochemical experiment. A 0.5 M stock solution of H_2SO_4(aq) (prepared with ultrapure water from a 95-98 wt.% H_2SO_4 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).

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 aluminium 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^2). Wires were soldered onto the connecting pads of the chip. The WE was electrochemically activated prior to each experiment by CV cycling (≈ 100 times) at 1 V s^{-1} in nitrogen purged 0.5 M $H_2SO_{4(aq)}$ 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[40-41] have shown an excellent reproducibility (within ~2–5 %) for electrochemical current responses on these TFEs.

1 µL 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^{-1} 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^{-1} was introduced into one arm of a modified glass T-cell[42] for the potential window and DmFc experiments. For the NH_3 experiments, dry ammonia gas with a flow rate on 125 mL min^{-1} 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^{-1}. The detailed experimental set-up is shown in our previous work.[31]

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 ~10–100 ppm range)[11] 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_3 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,[43] 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. 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 is studied via cyclic voltammetry (CV), showing how water reduces the electrochemical window (EW) and promotes the observation of dissolved impurities already present in the ionic liquids. We also demonstrate how the presence of moisture in [C_4mpyrr][NTf_2] affects the voltammetry of two dissolved species (decamethylferrocene (DmFc) and ammonia (NH_3)), whose electrochemical reaction mechanisms are known to be unaffected by follow-up reactions in the presence of water.

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 analysing the cyclic voltammetry response on a platinum thin-film electrode (Pt-TFE) at a scan rate of 100 mV s^{-1}. 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^{-2}.[11, 39, 44-45] 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^{-2} current density) (blue) as well as 1.5 µA (~0.19 mA cm^{-2} current density) (red) (Figure 1). 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.[11, 14, 45-48] Due to the use of a pseudo platinum 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 1 a, b, d, e and g), the trend of the widest electrochemical window, and therefore most electrochemically 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[49], imidazolium based cations are more easily reduced compared to single centred cations like pyrolidinium 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 1 c, e, f and i) is: $[BF_4]^- < [PF_6]^- \approx [NTf_2]^- < [FAP]^-$. This is in contrast to the trend of increasing stability from $[NTf_2]^- < [BF_4]^- < [PF_6]^-$ established via computational calculations by Kazemiabnavi et al.[50]. 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_4mpyrr][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.[51] De Giorgio et al.[52] 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 cut-off current of 1.5 µA because this is a typical current response for gases (e.g. for 20% of oxygen on these TFEs), therefore the CV scan was reversed at +/- 1.5 µA to determine the EWs (see narrower dashed lines in Figure 1 and solid black line in Figure 2). 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 centred 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.

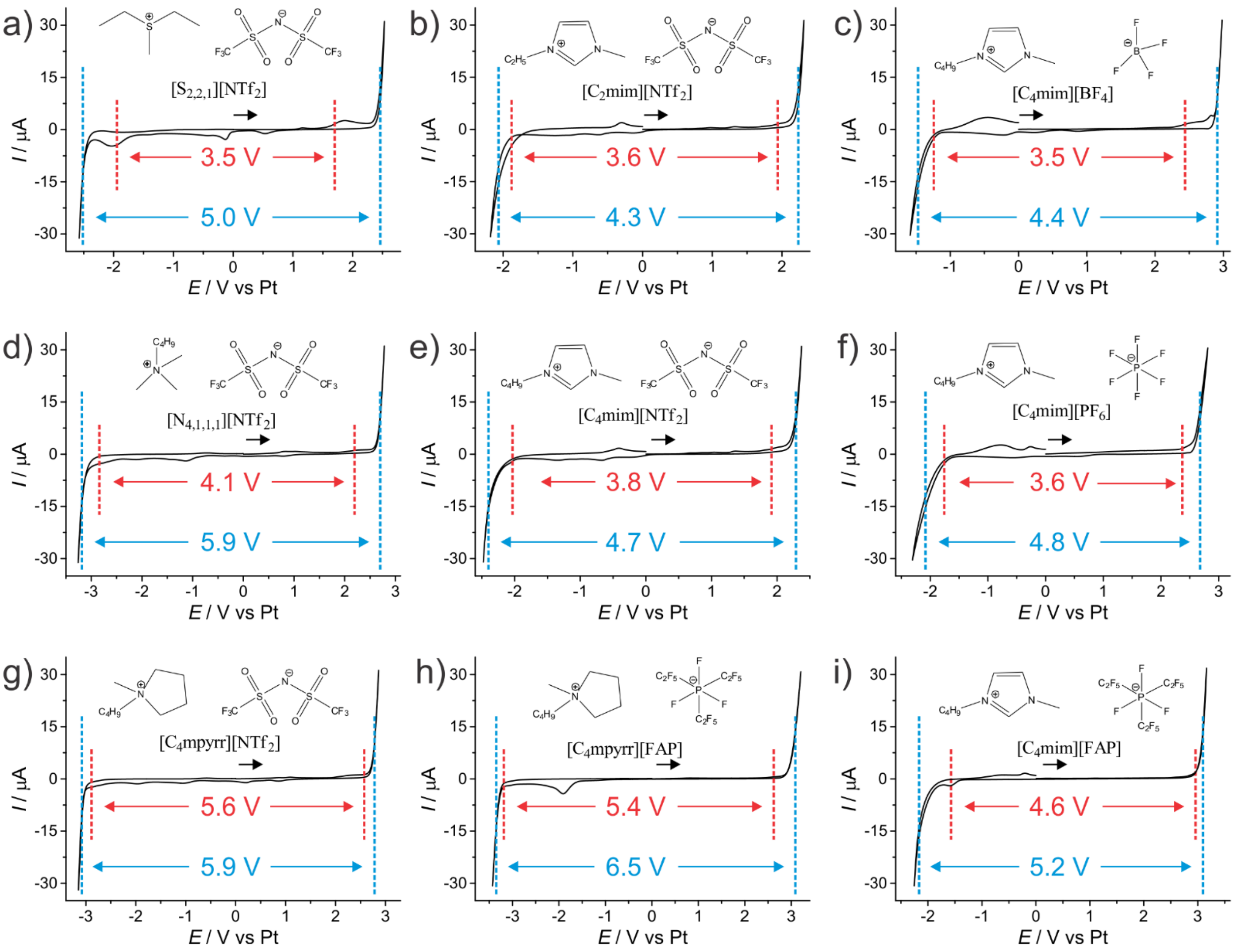

Figure 1. Electrochemical window and chemical structures of a) $[S_{2,2,1}][NTf_2]$, b) $[C_2mim][NTf_2]$, c) $[C_4mim][BF_4]$, d) $[N_{4,1,1,1}][NTf_2]$, e) $[C_4mim][NTf_2]$, f) $[C_4mim][PF_6]$, g) $[C_4mpyrr][NTf_2]$, h) $[C_4mpyrr][FAP]$ and i) $[C_4mim][FAP]$ on a platinum thin-film electrode at <1 RH%. The red dashed lines represent a cut-off current of 1.5 µA and the blue dashed line shows a cut-off current of 15 µA. All scans were taken at 100 mV s^{-1}. The black arrows indicate the start potential and the scan direction.

Figure 2 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^{-1}, with a cut-off current of +/- 1.5 µA to minimise 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 $[C_2mim][NTf_2]$ (Figure 2b) and $[N_{4,1,1,1}][NTf_2]$ (Figure 2d), still contain redox active impurities in the available EW. Also $[C_4mpyrr][NTf_2]$ (Figure 2g) shows large quasi-reversible voltammetric responses close to both the cathodic, as well as the anodic, limit of the scanned window.

As can be seen in Figure 2, most of the imidazolium based ionic liquids (Figure 2 b, 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.[31] Similar behaviour is observed for the ammonium RTIL in Figure 2d. As mentioned, the purification of ionic liquids is quite challenging due to their good solubilisation properties and low vapour pressures. Residues from the synthesis are therefore most likely causing voltammetric responses, e.g. imidazole is known to be a common impurity in commercially synthesised ILs.[53] 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 2.

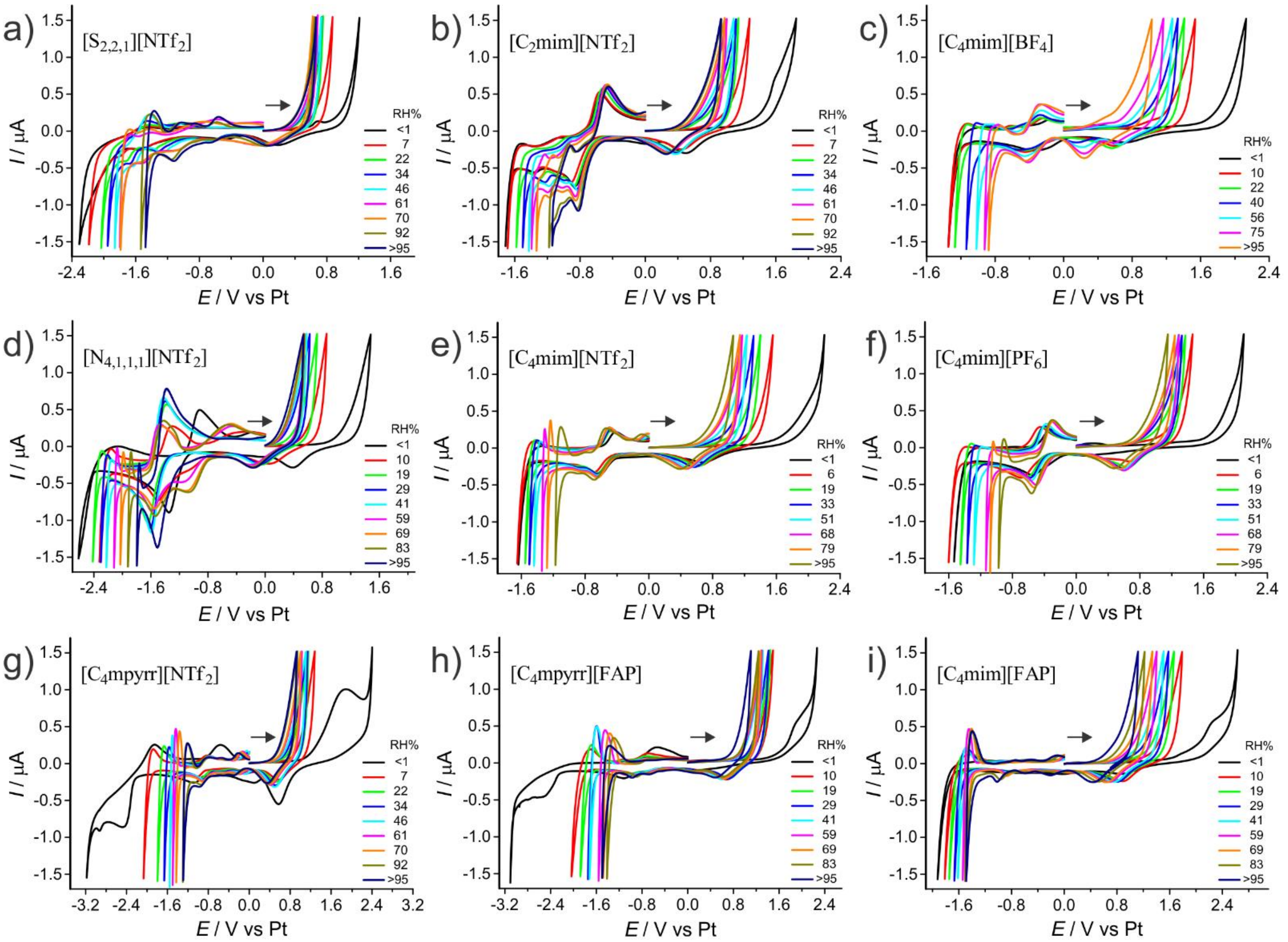

Figure 2. Effect of increasing relative humidity (RH%) on the electrochemical window of the RTILs a) [S$_{2,2,1}$][NTf$_2$], b) [C$_2$mim][NTf$_2$], c) [C$_4$mim][BF$_4$], d) [N$_{4,1,1,1}$][NTf$_2$], e) [C$_4$mim][NTf$_2$], f) [C$_4$mim][PF$_6$], g) [C$_4$mpyrr][NTf$_2$], h) [C$_4$mpyrr][FAP] and i) [C$_4$mim][FAP] on a platinum thin-film electrode at a scan rate of 100 mV s^{-1}. 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.[39] 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 using the intentionally dissolved species decamethylferrocene (DmFc), where the electrochemical behaviour is quite well known.

Table 1 summarizes the total electrochemical window (EW$_{\text{total}}$) of all nine RTILs at a cut-off current of 15 μA (at <1 RH%), 1.5 μA (at <1 RH%) and 1.5 μA (at >95 RH%). Table S1 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.[54] 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 1. Total electrochemical windows of nine RTILs at cut-off currents of 15 µA (~1.9 mA cm^{-2} current density) at <1 RH%, 1.5 µA (~0.19 mA cm^{-2} current density) at <1 RH% and 1.5 µA at >95 RH%.

	I_{cutoff} = 15 uA, <1 RH%	I_{cutoff} = 1.5 uA, <1 RH%	I_{cutoff} = 1.5 uA, >95 RH%
RTIL	EW$_{\text{total}}$ / V	EW$_{\text{total}}$ / V	EW$_{\text{total}}$ / 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_4mpyrr][NTf_2]	5.9	5.6	2.3
[C_4mpyrr][FAP]	6.5	5.4	2.6
[C_2mim][NTf_2]	4.3	3.6	2.0
[C_4mim][BF_4]	4.4	3.5	1.8
[C_4mim][PF_6]	4.8	3.6	2.1
[C_4mim][NTf_2]	4.7	3.8	2.2
[C_4mim][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.[55]. 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 S1 in the supporting information shows that scanning over a much wider potential range results in a plateau current where water has been electrolysed. However, consecutive scans bring about a colour change of the RTIL from colourless 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.[11] are expected. Comparing the “vacuum-dried” values at current densities of 1 mA cm^{-2} with our values at currents of 15 µA at <1 RH% (which equals 1.9 mA cm^{-2} considering our geometric working electrode area of 0.785 mm^2), similar values are observed. The “wet” values reported by O’Mahony et al.[11] are between 1.6 V for [C_4mim][I] to 2.9 V for [C_4dmim][NTf_2], which is in the same range as our reported values at >95 RH% (between 1.8 V for [C_4mim][BF_4] and 2.6 V for the two [FAP]$^-$-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.[56]

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 2 that the presence of water causes further limitations to the electrochemical window. Figure 3 shows the cathodic and anodic electrochemical window values at a cut-off current of 1.5 µA as a function of the relative humidity (RH) for a range of RTILs with the same cation, [C_4mim]$^+$, (Figure 3a) and a range of RTILs with the same anion, [NTf_2]$^-$, (Figure 3b). 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

[C4mim][FAP] in dry conditions, but the effect of water under saturated conditions is mostly the same (Figure 3a). For the same anion (Figure 3b), only [C4mpyrr][NTf2] 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.

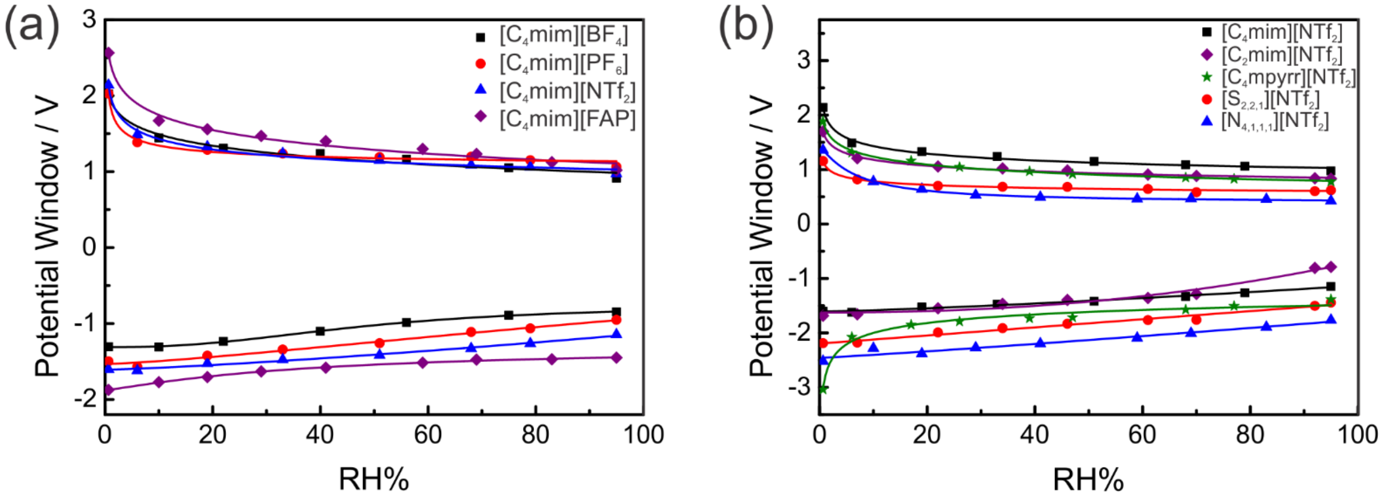

Figure 3. Plot of electrochemical window at cut-off currents of +/- 1.5 µA versus relative humidity level (RH%) for RTILs with the same cation (a) and the same anion (b).

Various literature articles have shown the formation of well-defined interfacial structures of RTILs at charged interfaces[36, 57], which has been investigated using different experimental methods, including atomic force microscopy (AFM)[38, 58], surface-enhanced infrared absorption spectroscopy (SEIRAS)[59] and sum frequency generation vibrational spectroscopy (SFG-VS).[60] These studies reveal that the electric 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.[61] 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.[62] 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.[62] This can be also seen in our results in Figure 3, 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), supports the predictions by Feng et al.[62], 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[31] 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 are 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 nonpolar moieties in the chemical structure can result in hydrophobic pockets formed by nonpolar groups in the RTIL structure, especially in the presence of water as has been discussed by Hayes et al.[36] However, this behaviour 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 4. 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 4a). In the presence of water, it is likely that partially solvated RTIL ions balance the electrode charge (Figure 4b). 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 nonpolar 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 oxidised. We suggest that the electrolyte composition inside the electrical double layer changes from 'water-in-RTIL'- to 'RTIL-in-water' behaviour from 'dry' to 'humidified' conditions (see Figure 4), i.e. comparable to a conventional electrolyte/solvent system.[63] In hydrophobic RTILs such as [C$_4$mpyrr][NTf$_2$], the bulk-phase water content in a water-saturated sample is around 1.1 wt.%[11], 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 4) in water-controlled environments, as well as the influence of the RTIL structure.

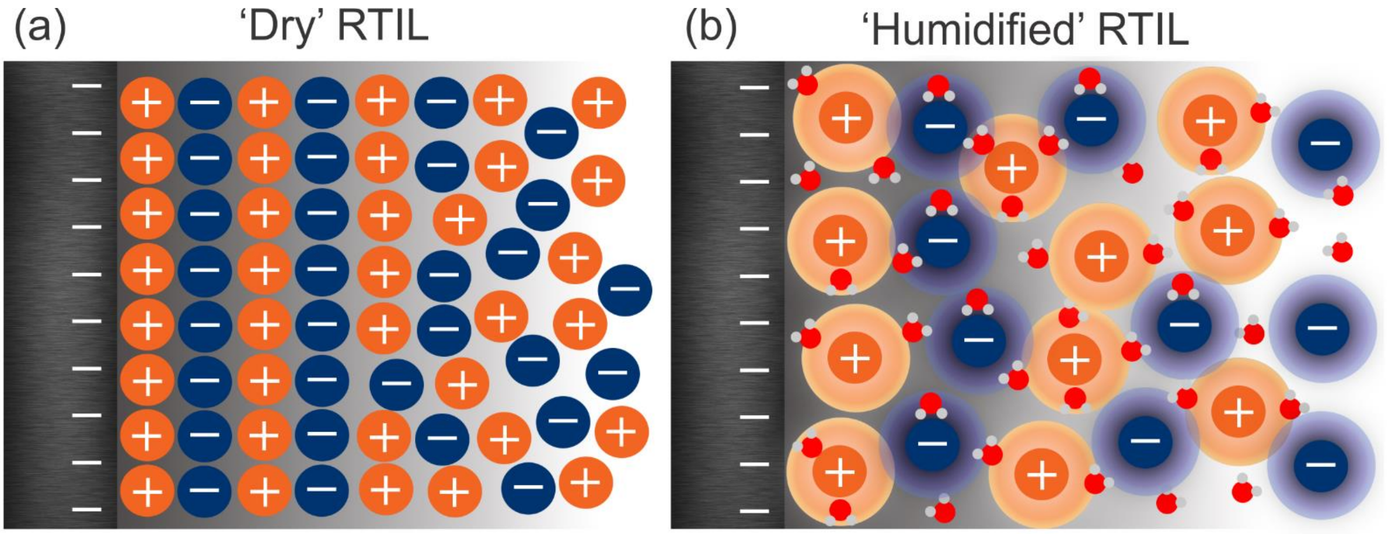

Figure 4. Schematic illustration of the suggested structures of room temperature ionic liquids at a negatively charged surface in dry (a) and highly humidified conditions (b).[64] The ionic liquid ions are shown in orange (cation) and blue (anion) and the water is shown in red (oxygen) and grey (hydrogen).

3.2. Electrochemistry of dissolved species at different RH% in [C_4mpyrr][NTf_2]

Ionic liquids are considered to be hygroscopic, and the extent of water uptake depends on their cation and anion structure.[65] 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.[12-13] The impact of relative humidity on the electrochemical window (EW) of RTILs[11] and on the voltammetry of dissolved species in RTILs[39] has also been previously discussed.[11] Yaghini et al.[66] 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.[66] 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_3), in an environment with controlled relative humidity levels.

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 1.[67] 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.[67-68] Therefore, DmFc has been used as a model probe to study the effect of water on the diffusion behaviour in the ionic liquid [C_4mpyrr][NTf_2] by cyclic voltammetry (CV).

$$\mathrm{DmFc} \rightleftharpoons \mathrm{DmFc}^{+} + e^{-} \tag{1}$$

Figure 5 shows the voltammograms at a scan rate of 100 mV s^{-1} of the oxidation of DmFc and subsequent reduction of decamethylferrocenium ($DmFc^+$) (according to equation 1) in [C_4mpyrr][NTf_2] as a function of different humidity levels, with the normalised 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_4mpyrr][NTf_2] is chemically reversible with a peak-to-peak separation of ΔE_p = 63.5 ± 2 mV for all humidity levels.

As can be seen in Figure 5, 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 [C_4mpyrr][NTf_2]. In contrast, Schröder et al.[39] 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_4mim][BF_4] and [C_4mim][PF_6]. 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 methylviologen (MV^{2+}), 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_4mpyrr][NTf_2]. 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 2 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.

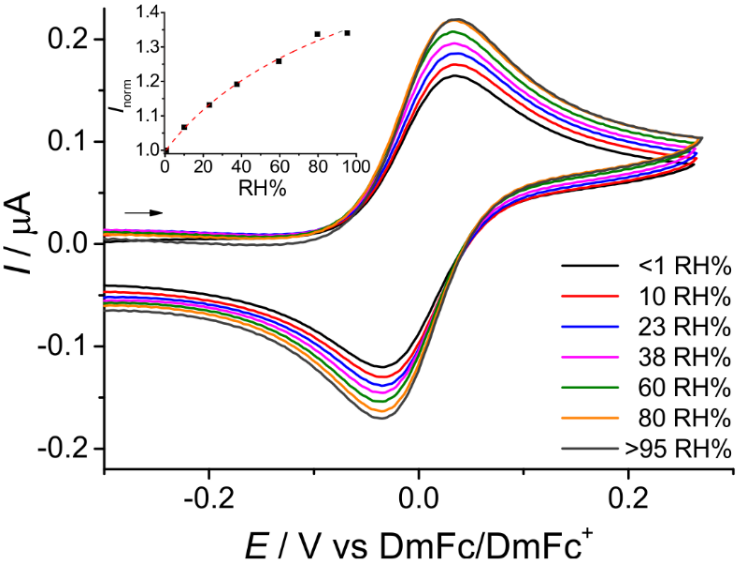

Figure 5. Cyclic voltammetry response of decamethylferrocene (saturated concentration) in [C_4mpyrr][NTf_2] as function of different relative humidity levels (RH%) on a platinum thin-film electrode at a scan rate of 100 mV s^{-1}. The inset plot shows the normalised current (I_{norm}) as a function of the relative humidity, where the oxidation peak currents were normalised to the current recorded at the driest condition, i.e. <1 RH%.

3.2.2. Ammonia gas

Ammonia (NH_3) was chosen because its mechanism is not expected to be affected by water, but the oxidation potential is closer to the edge of the electrochemical window[69] 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 2-4.[70-72]

$$4\ \mathrm{NH_3}(g) \rightarrow 3\ \mathrm{NH_4^+} + \tfrac{1}{2}\ \mathrm{N_2}(g) + 3\ e^- \qquad (2)$$

$$\mathrm{NH_4^+} \rightleftharpoons \mathrm{NH_3} + \mathrm{H^+} \qquad (3)$$

$$\mathrm{H^+} + e^- \rightarrow \tfrac{1}{2}\ \mathrm{H_2} \qquad (4)$$

In an extension of the mechanism, Buzzeo et al.[70] 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 µL of [C_4mpyrr][NTf_2] on a Pt-TFE. The full redox response at <1 RH% (see supporting information Figure S2) shows the same features as previously reported in dry conditions[70], 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. For simplicity, only linear sweep voltammetry (LSV) for the ammonia oxidation is further shown.

Figure 6 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 2g.

For DmFc (section 3.2.1), an approximate 35% increase in current over the whole humidity range was observed. The DmFc/DmFc$^+$ 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_3 diffusion coefficient) and also a shift in the onset of the anodic limit of the electrochemical window which, according to Table S1, reduces by approximately 1.6 V form 'dry' to 'wet' [C_4mpyrr][NTf_2]. 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.[73] previously reported the "nonadditivity" of faradaic currents in ionic liquids when two electrochemically active analytes (ferrocene and cobaltocenium) were present in the same solution, resulting in a different current response with an alteration in the capacitive currents. This non-conventional behaviour may be important to consider in our work, because water as an impurity could also cause a faradaic current contribution to the ammonia response.

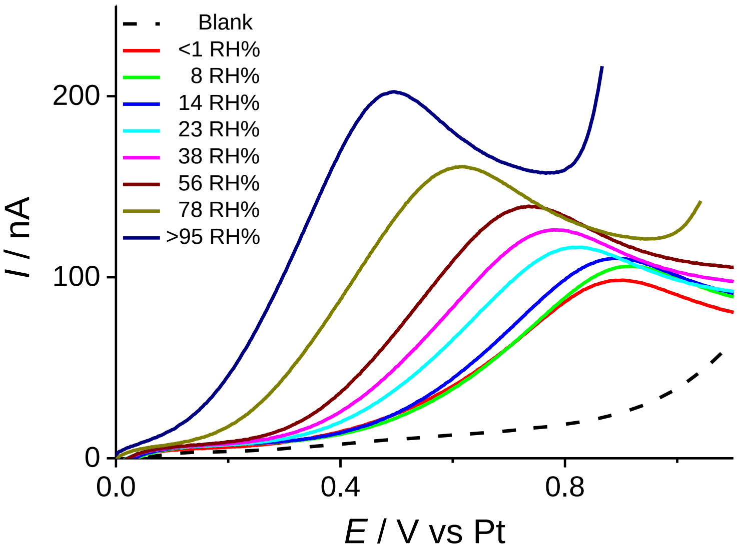

Figure 6. Linear sweep voltammetry for the oxidation of 200 ppm of ammonia gas in [C_4mpyrr][NTf_2] on a Pt-TFE at a scan rate of 100 mV s^{-1} at different relative humidity levels (RH%). Dashed line represents the blank in the absence of ammonia gas at <1 RH%.

Ammonia oxidation was further studied in ionic liquids with different cations and anions, and the results are shown in full in the supporting information (Figures S3 and S4). In general, all ionic liquids show the same behaviour as for [C_4mpyrr][NTf_2], showing a shift of the NH_3 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 normalised to the response at the driest condition.

Figure 7 shows the normalised 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_4mim][BF_4] and [C_4mim][PF_6], for the reasons discussed in more detail in the supporting information. All RTILs show a similar trend: a gradual increase of the normalised current by approximately 100% with increasing humidity. These ionic liquids cover a range of relatively hydrophilic electrolytes like [C_2mim][NTf_2] and [$S_{2,2,1}$][NTf_2] 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[31]), supporting the assumption that the ammonia oxidation reaction mechanism remains the same. In the case of a change of the redox mechanism of NH_3 gas in the presence of water, much more dramatic trends of I_{norm} 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.[31] 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.

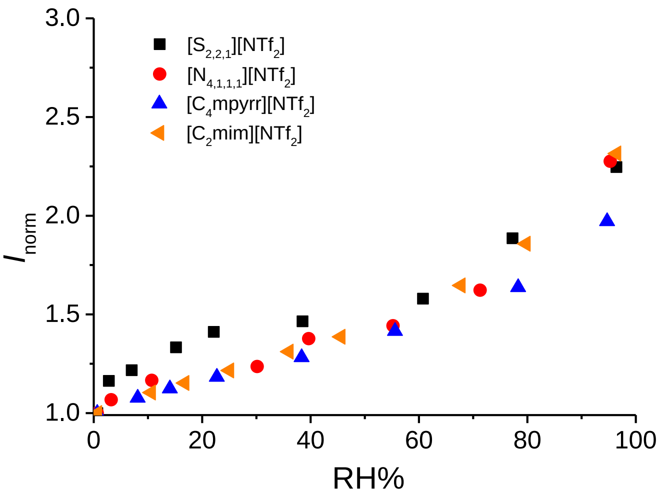

Figure 7. Normalised ammonia oxidation current as a function of different relative humidity level (RH%) for four ionic liquids. Currents were normalised to the oxidation current at the lowest humidity level for easy comparison between different electrolytes.

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 behaviour 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.

Supporting Information

Anodic and cathodic potentials as well as total electrochemical windows at cut-off currents of 15 µA at <1 RH%, 1.5 µA at <1 RH% and 1.5 µA at >95 RH%. Discussion and experimental cyclic voltammetry responses over a wide potential range of [C_4mpyrr][NTf_2] and [C_4mim][BF_4] at different humidity levels including photos of the electrode after the experiment. Effect of relative humidity on the full electrochemical redox mechanism of ammonia in [C_4mpyrr][NTf_2]. Linear sweep voltammetry for the oxidation of ammonia gas in various ionic liquids and discussion of the experimental responses in [C_4mim][BF_4] and [C_4mim][PF_6]. This material is available free of charge via the Internet at http://pubs.acs.org.

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TOC Graphic: