

Achievement of Prolonged Oxygen Detection in Room Temperature Ionic Liquids on Mechanically Polished Platinum Screen-Printed Electrodes

Junqiao Lee, Damien W. M. Arrigan and Debbie S. Silvester*

*Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPOBox U1987, Perth,
Western Australia 6845*

Submitted to Analytical Chemistry

* Author to whom all correspondence should be addressed

E.mail: d.silvester-dean@curtin.edu.au

Tel: +61 (0) 892667148

FAX: +61 (0) 892662300

Abstract

The demonstration of prolonged amperometric detection of oxygen in room temperature ionic liquids (RTILs) was achieved by the use of mechanical polishing to activate platinum screen-printed electrodes (Pt-SPEs). The RTILs studied were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$) and *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{mpyrr}][\text{NTf}_2]$). It was found that voltammetry on polished Pt-SPEs exhibited less deterioration (in terms of voltammogram shapes, stability of peak currents, and appearance of contaminant peaks) from long-term consecutive cyclic voltammetry cycling under 100 % vol. oxygen flow in both RTILs. The detection capability of these RTIL/Pt-SPE systems, initially subjected to long-term consecutive voltammetric cycling, was also investigated by cyclic voltammetry (CV) and long-term chronoamperometry (LTCA). Current vs. concentration plots were linear on both unpolished and polished electrodes for 10-100 % vol. O_2 (using CV) and 0.1-5 % vol. O_2 (using LTCA). However, sensitivities and limits of detection (LODs) from CV were found to improve significantly on polished electrodes compared to unpolished electrodes, particularly in $[\text{C}_2\text{mim}][\text{NTf}_2]$, but also moderately in $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$. The lowest LODs (of ca. 0.1 % vol. O_2) were found on polished SPEs using LTCA, with the most stable responses observed in $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$. Calibration graphs could not be obtained on unpolished electrodes in both RTILs using LTCA. The results show that polishing markedly improves the analytical performances of Pt-SPEs for oxygen sensing in RTILs. The reusability of such disposable Pt-SPEs, after the surfaces had been experimentally fouled, was also demonstrated through the use of polishing. Mechanical polishing of Pt-SPE devices offers a viable approach to performance improvement for amperometric gas sensing.

Keywords: Oxygen reduction, screen printed electrodes, polishing, room temperature ionic liquids, cyclic voltammetry, chronoamperometry

1. Introduction

The oxygen (O₂) reduction reaction (ORR) is vital for biological aerobic respiration and metabolism, and in fuel cells.¹ The sensing of O₂ gas is also crucial in many industrial processes and technological applications, ranging from combustion and steel-making processes (at high O₂ concentrations) to food preparation (e.g. monitoring leaks of O₂ at ppm levels).² Potentiometric semiconductor sensors are commonly used for oxygen detection due to their many advantages (e.g. low cost, robustness, compact sizes), however, their narrow dynamic ranges and high operation temperatures severely limit their applications.³ Thin-film luminescent oxygen sensors offer promising but limited trace-concentration detection.⁴ As a result, amperometric gas sensors (AGSs) are still relevant to this day due the wider linear response range that they offer.^{2,5} For oxygen sensing, platinum (Pt) is widely regarded as the most active electrode material.^{1,6}

Room temperature ionic liquids (RTILs) have attracted considerable attention as solvents for electrochemical experiments.⁷⁻⁹ RTILs are salts that are liquid at room temperature, possessing extremely low volatility and high intrinsic conductivity, in addition to other favorable properties as an electrochemical solvent. The application of RTILs as solvents in gas sensors has been extensively investigated,¹⁰⁻¹³ with suggestions for their use in membrane-free AGSs for a wide range of gases.¹⁰ RTILs have been recently combined with screen-printed electrodes (SPEs) to produce planar, low-cost, miniaturized sensing surfaces. These SPEs consist of three thick-film electrodes (working, reference and counter) printed onto a planar surface, with typical film thicknesses in the range 20-100 μm¹⁴. The detection of ammonia,¹⁵ oxygen,¹⁶⁻¹⁸ chlorine,¹⁹ methylamine²⁰ and hydrogen chloride²⁰ gases on commercially-available SPEs in RTILs has been reported. Whereas the electrochemical reaction mechanisms of most gases (i.e. ammonia, chlorine, methylamine and hydrogen chloride) on SPEs was found to be similar to that conventional metal disk electrodes, unusual voltammetry of the O₂/O₂^{•-} redox couple in imidazolium RTILs on Pt SPEs was observed.¹⁶ Cyclic voltammograms exhibited a cross-over characteristic and an absence of the superoxide oxidation peak, which together suggested a reaction of superoxide with the paste of the Pt SPE. Although linear calibration graphs were obtained (R²>0.99), the

follow-up chemical reactions suggested that these SPE/RTIL systems may only be suitable for “single-use” O₂ detection.¹⁶ In contrast, CVs performed in an aprotic pyrrolidinium based RTIL were comparable to those on standard Pt macrodisk electrodes.¹⁶

We have recently found that mechanical polishing of Pt-SPEs produced a superior electrochemical performance in aqueous electrolyte media compared to other, more conventional electrode surface treatments.²¹ In this paper, we therefore investigate the effect of mechanical polishing of Pt-SPEs for the detection of oxygen in two RTILs. Particular focus is given to the RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][NTf₂]), where non-ideal voltammetry for the O₂/O₂⁻ redox couple was observed on unpolished Pt-SPEs.¹⁶ The electrodes are subjected to extended monitoring of oxygen using cyclic voltammetry and the harsher technique of long-term chronoamperometry, where superoxide is continuously generated at the electrode. The results presented here clearly show that mechanical polishing improves the performances of Pt-SPEs for prolonged oxygen sensing in RTILs.

2. Experimental

2.1 Chemical Reagents

The RTILs 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][NTf₂]) and N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][NTf₂]) were kindly donated by the group of Professor Christopher Hardacre at Queens University, Belfast, synthesized and purified according to standard literature procedures.^{22,23} They were used as received, without any additional drying or purification procedures. Acetonitrile (MeCN 99.8 %, Sigma-Aldrich Pty Ltd., NSW, Australia), ethanol (EtOH, Sigma-Aldrich, 99%), and ultrapure water (with a resistance of 18.5 MΩ·cm prepared by a Milli-Q laboratory water purification system (Millipore Pty Ltd., North Ryde, NSW, Australia) were used for rinsing the electrodes after polishing. High-purity oxygen gas (O₂, >99.5 %) and high-purity nitrogen gas (N₂, 99.99 %) were purchased from BOC gases (North Ryde, NSW, Australia). Tetrahydrofuran (THF, Sigma-Aldrich, 99%) was used to remove the polymer coating of the

Pt-SPEs prior to polishing. 0.5 M sulfuric acid ($\text{H}_2\text{SO}_{4(\text{aq})}$, Ajax Finechem, WA, Australia), and 0.1 M potassium chloride (KCl , > 99.5 %, Fluka, Buchs, Switzerland) aqueous (aq) solutions were prepared using ultrapure water.

2.2 Preparation of polished Pt-SPEs

Pt-SPEs from DropSens (DRP-550, Oviedo, Spain) were chosen due to their reportedly better electrochemical performance and reproducibility compared to other commercially available SPEs.^{24,25}

The Pt-SPEs consist of a 4mm diameter Pt based working electrode (WE), a Pt based counter electrode (CE), and a silver based (quasi-) reference electrode (RE). Unpolished SPEs have the following estimated geometric areas: WE=12.6 mm², CE=12.0 mm² and RE=1.83 mm². Polished SPEs have the same WE area, but CE=17.9 mm² and RE=4.7 mm². Areas were estimated from optical images, and the larger CE and RE for polished SPEs is due to the additional electrode area exposed after the removal of the polymer mask. The Pt-SPEs were soaked and sonicated in THF (to remove the blue polymer material), followed by polishing on soft lapping pads on a rotating mechanical polisher at a rotation speed of 600 rpm for ca. 1 minute, until a glossy finish was obtained. The exposed Ag metal traces were then sealed with SELLEYS® Silicone Sealant (100% Silicone, purchased from local hardware store) to leave only the three electrode surfaces (WE, CE and RE) uncovered. Unless otherwise stated, the unpolished Pt-SPEs were used ‘as-is’ straight out of the box without subjecting to any pre-treatment.

2.3 Electrochemical experiments

Pt-SPEs were connected via soldered wires to a μ -Autolab Type III potentiostat (Eco-Chemie, Netherlands) controlled by a PC running NOVA 1.8 software. The step potential for CV experiments was fixed at 0.003 V and a scan rate of 0.1 V·s⁻¹ was consistently used. 30 μL of RTIL was dropcasted over the three electrodes for each experiment. The Pt-SPE was then inserted into a specially designed glass cell for gas sensing experiments.¹⁶ Oxygen gas was introduced from a cylinder, and was further diluted with nitrogen gas, as detailed previously.¹⁶ A total gas flow rate of 100 standard cubic

centimeters (sccm) was used for all the CV experiments. The RTIL was flushed with nitrogen for ca. 1 hour before commencing experiments in order to remove dissolved impurities such as oxygen and water naturally present in RTILs exposed to air. No obvious voltammetric features were observed in the blanks, suggesting that no significant impurities are present (e.g. water/unreacted starting materials).²⁶ This is important, especially as water and other impurities can affect the kinetics of reactions²⁷ and the mechanism of the ORR.²⁸ Before CVs of oxygen were recorded, consecutive CVs (from 0 to -1.8 V) were performed in a N₂-purged environment until the voltammetry stabilized (typically up to 12 cycles). After each CV of oxygen, 8 minutes was allowed before the commencement of the next scan for replenishment of the oxygen content of the RTIL.

Prolonged chronoamperometry experiments, referred to here as long-term chronoamperometry (LTCA), were conducted after 120 CV cycles in the presence of 100 % vol. O₂. The O₂ concentrations were varied between 0 and 5 % vol. (in the gas phase) with respect to N₂ carrier gas. The actual concentrations measured by CV or LTCA are those in the RTIL phase, and are dependent on the degree of partitioning of the gas from the gas phase to the liquid phase. The data was collected at 15 s time intervals with an overpotential of 200~300 mV relative to the CV peak for O₂ reduction. The response was allowed to stabilize (under N₂) for at least 30 mins before the introduction of O₂ gas. To ensure faster displacement of the previous concentration of oxygen within the cell, a higher total flow rate of 1000 sccm was used during the amperometric experiments. The cell was flushed with N₂-gas between each change of O₂-concentration, following which sufficient time (up to ~50 mins) was allowed for baseline stabilization.

Electrochemical activation of Pt-SPEs was carried out using a separate Pt-wire coil counter electrode and a Ag/AgCl reference electrode (BASi, West Lafayette, IN, USA). Pt-SPEs were subjected to 30 CV cycles between 1.25 V and -0.25 V (vs. Ag/AgCl) at a scan rate of 1 Vs⁻¹, in either 0.5 M H₂SO_{4(aq)}²⁹ or 0.5 M KCl_(aq)³⁰.

3 Results and Discussion

3.1 Consecutive CVs for O₂ reduction on unpolished and polished Pt-SPEs

Polished and unpolished Pt-SPEs were subjected to 120 repeated cyclic voltammetry (CV) scans under 100 % vol. O₂ flow, to enable the comparison of the effect of polishing on the short- and long-term performance of Pt-SPE/RTIL systems for O₂ sensing. Two RTILs were studied: [C₂mim][NTf₂], which provides the highest diffusion coefficient for O₂¹⁰ amongst the available RTILs, and [C₄mpyrr][NTf₂], which provides the best voltammetric response for O₂ on Pt-SPEs amongst eight RTILs tested in our previous work.¹⁶

Figure 1 shows CVs of the O₂/O₂⁻ redox couple in [C₂mim][NTf₂] and [C₄mpyrr][NTf₂] on both unpolished and polished Pt-SPEs. 120 consecutive cycles were performed in the presence of 100 % vol. O₂, with a wait time of 8 minutes between scans to allow for replenishment of depleted O₂. The 1st, 2nd and 120th cycles are overlaid in the main figure, with the initial blank under N₂ shown as dotted lines. The 120th cycle (with the blank also subjected to 120 CV cycles) is presented individually in the inset. In [C₂mim][NTf₂] on an unpolished electrode (Figure 1a), chemically irreversible voltammetry was observed (i.e. no superoxide oxidation peak), with the appearance of a ‘cross-over’ of current in the forward and reverse scans on the second cycle, consistent with that reported previously.¹⁶ This was proposed to be due to the reaction of the electrogenerated superoxide with components of the ink matrix in the mildly acidic imidazolium RTIL;¹⁶ the cross-over likely occurs as a result of the changing nature of the working electrode during the course of a CV cycle, due to that reaction. Once the components of the ink are consumed, the reaction no longer proceeds and the crossover is not present (typically after ca. 35-40 scans in the presence of 100 % vol. O₂). The reaction of superoxide with the imidazolium cation has been previously suggested by AlNashef et al.³¹ and Islam et al.³² Later, Frith et al.³³ used in-situ Raman spectroscopy to prove the degradation of [C₂mim][NTf₂] by superoxide attack. Importantly, the degradation of [C₄mpyrr][NTf₂] was not observed in their work,³³ as is consistent with our results.¹⁶ However, in our case, it appears that the compounds in the paste of the screen-printed ink are linked to the degradation of [C₂mim]⁺ observed within the voltammetric timescale.¹⁶

Figure 1a also shows a ca. 600 mV shift in the reduction peak potential from the first to the second scan, as reported previously.¹⁶ This is mainly due to a shift in the quasi-reference electrode potential, as a similar potential shift was observed for the ferrocene/ferrocenium redox couple when added in-situ.²¹ In [C₄mpyrr][NTf₂], the voltammetry on the unpolished electrode (Figure 1c) is more chemically reversible (the superoxide oxidation peak is clearly seen, as reported previously).¹⁶ However, the CV has a less ideal shape compared to O₂ reduction on macrodisk electrodes¹⁶ and varies slightly from the first to the second scan. The peak current is smaller in [C₄mpyrr][NTf₂] compared to [C₂mim][NTf₂] probably due to differences in the diffusion coefficient and solubility of O₂ in the two RTILs.

Continued cycling on unpolished Pt-SPEs in [C₂mim][NTf₂] leads to deterioration in the voltammetry, with the growth of additional peaks in the cathodic scan (Figure 1a inset). The identities of these peaks are currently unclear, but are thought to be due to the build-up of reaction products of the ink binding materials with superoxide in the presence of [C₂mim][NTf₂]. A significantly smaller but still noticeable degradation was observed on unpolished SPEs in [C₄mpyrr][NTf₂] after 120 cycles (Figure 1c inset). It is noted that there was some variability in the peak shapes on unpolished SPEs (from 5 samples in the same batch) and not every SPEs gave exactly the same CV responses after 120 cycles.

However, in both RTILs, CVs on polished Pt-SPEs were much improved. In [C₂mim][NTf₂] (Figure 1b), the reduction peak potential did not shift between the first and second scans, suggesting a more stable quasi-reference electrode surface after polishing. However, potential shifting was observed on all electrodes over the course of 120 scans which means that instability in the reference electrode still persists after polishing. Additionally, peak currents were smaller than on unpolished Pt-SPEs, which could imply a reduction in the number of electrons exchanged or a change in the electrode surface area.²¹ After 120 cycles (Figure 1b inset), the voltammetry resembled that of an ideal CV for oxygen reduction (e.g. on an polished macrodisk electrode).¹⁶ The currents are also significantly smaller, suggesting the number of electrons involved in the reduction step is lower (estimated here to be $n = 1$,

based on the wave-shape and the known oxygen voltammetry in RTILs on conventional Pt disk electrodes).^{16,34} The generation of this ‘ideal’ CV wave-shape for the $O_2/O_2^{\bullet-}$ redox couple in $[C_2mim][NTf_2]$ simply by polishing is remarkable. For $[C_4mpyrr][NTf_2]$ (Figure 1d), the wave-shapes for all CVs from the first to 120th cycles showed chemically reversible behavior with similar peak currents and were much more stable over time, suggesting suitability for long-term measurements (although possible reference potential shifting over time would have to be accounted for). The most likely explanation for the improved behavior with polishing is the exposure of a fresh screen-printed Pt material by the removal of surface contaminants (e.g. excess residual binding materials or absorbed organic oils from the manufacturing and packaging processes).²¹

Attempts were also made to electrochemically activate the Pt-SPEs (both polished and unpolished) using conventional methods by cycling in 0.5 M $H_2SO_4(aq)$ ²⁹ and 0.5 M KCl ³⁰. However, the CVs for oxygen reduction on both polished and unpolished electrodes were highly unusual, showing larger background currents and poorly shaped peaks. This demonstrates that these methods are unsuitable for the activation of Pt-SPEs for use with RTILs in O_2 gas-sensing experiments.

3.2 Analytical response of unpolished and polished Pt-SPEs

To assess the advantages of using polished Pt-SPEs for extensive continuous O_2 gas monitoring, CV and LTCA at different concentrations of oxygen were performed after the electrodes had been subjected to 120 CV cycles in the presence of 100 % vol. O_2 .

3.2.1. Cyclic Voltammetry

Figure 2 shows CVs of the $O_2/O_2^{\bullet-}$ redox couple at various concentrations (0-100 % vol. O_2) in both $[C_2mim][NTf_2]$ and $[C_4mpyrr][NTf_2]$ on unpolished and polished Pt-SPEs. In $[C_2mim][NTf_2]$ on an unpolished SPE (Figure 2a), contaminant peaks are evident even in the absence of oxygen (dotted line). These were not present initially in the blank CVs in Figure 1, and even after 120 CV cycles in the absence of superoxide (insets to Figure 2). This suggests that they have built-up during 120 cycles as a

result of electrochemically-generated products of the superoxide/SPE paste/RTIL reaction. As the oxygen concentration is increased, the peak current at ca. -1.3 to -1.6 V also increased. For all other SPE/RTIL systems, reasonable single-peak CVs were observed, with the oxygen reduction current increasing with concentration. For all other SPEs, single-peak CVs were observed, with the oxygen reduction currents increasing with concentration. Figures 2b and 2c show the presence of a small pre-peak before the onset of oxygen reduction, however this is not present in Figure 2d (polished SPE in [C₄mpyrr][NTf₂]), despite already being subjected to 120 CV cycles in 100 % vol. O₂. The insets to Figure 2 show plots of background-subtracted reduction current vs. oxygen concentration. For Figure 2a, the currents of the largest peak at potentials of ca. -1.3 to -1.6 V were used to construct the calibration graph. Despite the presence of additional contaminant peaks in Figure 2a, a linear correlation was still obtainable at high concentrations (with large standard deviations), however the plot diverged from linearity at lower concentrations. All other plots were linear ($R^2 > 0.99$). The equations for the lines of best-fit and corresponding limits of detection (LODs, based on 3 standard deviations of the regression) are presented in Table 1, along with the peak-to-peak separations (ΔE_p) for the O₂/O₂^{•-} redox couple, averaged over the concentrations 10-100 % vol. O₂.

The LOD in [C₂mim][NTf₂] was significantly improved on polished Pt-SPEs (12.5 % vol. O₂) compared to unpolished SPEs (23.0 % vol. O₂), but remains too high for most analytical applications. However, in [C₄mpyrr][NTf₂] the performance was significantly better than in [C₂mim][NTf₂], with LODs of 0.82 and 0.78 % vol. O₂ on unpolished and polished SPEs, respectively. The ΔE_p values also showed a substantial improvement on polished electrodes, suggesting either faster kinetics or lower resistance on polished electrodes after long-term cycling. These results demonstrate a significant advantage of using polished Pt-SPEs to improve O₂ sensing performance in RTILs, particularly in [C₂mim][NTf₂].

3.2.2 Long-term Chronoamperometry

Figure 3 shows the LTCA response for different concentrations of O₂ (descending from 5 to 0.1 % vol. and ascending back up to 5 %) in (a) [C₂mim][NTf₂] and (b) [C₄mpyrr][NTf₂] on unpolished and

polished Pt-SPEs. The potential was held at a suitable overpotential relative to the oxygen reduction peak and the current was monitored over time. 100 % vol. N₂ gas was used between each oxygen concentration to observe any change in the baseline currents. Higher concentrations than 5 % vol. O₂ were avoided in these experiments due to the very rapid deterioration in the current response (results not shown) and the observation of a brown-colored product building up in the RTIL. This deterioration was observed for both unpolished and polished Pt-SPEs, even when the Pt-SPE was not subjected to the initial 120 CV cycles. In contrast, Pt-SPEs exposed only to nitrogen did not show any indication of baseline changes or deterioration. It should be noted that long-term constant biasing is considered a much harsher experiment compared to CV (or short-term chronoamperometry) due to the constant generation and accumulation of superoxide at the WE. Thus, CV may be a better method for monitoring O₂ at concentrations higher than 5 % vol.

As seen in Figure 3a, in [C₂mim][NTf₂], the current axis has been shifted for the unpolished electrode (dotted line) to allow for a better comparison to the polished electrode (solid line). The results show that the unpolished Pt-SPE in [C₂mim][NTf₂] is much less responsive to O₂ concentrations than a polished Pt-SPE, with a large and increasing background current. This suggests a continuous change of the background signal, perhaps by the accumulation of electrogenerated products at the working electrode, which is unsurprising given the unusual CV on this electrode (inset, Figure 1a). There is also a noticeable background current in [C₄mpyrr][NTf₂] on an unpolished electrode (Figure 3b, dotted line). Although a response to different concentrations of O₂ is still appreciable above the background, the current transient is far from ideal, which makes analysis difficult. In contrast, for both RTILs on polished SPEs, the chronoamperometric transient is better with larger and well-defined current responses above background at different concentrations. In [C₂mim][NTf₂] on polished SPEs, the baseline is still observed to vary appreciably over time. This could be due to build-up of a contaminant product as indicated by the small pre-peak in the voltammetry (Figure 2b). The baseline is more stable in [C₄mpyrr][NTf₂] on polished SPEs, where a more “ideal” CV shape was observed (Figure 2d).

Figure 4 shows the calibration graphs for the LTCA experiments on polished SPEs presented in Figure 3. Both the ‘ascending’ and ‘descending’ concentration plots are shown, with their lines of best fit. Each concentration response was taken at the current plateau, or at the peak in cases where the current did not reach a plateau. The background currents for each O₂ concentration were measured just prior to the introduction of oxygen. There appears to be a difference in the gradients for the ‘descending’ and ‘ascending’ plots in [C₂mim][NTf₂]. It is further observed in Figure 3a that the decline of the current response after reaching a peak becomes more severe over time and as a result of exposure to higher O₂ concentrations. The equations of the calibration graphs and the corresponding limits of detection are presented in Table 2.

As seen in Table 2, the sensitivity is higher in [C₂mim][NTf₂] compared to [C₄mpyrr][NTf₂], probably due to the lower viscosity and faster partitioning of O₂ gas into [C₂mim][NTf₂]. The sensitivities in both RTILs from LTCA (Table 2) were worse than those from CV (Table 1), but the LODs were better. However, it is noted that the concentration range chosen for the two studies were different (0.1-5 % vol. for LTCA and 10-100 % vol. for CV). The choice of concentration ranges was based on the lowest O₂ concentration that was detectable via CV, and the instability of the response at higher concentrations during LTCA.

The 90 % response times, t_{90} (defined as the time taken to reach 90 % of the plateau current from the baseline), were also estimated from Figure 3. The relatively slow response times (t_{90}) of ca. 3.5 mins for [C₂mim][NTf₂] and ca. 5 mins for [C₄mpyrr][NTf₂] on polished Pt-SPEs are probably due to the large volume (30 μ L) of RTIL used. This was necessary to ensure proper coverage of the exposed area of the three electrode surfaces, particularly on polished SPEs. It is expected that the response time could be improved with a smaller volume (e.g. thinner layers) of RTIL solvent.

3.3 Recovery of ‘fouled’ Pt-SPE surfaces by polishing

Figure 5 illustrates the recovery of an unpolished Pt-SPE surface that has been fouled by extensive consecutive CV (i.e. 120 cycles in the presence 100 % vol. O₂) in [C₄mpyrr][NTf₂]. The dotted line is

the CV response of the fouled Pt-SPE, clearly showing non-ideal voltammetry, with a reductive pre-peak (at ca. -1.1 V) and a follow-up oxidation peak (at ca. -0.1 V) present. When the RTIL was rinsed off and replaced with a fresh aliquot, the CV shape changed significantly and did not recover (dashed line). However, polishing the fouled SPE recovered the CV to one resembling a typical reversible $O_2/O_2^{\bullet-}$ redox couple (solid line). The Pt-SPE could be successfully re-polished more than 12 times before the screen printed platinum surface became visually worn out and the typical O_2 voltammetry in $[C_4mpyrr][NTf_2]$ was unachievable. The number of times that a SPE can withstand repeated re-polishing is dependent on various factors, such as the extent (i.e. pressure and duration) of the initial and subsequent polishing. Additional unidentified peaks occasionally appeared after re-polishing, but a stable voltammogram is achieved after only a few cycles (i.e. < 3) in the presence of 100 % vol. O_2 . The results show that SPEs, typically marketed as single-use devices, can be reused multiple times by simply polishing the surface.

4. Conclusions

The long-term sensing of O_2 gas in two RTILs on platinum SPEs before and after mechanical polishing has been studied. Polishing provides a substantial improvement in the voltammetric wave-shapes and stabilities when subjected to prolonged repeated scanning. In particular for $[C_2mim][NTf_2]$, where the behavior is less than ideal on an unpolished electrode, the cross-over characteristic was removed simply by polishing, and eventually evolved to a voltammetric characteristic resembling that on a typical platinum macrodisk electrode. This is in contrast to the severe degradation that was observed on unpolished Pt-SPEs. There was also appreciable improvement in the CV response for $O_2/O_2^{\bullet-}$ in $[C_4mpyrr][NTf_2]$ after polishing. Analytical responses for unpolished and polished Pt-SPEs were examined using both CV and LTCA at different O_2 concentrations, with the lowest LODs observed on polished electrodes in $[C_4mpyrr][NTf_2]$, but the highest sensitivities on polished electrodes in $[C_2mim][NTf_2]$. Overall, we have shown that polishing is a simple and highly effective pre-treatment method for Pt-SPEs, and can be used to re-vitalize fouled Pt-SPEs (generally regarded as single-use

electrodes) multiple times. This provides a method to extend the reusability and lifetime of SPEs in low-cost O₂ sensors based on Pt-SPE/RTIL systems and for other analytical applications.

Acknowledgements

The authors thank Professor Christopher Hardacre at Queens University Belfast for the kind donation of the ionic liquids used in this work. DSS thanks the Australian Research Council for a Discovery Early Career Researcher Award (DECRA: DE120101456). JL acknowledges PhD funding through an Australian Postgraduate Award and a Curtin Research Scholarship.

Tables

Table 1. Analytical performances by CV of Pt-SPEs in RTILs; equations for the linear calibration graphs presented in Figure 2, and corresponding limits of detection (LODs) for unpolished and polished Pt-SPEs. Also given are the peak-to-peak separations (ΔE_p) for the $O_2/O_2^{\cdot-}$ redox couple, averaged over all concentrations (10-100 % vol. O_2). The electrodes were subjected to 120 CV cycles before recording calibration data.

RTIL	Treatment	Calibration Equation (where I / A and $[O_2] / \% \text{ vol.}$)	R^2	LOD / % vol.	$\Delta E_p / \text{mV}$
[C ₂ mim][NTf ₂]	Unpolished	$-I = 9.0 \times 10^{-7} [O_2] + 3.6 \times 10^{-5}$	0.9537	23.0	-
	Polished	$-I = 1.0 \times 10^{-6} [O_2] + 1.3 \times 10^{-5}$	0.9972	12.5	420 ± 13
[C ₄ mpyrr][NTf ₂]	Unpolished	$-I = 6.9 \times 10^{-7} [O_2] + 1.8 \times 10^{-6}$	0.9967	0.82	395 ± 15
	Polished	$-I = 7.3 \times 10^{-7} [O_2] + 4.6 \times 10^{-7}$	0.9999	0.78	266 ± 10

Table 2. Analytical performances by LTCA of polished Pt-SPEs in RTILs; equations for the linear calibration graphs presented in Figure 4, and limits of detection (LODs), for the initial ‘descending’ and subsequent ‘ascending’ sequence of O_2 concentrations from LTCA (after being subjected to 120 CV cycles).

RTIL	Order	Calibration Equation (where I / A and $[O_2] / \% \text{ vol.}$)	R^2	LOD / % vol.
[C ₂ mim][NTf ₂]	Descending	$-I = 2.7 \times 10^{-7} [O_2] - 3.1 \times 10^{-8}$	0.9978	0.28
	Ascending	$-I = 3.2 \times 10^{-7} [O_2] - 3.8 \times 10^{-9}$	0.9999	0.08
[C ₄ mpyrr][NTf ₂]	Descending	$-I = 1.1 \times 10^{-7} [O_2] + 4.5 \times 10^{-9}$	0.9954	0.13
	Ascending	$-I = 1.1 \times 10^{-7} [O_2] + 7.0 \times 10^{-9}$	0.9998	0.09

Figure. Legends

Figure 1. Main Figures: Comparison of the 1st (dashed), 2nd (dot-dashed) and 120th (solid) CV cycles of the O₂/O₂^{•-} redox couple with 100 % vol. O₂ in: [C₂mim][NTf₂] on (a) unpolished and (b) polished Pt-SPEs, and [C₄mpyrr][NTf₂] on (c) unpolished and (d) polished Pt-SPEs. The response in the absence of O₂ is shown as a dotted line. Insets: Comparison of the 120th CVs (solid) with the blank (100% N₂, dots) also subjected to 120 CV scans. Scan rate is 100 mVs⁻¹. The waiting time between consecutive scans was 8 min. Potential shifting is due to the unstable reference electrode of the SPE, but the magnitude of the shift is smaller on the polished surface.

Figure 2. CV for O₂ reduction in: [C₂mim][NTf₂] on (a) an unpolished Pt-SPE and (b) a polished Pt-SPE, and in [C₄mpyrr][NTf₂] on (c) an unpolished Pt-SPE and (d) a polished Pt-SPE. Scan rate of 100 mVs⁻¹ at 10, 20, 40, 60, 80 and 100 % vol. O₂ after 120 CV cycles in the presence of 100 % vol. O₂ was performed. The dotted lines are CVs in the absence of oxygen (after 120 CV cycles in 100 % vol. O₂). The insets are the corresponding plots of O₂ reduction peak current (background corrected) vs. % vol. O₂ in the flow, and the line of best-fit. Error bars are represented as one standard deviation of three separate calibrations on different days. Where they are not clearly visible, the error bars are smaller than the symbol size.

Figure 3. LTCA at different O₂ gas concentrations in (a) [C₂mim][NTf₂] and (b) [C₄mpyrr][NTf₂] on unpolished (dotted line) and polished (solid line) Pt-SPEs. The gas flow was alternated between N₂ and varying concentrations of O₂ in the following order: 5, 4, 3, 2, 1, 0.5, 0.3, 0.1, 0.3, 0.5, 1, 3, 5 % vol. O₂.

Figure 4. Plots of background corrected oxygen reduction currents vs. % vol. O₂, and the lines of best-fit for (a) [C₂mim][NTf₂] and (b) [C₄mpyrr][NTf₂] on polished Pt-SPEs, extracted from LTCA measurements presented in Figure 3. The solid lines (–) represent the linear regression for the first eight ‘descending’ oxygen concentrations (5, 4, 3, 2, 1, 0.5, 0.3, 0.1 % vol.), and the dashed lines (- -) for the last six ‘ascending’ oxygen concentrations (0.1, 0.3, 0.5, 1, 3, 5 % vol., see Figure 3).

Figure 5. Recovery of fouled Pt-SPE surfaces after polishing. The dotted line (···) shows CV of 100 % O₂ reduction on an unpolished Pt-SPE surface, degraded after long-term CV experiments (120 cycles) in [C₄mpyrr][NTf₂]. The dashed line (- -) shows the CV after the RTIL (visibly browned) was rinsed off and a fresh 30 μL aliquot applied. The solid line (–) shows the CV after the RTIL was rinsed off, and the surface polished before applying a fresh 30 μL aliquot of the RTIL. Scans were conducted with a scan rate of 100 mVs⁻¹.

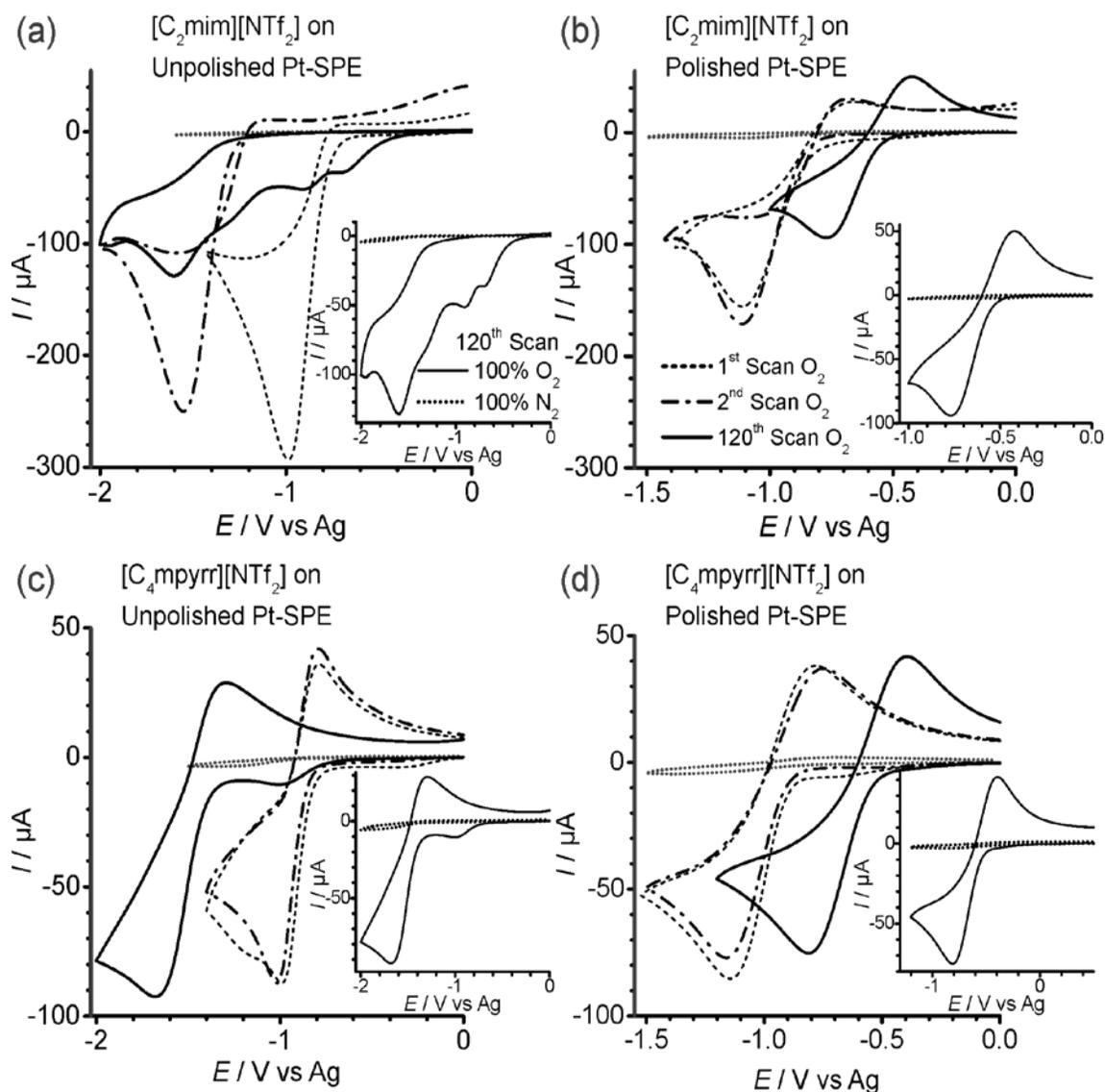


Figure 1. Main Figures: Comparison of the 1st (dashed), 2nd (dot-dashed) and 120th (solid) CV cycles of the $\text{O}_2/\text{O}_2^{\bullet-}$ redox couple with 100 % vol. O_2 in: $[\text{C}_2\text{mim}][\text{NTf}_2]$ on (a) unpolished and (b) polished Pt-SPEs, and $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ on (c) unpolished and (d) polished Pt-SPEs. The response in the absence of O_2 is shown as a dotted line. Insets: Comparison of the 120th CVs (solid) with the blank (100% N_2 , dots) also subjected to 120 CV scans. Scan rate is 100 mVs^{-1} . The waiting time between consecutive scans was 8 min. Potential shifting is due to the unstable reference electrode of the SPE, but the magnitude of the shift is smaller on the polished surface.

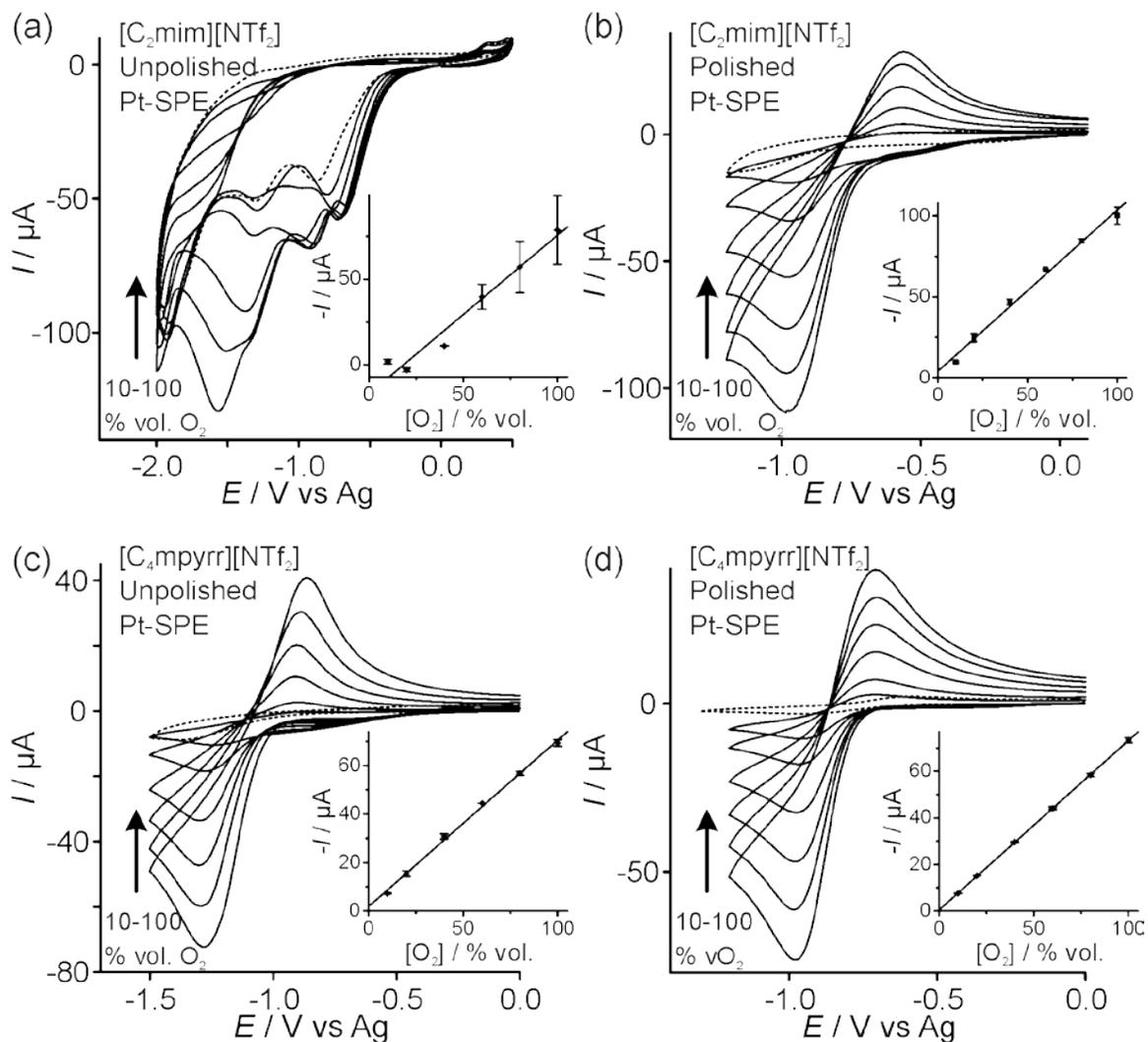


Figure 2. CV for O_2 reduction in: $[C_2mim][NTf_2]$ on (a) an unpolished Pt-SPE and (b) a polished Pt-SPE, and in $[C_4mpyrr][NTf_2]$ on (c) an unpolished Pt-SPE and (d) a polished Pt-SPE. Scan rate of 100 mVs^{-1} at 10, 20, 40, 60, 80 and 100 % vol. O_2 after 120 CV cycles in the presence of 100 % vol. O_2 was performed. The dotted lines are CVs in the absence of oxygen (after 120 CV cycles in 100 % vol. O_2). The insets are the corresponding plots of O_2 reduction peak current (background corrected) vs. % vol. O_2 in the flow, and the line of best-fit. Error bars are represented as one standard deviation of three separate calibrations on different days. Where they are not clearly visible, the error bars are smaller than the symbol size.

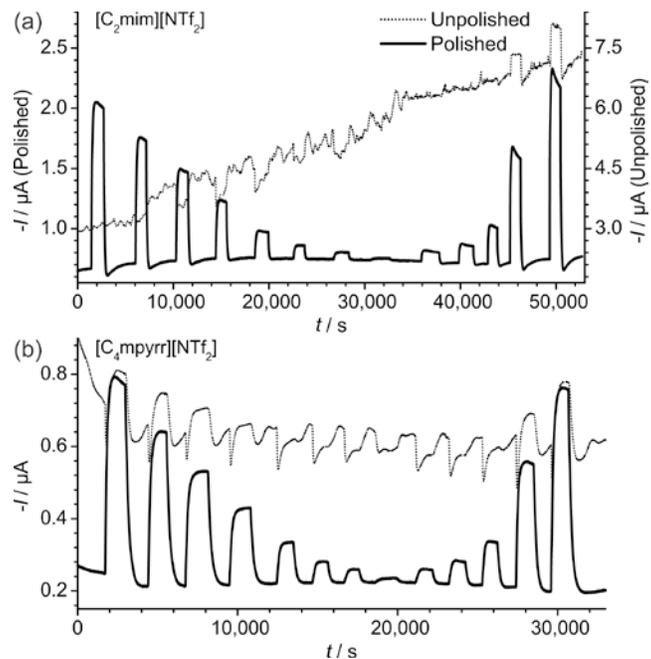


Figure 3. LTCA at different O_2 gas concentrations in (a) $[\text{C}_2\text{mim}][\text{NTf}_2]$ and (b) $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ on unpolished (dotted line) and polished (solid line) Pt-SPEs. The gas flow was alternated between N_2 and varying concentrations of O_2 in the following order: 5, 4, 3, 2, 1, 0.5, 0.3, 0.1, 0.3, 0.5, 1, 3, 5 % vol.

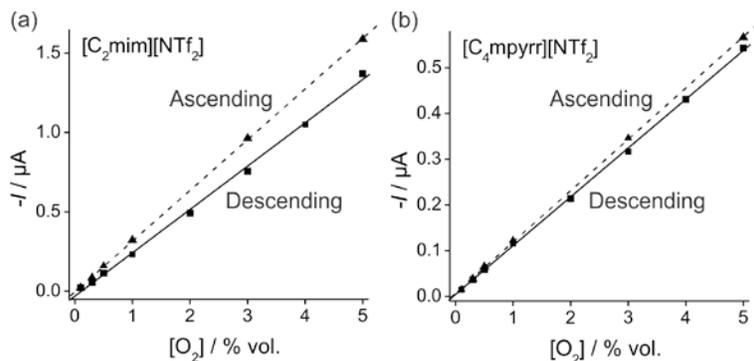


Figure 4. Plots of background corrected oxygen reduction currents vs. % vol. O₂, and the lines of best-fit for (a) [C₂mim][NTf₂] and (b) [C₄mpyrr][NTf₂] on polished Pt-SPEs, extracted from LTCA measurements presented in Figure 3. The solid lines (—) represent the linear regression for the first eight ‘descending’ oxygen concentrations (5, 4, 3, 2, 1, 0.5, 0.3, 0.1 % vol.), and the dashed lines (- -) for the last six ‘ascending’ oxygen concentrations (0.1, 0.3, 0.5, 1, 3, 5 % vol., see Figure 3).

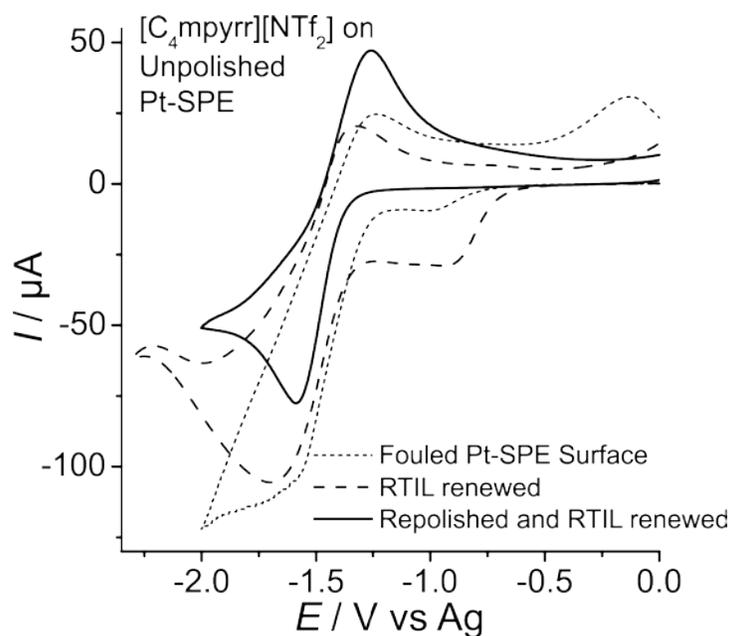


Figure 5. Recovery of fouled Pt-SPE surfaces after polishing. The dotted line (···) shows CV of 100 % O₂ reduction on an unpolished Pt-SPE surface, degraded after long-term CV experiments (120 cycles) in [C₄mpyrr][NTf₂]. The dashed line (- -) shows the CV after the RTIL (visibly browned) was rinsed off and a fresh 30 μL aliquot applied. The solid line (—) shows the CV after the RTIL was rinsed off, and the surface polished before applying a fresh 30 μL aliquot of the RTIL. Scans were conducted with a scan rate of 100 mVs⁻¹.

References:

- (1) Song, C.; Zhang, J.: Electrocatalytic Oxygen Reduction Reaction. In *PEM Fuel Cell Electrocatalysts and Catalyst Layers*; Zhang, J., Ed.; Springer London, 2008; pp 89-134.
- (2) Toniolo, R.; Dossi, N.; Pizzariello, A.; Doherty, A. P.; Susmel, S.; Bontempelli, G. *J. Electroanal. Chem.* **2012**, *670*, 23-29.
- (3) Göpel, W.; Reinhardt, G.; Rösch, M. *Solid State Ionics* **2000**, *136–137*, 519-531.
- (4) Mills, A.; Tommons, C.; Bailey, R. T.; Crilly, P.; Tedford, M. C. *Anal. Chim. Acta* **2011**, *702*, 269-273.
- (5) Wang, R.; Okajima, T.; Kitamura, F.; Ohsaka, T. *Electroanalysis* **2004**, *16*, 66-72.
- (6) Xiang, L.; Yu, P.; Zhang, M.; Hao, J.; Wang, Y.; Zhu, L.; Dai, L.; Mao, L. *Anal. Chem.* **2014**, *86*, 5017-5023.
- (7) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, *5*, 1106-1120.
- (8) Barrosse-Antle, L. E.; Bond, A. M.; Compton, R. G.; O'Mahony, A. M.; Rogers, E. I.; Silvester, D. S. *Chem. Asian J.* **2010**, *5*, 202-230.
- (9) Silvester, D. S.; Compton, R. G. *Z. Phys. Chem.* **2006**, *220*, 1247-1274.
- (10) Buzzeo, M. C.; Hardacre, C.; Compton, R. G. *Anal. Chem.* **2004**, *76*, 4583-4588.
- (11) Rehman, A.; Zeng, X. *RSC Adv.* **2015**, *5*, 58371-58392.
- (12) Silvester, D. S. *Analyst* **2011**, *136*, 4871-4882.
- (13) Rogers, E. I.; O'Mahony, A. M.; Aldous, L.; Compton, R. G. *ECS Trans.* **2010**, *33*, 473-502.
- (14) Metters, J. P.; Kadara, R. O.; Banks, C. E. *Analyst* **2011**, *136*, 1067-1076.
- (15) Murugappan, K.; Lee, J.; Silvester, D. S. *Electrochem. Commun.* **2011**, *13*, 1435-1438.
- (16) Lee, J.; Murugappan, K.; Arrigan, D. W. M.; Silvester, D. S. *Electrochim. Acta* **2013**, *101*, 158-168.
- (17) Gębicki, J.; Kloskowski, A.; Chrzanowski, W. *Electrochim. Acta* **2011**, *56*, 9910-9915.
- (18) Xiong, S.-Q.; Wei, Y.; Guo, Z.; Chen, X.; Wang, J.; Liu, J.-H.; Huang, X.-J. *J. Phys. Chem. C* **2011**, *115*, 17471-17478.
- (19) Murugappan, K.; Arrigan, D. W. M.; Silvester, D. S. *J. Phys. Chem. C* **2015**, *119*, 23572-23579.
- (20) Murugappan, K.; Silvester, D. S. *Sensors* **2015**, *15*, 26866-26876.
- (21) Lee, J.: PhD thesis: Electrochemical Sensing of Oxygen Gas in Ionic Liquids on Screen Printed Electrodes. Curtin University, 2014.
- (22) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168-1178.
- (23) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164-4170.
- (24) Fanjul-Bolado, P.; Hernández-Santos, D.; Lamas-Ardisana, P. J.; Martín-Pernía, A.; Costa-García, A. *Electrochim. Acta* **2008**, *53*, 3635-3642.
- (25) Kadara, R. O.; Jenkinson, N.; Banks, C. E. *Sens. Act. B* **2009**, *138*, 556-562.
- (26) Zhao, C.; Bond, A. M.; Lu, X. *Anal. Chem.* **2012**, *84*, 2784-2791.
- (27) Zhang, J.; Bond, A. M.; MacFarlane, D. R.; Forsyth, S. A.; Pringle, J. M.; Mariotti, A. W. A.; Glowinski, A. F.; Wedd, A. G. *Inorg. Chem.* **2005**, *44*, 5123-5132.
- (28) Switzer, E. E.; Zeller, R.; Chen, Q.; Sieradzki, K.; Buttry, D. A.; Friesen, C. *J. Phys. Chem. C* **2013**, *117*, 8683-8690.
- (29) James, S. D. *J. Electrochem. Soc.* **1967**, *114*, 1113-1119.
- (30) Huang, X. J.; Aldous, L.; O'Mahony, A. M.; del Campo, F. J.; Compton, R. G. *Anal. Chem.* **2010**, *82*, 5238-5245.
- (31) AlNashef, I. M.; Hashim, M. A.; Mjalli, F. S.; Al-haj Ali, M. Q.; Hayyan, M. *Tetrahedron Lett.* **2010**, *51*, 1976-1978.
- (32) Islam, M. M.; Imase, T.; Okajima, T.; M., T.; Niikura, Y.; Kawashima, N.; Nakamura, Y.; Ohsaka, T. *J. Phys. Chem. A* **2009**, *113*, 912-916.
- (33) Frith, J. T.; Russell, A. E.; Garcia-Araez, N.; Owen, J. R. *Electrochem. Commun.* **2014**, *46*, 33-35.

(34) Buzzeo, M. C.; Klymenko, O. V.; Wadhawan, J. D.; Hardacre, C.; Seddon, K. R.; Compton, R. G. *J. Phys. Chem. A* **2003**, *107*, 8872-8878.

Table of Contents Figure

