Ionic liquids (ILs) are promising electrolytes for metal-air batteries since they are non volatile, non flammable and liquid at room temperature with high oxygen solubility, and high stability particularly for Li-O2[1,2] and Na-O2[3–5] batteries. One of the most widely investigated ILs for metal-O2 batteries is N-butyl-N-methylpyrrolidinium bis(trifluoromethylene sulfonyl)amide PYR14 TFSI, (Io-Li-Tec) and bis(trifluoromethane) sulfonimide lithium salt (544094, LiTFSI, sigma Aldrich) were stored in the argon-filled MBRAUN glove box with an oxygen content ≤ 0.1 ppm and water content below 2 ppm. All solutions were prepared inside the glove box, dried for several hours at 80 °C under vacuum and the water content was measured using the Karl Fisher 831 KF Coulometer (Metrohm). Solutions were found to contain around 20 ppm of water.

Rotating ring disc electrode (RRDE) system has been described in details elsewhere. An Au/Au RRDE with r1 = 0.25, r2 = 0.26, and r3 = 0.30, where r1 is the radius of disc electrode, r2 and r3 are respectively the inner and outer radii of the RRDE system with a geometric area of 0.196 cm2, and collection coefficient 0.28 was employed.

The reference Li2Mn2O4/LiMn2O4 electrode (2.61 V Li/Li+) was added stepwise in order to increase the Li+/Li concentration in the IL competition of LiO2 and PYR14TFSI. Electrode potential calibration with ferrocene was done.

A large area Pt gauze was the counter electrode. The Pt counter electrode was not shielded during the electrochemical measurements, however it was positioned far enough from the working electrode in order to avoid possible contamination of the electrolyte with its oxidation by-products, moreover the ionic liquid is viscous and the diffusion of side products is expected to be slow.

Differential electrochemical mass spectrometry (DEMS) was accomplished using a Pfeiffer vacuum Omnistar GSD 320 gas analysis system with a quadrupole mass spectrometer QGM 220 (mass range 1–200 amu) with ion gastight ion source, yttriated iridium-filament with secondary electron multiplier C-SEM and Faraday detectors. The DEMS cell setup was used as described elsewhere. An EQCM system with shear wave dissipation that has been described elsewhere has been employed.

For the experiments the Li+ was added stepwise in order to increase the Li+ concentration in the ionic liquid, however the RRDE was dissembled prior each measurement as its surface was cleaned and polished with 0.05 μm alumina. The procedure was done in order to clean any possible ORR products side products, such as passivating Li2O2 or Li2CO3 films.

Results and Discussion

Figure 1 depicts cyclic voltammetry of an Au electrode in PYR14TFSI + LiTFSI at different Li+ concentrations, 0–50 mM, at 50 mVs−1. In pure ionic liquid PYR14TFSI a quasi-reversible one-electron wave is observed with a mid-peak potential of 2.04 V, while
a cathodic ORR peak at 1.91 V in good agreement with previous reports.\textsuperscript{14,15} In the reverse scan an oxidation peak at 2.16 V corresponds to the oxidation of superoxide at the electrode surface which has not diffused away from the electrode surface, i.e. the reaction \( \text{O}_2/\text{PYR}_{14}\text{O}_2^- \) is reversible.

As we introduce 1 to 25 mM LiTFSI in the ionic liquid the quasi reversible peak is still observed but a second oxygen reduction peak at more positive potential, i.e. 2.15 V is now present due to the formation of \( \text{Li}^+\text{O}_2^- \) ion pair. The \( \text{O}_2/\text{Li}_2\text{O}_2 \) redox couple exhibits a more positive potential than \( \text{O}_2/\text{PYR}_{14}\text{O}_2^- \) due to the effect of a better acceptor cation.\textsuperscript{20}

At 50 mM LiTFSI a single cathodic peak at 2.15 V is observed and the superoxide re-oxidation peak disappears, while anodic current is observed above 3.4 V from 25 mM lithium ion concentration. Under stirring with a rotating disc electrode system convective-diffusion ORR plateau is observed in Figure 2 for the lithium free PYR\(_{14}\)TFSI and cathodic peaks are present in lithium containing electrolyte.

An RRDE study of the ORR in PYR\(_{14}\)TFSI containing LiTFSI shows that superoxide ion can be detected at the ring electrode, see Figure 2. However the ring electrode response is delayed in time (potential in the cyclic voltammetry) with respect to the ORR onset at the disc electrode. Similar findings have been reported for O\(_2\) saturated pure PYR\(_{14}\)TFSI and have been ascribed to the slow diffusion of \( \text{O}_2^- \) radical anion in the ionic liquid.\textsuperscript{17} While the diffusion coefficient for neutral \( \text{O}_2 \) in PYR\(_{14}\)TFSI is 2.9 \( \times 10^{-6} \) cm\(^2\)s\(^{-1}\),\textsuperscript{19} superoxide exhibits a negative charge and therefore the diffusion coefficient in the highly charged ionic liquid is much lower, i.e. 1.1 \( \times 10^{-7} \) cm\(^2\)s\(^{-1}\).\textsuperscript{17} The slow diffusion of superoxide is also responsible for the positive currents in the back scan due to the oxidation of superoxide radical that has not completely diffused away from the disc electrode surface at positive enough potentials for its anodic oxidation.

Figure 2 features the strong effect of lithium ion concentration: The yield of superoxide ion detected at the ring electrode decreases and the disc current pre-peak at 2.15 V increases the higher the LiTFSI concentration. Therefore, insoluble \( \text{Li}_2\text{O}_2 \) becomes the main interfacial electrode reaction product at 50 mM LiTFSI with no detection of superoxide at the ring electrode.

Notice that the solubility of oxygen in PYR\(_{14}\)TFSI is 13.6 mM,\textsuperscript{6} and therefore the \( \text{O}_2^- \) concentration is much less than the ionic liquid cation PYR\(_{14}^+\) concentration, thus PYR\(_{14}^+\) \( \text{O}_2^- \) prevails, but above 25 mM \( \text{Li}^+ \), surface \( \text{Li}^+\text{O}_2^- \) is more favorably formed due to the strong Lewis acidity of small \( \text{Li}^+ \) cations and the shortly lived \( \text{Li}^+\text{O}_2^- \) disproportionates into \( \text{Li}_2\text{O}_2 \) and oxygen.

Superoxide is the first oxygen reduction product as shown by Frith et al.,\textsuperscript{21} who have reported a Raman band at 1107 cm\(^{-1}\) assigned to superoxide anions during the ORR in O\(_2\) saturated PYR\(_{14}\)TFSI containing 10 mM LiTFSI. At low concentration of hard Lewis acid \( \text{Li}^+ \) cations and high concentration of soft organic cations PYR\(_{14}^+\) these can associate to the superoxide ion, and therefore, prevent them from combining to form \( \text{Li}_2\text{O}_2 \). As the LiTFSI concentration increases, the main surface reaction product is \( \text{Li}_2\text{O}_2 \) as has been shown in this electrolyte by ex-situ the 805 cm\(^{-1}\) Raman spectroscopy band characteristic of lithium peroxide\textsuperscript{22} and confirmed in the present study by the EQCM mass increase in Figure 3. In spite of the noisy data due to the high viscosity of the ionic liquid, there is a clear gravimetric evidence of formation of insoluble \( \text{Li}_2\text{O}_2 \) at low overpotentials. Furthermore, notice that the mass increases at the peak due to formation of \( \text{Li}^+\text{O}_2^- \), which we take as an evidence of disproportionation.

DEMS for \( \text{O}_2 \) (q/m = 32) and \( \text{CO}_2 \) (q/m = 44) simultaneous to the ORR and re-oxidation in pure PYR\(_{14}\)TFSI ionic liquid and in 25 mM LiTFSI in PYR\(_{14}\)TFSI under constant current pulses are shown in Figure 4. In both systems \( \text{I}_{32} \) current decreases due to the \( \text{O}_2 \) depletion during the ORR. After correction for the mass spectrometry ionic current delay (22 seconds) due to transport in the IL and DEMS vacuum, positive \( \text{I}_{32} \) current for oxygen evolution in pure ionic liquid occurs at about 2 V confirming the anodic peak voltammetry evidence.

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**Figure 1.** Cyclic voltammetry experiment of \( \text{O}_2 \) saturated PYR\(_{14}\)TFSI + LiTFSI at different \( \text{Li}^+ \) concentrations 0–50 mM at 50 mVs\(^{-1}\).

**Figure 2.** Au-Au RRDE experiment of \( \text{O}_2 \) saturated PYR\(_{14}\)TFSI + LiTFSI at different \( \text{Li}^+ \) concentrations 0–50 mM, 4 Hz, 50 mVs\(^{-1}\)., ring potential 3.0 V, \( \text{A} = 0.2 \text{ cm}^2, \text{N}_o = 0.28 \).

**Figure 3.** Cyclic voltammetry experiment of \( \text{O}_2 \) saturated PYR\(_{14}\)TFSI + 0.18 M LiTFSI at 50 mVs\(^{-1}\) and 10 MHz EQCM mass increase (\( \Delta \text{m/A} \)) simultaneous to the cyclic voltammetry.
during the back scan and the RRDE detection of superoxide. In 25 mM Li+ solution in PYR14TFSI, the mass 32 ionic current peak due to superoxide oxidation is smaller. It should be noted that there is no DEMS evidence for O2 evolution expected from Li2O2 oxidation above 3.2 V while anodic currents are observed in Figures 1 and 2. However, I32 mass spectroscopic current due to CO2 increases above 4.2 V consistent with the FTIR evidence of PRY14+ degradation and mass loss in the EQCM experiment. Therefore the parasitic reaction of Li2O2 with the ionic liquid cation is expected to yield surface species that can only be oxidized at high overpotentials.

Summary

Competition of ORR product O2− for the PYR14+ and the strong Lewis acid Li+ is reflected in the lower yield of soluble superoxide, EQCM mass increase and the positive shift of the O2/O2− potential while increasing the Li+ concentration in the ionic liquid.

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The first author’s last name, corrected above, was misspelled.