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 and Na-O2 batteries. One of the most widely investigated ILs for metal-O2 batteries is N-butyl-N-methylpyrrolidinium bis(trifluoromethane sulfonyl)amide (PYR14TFSI) also denominated [C4mpyr][TFSI].

In ionic liquids, including PYR14TFSI, in the absence of protons and alkali metal ions, the reversible formation of O2/O2− couple is observed6–12 due to the stabilization of superoxide radical ion by IL cation like the tetralkyl ammonium cations in aprotic organic solvents. However, the ORR in ionic liquids changes in the presence of cation like the tetralkyl ammonium cations in aprotic organic solvents. Allen et al.13,14 described the mechanism of ORR in PYR14TFSI in 25 mM Li+ as follows:

\[
\text{Li}^+ + O_2 + e^- \rightarrow \text{Li}_2O_2 \tag{1}
\]

\[
2\text{Li}_2O_2 \rightarrow \text{Li}_2O_2 + O_2 \tag{2}
\]

\[
\text{PYR}_{14}^+ + O_2 + e^- \rightarrow \text{PYR}_{14}^{+} - O_2^- . \tag{3}
\]

Following for the oxygen evolution reaction (OER) in the anodic sweep:

\[
\text{PYR}_{14}^{+} - O_2^- \rightarrow \text{PYR}_{14}^{+} + O_2 + e^- \tag{4}
\]

\[
\text{Li}_2O_2 \rightarrow \text{Li}^+ + O_2 + e^- \tag{5}
\]

\[
\text{Li}_2O_2 \rightarrow 2\text{Li}^+ + O_2 + 2e^- \tag{6}
\]

Herranz et al. have quantified the stability of pure PYR14TFSI in the presence of superoxide with RRDE.17 The stability of PYR14+ studied by FTIR has been reported recently.18

Brieﬂy, in oxygen saturated LiTFSI containing PYR14TFSI electrolyte carbon dioxide and water were formed at potential 4.3 V either with or without previous O2 electrodeuction reaction. However in deoxygenated LiTFSI contacting ionic liquid no formation of CO2 or water was observed, suggesting oxygen presence to be crucial in carbon dioxide production.

In this communication we report for the first time RRDE ORR experiments in PYR14TFSI ionic liquid containing Li+ at concentrations from 0 to 50 mM, complemented by EQCM and DEMS, and discuss the mechanism of ORR in this ionic liquid.

Communication—Lithium Ion Concentration Effect in PYR14TFSI Ionic Liquid for Li-O2 Battery Cathodes

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The oxygen reduction reaction (ORR) has been studied on Au cathodes in O2 saturated PYR14TFSI liquid electrolyte using cyclic voltammetry, rotating ring disc electrode (RRDE), electrochemical quartz crystal microbalance (EQCM) and differential electrochemical mass spectrometry (DEMS). At different Li+ concentrations in the IL competition of Li+ and PYR14+ for superoxide ion results in dismutation of Li2O2 and formation of insoluble Li2O2.

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a cathodic ORR peak at 1.91 V is 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 Li\(^+\)/\(\text{LiO}_2^-\) ion pair. The \(\text{O}_2/\text{LiO}_2\) 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. Thus, the ring current decreases due to the oxidation of superoxide radical anion in the ionic liquid.\textsuperscript{17} While the diffusion coefficient for neutral \(\text{O}_2\) in \(\text{PYR}_{14}\text{TFSI}\) is 2.9 \(\times 10^{-6}\) cm\(^2\)s\(^{-1}\),\textsuperscript{15} 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 LiTFSI concentration. Notice that the solubility of oxygen in \(\text{PYR}_{14}\text{TFSI}\) is 13.6 mM,\textsuperscript{6} and therefore the \(\text{O}_2^-\) concentration is much less than the ionic liquid cation \(\text{PYR}_{14}^+\) concentration, thus \(\text{PYR}_{14}^+\text{O}_2^-\) 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 \(\text{O}_2\) saturated \(\text{PYR}_{14}\text{TFSI}\) containing 10 mM LiTFSI. At low concentration of hard Lewis acid \(\text{Li}^+\) cations and high concentration of soft organic cations \(\text{PYR}_{14}^+\) 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 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 \(\text{O}_2\) (\(\varphi/m = 32\)) and \(\text{CO}_2\) (\(\varphi/m = 44\)) simultaneous to the ORR and re-oxidation in pure \(\text{PYR}_{14}\text{TFSI}\) ionic liquid and in 25 mM LiTFSI in \(\text{PYR}_{14}\text{TFSI}\) under constant current pulses are shown in Figure 4. In both systems \(I_{\text{L}/2}\) 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 \(I_{\text{L}/2}\) current for oxygen evolution in pure ionic liquid occurs at about 2 V confirming the anodic peak voltammetry evidence of the positively charged superoxide ion.

An RRDE study of the ORR in \(\text{PYR}_{14}\text{TFSI}\) 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 \(\text{O}_2\) saturated pure \(\text{Py}_{14}\text{LiO}_{14}\text{TFSI}\) and have been ascribed to the slow diffusion of \(\text{O}_2^-\) radical anion in the ionic liquid.\textsuperscript{17}
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 O\(_2\) evolution expected from Li\(_2\)O\(_2\) oxidation above 3.2 V while anodic currents are observed in Figures 1 and 2. However, \(I_{\text{L}}\) mass spectroscopic current due to CO\(_2\) increases above 4.2 V consistent with the FTIR evidence of PYR\(14^{+}\) degradation\(^1\) and mass loss in the EQCM experiment. Therefore the parasitic reaction of Li\(_2\)O\(_2\) with the ionic liquid is expected to yield surface species that can only be oxidized at high overpotentials.

**Summary**

Competition of ORR product O\(_2^-\) for the PYR\(_{14}^{+}\) and the strong Lewis acid Li\(^+\) is reflected in the lower yield of soluble superoxide, EQCM mass increase and the positive shift of the O\(_2\)/O\(_2^-\) potential while increasing the Li\(^+\) concentration in the ionic liquid.

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**References**