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### An in-situ Raman study of the oxygen reduction reaction in ionic liquids

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### Abstract

In-situ Raman spectroscopy is applied, for the first time, to elucidate the reaction products of oxygen reduction in two types of ionic liquids: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C<sub>2</sub>mimTFSI) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr<sub>14</sub>TFSI). The degradation of C<sub>2</sub>mimTFSI by superoxide attack is evidenced by the appearance of bands characteristic of amide and carbonate compounds. On the contrary,  $Pyr_{14}TFSI$  is found to be resistant towards degradation. It is observed that superoxide is the first product of oxygen reduction in  $Pyr_{14}TFSI$ , and the formation of  $Li_2O_2$  is observed at longer times.

### **1. Introduction**

Oxygen reduction in non-aqueous electrolytes has attracted much interest, especially in the last few years, because of its involvement in the discharge reaction in lithium- $O_2$ batteries. Having a theoretical specific energy around 5 times higher than lithium-ion, lithium- $O_2$  cells could become the technology that powers tomorrow's electric cars. However, several issues need to be addressed before lithium- $O_2$  cells could reach their full potential. In particular, the choice of the electrolyte is critical, since most electrolytes have been found to degrade under the operating conditions in lithium- $O_2$ cells [1–4]. In addition, electrode passivation limits the energy delivered by lithium- $O_2$ cells because the discharge product,  $Li_2O_2$ , is insoluble and insulating and deposits on the surface of the electrode [5].

Previous studies have shown that lithium- $O_2$  batteries operated with ionic liquids such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $C_2$ mimTFSI) and 1butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ( $Pyr_{14}TFSI$ ) exhibit promising electrochemical performance [6–18]. These electrolytes are also attractive because they are hydrophobic, non-volatile and non-flammable. In this work, in-situ Raman spectroscopy is used to detect the products of oxygen reduction in  $C_2$ mimTFSI and  $Pyr_{14}TFSI$ . Compared to cyclic voltammetry, the test of the chemical stability of the ionic-liquids by in-situ Raman spectroscopy is much more demanding, because of the longer time scale and the high sensitivity towards small amounts of degradation products achieved by using nanostructured gold electrodes. It is found that  $C_2$ mimTFSI degrades during the reduction of oxygen, most likely due to attack by superoxide radical anions,  $O_2^{--}$ . On the other hand, the  $Pyr_{14}TFSI$  is found to be resistant to degradation, and the first reaction product is found to be superoxide, with Li<sub>2</sub>O<sub>2</sub> formed at longer times.

### 2. Experimental

Electrolytes were prepared by mixing C<sub>2</sub>mimTFSI (IoLiTec, 99%wt., <25 ppm halides, <10 ppm Li<sup>+</sup>) or Pyr<sub>14</sub>TFSI (IoLiTec, 99%wt., <25 ppm halides, <25 ppm Li<sup>+</sup>) with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Aldrich, 99.95%wt.) in an argon-filled glovebox (<1 ppm water, <10 ppm oxygen). The final water content of the electrolytes was <10ppm, as determined by Karl-Fisher titration. Prior to transferring them to the glovebox, all reagents were dried under vacuum at 120 °C for 24 h. The cell and electrodes were dried in an oven at 80 °C for a minimum of 12 h. The cell was

assembled and filled with 0.25ml of Ar-saturated electrolyte inside the glovebox. In order to dose  $O_2$  into the cell, the cell was connected to a gravity flow apparatus, and around 10 ml of  $O_2$ -saturated electrolyte were flowed through the cell. Oxygen (BOC, 99.5%, dried through a bed of molecular sieves before use) was bubbled in the electrolytes for 30 minutes to achieve saturation.

The spectro-electrochemical Raman cell (Ventacon Ltd) comprised a structured gold working electrode with a geometric surface area of 0.5 cm<sup>2</sup>, a platinum wire counter electrode (0.5 mm diameter, Advent research materials, >99.95%wt.) and an in-house prepared Li<sub>1.5</sub>Mn<sub>2</sub>O<sub>4</sub> coated platinum wire as the reference electrode (with potential of 3V vs. Li/Li<sup>+</sup>). Structured gold working electrodes formed of sphere segment voids (SSV) of 600 nm diameter and 400 nm height were prepared in-house as described previously [19]. These electrodes produce a strong surface enhancement for Raman scattering at the surface [18]. Raman spectra were acquired using the static-scan mode with a 50X objective on a Renishaw 2000 microscope instrument equipped with a 632.8 nm He-Ne laser. The diameter of the laser spot was 1 µm. The Raman spectra presented were baseline corrected using a linear multipoint fitting function. Electrochemical measurements were carried out at room temperature on a µAutolabIII potentiostat.

Raman spectra were first recorded in O<sub>2</sub>-saturated electrolyte at the open circuit potential (3 V *vs* Li/Li<sup>+</sup>). Then, in the case of C<sub>2</sub>mimTFSI, the potential was stepped to lower values (sequentially: 1.85, 1.35 and 0.85V *vs* Li/Li<sup>+</sup>) and spectra were recorded after 6 minutes of the application of the potential step. In the case of Pyr<sub>14</sub>TFSI, more drastic conditions were applied in order to test the presence of degradation reaction. The potential was stepped to 0.85 V *vs* Li/Li<sup>+</sup>, and Raman spectra were collected after 14, 15, 16, 17, 19 and 21 minutes. These values of the applied potentials are not corrected from IR-contributions.

#### 3. Results and discussion

Fig. 1 shows in-situ Raman spectra collected from a gold structured electrode in  $O_2$ saturated  $C_2$ mimTFSI containing 10 mmol·dm<sup>-3</sup> LiTFSI. The spectrum collected at 3 V vs. Li/Li<sup>+</sup> agrees well with the spectrum of  $C_2$ mimTFSI [20,21]. After decreasing the applied potential up to 0.85 V vs Li<sup>+</sup>/Li, several new bands appear. A small band at 1110 cm<sup>-1</sup> can be ascribed to superoxide anions [22]. Several additional bands appear at around 1600 cm<sup>-1</sup> that can be ascribed to the formation of amide compounds (and possibly carbonates) [23]. Indeed, previous studies have found that superoxide slowly reacts when it is dissolved in a solution containing  $C_2$ mim<sup>+</sup>, producing "ring-opening products" [24] and 2-imidazolones [25]. We believe that this work presents the first insitu spectroscopic evidence of  $C_2$ mim<sup>+</sup> degradation in Li-O<sub>2</sub> cells.



Fig. 1. Raman spectra recorded on a gold electrode in O<sub>2</sub>-sturated C<sub>2</sub>mimTFSI with 10 mmol·dm<sup>-3</sup> LiTFSI at different potentials, as indicated. Raman spectra were collected 6 minutes after the start of each potential step. Bands present due to the C<sub>2</sub>mim<sup>+</sup> cation are marked with (°)[20]. Bands present due to the TFSI<sup>-</sup> anion are marked with (<sup>°</sup>)[21]. New bands appearing during the discharge of the cell, and ascribed to the reaction of superoxide with the C<sub>2</sub>mim<sup>+</sup> cation, are marked with (<sup>°</sup>).



Fig. 2. Raman spectra recorded on a gold electrode in  $O_2$ -sturated in  $Pyr_{14}TFSI$  with 10 mmol·dm<sup>-3</sup> LiTFSI. Spectra were first recorded at 3V and then at 0.85V after different holding times, as indicated. Bands present due to the  $Pyr_{14}^+$  cation are marked with (<sup>+</sup>)[20,26]. Bands present due to the TFSI anion are marked with (<sup>□</sup>) [21,26].

Fig. 2 shows in-situ Raman spectra recorded in O<sub>2</sub>-saturated Pyr<sub>14</sub>TFSI containing 10 mmol·dm<sup>-3</sup> LiTFSI. The spectrum at 3V vs. Li/Li<sup>+</sup> agrees well with that of Pyr<sub>14</sub>TFSI[20,21,26]. In contrast to the case of C<sub>2</sub>mimTFSI, fewer bands emerged during the reduction of oxygen. Bands due to the degradation of the electrolyte were not observed, demonstrating the chemical stability of Py<sub>14</sub>TFSI in lithium-oxygen batteries, as suggested previously by ex-situ measurements [15]. The band at 1107 cm<sup>-1</sup> is assigned to superoxide anions. The frequency of this band is in good agreement with the band at 1109 cm<sup>-1</sup> assigned to superoxide anions on gold in tetraalkylammonium solutions of acetonitrile [22]. The growth of a smaller band at 805 cm<sup>-1</sup> can be explained by the formation of lithium peroxide [22,27], which was observed previously in ex-situ Raman measurements in this ionic liquid [15].

In conclusion, the first reaction product of oxygen reduction in  $Pyr_{14}TFSI$  is superoxide, while  $Li_2O_2$  formation is observed at longer times. The relatively slow conversion of superoxide to  $Li_2O_2$  shown in Fig. 2 can be ascribed to the low concentration of lithium salt and the high concentration of soft organic cations which can associate to the superoxide ions [28], and hence, prevent them for combining to form  $Li_2O_2$ .

The chemical stability of Pyr<sub>14</sub>TFSI against nucleophilic attack by superoxide is clearly an advantage; a less obvious but significant advantage of this solvent may be the stabilisation of superoxide against disproportion into lithium peroxide and oxygen. As the rate of disproportionation decreases, superoxide anions have more time to diffuse away from the electrode surface, and hence the formation of lithium peroxide would take place in solution at a certain distance from the electrode. This would hamper electrode passivation due to deposition of lithium peroxide, which is accepted to be one of the most important limiting factors that limits the practical capacity delivered by lithium-air batteries [5]. Evidence for a slowdown in electrode passivation may be obtained from the observed enhancement in discharge capacity of lithium-oxygen cells when the mass transport rate is increased, as shown with rotating disc electrodes by Monaco *et al.* [16]. Our calculations show that, at rotation rates > 200 rpm, the rate of oxygen supply to the surface is high enough to sustain the applied current, and therefore, the electrochemical measurements should not be affected by oxygen starvation near the surface.<sup>i</sup> Therefore, we propose that peroxide deposition on the electrode surface may be a more important limiting factor than oxygen starvation, and that the positive correlation between the capacity and rotation was due to a faster removal of superoxide from the surface, leading to a slower rate of lithium peroxide nucleation and growth at the surface. This scenario suggests that lithium peroxide deposition on the electrode can indeed be significantly slowed down by hydrodynamic means in this ionic liquid, even at realistically high lithium salt concentrations.

Since the increased capacity due to the suppression of electrode fouling by lithium peroxide will only be effective at unusual hydrodynamic conditions as the above, we seek an alternative method of reducing the residence time of superoxide at the electrode. A possible method already exists, in fact, in the form of the redox shuttle described by Lacey *et al.* [29] as means of separation of oxygen reduction from the electrode interface. Interestingly, that work showed that although some electrode fouling did take place in the presence of the shuttle over many cycles, the effect was far less significant than that obtained at the same concentration of lithium salt without the shuttle.

#### 4. Conclusions

In conclusion, in-situ Raman spectroscopy is a powerful technique used to investigate the reaction products of oxygen reduction in non-aqueous electrolytes. This approach is used to study, for the first time, ionic liquids, and it is concluded that pyrrolidiniumbased ionic liquids are chemically resistant to degradation under the conditions relevant to lithium-air batteries, in agreement with previous studies [6–17]. In addition, we have found that superoxide was the main reaction product of the reduction of oxygen in this ionic liquid, with slow conversion to  $Li_2O_2$ . The long lifetime of superoxide anions is probably related to the high concentration of soft organic cations in ionic-liquids. As a result, the rate of electrode passivation by  $Li_2O_2$  deposition can be in principle slower in ionic liquids, since superoxide anions could diffuse fast enough away from the electrode

surface before they could disproportionate forming  $Li_2O_2$ . Indeed, our interpretation of the experimental data reported by Monaco *et al.* [16] indicates that the capacity of Li-O<sub>2</sub> cells operated with pyrrolidinium-based ionic liquids is limited by the rate of mass transport of superoxide.

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Highlights

-First in-situ Raman measurement on the reduction of oxygen in ionic liquids -Degradation of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $C_2$ mimTFSI) during the reduction of oxygen by attack by superoxide -Absence of degradation reactions during the reduction of oxygen in 1-butyl-1methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr<sub>14</sub>TFSI). -New interpretation of the enhancement of the discharge capacity of lithium-oxygen cells with increased mass transport rate

<sup>i</sup> Two scenarios can be considered for galvanostatic experiments on the reduction of oxygen at rotating disc electrodes. If the applied current is lower than the oxygen diffusion limiting current, then the electrode potential will reach a steady state, after which the oxygen reduction reaction will continue at a constant rate, unless factors other than oxygen diffusion intervene to produce an end point in the reaction. On the other hand, if the applied current is higher than the limiting current, the oxygen reduction reaction will end at the time when the concentration of oxygen at the surface drops to zero, with a sharp decrease of the electrode potential. Estimations of the oxygen diffusion limiting current under the conditions in the work by Monaco *et al.* [16] indicate that the applied current is lower than the limiting current. Furthermore, we can estimate the charge required to deplete the oxygen concentration to approach zero before reaching steady state conditions. This can be done by using the theory for a transient at a Rotating Disk Electrode (RDE), since in order to deplete the oxygen concentration to zero, the thickness of the diffusion layer should be smaller than the thickness of the stagnant layer in a RDE [28]. Thus, the charge is obtained as:

$$q = (n^2 F^2 D \pi c^2) / (4j) \qquad (\text{Equation 1})$$

Where: n is the number of electrons, F is the Faraday constant, D is the diffusion coefficient of oxygen, c is the oxygen solubility and j is the experimentally applied current density.

For the experimental conditions in the work by Monaco et al, we obtain  $q = 4.5 \text{ mC} \cdot \text{cm}^{-2}$ . For this calculation, we have used n = 2,  $D = 8.6 \times 10^{-6} \text{cm}^2 \cdot \text{s}^{-1}$  (as estimated using the value of the diffusion coefficient in pure Py<sub>14</sub>TFSI and taking into account the change in viscosity upon addition of 100 mmol·dm<sup>-3</sup> of LiTFSI using the Stokes-Einstein relationship),  $c = 3 \text{ mmol·dm}^{-3}$  and  $j = 0.5 \text{ mA} \cdot \text{cm}^{-2}$ . When the value of the oxygen diffusion coefficient in pure Py<sub>14</sub>TFSI is used, the calculation gives  $q = 6.3 \text{ mC} \cdot \text{cm}^{-2}$ . Taking into account the carbon loading used in these experiments (1 mg·cm<sup>-2</sup>), these charges correspond to specific capacities of 1.3 mA·h·g<sup>-1</sup> and 1.8 mA·h·g<sup>-1</sup>, respectively. The specific capacities measured experimentally are much higher than that: > 300 mA·h·g<sup>-1</sup> at rotation rates > 200 rpm. In addition, if the observed sharp drop in potential during the galvanostatic discharge was due to oxygen starvation, the same value of discharge capacities increase with rotation rates, while the experimental discharge capacities increase with rotation rate. Therefore, we can conclude that, at these rotation rates, the supply of oxygen towards the surface was fast enough to sustain the applied current.