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Tailoring oxygen redox reactions in ionic liquid based Li/O₂ batteries by mean of the Li⁺ dopant concentrationLaura Cecchetto,^a Alvaro Y. Tesio,^{a,b} Mara Olivares-Marín,^{a,e} Marc Guardiola Espinasa,^c Fausto Croce^d and Dino Tonti^{*a}Received 00th January 20xx,
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Ionic liquids' (ILs) reusability, non-volatility and non-corrosiveness, as well as their ease of isolation and a large electrochemical stability window make them an interesting choice as environment-friendly electrolyte for metal/air batteries. ILs have been described as designer solvents as their properties and behaviour can be adjusted to suit an individual reaction need. In the framework of this study we applied a conceptually similar designer approach and show that a simple parameter as the concentration of a Li⁺ dopant dramatically affects the reactions yields of Li/O₂ based energy storage devices. We studied the effect of Li⁺ concentration from 0.1 to 1 M in a LiTFSI:PYR₁₄TFSI ionic liquid electrolyte on the kinetics of the oxygen reduction reaction (ORR) and on the formation rate of different Li-O species at two different temperatures, finding that discharge capacity, rates and product distribution change in a non-linear way. At 60 °C highest rates and up to one order of magnitude larger capacities were observed at intermediate LiTFSI concentrations, implying a complete mechanism switch from surface to volume phase mediation for Li₂O₂ precipitation. At room temperature the same evolution was observed, even if in this case the surface mediation remained predominant at all concentrations. These results suggest the possibility to optimise the ionic liquid based Li/O₂ battery performances in terms of discharge capacity and lithium use, by playing on temperature and alkali cation concentration.

1. Introduction

Lithium-oxygen (Li/O₂) rechargeable batteries utilizing aprotic electrolytes overcome all other practically interesting electrochemical battery storage devices in terms of theoretical specific energy. Consequently, these batteries have recently received considerable attention,¹⁻⁸ being an important candidate for energy storage devices for electric vehicles, and other large scale high-energy storage applications. In spite of these promising perspectives, the practical exploitation of Li/O₂ systems in organic electrolytes is still far, due to the numerous scientific challenges that need to be addressed. The main critical points are a low efficiency due to a significant overpotential and a poor reversibility upon cycling. These are mainly related to the formation of the insoluble and insulating Li₂O₂ product⁹⁻¹² whose morphology and structure can greatly affect the cell overpotential and reversibility, and to the

presence of parasitic products mostly from solvent decomposition, product of the reaction of the intermediates of oxygen reduction with the organic electrolytes.¹³⁻¹⁶ Moreover, as volatile organic solvents are highly polluting and difficult to recycle, their replacement on large energy storage devices also represents an advantage to the environment. Ionic liquids reusability, non-volatility and non-corrosiveness, as well as their conductivity and a large electrochemical stability window make them an interesting choice as environmentally friendly electrolyte for rechargeable Li-ion batteries^{17,18} as well as for metal-air batteries.¹⁹ Besides their interest as "green" solvents,²⁰ different studies have showed that ionic liquid electrolytes are generally more stable, compared to other organic electrolytes, to the superoxide radical anion attack,²¹ and that their use could lower the overpotential^{22,23} while increasing the rechargeability of the Li/O₂ cells.²⁴ In particular, Elia et al. could recently demonstrate exceptional energy efficiency in the order of 82%.²³ However, their high viscosity generally introduces mass transport limitations that may results in film-like coating and poor discharge capacity.²⁵⁻²⁷ In effect these limitations can be reduced by stirring the electrolyte and operating above room temperatures.²⁵ Nonetheless, stirred cells require larger electrolyte volumes, which tend to increase cost and lower energy density. Quaternary ammonium ionic liquid electrolytes, are the most studied in combination with Li/O₂ cells, in particular 1-methyl-1-butylpyrrolidinium bis(tri-fluoromethane sulfonyl) imide (PYR₁₄TFSI). Several investigations have already been reported

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on the O_2 reaction in cells containing $PYR_{14}TFSI$ pure^{21,28-30} or at different concentrations of $LiTFSI$,^{25,28,29,31-33} where glassy carbon²⁹ or porous carbons^{25,28,31,32} were used as cathodes. The presence of Li^+ has been found to remarkably affect the O_2 electrochemistry,^{25,28} however the effect of its concentration has not been discussed in detail. The aim of this work was to tune a $PYR_{14}TFSI$ electrolyte and optimize it for Li/O_2 batteries, by acting on parameters that affect interactions with O_2 and its reduction products. We especially investigated the effect of Li^+ concentration at two different temperatures on the formation rate of different $Li-O$ species. We performed a galvanostatic, cyclic voltammetry study and SEM morphological characterisations at room temperature (RT) and at 60 °C with a $PYR_{14}TFSI$ solution containing different $LiTFSI$ concentrations. We show that the peroxide/superoxide ratio and even the discharge mechanism in a $PYR_{14}TFSI$ based electrolyte can be modulated by controlling the Li salt concentration and the temperature, showing the possibility to largely control Li/O_2 batteries by these two parameters.

2. Experimental methods

The electrochemical cell was based on ISO-KF standard high vacuum components supplied from ITL Vacuum Components. A detailed description of the cell is reported in a previous work.³¹ The electrodes consisted of a layer of commercial carbon black (Super P, M.M.M. Carbon) supported on a stainless steel mesh (AISI 316, 180 mesh per inch, ADVENT Research Materials Ltd). Super P (90 wt.%) was mixed with 10 wt.% of polyvinylidene fluoride (PVDF) as a binder in N-methylpyrrolidone (NMP). The slurry obtained was used to impregnate the mesh, which was finally dried at 100 °C for 12 h. The carbon load used was close to 1 mg cm⁻². The electrolyte used was 1-methyl-1-butylpyrrolidinium bis(trifluoromethane sulfonyl)-imide ($PYR_{14}TFSI$, 99.5%, Solvionic) containing $LiTFSI$ (99.95%, SigmaAldrich). $PYR_{14}TFSI$ was stored in dry box and used as received, while $LiTFSI$ was dried at 120 °C under vacuum for 48 h before use. The separator was a fiberglass filter (FilterLab MFV1, 260 µm thick) soaked with ~100 ml of electrolyte, the anode was a Li metal foil (Sigma Aldrich, 0.4 mm thick, cut to approx. 0.8 cm²). A nickel foil was used as a current collector. All lithium-oxygen cells were assembled in an argon-filled glove box. Subsequently, oxygen was forced to pass continuously through the cell for at least 20 min before starting the electrochemical measurements, and a constant flow (5 ml min⁻¹) was kept during the measurements. Tests at room temperature were done in a lab with temperature set at 25 °C. For tests at 60 °C cells were placed in a heating cabinet designed specifically for this purpose.

3. Results and discussion

To compare the oxygen reduction reaction (ORR) activity using $LiTFSI$ concentrations between 0.1 M and 1 M we performed cyclic voltammeteries at a scan rate of 100 mV s⁻¹ and 20 mV s⁻¹

at room temperature (RT) and 60 °C under an oxygen flow. The results are reported in Fig. 1.

Fig. 1 Cyclic Voltammetry curves obtained at different $LiTFSI$ molar concentration in $PYR_{14}TFSI$ at RT and at 60 °C with an applied scan rate of 100 mV s⁻¹.

The typical peak position observed and the cyclic voltammetry shapes are very similar to what previously observed by Allen et al. in a lithium oxygen cell containing 0.025 M $LiTFSI$ in $PYR_{14}TFSI$ on Au.³³ The agreement is remarkable, if we keep into account that in our case we are using not an ideal substrate, but a common porous carbon electrode. We therefore propose the same reaction scheme to explain the different peaks observed in our study and use the same labelling, as summarized in Table 1. The cathodic peak C1 may correspond to more than one reduction reaction of O_2 , occurring almost at the same potential, leading to LiO_2 , Li_2O_2 or in some cases to Li_2O . Lithium peroxide can be obtained from superoxide via second electrochemical reduction and/or via chemical disproportionation. The different species generated

in the C1 region of the cathodic scan are oxidized at different potentials, originating different anodic peaks. During the anodic scan, lithium peroxide, considered the most stable in aprotic electrolytes, is oxidized to O_2 and Li^+ in a two-electron reaction corresponding to peak A3, while peak A2 has been previously assigned to oxidation of lithium superoxide to O_2 and Li^+ ^{24,28} as also confirmed by Raman measurements.^{34,35} In the 1 M solutions, where viscosity is expected to be particularly high, the anodic peaks are hardly visible, and rather a sort of diffusion plateau is observed; in this case, labels A2 and A3 barely mark their expected position. According to the peak attribution illustrated in Table 1, the ratio between A2 and A3 can provide qualitative information on the relative amounts and stability of LiO_2 and Li_2O_2 formed in C1. This ratio between the formed products may affect capacity and reversibility of the Li/O_2 cell in the different electrolytes.²⁴

Table 1 Electrochemical (EC) and chemical (Ch) reactions and corresponding labelling

$Li^+ + O_2 + e \rightarrow LiO_2$	EC C1	$LiO_2 \rightarrow Li^+ + O_2 + e$	EC A2
$Li^+ + LiO_2 + e \rightarrow Li_2O_2$	EC C1'	$Li_2O_2 \rightarrow 2 Li^+ + O_2 + 2e$	EC A3
$2LiO_2 \rightarrow Li_2O_2 + O_2$	Ch		

At both temperatures the onset potentials, as well as the anodic and cathodic current densities are all affected by the Li^+ content. In Fig. 2 are reported the absolute values of the cathodic current recorded at 2 V at RT and 60 °C in the 100 mV s^{-1} scans. At RT the lowest cathodic currents are observed in the 1 M LiTFSI:PYR₁₄TFSI solution. Instead, increasing the LiTFSI content from 0.1 M up to 0.8 M the cathodic current progressively increases. This is associated with an increase of the anodic peak contribution at higher potential (peak A3), confirming the rapid LiO_2 conversion to Li_2O_2 , according to what already observed by Allen et al.²⁴ At 60 °C the cathodic current steeply increases, as a function of the LiTFSI concentration in the PYR₁₄TFSI solution, reaching a maximum value in the 0.6 M solution and then decreasing at higher LiTFSI concentrations. In this case, when the cathodic peak is increased, a greater A2 peak contribution is observed, while peak A3 becomes negligible compared to what observed at RT. Thus, in spite of the similar trend of larger cathodic currents at intermediate concentrations, the rise of temperature makes the LiTFSI concentration in the PYR₁₄TFSI solution a more critical parameter for the ORR at the electrode interface.

Recent studies have explained that formation of solid Li_2O_2 from O_2 reduction proceeds by an electrode surface or solution pathway depending on the influence of the solvent donor number on the solubility of the LiO_2 intermediate.³⁶ Being LiO_2 partitioned between LiO_2 dissolved in the electrolyte and LiO_2 adsorbed on the electrode, the ORR can take place on the electrode surface or in the electrolyte bulk, depending on the electrolyte stabilisation properties. In our case, the increase of the A2 anodic peak with temperature and with LiTFSI concentration could be explained in terms of an increase of soluble LiO_2 , most likely due to a faster desorption, at the expense of its disproportionation at the immediate surface. LiO_2 solubilisation strongly increases its further production and a larger number of molecules would remain

within their diffusion length from the electrode surface. The weak temperature-dependence of the A2 overvoltage compared to A3, further supports the attribution of peak A2 to mainly solubilised LiO_2 . The increase of peak A2 at the expense of A3, observed at 60 °C, would thus suggest that the LiO_2 dissolution in the electrolyte is promoted at higher temperatures so that a larger extent of solution phase mechanism for Li_2O_2 precipitation takes place. It is worth to notice that the A2/A3 ratio takes smaller values as the scanning speed decreases (Fig. 1f), consistent with peak A2 being related to a LiO_2 soluble species, whose diffusion far from the electrode would be favoured at lower scan rate.

Fig. 2 Absolute value of cathodic current at 2 V in cyclic voltammograms at a scan rate of 100 mV s^{-1} as a function of LiTFSI molar concentration at RT and at 60 °C.

Galvanostatic tests under different Li^+ concentrations reflect cycling voltammetry results. Fig. 3 depicts the behaviour at RT and 60 °C of discharge capacity at different LiTFSI concentrations, applying a current of 0.1 mA cm^{-2} . At both temperatures, the graphics show a “volcano” shape evidencing optimal performances for a concentration of 0.6 M. The low capacity at RT compared to the work of Elia et al.²³ could be mainly attributed to our cathode geometry, which in our case was flooded and not supported on a gas-diffusion layer. Nevertheless, as it is possible to see from Fig. 4, we also observed a remarkably low charge voltage (especially at 60 °C) compared to literature using other organic electrolytes.^{6,7,23} While a smaller particle size may play a role, we attribute this lower charge voltage mainly to the smaller quantity of secondary products wrapping the deposits discharged in Room Temperature Ionic Liquids (RTIL)-based electrolytes, as recently shown by us using soft x-ray transmission microscopy.³⁷

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Fig. 3 Discharge capacity values as a function of LiTFSI molar concentration in PYR₁₄LiTFSI at RT and at 60 °C.

Fig. 4 Voltage (vs. Li^+/Li^0) as a function of specific capacity (Ah g^{-1}) for a 0.1 M, 0.6 M and 1 M LiTFSI concentration in PYR₁₄LiTFSI at RT and 60 °C.

Remarkably, the volcano shape obtained for the discharge capacity is similar to the behaviour already observed for the cathodic current as a function of the LiTFSI content (Fig. 2). We can therefore conclude that the non-linear evolution of the Li^+ availability for the ORR at the interface equally affects cathodic current and discharge capacity when increasing the Li^+ concentration. This evolution is analogous to that reported by Liu et al. as a function of LiTFSI concentration in TEGDME³⁸ although the maximum is here observed with lower Li^+ concentration, which can be attributed to the stronger effect of Li^+ on viscosity as discussed above. Nevertheless, the most intriguing aspect is the large capacity increase obtained at intermediate concentrations. These values - ranging from 1500 mAh g^{-1} to 3000 mAh g^{-1} at 60°C - correspond to those previously observed with the same electrodes in presence of a solution-mediated mechanism.²⁶ The theoretical capacity for a film-like discharge on Super P can be estimated as 1200 mAh g^{-1} considering the specific surface area of $62 \text{ m}^2 \text{ g}^{-1}$, the Li_2O_2 film thickness and the capacity density,^{6,27} however this is considered a limit value that is usually not approached, as it is difficult to homogeneously cover all the carbon surface.

Therefore, the observed higher capacities can only be explained by a solution phase mechanism. In effect, SEM images of the electrode surfaces after discharge at 60°C in 0.1 M, 0.6 M and 1 M LiTFSI solutions (Fig. 5) are consistent with a mechanism change for intermediate concentrations.

A heterogeneous precipitate characterised by large particles is evident with the 0.6 M solution, while in the other two cases just the texture of the supporting carbon can be appreciated, as expected with formation of a nm-thick conformal Li_2O_2 film. The role of soluble LiO_2 to obtain a solution mediated mechanism and thus large discharge capacity is highlighted by the evident A2 peak at intermediate concentration at 60°C . We report in Fig. 6 the discharge capacity as a function of the A2/A3 ratio (considering the respective absolute peak currents) at RT and 60°C . In effect, a remarkable linear trend is observed at 60°C , while at RT no clear correlation can be noticed.

Fig. 5 Secondary electrons images of the electrode surface after discharge in a 0.1 M, 0.6 M and 1 M LiTFSI concentration in PYR₁₄TFSI at 60°C .

Fig. 6 Discharge specific capacity obtained as a function of the A2/A3 ratio, at RT and 60°C and linear trend of points obtained at 60°C .

In the latter case, the relatively low capacities and the high peak A3 contribution suggest a main surface precipitation process that is expected to partly mask the effect of the Li^+ concentration on LiO_2 solubility, although the highest discharge capacity was still observed for the Li^+ concentration of 0.6 M, where the anodic peak A2 reaches its limiting value. We can therefore conclude that a complete mechanism switch from surface to volume phase mediation takes place at intermediate concentrations at 60°C , while at RT the same

tendency is likely, even if the surface mediation remains present at all concentrations.

Several causes can be considered for this mechanism change, and the present knowledge of the system makes difficult a precise description. Both, concentration and temperature affect viscosity, the electrolyte association, and the cathode wettability by the electrolyte.^{39,40} Viscosity determines electrolyte conductivity and mass transport of reactants and products. The electrolyte association interacts with solvation of possible soluble intermediates. Wettability in turn affects the available area for charge transfer, and may influence the nucleation of Li_2O_2 deposits on the surface of the electrode. The increase of temperature is generally expected to enhance electrochemistry via these effects, while the effect of concentration is not monotonous. However, the switch from a surface- to a solution-mediated mechanism necessarily involves enhanced LiO_2 solubilisation.

Mass transport is likely responsible of the generally improved kinetics at higher temperature, when viscosity decreases⁴¹ and the Li^+ mobility substantially increases.⁴² It could also be involved in the mechanism switch at 60 °C. In effect, previous studies in this RTIL system showed that electrolyte stirring can largely affect the discharge capacity²⁵ by inducing a similar change of the peroxide deposition mechanism.²⁶ This indicates that depletion of either oxygen or Li^+ hinders LiO_2 formation and desorption. The strong sensitivity to the LiTFSI concentration suggests that even if in larger concentration than O_2 (which is in the order of 2-3 mM²⁸), Li^+ could be at least as limiting. This can be explained by the Li^+ diffusivity more than one order of magnitude smaller and more dependent on LiTFSI concentration than oxygen.^{42,43} Our results suggesting faster ORR kinetics at the intermediate concentrations used, could be ascribed to a higher Li^+ availability at the electrode interface. However, when the LiTFSI content further increases, coordination of Li^+ with TFSI neighbouring anions starts forming bridged structures limiting mass transport.^{41,44,45} In this case, the slower diffusion prevails over the increased Li^+ content, and the ORR rate declines.

In addition to its effect on mass transport, we think that the Li^+ content could also affect electrolyte association, which also plays a role on LiO_2 solubility, as it has been showed recently in the literature.^{46,47} Sharon *et al.*⁴⁷ especially highlighted how the level of lithium salt association, which strongly depends on its concentration in the electrolyte, could affect LiO_2 stability: the more associated Li salt would improve the Li^+ soft acid character and thus its affinity for the O_2^- soft base. This favours LiO_2 desorption, and again its solution phase disproportionation, as long as the increased LiTFSI bridging affects viscosity. Further studies are needed to demonstrate what phenomena govern the reaction path in this system.

Conclusions

A cyclic voltammogram study performed with a Super P electrode with LiTFSI:PYR₁₄TFSI ionic liquid solutions at different concentration gave features similar to those previously reported in literature on Au or glassy carbon.

According to the Li^+ content and temperature, it is possible to significantly affect the reaction product ratio as well as the reduction and oxidation voltage and kinetics. The delivered discharge capacity is also affected. At a given temperature, the Li^+ concentration affects the delivered current as well as the reaction product ratio. We could confirm that higher temperature improves kinetics and also favours superoxide stability for given Li^+ concentrations. The highest capacities are observed at the intermediate composition of 0.6 M at RT and 60 °C. This dependence could involve both mass transport and an electrolyte association effect acting on the way LiO_2 is partitioned between electrode surface and electrolyte bulk, affecting where Li_2O_2 precipitation takes place, with dramatic effects on capacity. These results show that by playing on Li^+ concentration and temperature it is possible to switch from surface mediated to solution-phase Li_2O_2 growth mechanism for optimal Li/O₂ cell performances. Further investigations focusing on a more precise understanding of the mechanisms, and on the effect of temperature and other electrolytes additives may still largely improve discharge capacity, reversibility and efficiency, nevertheless the present study confirms that ionic liquids are a promising choice for metal-oxygen batteries.

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Li⁺ dopant concentration in RTIL electrolyte controls the discharge mechanism in Li/O₂ batteries