

A redox shuttle to facilitate oxygen reduction in the lithium air battery

Matthew J. Lacey, James T. Frith and John R. Owen

5 University of Southampton, UK

Abstract

10 A novel design of the non-aqueous lithium air cell is presented with a demonstration of a new reaction concept, involving a soluble redox shuttle to catalyse oxygen reduction. In principle, this can relieve the requirement for fast diffusion of molecular oxygen from the air interface to the positive electrode. To demonstrate this concept, ethyl viologen ditriflate was dissolved in BMPTFSI, reduced at a carbon electrode and regenerated by aspiration with oxygen. Useful shuttle behaviour, confirmed by several reduction-oxidation cycles, was observed in 15 the case where the electrolyte contained at least 0.3M lithium salt. The beneficial effect of the salt was attributed to its critical role in converting superoxide, which would otherwise destroy the shuttle, into the more desirable product of oxygen reduction, lithium peroxide.

Keywords

20 Li-air, viologen, redox shuttle, oxygen reduction, catalysis, ionic liquid

Introduction

25 The rechargeable lithium air battery is expected to have a high mass-specific energy due to the low mass of its discharge products such as Li_2O and Li_2O_2 [1–4] and this battery has been proposed as a solution to the challenge of extending the range of electric vehicles to many times what is possible using today's lithium ion technology. The negative electrode, lithium metal, is very reactive towards water and must be used with a non-aqueous electrolyte, except 30 in some cases where it is protected from water by a ceramic membrane[5]. The positive electrode is analogous to a fuel cell, where oxygen reduction can occur at a three-phase interface between the gas, electrolyte, and the catalytic electrode surface within a partially wetted current collector. Alternatively, adsorption and diffusion of molecular oxygen through the electrolyte to the electrode surface can occur prior to the electron transfer. The latter 35 mechanism is particularly important in the cell design addressed in this work, which has an already oxygen-saturated electrolyte flowing over the electrode surface (LABOHR – Lithium Air Battery with Split Oxygen Harvesting and Redox processes)[6]. The discharge rate is usually limited by the rate of oxygen adsorption and permeation from the gas phase to the electrode surface through the electrolyte and insoluble reaction products. The solubility 40 constant limits the concentration of oxygen in the electrolyte to below 10 mM/bar in most liquid electrolytes.

The new concept, presented in Scheme I begins with a highly soluble redox shuttle $\text{M}^{(n+1)+}$ that can be reduced at the electrode. The reduced form then diffuses to the air interface to be 45 reoxidised by oxygen to form an oxide of lithium as the discharge product. Forming the product at the gas interface instead of the electrode surface is preferable in avoiding the problem of a solid product blocking further access to the electrode surface. The cycle is completed on diffusion of the shuttle to its original location at the electrode surface. Two variations are suggested, involving lithium peroxide or superoxide as the discharge product.

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Scheme I

(A) $M^{n+1} + e^- \rightarrow M^{n+}$ at the cathode

(B) $2M^{n+} + O_2 + 2Li^+ \rightarrow 2M^{(n+1)+} + Li_2O_2$ at the air interface

55 or (B') $M^{n+} + O_2 + Li^+ \rightarrow M^{(n+1)+} + LiO_2$ at the air interface

(C) $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$ overall $E^0 = 2.9 \text{ V vs Li}$

or (C') $O_2 + Li^+ + e^- \rightarrow LiO_2$ overall $E^0 = \sim 2.3 \text{ V vs Li}$

60 Scheme I is an example of an electrochemical-chemical EC' catalytic reaction described in the electrochemical literature[7] and here applied to two possible oxide products. A one-electron transfer reaction is expected as a first step, and the extent of the two-electron transfer reaction will depend on kinetic factors which are not yet established and catalyse by certain cations, including Li^+ . To ensure thermodynamic feasibility, the free energy change for the chemical step (B) must be negative. This means that the thermodynamically reversible potential of the shuttle couple (A) should be comparable to, or more negative than that of the overall reaction (C).

70 In this work, the ethyl viologen redox couple, $EtV^{2+}/EtV^{.+}$ is analogous methyl viologen (Paraquat) which is well known for mediation of oxygen reduction in biological reactions, ultimately producing superoxide[8]. $EtV(OTf)_2$ was chosen for this work because of its relatively high solubility and stability in the ionic liquid electrolyte used for lithium cells.

Experimental

75 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI, IoLiTec) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Aldrich) were dried under vacuum at 80 °C prior to use and transferred to an argon-filled glove box.

80 Ethyl viologen ditriflate ($EtV(OTf)_2$) was prepared by the reaction of the diiodide salt with a stoichiometric amount of silver triflate ($AgOTf$, Aldrich) in aqueous solution. The solution was separated from the AgI precipitate and the water was removed under reduced pressure. The solid $EtV(OTf)_2$ was purified by recrystallization from ethanol and was dried under vacuum as described above.

85 1. Electrochemistry of oxygen and viologen in BMPTFSI

90 The electrochemistry of oxygen and viologen in ionic liquid was investigated using a two-electrode electrochemical cell comprising two glass compartments separated by a glass frit. The total electrolyte volume in each compartment was 4 mL. The working electrode was a 3 mm diameter glassy carbon disc and the counter and reference electrode was a piece of Li metal foil (0.5 mm, Rockwood Lithium). The glass frit minimises mixing of the two solutions by convection and improves the estimation of the extent of EtV^{2+} reduction according to Faraday's law

95 Solutions were prepared by dissolving the required amount of LiTFSI and $EtV(OTf)_2$ in BMPTFSI with vigorous stirring at 70 °C in the glove box. Oxygen saturation was achieved by bubbling the working electrode compartment solution with dry oxygen through a syringe needle for at least 20 minutes. The experiments were run at RT using a variable multichannel potentiostat (VMP2, Princeton Applied Research – Bio-Logic Science Instruments).

100 2. Chemical reactions of viologen, oxygen and Li^+

105 A two electrode cell comprising a copper foam working electrode (ERG Duocel, 40 ppi, 5 mm thick) and a Li metal counter and reference electrode was assembled. The electrolyte was 2 mM EtV(OTf)₂ in BMPTFSI. Two experiments were run, one with no added lithium salt and one with LiTFSI added at a 0.3 M concentration.

110 The blue reduced form of EtV was produced in the cell by holding the cell potential at 2.0 V until the correct charge had been passed according to complete reduction of EtV²⁺ to EtV⁺ in the electrolyte. The reduction was assisted by bubbling of Ar gas in the cell. Once the reduction was complete, the cell was left at open circuit and oxygen was bubbled through the cell until the blue colour of EtV⁺ had been completely bleached. This reduction/oxidation cycle was then repeated multiple times.

115 Results and discussion

1. (a). Electrochemistry of oxygen in Li⁺-containing ionic liquids

120 The voltammogram of Fig. 1 shows reduction of oxygen dissolved in the electrolyte during fast scans in the presence of 1 mM LiTFSI. The voltammetry due to the major redox couple has been fitted using EC-Lab's CV Sim utility.

125 The fit indicates that the redox couple at 2.04 V is consistent with a reversible one-electron transfer with a peak separation of approx. 59 mV plus IR drop. Following Ó'Laoire *et al*[9] we identify the reduced form as superoxide anion associated with the BMP cation via a soft base-soft acid interaction. An oxygen diffusion coefficient of approximately $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ can be estimated assuming an oxygen solubility of approximately 3 mM. A diffusion coefficient of superoxide an order of magnitude lower than that of oxygen has been estimated based on work reported by Evans *et al*[10]. A smaller cathodic peak at 2.3 V is attributed to lithium superoxide formation. Re-oxidation of the lithium species is delayed until 3.6 V, presumably due to its slow disproportionation to form a lithium peroxide at a higher oxidation potential. The additional current near the cathodic limit is attributed to further reduction of superoxide to peroxide.

130 When the Li⁺ concentration is increased to 0.3 M, which is a practical concentration for battery operation, it can be seen that the onset of oxygen reduction is shifted positive to approximately 2.6 V, peaking at 1.95 V with half the peak current compared to the 1 mM Li⁺ case. On the anodic scan, the reversible oxidation peak is completely suppressed, indicating disproportionation of lithium superoxide to lithium peroxide, which is reoxidised back to O₂ in the range 3.0 – 4.4 V. These findings are consistent with those reported elsewhere[9,11,12].

1. (b). Electrochemistry of viologen at low concentration

145 Fig. 2 shows the cyclic voltammetry of ethyl viologen ditriflate (EtV(OTf)₂) in oxygen-free BMPTFSI in the presence of 1 mM LiTFSI. The reversible redox couple centered at approximately 2.4 V is due to the EtV^{2+/-+} couple. This potential is notably lower than the thermodynamic potential for lithium peroxide, thus satisfying the condition for Scheme 1A.

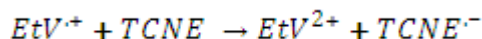
150 The effect of added oxygen is seen as an enhancement of the EtV reduction peak by regeneration of the oxidised form according to Scheme 1B. This result, obtained with a

relatively low concentration of shuttle confirms the shuttle mechanism. On the anodic sweep, there is no observed reoxidation of EtV^{+} , which is consumed by O_2 with regeneration of EtV^{2+} . Furthermore, there is no observed reoxidation of O_2^- , which must also be consumed. Of course, in order for this shuttle to be applicable to the Li-air concept, the ultimate product of the reaction must be Li_2O_2 . Evidence for this can be seen on the anodic sweep, where an oxidation peak appears at approximately 3.1 V. This peak is not seen in the voltammetry for oxygen reduction without the shuttle and with the same concentration of lithium salt (Fig. 1), but this peak is consistent with the anodic peak in Fig. 1 where the concentration of lithium salt is 0.3 M. Over multiple cycles, the voltammetry does not change and there is no significant degradation of any of the peaks. The voltammetry provides strong evidence for efficient viologen-promoted production of Li_2O_2 compared to direct oxygen reduction for the same low concentration of lithium salt, although the mechanism for this process is unclear.

The peak current for viologen in the absence of oxygen indicates a diffusion coefficient significantly lower than that of oxygen. As such, in order for this scheme to relieve the oxygen transport limitation in the discharge reaction, a high concentration of the shuttle must be used. A significant advantage of this scheme is that it is selective for oxygen at the air interface, whereas physical absorption from the gas is not selective.

2. Chemical reaction of EtV^{+} at high concentration with oxygen

A concentrated solution of EtV^{+} was prepared by reaction of a solution of $\text{EtV}(\text{OTf})_2$ (approx. 0.18 M) in BMPTFSI with metallic lithium with stirring for 48 hours in an argon atmosphere. A portion of the intensely dark blue solution was titrated against tetracyanoethylene (TCNE), according to the reaction:



The disappearance of the blue colour due to the titration of EtV^{+} against TCNE was monitored by colorimetry. The concentration of EtV^{+} was determined to be 20.5 mM. LiTFSI was added to a 5 mL portion of this solution to a concentration of approximately 0.1 M, the sample was removed from the glove box and was bubbled with oxygen for 15 minutes. During this time the colour of the solution changed from deep blue to bronze, and no precipitate was formed. The solution was left overnight, and a precipitate was observed the next day. This precipitate was readily soluble in tetraglyme to give a green solution. The product of this reaction, therefore, is not Li_2O_2 , and is consistent with the reaction of EtV^{+} with superoxide as described by Nanni *et al*[13]. This reaction would be expected to dominate where the concentration of EtV exceeds the solubility of oxygen and where the concentration of Li^{+} is too low to remove the produced superoxide as LiO_2 and, ultimately, Li_2O_2 .

The cycling behaviour of EtV^{+} was investigated by complete bulk electrolysis of EtV^{2+} to EtV^{+} at a concentration of 2 mM in BMPTFSI by applying a constant potential, with no added lithium salt. When the electrolysis was complete, oxygen was bubbled through the cell and bleaching of the blue colour gave way to a brown solution. The solution was then re-purged with Ar gas. Upon application of the electrolysis potential, only one-tenth of the first cycle electrolysis current was passed and no blue colour was observed. This is consistent with the viologen decomposition reaction as previously described.

200 The experiment was re-run with a solution containing the same concentration of EtV but
containing 0.3 M LiTFSI. In this case, the solution became colourless, on oxygen bubbling
and on subsequent electrolysis a similar current was passed compared to the first cycle, and
the blue colour was re-evolved. This process can be repeated many times, showing that EtV²⁺
205 is not consumed but instead acts as a catalyst. While a solid Li₂O₂ product has not yet been
detected directly, the conditions of this experiment cause the formation of the product away
from the electrode surface. The recyclability of viologen in the presence of a high
concentration of lithium salt provides strong evidence that lithium competes with EtV⁺ for
superoxide.

210 Our current work is focused on determining conditions under which the shuttle can achieve
high performance with good cyclability, as well as identifying potential shuttles with
improved stability against superoxide. Further investigation will address the possibility of
increasing the energy density of this system as compared with the standard Li-air system
215 where the capacity is limited by the resistance of the product formed as a solid layer on the
electrode surface.

Conclusions

220 The redox shuttle properties of ethyl viologen have been investigated electrochemically.
Under CV conditions at low concentration, EtV shows efficient redox cycling, being reduced
at the electrode and regenerated by reaction with oxygen near the air interface. The cycle is
stable over multiple voltammetric cycles. Comparison with direct oxygen electrochemistry in
Li⁺ solutions in the same ionic liquid leads us to suggest that EtV can efficiently promote
225 Li₂O₂ formation, although the exact mechanism is as yet unknown. However, we have also
demonstrated that at high concentrations of EtV⁺, the shuttle decomposes upon reaction with
superoxide. While controlled redox cycling of a low concentration of EtV in 0.3 M LiTFSI in
BMPTFSI has shown to be repeatable and demonstrates the concept of a redox shuttle for a
lithium air battery, a higher concentration of the shuttle is required in order to offset the
230 significantly lower diffusion coefficient of the shuttle relative to that of oxygen. For this
reason, further work will continue to focus on the search for a superoxide-stable redox
shuttle, such that a higher concentration can be used for successful cell operation.

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