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A rotating ring disk electrode study of the oxygen reduction reaction in lithium containing non aqueous electrolyte



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ABSTRACT

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1. Introduction

There is a growing interest in the rechargeable lithium-air battery that exhibits a very large theoretical energy density (5280 Wh/kg) comparable to fossil fuels for electric vehicle applications with extended millage range [1–3]. The non aqueous Li–air battery was introduced in 1996 by Abraham [4]. During discharge a lithium metal anode dissolves in non aqueous electrolyte and the resulting Li⁺ ions react with oxygen reduction products to form insoluble Li₂O₂ at a porous carbon cathode. Bruce et al. [5] demonstrated that the electrochemical reaction of Li⁺ with oxygen to yield insoluble Li₂O₂ in non aqueous electrolyte is reversible sustaining more than ten charge/discharge cycles. However, there are a number of challenges to achieve a large practical number of cycles with high charge capacity since the intermediaries of the ORR attack the solvent and cathode material reducing the re-chargeability [2]. Infrared and mass spectrometry coupled to electro-chemical cycling have shown in several aprotic solvents, including alkyl carbonates, ethers, and DMF degradation during recharging due to the nucleophillic attack by superoxide radical anion [6–9].

Among recent successful reports, Bruce [10] has demonstrated that the Li–air battery can be recharged with 95% capacity retention in 100 cycles using DMSO electrolyte and porous gold electrode. Scrosati [11] also reported a lithium–air battery with tetra-(ethylene) glycol dimethyl ether–lithium triflate (TEGDME–LiCF₃SO₃) electrolyte capable of 100 cycles of charge–discharge and high rate values.

We show the effect of a very small addition of LiClO₄ to tetraethyl ammonium perchlorate (TEAP) in acetonitrile on the electro-reduction of molecular oxygen (ORR) at a rotating ring (Pt) glassy carbon (GC) disk electrode. While TEA⁺ cations stabilize the first electron reduction product in acetonitrile, superoxide O_2^- , in the absence of Li⁺ the ORR proceeds by two one-electron sequential steps to the stabilized peroxide. Addition of 10 μ M LiClO₄ (<1:800 Li⁺ to TEA⁺ ratio) strongly affects the ORR mechanism: Both disk (I_D) and ring (I_R) currents strongly decrease, with less than 0.5% O_2^- produced at the GC disk reaching the ring electrode, but still I_R follows the same potential dependence as I_D. On the other hand, addition of DMSO to acetonitrile 0.1 M LiClO₄ stabilizes soluble O_2^- detected at the ring since DMSO preferentially solvates Li⁺ preventing disproportionation of LiO₂ into O₂ and passivating Li₂O₂.

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Solvation of Li^+ and oxygen species such as O_2^- plays a major role on the nature of discharge products, rechargeability and capacity of non aqueous Li–air batteries [12–14].

The redox potential for the O_2/O_2^- couple shows a strong dependence on the solvent due to different solvations of O_2^- [15,16], also solvation of the electrolyte cation influences the redox potential due the stabilization of the intermediate O_2^- [12,17].

It has also been shown that the electrode kinetics of the ORR in lithium air battery cathodes strongly depends on the solvent [9,12], electrolyte cation [18] and electrode material. On carbon electrodes the first reduction product, superoxide is stable in non aqueous solutions containing tetra alkylammonium cations. In acetonitrile, O_2^- has been described as produced by an outer sphere ORR on HOPG with a heterogeneous rate constant, an order of magnitude lower than on ordinary pyrolytic graphite (OPG) [19].

Furthermore, O_2^- can nucleophillically attack most aprotic solvents employed [1,7,8] as in situ infrared experiments and mass spectrometry have suggested [9,20–22]. The rotating ring disk electrode (RRDE) has been employed recently to quantify the stability of superoxide in aprotic solvents such as propylene carbonate and an ionic liquid by measuring the ring current transient response to a potential step at the disk electrode [23].

The present communication discloses new important RRDE evidence on the role of superoxide, lithium ions and their solvation with respect to the recharge capacity of lithium air batteries.

2. Experimental

A glassy carbon (Tokay Carbon Co., Japan) disk electrode with a Pt ring embedded in Araldite epoxy resin cylindrical body (Ciba-Geigy)

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was employed with $A_D = 0.196 \text{ cm}^2$. The geometrical dimensions of the RRDE were $r_1 = 0.250$, $r_2 = 0.265$ and $r_3 = 0.300$ with a collection efficiency $N_o = 0.22$ [24]. A RRDE system described elsewhere [25] has been used in an air tight three-electrode cell. An Ag/AgCl, 3 M KCl reference electrode in a fritted glass compartment with the aprotic electrolyte was employed and potentials are referred to the Li/Li⁺ system after calibration with ferrocene. Acetonitrile (HPLC, Merck) was purified in a solvent purification system (Innovative Technology). The water content evaluated by coulomb metric Karl Fischer titration (Metrohm 831 KF coulometer) was typically 50 ppm. Lithium tetraethyl-ammonium perchlorate (Aldrich) and lithium perchlorate (Aldrich) have been employed.

3. Results and discussion

Fig. 1 depicts the ORR disk and superoxide oxidation ring current vs. disk potential curves for W $(2\pi\omega) = 18$ Hz. The ORR disk current shows little hysteresis and approaches a limiting value while the ring current collecting O_2^- under convective-diffusion exhibits a maximum at -1.6 V.

At the disk electrode the possible potential dependent sequential reactions are:

$$O_2 + TEA^+ + e \rightarrow \left[O_2^- TEA^+\right] \tag{1}$$

$$\left[O_2^- TEA^+\right] + TEA^+ + e \rightarrow \left[O_2^{2-} TEA_2^+\right]$$
(2)

with two one-electron superimposed waves (see below). The bulky tetra-alkyl ammonium cation stabilizes O_2^- and $O_2^2^-$ by cation–anion pairing [12]. The ORR is reversible with large bulky counter-ions, but highly irreversible in the presence of small cations, such as lithium, because of the instability of LiO₂ and electrode surface passivation by solid lithium peroxide, Li₂O₂ [12,26–28].

The convective-diffusion O_2 reduction current, I_L , in Fig. 1 can be described by the Levich equation [29]:

$$I_L = 1.554 n FAD_{0_2}^{2/3} \nu^{-1/6} C_{0_2} W^{1/2}$$
(3)

with F as the Faraday constant, n as the number of electrons per O₂ molecule, A as the electrode geometric area, D_{O2} O₂ as the diffusion coefficient in acetonitrile, c.a. $4.64\times10^{-5}~{\rm cm}^2{\rm s}^{-1}$, C_{O2} = 8.1×10^{-3} M, the kinematic viscosity, and ν = 0.0036 cm $^2{\rm s}^{-1}$ and W (f = $2\pi\omega$) are the rotation frequency in Hz.



Fig. 1. O_2 reduction on a GC disk electrode in O_2 (1 atm) saturated 0.1 M TEAP in purified CH₃CN at W = 18.5 Hz and scan rate of 0.1 V s⁻¹, ring current at $E_R = 3$ V. The inset depicts a CV of O_2 reduction under unstirred conditions. $A_D = 0.2$ cm².

At the ring electrode ($E_R = 3 \text{ V}$) the superoxide radical anion is oxidized under convective-diffusion conditions (see inset CV for ORR under unstirred condition):

$$[O_2^- TEA] \rightarrow O_2 + TEA^+ + e. \tag{4}$$

Considering $N_o = 0.22$, the ring current is only a fraction of the expected value ($N_o.I_D$); therefore a fraction of the superoxide formed at the disk electrode should decompose in transit to the ring electrode. In the presence of traces of water (50 ppm in the CH₃CN represents 2–3 mM as compared to O_2 solubility 8.1 mM and thus superoxide concentration) the fast reaction ($k_2 > 10^4 \text{ M}^{-1} \text{ s}^{-1}$):

$$\mathrm{HO}_{2}^{\bullet} + \mathrm{HO}_{2}^{\bullet} \rightarrow \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{O}_{2} \tag{5}$$

yields H_2O_2 . Also with traces of H_3O^+ the reaction:

$$HOO' + H_3O^+ + e \rightarrow H_2O_2 \tag{6}$$

with $E^{o'} = 0.8$ V would also account for the loss of superoxide.

In LiClO₄ containing electrolyte in acetonitrile the ORR proceeds with very different kinetics as has been shown on Au [16] and glassy carbon [18] with the formation of Li_2O_2 [14,18].

The following reactions at low overpotential:

$$O_2 + Li^+ + e \rightarrow [O_2 Li] \tag{7}$$

$$O_2Li] + [O_2Li] \rightarrow Li_2O_{2\downarrow} + O_2 \tag{8}$$

and, at lower potentials:

$$[O_2Li] + Li^+ + e \rightarrow Li_2O_2$$

should be considered in lithium containing electrolytes.

In our hands, the RRDE has failed to detect (zero ring current) soluble O_2^- in LiClO₄ electrolyte above 1 mM. This implies that either solution soluble O_2^- is not formed at GC disk in Li⁺ bearing electrolytes of comparable concentration to O_2 solubility or it undergoes rapid dismutation to yield insoluble Li₂O₂.

However, adding 10 μM LiClO₄ to the tetraethyl ammonium perchlorate solution, I_D is much smaller with a shoulder at 2.5 V and a peak at = 1.9 V as depicted in Fig. 2 with surface passivation in the reverse scan. Surprisingly a non zero I_R is only a very small fraction of the disk current (i.e. 1–2 μA vs 400 μA) but follows the I_D vs. E_D curve shape with the shoulder and the peak [30].

In 10 μ M LiClO₄ the concentration of Li⁺ ions is some 800 times less than that of dissolved oxygen, and 10⁴ times less than (TEA⁺),



Fig. 2. O_2 reduction on a GC/Pt RRDE in O_2 saturated 0.1 M TEAP in purified CH₃CN containing 10 μ M LiClO₄ at W = 9 Hz and scan rate 0.1 V s⁻¹. Ring current at E_R = 3 V. A_D = 0.2 cm².

therefore the capacity of Li^+ ions in the weakly coordinating solvent acetonitrile to unstabilize LiO_2 by disproportionation into Li_2O_2 and O_2 is extremely high.

Unlike in acetonitrile, in the strong Lewis base DMSO with 0.1 M LiPF₆ electrolyte it has very recently been shown that soluble superoxide formed at a glassy carbon disk can be detected at a gold ring [14] due to the strong Li⁺ solvation in the highly polar DMSO and the stabilization of the solvated O_2^- Li⁺ ion pair in solution. We have studied the ORR in 0.1 M LiClO₄ containing DMSO in an equivalent concentration to the lithium ion in a large excess of acetonitrile (1:200). Fig. 3 depicts the resulting RRDE ORR curve with hysteresis, surface passivation and oxidation of Li₂O₂ at positive potentials and detection of superoxide oxidation ring current. Notice that the soluble O_2^- reaching the ring is an important fraction of the flux at the disk electrode, i.e. $-I_R N_0^{-1}$ compared to I_D .

Even in large excess of acetonitrile, Li^+ ions seem to be preferentially solvated by DMSO with solvated $Li^+-O_2^-$ ion pair stable with respect to disproportionation into Li_2O_2 and O_2 . The decrease in $O_2^$ concentration at more reducing potentials, i.e. a maximum ring current, indicates that a second electron transfer occurs and soluble $Li^+-O_2^-$ produces Li_2O_2 collecting less superoxide at the ring. We cannot completely rule out some slow reaction of DMSO and O_2^- into dimethylsulfone and spectroscopic studies are under way to unravel this question.

The competition of i) two sequential one-electron transfer steps with intermediate superoxide and ii) disproportionation of soluble



Fig. 3. O_2 reduction on a GC/Pt RRDE in O_2 saturated 0.1 M LiClO₄ in purified CH₃CN containing 0.1 M DMSO at W = 9 Hz and scan rate 0.1 Vs⁻¹. Ring current at $E_R = 0$ V. $A_D = 0.2$ cm².

superoxide into O_2 and insoluble Li_2O_2 may determine the ability to recharge the lithium-air battery. While the former hetero-geneous electrochemical reactions limit the amount of insoluble Li_2O_2 to monolayer or few layers due to tunneling distance and diffusion of Li^+ and O_2 limitations, precipitation of Li_2O_2 from the solution adjacent to the cathode may lead to the formation of bulky deposits that block the availability of electrons and O_2 during charge discharge cycles.

4. Conclusions

In conclusion, we have shown with RRDE experiments in acetonitrile based electrolytes that small additions of Li⁺ and DMSO respectively can operate in opposite directions on the kinetics of the ORR by strongly affecting the solvation of cations and the stability of the $O_2^$ with respect to O_2 and insoluble Li₂ O_2 . A combination of solvent properties, such as high oxygen solubility in acetonitrile and enhanced stability of superoxide in DMSO seems to be interesting for the design of advanced lithium air batteries with high discharge–charge capacity.

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