

Solvent and Conducting Salt Effects on the Oxygen Reduction Mechanism in the Non-Aqueous Lithium Air Battery

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The Lithium-air battery is attractive because fully developed, practical batteries could exceed specific energies of 2000 Wh/kg. The battery is composed of a Li metal anode and an air cathode in which the cathode active material, oxygen, is accessed from the environment (1). The early versions of the non-aqueous Li-air batteries utilized gel polymer electrolyte membranes as both the separator and the ion-transporting medium in the battery cell (1,2). More recent studies (3) have utilized organic carbonate and ether based electrolytes of the types used in Li metal and Li-ion batteries. Lithium peroxide, Li_2O_2 , has been identified as a discharge product of the Li-air battery (1), consistent with the observed cell voltage according to the reaction,



This study is a continuation of our efforts (3) to elucidate the effects of conducting salts and solvents on the kinetics and reduction of oxygen in non-aqueous electrolytes in relation to the development of the Li-air battery.

In solutions of the tetrabutylammonium (TBA) salts, $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ or $(\text{C}_4\text{H}_9)_4\text{NClO}_4$, in acetonitrile, the reduction of oxygen involves a highly reversible one-electron process with superoxide (O_2^-) as the only reduction product in the cyclic voltammogram when the potential is swept between 2.0 and +0.5 V versus Ag/AgCl. Rotating disk electrode (RDE) voltammetry scans under mass transport control are presented in Figure 1. Analysis of the data using the Levich relationship (equation 2) produced a straight line when the current, i , is plotted versus the square root of rotation speed, $\omega^{1/2}$ (Figure 1). The slope of this line runs parallel to the theoretical plot for a one-electron reaction.

$$i_L = (0.620) n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C \quad [2]$$

The results indicate that the reduction of oxygen in this electrolyte involves the initial formation of superoxide, O_2^- , according to Equation 3 as the first reduction product



When the potentials are scanned between -3.0 V and +3.0 V versus Ag/AgCl, a second reduction peak is observed at about -2.5 V which is irreversible. The formation of this peak is accompanied by a decrease in the intensity of the superoxide formation peak at about -1.25V. Consequently, the reduction process at -2.5 V is most probably the reduction of superoxide to peroxide according to equation 4.



The reduction of O_2 in the presence of the alkali metal cations is irreversible in this and several of other solvents investigated.

Substituting alkali metal cations Li^+ , Na^+ , or K^+ for TBA^+ produced significant changes in O_2 reduction and subsequent oxidation reactions. In solutions containing the smaller Li (\AA), an irreversible one-electron reduction of O_2 to LiO_2 is the first process. At fast sweep rates some reduction of this LiO_2 to Li_2O_2 is evident in the voltammograms. However, the LiO_2 formed initially appeared also to decompose to Li_2O_2 as evidenced by the decreased intensity of the peak for LiO_2 reduction to Li_2O_2 in the CV at slow sweep rates. The electrochemistry of O_2 in presence of Na^+ is somewhat similar to that in presence of Li^+ , except for the fact that the NaO_2 first formed appears to decompose rapidly to Na_2O_2 .

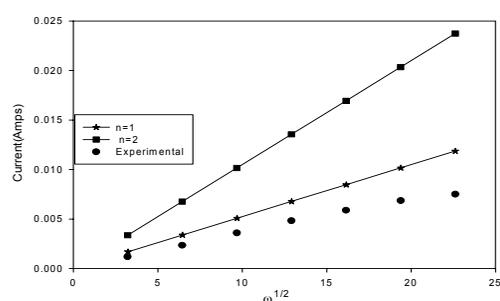
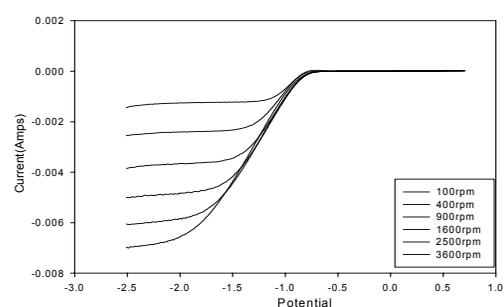
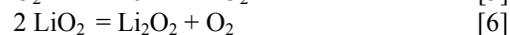


Figure 1: RDE Current-potential curves (upper) for the reduction of O_2 on a rotating disk electrode in 0.1 M TBClO_4 MeCN vs. Ag/AgCl at different rotation speeds and a scan rate of 100mVs^{-1} . The Levich plot of limiting current i vs. square root of rotation speed is also shown (lower).

References

1. K. M. Abraham and Z. Jiang, *Journal of The Electrochemical Society*, **143**, 1 (1996).
2. K.M.Abraham and Z.Jiang, U.S.Patent **5,510,209** (1996)
3. Cormac O' Laoire, Sanjeev Mukerjee and K. M. Abraham, Electrochemical Society Fall Meeting, October 2008, Hawaii, Extended Abstract No. 404

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