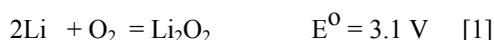


### Solvent and Conducting Salt Effects on the Oxygen Reduction Mechanism in the Non-Aqueous Lithium Air Battery

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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,  $\text{Li}_2\text{O}_2$ , 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 ( $\text{O}_2^-$ ) 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,  $\text{O}_2^-$ , 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  $\text{O}_2$  in the presence of the alkali metal cations is irreversible in this and several of other solvents investigated.

Substituting alkali metal cations  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  for  $\text{TBA}^+$  produced significant changes in  $\text{O}_2$  reduction and subsequent oxidation reactions. In solutions containing the smaller Li ( $\text{\AA}$ ), an irreversible one-electron reduction of  $\text{O}_2$  to  $\text{LiO}_2$  is the first process. At fast sweep rates some reduction of this  $\text{LiO}_2$  to  $\text{Li}_2\text{O}_2$  is evident in the voltammograms. However, the  $\text{LiO}_2$  formed initially appeared also to decompose to  $\text{Li}_2\text{O}_2$  as evidenced by the decreased intensity of the peak for  $\text{LiO}_2$  reduction to  $\text{Li}_2\text{O}_2$  in the CV at slow sweep rates. The electrochemistry of  $\text{O}_2$  in presence of  $\text{Na}^+$  is somewhat similar to that in presence of  $\text{Li}^+$ , except for the fact that the  $\text{NaO}_2$  first formed appears to decompose rapidly to  $\text{Na}_2\text{O}_2$ .

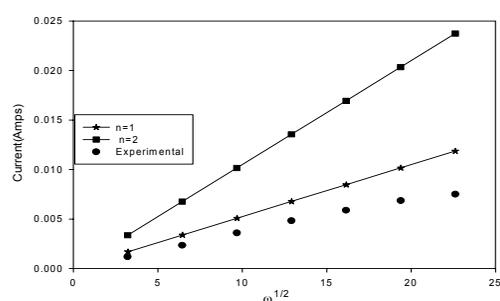
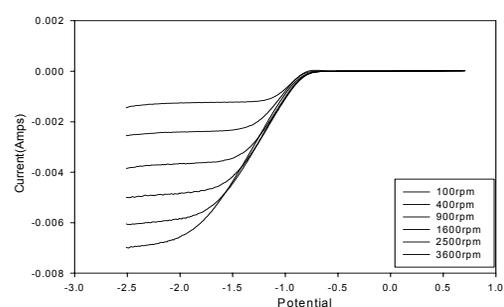
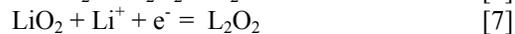
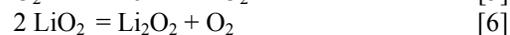


Figure 1: RDE Current-potential curves (upper) for the reduction of  $\text{O}_2$  on a rotating disk electrode in 0.1 M  $\text{TBClO}_4$  MeCN vs. Ag/AgCl at different rotation speeds and a scan rate of  $100\text{mVs}^{-1}$ . The Levich plot of limiting current  $i$  vs. square root of rotation speed is also shown (lower).

### References

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