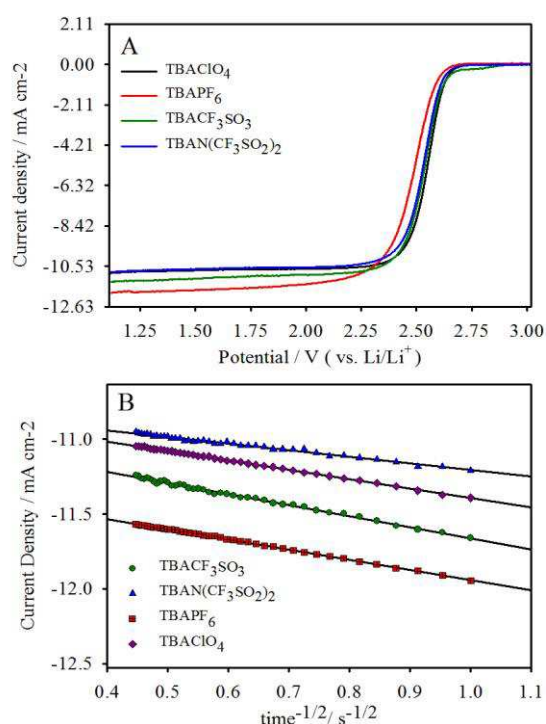


## Microelectrode Investigations of Oxygen Reduction Reactions in Lithium-air Batteries

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Despite recent progress in elucidating the electrochemistry of the oxygen electrode reactions in non-aqueous electrolytes, the irreversibility of the oxygen reduction reaction (ORR) has become a major challenge to developing practical rechargeable Li-air batteries<sup>1-3</sup>. In this connection, electrochemistry on microelectrodes can provide valuable information to delineate the



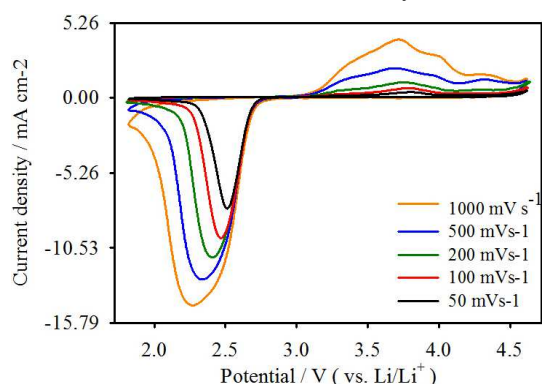
**Figure 1 A): Current vs. potential scans at a microelectrode in 0.1 M TBA/DMSO. Scan rate 50 mVs<sup>-1</sup> B): Cottrell plots calculated for the current-time transients obtained from potential jump chronoamperometry experiments.**

role of mass transport from reaction kinetics on the rechargeability of the oxygen electrode.

We have studied the ORR in dimethyl sulfoxide (DMSO)-based electrolytes containing Li and tetrabutylammonium (TBA) salts at a 11 $\mu$ m diameter carbon microelectrode. Due to efficient mass transport of the electroactive species onto and the removal of reduction products from the microelectrode surface (radial diffusion), limiting current behavior is expected for ORR even at scan rates high as 500 mV s<sup>-1</sup>. Indeed, we have observed steady state voltammograms with the characteristic limiting currents in all TBA salt-based electrolytes (Figure 1A). This confirms that the reversible one-electron reduction product, superoxide (O<sub>2</sub><sup>-</sup>), proposed by Cormac et al<sup>1</sup>, is soluble in TBA salt-based electrolytes. Oxygen transport parameters calculated from the Cottrell plots (Figure 1B) derived from chronoamperometric current-time transients on the

microelectrode in TBAPF<sub>6</sub>, TBAClO<sub>4</sub>, TBACF<sub>3</sub>SO<sub>3</sub>, TBAN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> in DMSO reveal that oxygen transport is not affected by the anions of these salts.

In contrast to the behavior of TBA salt solutions, peak-shaped (non-steady state) current-voltage profiles were observed in the electrolytes containing their Li salt counterparts (Figure 2). These voltammograms depicted in Figure 2 are attributed to electrode passivation by insoluble discharge products. As the microelectrode is passivated by insoluble ORR products, O<sub>2</sub> diffusion through the passivation film becomes increasingly inefficient and at the same time the effective area of the electrode available for ORR is greatly reduced. These two effects lead to a classical CV type current-voltage profile as the potential is scanned. We have confirmed passivation film formation on the microelectrode from SEM/EDAX and Raman spectroscopic data, which indicated that Li<sub>2</sub>O and Li<sub>2</sub>O<sub>2</sub> were formed at different reduction potentials. The trend in Columbic efficiencies for ORR in the various electrolytes containing



**Figure 2: Current-voltage scans at the microelectrode in O<sub>2</sub> purged 0.1 M LiPF<sub>6</sub>/DMSO recorded at scan rates ranging from 50 - 1000 mV s<sup>-1</sup>.**

Li salts suggested that LiCF<sub>3</sub>SO<sub>3</sub>/DMSO electrolyte has the best ORR product solubility out of the four Li<sup>+</sup>-conducting electrolytes, namely LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, or LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> in DMSO. Additional ORR studies on microelectrodes are being carried out in several ether electrolytes which together with the data in DMSO are expected to provide a deeper understanding of the influence of both organic solvents and ion-conducting salts on the rechargeability of the ORR reactions in non-aqueous Li-air batteries.

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