



## Studies of Li-Air Cells Utilizing Dimethyl Sulfoxide-Based Electrolyte

Matthew J. Trahan,<sup>a,\*</sup> Sanjeev Mukerjee,<sup>a,\*\*</sup> Edward J. Plichta,<sup>b</sup> Mary A. Hendrickson,<sup>b</sup> and K. M. Abraham<sup>a,\*\*\*,z</sup>

<sup>a</sup>Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, USA

<sup>b</sup>US Army RDECOM CERDEC CP&I, Army Power Division, Aberdeen Proving Ground, Maryland 21005, USA

Dimethyl Sulfoxide (DMSO) was evaluated as a practical solvent for the rechargeable lithium air battery. Redox characteristics of the dissolved oxygen and its reduction products in the presence of lithium hexafluorophosphate (LiPF<sub>6</sub>) supporting electrolyte were studied via cyclic, rotating disk (RDE) and ring-disk (RRDE) electrode voltammetry. The DMSO medium facilitates reversible reduction and oxidation processes in contrast to other solvent-based electrolytes studied. Galvanostatic discharge-charge cycling of the Li-O<sub>2</sub> cells has shown characteristics of rechargeability expected from voltammetric studies. Multiple high-efficiency discharge-charge cycles are possible if the depth of discharge of the carbon cathode is limited to avoid excessive passivation by the discharge products. The discharge voltage of this Li-O<sub>2</sub> cell is higher than cells assembled with other non-aqueous organic electrolytes, an attribute ascribed to the stability of superoxide (O<sub>2</sub><sup>-</sup>), the one-electron reduction product of oxygen.

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Manuscript submitted August 6, 2012; revised manuscript received October 29, 2012. Published December 4, 2012. This was Paper 1328 presented at the Boston, Massachusetts, Meeting of the Society, October 9-14, 2011.

The theoretical specific energy of the Li-air battery of 5280 Wh/kg approaches the energy density limit of electrochemical energy conversion and storage systems. However, such a high specific energy can be harnessed in a practical battery only if a four-electron reduction of oxygen to form Li<sub>2</sub>O can be reversibly achieved. The primary discharge product of the Li-air battery has been identified to be Li<sub>2</sub>O<sub>2</sub><sup>1-5</sup> involving an overall two-electron oxygen reduction which makes the theoretical specific energy 3500 Wh/kg.

Following the discovery of the non-aqueous Li-O<sub>2</sub> battery in 1996 was a surge of investigations into the oxygen electrode's electrochemical behavior utilizing traditional lithium ion battery electrolytes dissolved in organic carbonate, ether, and glyme solvents. It has become apparent from these studies that many or all of these solvents may not have long-term chemical stability in the presence of the superoxide radical.<sup>6-14</sup> Although the battery can be discharged and charged in these media, the cycling is shown to cause irreversible chemical changes in the electrolyte. As a result, research efforts have shifted toward developing and characterizing new electrolyte media to support prolonged cycling in the Li-O<sub>2</sub> battery.<sup>7,15-21</sup> This entire progress has been summarized in a recently published review.<sup>22</sup>

Our previous study of the oxygen reduction reactions (ORR) in non-aqueous electrolytes<sup>3</sup> has led to the realization that Li<sup>+</sup>-conducting electrolytes in dimethyl sulfoxide (CH<sub>3</sub>SOCH<sub>3</sub>) (DMSO), a solvent with very high Lewis basicity as measured by its Gutmann donor number of 29.8, are good media to fully elucidate ORR and oxygen evolution reaction (OER) mechanisms, and ultimately to utilize in Li-air cells. A major reason for this is their ability to stabilize oxygen reduction reaction intermediates and products, and facilitate the reverse (recharge) reactions. The fundamental concepts understood from these half-cell experiments lead us to continue investigating the DMSO-based electrolyte, evolving into full cell galvanostatic studies, preliminary results of which we first reported at the Electrochemical Society meeting in Boston.<sup>23</sup> A full account of our work is presented here. A recent paper has shown that the DMSO electrolyte is promising for repeated galvanostatic cycling of Li-O<sub>2</sub> cells with a porous gold electrode.<sup>24</sup>

Included in this work is a detailed study of the rechargeability of the oxygen electrode via half-cell voltammetry in DMSO-LiPF<sub>6</sub> electrolytes and Li/O<sub>2</sub> cell performance evaluation. With respect to the latter we report on the Li/O<sub>2</sub> cell reaction products, and elucidation of the factors affecting its rechargeability. We demonstrate here that the ORR reduction products in DMSO-LiPF<sub>6</sub> electrolytes can be fully

recharged. Importantly, we have found that a Li/O<sub>2</sub> cell with DMSO-LiPF<sub>6</sub> electrolyte and no cathode catalyst can be recharged at lower charge potentials than cells utilizing other non-aqueous electrolytes such as electrolytes in organic ethers and carbonates. These more detailed electrochemical results are reported in this paper.

### Experimental

All solvents utilized in electrolyte media were anhydrous grade purity purchased from Sigma Aldrich and used as received. Specifically, anhydrous grade DMSO certified to contain less than 50 ppm water was used as received after performing Karl Fischer titrations as described below. The DMSO solvent was found to contain 20.5 ppm H<sub>2</sub>O. Purolyte LiPF<sub>6</sub> certified to contain less than 20.0 ppm water was purchased from Novolyte Technologies and used as received. Metals basis 99.9% Li foil was used as received from Alfa Aesar Company. Upon receipt from the vendor, all these reagents were immediately stored in an MBraun Labmaster 130 argon-filled glove box with water vapor concentrations maintained below 1 ppm.

Coulometric Karl Fischer titrations were performed via a compact Meter Toledo C20 Coulometric titration apparatus in conjunction with a Meter Toledo XP56 microbalance. All measurements were made only after the titration drift value had settled to 1 µg/min or less. Hydranal water standards of 100 ppm were analyzed before and after samples of interest were measured. All measurements were made utilizing a 3 mL aliquot of the solution of interest delivered via a Whatman gastight syringe.

Air cell cathodes were fabricated by curing slurries of Ketjen300 JD carbon black powder from AkzoNobel dispersed in 1-methyl-2-pyrrolidone with 10% Kynar 2801 binder onto 1 inch diameter Panex30 carbon cloth substrates. Typical cathode loadings were between 5 and 10 mg carbon powder per cathode substrate, which had an area of 5.1 cm<sup>2</sup>. Anodes were cut from lithium foil as received from Alfa Aesar and pressed onto copper mesh current collectors. A standard polypropylene separator was used after it was soaked in electrolyte for 12 hours. Air cell components were assembled into custom-designed air cell containers fabricated from polypropylene. All assembly procedures were conducted in the argon-filled glove box described above. Prior to cell assembly the dried cathodes were submerged in electrolyte solution while vacuum impregnated in the anti chamber of the glove box for approximately 30 minutes. The mass change of the electrode as a consequence of the impregnation was measured roughly to be 250 mg. Assembled cells were transferred to 3 mil thick multilayered aluminized polyethylene bags and heat impulse sealed. Sealed bags were transferred to a Labconco dry atmosphere glove box where moisture levels are maintained below

\*Electrochemical Society Student Member.

\*\*Electrochemical Society Active Member.

\*\*\*Electrochemical Society Fellow.

<sup>z</sup>E-mail: kmabraham@comcast.net