



Enhancement of oxygen reduction reaction rate by addition of water to an oxidatively stable ionic liquid electrolyte for lithium-air cells



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ABSTRACT

The oxygen reduction reaction in an ionic liquid (IL) consisting of *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium (DEME) cation and the bis(trifluoromethanesulfonyl)imide (TFSI) anion was investigated in the anhydrous and water saturated conditions respectively. The IL was demonstrated to be stable in the operating range of a lithium air cell in both the anhydrous and water saturated conditions. The addition of water was found to lower the overpotential for the oxygen reduction reaction by 40 mV. Finally, the reaction rate constant was found to increase by an order of magnitude with the addition of water hence demonstrating the tendency of water to promote/catalyze the oxygen electrochemistry in non-aqueous systems.

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1. Introduction

The practical realization of lithium-air cells with its high theoretical specific energy of 3505 Wh kg⁻¹ is impeded by problems of (i) poor cycle life; (ii) low columbic efficiency and low power density due to high charge and discharge overpotentials [1]; (iii) operation in ambient air and the consequent side reactions with N₂, CO₂ and moisture. The oxidative instability of the electrolyte [2,3,4], electrode passivation due to electrochemically irreversible product deposits and high overpotentials for decomposing Li₂O₂ [5,6] are believed to be the major causes of poor cycle life. The electrolyte stability issue has led to studies on acetonitrile [7], ethers [3], dimethylformamide [4], dimethylsulfoxide (DMSO) [8], ionic liquids (ILs) [9,10] and relatively stable electrolytes were identified [11]. ILs are an attractive option due to their favorable oxidative stability properties and their inherently good conductivity [9,10] which allowed us to demonstrate a highly improved Li-O₂ cell with the *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) IL [9]. Further, our recent investigations [15] have demonstrated that the Li metal anode is stable and LiOH passivation is very limited during galvanic cycling in a water saturated ionic liquid (WSIL).

While this is promising in the context of using ILs for a true lithium-“air” cell, the effect of water addition on the superoxide electrochemistry in ILs has not been previously reported in the literature. This study is the first, to the best of our knowledge, to do so.

The present study sought to examine the oxygen reduction reaction (ORR) in the *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) IL and evaluate its suitability for use in ambient air conditions with moisture present. The rotating disk electrode (RDE) technique was applied to this non-aqueous system following the procedures outlined by us elsewhere [12] and the rate constants for the ORR in the presence and absence of moisture was calculated. The measured enhancement of the ORR rate in the presence of water allowed us to extend the suggestion of Markovic and coworkers [13] about the catalytic effect of water beyond non-aqueous solvent-salt electrolytes to ILs.

2. Experimental methods

The DEME-TFSI IL (Kanto Chemical Co., Japan) was stored in a MBraun argon filled glove box with H₂O and O₂ levels <0.5 ppm. The anhydrous tests were carried out filling the glassware with the IL in the glovebox, sealing it and transferring it to the test stand. For the water-saturated tests, equal volumes of the IL and de-ionized water were sonicated for 3 h and allowed to phase separate. The IL-rich phase was decanted into the glassware and further tests were carried out. The water content of the “as-received” IL and the WSIL was measured by Karl-Fisher titration (Mettler Toledo C30 Coulometric KF Titrator) and

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was found to be 120 ppm and 15,456.6 ppm respectively. The corresponding viscosities were measured using a cone-plate viscometer (Thermo Scientific HAAKE RheoStress 1) and were found to be 69 cP and 40 cP respectively.

The electrochemical measurements were carried out in a setup that consisted of a three-neck electrochemical cell with Teflon stoppers for the openings for counter and reference electrodes and a gas purge line. The working electrode was used with a Pine Instruments gas purged bearing assembly to maintain a continuous argon purge to prevent any leakage from the atmosphere during RDE rotation. The working electrode was a Pine Instruments RDE assembly with a disk of glassy carbon (GC) polished to a mirror finish with 0.05 μm alumina suspension. The counter and reference electrodes each consisted of a Pt mesh attached to a Pt wire. The Pt pseudo-reference was calibrated against a standard reference consisting of an Ag wire dipped in a solution of 0.1 M AgNO_3 in CH_3CN . The gas purge line consisted of a tube inserted through one of the stoppers and immersed in the electrolyte. A conventional gas regulator was used to control the gas flow rate and sufficient time was allowed for saturation of the electrolyte. The entire setup was assembled in the glovebox, sealed and then transferred to a glove-bag which was kept at a positive pressure relative to the atmosphere using a continuous argon feed to prevent unintended moisture contamination. The electrochemical impedance spectra (EIS) were recorded using a Solartron analytical frequency response analyzer to measure the resistance of the setup prior to electrochemical measurements

and was later used in iR correction of the RDE voltammograms. The electrochemical measurements were performed using a multi-channel potentiostat (Solartron analytical).

3. Results and discussion

The cyclic voltammograms (CVs) in Fig. 1(a) and (b) allowed the identification of the potentials at which reactions occur in this model system under cathodic and anodic conditions. The voltammograms in the Ar saturated condition showed that the electrolyte was electrochemically stable within the potential window of operation of lithium-air cells. The reduction and oxidation peaks in the oxygen saturated condition were believed to correspond to the O_2/O_2^- redox couple as there is no other strongly electropositive species present. After saturation with oxygen, the voltammogram in the anhydrous condition showed the onset of ORR at 2.45 V whereas the WSIL showed the onset as being at 2.49 V. The occurrence of oxygen evolution reaction (OER) peaks at 2.41 V and 3.65 V for the anhydrous and water saturated conditions respectively and the corresponding peak separations of 0.3 V and 1.35 V suggested a degree of irreversibility. The CVs were found to be stable over multiple cycles. Further, the CVs were measured at progressively increasing scan rates as depicted in Fig. 1(c) and (d) and were found to be stable and to show the characteristic $30/\alpha$ mV shift for a 10-fold increase in scan rate proposed by Bard and Faulkner [16].

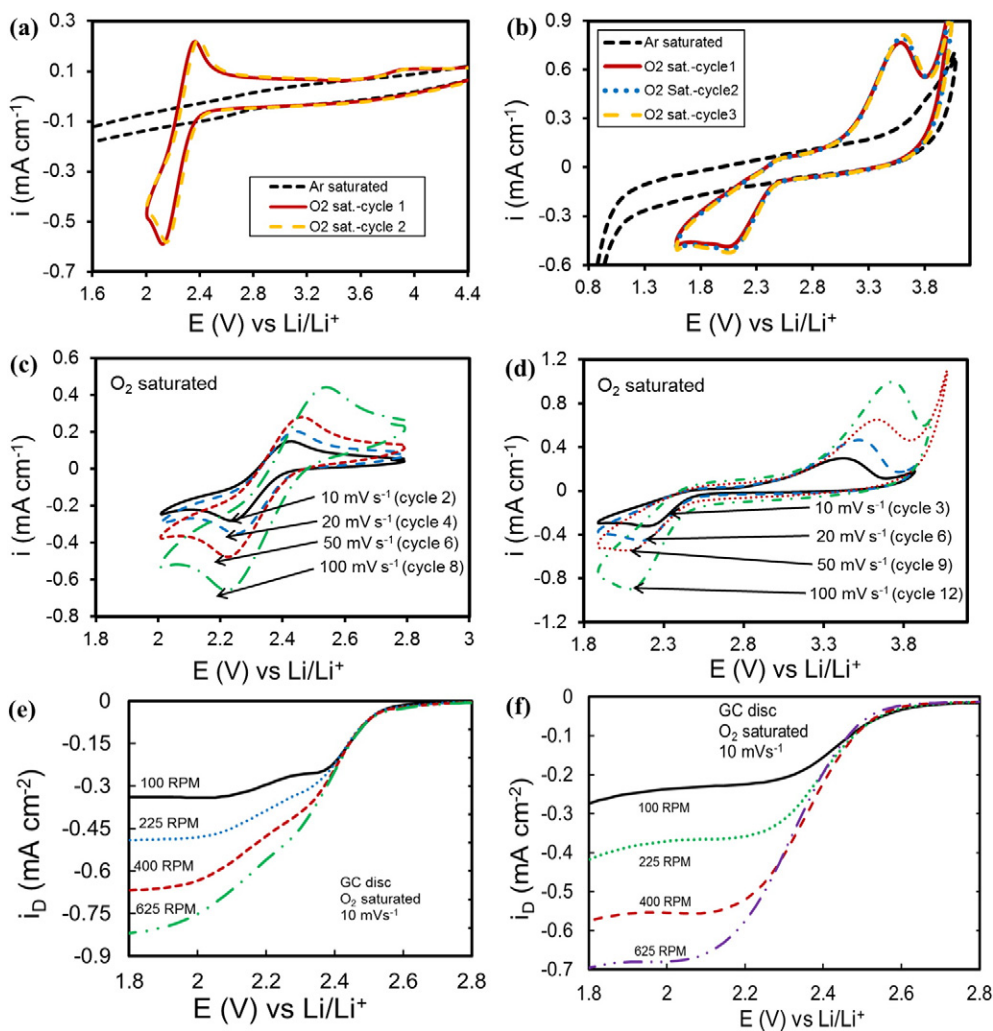


Fig. 1. Cyclic voltammograms of - (a) anhydrous DEMETFSI on glassy carbon (GC) electrode scanning at 50 mV s^{-1} ; (b) water saturated DEMETFSI on GC electrode scanning at 50 mV s^{-1} ; (c) O_2 saturated anhydrous DEMETFSI on GC electrode at various scan rates; (d) O_2 saturated, water saturated DEMETFSI on GC electrode at various scan rates. Rotating disk voltammograms on - (e) GC disk scanning at 10 mV s^{-1} in O_2 saturated anhydrous DEMETFSI (f) GC disk scanning at 10 mV s^{-1} in O_2 saturated, water saturated DEMETFSI.

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