

Oxygen Electrode Rechargeability in an Ionic Liquid for the Li–Air Battery

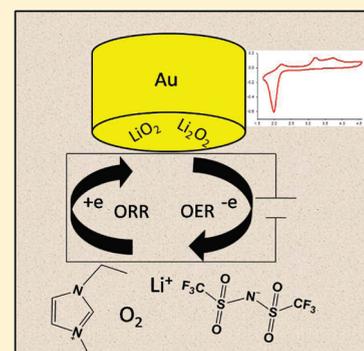
Chris J. Allen,[†] Sanjeev Mukerjee,[†] Edward J. Plichta,[‡] Mary A. Hendrickson,[‡] and K. M. Abraham^{*,†}

[†]Department of Chemistry and Chemical Biology, Northeastern University Center for Renewable Energy Technology (NUCRET), Northeastern University, Boston, Massachusetts 02115, United States

[‡]U.S. Army CERDEC, Army Power Division, Fort Monmouth, New Jersey 07703, United States

ABSTRACT: Oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs) on glassy carbon (GC) and gold electrodes were investigated in a neat and Li⁺-containing room-temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI). The presence of Li⁺ significantly changes the ORR mechanism. While similar one-electron O₂/O₂^{•-} reversible couples result on both electrodes in neat EMITFSI, in the presence of added LiTFSI, the initially formed LiO₂ decomposes to Li₂O₂. In addition, the ORR and OER in the Li⁺-doped solution exhibit strong distinctions between the Au and GC electrodes. The voltammetric data on the Au electrode revealed a highly rechargeable ORR, yielding LiO₂ and Li₂O₂, which underwent multiple cycles without electrode passivation.

SECTION: Energy Conversion and Storage

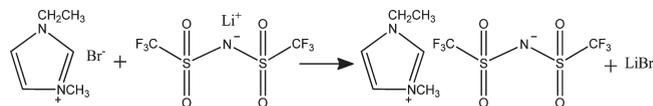


In our continuing efforts to develop practical electrolytes for the nonaqueous Li–air battery,^{1–4} we have studied O₂ electrode processes in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI). The use of room-temperature ionic liquids (RTILs) in Li–air batteries is attractive due to their low flammability, hydrophobic nature, low vapor pressure, wide potential window, and high thermal stability. In particular, the extended anodic voltage window in RTILs is of interest as the presence of cathode catalysts, frequently employed in the Li–air system, can shorten the potential window of many organic electrolytes (e.g. carbonate solvents) and affect cell performance. The influence of solvents on the kinetics of the oxygen reduction reaction (ORR) products and/or the nature of the oxidation reactions in the Li–air cell is now recognized.^{3–8} Previous studies have reported on the O₂ one-electron reduction product superoxide, O₂^{•-}, and its electrochemistry in different RTILs,^{9–12} yet a good understanding of the influence of Li⁺ on the oxygen electrode in these media has not yet been obtained. In this work, we have investigated in detail ORRs and oxygen evolution reactions (OERs) in a RTIL doped with Li salt on both GC and Au electrodes to establish the reaction mechanism and products and their rechargeability. Surprisingly, we have found a strong influence of the nature of the electrode material and the charging potential on the rechargeability of the O₂ electrode, along with changes in ORRs and OERs when a Li salt is present. These results are reported.

The EMITFSI was synthesized via anion exchange, as shown in the following reaction.

An aqueous solution containing 1-ethyl-3-methylimidazolium bromide (EMIBr)-98% (Alpha Aesar) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-98% (Alpha Aesar) was stirred at 80 °C for 3 h until the materials reacted completely. The solution was then washed several times with water and

further purified with decolorizing carbon and neutral alumina, as



described elsewhere.¹³ The product was finally dried under vacuum for 24 h at 130 °C to remove residual water. ¹H NMR, 10 mM in CO(CD₃)₂, δ/ppm relative to TMS: (s, 9.08, 1H), (t, 7.81, 1H), (t, 7.74, 1H), (q, 4.43, 2H), (s, 4.09, 3H), (t, 1.58, 3H). A moisture content of <25 ppm was confirmed with Karl Fisher coulometry.

Cyclic voltammetry (CV) measurements were performed on an Autolab potentiostat (Eco Chemie B.V.) equipped with a frequency response analyzer for iR correction. A conventional three-electrode set up was used, which included a 5 mm gold (Au) or 6 mm diameter glassy carbon (GC) working electrode along with a platinum counter electrode. The reference electrode consisted of a silver wire immersed in a 0.1 M AgCF₃SO₃ solution contained in a glass tube placed close to the working electrode, separated with a Vycor frit. Potentials were converted to the Li/Li⁺ reference electrode by measuring the potential of the Ag/Ag⁺ electrode against a Li foil and are used throughout this paper. Gas purging of the IL solutions (1 h of argon followed by 1 h of oxygen) and the electrochemistry were carried out in a controlled atmosphere glovebox.

Oxygen Electrochemistry in Neat EMITFSI. The ORRs and OERs on GC and gold (Au) electrodes were studied in a neat and

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