



Rechargeable Lithium/TEGDME-LiPF₆/O₂ Battery

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A rechargeable Li–air cell utilizing an electrolyte composed of a solution of LiPF₆ in tetraethylene glycol dimethyl ether, CH₃O(CH₂CH₂O)₄CH₃ (TEGDME), and an uncatalyzed porous carbon electrode, investigated to elucidate the baseline Li–air battery chemistry, is reported. From the x-ray diffraction patterns of the discharged carbon electrodes, the discharge product of the cell was identified to be Li₂O₂ during normal discharge to 1.5 V. Discharging the cell to 1.0 V or below produces Li₂O as well. The cell can be recharged without a catalyst in the carbon cathode, albeit at low depths of discharge. The high resistance of the discharged carbon cathode is a major impediment to recharging cells displaying a high specific capacity. The cell capacity decreases with continued cycling, which was found to be due to the poor cycling efficiency of the Li anode and the high resistance of the discharge products, which slowly accumulate in the porous electrode.

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Rechargeable Li–air batteries utilizing the oxygen in the air as the positive electrode material are attractive electrochemical power sources because of their potential for ultrahigh energy densities.^{1,2} Despite the increasing levels of research and development interest in these batteries,^{2–11} the full energy density promised by the four-electron reduction of O₂ to Li₂O has not yet been realized. Furthermore, practically useful electrolytes with low vapor pressures to enable the operation of the Li–air batteries in which O₂ is accessed into the cell from open air without solvent loss by evaporation has not yet been satisfactorily demonstrated. Recently, we have reported the results of our detailed studies of the oxygen reduction reactions (ORR) in nonaqueous electrolytes, showing how the solvent in the electrolyte strongly influences the reduction products and their rechargeability.^{7–9} We have shown from these and earlier investigations¹⁰ that polyethylene oxide oligomers are potentially useful low volatile solvents to build practical Li–air cells. In order to demonstrate this experimentally and to study the cell chemistry in the absence of catalysts in the cathode, we have built Li/O₂ cells utilizing one of these polyethylene oxide oligomer-based electrolytes, namely, a solution of LiPF₆ in tetraethylene glycol dimethyl ether, CH₃O(CH₂CH₂O)₄CH₃ (TEGDME). Our principal objectives of this study were the following:

- (i) Identify the discharge products of the Li/O₂ cell in the absence of a catalyst in the cathode using a commonly available analytical technique such as x-ray diffractometry.
- (ii) Determine if the cell is rechargeable without a catalyst in the carbon cathode and characterize the relevant cell chemistry.
- (iii) Elucidate the factors limiting the rechargeability of the Li/O₂ cell.

We have found that the Li/air cell utilizing this electrolyte is rechargeable though at low depths of discharge (DOD) and with limited cycle life. We have identified the discharge products of the Li/air cell from the x-ray diffraction (XRD) pattern of the discharged carbon cathodes, which is believed to be the first using this technique. We have also made an attempt to determine the factors affecting the rechargeability of the Li/O₂ cells from the ac impedance spectra of the discharged–charged cathode. Our results are reported.

Experimental

Materials.—Pursis TEGDME and anhydrous *N*-methyl pyrrolidinone (NMP) were purchased from Sigma-Aldrich, Allentown, PA.

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The solvents were dried by stirring with 0.3–0.4 nm dry molecular sieves, and prior to preparing electrolytes, it was degassed under vacuum. Lithium hexafluorophosphate (LiPF₆) (battery grade, >99.9%, H₂O < 20 ppm) dried under reduced pressure at room temperature was obtained from Novolyte Corporation, Cleveland, OH.

The 1 M electrolyte of LiPF₆ in TEGDME was further dried by stirring over lithium foil and stored in an MBraun dry box filled with purified argon where the moisture and oxygen content was less than 1 ppm.

Li/O₂ cells.—Porous carbon electrodes were prepared as follows. First, ink slurries were prepared by dissolving a 95 wt % of BP2000 carbon black (Cabot Corporation) and 5 wt % Kynar PVDF (Arkema Corporation) in NMP. Air electrodes were prepared with a carbon loading of 5–8 mg/cm² by hand-painting the inks onto a carbon cloth (PANEX 35, Zoltek Corporation), which was then dried at 180°C overnight.

The Li/O₂ test cells were assembled in an argon-filled glove box. The cell consists of metallic lithium foil anode (~60 mil thick) and the aforementioned carbon cathode. A Celgard 2320 separator separated the two electrodes. Both the cathode and the separator were soaked in a TEGDME/1 M LiPF₆ solution for a minimum of 24 h. An in-house built Li/O₂ cell was used. The cell was placed in an oxygen-filled glove bag where oxygen pressure was maintained at slightly higher than 1 atm. The cell discharge and charge were carried out with an Arbin battery cycler.

The ac impedance was measured using an Autolab PG 30 fitted with a frequency response analyzer (FRA 2 module), operating in the frequency range of 0.01–10⁶ Hz with an ac voltage amplitude of 5 mV.

Powder XRD was carried out using a Rigaku RINT 2500 x-ray diffractometer with a rotating copper K α radiation. The patterns were recorded at slow scan rates. Scanning electron microscope (SEM) images and energy-dispersive x-ray spectroscopy (EDAX) were measured using Hitachi SEM S-4800. All the cell cycling studies were carried out at room temperature.

Results and Discussion

Lithium–air batteries differ from the conventional batteries in that the porous carbon electrode in the cell is used to continuously reduce oxygen accessed from the environment. Consequently, the electrolyte in the cell is exposed to the atmosphere, and the loss of solvent from the cell is a concern. Abraham and Jiang,¹ who demonstrated the first nonaqueous rechargeable Li–air cell in 1996, employed a cell composed of an Li metal anode, a polyacrylonitrile-based gel polymer electrolyte, and a catalyzed carbon cathode. We showed that the oxygen in air is the cathode active material with the