Rechargeable Lithium/TEGDME-LiPF₆/O₂ Battery

Cormac Ó Laoire,a Sanjeev Mukerjee,a Edward J. Plickta,b Mary A. Hendrickson,b and K. M. Abrahamab

aDepartment of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, USA
bUS Army CERDEC, Army Power Division, Ft. Monmouth, New Jersey 07703, USA

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 porou electrode.

© 2011 The Electrochemical Society. [DOI: 10.1149/1.3531981] All rights reserved.

Manuscript submitted September 14, 2010; revised manuscript received December 1, 2010. Published January 19, 2011.

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,3-14 the full energy density promised by the four-electron reduction of O₂ to Li₂O has not yet been realized. Further, practically useful electrolytes with low vapor pressures to enable the operation of the Li–air batteries in which O₂ is accessed 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 rechargability.15 We have shown from these and earlier investigations16-19 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 diffraction.
(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 rechargability 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 rechargability of the Li/O₂ cells from the ac impedance spectra of the discharged-charged cathode. Our results are reported.

Experimental

Materials.— Puris TEGDME and anhydrous N-methyl pyrrolidinone (NMP) were purchased from Sigma-Aldrich, Allentown, PA. 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 (PAXEN 35, Zoltek Corporation), which was then dried at 180°C overnight.

The Li₂O₂ 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 Kα 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,20 who demonstrated the first nonaqueous rechargeable Li–air cell in 1996, employed a cell composed of a 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
TEGDME is a polar versatile solvent, which displays a high LiPF₆ solubility to produce well-conducting solutions with a wide electrochemical window. Table I lists some relevant properties of TEGDME.

We first studied the redox electrochemistry of O₂ in 1 M LiPF₆/TEGDME using cyclic voltammetry (CV) on a glassy carbon electrode in order to establish the voltage window of the electrolyte and to assess the degree of reversibility of the oxygen reduction reaction. The voltammogram (Fig. 1) recorded under an atmosphere of argon shows a nearly 5 V wide stability window in which there is a very little electrochemical activity. Solvent decomposition is seen as an anodic current at ≈4.8 V and the onset of lithium plating is seen only near 0.0 V. A high electrolyte stability led us to use this electrolyte in the Li–air battery. Figure 1 also shows a CV for the reduction of O₂ in a 1 M LiPF₆/TEGDME electrolyte saturated with oxygen. The peak potential separation ΔEₚ between the anodic (Eₚ₁ = 2.30 V) and cathodic (Eₚ₉ = 4.06 V) peaks is almost 1.8 V, suggesting that O₂ reduction in the presence is only a quasi-reversible process at best. The charge ratio under the curves was integrated to yield Qₐ/Q₉ = 95%, which indicated that the reduction products are rechargeable, albeit at high overpotentials.

We recently reported elsewhere on the detailed kinetic analysis of the CV data in several nonaqueous electrolytes and reported that O₂ reduction is highly solvent dependent as depicted schematically in Scheme 1 using dimethyl sulfoxide (DMSO) as the example. Here the O₂⁻ formed as the first reduction product is complexed by the solvated Li⁺, probably becoming a stable specie with a finite lifetime in solution. High donor number (DN) solvents such as DMSO afford better stability to the one-electron reduction product LiO₂ whereas lower DN solvents such as TEGDME promote the formation of Li₂O₂ and Li₂O.

The observed behavior of oxygen has been explained through the hard–soft acid-base theory. The following reduction and subsequent oxidation reactions of O₂ have been provided based on a large body of electrochemical data.

**Table I. Tetraethylene glycol dimethyl ether properties.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constantε (25°C)</td>
<td>7.79⁶</td>
</tr>
<tr>
<td>DN (kcal/mol)</td>
<td>16.6⁶</td>
</tr>
<tr>
<td>Viscosity η (cP)</td>
<td>4.0⁴</td>
</tr>
<tr>
<td>Oxygen solubility (mM/cm³)</td>
<td>4.43¹</td>
</tr>
<tr>
<td>bp/mp (°C)</td>
<td>275/−30⁴</td>
</tr>
</tbody>
</table>

*a Reference 12  
*b Reference 13  
*c Reference 14  
*d Reference 15

![Scheme 1](image-url)  
**Scheme 1.** (Color online) A depiction of O₂ reduction at the electrode followed by the formation of a stable complex between superoxide and solvated Li⁺ in solution.

![Figure 1](image-url)  
**Figure 1.** (Color online) Cyclic voltammograms for oxygen in 0.1 M LiPF₆/TEGDME (red) and the argon background (black). Scan rate, 100 mV/s.

**Cathodic**

O₂ + Li⁺ + e⁻ = LiO₂ (Eₚ₁)  
2LiO₂ = Li₂O₂ + O₂ (chemical)  
LiO₂ + Li⁺ + e⁻ = Li₂O₂ (Eₚ₂)  
Li₂O₂ + 2Li⁺ + 2e⁻ = 2Li₂O (Eₚ₃)

**Anodic**

LiO₂ = O₂ + Li⁺ + e⁻ (Eₚ₉)  
Li₂O₂ = O₂ + 2Li⁺ + 2e⁻ (Eₚ₁₉)
Li₂O = 1/2O₂ + 2Li⁺ + 2e⁻ (Eₚc3) \[10\]

In Eqs. 4-6, Eₚc1, Eₚc2, and Eₚc3 refer to the potentials corresponding to the first, second, and third cathodic processes, respectively, and in Eqs. 8-10, Eₚa1, Eₚa2, and Eₚa3 refer to the potentials corresponding to the three anodic processes, as discussed in Ref. 8. The chemical reversibility of the observed O₂ reduction reactions in Fig. 1 served as an impetus to construct an Li/O₂ cell using this electrolyte and study its discharge reaction and rechargeability, and fully characterize the discharge products formed on the carbon cathode.

**Li/O₂ cell discharge behavior and products.**—The full discharge curves for two Li/O₂ cells obtained with BP2000 carbon electrodes exposed to a dry oxygen atmosphere are depicted in Fig. 2. The OCV of the cells varied slightly, 3.37 V (black) and 3.18 V (blue), depending on cell, oxygen saturation, and atmospheric variables. The latter refers to small amounts of moisture that may be present in the O₂ atmosphere in plastic bag where the cells were tested. The working voltages of the cells differed on average by 150 mV, attributable to the polarizations from different discharge currents. The discharge current density affects the specific capacity. The discharge current density of 0.25 mA/cm² is 2.0 times that of 0.16 mA/cm² in 1 M LiPF₆/TEGDME. Capacities are expressed per gram of carbon in the electrode.

![Figure 2.](Color online) Li/air cell discharge curves at 0.25 (blue) and 0.16 (black) mA/cm² in 1 M LiPF₆/TEGDME. Capacities are expressed per gram of carbon in the electrode.

![Figure 3.](Color online) The XRD pattern of fully discharged O₂ cathode to 2 V.

We found if the cell was fully discharged (1452 mA/h), only 30% of the discharge capacity could be charged (Fig. 6). In this cell, the following cycle yielded 488 mA/h of discharge capacity and 200 mA/h charge capacity before the voltage runs to 4.9 V and the cell ultimately fails. There are possibly two factors that limited the rechargeability of this cell, the current density for charge and the higher resistance of the electrode from the deposited Li₂O₂ di-
charge product. We investigated this further. Several cells were cycled at various DOD, and charge, at different current densities, and their impedances followed as a function of charge and discharge.

Figure 7a illustrates capacity versus cycle number for a cell discharged and charged for 2-h periods at 0.13 mA/cm$^2$. The voltage is monitored as a function of time. The average discharge potential varied between 2.7 V for the initial cycles and dropped to 2.45 V at the later stages of the cell’s life. The charge plateau steadily increased from 3.2 V initially to 4.7 V before cell termination. Figure 7b presents a plot of the discharge and charge capacities versus cycle number. Cycling is demonstrated for over 40 cycles during which 100% coulombic efficiency is achieved with a capacity utilization of 175 mAh/g. The discharge fell below 2 h at cycle 41.

A high discharge/charge capacity was maintained after increasing the discharge time to 14 h with a discharge capacity of about 700 mAh/g capacity, but the cells exhibited decreasing capacity along with increased charge voltage polarization after four cycles (Figs. 8a and 8b). The discharge profile remains unchanged after the first cycle until the sudden cell failure observed during cycle 7, where capacity drops to 400 mAh/g. Efficient cycling was observed during the first three charge cycles; however, the charge profile polarization increases with cycle number. As polarization increases, capacity drops and charge voltage increases. The sudden drop in capacity at the eighth discharge coupled with the impedance data and the physical examination of the Li anode after cycling (see below) led us to believe Li anode failure is also a major contributor to cell failure. The poor recharge efficiency may be attributed to the inability to oxidize the nonconducting discharge product Li$_2$O$_2$ deposited in the pores of the carbon cathode, perhaps due to the increased resistance and the associated overvoltage of the electrode. It should be noted we have not fully elucidated all the sources of impedance changes in the cell, which require significant further investigation. The impedance data discussed below as well as post-test examination of the Li anode revealed that, along with impedance,
the deterioration of the Li anode is also a major contributing factor for the capacity decline and eventual failure of the Li/air cell.

Factors affecting the cycle life of the LiO2 cell.—Figure 9a shows the voltage discharge profile of an LiO2 cell discharged to 0.85 V. Figure 9b shows that there is a significant increase in the cell impedance during the full discharge. The polarization resistance (Rp), as measured by the diameter of the semicircle in the Nyquist

diagram, increases from about 84 to 241 Ω. This supports the view that the high resistance of the carbon electrode is a possible cause of the poor rechargeability of the cell after full discharge.

Figure 10 displays the ac impedance spectra recorded at various intervals during the cycling of the cells displayed in Figs. 7 and 8. Generally, the spectra consist of a semicircle offset at high frequencies from the origin. At low frequencies, the semicircle connects with a line inclined at approximately 45° to the x axis. Initially, the impedance, as indicated by the diameter of the semicircle, increases with cycle number. However, after cycle 4 in the cell in Fig. 7 and after cycle 3 for the cell described in Fig. 8, impedance drops slowly. Several qualitative changes in the spectra recorded during the course of the cell cycling are noticeable. First, there is a large increase in the diameter of the semicircle without any significant change in the position of its first intersection with the x axis. The diameter of the semicircle reached a maximum at about the fourth (Fig. 10a) and third (Fig. 10b) cycles. Contrary to what we believed prior to the experiment, there was no significant difference in the impedance between a discharge step and a following charge step. We do not understand the reason for this. In addition to increased electrode resistance from the deposited discharge product, the change in the electrode structure may be another reason. Fitting the impedance spectrum to an appropriate equivalent circuit is difficult because the cell does not have reference electrodes, which prohibits assigning the contributions of the anode and cathode interfacial reaction impedances to the total cell impedance. For the purpose of our discussion here, a simple equivalent circuit shown in Fig. 10d may describe the observed impedance spectrum at the early stages of the cycling. The circuit consists of an Ohmic resistance

Figure 6. First full discharge of Li/air cell at 0.16 mA/cm². The cell was then charged to 4.5 V.

Figure 7. (Color online) (a) The cycling data for an LiO2 cell at room temperature. The cell was discharged and charged for 2 h at 0.13 mA/cm². Capacities are expressed as per gram of BP2000 carbon + polyvinylidifluorine (PVDF) in the electrode. (b) Discharge/charge capacities as a function of cycle number for the same cell.

Figure 8. (Color online) (a) The cycling data for a 1 M LiPF6/TEGDME/oxygen cell at room temperature. The cell was discharged and charged for 14 h at 0.13 mA/cm². Capacities are expressed as per gram of BP2000 carbon + PVDF in the electrode. (b) Discharge/charge capacities as a function of cycle number for the same cell.
We can only discuss overall cell polarization
anode and the cathode contribute to this phenomenon. Without a
Clearly the charge transfer resistances of the reactions at both the
LiPF$_6$
various stages of discharge for 2 h
Figure 10. (Color online) Nyquist ac impedance plots of the Li-air cell at
Discharge Capacity (mAh/g)
Figure 9. (Color online) (a) Full discharge of Li/air cell in 1 M
LiPF$_6$/TEGDME (--0.13 mA/cm$^2$). (b) Nyquist ac impedance plot.
(R$_p$) (due to electronic resistances of the electrodes and their contacts
to the current collectors, and electrolyte resistance), which is in a
series with a constant-phase element (CPE) that represents the
capacitive contributions of the two electrodes in parallel with the
polarization (charge transfer) resistances (R$_p$) at the two electrodes.
Clearly the charge transfer resistances of the reactions at both the
anode and the cathode contribute to this phenomenon. Without a
reference electrode we can only discuss overall cell polarization
impedance, and with that in mind, the capacitance is represented by
a CPE. The precycling spectrum of the cell reveals one semicircle with
R$_s$ = 11.50 $\Omega$ and R$_p$ = 14.00 $\Omega$. The linear Warburg element
following the semicircle may be attributed to the diffusion of the
electroactive species to the electrode. The polarization resistance in the
2-h cycled cell increased after the first discharge to R$_p$ = 46.4 $\Omega$. Overall impedance of the carbon electrode gradually increases with cycle number. However, toward the end of the cell
cycle life, the initial semicircle becomes depressed and a second
semicircle emerges. There is little change in the intercept R$_s$ at high
frequencies throughout the cycling. The impedance increase at the end of discharge is attributed to the deposition of the discharge products in the pores and the surface of the carbon electrode, resulting in sluggish ORR kinetics and diffusion of the electroactive spe-
cies to the electrode surface. As these spectra are of the whole cell,
the reactions at the Li electrode, the changing morphology of the
plated lithium, and the surface films formed on it also contribute to
this polarization.

Figure 10 displays the photograph of the Li anode after cycling.
The morphology of the lithium electrode plated with granular lithium particles deposited on the surface after many charge/discharge cycles is clearly seen. The growth results in an increase in the overall surface area of the Li anode. We believe this in turn leads to a decrease in the resistance of the surface films on the Li anode and an overall lowering of the anode’s contribution to the total im-
pedance. This explains the drop in the total cell impedance after several cycles. The evidence gathered suggests that the point where the total cell impedance begins to decrease is a marker of a signifi-
cant change in the morphology of the Li anode. The cycled Li elec-
trode surface becomes covered with a brown precipitate, probably the reaction product between the electrolyte and plated Li. Further-
more, the thickness of the original metallic Li foil is substantially reduced as the precipitate is accumulated on the anode surface with
continued cycling. These are tell-tale signs of an Li electrode failure.

**Conclusions**

The use of the low volatile electrolyte TEGDME-LiPF$_6$ allowed
the discharge reaction and rechargeability of the Li/O$_2$ cell to be studied without the uncertainties associated with solvent evaporation on cell failure. The cell was fabricated without a catalyst in the carbon cathode in order to characterize the baseline Li/O$_2$ cell chemistry. From the x-ray diffraction patterns of discharged carbon electrodes, we identified Li$_2$O$_2$ in cells discharged to 2.0 V, and, additionally, small amounts of Li$_2$O in cells discharged to 1.0 V. The rechargeability of the uncatalyzed cell is limited, which, to a
large extent, is attributed to the poor cycling efficiency of the Li anode and to the high impedance associated with the Li$_2$O$_2$ deposit in the carbon cathode.

Acknowledgments

US Army CERDEC through Subcontract no. GTS-S-6-1-437 supported this work.

Northeastern University assisted in meeting the publication costs of this article.

References