ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery

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ABSTRACT

A novel rechargeable Li/O_2 battery is reported. It comprises a Li^+ conductive organic polymer electrolyte membrane sandwiched by a thin Li metal foil anode, and a thin carbon composite electrode on which oxygen, the electroactive cathode material, accessed from the environment, is reduced during discharge to generate electric power. It features an all solid state design in which electrode and electrolyte layers are laminated to form a 200 to 300 μm thick battery cell. The overall cell reaction during discharge appears to be $2Li + O_2 \rightarrow Li_2O_2$. It has an open-circuit voltage of about 3 V, and a load voltage that spans between 2 and 2.8 V depending upon the load resistance. The cell can be recharged with good coulombic efficiency using a cobalt phthalocyanine catalyzed carbon electrode.

Introduction

Electrochemical power sources based on metal/oxygen chemical couples are unique because oxygen, the cathode active material, does not have to be stored in the battery, but rather it can be accessed from the environment. Past efforts to develop such batteries emphasized aqueous systems, utilizing either a KOH/H_2O alkaline electrolyte or a quasi-neutral electrolyte consisting of aqueous solutions of NaCl, NH_4Cl, $(NH_4)_2SO_4$, or KNO_3, and conventional design,[1] for example as in the alkaline Zn/MnO_2 battery. Examples of aqueous metal/O_2 batteries include the Zn/O_2, Al/O_2, Ca/O_2, and Li/O_2 systems,[1] although only the Zn/O_2 battery has become a commercial product; it is used for powering hearing aids.

In this paper we report on a novel Li/O_2 battery that is unlike any metal/oxygen power sources developed to date. It is a nonaqueous thin film battery and consists of a thin Li metal foil anode, a thin solid polymer electrolyte membrane that conducts Li ions, and a thin carbon composite electrode sheet made up of high surface area carbon on which oxygen, the electroactive cathode material, accessed from the environment, is reduced during battery discharge to generate electric power. The organic polymer electrolyte membrane serves both as the separator that electronically insulates the cathode from the anode and the medium through which Li ions are transported from the Li anode to the oxygen cathode during discharge.[2] The present Li/oxygen cell appears to be rechargeable due to the use of nonaqueous electrolyte. The design of this novel battery is a radical departure from that of traditional polymer electrolyte-based Li batteries in which the cathode comprises Li intercalating solid-state materials such as TiS_2, V_6O_{13}, $LiMn_2O_4$, and $LiCoO_2$.[2]

Experimental

The general experimental procedures, materials treatment, and cell construction were as follows. All experiments were carried out either in a Vacuum Atmospheres Corporation argon-filled dry box or in a dry room maintained with less than 1% humidity.

The Chevron acetylene black carbon (Chevron Chemical Company, Houston, TX) and graphite powder (Johnson Matthey Catalog Company, Inc., Ward Hill, MA) were dried at 250°C for 48 h under vacuum. Polyacrylonitrile (PAN) (Polysciences, Inc., Warrington, PA) was dried at 50°C for 48 h under vacuum. Ethylene carbonate (EC) and propylene carbonate (PC) (99.98% and battery grade, Grant Chemicals, Baton Rouge, LA), Li (Cyprus Foote Mineral, Exton, PA), and $LiPF_6$ (Advance Research Chemicals, Inc., Caloosa, OK) were used as-received.

Chevron carbon containing cobalt catalyst was prepared as follows: 0.5 g of cobalt phthalocyanine was dissolved in about 30 ml of concentrated [30 weight percent (w/o)] sulfuric acid. The resulting viscous liquid was poured onto 9.5 g of Chevron carbon forming a wet paste. When water was added to the paste, cobalt phthalocyanine precipitated and deposited in the Chevron carbon matrix. Then the resultant solid mixture was filtered and washed with distilled water until the supernatant had a neutral pH. After drying overnight at 100°C, the solid mixture was heated at 800°C for 5 h under a flow of argon.

For the preparation of the polymer electrolyte film, a 12:40:40:8 w/o mixture of PAN, EC, PC, and $LiPF_6$ was heated in a glass vial, inside the dry box, to 135°C to obtain a homogeneous solution. The solution was then poured between two stainless steel shims coated with Teflon films, and rolled into thin membranes. On cooling, dimensionally stable, freestanding electrolyte films with thicknesses ranging from 75 to 100 μm were formed. The carbon composite electrodes were prepared from a 20:80 by weight percent mixture of Chevron carbon (or graphite) and the polymer electrolyte by pressing it onto a Ni or Al screen current collector. The carbon electrode thickness varied between 75 and 100 μm.

The Li/PAN-based polymer electrolyte/oxygen cell was fabricated by sandwiching the polymer electrolyte membrane between a 50 μm thick Li foil and a carbon composite electrode. The Li/polymer electrolyte/carbon electrode laminate was enclosed in a metallized plastic bag and heat sealed. The plastic envelope contained pores on the carbon electrode side to let oxygen into the electrode. Prior to cell activation, the pores were sealed with a tape. For experiments in known gaseous atmospheres the cell package was

enclosed in a D cell metal can and a flowing atmosphere of oxygen or air was maintained inside the can during discharge at room temperature. Cells were discharged or charged at constant currents using a microprocessor-controlled battery cycler manufactured by Arbin Corporation (College Station, TX). Open-circuit voltage measurements during the course of discharge were done after interrupting discharge and allowing the cell to equilibrate for at least 15 min.

The identification of the discharge product of the Li/O_2 electrochemical couple was made from qualitative analysis and by means of Raman spectrometry. The qualitative analysis is based on the reaction $MnO_4^- + H_2O_2 \rightarrow O_2 + MnO_2$ in neutral solution.[3] It was performed by adding carbon (0.2 g) containing the discharge product from a discharged cell or the same amount of carbon from an undischarged carbon electrode to 5 ml of 2.5×10^{-3} M $KMnO_4$ solution. If Li_2O_2 was present the purple color of the solution changed with the evolution of oxygen.

Raman spectra of both the discharged and fresh carbon electrodes were obtained using the 647 nm line of a 200 mW Kr laser at EIC's Raman Laboratory. Before the Raman analyses, the materials from the electrodes were washed with tetrahydrofuran (THF) to remove the Li salt as well as plasticizer solvents, and then dried at 100°C in argon.

Results and Discussion

The theoretical specific energies of some selected metal/O_2 chemical couples given in Table I illustrate the very high energy density available from a Li/O_2 electrochemical cell. The polymer battery described here is a novel and convenient way to harness this energy. A schematic of the cell is given in Fig. 1. The solid polymer electrolyte can be one of the many that we[2,4] or others[5] have developed. The cells being reported here were constructed using the polyacrylonitrile (PAN)-based plasticized polymer electrolytes.[2,6] A typical composition of this electrolyte used in the Li/O_2 cell is 12 w/o PAN-40 w/o ethylene carbonate (EC)-40 w/o propylene carbonate (PC)-8 w/o $LiPF_6$. The relative amounts of the plasticizers, EC and PC, can be varied or other solvents can be substituted for them. Lithium salts other than $LiPF_6$ can also be used. Although, the polymer electrolyte contains a substantial amount of solvent, it is fully absorbed by the polymer, and it can be isolated as a mechanically strong, freestanding film. The carbon composite electrode consists of an intimate mixture of the polymer electrolyte and a high surface area carbon.[6] Chevron acetylene black with a surface area of about 40 m^2/g or graphite powder with a surface area of about 5 m^2/g was used. A 50 μm thick Li foil was used as

Table I. Characteristics of some metal/oxygen battery couples.

Metal/O_2 Couple	Idealized cell reaction[a]	Calculated open-circuit voltage (V)	Theoretical specific energy[b] (Wh/kg)	
			Including O_2	Excluding O_2
Li/O_2	$4Li + O_2 \rightarrow 2Li_2O$	2.91	5,200	11,140
Al/O_2	$4Al + 3O_2 \rightarrow 2Al_2O_3$	2.73	4,300	8,130
Ca/O_2	$2Ca + O_2 \rightarrow 2CaO$	3.12	2,990	4,180
Zn/O_2	$2Zn + O_2 \rightarrow 2ZnO$	1.65	1,090	1,350

[a] The reduction of O_2 to O^{2-} usually occurs only in the presence of a catalyst; often the product is the peroxide, O_2^{2-}.
[b] Includes only the active materials. Since O_2 does not have to be carried in the battery, values are given for the cases of including and excluding O_2. The battery weight will increase once the discharge begins.

the anode. The highly flexible cell package can be fabricated in a variety of geometric shapes, and activated, as needed by exposing the carbon cathode to atmospheric oxygen. The air permeates the pores on the metallized plastic envelope into the carbon composite electrode where it undergoes electrochemical reactions during discharge of the cell.

Discharge behavior.—The discharge curve obtained with the carbon electrode exposed to an atmosphere of laboratory air is depicted in Fig. 2. This cell had an open-circuit voltage (OCV) of 3.05 V. Another cell identical to the one in Fig. 2, in terms of electrode and electrolyte compositions, was discharged with the cathode exposed to an atmosphere of dry oxygen (Fig. 3). This cell had an OCV of 2.85 V. (Although the OCV varied slightly depending on whether dry oxygen or atmospheric air was used, the discharge voltages and capacities were similar in the presence of both gases.) The virtually identical discharge voltage profiles in Fig. 2 and 3 suggest that the discharge reaction in both cells involves the reduction of oxygen on the carbon electrode. Note that cells discharged in the absence of either air or O_2 showed no electrochemical activity between 3.5 and 1.5 V. The open-circuit voltage of a cell similar to the one in Fig. 3 was monitored as a function of its depth of discharge. The results, presented in Fig. 4, indicate that the OCV remains practically constant during the course of the discharge. It was about 2.85 V during the first 60% of the discharge and then decreased to about 2.75 V by the end of discharge. A constant OCV with depth of discharge is consistent with a two-phase equilibrium at the cathode between the reactants and products. A reaction process involving the adsorption of O_2 onto the carbon
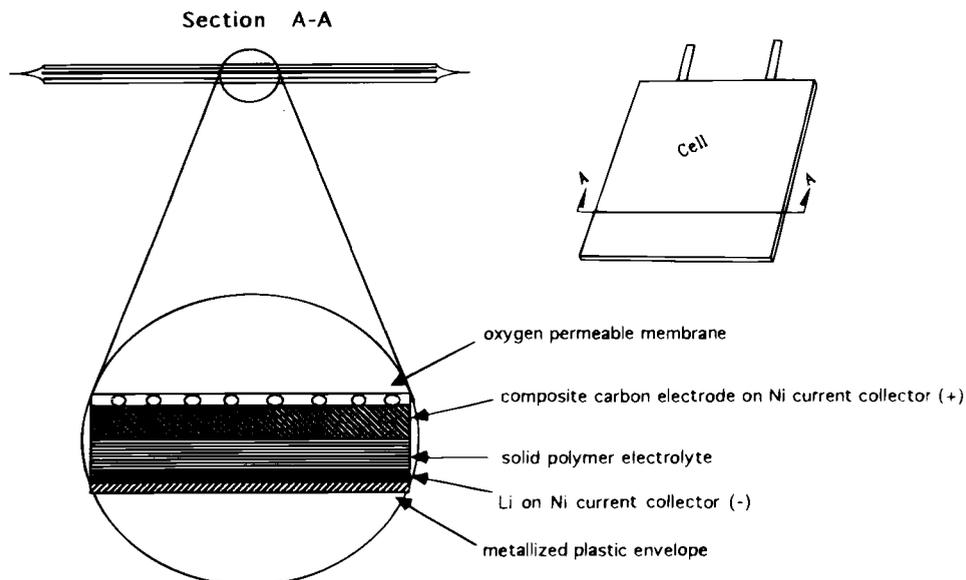
Section A-A

Fig. 1. A schematic representation of the Li/O$_2$ plastic battery.

oxygen permeable membrane

composite carbon electrode on Ni current collector (+)

solid polymer electrolyte

Li on Ni current collector (-)
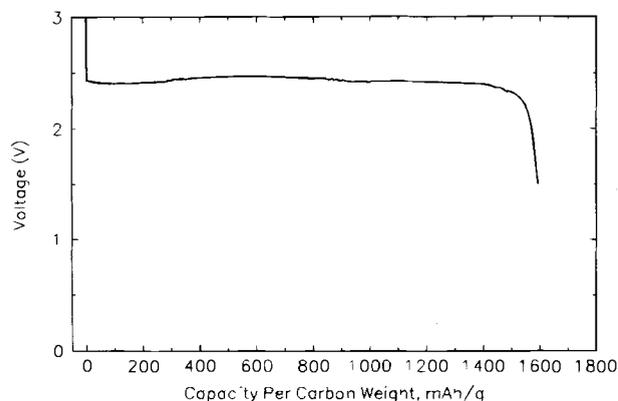
metallized plastic envelope

Fig. 2. The discharge curve of a Li/PAN-based polymer electrolyte/oxygen cell at a current density of 0.1 mA/cm² at room temperature. The cathode contained Chevron acetylene black carbon. The cell was packaged in metallized plastic envelope and discharged by exposing the carbon electrode to laboratory air.
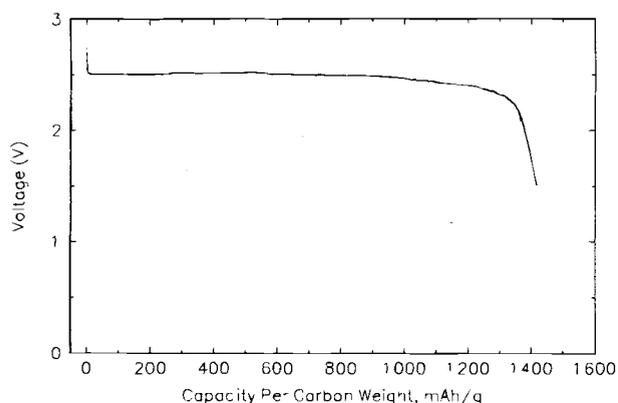

Fig. 3. The discharge curve of a Li/PAN-based polymer electrolyte/oxygen cell at a current density of 0.1 mA/cm² at room temperature in an atmosphere of oxygen. The cathode contained Chevron acetylene black carbon. The cell was packaged in the D cell can and O_2 from a tank was used to maintain a flowing O_2 atmosphere.

electrode and its reduction according to reaction 1 and/or 2 can explain the observed results

$$2Li + O_2 \rightarrow Li_2O_2 \quad E° = 3.10 \text{ V} \qquad [1]$$

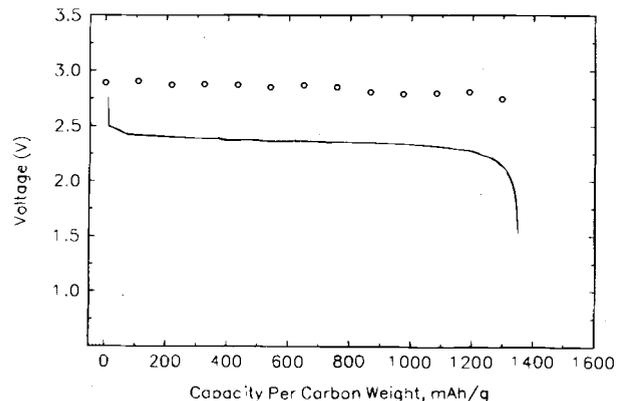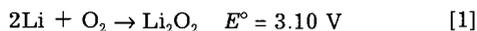$$4Li + O_2 \rightarrow 2Li_2O \quad E° = 2.91 \text{ V} \qquad [2]$$

Fig. 4. The intermittent discharge curve and the open-circuit voltages of a Li/PAN-based polymer electrolyte/oxygen cell at a current density of 0.1 mA/cm² at room temperature in an atmosphere of oxygen. The cathode contained Chevron acetylene black carbon. The cell was discharged in 1.5 h increments with an open-circuit stand of about 15 min between discharges. (ooo) OCV, (____) load voltage.
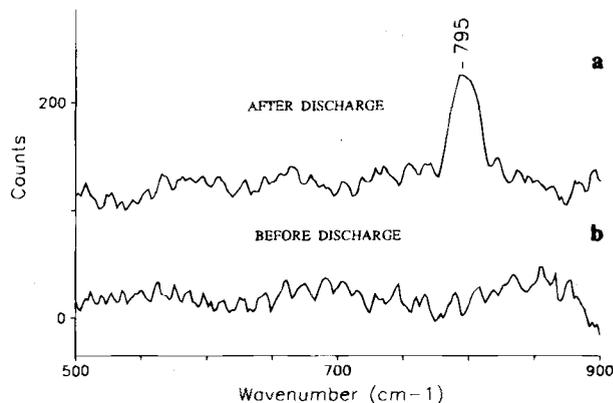

Fig. 5. Raman spectra of (a) the discharged carbon electrode and (b) the undischarged carbon electrode.

Standard cell potentials, $E°$, in Eq. 1 and 2 were calculated using the standard Gibbs free energy of formation ($\Delta G°$) of -134 kcal/mol for Li_2O and -145 kcal/mol for Li_2O_2. A reaction between Li and H_2O could be ruled out as the source of the cell potential since $E°$ for the reaction, $Li + H_2O \rightarrow LiOH + 1/2H_2$ is only 2.08 V.

Qualitative analysis indicated that the discharge product most probably is Li_2O_2. Thus, when the carbon containing the discharge product from a discharged cell was mixed with the $KMnO_4$ solution, the purple color of the solution disappeared with the evolution of a gas; a similar phenomenon was observed by adding Li_2O_2 to the $KMnO_4$ solution. However, the addition of carbon containing undischarged carbon electrode to $KMnO_4$ did not change the solution color. Li_2O also does not change the color of $KMnO_4$ solution. Li_2O_2 was confirmed from Raman spectra of discharged cathodes.

The Raman spectrum (Fig. 5a) of the discharged carbon electrode, recorded in the range of 900 to 500 cm⁻¹, shows one strong absorption peak at 795 cm⁻¹, which is characteristic of the O-O stretch in Li_2O_2.[7] The Raman spectrum also shows that there is little or no Li_2O in the discharged carbon electrode since its absorption at 521 cm⁻¹ is absent.[8] The Raman spectrum (Fig. 5b) of the undischarged carbon electrode shows no absorption between 900 and 500 cm⁻¹.

Based on both the qualitative and the Raman analyses the reaction in Eq. 1 appears to be the most probable discharge process in the Li/O_2 cell. This is consistent with prior observations that in the absence of a catalyst reduction of oxygen usually does not proceed beyond the peroxide stage.[9] A load voltage of approximately 2.5 V which is 0.35 V lower than the OCV of 2.85 V can be explained in terms of reaction overvoltages at the electrodes.
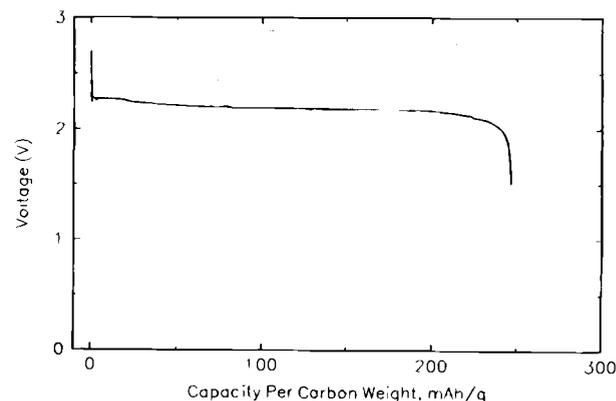

Fig. 6. The discharge curve of a Li/PAN-based polymer electrolyte/oxygen cell at a current density of 0.1 mA/cm² at room temperature in an atmosphere of oxygen. The cathode contained 40 w/o graphite powder and 60 w/o polymer electrolyte. The cell was packaged in the D cell can and O_2 from a tank was used to maintain a flowing O_2 atmosphere.

Table II. Discharge capacities of Li/O₂ cells[a] at different current densities.

Current density (mA/cm^2)	Cell voltage (V)	Capacity (mAh/g)
0.1	2.5	1410
0.25	2.4	1390
0.50	2.3	800
1.0	2.2	800
2.0	2.2	600

Discharged in an O_2 atmosphere with cells containing Chevron acetylene black carbon electrodes and $PAN-EC/PC-LiPF_6$ electrolyte.

The capacity of the cell is expressed as milliampere-hour (mAh) per gram (g) of carbon since it appears that the end-of-discharge of the cell is reached when the carbon electrode is choked by the deposition of Li_2O_2 in its pores. This behavior resembles that in $Li/SOCl_2$ and Li/SO_2Cl_2 cells in which the end of discharge occurs when the carbon electrode is choked by LiCl. As in these cells, the Li/O_2 polymer cell capacity strongly depended on the surface area of the carbon. For example, a capacity of only 250 mAh/g was obtained (Fig. 6) with an electrode containing 10 μm size graphite powder having a surface area of 5 m²/g as opposed to 1400 mAh/g for an electrode based on submicron Chevron acetylene black, having 40 m²/g surface area.

The effect of discharge rate on the capacity obtained in a cell with Chevron acetylene black-based carbon electrode is presented in Table II. A capacity of 800 mAh/g was realized at 1 mA/cm² and 600 mAh/g was obtained at 2 mA/cm². It should be noted that these results were obtained with carbon electrodes which were not optimized with respect to composition; for example, the ratio of carbon to the polymer electrolyte, the surface area of the carbon, electrode thickness, and electrode porosity. For example, carbons such as Ketjenblack (available from Akzo Chemical, Inc., Chicago, IL) and Black Pearl-2000 (available from Cabot Corporation, Billerica, MA) have surface areas of 1000 to 2000 m²/g and should provide substantially higher rate capability than that realized so far with Chevron acetylene black.

A preliminary study of the shelf-life of the Li/O_2 battery was carried out by exposing a cell package containing a Chevron acetylene black electrode to an atmosphere of flowing O_2 for 5 days and subsequently discharging it at 0.1 mA/cm². A capacity of 1350 mAh/g was obtained from the cell with an average load voltage of 2.4 V. It appeared that if the Li anode can be shielded by the polymer electrolyte from direct contact with moist air, the shelf-life of the Li/O_2 polymer cell is satisfactory for practical use. In
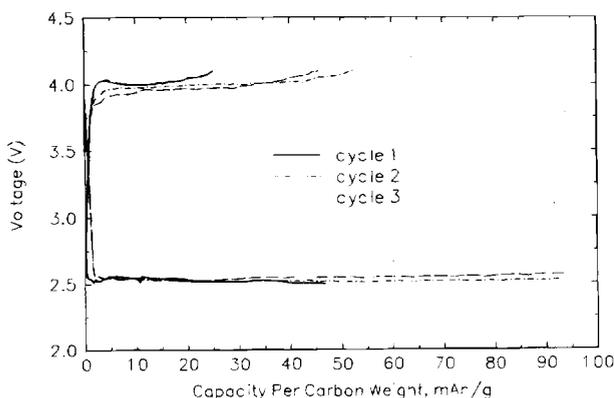
Fig. 7. The cycling data for a Li/PAN-based polymer electrolyte/oxygen cell at room temperature in an atmosphere of oxygen. The cathode contained 20 w/o Chevron carbon black and 80 w/o polymer electrolyte. The cell was discharged at 0.1 mA/cm² and charged at 0.05 mA/cm².
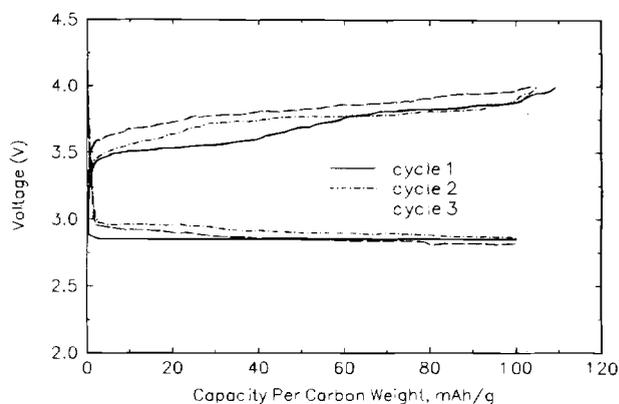
Fig. 8. The cycling data for a Li/PAN-based polymer electrolyte/oxygen cell at room temperature in an atmosphere of oxygen. The cathode contained 20 w/o catalyzed Chevron carbon black and 80 w/o polymer electrolyte. The cell was discharged at 0.1 mA/cm² and charged at 0.05 mA/cm².

practice, the Li anode will be shielded from direct contact with air by the plastic envelope as well as the polymer electrolyte wrapped around the edges of the Li foil. Oxygen that diffuses to the Li anode through the electrolyte will react with it and form a protective solid electrolyte interphase of either Li_2O or Li_2O_2.

Rechargeability.—Figure 7 shows the discharge/charge data for a Li/oxygen cell with Chevron carbon cathode. In the first cycle the cell was partially discharged to a capacity of 47 mAh/g before it was charged. The charge plateau at ~4 V yielded a capacity of 25 mAh/g and a definite end point was observed. In the second and the third cycles, a higher discharge capacity of 94 mAh/g was extracted from the cell. The capacities in the respective charges were 52 and 47 mAh/g. In order to see if the charge capacity at 4 V was due to electrolyte oxidation, we charged a fresh Li/oxygen cell at 0.05 mA/cm² in an atmosphere of oxygen. At the voltage cutoff of 4.1 V, a capacity of only 3 mAh/g was obtained; and at the voltage cutoff of 4.5 V, the charge capacity increased just to 9 mAh/g. Thus, the capacity due to oxidation of the polymer electrolyte on the carbon surface is very small, and the charge capacity realized in Fig. 7 clearly corresponds to the reversible reaction of 1.

The overvoltage for recharge can be decreased and its coulombic efficiency increased with the use of cobalt phthalocyanine catalyzed electrodes. These electrodes are similar to the ones we previously used in $Li/SOCl_2$ cells,[10] and by others in aqueous oxygen cells.[9] Figure 8 displays cycling data for a cell using the catalyzed Chevron carbon electrode. The cell had an OCV of 3.07 V. It was partially discharged to a capacity of 100 mAh/g and then charged. In the first charge, a capacity of 112 mAh/g was obtained to a 4.1 V cutoff. In the second and the third charges, the capacities were 108 and 105 mAh/g, respectively. When a catalyzed fresh Li/oxygen cell was charged, a capacity of only 4 mAh/g was obtained to the 4.1 V cutoff. Thus, the catalyst had no effect on the oxidation of the electrolyte, and the charge capacity observed in the Li/O_2 cell in Fig. 8 is ascribed due to the recharge of the cell reaction. The presence of cobalt catalyst in the carbon electrode increases the discharge voltage by ~0.35 V and decreases the charge overvoltage by ~0.3 V. As a result, the overpotential between the charge and the discharge is reduced by ~0.65 V. At the fourth cycle, the cell was fully discharged to 2 V and analysis of the carbon electrode indicated that Li_2O_2 was the discharge product. The major effect of this cobalt catalyst appears to be a reduction in the activation overpotentials for the discharge and charge and not a change in the mechanism of the cell reactions since the discharge product is the same with and without the catalyst.

Figure 9 shows cycling data for another catalyzed Li/oxygen cell. The cell was first discharged to a 1.5 V cut-
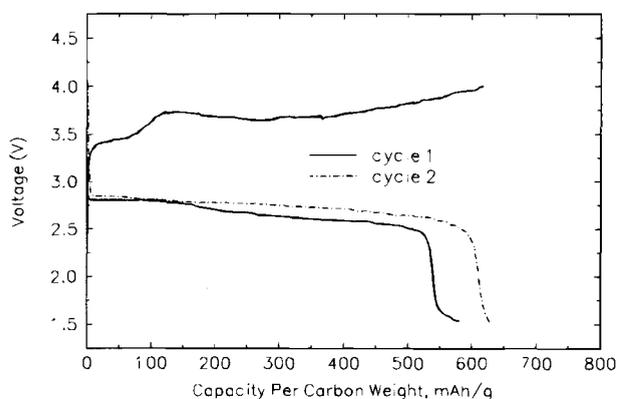
Fig. 9. The cycling data for a Li/PAN-based polymer electrolyte/oxygen cell at room temperature in an atmosphere of oxygen. The cathode contained 20 w/o catalyzed Chevron carbon black and 80 w/o polymer electrolyte. The cell was discharged at 0.1 mA/cm² and charged at 0.05 mA/cm².

off to yield a capacity of 580 mAh/g. In the following charge to 4.0, a capacity of 630 mAh was obtained. In the second discharge the capacity was 630 mAh/g. The capacity of this cell is smaller because the cathode was about 250 μm thick as opposed to 75 to 100 μm in the other cells. These results indicate that the discharge capacity in the Li/oxygen cell can be fully recovered by charging to a potential of ~4 V.

Conclusions

A nonaqueous rechargeable Li/O₂ cell is described. The polymer electrolyte-based design offers a convenient way to harness the energy from the Li/O₂ couple.

The Li/O₂ polymer battery can conceivably be fabricated with the oxygen-permeable membrane on the cathode side of the plastic envelope sealed with a peelable tape, resembling that in a Band-Aid. Prior to use, the tape will be removed to let oxygen into the carbon electrode and activate the battery. The battery can be resealed after each use or it can be recharged and used. The materials used for the polymer electrolyte and other components of the battery are nontoxic so that it is possible to fabricate a completely environmentally friendly battery. A convenient way of distributing the polymer battery would be as packages of Band-Aid-type strips, or as large rolls of Z-folded stacks from which individual strips may be cut off and used as needed. Its unique design features make this polymer battery especially suitable for powering small portable devices.

The cells studied so far showed a specific energy between 250-350 Wh/kg. Considerably higher specific energy should be possible with optimized cells. The specific energy was calculated using the capacity and voltage of the cell and the weights of the electrodes and electrolytes. The weight of the plastic envelope was not included in the calculation since the aspect ratio of the plastic envelope is too large in small cells.

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