

## A Brief History of Non-aqueous Metal-Air Batteries

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### Abstract

A new family of non-aqueous metal-air batteries has been discovered during the course of experiments carried out to study the Li intercalation behavior of graphite in a Li/C cell utilizing propylene carbonate containing gel-polymer electrolytes. Some of these batteries when fully developed could have practical specific energies of 1000-3000 Wh/kg. The Li/O<sub>2</sub> battery is rechargeable and efforts should be made to fully develop it.

### Introduction

Non-aqueous metal-air batteries utilizing alkali and alkaline earth metal anodes are very attractive because they offer potentially very high energy densities. They are unique power sources because the cathode active material, oxygen, does not have to be stored in the battery but can be accessed from the environment. Of the various metal-air battery chemical couples, the Li-air battery is the most attractive since the cell discharge reaction between Li and oxygen to yield Li<sub>2</sub>O, according to  $4\text{Li} + \text{O}_2 = 2\text{Li}_2\text{O}$ , has an open circuit voltage of 2.91 V and a theoretical specific energy of 5200 Wh/kg (Table 1). In practice, oxygen is not stored in the battery, and the theoretical specific energy excluding oxygen is 11140 Wh/kg. In early nineteen nineties we demonstrated the first practical non-aqueous Li-air battery with the use of a Li/C cell in which a gel polymer electrolyte membrane served as both the separator and ion-transporting medium (1,2). The Li ion conducting gel polymer electrolytes used to construct polymer Li-air cells included those based on polyacrylonitrile (PAN) (3) and polyvinylidene fluoride (PVdF) (4). In this paper, I present a brief account of the circumstances that led to our discovery of the Li-air battery. The potentially very high energy density of the Li-air battery has spurred considerable recent interest in developing it for applications such as unmanned aerial vehicles and portable power sources.

Table 1  
Properties of metal-air batteries

Metal/air battery	Calculated OCV, V	Theoretical specific energy, Wh/kg	
		Including oxygen	Excluding oxygen
Li/O <sub>2</sub>	2.91	5200	11140
Na/O <sub>2</sub>	1.94	1677	2260
Ca/O <sub>2</sub>	3.12	2990	4180
Mg/O <sub>2</sub>	2.93	2789	6462
Zn/O <sub>2</sub>	1.65	1090	1350

## Results and Discussion

The Li-ion conducting polymer electrolytes we used and their conductivities are summarized in Figure 1. They were all isolated as free-standing films and, except for those based on poly(vinyl sulfone), exhibited room temperature conductivities of  $2-3 \times 10^{-3}$  S/cm (3,4).

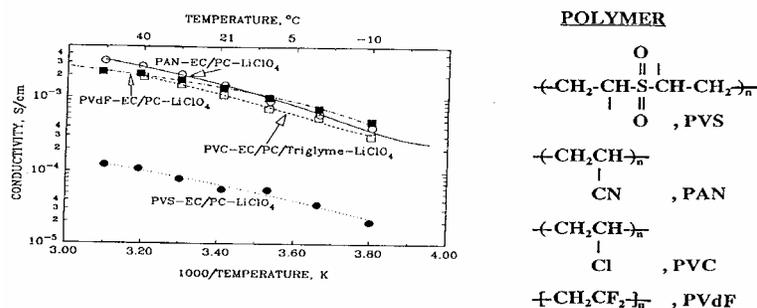


Figure 1. Gel Polymer electrolytes and their conductivities

We did not set out to invent a Li-air battery, rather its discovery in our laboratory was serendipitous. We were investigating the electrochemical properties of a Li/graphite cell with the polymer electrolyte of the composition, PAN(12w/o)-EC(39w/o)-PC(39w/o)-LiPF<sub>6</sub>(10w/o). Schematics of the cell used are shown in Figure 2 and a picture of the cell is shown in Figure 3.

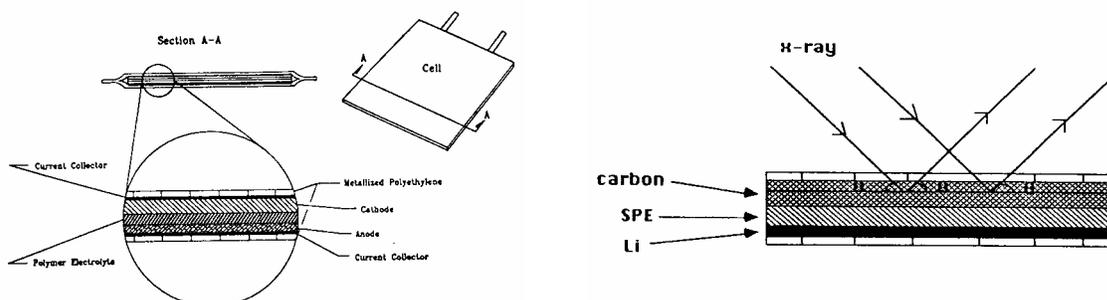


Figure 2: Schematics of the Polymer Electrolyte-based Li/C Cell (left) used to measure *in-situ* X-ray diffraction of graphite (right) and infrared spectral analysis of gases produced during discharge (see Z. Jiang, M. Alamgir and K. M. Abraham, J. Electrochem. Soc, 142,333(1995))



Figure 3: Photograph of the Li/C cell

We had two purposes for our study: i) to perform an insitu X-ray diffraction analysis of the graphite during discharge of the Li/C cell, and ii) analysis of the gases produced in the cell as its discharge proceeded. We found that the discharge of this cell leads to the reduction of PC at about 0.9V with the generation of gases we identified by gas-phase infrared (IR) spectroscopy to be mostly propylene. For the IR analysis we used a gas syringe to withdraw gases from the plastic-sealed Li/C cell at various stages in its discharge. When we resumed discharge after withdrawing the gases, each time the OCV of the cell increased to  $\sim 2.5$  V and it delivered a small amount of capacity at about 2.3V, Figure 4.

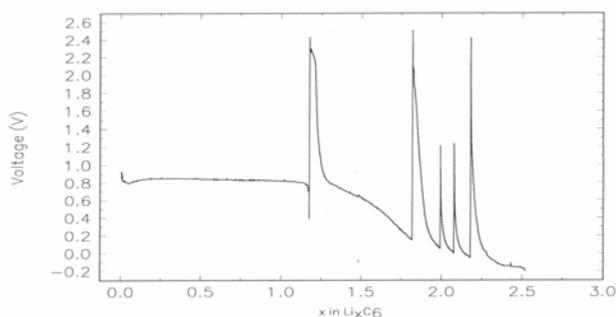
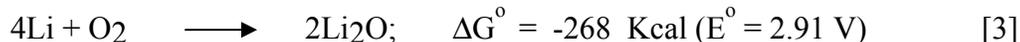


Figure 4: The voltage of the Li/C cell each time after withdrawing gases form it

Having repeatedly seen this behavior we recognized, supported by the thermodynamic calculations shown in equations 2- 4, that we were inadvertently introducing oxygen into the cell from the syringe.

$$\Delta G^{\circ} = -nFE^{\circ} \quad [1]$$



We then built a Li cell with Teflon-bonded carbon black cathode and an inlet to introduce oxygen or air into the Li/C cell, Figure 5. We demonstrated that we could build a practical Li battery with oxygen being accessed from the atmosphere, Figures 6 and 7.

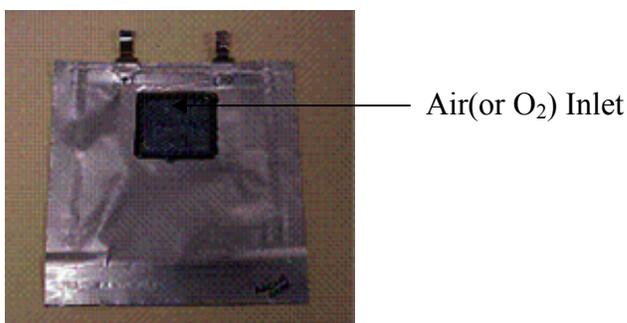
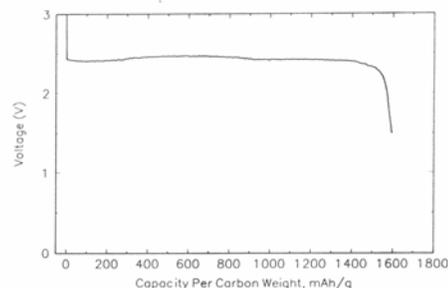
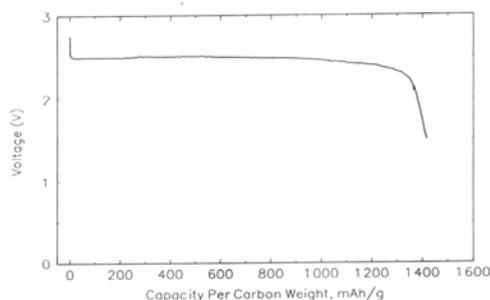
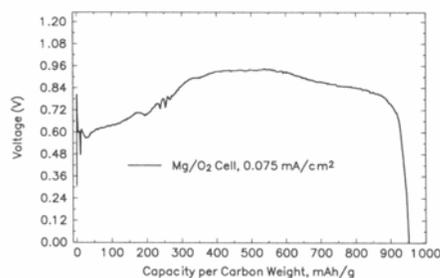
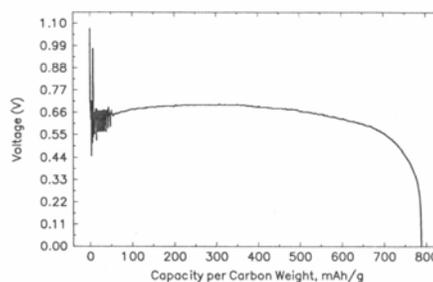
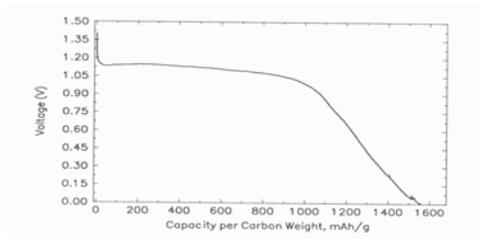
Figure 5: Plastic Li/air (O<sub>2</sub>) CellFigure 6: Discharge of Li/O<sub>2</sub> cell at 20 °C

Figure 7: Discharge of a Li/Air cell at room temperature

In the discharge of this cell, the oxygen is reduced on the carbon cathode and the products are stored inside the pores of the Teflon-bonded carbon electrode. As a result the cell capacity is expressed as ampere-hour per gram of the carbon in the cathode. We showed that the main discharge reaction in the absence of a catalyst in the porous carbon cathode is the reduction of oxygen to form Li<sub>2</sub>O<sub>2</sub> (1). In the presence of a transition metal catalyzed carbon cathode, oxygen reduction can proceed further to form Li<sub>2</sub>O (2).

We found that the Li/oxygen cell is rechargeable when the carbon cathode contains catalysts derived from complexes of metals such as cobalt (1). The catalyst can be viewed as lowering the overvoltage for the oxidation of Li<sub>2</sub>O<sub>2</sub> or Li<sub>2</sub>O to form metallic Li and oxygen. Alternatively, the cobalt may be catalyzing the oxidation reaction by accepting the oxygen from the lithium oxide to form a cobalt oxide and metallic lithium. The reactions and products in the rechargeable Li-air battery remain to be fully elucidated. Recent studies have shown that the utilization of the carbon cathode can be significantly increased with the used of metal-catalyzed carbon black (5).

We have also found that a Magnesium/Oxygen battery can be constructed with a Mg ion conducting polymer electrolyte of the composition, 30PVdF-HFP-62.5 EC/PC-7.5Mg(ClO<sub>4</sub>)<sub>2</sub>, with a conductivity of 1.2x10<sup>-3</sup> S/cm at 20 °C. This Mg/O<sub>2</sub> cell showed an open circuit potential of ~1.2 V at room temperature, lower than the calculated value of 2.93 V, and its discharge voltage ranged between 0.7 to 1.1 V depending on the current density, carbon cathode and electrolyte composition, Figures 8-10.

Figure 8: Discharge of a Mg/O<sub>2</sub> CellFigure 9: Discharge of a Mg/O<sub>2</sub> Cell at 50 °CFigure 10: Discharge of a Mg/O<sub>2</sub> cell with a few drops of water added to the electrolyte

The departure of the discharge behavior of the Mg/O<sub>2</sub> cell from that expected from thermodynamic data is attributed to the chemistry of the Mg anode. For constructing the cell in Figure 8 the Mg foil had been dipped in hydrochloric acid and polished to remove surface films. Remarkably, the cell showed a steady voltage at about 1.1 V at 0.075 mA/cm<sup>2</sup> after adding a few drops of water into the Mg ion conducting polymer electrolyte (Figure 10).

## Conclusions.

The non-aqueous metal-air batteries represent a class of potentially ultrahigh energy density power sources useful for military and civilian applications. When fully developed these batteries could exhibit practical specific energies of 1000-3000 Wh/kg. Some of them are rechargeable and efforts should be made to fully develop them

## References

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