

Non-aqueous Lithium-Air Batteries with an Advanced Cathode Structure

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Abstract

Lithium-air batteries consist of lithium anodes electrochemically coupled to atmospheric oxygen through an air cathode. Oxygen gas introduced into the battery through an air cathode is essentially an unlimited cathode reactant source. Theoretically with oxygen as an unlimited cathode reactant, the capacity of the battery is limited by the Li anode. The theoretical specific energy of the Li-oxygen cell is 13.0 kWh/kg, the highest for a metal air battery. In addition to this very high specific energy, the Li air battery offers a flat discharge voltage profile, environmental friendliness and long storage life. A cell design utilizing a non-aqueous electrolyte alleviates the parasitic corrosion reactions of the Li aqueous anode that plagued past lithium-air batteries based on alkali electrolytes. The non-aqueous electrolyte-based cell design also overcomes safety concerns of the Li-air system.

In this paper we report the results of our efforts to increase the practical energy density of the Li-air battery through improved air cathode structures. Transition metal catalysts incorporated into the carbon electrode enhance the oxygen reduction kinetics and increase the specific capacity of the cathode. Yardney's experience and technologies in the zinc-air and aluminum-air power sources were adopted in the design of the new air cathode structure and the Li air-cell. These batteries have the potential to power portable electronic equipment, unmanned aerial vehicles, camping equipment, or any equipment where air is present.

Keywords

Lithium air; air cathode; non-aqueous; Li-air; SEM.

Introduction

Lithium air batteries, like all metal air batteries, consist of a metal anode electrochemically coupled to atmospheric oxygen through an air cathode. Lithium is an extremely light metal, and possesses the greatest theoretical specific energy at 13 kWh/kg (Table I). Oxygen, the cathode reactant, is a virtually unlimited source in the air. Since the atmosphere is the source of oxygen the battery is very light in weight. The two discharge reactions of the lithium air battery are:



Much of the development efforts on lithium air batteries in the past focused on aqueous electrolyte of KOH that resulted in high self-discharge, excessive parasitic

corrosion of the lithium anode, and safety problems [1]. By using a non-aqueous electrolyte the parasitic reactions can be avoided and the safety concerns alleviated. The first non-aqueous lithium air battery reported in the literature was the polymer electrolyte lithium air battery developed by Abraham [2]. The main advantages this system has over the previous battery designs are that it is non-aqueous and contains a solid electrolyte. This polymer electrolyte lithium air battery system uses lithium metal as the anode, a lithium ion conducting polymer, and an air cathode. The polymer in the original work is either a polyacrylonitrile plasticized with a LiPF₆ solution in a mixture of ethylene carbonate and propylene carbonate or a copolymer composed of polyvinylidene fluoride (PVDF) and hexafluoropropene (HFP) with the plasticizer poly(ethylene glycol) dimethyl ethers (PEGDME) plus a small amount of LiN(SO₂CF₃)₂ [3]. Abraham discovered the remarkable polymer lithium air battery, but did not make an effort to improve the air cathode structure. The next researcher to investigate lithium air batteries has been J. Read [4]. He investigated organic electrolytes in lithium air batteries and their interaction with the air cathode [4]. Electrolyte formulation and its matching to the specific cathode, he surmised, are the most important factors. Later Read et al. looked at the oxygen transport properties of electrolytes for lithium air batteries [5]. They concluded that increasing the oxygen content of the electrolyte, by electrolyte reformulation, the discharge capacity of the cell might be improved. The limiting factor in this system, and nearly all of the metal air batteries, is the air cathode [1,2]. The performance of the lithium air battery has been limited by a low rate of oxygen diffusion in the porous cathode. Recognizing that improving the cathode structure is the key to increasing the energy density of the Li air battery, we focused on improving and optimizing the air cathode structure. Yardney's experience and technologies in the Zn and Al air power sources was combined with our extensive knowledge of lithium batteries in the design of the new air cathode structures.

Table I. Properties of metals used in metal air batteries [1].

Metal Anode	Ah/g	Theor. V	Theor. kWh/kg
Li	3.86	3.4	13.0
Ca	1.34	3.4	4.6
Mg	2.20	3.1	6.8
Al	2.98	2.7	8.1
Zn	0.82	1.6	1.3
Fe	0.96	1.3	1.2

Experimental

Cell Design: A pouch cell design was used to test the new air cathodes in lithium air cells. These cells are self-contained cells suitable for testing in different environments. The cell construction involves layering the cell components and sealing them in a plastic case resembling a packet. The lithium metal anode, separator, electrolyte, and carbon air cathodes are sealed inside the metallized plastic packaging material. A picture of the pouch cell used for testing is in Figure 1.

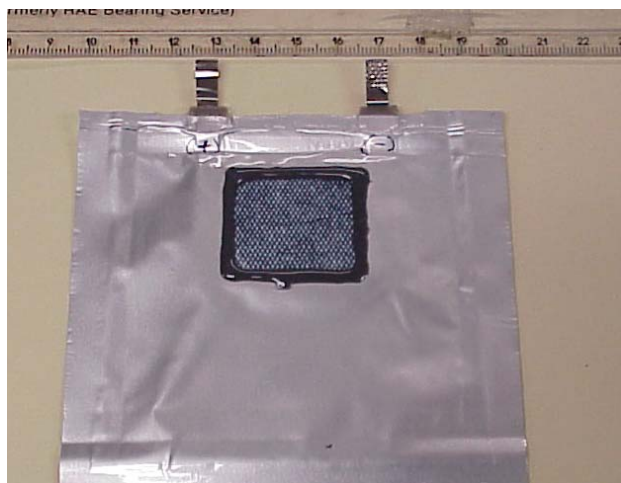


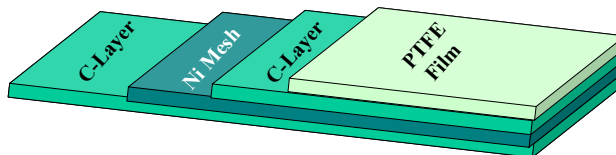
Figure 1. A photo of lithium air pouch cell designed to test the air cathodes.

The anode is composed of a lithium metal foil, pressed into a nickel mesh current collector that was welded to a nickel tab. The area of the anode is slightly larger than the 10 cm^2 cathode to provide full usage of the air cathode. The separator used was Setela, which is an organic polymer film 20 microns thick. The liquid electrolyte used was 1M LiPF_6 in 1:1:1 EC/DEC/DMC. EC is ethylene carbonate, DEC is diethyl carbonate, and DMC is dimethyl carbonate. The air cathode is a carbon composite made by combining carbon, a metal catalyst, and a binder, deposited on a metal current collector. The ratios of these components together with the particular types of component were varied to investigate the optimal composition. The binder used was Teflon combined with latex. The metal current collector was Ni expanded metal mesh. The air cathode structure is a layered composite with an increased capacity (Figure 2). A thin Teflon film between the air cathode and the atmosphere provides hydrophobicity to the cathode to repel atmospheric water and creates channels for oxygen diffusion. The active area of the cathode is 10 cm^2 .

Cathode Preparation: A typical machine cathode preparation would entail two layers of a carbon, binder, and catalyst mixture being deposited on both sides of a metal current collector (Figure 2). Carbon mats are impregnated with slurry of carbon, binder, and catalyst. Two of these impregnated mats are laminated around a current collector. All air cathodes would have a microporous Teflon layer

added to the side exposed to the environment. This produces a double-sided air cathode.

Figure 2. A diagram of the layered air cathode.



Test Chamber: The lithium air cells were discharged in test bags filled with oxygen. The entire bag is sealed and is gas tight. The bag can be opened at one end, and cells inserted or removed. A valve is in the bag allowing gas flow and evacuation. A wire feed-through allows leads to connect to the cell and maintain a gas tight seal. The bags are reusable. Li air cells are placed inside, connected to the wires, then flushed and filled with oxygen, before being discharged. The cells were discharged in a temperature chamber at 20°C . The bags were only slightly filled with oxygen gas so the pressure of oxygen inside the bag is about one atmosphere.

Cell Discharge: Cells were discharged at constant current using the Maccor battery cycler as the power supply. Typically a 1mA constant current (a current density of 0.1 mA/cm^2) discharge was used to test the different cathodes. The electrode area was 10 cm^2 . Since these cells are primary cells new cells were used to test higher rates, for example 0.2 mA/cm^2 . The cells were typically discharged to 1.5 V .

SEM Analyses: The scanning electron microscope (SEM) was used to characterize the structure of the air cathodes, and investigate the distribution of the metal catalyst.

Results and Discussion

SEM Analyses: The scanning electron microscope (SEM) was used to view the structure of the air cathodes and locate the catalysts. The image below (Figure 3) is representative of the Mn cathodes viewed. The cathode must contain pores to allow both the oxygen gas and electrolyte to come in contact with the catalysts and carbon. Carbons provide the reactive surface for the reduction of the oxygen gas. The best type of carbon investigated was Black Pearls 2000. Metals such as Mn catalyze the reduction of oxygen on the air cathode structure to increase the depth of oxygen reduction from a 2 electron to a 4 electron per mole of oxygen (O_2) process. Binders are primarily used for structural stability. The image shows dark pores throughout the cathode structure. The long fibers are the carbon mats, while the lightly colored patches are the dried slurry containing the carbon powder, binder and catalyst. It is important to distribute the catalysts in the carbon cathode and prevent agglomeration. Distributing the catalysts increases the reactivity of the cathode, and decreases material cost. Elemental analysis showed that the

Mn catalyst was evenly distributed amongst the cathode structure.

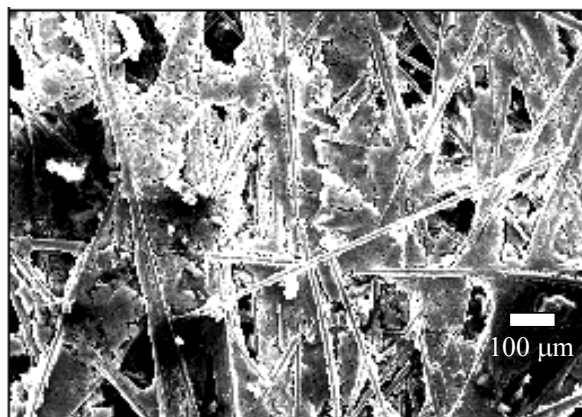


Figure 3. The SEM image showing the porous nature of the air cathode.

Several cells with the Mn catalyst were discharged. Doubling the rate of discharge did not result in half of the capacity but less. This might be due to partial clogging of the cathodes pores at the higher rate thus preventing complete utilization of the carbon in the cathode structure. The Mn catalyzed cell had a capacity of 91 mAh with a relatively flat discharge profile (Figure 4).

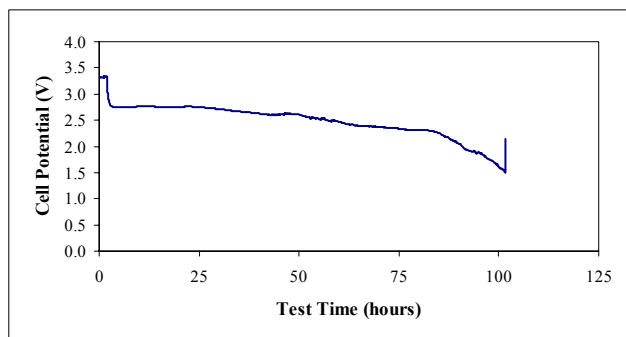


Figure 4. The discharge profile of the Mn catalyzed cathode at 0.1 mA/cm² shown with an initial open circuit rest of two hours.

Discharging further to 1.5 volts resulted in 100 mAh total capacity. The corresponding energy yield is 246 mWh. The air cathodes demonstrated very high specific capacities of 3471 mAh/g (at 0.1 mA/cm²) and 1850 mAh/g (at 0.2 mA/cm²) (Table II). The specific capacity is based upon the weight of the carbon in the cathode that is the active

material. These are the highest values of specific capacity reported in the literature to date [2-5].

Table II. Discharge data from the Mn catalyzed air cathode at two different rates. Cells were discharged to 1.5 V at constant current.

Initial potential (volts)	Discharge Capacity (mAh)	Discharge Current (mA)	Average Potential (volts)	Specific Capacity (mAh/g)
3.34	99.6	1.0	2.47	3471
3.31	53.1	2.0	2.27	1850

Conclusion

The main goal of developing high capacity improved air cathodes for lithium cells was achieved and demonstrated in the discharge of these lithium air cells. The improved cathode utilizing Mn catalysts may account for the high capacity. These electrodes will be optimized in further studies.

Acknowledgement

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