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8.1 Large Prototype Lithium Air Batteries

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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 anode that plagued past lithium-air batteries based on alkali aqueous 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 create a manufacturable Lithium-air battery through optimized air cathode structures, oxygen transport molecules, and a lightweight cell case. Transition metal catalysts incorporated into the carbon electrode enhance the oxygen reduction kinetics and increase the specific capacity of the cathode. Advanced electrolyte compositions, using oxygen transport molecules, increase the oxygen diffusion rate into the cell and throughout the air cathode structure. Yardney's experience and technologies in the zinc-air and aluminum-air power sources were adopted in the design of the new Lithium-air cell suitable for manufacturing. These batteries have the potential to power portable electronic equipment, unmanned aerial vehicles, camping equipment, or any equipment where air or oxygen is present.

Keywords

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

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).

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

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:

$2Li + O_2 \rightarrow Li_2O_2$ $\quad E^o = 3.10$ V

$4Li + O_2 \rightarrow Li_2O$ $\quad E^o = 2.91$ V

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 $LiPF_6$ solution in a mixture of ethylene carbonate and proplylene carbonate or a copolymer composed of polyvinylidene fluoride (PVDF) and hexaflouropropene (HFP) with the plasticizer poly (ethylene glycol) dimethyl ethers (PEGDME) plus a small amount of $LiN(SO_2CF_3)_2$ [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 was 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. Since oxygen diffusion often limits the rate of discharge for metal-air cells, oxygen transport molecules were investigated. This new lithium-air technology required novel designs for a cell case. 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 prototype lithium-air batteries.

Experimental

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 1). 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.

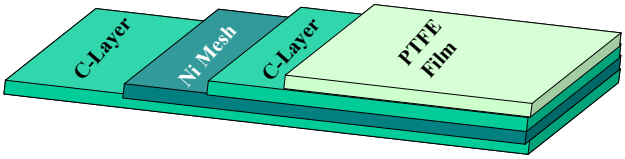
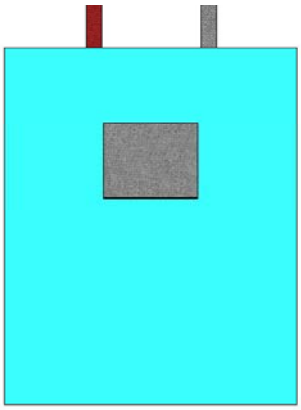
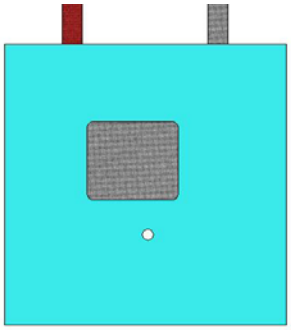


Figure 1. A diagram of the layered air cathode.

Cell Design: Three cell designs were used to test various air cathodes, oxygen transport molecules, and a new cell case design suitable for manufacturing. The three cases are identified as small, medium, and large referring to the size of the cathode and case. First, a small pouch cell design was used to test the new air cathodes and oxygen transport molecules 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 2). Second, a hard plastic case design was used to test anodes, cathodes, and assembly. A drawing of the machined medium case is shown in Figure 3. Similar to the small case design, the electrodes and separator are stacked together and placed



between two pieces of the case. Third, is the large prototype cell composed of a two piece molded plastic case (Figure 4). The case is about five inches square. This case



was made to test assembly procedures and manufacturing processes for non-aqueous lithium-air batteries.

Figure 2. A drawing of the small lithium air pouch cell designed to test the air cathodes.

Figure 3. A drawing of the medium lithium air cell designed to test the air cathodes.

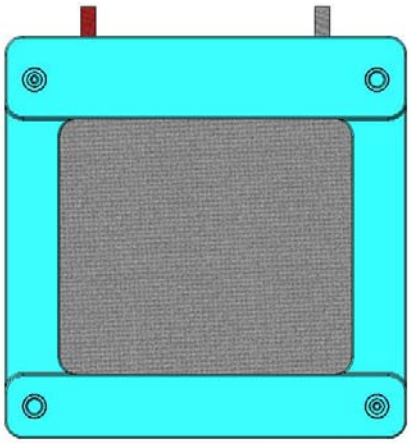


Figure 4. A generalized drawing of the large lithium air prototype cell.

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 area of cathode to provide full usage of the air cathode. The separator used was Setela, which is an organic polymer film 20 micron 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 1). 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 areas of the cathode sizes were 10, 15, and 250 cm^2. The oxygen transport molecules are organic compounds with high affinities for oxygen that carry the oxygen from the air into the cell. The chemical names are currently proprietary. The large cell design is a moldable product to increase reproducibility and lower cost. It also allows for easy assembly by hand or automated machinery.

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 1.5 mA constant current (a current density of 0.15 mA/cm^2) discharge was used to test the different cathodes. Since these cells are primary cells, new cells were used to test various rates. Current densities tested included 2.0, 1.0, 0.5, 0.2, 0.1, and 0.5 mA/cm^2. The cells were typically discharged to 1.5 V.

Results and Discussion

Several accomplishments to date include: the optimization of the air cathode structure, the utilization of oxygen transport molecules, and the fabrication of a large test cell. Of the six different metal catalysts studied, the manganese catalyzed air cathodes gave the highest specific energy (Figure 5). The air cathode structure was optimized by investigating various carbons, catalysts, and lamination pressures. 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]. Oxygen transport molecules were shown to increase the energy of the system when added to the electrolyte. The specific energy (based upon carbon) increased by about 50% (Table II). The cell case designs drastically increased the percent of the air cathode area, while decreasing the cell case area (Table III). The large prototype cells cover over 60% of the cell case area. This will further increase the energy of the cell.

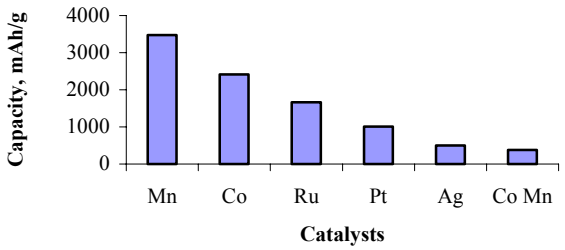


Figure 5. The specific capacities of the air cathodes utilizing the various metal catalysts.

Table II. The oxygen transport molecules increase the specific capacity when added.

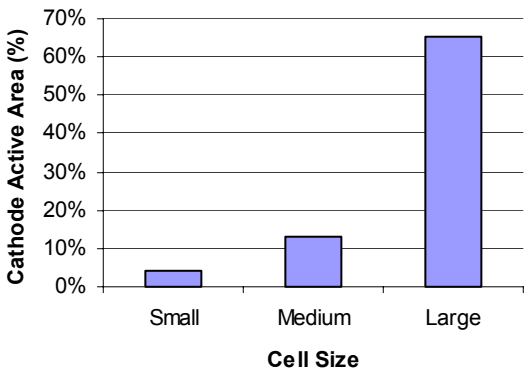


Figure 6. The cell case sizes with the percent of active area of the cathode.

Cells were discharged at current densities from 0.05 to 2 mA/cm^2 to determine their specific energy at various discharge currents (Table III). To date, and without the oxygen transport molecules added, the cells exhibited greater specific capacities at the lower current densities of 0.05 to 0.15 mA/cm^2. The ability to discharge at higher current densities is expected with the oxygen transport molecules.

Table III. Initial results of various discharge current densities with their corresponding specific capacity values based on the weight of carbon.

Current Density (mA/cm^2)	Specific Capacity (mAhr/g)
0.05	2500
0.1	3300
0.15	4300
0.2	1400
0.5	700
1	300
2	200

Conclusion

Transport Molecule	Discharge Current (mA)	Specific Capacity Increase % (mAh/g)
3	1.5	40
1	1.5	40
9	1.5	60

The goal of developing high capacity improved air cathodes for lithium cells was achieved and demonstrated in the discharge of lithium-air cells. The incorporation of oxygen transport molecules into lithium-air cells to improve performance has been successful, and studies continue. The large prototype cell has been fabricated and initially tested. The large cell will continue testing, and the oxygen transport molecules will be optimized within this large cell.

Acknowledgement

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