



A hybrid Li-air battery with buckypaper air cathode and sulfuric acid electrolyte

Yunfeng Li, Kan Huang, Yangchuan Xing*

Department of Chemical and Biological Engineering, Missouri University of Science and Technology, Rolla, MO 65409, United States

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ABSTRACT

We demonstrate a type of carbon nanotube based buckypaper cathode in a hybrid electrolyte Li-air battery (HyLAB) that showed outstanding discharging performances. The HyLAB has sulfuric acid as the catholyte and a large active electrode area (10 cm^2). The active cathode layer was made from a buckypaper with 5 wt.% Pt supported on carbon nanotubes (Pt/CNTs) for oxygen reduction and evolution. A similar cathode was constructed with a catalyst of 5 wt.% Pt supported on carbon black (Pt/CB). It is demonstrated that sulfuric acid can achieve high discharging current densities while maintaining relatively high cell potentials. The cell with Pt/CNTs showed a much better performance than with Pt/CB at high current densities. The HyLAB with Pt/CNTs achieved a discharging capacity of 306 mAh/g and a cell voltage of 3.15 V at 0.2 mA/cm^2 . The corresponding specific energy is 1067 Wh/kg based on the total weight of the sulfuric acid. Slow decrease in performance was observed, but it can be recovered by refilling the cell with new electrolyte after continuous discharging of more than 75 h. A charge–discharge experiment at 0.2 mA/cm^2 showed that the cell was rechargeable with a capacity of more than 300 mAh/g.

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1. Introduction

Li-air batteries have gained much attention as energy storage systems due to their high energy densities, comparable to that of gasoline in theoretical values [1–3]. An advantage of Li-air batteries is that oxygen is not stored in the cathode but acquired free from ambient air during discharge. Major efforts have been focused on non-aqueous electrolyte Li-air batteries to avoid the intensive reaction between water and the Li metal [4–10]. However, Li-air battery with non-aqueous electrolytes is cathode-limited due to that the electrolytes cannot dissolve the solid lithium oxide products, which clog the pores and choke the air breathing cathode. In addition, moisture in ambient air can still degrade non-aqueous electrolytes and react with lithium metal causing self-discharge. These problems directly lead to a short life of non-aqueous Li-air battery.

Aqueous-based systems represent an alternative approach to long operational battery life. A water-stable lithium electrode can be developed by employment of a LISICON-type lithium ion conducting glass ceramic (LiCGC) membrane [11–14]. This impermeable LiCGC membrane can prevent direct lithium reaction with water. Consequently, a hybrid electrolyte Li-air battery (HyLAB) can be constructed. Already demonstrated, aqueous electrolytes of acidic [13,15], neutralized [12], and basic [14,15] solutions have been used in HyLABs in recent years. Neutralized and basic

electrolytes have an overall reaction of $2\text{Li} + \text{H}_2\text{O} + 0.5\text{O}_2 = 2\text{LiOH}$, and the theoretical cell potential is 3.43 V [15]. In acidic electrolytes, especially strong acid solutions, the cell reaction is $2\text{Li} + 0.5\text{O}_2 + 2\text{H}^+ = 2\text{Li}^+ + \text{H}_2\text{O}$, which yields a theoretical open circuit voltage (OCV) of 4.274 V. Acids can dissolve lithium oxide, preventing clogging in the air breathing channels in the cathode. Such cells can have a practical discharge potential about 3.5 V or higher at a discharge current density of 0.2 mA/cm^2 [12,13], which is much higher than that of non-aqueous electrolyte cells (*ca.* 2.6–2.7 V) [5,6,15]. Furthermore, smaller charge–discharge polarizations have been observed in acidic electrolyte cells with the use of Pt catalyst, necessary for the oxygen reduction reaction (ORR) at the cathode, which is $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$, involving 4 electron transfer in acidic medium.

There are two most relevant studies of rechargeable HyLAB using acidic electrolytes. Zhang et al. [13] reported a HyLAB using an acetic acid–lithium acetate electrolyte, and most recently Li et al. [16] reported a HyLAB based on 0.1 M phosphorous acid and 1 M lithium dihydrogen phosphate as catholyte. Both cells reached a high discharge capacity of *ca.* 220 mAh/g and a specific energy of *ca.* 770 Wh/kg, where the mass is based on that of the acid in the electrolytes. The test duration of the charge–discharge to reach this capacity was between 1 and 3 h. Those cells used high loading Pt catalysts (Pt-black or 40 wt.% Pt/C) in the cathodes. In a primary Li-air cell, Kowalczyk et al. [15] showed that it can be discharged for more than 6 days at 0.1 mA/cm^2 in 5.25 M H_2SO_4 catholyte at a cell potential of 3.2 V.

In this work, we demonstrated a rechargeable HyLAB with sulfuric acid aqueous solution as the catholyte and investigated its charge–discharge performance. We chose sulfuric acid as the

* Corresponding author. Current address: Department of Chemical Engineering, University of Missouri, Columbia, MO 65211, United States. Tel.: +1 573 884 1067.
E-mail address: xingy@missouri.edu (Y. Xing).

catholyte, in addition to the advantages of acids mentioned above, due to its electrochemical stability and non-volatility during battery charge–discharge. As lithium sulfate has much solubility in water, and theoretically, all sulfuric acid in 1.0 M H_2SO_4 can be electrochemically converted into lithium sulfate, it can keep the product, lithium sulfate, completely dissolved in the solution. Sulfuric acid also has a relatively high theoretical capacity (479 mAh/g with Li mass included and 546 mAh/g without Li metal) and a specific energy (2046 Wh/kg) [17]. Since carbon nanotubes (CNTs) and carbon black (CB) can yield different porosity and structures in the air diffusion cathode, we prepared two structures of the catalyst layer, one with CNTs and the other with CB, and made a comparison on their cell performances. In addition, a large electroactive area cell (10 cm^2) is demonstrated in a full cell charge–discharge experiment.

2. Experimental methods

2.1. Air cathode preparation

The air cathode consists of an active catalyst layer, a transition layer and the backing layer of Toray[®] paper, which are laminated together. The preparation of Pt/CNT catalysts (CNTs from NanoLab, $50 \pm 15\text{ nm}$) was reported elsewhere [18]. The air-breathing cathodes were prepared as follows. 10 mg carbon nanofibers (CNF $\sim 150\text{ nm}$ in diameter and $\sim 10\ \mu\text{m}$ long, Pyrograf, PR-24-XT-LHT) and 10 mg Pt/CNT catalysts (5 wt.% Pt) were dispersed under sonication in ca. 8 mL ethanol in two separated beakers. First, the CNF ethanol dispersion was vacuum filtered through a $0.4\ \mu\text{m}$ Millipore ISOPORE[®] membrane (47 mm diameter). Then filtration of the 10 mg Pt/CNT ethanol dispersion was done on the same Millipore membrane covered with the CNF layer. This produced a buckypaper of catalyst layer based on the Pt/CNTs. The resulted total thickness of this buckypaper layer is ca. $60\ \mu\text{m}$. This buckypaper was laminated onto a Toray carbon paper (Fuel Cell Store, TGP-H-030) at 140°C and a pressure of 2 atm, with the CNF side on the Toray paper. Repeating the same process using 5 wt.% Pt/CB E-TEK catalysts produced the catalyst layer with the CB structure. Again, the transition layer is CNF. We found that the transition CNF layer can serve well to support both the Pt/CNT and the Pt/CB catalyst layers. The whole cathode thickness after hot press was at ca. $150\ \mu\text{m}$.

2.2. Li-air cell assembly

The HyLAB assembled in this work consists of a sealed anode made by MaxPower Inc. (a pouch half-cell) [15] and an air-breathing cathode described above. Fig. 1 shows a schematic structure of the Li-air cells. The effective area of electrode reported here is 10 cm^2 . In order to prevent electric shorts between the carbon paper and the Li anode pouch cell, a Teflon[®] tape was used to cover the rim of the pouch. The advantage of using a Teflon tape

is that its hydrophobic property prevents the aqueous electrolyte solution from leaking. The catholyte in our study of cell discharge is a pure 1.0 M H_2SO_4 to start with. The volume of the acid was 5.0 mL, to fill up the recess in the pouch in the cathode side.

2.3. Li-air cell test

Tests of the HyLABs were performed in an ambient environment and at room temperature (25°C). An Arbin battery test station (GT2000) connecting to a computer installed with the Arbin Data Pro software was used in the charge–discharge and data collection. For each cell tested, the discharge current density was chosen as 0.01 mA/cm^2 , 0.1 mA/cm^2 , 0.2 mA/cm^2 , 0.5 mA/cm^2 , or 1.0 mA/cm^2 . For long-term discharge and charge experiments, a current density of 0.2 mA/cm^2 was used.

3. Results and discussion

The thickness of 10 mg of CNFs filtered onto the filter membrane produced a transition layer of $30\text{--}35\ \mu\text{m}$ in thickness and 10 mg of Pt-loaded carbon produced $20\text{--}25\ \mu\text{m}$ active layer, which were confirmed by their cross-sections through SEM. The cross-section and surface morphology of typical air-breathing cathodes were characterized by SEM and shown in Fig. 2. In either case of Pt/CNT or Pt/CB, the total thickness of the buckypaper is about $50\ \mu\text{m}$ after hot press, as can be seen from Fig. 2. Similar to proton exchange membrane (PEM) fuel cell electrode preparation, a hot press procedure was needed in order to yield a strong interaction between the carbon paper backing and catalyst layers. It is inevitable that CB particulate structure (with low aspect ratio particulates) was constricted in each direction under high pressure, and this leads to compactness, low porosity, as well as formation of lots of dead-ended channels in this process. However, due to the fibrous structure of CNTs. They were compressed only along the direction of pressure (perpendicular to the electrode surface) in the hot press process. The CNTs are intertwined in the horizontal directions (in plane), forming open channels for air diffusion. Consequently, Pt/CNT formed an open buckypaper layer (see Fig. 2(A) and (B)) on the transition layer and remained porous after hot press, but Pt/CB formed a compact layer with less porous channels after hot press (see Fig. 2(C) and (D)). The surface morphologies of these cathodes are very much different in the catalyst layers, as can be seen from their SEM images. Consequently, their porous structures have direct effect on the Li-air cell performance as shown below.

For acidic electrolytes, the calculated discharge OCV is 4.274 V at 25°C , assuming a 4 electron reaction for the reduction of oxygen [15]. The cells exhibited OCVs in the range of 3.95–4.02 V, depending on the different carbon materials and electrocatalysts. Therefore, the difference between the theoretical and actual OCVs is small. The result was attributed to the better ORR activity in H_2SO_4 because of higher concentration of protons in the H_2SO_4 solution, despite that the air cathode used a low loading Pt catalyst (5 wt.%). Geometrical loading of Pt in the cathode is calculated to be only 0.05 mg/cm^2 (electrode area), but it was found good enough to produce a current flow comparable to that of non-aqueous electrolyte cells. It noted that this loading is much less than the long term (for the year of 2015) DOE target (0.125 mg/cm^2) for noble metal loading in PEM fuel cells.

The HyLAB cell potential dropped from 3.72 V discharging at 0.1 mA/cm^2 to 3.43 V at 0.5 mA/cm^2 for the buckypaper cathode (Pt/CNTs), as shown in Fig. 3. The polarization of the cell was mainly due to the cell resistance derived from contact resistance at the anode side, especially the one between the aprotic electrolyte and the LiCGC membrane [13,19]. At low discharge currents, the cell performance (potential) was about the same as the one based on

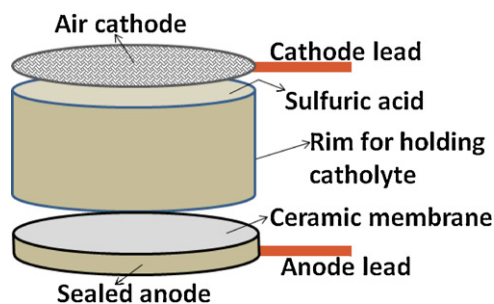


Fig. 1. Schematic diagram of the HyLAB with sulfuric acid catholyte. Sealed anode contains a Li foil, an aprotic buffer, and the top ceramic membrane.

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