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Carbon/PTFE Electrode for Lithium/Air-Water Batteries

by Benjamin Margulies and Jeffrey Read

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT For this project we constructed an inexpensive air cathode free of catalyst, capable of functioning in both acidic and neutral electrolytes, for use in a lithium/air-water battery. The use of acidic electrolyte is necessitated by the formation of the discharge product LiOH from the lithium/air-water reaction. We present a procedure for the construction of a carbon/PTFE air cathode for use with both acidic and neutral electrolytes. We evaluated the performance of the cathode in electrolytes ranging from pH=0 to pH=8 by applying voltage to a half cell, in reference to a Ag/AgCl reference electrode, and then measuring the steady state current. Current densities were found to be the highest in 1M H ₂ SO ₄ , the most acidic electrolyte tested, and decreased as the pH of the electrolyte increased. The cathode performed well enough over the entire pH range to be useful for the lithium/air-water battery.					
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1. Introduction

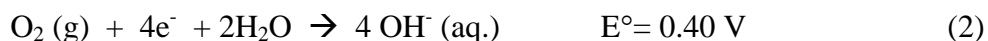
In a lithium/air-water cell, electrons flow between a lithium anode in contact with a non-aqueous electrolyte and an air-cathode in contact with an aqueous electrolyte. The non-aqueous and aqueous electrolytes are kept separate by a non-electronically conducting ceramic membrane impervious to water but with a high ionic conductivity for lithium-ions. $\text{LiTi}_x\text{Al}_y(\text{PO}_4)_3$ is one such example of a ceramic composition that has been used in this manner. The lithium ion can be thought of as being solvated by the ceramic membrane as it passes from non-aqueous to aqueous electrolyte.

At the lithium anode, the following reaction occurs:



At the air cathode, oxygen and either water or hydronium ion undergo reduction as shown in equations 2 through 5 depending on conditions (I).

In a basic electrolyte, the direct 4 electron reaction occurs as:

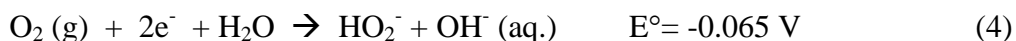


In acidic electrolyte, the direct 4 electron reaction proceeds as:

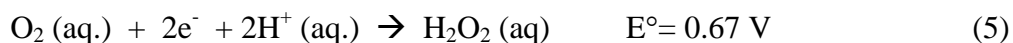


At higher current densities on the air cathode, a 2 electron reaction tends to dominate with the formation of peroxide.

In a basic electrolyte, the 2 electron reaction occurs as:



In acidic electrolyte, the 2 electron reaction proceeds as:



In both basic and acidic electrolytes, carbon black based air cathodes can be used as peroxide generators (2). On gold, mercury, graphite, and most carbons, the formation of peroxide is the predominant reaction pathway. Peroxide decomposes to form water and oxygen, which can then be reduced again on the air cathode.



The flow of electrons from the lithium anode (equation 1) to the air cathode (equations 2 through 5) provides current. To balance the overall charge in the reaction, positive lithium ions flow

through an ionically conducting ceramic membrane from the non-aqueous anode compartment to the aqueous cathode compartment.

For this project we constructed an inexpensive air cathode free of catalyst that is capable of functioning in both acidic and neutral electrolytes. In the lithium/air-water cell, a major failure mode occurs when LiOH saturates the electrolyte and precipitates into the air cathode. This tends to impede the function of the air electrode and limits discharge capacity. The use of an acidic electrolyte is meant to mediate this problem. In acidic solution, lithium salts will not reach the saturation point and precipitate into the electrode until later in discharge. The choice to use an uncatalyzed air cathode results from the fact that the only catalyst stable in acid environments for long periods are ones based on Platinum.

The use of acidic electrolytes in room temperature metal/air cells has not been a major area of research due to the reactivity or corrosion of anode metals in acid electrolytes. The use of an ionically conducting membrane between the anode and cathode compartments prevents contact between the metallic lithium anode and the aqueous acid electrolyte and therefore allows the use of these electrolytes in lithium/air-water cells.

2. Considerations for the Air Cathode

In a metal/air battery, the air cathode is multifunctional. First, the material must be permeable to oxygen gas from the atmosphere. Second, the material must be impermeable to liquid water so that the aqueous electrolyte remains in the cell. Third, the material must provide active sites for the oxygen reduction reaction.

Previous studies (1, 3) indicate that an inexpensive metal air battery cathode can be constructed from layers of PTFE bonded carbon black. The air cathode is constructed using a hydrophobic “wet-proofing” layer, which is permeable to oxygen but not water, and an “active” or catalytic layer, which provides sites for oxygen reduction in the aqueous electrolyte solution. Previous research by Kenjo and Kawatsu (4) and Giordano (5) discuss fabrication parameters for double-layered oxygen electrodes and conclude that current density increases when PTFE content of the electrode decreases.

This project, as stated above, calls for the construction of an inexpensive air cathode for use in lithium/air-water cells. The PTFE bonded carbon cathode using a layered structure should satisfy this goal. The choice of “active” layer carbon will have to be investigated to determine if a carbon, free of catalyst, can provide enough activity for oxygen reduction to be useful in a functioning battery. We define functioning as a current density of 1 to 2 mA/cm² at a potential of -200 mV versus Ag/AgCl. Titanium grid will be used as the collector in the air cathode as it will not corrode in acid environments.

3. Experimental

3.1 Electrode Construction

The procedure for fabrication of the electrode is a modified version of that given by Read (3). We made a wet proofing layer by combining Super P carbon black, distilled water, 2-propanol, and PTFE-30 in a Kitchenaid mixer. The wet paste was allowed to dry overnight and the resulting material was chopped using a Waring blender. The powdered “wet-proofing” layer was 26% PTFE and 74% Super P by weight. The “active” layer was prepared in a similar fashion but with only 16 wt% PTFE and 84% carbon. The carbons used for the “active” layer were Acetylene Black (AB50), Black Pearls 2000 (BP2000), and Platinized Vulcan containing 10 wt% Pt (Pt Vulcan). An “active” layer made from a 1:1 mixture of AB50 and BP2000 was also prepared (AB50/BP2000).

To make the double-layered electrodes, 3.0 grams of the “wet proofing” layer was pressed onto Titanium grids having a 74 cm² area. The electrode was hot-pressed at 9000 psig and 400 °F for 15 minutes. Then, 1.3 g of the dry “active” layer was applied to one side of the electrode. This was cold pressed at 2000 psig for 10 minutes, and then hot pressed at 560 °F and 8000 psig for 15 minutes.

3.2 Three Electrode Steady State Measurements

Three electrode cells were constructed from glass T-cells. A cathode disk was cut from the layered electrodes and sealed to a threaded PTFE holder with an O-ring and PTFE disk with a hole in the center for air access as shown in figure 1. The cathode area with access to air was 0.712 cm². Titanium metal grid was used as a counter electrode, and a Ag/AgCl electrode was used as a reference. The Ag/AgCl reference electrode was placed in a separate vessel with electrolyte and connected to the T-cell using a 1/16” piece of plastic tubing functioning as a salt bridge. The reference electrode was separated from the T-cell to prevent chloride ions from interfering in the oxygen reduction reaction (6). For measurements from pH 0 to pH 8, mixtures of 1M H₂SO₄ and 1M Na₂SO₄ were used.

Electrochemical measurements were carried out using a Solartron SI 1287 electrochemical interface running Corrware software. The cathode was “wet-up” before measuring performance by running a potentiodynamic sweep from open circuit to -700 mV versus Ag/AgCl. Once wet-up was complete, potentiostatic measurements were carried out at voltages ranging from 0 V to -600 mV versus Ag/AgCl until a steady state current was reached.

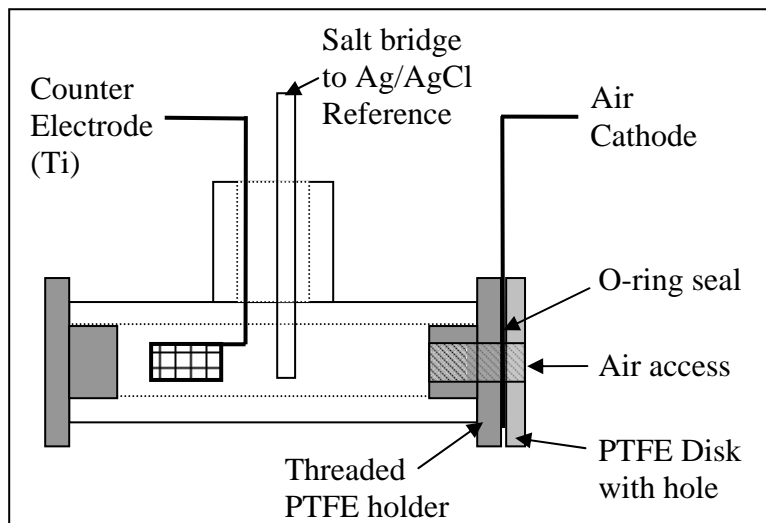


Figure 1. Glass T-cell for 3 electrode measurements on air cathodes.

4. Results

The results of the steady state current measurements on 3 cathode formulations are given in table 1. These measurements were carried out in 1M H₂SO₄ with a pH of 0. Table 2 gives the results of steady state current measurements on the AB50/BP2000 cathode formulation at pH values from 0 to 8.

Table 1. Current density (mA/cm²) versus voltage of various air cathodes in 1M H₂SO₄.

Voltage versus Ag/AgCl	AB50	Pt/Vulcan	AB50/BP2000
0 mV	0.22	5.76	5.70
-100 mV	0.41	12.94	10.80
-200 mV	0.73	24.30	17.20
-300 mV	1.80	33.71	24.70
-400 mV	5.84	43.68	33.40
-500 mV	12.37	54.49	43.30
-600 mV	20.08	64.89	53.50

Table 2. Current density (mA/cm^2) versus voltage and pH for AB50/BP2000 cathode.

Voltage versus Ag/AgCl	0.0	0.8	pH 1.2	2.2	3.7	8.0
0 mV	5.70	2.70	1.70	1.37	0.47	0.01
-100 mV	10.80	5.25	3.85	3.09	0.93	0.44
-200 mV	17.21	8.38	6.11	4.92	1.69	1.50
-300 mV	24.72	12.15	8.58	6.85	2.96	3.29
-400 mV	33.43	16.57	11.26	8.86	4.62	5.44
-500 mV	43.26	21.49	14.02	10.53	6.46	7.77
-600 mV	53.51	26.97	16.99	12.68	8.36	10.18

Figure 2 shows the data from table 1 in graphical form comparing the performance of the three cathode formulations as a function of polarization versus the Ag/AgCl reference potential. The best performing cathode was the Pt Vulcan, especially at high overpotentials. The AB50/BP2000 cathode is comparable to the Pt Vulcan at low overpotentials and at current densities of $< 10 \text{ mA}/\text{cm}^2$. The AB50 cathode did not perform well enough to be considered for use in this application. Given that it is desirable to use an un-catalyzed cathode, the AB50/BP2000 looks like a good choice. The AB50/BP2000 cathode was easy to fabricate and had good durability. Cathodes fabricated from BP2000 alone performed similarly to the AB50/BP2000 cathode but were difficult to fabricate and lacked durability.

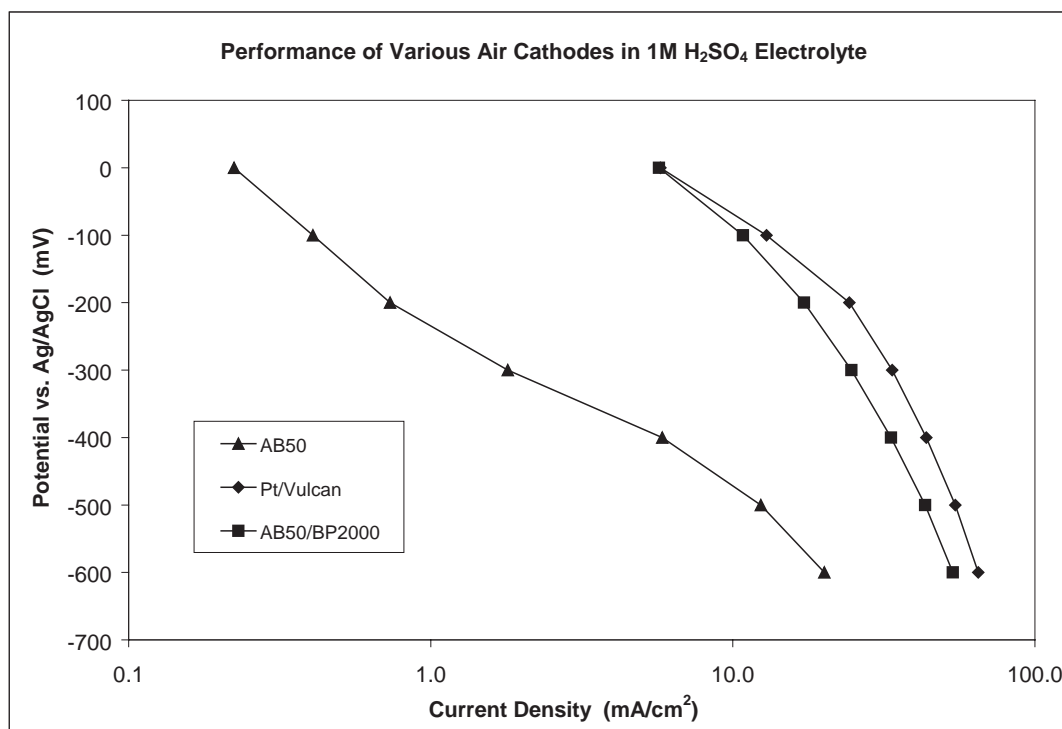


Figure 2. Voltage (mV) versus current density (mA/cm^2) for air cathode formulations in 1M H₂SO₄.

Figures 3 and 4 show the data from table 2 in graph form. Figure 3 gives the steady state current density for the AB50/BP2000 cathode as a function of polarization versus the Ag/AgCl reference potential for the different pH values. Figure 4 shows the same data plotted as current density versus pH at the various cathode polarizations. Figure 4 shows some interesting trends as the pH changes. The current density for a particular polarization voltage is highest in the most acidic electrolyte and generally declines as the electrolyte becomes more neutral. The data shows a plateau in the current density between pH 1 and 2 which corresponds to the $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$ equilibrium. This equilibrium provides protons that facilitate the oxygen reduction reaction (equation 5). Beyond pH 2.2 the current density continues to decline to pH 3.7. For the higher overpotentials (≥ 300 mV) the current density again rises as the pH increases to 8.0. For the lower overpotentials (≤ 200 mV), the current density does not rise as the pH increases. The rise in current density, although slight, may indicate a change in reaction mechanism from equation 5 to equation 4 at the higher overpotentials.

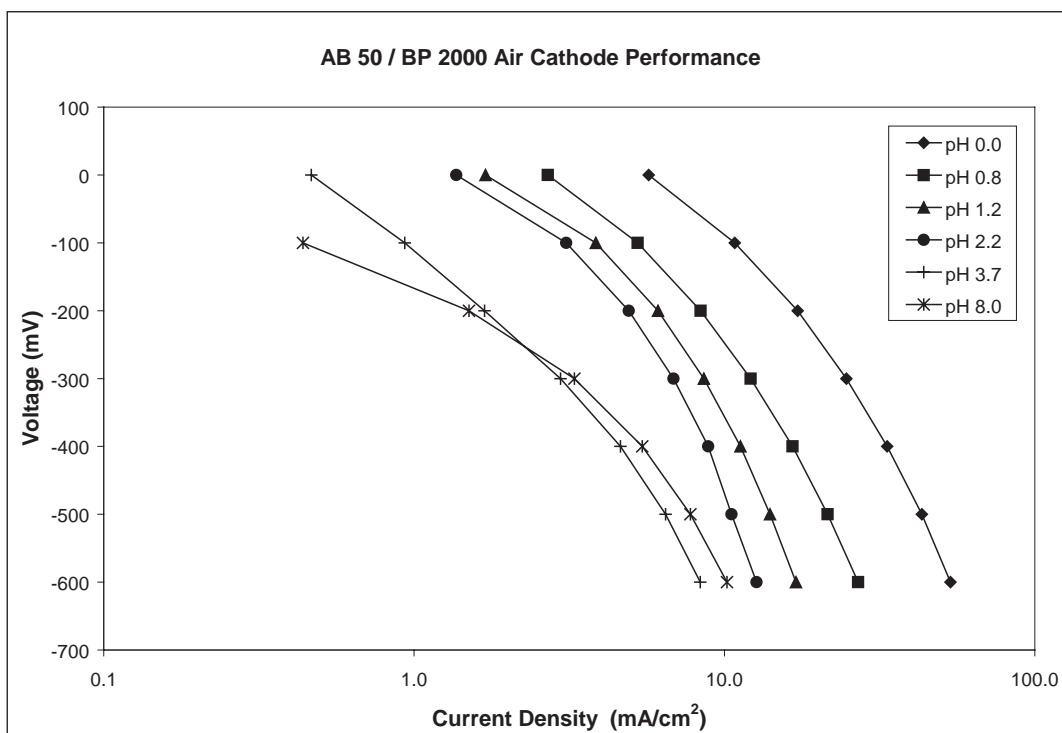


Figure 3. Voltage (mV) versus current density (mA/cm²) for AB50/BP2000 air cathode at pH values of 0 to 8.

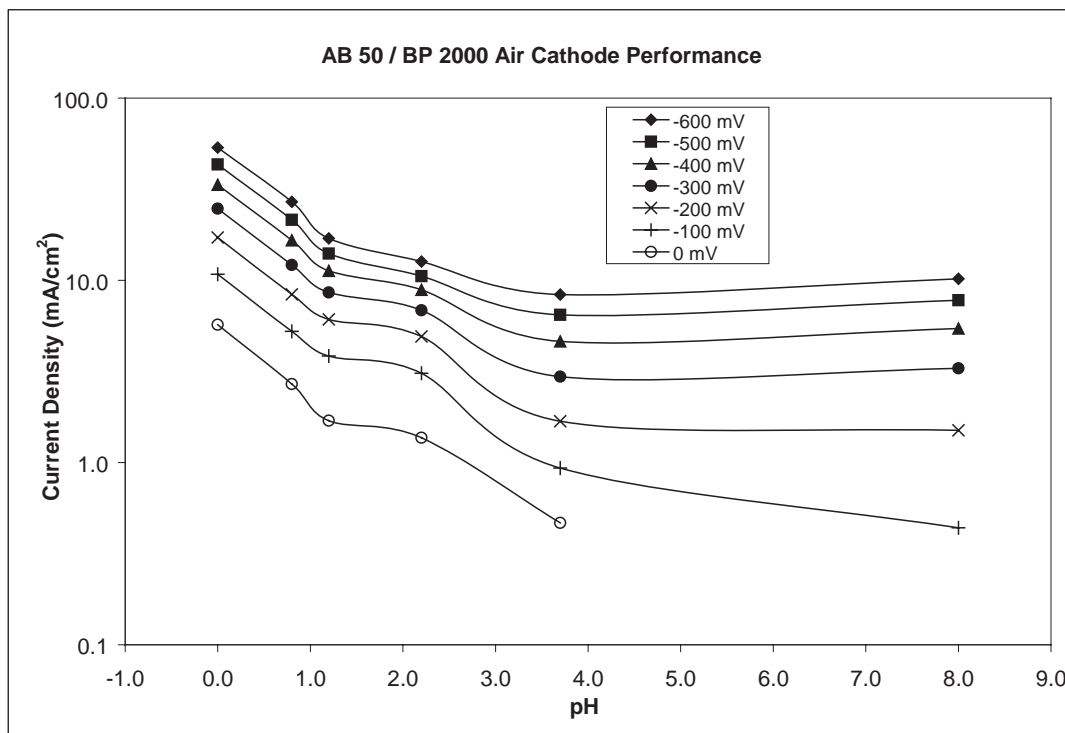


Figure 4. Current density (mA/cm^2) versus pH for AB50/BP2000 air cathode at polarization voltages of 0 to -600 mV.

The AB50/BP2000 cathode meets all of our requirements for performance. It has no expensive catalyst, it performs at the required current density at a polarization of -200 mV versus Ag/AgCl over the pH range of 0 to 8, and it is robust and easy to prepare.

5. Conclusions

The AB50/BP2000 air cathode provides current densities in the range of 1 to 20 mA/cm^2 with an applied voltage of -200 mV versus Ag/AgCl. The more acidic the electrolyte is, the higher the resulting current density. These current densities are adequate for use in lithium-air primary cells and allow the use of a catalyst free air cathode.

Future research is needed to answer a number of questions. In the above experiment, the area of the cathode remained constant. Larger cathodes should be tested to determine if current density values continue to follow the established trends. Additional acidic electrolytes, such as those based on nitric and perchloric acid, should be tested. Although sulfuric acid based electrolytes performed well, Schmidt (6) describes adsorbed bisulfate ions as adversely affecting the oxygen reduction reaction.

Furthermore, in a prototype cell, the proximity of lithium metal to an acidic electrolyte is a serious safety concern. While lithium metal will form a layer of corrosion products that slow reaction when exposed to strongly alkaline aqueous solutions (7), the reaction between lithium metal and acid is violent. The lithium ion conductor separating the aqueous electrolyte from the lithium metal must be robust and some additional interlayer material between the membrane and the aqueous electrolyte will be needed to slow reaction in the case of membrane leakage.

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