



**Performance of Carbon/Polytetrafluoroethylene (PTFE)
Air Cathodes from pH 0 to 14 for Li-Air Batteries**

by Michelle B. Marx and Jeffrey A. Read

ARL-TR-4334

December 2007

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ARL-TR-4334

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) December 2007		2. REPORT TYPE Summary		3. DATES COVERED (From - To) 05/28/2007 – 09/1/2007	
4. TITLE AND SUBTITLE Performance of Carbon/Polytetrafluoroethylene (PTFE) Air Cathodes from pH 0 to 14 for Li-Air Batteries				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Michelle B. Marx and Jeffrey A. Read				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-SE-DC 2800 Powder Mill Road Adelphi, MD 20783-1197				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-4334	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The performance of an uncatalyzed air cathode for use in a Li-Air battery was evaluated over the pH range from 0 to 14. This study was undertaken to determine if air cathodes constructed solely from carbon black and polytetrafluoroethylene (PTFE) can function at a sufficient rate in sulfate based electrolytes to be useful in Li-Air batteries. Layered cathodes were constructed with a hydrophobic wet-proofing layer and an active hydrophilic layer that utilizes a high surface area carbon black. Electrolytes were formulated using H ₂ SO ₄ , Na ₂ SO ₄ , and NaOH in various combinations giving pH values ranging from 0 to 14. Electrolytes were also formulated using H ₂ SO ₄ , Li ₂ SO ₄ , and LiOH in combination, and HCl, LiCl, and LiOH in combination giving electrolytes with pH values ranging from 0 to 14. The cathodes were discharged in a three electrode cell from 0.0 V to -0.6 V vs. a Ag/AgCl reference electrode. The cathode performed well and met the requirement that a current density of at least 1-2 mA/cm ² was maintained at -0.3 V vs. Ag/AgCl.					
15. SUBJECT TERMS Air Cathodes, Acid, Alkaline, Battery					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON Jeffrey Read
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) (301) 394-0313

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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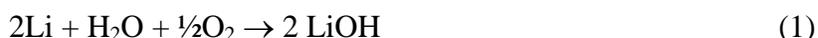
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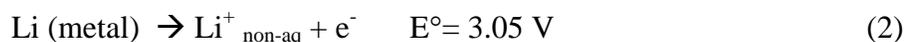
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1. Introduction

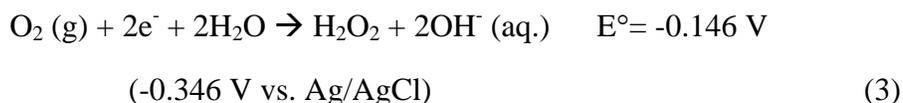
Li-Air batteries are proposed for use in applications where a high specific energy primary power source is needed and rate capability is not a limiting factor. The overall discharge reaction of a lithium-air battery is shown in equation 1.



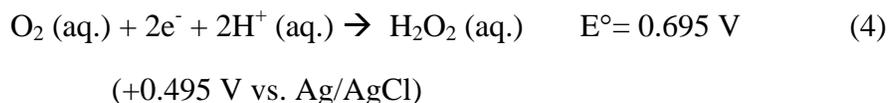
In a Li-Air battery, electrons flow between a lithium anode in contact with a non-aqueous electrolyte, and an air cathode in contact with an aqueous electrolyte. The non-aqueous and aqueous electrolytes are kept separate by a non-electronically conducting ceramic membrane impervious to water, but with 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. The half-cell reaction at the lithium anode is:



On gold, mercury, graphite, and most carbons, the 2 electron reaction resulting in the formation of peroxide ion is the predominant pathway (1). It has been demonstrated that in both basic and acidic electrolytes, carbon black based air cathodes can be used as peroxide generators (2). In basic electrolyte, the 2 electron reaction occurs as:



In acidic electrolyte, the 2 electron reaction proceeds as:



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 2) to the air cathode (equations 3 and 4) provides the 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.

One critical component of the Li-Air battery is an air cathode that can reduce oxygen at a sufficient rate; function for a number of days without flooding; operate in both strongly acidic

and strongly basic electrolytes; and not be cost prohibitive to throw away. Previous studies have shown that carbon/polytetrafluoroethylene (PTFE) cathodes, with an active layer composed of Acetylene Black 50 (AB-50) and Black Pearls 2000 (BP-2000), have performed well in acid electrolytes. The objective of this study was to determine if a similarly constructed cathode could perform over the entire pH range where a Li-Air battery might operate. Air cathodes are constructed such that the outer layer of the cathode is hydrophobic and permeable to oxygen, which prevents bulk electrolyte from leaking out of the cell. The inner layer is hydrophilic and “active” towards oxygen reduction (3, 4). A functioning cathode is defined as being able to support a current density of 1–2 mA/cm² at a potential of -0.3 V vs. a Ag/AgCl reference electrode.

The purpose of this project was to construct an inexpensive air cathode free of catalyst that is capable of functioning in both acidic and basic 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. Experiment

2.1 Construction of an Air Electrode

The carbon/PTFE double-layered electrode was constructed using a procedure similar to that used by Read and Margulies (3, 4). A hydrophobic air cathode paste was made using Super P carbon black, PTFE-30, distilled water, and isopropanol, which were combined and mixed for 5 min in a Kitchenaid mixer at setting two. The paste was then dried before being ground into a fine powder using a 2-liter laboratory blender. The hydrophobic layer composition was 70% Super P and 30% PTFE by weight. The active layer paste was made using BP-2000, AB-50, PTFE-30, distilled water, and isopropanol, which were combined and mixed for 5 min in a Kitchenaid mixer at setting two. The paste was then dried under vacuum and ground to a fine powder using the laboratory blender. The active layer composition was 42% BP-2000, 42% AB-50, and 16% PTFE by weight; 3.0 g of the hydrophobic powder was spread evenly

onto 7 by 10 cm titanium expanded metal grids. It was cold pressed for 5 min at 2000 psig and then hot pressed for 15 min at 400°F and 9000 pound-force per square inch gauge (psig). On top of the hydrophobic layer, 1.5 g of the active layer powder was cold pressed for 10 min at 2000 psig and then hot pressed for 15 min at 560°F and 8000 psig.

2.2 Setup for Three Electrode Cell

The experiments were carried out in a glass T-cell, which functioned as a three electrode cell. carbon/PTFE cathodes, cut from the double-layered electrodes, were used with titanium mesh acting as the counter electrode and a Ag/AgCl reference electrode. The Ag/AgCl electrode was placed into a beaker containing the same electrolyte as in the T-cell. The T-cell and the beaker were connected by a 1/16 inch plastic tube acting as a salt bridge. The Ag/AgCl with 4M KCl reference electrode used has a standard potential of +0.20 V vs. standard hydrogen electrode (SHE). The cathode was attached to the cell by a threaded PTFE holder with an O-ring and a PTFE disk with a hole in the center. The active, or hydrophilic, layer was positioned toward the electrolyte allowing for oxygen reduction to occur. The cathode area with air access was 0.712 cm². The set-up for the three electrode cell can be seen in figure 1.

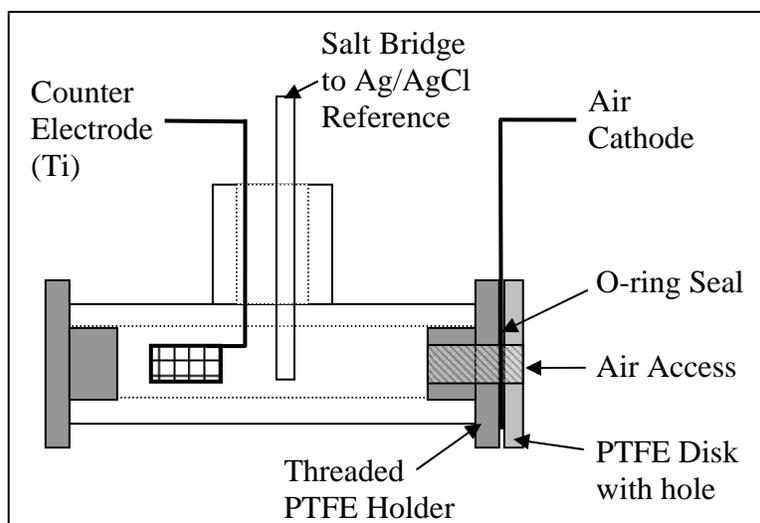


Figure 1. Set-up for three electrode cell.

2.3 Measurements

Solutions of H₂SO₄, Na₂SO₄, and NaOH were used to prepare sulfate electrolytes from pH 0-14. Sulfate electrolytes were also prepared from H₂SO₄, Li₂SO₄, and LiOH while chloride electrolytes were prepared from HCl, LiCl, and LiOH. Measurements were carried out using a Solartron SI 1287 electrochemical interface and Corrware software. A potentiodynamic sweep from open circuit to -0.6 V vs. Ag/AgCl was run to “wet-up” the cathode. Measurements were obtained for voltages ranging from 0.0 to -0.6 V vs. Ag/AgCl until a steady state current was reached. This was typically reached within 15 min.

3. Results and Discussion

The air cathode current response as a function of pH in Na₂SO₄, Li₂SO₄, and LiCl electrolytes is given in tables 1, 2, and 3. The same data is shown graphically in figures 2, 3, and 4.

Table 1. Voltage vs. current density (mA/cm²) for pH values 0-14 in Na₂SO₄ based electrolytes.

Voltage vs. Ag/AgCl	pH										
	0	0.7	1.5	2.5	3.8	4.1	8.3	11.9	12.7	13.4	13.7
0	3.8	1.7	0.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.1
-0.1	7.2	3.3	1.9	0.7	0.5	0.5	0.5	0.5	0.4	0.2	0.1
-0.2	11.5	5.5	3.4	1.7	1.4	1.4	1.4	1.4	1.3	1.1	1.1
-0.3	16.4	7.8	5.0	3.1	2.7	2.8	2.9	2.6	2.5	2.7	3.3
-0.4	21.6	10.4	6.2	5.0	4.1	4.3	4.7	3.9	3.8	4.6	5.8
-0.5	27.1	12.9	7.8	7.0	6.1	6.1	6.8	5.4	5.2	6.6	8.4
-0.6	32.6	15.6	9.8	9.0	7.7	7.8	8.8	6.9	6.7	8.7	11.2

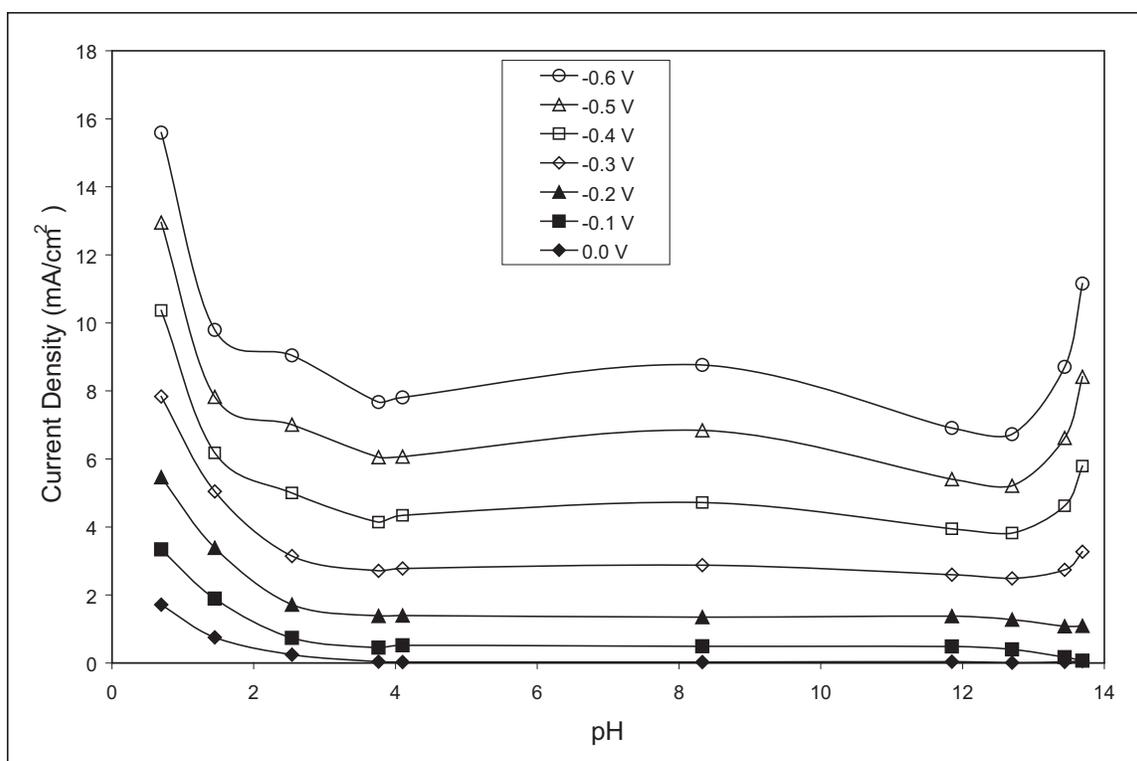


Figure 2. Current density (mA/cm²) vs. pH in Na₂SO₄ based electrolytes.

Table 2. Voltage vs. current density (mA/cm²) for pH values 0-14 in Li₂SO₄ based electrolytes.

Voltage vs. Ag/AgCl	pH										
	0.0	0.2	0.9	1.6	2.3	5.3	8.4	10.2	10.7	11.6	12.6
0	3.8	2.2	1.1	0.5	0.2	0.0	0.0	0.0	0.1	0.0	0.0
-0.1	7.2	4.0	2.3	0.9	0.6	0.5	0.4	0.5	0.5	0.4	0.1
-0.2	11.5	6.3	3.9	1.8	1.4	1.4	1.1	1.2	1.1	1.0	0.9
-0.3	16.4	9.0	5.7	2.7	2.5	2.7	1.9	2.0	1.9	1.8	2.6
-0.4	21.6	11.9	7.6	4.1	3.8	4.1	2.8	3.0	2.8	2.7	4.6
-0.5	27.1	14.9	9.6	5.6	5.2	5.7	3.8	4.1	3.8	3.6	6.7
-0.6	32.6	18.0	11.6	7.2	6.6	7.2	4.8	5.2	4.8	4.6	8.8

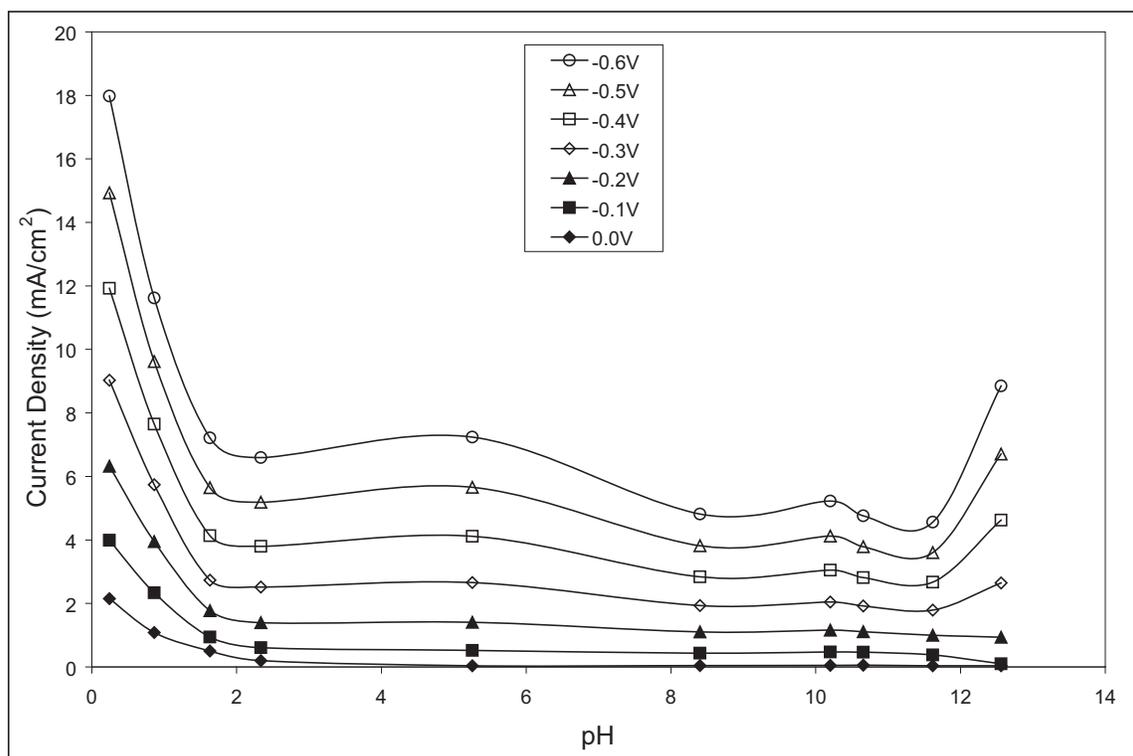


Figure 3. Current density (mA/cm²) vs. pH in Li₂SO₄ based electrolytes.

Table 3. Voltage vs. current density (mA/cm^2) for pH values 0-14 in LiCl based electrolytes.

Voltage vs. Ag/AgCl	pH							
	0.9	1.5	2.4	4.7	7.2	11.4	11.8	12.7
0	0.6	0.1	0.1	0.3	0.0	0.0	0.0	0.1
-0.1	1.3	0.6	0.6	0.7	0.3	0.3	0.4	0.1
-0.2	2.2	1.4	1.4	1.6	0.9	0.9	1.0	1.0
-0.3	3.2	2.4	2.5	2.5	1.6	1.6	1.7	3.0
-0.4	4.2	3.7	3.7	3.6	2.3	2.4	2.5	5.3
-0.5	5.1	5.0	5.0	4.8	3.2	3.2	3.4	7.7
-0.6	6.3	6.3	6.3	6.0	4.0	4.0	4.3	10.2

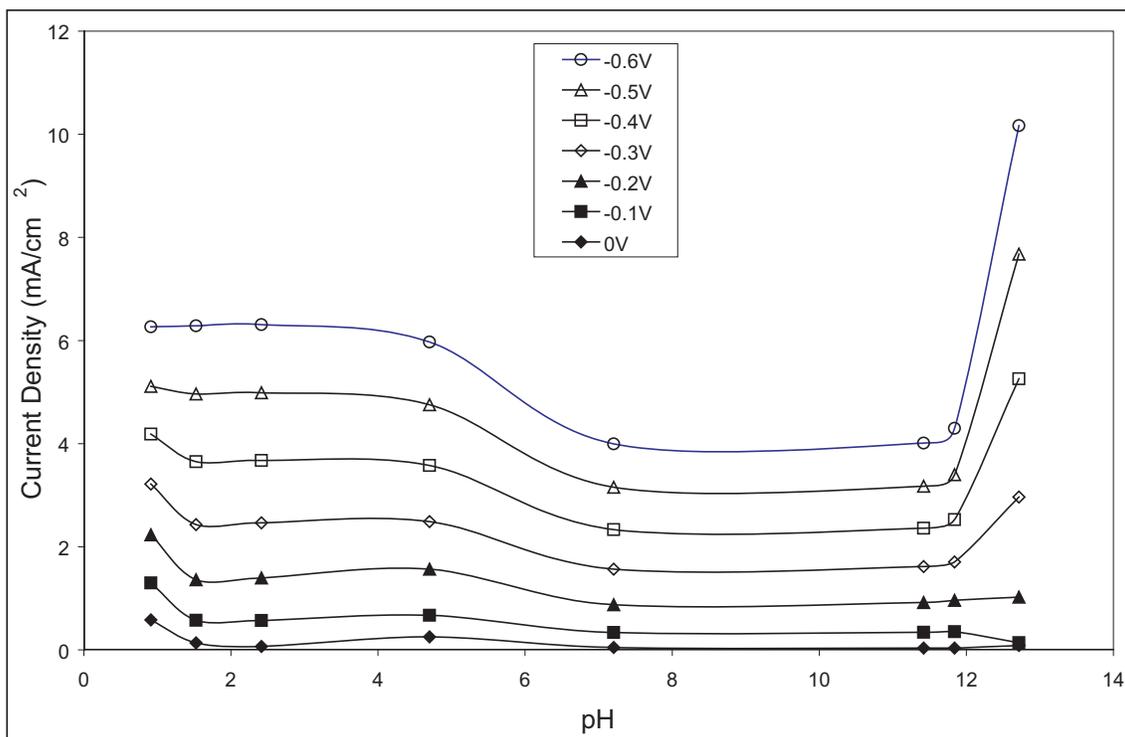


Figure 4. Current density (mA/cm^2) vs. pH in LiCl based electrolytes.

The performance of this air electrode follows the typical behavior for this type of electrode with the current density increasing as the voltage is decreased from 0.0 V to -0.6 V vs. the Ag/AgCl reference electrode. The performance of the cathode is sufficient to meet our criteria of 1-2 mA/cm² at -0.3 V vs. Ag/AgCl even in the LiCl based electrolyte. The increase in current density with electrode polarization results from an increase in the over potential for the electrochemical reaction (equation 3 or 4 depending on pH). As the difference between the electrode potential and the thermodynamic potential increases, the driving force, and therefore the current density, increases.

We will not attempt a complete explanation of the change in air electrode performance as the pH increases from 0 to 14, but simply identify several factors that are of importance. The first effect is the change in thermodynamic potential for the electrochemical reaction with increasing pH. The thermodynamic potential decreases from 0.49 V vs. Ag/AgCl for pH = 0 to -0.21 V vs. Ag/AgCl for pH = 12. The over potential at pH = 0 when the cathode is polarized to -0.30 V vs. the Ag/AgCl electrode is therefore -0.79 V (-0.30 V - 0.49 V) while the over potential at pH = 12 is much less at -0.09 V (-0.30 V + 0.21 V). This change in over potential should contribute to a decrease in current density with increasing pH. The second effect relates to the concentration of protons in the electrolyte. At low pH values when the concentration of protons is large, the reaction shown in equation 4 proceeds rapidly. As the pH increases, the reaction shown in equation 3 appears to take over and the concentration of protons is not a factor with the current density becoming nearly independent of pH above pH = 3.

The rise in current density for pH values greater than 12 is thought to arise from a change in mechanism (5-14), although there is some disagreement on the mechanism. Most of the proposed mechanisms involve the one electron reduction of oxygen to form the superoxide ion and the participation of the hydroperoxyl radical. Each of the three electrolytes studied demonstrate this small rise in current density at pH values greater than pH = 12.

The air cathode performance in LiCl electrolytes demonstrates the strong effect that chloride ion absorption has on oxygen reduction even at low pH. The chloride ion absorbs to the catalytic sites where O₂ would normally absorb and prevents the electrochemical reaction. This poisoning effect of chloride ion demonstrates that O₂ adsorption onto a catalytic site is important to the functioning of a normal air electrode.

4. Summary and Conclusions

Carbon/PTFE cathodes with an active layer, composed of AB-50, BP-2000, and PTFE, can be used for Li-Air batteries. The definition of a functioning cathode was satisfied for current densities at -0.3 V vs. the Ag/AgCl reference electrode. Similar results were obtained for both the Na₂SO₄ and Li₂SO₄ based electrolytes. For the most part, the LiCl based electrolyte followed the trends of the sulfate based electrolytes, except for the suppressed current density at low pH values.

References

1. Kinoshita, K., *Electrochemical Oxygen Technology*; John Wiley and Sons: New York, 1992.
2. Alcaide, F.; Brillas, E.; and Cabot, P. L. Oxygen Reduction on Uncatalyzed Carbon-PTFE Gas Diffusion Cathode in Alkaline Medium. *J. Electrochem Soc.* **2002**, *149*, E64-E70.
3. Margulies, B. and Read, J. Carbon/PTFE Electrode for Lithium/Air-Water Batteries; ARL-TR-4066; U.S. Army Research Laboratory: Adelphi, MD, March 2007.
4. Read, J. A. Recharge Catalyst with Thin Film Low Corrosion Coating Metal Air Electrode Including said Catalyst and Methods for Marking said Catalyst and Electrode. U.S. Patent 6,127,060, 1998.
5. Yeager, E.; Krouse, P.; Rao, K. V. *Electrochim. Acta.* **1964**, *9*, 1057.
6. Morcos, I.; Yager, E. *Electrochim. Acta.* **1970**, *15*, 953.
7. Taylor, R. J.; Humffray, A. A. *J. Electroanal. Chem.* **1975**, *64*, 63.
8. Appel, M.; Appleby, A. *J. Electrochim. Acta.* **1977**, *23*, 1243.
9. Appleby, J.; Marie, J. *J. Electrochim. Acta.* **1978**, *24*, 195.
10. Kukushkina, G. V.; Shteinberg, M. R.; Tarasevich, Bagotskii, V. S. *Sov. Electrochem.* (Engl. Transl.) **1981**, *17*, 193.
11. Yeager, E. *Electrochim. Acta.* **1984**, *29*, 1527.
12. Zhang, Z. W.; Tryk, D. A., Yeager, E. The Electrochemistry of Carbon; Saragapan, S.; Akridge, J. R.; Schumm B. Editors, PV 84-5, p. 158, *The Electrochemical Society Proceedings Series*, Pennington, NJ (1984).
13. Xu, J.; Huang, W.; McCreery, R. L. *J. Electroanal. Chem.* **1996**, *410*, 235.
14. Yang, H.-H.; McCreery, R. L. *J. Electrochem. Soc.* **2000**, *147*, 3420.

Acronyms

AB-50	Acetylene Black 50
aq.	aqueous
BP-2000	Black Pearls 2000
min	minute
psig	pound-force per square inch gauge
PTFE	polytetrafluoroethylene
SHE	standard hydrogen electrode
V	volt

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