The Role of PTFE in Cathode Transition Layer in Aqueous Electrolyte Li-Air Battery

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Abstract

To optimize the performance of aqueous lithium-air battery (LAB), a series of experiments were conducted on the structure and composition of the air-breathing cathode. Using a thin 100 μ m carbon paper as the backing of cathode yielded good battery discharge performance. However, this thin carbon paper does little to prevent an aqueous catholyte from evaporating. A thin transition carbon nanofiber (CNF) layer bonded with PTFE (Teflon) was introduced into the cathode to alleviate water evaporation, while keeping oxygen diffusion through the cathode. Since oxygen diffusion is a limiting factor when the battery discharges at high current densities, the influence of PTFE content in the transition CNF layer was investigated, together with electrode thickness. An optimal value of 30 wt.% PTFE in CNF was found to be the best to balance water evaporation and battery discharge performance. It is shown that a PTFE bonded CNF transition layer can significantly enhance cathode performance for air-breathing aqueous LABs.

Key words: Air-breathing cathode, Aqueous catholyte, Li-air batteries, PTFE content, Backing carbon papers.

Introduction

Li-air batteries (LABs) have gained much attention for their potential as a source of energy, which is comparable to gasoline in their high theoretical energy densities [1-5]. Typically, two types of catholytes, namely, non-aqueous (aprotic) and aqueous, are employed in such LABs. Compared to aprotic catholytes, aqueous catholytes provide several advantages, such as high solubility of discharged products, high ionic conductivities, and low catholyte flammability [6]. During the operation of an aqueous LAB, electrons flow through the external circuitry between a lithium anode and an air-breathing cathode (e.g., carbon) in contact with aqueous catholyte. To balance the overall charge in the cell, positive lithium ions flow internally through a lithium-ion-conducting glassy ceramic (LiCGC) membrane separating the anode compartment and the cathode compartment.

We have previously reported discharge/charge performance of such hybrid Li-air batteries (HyLABs) with both acidic and alkaline solutions as aqueous catholytes [4,7]. A multifunctional cathode is needed to meet some basic requirements for such batteries [8-12]. First, an air cathode must be as permeable to oxygen from ambient air as possible, since oxygen transport is a limiting factor at high discharging rates. Second, the evaporation/diffusion of water vapor should be minimized in order to retain the catholyte to wet the gas-solid interface. Finally, the cathode is expected to have a high surface area to provide sufficient active reaction sites or supported catalysts for oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs). To

accommodate these requirements, a thin, sheet-like air cathode is desired, having one side exposed to the ambient air and the other to an aqueous electrolyte [4].

As either an ORR or an OER requires a three-phase reaction zone in rechargeable metal-air batteries, consisting of oxygen, the electrolyte and a supported catalyst, the catalyst layer must be wetted in order for oxygen reduction to occur. Sufficient wetting of this layer is important to both ORR and OER. However, if too much wetting happens, the cathode can be flooded, which causes the cell polarized and the cell overpotential increases sharply. More seriously, the catholyte could easily evaporate from a wetted-through cathode, leading to loss of water. Consequently, the contacting area between the cathode and the electrolyte is reduced, resulting in a decreasing battery performance. Gradual loss of water in catholyte could also increase the lithium ion concentration leading to precipitation of the lithium salts during discharge. All these conditions will negatively affect the battery performance, especially for continuous operation of a battery.

Because water molecules are smaller than oxygen molecules, it is impossible for O_2 to be more permeable than water through porous structures. Also since oxygen diffusion is highly dependent on the porous properties of air-breathing cathodes, evaporation and the escape of water molecules from the catholyte pouch to the ambient air would be inevitable. Therefore, the clear choice for an air breathing cathode is to reduce water from evaporating without sacrificing oxygen diffusion. The other side of the air cathode facing ambient air has to be hydrophobic, enough to keep water staying inside these batteries.

In order to counteract or at least partially diminish those negative factors, the catalytic layer in the cathode has to be partially hydrophilic. Polytetrafluoroethylene (PTFE or Teflon) has been widely used for water management in polymer electrolyte membrane fuel cells to avoid flooding because of its excellent hydrophobicity and chemical inertness [13,14]. Thus, PTFE would be a good choice to achieve a stable operation of these porous air-breathing cathodes and prevent water evaporation. For this purpose, herein we report our study on incorporating PTFE in a transition layer made from carbon nanofibers (CNFs) in the air-breathing cathode. Results include Li-air battery discharge performances and water evaporation control in acid catholytes.

Experimental

Toray papers (Fuelcellstore.com) with thickness of 100 μ m (TGP-030), 190 μ m (TGP-060), 280 μ m (TGP-090), and 370 μ m (TGP-120) were used to investigate water evaporation from 1.0 M sulfuric acid. The methods of air cathode preparation, LAB assembly and cell test were reported previously [4]. The CNFs (Pyrograf III) are *ca.* 100 μ m long and *ca.* 100 nm in diameters. During the preparation of the transition layers, different amounts of PTFE (Dupont, Zonyl® MP1200) were added into the CNF dispersion of ethanol. The whole dispersion was sonicated thoroughly before vacuum filtration was performed to make the transition layer. The catalyst layer was made similarly with carbon nanotubes (CNTs) with 5% Pt catalyst. A 5 wt.% PTFE was also added to the catalyst layer. The transition and catalyst layers were laminated onto the Toray papers and hot pressed (temperature and pressure were 140°C and 2 atm) [4].

The prepared cathodes with different PTFE contents were characterized by scanning electron microscopy (SEM, Hitachi S4700). They were used to investigate electrolyte evaporation and LAB cell discharge in 1.0 M sulfuric acid solutions. The tests of water evaporation through the cathodes with PTFE were performed in an ambient environment. A cathode was attached using epoxy glue onto the rim of a glass vial containing 10mm-deep 1.0 M sulfuric acid. The glass vial was put upside down and the electrolyte sits on top of the cathode. In this way, the electrolyte is always in contact with the cathode. No liquid leaking was observed during the testing period of four days.

In order to investigate the influence of PTFE on battery discharge performance, we used the same protected anode, fresh catholyte with the same composition, and same test method. Current and cell voltage were recorded when the battery discharge performance was stabilized. The test followed to the previous reported method [4]. All cathode and catalysts were freshly made before testing.

Results and Discussion

Figure 1 shows SEM images of the air cathode used in this work. In Figure 1(A), a cross-section view of the cathode is shown, in which the three layers are clearly seen. The transition layer is made of CNFs, which forms a porous structure, as can be seen in Figure 1(B). Since the fibers are quite hydrophilic after surface treatment, those channels in the porous structure were also hydrophilic and water can creep through it due to the capillary effect. In order

to make them fully hydrophobic, PTFE particles are mixed with CNFs in the process of making this layer. By making this layer hydrophobic, aqueous electrolyte can no longer leak out. However, capillary evaporation of water was still observed, as will be discussed below.

Figure 1(C) exhibits the SEM images of a carbon paper supported CNF transition layer with 30 wt.% PTFE and its surface morphology. This backing carbon paper is not the limiting factor for air-diffusion. Addition of PTFE in the transition layer of CNFs (*ca.* 30 μm in thickness) makes the cathode backing less porous, shown in Figure 1(B) and keeps more water in the battery. However, it becomes a factor of limiting air diffusion under this circumstance. The 30 μm CNF transition layer possesses both hydrophobic and hydrophilic channels after being blended with PTFE, shown in Figure 1(D). Due to the non-uniform PTFE particles ranging from sub-microns to a few microns, these PTFE particles could either attach on the surface of CNFs or mix with CNFs. Apparently, these surface-attached PTFE particles also play a binder role during the air cathode preparation process, binding together the CNFs, Pt/CNTs catalyst, and the backing carbon paper [4]. This is deemed necessary for long-term stable operation of a LAB.

By varying the thickness of the carbon paper, it was reported that porosity, tortuosity, and thickness of porous media decide the through-plane fluid diffusion rate [15-18]. Toray-030 (100 microns thick, 80% in porosity) and Toray-060 (190 microns, 76%) have a little higher porosity than Toray-090 (290 microns) and Toray-120 (370 microns, 72%) [17]. The tortuosity of the latter two are much larger and more complex than the first two [15]. We have found that a thinner and more permeable paper yields better battery discharging performance, which is

something expected, as shown in Figure 2. Thus, air diffusion through Toray-030 yields the least gas transport resistance amongst all and correspondingly, its battery discharge performance is the highest at relatively high current densities.

According to the Fick's law,

$$J_{O_2} = -D \frac{dC_{O_2}}{dy} \quad (1)$$

where J_{O_2} is oxygen molar flux, D oxygen diffusion coefficient, C_{O_2} oxygen concentration in bulk, y cathode diffusion thickness. The flux is related to the reaction current,

$$J_{O_2} = \frac{i}{nF} \quad (2)$$

where i is current density, and n the number of electrons, and F the Faraday constant. Within the backing layer and transition layer, there is only diffusion, and therefore mass transfer is only controlled by diffusion (Eq. 1), which determines the oxygen concentration at the interface of the catalyst layer and the transition layer. The increase of thickness of gas diffusion layer would result in the increase of mean free path for diffusion, leading to the higher gas diffusion resistance in the backing layer.

In the catalyst layer, where both equations apply, a linear portion on the polarization curve in the middle is a result of Ohmic loss. However, for different thicknesses of the backing paper, we see that the curves decrease in cell voltage as the backing paper thickness is increased. As the backing paper thickness is increased, the oxygen concentration at the interface of the catalyst layer

and the inert transition layer is decreased, leading to a decrease in current density based on the Butler-Volmer equation. To keep the current density constant, the overvoltage must be increased, or cell voltage decreased. This is what observed from Figure 2 that the slopes change in the linear portions of the polarization curves since the oxygen concentration at the interface is diffusion limited by the thickness of the backing layer.

Water evaporation through these paper cathodes was conducted by attaching a cathode to the mouth of a glass vial and measuring the water level in the vial, as shown in Figure 3(A). Four different thicknesses of the carbon papers were tested, with results shown in Figure 3 (B).

Although all the carbon papers have 5 wt.% PTFE in them as received (they are hydrophobic with water contact angle at 100-110°), the water evaporation rates are different due to different thicknesses of these papers. The 100 μ m-thick carbon paper had about 25% loss of electrolyte in every 4 days, and this loss is reduced to 20%, 13.5%, and 13.1% for papers having thicknesses of 190 μ m, 280 μ m and 370 μ m, respectively. The explanation of air diffusion is also applicable to the water evaporation through the carbon papers. When the carbon paper thickness increases, the tortuosity of carbon paper also greatly increases. Therefore, the water evaporation rate was reduced significantly. The standard deviation also decreased along with the increase of carbon paper thickness, indicating that the water evaporation is more consistent for thicker carbon papers. The water evaporation rates in these carbon papers are too high for them to be practical in air battery applications. Obviously, it is necessary to add a CNF transition layer to reduce water evaporation.

The results from Figure 3 show, that the 100 μm backing carbon paper has much larger channels and higher porosity, indicative of its inability to retain water in the catholyte, although it demonstrates the best battery discharge performance, as shown previously. In order to balance the oxygen transport resistance and depress the water evaporation through the cathode, we added a CNF transition layer onto the carbon paper, made partially hydrophobic with the addition of PTFE. Figure 4 presents the relationship of PTFE contents in the CNF layer vs. the water evaporation rate with the same experimental method for testing. It was found that the average rate of water evaporation from the cathode was reduced from 25% to 16.7% with 15 wt.% PTFE in the CNF layer. The standard deviation of the evaporation rate had the same relationship as the average rate vs. PTFE percentage, showing that the evaporation was more stabilized. The water evaporation rate is roughly linear to the content of PTFE. When the PTFE has 50% of the weight, the evaporation rate was reduced to 5.6%. The general trend is that PTFE creates hydrophobic channels and reduces the porosity of the layer, all are beneficial to reducing water evaporation.

Figure 5 shows that more PTFE does not always yield good battery performance. The PTFE content has an optimal value when battery performance is taken into account, which might be more important. As shown in Figure 5, the cathode with 30 wt.% PTFE has the highest battery power density and cell potential, especially when the current densities are higher than 4 mA/cm^2 . The optimized PTFE content is a result of balancing of several factors. When less PTFE exists in the transition layer, fewer three phase sites exist at the interface of CNF transition layer and the CNT catalyst layer. As most of the interface is in the catholyte and diffusion of oxygen in

aqueous solutions is slow, limited three phase sites are clearly not beneficial to the improvement of battery discharge performance. On the other hand, too much PTFE in the CNF layer will reduce porosity and increase tortuosity of the transition layer, limiting air diffusion [15]. It was estimated that the layer porosity will be reduced by 5 – 8% when the PTFE content increases from 10 wt.% to 50 wt.%. Thus, a 30 wt.% PTFE may be optimal in making the CNF transition layer to achieve the best performance of the Li-air battery air.

Conclusions

In summary, the CNF transition layer plays an essential role in regulating the flow of water evaporation from the catholyte in aqueous catholyte Li-air batteries. The effects of PTFE content in the CNF layer on water retention and LAB discharge performance were studied. The results showed that the addition of PTFE can effectively mitigate water evaporation through the battery cathode into the ambient environment. It was found that a higher PTFE content in the LAB cathode can be more effective in preventing water evaporation from the catholyte due to the hydrophobicity of the PTFE. However, there is a limit. An optimal PTFE is found at 30 wt.% that can provide a compromise between water management and oxygen diffusion to achieve the best cell performance.

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References

- [1] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, Li-O₂ and Li-S batteries with high energy storage, *Nature Materials*, 11 (2012) 19-29.
- [2] J. Christensen, P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, A Critical Review of Li/Air Batteries, *Journal of The Electrochemical Society*, 159 (2012) R1-R30.
- [3] L. Li, X. Zhao, A. Manthiram, A dual-electrolyte rechargeable Li-air battery with phosphate buffer catholyte, *Electrochemistry Communications*, 14 (2012) 78-81.
- [4] Y. Li, K. Huang, Y. Xing, A hybrid Li-air battery with buckypaper air cathode and sulfuric acid electrolyte, *Electrochimica Acta*, 81 (2012) 20-24.
- [5] Z. Peng, S.A. Freunberger, Y. Chen, P.G. Bruce, A Reversible and Higher-Rate Li-O₂ Battery, *Science*, 337 (2012) 563-566.
- [6] K. Huang, Y. Li, Y. Xing, Increasing round trip efficiency of hybrid Li-air battery with bifunctional catalysts, *Electrochimica Acta*, 103 (2013) 44-49.
- [7] Y. Li, Z. Huang, K. Huang, D. Carnahan, Y. Xing, Hybrid Li-air battery cathodes with sparse carbon nanotube arrays directly grown on carbon fiber papers, *Energy & Environmental Science*, 6 (2013) 3339-3345.
- [8] S. Müller, F. Holzer, H. Arai, O. Haas, A study of carbon-catalyst interaction in bifunctional air electrodes for zinc-air batteries, *Journal of New Materials for Electrochemical Systems*, 2 (1999) 227-232.
- [9] Y. Takeshita, S. Fujimoto, M. Sudoh, Design of Rechargeable Air Diffusion Cathode for Metal-Air Battery Using Alkaline Solution, *ECS Transactions*, 50 (2013) 3-12.
- [10] N. Imanishi, A.C. Luntz, P.G. Bruce, Editors, *The Lithium Air Battery: Fundamentals*, Springer, New York, 2014.
- [11] W. Hago, I.M. Lorkovic, Cathode for metal-air rechargeable battery, patent, US8557449 B2, 2013.
- [12] V. Neburchilov, H. Wang, J.J. Martin, W. Qu, A review on air cathodes for zinc-air fuel cells, *Journal of Power Sources*, 195 (2010) 1271-1291.
- [13] C. Lim, C.Y. Wang, Effects of hydrophobic polymer content in GDL on power performance of a PEM fuel cell, *Electrochimica Acta*, 49 (2004) 4149-4156.
- [14] G.-G. Park, Y.-J. Sohn, T.-H. Yang, Y.-G. Yoon, W.-Y. Lee, C.-S. Kim, Effect of PTFE contents in the gas diffusion media on the performance of PEMFC, *Journal of Power Sources*, 131 (2004) 182-187.
- [15] J.Z. Fishman, Investigation of Surface Properties and Heterogeneity in Gas Diffusion Layers for Polymer Electrolyte Membrane Fuel Cells, Master's thesis, Department of Mechanical and Industrial Engineering, University of Toronto, 2010.
- [16] T.V. Nguyen, G. Lin, H. Ohn, D. Hussey, D. Jacobson, M. Arif, Measurements of Two-Phase Flow Properties of the Porous Media Used in PEM Fuel Cells, *ECS Transactions*, 3 (2006) 415-423.

- [17] I.S. Hussaini, C.Y. Wang, Measurement of relative permeability of fuel cell diffusion media, *Journal of Power Sources*, 195 (2010) 3830-3840.
- [18] A. Tamayol, F. McGregor, M. Bahrani, Single phase through-plane permeability of carbon paper gas diffusion layers, *Journal of Power Sources*, 204 (2012) 94-99.

Figure captions

Figure 1. SEM images of air cathode with PTFE: (A) Overview of the air cathode, with 10 mg 5wt.% Pt/CNT; (B) overview of backing paper and CNF transition layer; (C) Surface morphology of CNF layer with 30 wt.% PTFE; (D) enlarged view of PTFE distribution in CNF layer.

Figure 2. Li-air battery discharge performance with cathodes prepared with backing carbon papers of different thicknesses but maintaining the same CNF transition layer. Catalyst loading is 5wt.% Pt/CNT.

Figure 3. Water evaporation tests on backing carbon papers. (A) A photo of the 4 carbon papers attached (glued) to glass vials. (B) Liquid level changes (in percentage) in the vials. Inset is a photo showing a vial with 10 mm acid solution, put upside down during the test. The test was over 4 days.

Figure 4. Water evaporation rates under different PTFE content (in weight fractions) in the CNF transition layer with the 100 μ m carbon backing paper, over a period of 4 days.

Figure 5. LAB discharge performances using air-breathing cathodes with different PTFE loading in the CNF transition layer with the 100 μ m carbon backing paper.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5