Hydration Tunable Air/Oxygen Cathodes for Li-Air Batteries

Fan Xu[1], Meixian Wang[1], and Jian Xie[1]*
[1]Department of Mechanical Engineering, Purdue School of Engineering and Technology, Indiana University-Purdue University, Indianapolis, IN 46202, USA

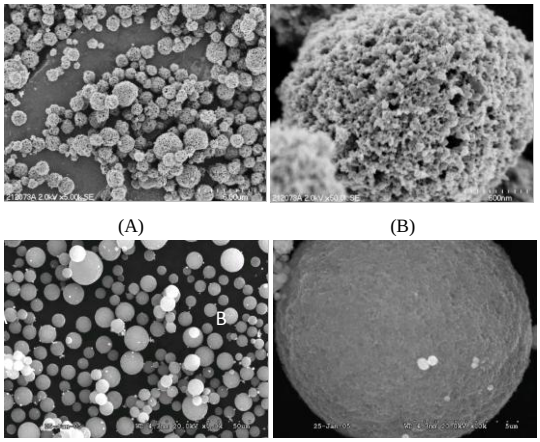
Lithium-air battery as the next generation battery, which uses the Li metal anode and oxygen cathode, has attracted more attention due to its highest specific energy (13.0 kWh/kg)[1] among all the known metal/air batteries. Li-air battery consists of lithium anodes, polymer electrolyte, and air cathode. Atmospheric oxygen is reduced at the air cathode. One of the major challenges is the control of the cathode water which will back diffuses from air cathode to the anode, particular sever at high current density. Another challenge is the humidification of the air cathode to maintain the oxygen reduction reaction at high potential (low current density).

We have taken an approach to effectively control the hydration in the air cathode using the surface functionalized carbon blacks. In this work, carbon blacks were functionalized for either higher hydrophilicity or hydrophobicity. Three different functional groups, hydrophilic group, *p*-aminobenzoic acid, *p*-COOH; phenyl sulfonic acid, *p*-SO_3H; and hydrophobic group, perfluorooctyaniline (PFOA), $C_{14}H_6F_{17}N$, group have been chemically attached to XC72 carbon black through the diazonium cation reaction[2]. Then, the catalysts were made using these functionalized carbon blacks for controlling the air cathode hydration. For air cathodes using both XC72- *p*-COOH and XC72- *p*-SO_3H, 1.26A/cm^2 @ 0.58 V (*vs.* SHE) and 0.731 w/cm^2 have been achieved for ambient air (30% RH) without humidification.

The structures of the catalyst using functionalized carbon black, XC72- *p*-COOH group (Pt/FXC72-*p*-COOH) and catalyst (Pt/XC72) are shown in Fig. 1(A) to (D). It can be clearly seen that after functionalization, spherical carbon aggregated particles become more porous. Compared to XC72 (0.5 – 2.56 µm), the particle size of the spherical carbon particles with a seemingly porous structure was only 0.2-1.14 µm.

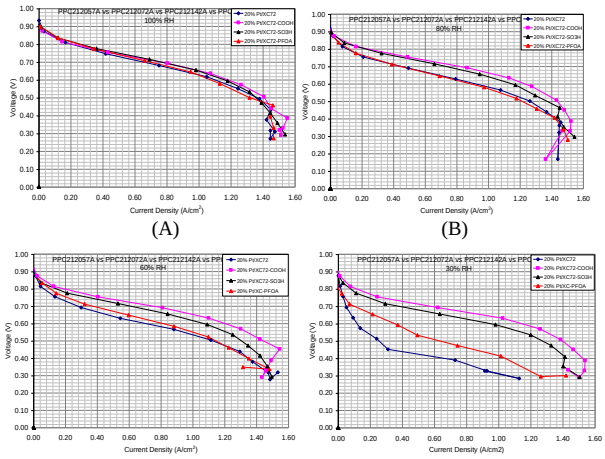
The performance of air cathode using different functional carbon black catalysts was measured using membrane electrode assembly (MEA) configuration for different relative humidity (RH) airs. The results were shown in Figure 2 (A) to (D). Under 100% RH, Pt/FXC72-*p*-COOH and Pt/FXC72- *p*-SO_3H had a little better performance than Pt/XC72 and Pt/XC72-PFOA. When the RH was decreased to 80%, Pt/XC72- *p*-COOH and Pt/FXC72-*p*-SO_3H had better performance due to higher hydrophilicity, which help to retain water. The same trend will remain for 60 and 30% RH.

From the above results, it can be concluded that functional carbon black catalyst can effectively control the hydration in catalyst layer. Appropriate combination of hydrophobic and hydrophilic carbon balcks can effectively control the hydration while allowing the use of ambient air for high performance.



(A) (B) (C) (D)

Fig.1 (A) and (B) SEM images of the Pt/FXC72-COOH; (C) and (D) SEM images of the Pt/XC72



(A) (B) (C) (D)

Fig.2 Performance of cathode catalyst with different functional groups at different RHs (anode 100%RH) (Pt/FXC72-COOH,Pt/FXC72-SO3H, Pt/FXC72-PFOA and Pt/XC72). Catalyst loading: C/A= 0.20/0.05 mg Pt/cm2, 20%/10 % Pt/XC72, membrane: N112, 28% Nafion (EW1100), Anode:100% RH, Temperature: 80/80/80 °C (cell/anode/cathode), Back pressure: 30 Psig, Flow rate: 520/2060 sccm (A/C). (A). 100% RH, (B). 80% RH, (C). 60% RH and (D). 30% RH.

References

[1] Arthur Dobley, Joseph DiCarlo and K. M. Abraham, Non-aqueous Lithium-Air Batteries with an Advanced Cathode Structure

[2] Downard, A. J.; Garrett, D. J.; Tan, E. S. Q., Microscale Patterning of Organic Films on Carbon Surfaces Using Electrochemistry and Soft Lithography†. Langmuir 2006, 22, (25), 10739-10746.

* Corresponding author, *E-mail:* jianxie@iupui.edu