U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Argonne NATIONAL LABORATORY

Develop New Non-aqueous Electrolytes for Rechargeable Li-Air Battery Application

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Background and Introduction

Li-air cells can be considered as the 'holy grail' of lithium batteries because they offer, in principle, a significantly superior theoretical energy density to conventional lithium-ion systems. This lithium-ion cell chemistry, the best to data, would provide a theoretical specific energy of ~900 Wh/kg if the calculation is based on the masses of the anode and cathode materials alone; in practice, 150-200 Wh/kg has been accomplished at the cell level. In contrast, a lithium-air cell, when discharged to the peroxide composition Li_2O_2 at an average 3.1 V would provide a theoretical specific energy of 3623 Wh/kg, or when discharged to Li_2O at the same voltage, 5240 Wh/kg.

Figure 1 The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline.

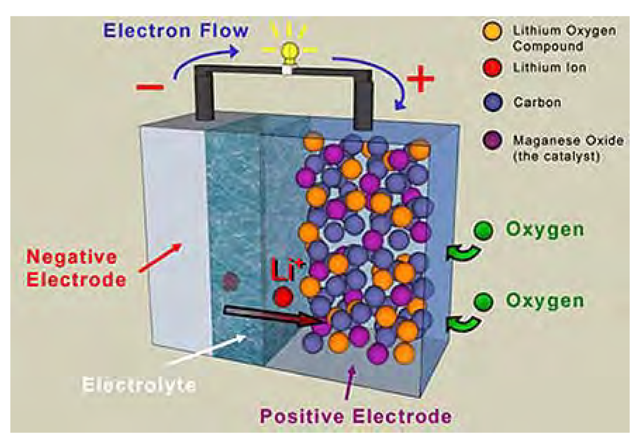


Figure 2 Li-air battery flow chart

Such larger theoretical energy density of Li-air battery is because the cell consists of lithium metal as an anode, and the cathode oxidant, oxygen, is stored externally since it can be readily obtained from the surrounding air. Figure 2 shows the schematic diagram of a typical lithium-air cell configuration, which consists of a porous carbon supported catalytic cathode designed to promote oxygen diffusion and reduction and a pure lithium metal anode. These two electrodes are separated by a lithium-ion conducting electrolyte. During discharge, lithium metal at the anode is oxidized to lithium ion and liberates electrons; while at cathode, oxygen is reduced in either a two-electron or four-electron process to form Li_2O_2 or Li_2O, respectively, both of which are thermodynamically possible.

There are still many challenges to be overcome, from finding suitable catalyst for cathode reactions (ORR and OER), to designing porous cathode structure for storing the oxygen reduction product, to optimizing the electrolyte composition and to elucidating the complex electrochemical reactions that occur during charge and discharge before it can be realized as high performance, commercially viable products. These scientific obstacles, which are closely related to the performance of the lithium-air batteries, open up an exciting window for researchers from many different backgrounds to utilize their unique knowledge and skills to bridge the knowledge gaps that exist in current research projects.

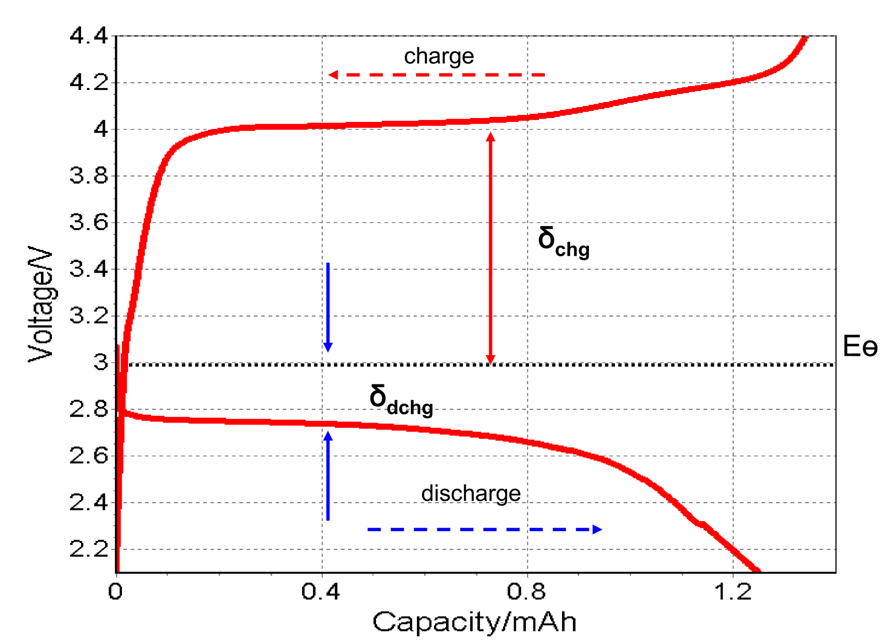
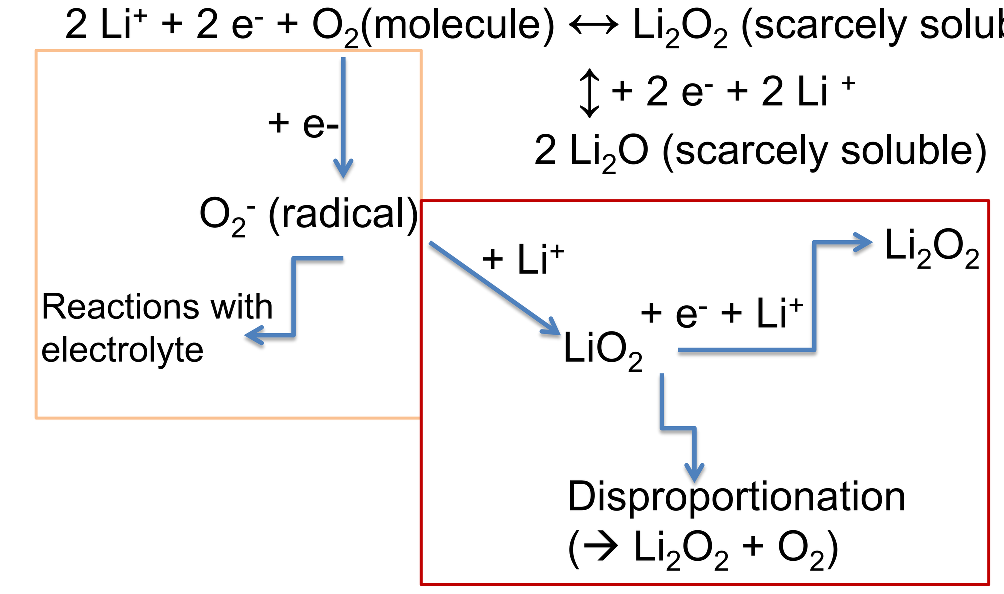


Figure 3 Typical voltage profile of Li-air battery using PC as electrolyte

Approach

Ideal reaction scheme (on the air cathode)

$2 Li^+ + 2 e^- + O_2$(molecule) ↔ Li_2O_2 (scarcely soluble)



- **Develop novel catalysts to facilitate cathode reactions**
- **Develop new electrolytes that can resist oxidation.**

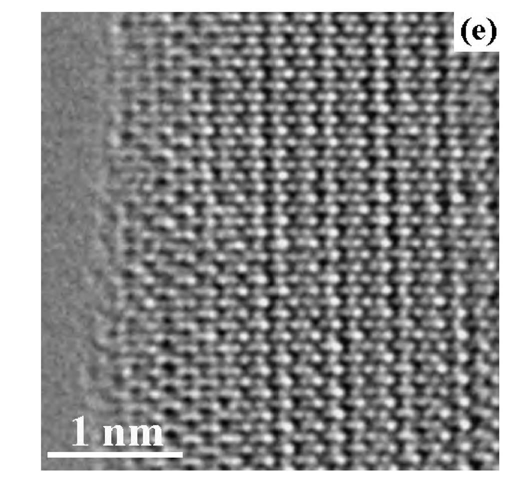


Figure 6 HRTEM image of MnO_2/C composite

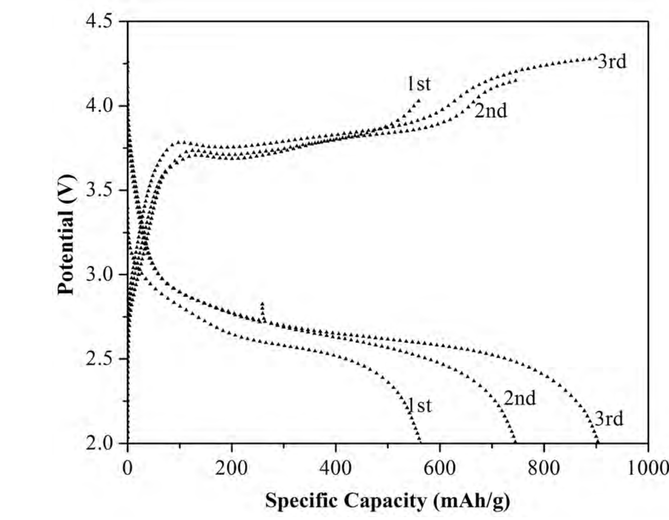


Figure 7 Voltage profile in 1M $LiPF_6$/PC

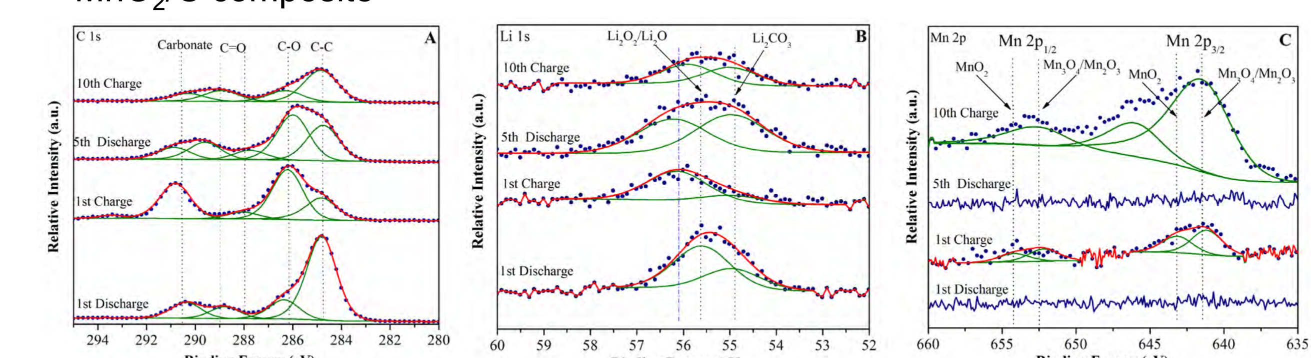


Figure 8 XPS spectra of C1s, Li 1s and Mn 2p core peaks of the cathode carbon electrodes at different charge/discharge status

Preliminary Results

I. In-situ Synthesis of Catalytic Air Cathode Materials

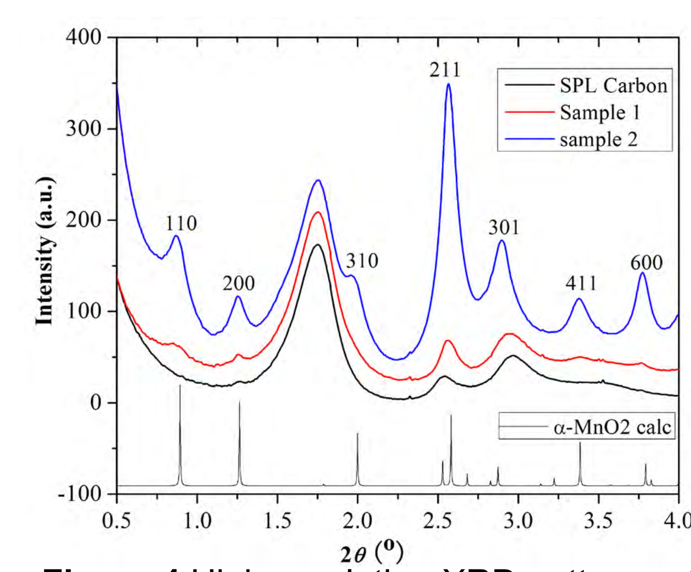


Figure 4 High-resolution XRD patterns of original SPL carbon and SPL carbon after being loaded with MnO_2 catalyst.

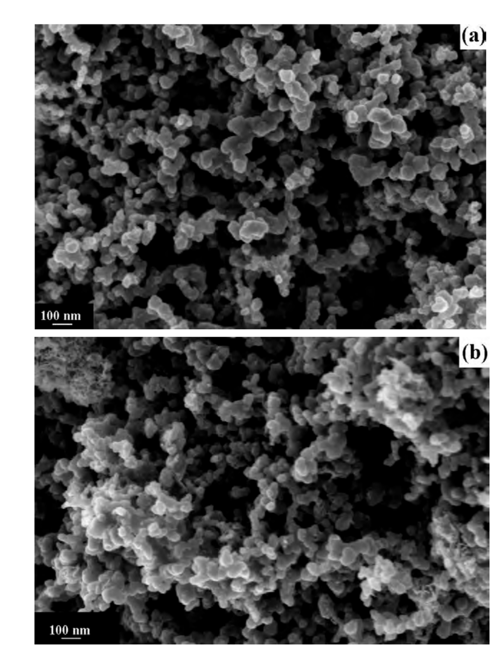


Figure 5. SEM images of (a) original carbon and (b) as-prepared MnO_2/C composite

II. Increase Stability Towards Oxygen Reduction Products with Oligoether-functionalized Silane Electrolytes

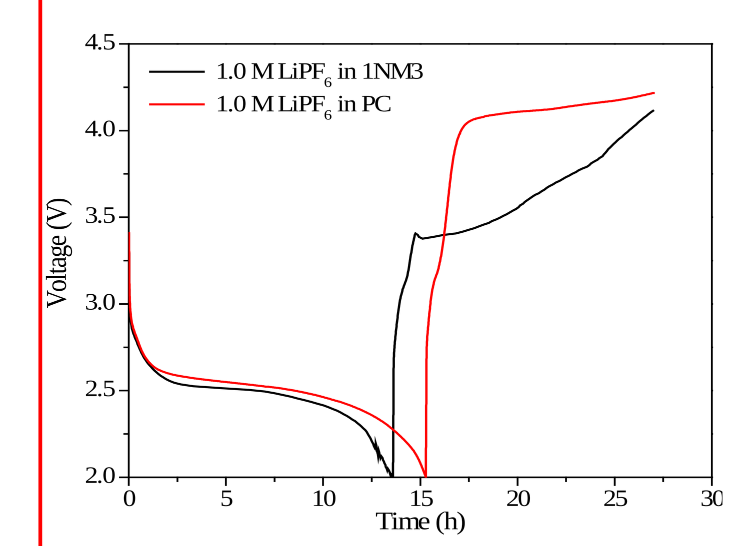


Figure 9 First charge and discharge cycles of a Li-air cell with propylene carbonate (PC) and 1NM3.

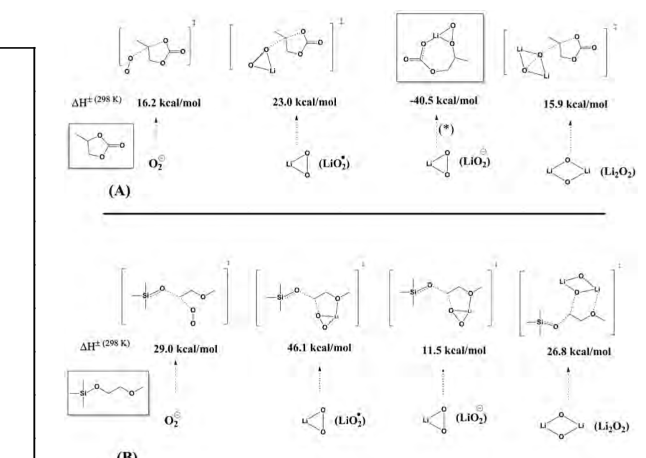


Figure 10 Comparison of the computed barriers (enthalpies) for activation of (A) PC decomposition and (B) 1NM1 decomposition by O_2 anion radical, Li_2O radical, Li_2O anion, and Li_2O_2.

Impact

- **Achieve highly reversible formation and decomposition of lithium oxide products at a very low charge overpotential.**
- **Understand the mechanism of the cell chemistry and identify the reaction products.**
- **Predict ways to discover novel catalysts to facilitate the oxygen reduction/evolution reactions and to develop new electrolytes to achieve good round trip efficiency and rechargeability in Li-air cells.**

Publications

- Jun Lu,et. al. "Increased Electrolyte Stability for Oxygen Reduction Products in Lithium Air Batteries" ***J. Phys. Chem. C*** 115(51), 25535 – 25542, 2011
- Jun Lu, et.al., "Uniformly Dispersed Fe/Fe_3O_4 Nanocomposites onto Porous Carbon: A Highly Active Electrocatalyst for Rechargeable Li-air Batteries" ***J. Am. Chem. Soc.***, Submitted.
- Jun Lu, et. al."In-situ Fabrication of Porous Carbon Supported α-MnO2 Nanoparticles: Application for Rechargeable Li-air Battery" ***Energy and Environ. Sci.***, Submitted.
- Jun Lu, et. al, "Synthesis of Porous Carbon Supported Pd/PdO Nanoparticles by Atomic Layer Deposition: Application for Rechargeable Li-air Battery" ***Adv. Funct. Mater.***, Submitted.

Acknowledgments

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Develop novel non-aqueous electrolytes, explore new approach to fabricate novel catalysts on carbon cathode and apply state-of-the-art characterization for Li-air batteries application