

Holistic View on Chemical Processes in Li-O₂ Battery Based on *Operando* Spatiotemporal Investigation

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Research on Li-O₂ battery has generated a great deal of interests due to the potential high energy storage capacity for future vehicular application.[1] Many studies have been reported on the understanding of catalysts, cathode structures and electrolytes to the battery performance and cycle span.[2] These investigations revealed that the actual redox mechanism in Li-O₂ battery could be significantly more complicated than originally thought. For example, the cell stability has become a significant issue when a non-aqueous electrolyte is used. [3] The actual reactions occurring at both electrodes of the Li-O₂ battery and their contributions to the overall cell durability are yet to be fully understood. Some fundamental questions on the structural and phase changes at different segments of the battery were raised and addressed only gradually by different characterization methods. In the cathode region, for example, whether the lithium peroxide is the sole redox intermediate during the discharge-charge cycle remains yet fully addressed. If Li₂O₂ is the key intermediate, how does its concentration or grain size distribute at different electrode depths? And how are they affected by oxygen and ion transports? Are there other lithium compounds formed or participated during the redox process? Another important area is the electrolyte stability in the presence of oxygen. Decomposition of electrolyte at cathode during cycling leads to the formation of insoluble lithium salts, which are attributed to the shortened battery lifespan. Does lithium salt precipitates impact only the cathode or throughout the battery? [4] Anode is another important region which has generated only limited discussion at the moment. Given the complexity of multiple electrochemical reactions inside of Li-O₂ cell, it is difficult to image that they will not affect the highly reactive lithium anode. If anode is affected, how does that impact to the rechargability of the battery?

At Argonne National Laboratory, we developed a holistic approach in studying electrochemical processes and mechanism of the lithium-oxygen battery. Various characterization techniques, such as SEM, TEM, FTIR, XRD, were used to analyze the structure, morphology and chemical species at the electrodes and separator regions of the operating battery. Particularly, we introduced the microfocused synchrotron X-ray diffraction (μ -XRD) and tomographic techniques for the spatiotemporal study on the phase and structural change in Li-O₂ battery. These tools offered some unique capabilities to characterize the battery properties under the actual discharge-charging condition. For example, the μ -XRD has a spatial resolution of less than 20 μ m and complete penetration of the battery from the radial direction, rendering it possible to probe battery's composition layer-by-layer under either *ex situ* or *in situ* conditions. The data collection at any given position usually takes only a few seconds, making the method particularly suitable to study the dynamic change in battery in real time.

In this presentation, we will discuss our recent result obtained from these *in situ* studies of the operating Li-O₂ batteries under the cycling condition. The cells we employed were fabricated based on the most representative design and materials in the current studies. We were able not only to reveal individually the changes at anode, cathode and separator, but also to assemble these data under the same discharge-charge time domain. Such information provides a holistic view of the chemical processes at different regions and their interdependence inside of a working battery.

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References:

- [1] a) G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193; b) F. T. Wagner, B. Lakshmanan, M. F. Mathias, *J. Phys. Chem. Lett.* **2010**, *1*, 2204
 [2] a) K. M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1; b) D. Shanmukaraj, S. Grugeon, G. Gachot, S. Laruelle, D. Mathiron, J. M. Tarascon, M. Armand, *J. Am. Chem. Soc.* **2010**, *132*, 3055; c) H. Cheng, K. Scott, *J. Power Sources* **2010**, *195*, 1370; d) J. Xiao, D. H. Wang, W. Xu, D. Y. Wang, R. E. Williford, J. Liu, J. G. Zhang, *J. Electrochem. Soc.* **2010**, *157*, A487; e) Y. C. Lu, Z. C. Xu, H. A. Gasteiger, S. Chen, K. Hamad-Schifferli, Y. Shao-Horn, *J. Am. Chem. Soc.* **2010**, *132*, 12170; f) T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390; g) A. Débart, A. J. Paterson, J. Bao, P. G. Bruce, *Angew. Chem. Int. Ed.* **2008**, *47*, 4521; h) B. D. McCloskey, D. S. Bethune, R. M. Shelby, G. Girishkumar, A. C. Luntz, *J. Phys. Chem. Lett.* **2011**, *2*, 1161;
 [3] a) F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoiishi, H. Iba, *Electrochemistry* **2010**, *78*, 403; b) W. Xu, V. V. Viswanathan, D. Y. Wang, S. A. Towne, J. Xiao, Z. M. Nie, D. H. Hu, J. G. Zhang, *J. Power Sources* **2011**, *196*, 3894; c) S. A. Freunberger, Y. H. Chen, Z. Q. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2011**, *133*, 8040; d) S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bardé, P. G. Bruce, *Angew. Chem. Int. Ed.* **2011**, *50*, 8609
 [4] Jiang-Lan Shui, John S. Okasinski, Dan Zhao, Jonathan D. Almer and Di-Jia Liu, *ChemSusChem*, **2012**, *5*, 2421 – 2426