

X-ray structural studies of Li-ion and Li-air battery materials

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Electrochemical energy storage devices will undoubtedly play an important role in future energy supply and demand. Currently, rechargeable lithium battery chemistries (e.g., lithium-ion, lithium-polymer, and lithium-air) are being touted as prime contenders to power a future generation of electric and hybrid-electric vehicles. However, much still needs to be done before these batteries meet the performance requirements for transportation applications. The performance of a rechargeable lithium battery is limited, to a large extent, by structural instabilities of the electrode components (both anode and cathode) during electrochemical cycling. Therefore, understanding the structural changes (stability) of the electrode materials during battery operation at the microscopic level is an important aspect of lithium battery research; such information is helpful for engineering new or improved electrode materials with superior performance. In this respect, various experimental techniques employing synchrotron x-rays, such as diffraction and absorption, particularly those that are conducted *in situ*, are well suited for unraveling the intricate details of active redox species, as well as the atomic and electronic structural changes that occur during electrochemical charge-discharge processes.

The experimental techniques that we employ in order to gain a fundamental understanding about atomic level structures include *in situ* X-ray Absorption Spectroscopic (XAS) and high-energy X-ray (60 to 120 keV) diffraction (XRD) measurements. The advantage of using high energy x-rays has opened up the possibility of going beyond traditional diffraction experiments and performing high resolution scattering experiments, such as Pair Distribution Function (PDF) analysis, which can yield valuable short-range structural information about complex materials. Complementing the high energy x-ray diffraction studies, we utilize XAS to obtain useful structural information, such as the average oxidation states of transition metal ions and the local atomic structure about the absorbing atom, which are used to interpret the electronic configuration of the absorber. XAS is an ideal method for the studies of electrochemical systems, due to the penetrating ability of hard x-rays, which allows *in-situ* characterization in a suitably designed cell or reactor. An important advantage is the element specific nature of the technique, which permits investigation of the local structure of a particular constituent element in a composite cathode/catalyst sample. These techniques are powerful and provide important information, for example, about 1) atomic level defects in catalytic materials and their role in controlling catalytic activity, and 2) changes in local structures (both crystallographic and electronic) around a particular element to help understand intermediate structures (or transition states) formed in an oxygen electrode during the operation of Li-air cells. Emphasis is placed on correlations that exist between the electrochemical activity and structure (electronic and crystallographic) of cathode/catalytic materials in rechargeable Li-ion and Li-air batteries. The objective is to use the information to tailor the composition and structure of electrode and electrocatalytic materials that will provide enhanced electrochemical properties.

In particular, this presentation will provide the results of 1) detailed quantitative analyses of XAS and XRD data of $\text{Li}[\text{Mn}_{0.5-x}\text{Cr}_{2x}\text{Ni}_{0.5-x}]\text{O}_2$ ($0 < 2x < 0.2$) Li-ion cathode materials¹⁻² at various states of charge/discharge, and 2) structural studies, using high energy-XRD and XAS, of lithia-rich cathode/catalysts³ for Li-air cells such as Li_2MnO_3 , $\text{Li}_2\text{MnO}_3\text{-LiFeO}_2$ and their acid treated analogues, before and after electrochemical activation.

References

1. N. K. Karan, D. P. Abraham, M. Balasubramanian, M. M. Furczon, R. Thomas and R. S. Katiyar, *J. Electrochem. Soc.*, **156**, A553 (2009).
2. N. K. Karan, M. Balasubramanian, D. P. Abraham, M. M. Furczon, D. K. Pradhan, J. J. Saavedra-Arias, R. Thomas, and R. S. Katiyar, *J. Power sources*, **187**, 586 (2009).
3. L. Trahey, C. S. Johnson, J. T. Vaughey, N. Karan, M. Balasubramanian, S.-H. Kang, M. M. Thackeray, poster presented at the "Energy Storage Beyond Lithium ion" symposium, Argonne National Laboratory, IL, May 3-4, 2010.