Understanding how Li-rich Cathode Materials Degrade Using X-ray Diffraction, Spectroscopy, and 3D Nano Imaging

Lithium-ion batteries are common in home and portable electronics due to their high energy density and slow self-discharge properties. The development of high capacity Li-ion materials is therefore vital for industry, in particular materials that have low voltage fade with repeated cycling. Typically, high storage capacity is accompanied by complex phase transitions, structural rearrangement and volume changes, which induce strain and morphological changes within the battery that affect the electrochemical behavior of the cathode material. A promising compound, $Li_2Ru_{0.5}Mn_{0.5}O_3$, is a lithium rich cathode material containing ruthenium (Ru) currently under study for battery production with high energy density and low voltage fade [1].

The current research employs a novel transmission x-ray microscope (TXM) to investigate the electrochemical reaction-induced morphological and chemical changes in the cathode particles at the meso-to-nano scale level. By combining x-ray spectroscopy, diffraction and microscopy measurements, cathode material evolution during repeated cycling is being studied to provide a comprehensive understanding of voltage fade at the structural level through 2D and 3D morphology reconstruction and heterogeneity change at fine scale lengths.

Collaborating with researchers from the Brookhaven National Laboratory, the Institute of Physics and the Donghua University in China, staff and students from SSRL are using the BL6-2C TXM facility to study *ex-situ* samples of $Li_2Ru_{0.5}Mn_{0.5}O_3$ at different stages of the battery lifetime from pristine up to 20 discharge cycles. The full-field TXM system is capable of 3D imaging at high resolution over a field of view up to 30x30 μm^2. The TXM tool is ideal for extracting spectroscopic information that can distinguish different morphological and chemical evolution processes between bulk and surface regions of the sample particles [2].

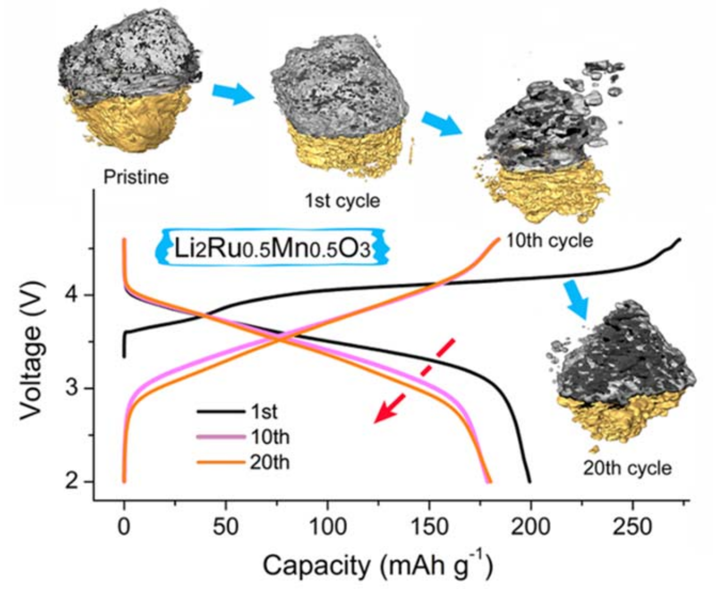

Figure 1. Room temperature charge-discharge curves for a $Li/Li_2Ru_{0.5}Mn_{0.5}O_3$ sample cycled between 2V and 4.6V at a current density of 22mA g^{-1}; 3D visualization of the different cycling stages (pristine, 1, 10, 20 cycles).

With computer enhancement of the data, researchers can visualize complex morphological changes during electrochemical cycling to determine predominant influences in the time-evolving reaction pathways. The research shows substantial structural rearrangements during the delithiation and lithiation process leading to the formation of micro-structural defects, thereby facilitating oxygen release and accelerating layered-to-spinel phase transitions.

An important aspect of the work is the detailed study of changes in the chemical composition and the degree of chemical heterogeneity within $Li_2Ru_{0.5}Mn_{0.5}O_3$ particles upon battery cycling. The x-ray optical density and the oxidation state of the electrode material were used in the processing of x-ray imaging data to evaluate the degree of heterogeneity. The observed phenomena suggest that electrochemical reactions and dissolution/precipitation processes occur at different rates at different locations within individual particles resulting in increased material complexity with cycling number.

The research suggests that atomic manipulation (e.g. doping substitution) and/or nano-fabrication techniques are important engineering strategies to mitigate internal material strain and defects induced by lithium insertion or extraction. The correlation between voltage fade and morphological changes at the nano-particle level provides valuable insight into the design of high storage capacity lithium-rich layered battery materials with improved cycle stability.

References

[1] D. Mori, H. Sakaebe, M. Shikano, H. Kojitani, K. Tatsumi and Y. J. Inaguma, *J. Power Sources* **196**, 6934 (2011).

[2] F. F. Yang, Y. J. Liu, S. K. Martha, Z. Y. Wu, J. C. Andrews, G. E. Ice, P. Pianetta, J. Nanda, *Nano Lett.* **14**, 4334 (2014).

Primary Citation

Y. Xu, E. Hu, F. Yang, J. Corbett, Z. Sun, Y. Lyu, X. Yu, Y. Liu, X.-Q. Yang and H. Li, "Structural Integrity—Searching the Key Factor to Suppress the Voltage Fade of Li-rich Layered Cathode Materials through 3D X-ray Imaging and Spectroscopy Techniques", *Nano Energy* **28**, 164 (2016), DOI: 10.1016/j.nanoen.2016.08.039.

Contacts

Yijin Liu, Stanford Synchrotron Radiation Lightsource

Xiqian Yu, Brookhaven National Laboratory / Institute of Physics, Chinese Academy of Sciences

Xiao-Qing Yang, Lawrence Berkeley National Laboratory

SSRL is primarily supported by the DOE Offices of Basic Energy Sciences and Biological and Environmental Research, with additional support from the National Institutes of Health, National Institute of General Medical Sciences.