

In-Situ chemical mapping of lithium-ion battery using full-field hard x-ray spectroscopic imaging

Jiajun Wang, Yu-chen Karen Chen-Wiegart, Jun Wang*

Brookhaven National Laboratory, 75 Brookhaven Avenue Building 725D, Upton, NY, USA.

In developing new electrode materials for lithium-ion batteries (LIBs), it is critical to understand the fundamental reactions occurring inside the electrode materials by observing the morphological/structural evolution during the operation of a battery. In order to better understand the lithiation-delithiation process and kinetic, serving for the exploration of the correlation between phase change/distribution and performance as well as the further optimization of material synthesis routes for advanced battery materials, it is still more desirable to obtain detailed chemical phase change and distribution information within an operating lithium-ion battery. Unfortunately, most of current in situ techniques cannot provide this chemical phase mapping information.

Synchrotron X-ray imaging technique is of increasing interest for applications in energy studies.^[1-4] Compared with conventional in situ techniques, synchrotron X-ray imaging is non-destructive, element sensitive, environmental friendly, and highly penetrating. An important and unique capability of this technique is that it can provide the chemical phase mapping information with sub-30 nm spatial resolution rather than only averaged information by conventional x-ray absorption near edge structure (XANES) spectroscopy. By collecting morphological information during cycling, and tuning x-ray energy at one cycling state across an absorption edge of an element of interest that generates a series of x-ray absorption spectra, transmission x-ray microscopy (TXM) enables the study of correlation between the morphology evolution and the chemical phase change (mapping) under in-situ conditions.

Here, we first demonstrated the capabilities of in-situ TXM-XANES technique on battery materials with nondestructive and quantitative characterization of the phase and chemical state as well as morphology evolution at nanometer resolution during cycling.^[5] CuO was selected as the study material, because it represents a typical conversion mechanism evolution. The obtained morphology evolution, chemical phase change, and detailed composition information from the statistical analysis with high spatial resolution at CuO anode material suggest a core-shell lithiation-delithiation mechanism.

The morphology evolution of CuO during the first two cycles was directly observed by our TXM with high resolution. The distributions of different chemical phases (CuO, Cu₂O, and Cu) within the sample under in situ electrochemistry conditions were analyzed by least-squares linear combination fitting. Fig. 1 shows the phase mappings, line profiles and composition of the active material during cycling. The fresh sample shows a major

CuO phase with a small amount of Cu₂O. The fresh sample shows a major CuO phase with a small amount of Cu₂O. After the first lithiation, the large sized CuO particle was reduced from the outer surface to the inner core, so the phase mapping shows a core (CuO)-shell (Cu) structure with an interface phase (Cu₂O). During the following rest and anodic scanning, the shell became thicker. The mapping shows the result of the combination process, including the lithium ion equilibrium, self-reaction during the rest period (the rising of open circuit potential), and the following delithiation to form Cu₂O (anodic scanning). A detailed phase composition was also obtained by the XANES analysis.

Our in-situ TXM-XANES phase analysis was first used to elucidate in situ the conversion reaction mechanism of a battery material. The information presented in this work will be a key for further modeling, simulation and design of new electrode materials. The methodology we reported in this work can be widely used in a variety of energy science.

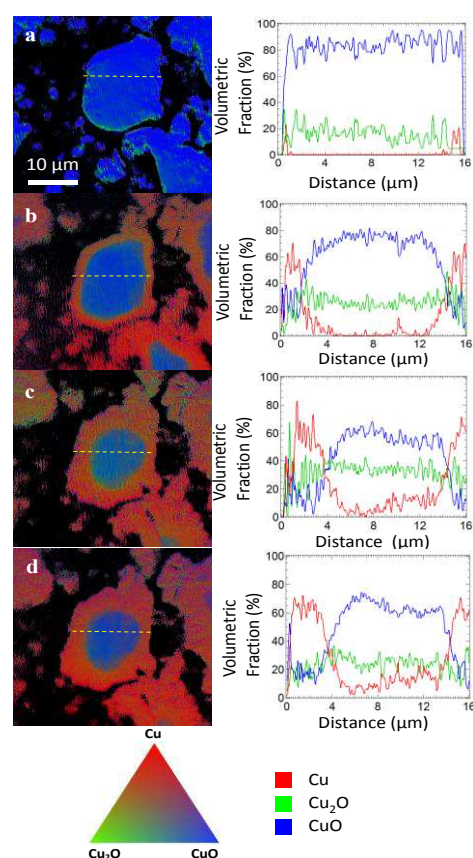


Fig. 1. (a) Chemical phase mappings of CuO during cycling. (b) Line profile of the corresponding particle during cycling.^[5]

Reference

1. Y. K. Chen-Wiegart, J. S. Cronin, Q. Yuan, K. J. Yakal-Kremski, S. A. Barnett, J. Wang, *J. Power Sources* 2012, 218, 348.
2. Y. K. Chen-Wiegart, Z. Liu, K. T. Faber, S. A. Barnett, J. Wang, *Electrochem. Commun.* 2013, 28, 127.
3. Y. K. Chen-Wiegart, W. M' Harris, J. J. Lombardo, W. K. S. Chiu, J. Wang, *Appl. Phys. Lett.* 2012, 101, 253901.
4. J. Wang, Y. K. Chen, Q. Yuan, A. Tkachuk, C. Erdonmez, B. Hornberger, M. Feser, *Appl. Phys. Lett.* 2012, 100, 143107.
5. J. J. Wang, Y. K. Chen-Wiegart, J. Wang, *Chem. Commun.* DOI: 10.1039/C3CC42667J