XAFS measurement of blended electrode materials in lithium-ion battery

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Introduction

Lithium-ion rechargeable battery has been utilized for mobile devices, vehicle application, and started for large scale energy storage of electric system recently. But, it need to rather improve the cycling performance for the system with renewable energies. Battery performance can be estimated by tracking a change of battery capacity, but the battery estimation is not enough to clarify the fading battery mechanism for the improvement in the battery. The battery capacity is directly proportional to lithium content migrated between positive and negative electrodes. The almost lithium is contained inside the positive electrode before charge-discharge test. Therefore, it is important to analyze the lithium content in the positive electrode for the battery mechanism. However, lithium is low scattering ability of X-ray for quantitative analysis of lithium content in the electrode. Chemical valence of $3d$ metal elements such as manganese or nickel change corresponding to lithium content in the electrode. Thus, X-ray absorption fine structure (XAFS) measurement is strong tool to estimate change in the valence in positive electrode during charge-discharge processes.

Electrode material mixtures have been frequently used in the positive electrode of the battery, for example, spinel oxide or layered oxide. Blended electrode has an issue of individual material estimation in the positive electrode of the fading battery. In this study, we estimate the individual materials in the fresh and the fading blended positive electrode in a model cell and a commercial battery by XAFS measurement.

Experimental methods

We use the modeled blended cathode (LN73) mixed a spinel oxide, $LiAl_{0.1}Mn_{1.9}O_4$ (LMO) and a layered oxide, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) using conductive materials and a binder together. The LN73 pouched cell and the 4 Ah-class commercial battery are tested by repeats of the charge-discharge processes at 45ºC and 50ºC.

In situ Ni, Co, and Mn K-edge XAFS spectra are obtained under various voltages during discharge process at BL16B2 of SPring-8 in Japan with transmission mode and fluorescence mode at room temperature for modeled cell and the battery. XAFS spectra of the highest and lowest voltages are used for reference data in the LN73 cell and the commercial battery of the XAFS analysis, which correspond to the highest and lowest chemical valences. Changes in the reference sample of each elements are obtained from the calculation optimized the ratio of the references in the blended electrodes by linear fitting analysis using Athena.

Results and discussion

Linear fitting is applied to the XAFS spectra of each elements at various voltages using spectra of highest and lowest voltages. The calculated spectra are coincident with the measured those. The tendency of reference ratio changes of Mn in the LMO and the NMC are coincident with their individual charge-discharge performances and their lattice parameters during charge-discharge processes. This analysis technique is also applied into the fading LN73 cell. The behaviors of the reference ratio are different from Mn and Ni, Co between the fresh and the fading LN73 cells. Also, A combination of XAFS, X-ray fluorescence analysis and X-ray diffraction

measurements indicates identification of a spinel oxide and a layered oxide in a blended positive electrode of the commercial battery and changes in the XAFS spectra of Ni and Mn at various voltages.

Conclusion

XAFS measurement and its linear fitting are applied into Ni, Co, and Mn K-edge XAFS spectra in blended positive electrodes the modeled cell and the commercial battery. Their approach can reveal the reference ratio change corresponded to the change in the chemical valences of the spinel oxide and the layered oxide during discharge process.