

Lab-Scale X-Ray Emission/Absorption Spectroscopy for Operando Measurement of Electronic Structure of Transition Metals in Battery Electrodes

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Abstract

Tracking the change in electronic structure of target elements is crucial to investigate the nature of redox reactions occurring in battery electrodes. X-ray emission spectroscopy (XES) and x-ray absorption fine structure (XAFS) perform this role well with high sensitivity and throughput, but the requisite of synchrotron facilities often limits those availability for material characterization.

Using a lab-scale x-ray emission/absorption spectrometer, we investigated the changes in the local structure and chemistry around the 3d transition metal elements of LiMO₂ cathodes for Li-ion batteries as a function of the battery state of charge (SoC). *Ex situ* measurement was prepared from the electrode samples with discrete difference in SoC. Coupled with *ex situ* measurement, *operando* measurement was performed using pouch cells with LiMO₂ cathode, which enabled a real-time monitoring of chemical shift in an element-specific manner resulted from changing electrode potential.

Through the XES mode of the bench-top spectrometer, fluorescence emissions from the LiMO₂ cathode, or the cell containing it, was monochromatized by a spherically bent crystal analyzer (SBCA). The K β emissions of 3d transition metal elements such as cobalt display position/shape difference of spectrum with varying SoC. The trend of chemical shift and change in spectral features provided the information on the electronic structure variation, such as oxidation state change of 3d transition metals in LiMO₂ during charge and discharge (i.e., delithiation and lithiation). Furthermore, valence-to-core (VtC) emission signals helped enable in-depth analysis such as spin structure characterization.

In addition to the XES analysis, we could measure K-edge XAFS for the same 3d transition metals in LiMO₂ as well. In the XAFS mode of the spectrometer, SBCA monochromatized bremsstrahlung x-ray generated from a high-power x-ray tube is used to make an incident source energy-dispersive. While

K β XES probed occupied levels, K-edge XAFS examined unoccupied levels providing comprehensive understanding on the change in electronic structure of 3d transition metals in LiMO₂.

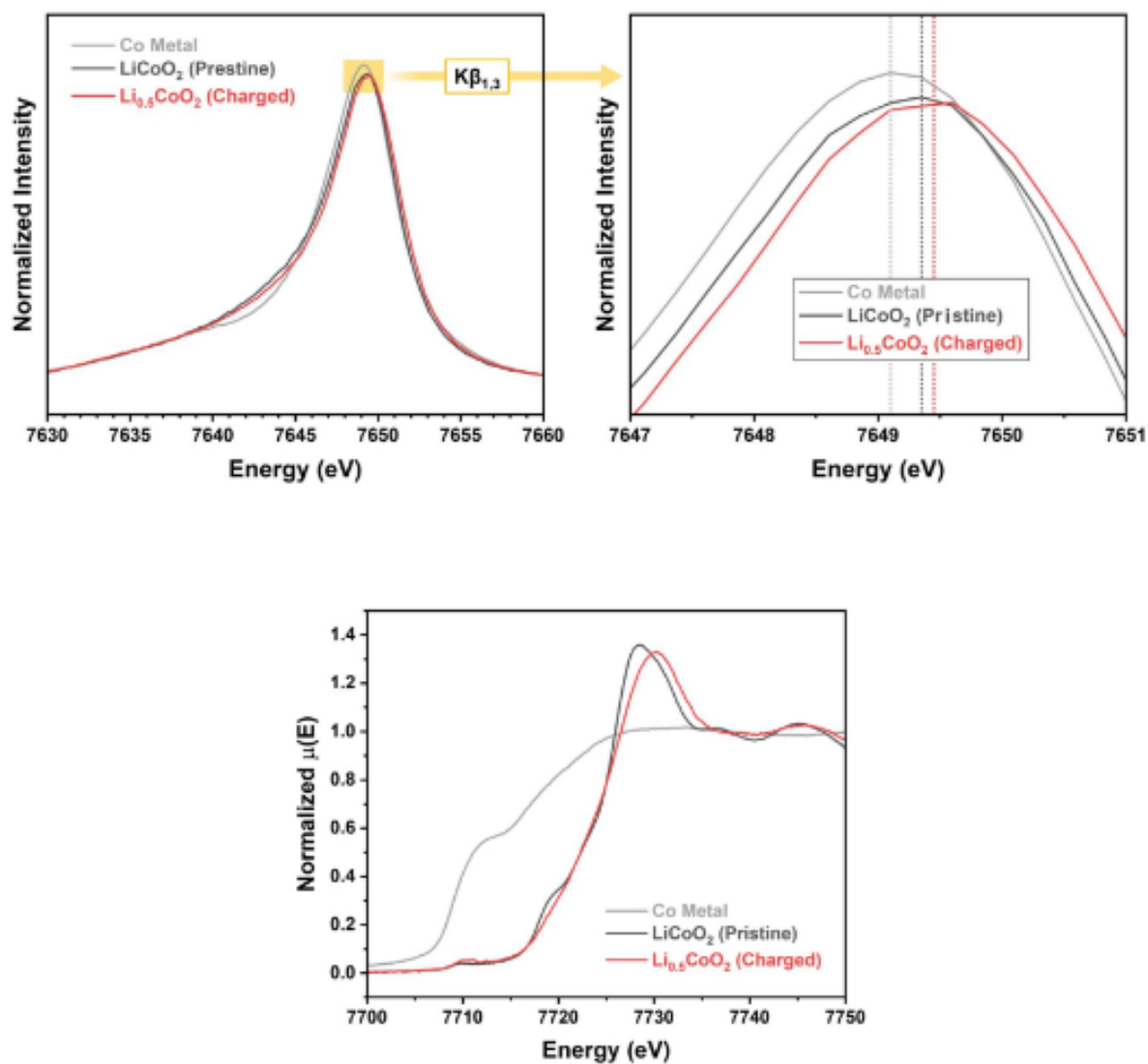


Figure 1