

Analyzing Lithium Ion Battery Materials with Valence EELS

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Many key structure-property relationships important to lithium ion battery (LIB) materials are revealed only at the nanoscale and below. Electron Energy Loss Spectroscopy (EELS) in the Scanning Transmission Electron Microscope (STEM) is an excellent tool for studying both static and dynamic phenomena in battery materials as the combination enables elemental characterization with spatial resolution down to the atomic scale. EELS is also one of the best methods of analyzing light elements like lithium and oxygen, which are of critical importance to LIB materials.

Routine EELS analysis of LIB materials typically examines the fine structure of lithium and oxygen edges, in addition to peak intensity ratios of the transition metal white-lines. Recently, studies used the low-loss valence EELS region (2 eV- 30 eV) of battery materials to visualize composition evolution. For example, an interband transition feature at ~6 eV was used to image the delithiation of LiFePO₄ with energy filtered TEM [1]. In-depth analysis of the plasmon region revealed the different compounds found in the solid electrolyte interface formed on Si after electrochemical cycling [2].

Here, we discuss the valence EELS structure of several LIB materials of interest, primarily using LiCoO₂ as a model system. EELS spectra were collected using a Hitachi HD2300 STEM, equipped with a FEG source operating at 200 kV. The typical energy resolution during acquisition was 0.8 eV, based on the full-width at half-maximum of the EELS zero-loss peak.

The valence EELS fine structures of several LIB materials are highlighted in Figure 1. Although the LiFePO₄/FePO₄ couple has the strongest feature differences, each material still has a distinct fine structure that can be used for analysis. Furthermore, comparing the valence EELS features of LiCoO₂ to its Li-K edge shows that the valence EELS features possess higher jump ratios than the Li-K edge. This holds true especially when minimal acquisition times are used, or the spectra are collected from regions with thicknesses greater than two inelastic mean free paths.

EELS spectrum image results using valence EELS (7 eV feature) of LiCoO₂ can also have some advantages over mapping the Li-K edge intensity. Both types of EELS maps highlight the thin edge of the LiCoO₂ region but have darker contrast in the thicker regions due to lower signal. However, calculating the 2nd derivative of the LiCoO₂ EELS spectrum isolates the 7 eV LiCoO₂ feature from other valence EELS contributions. This processing also reduces changes in contrast due to lower signal in thick regions. As a result, the 2nd derivative of the valence EELS region produces a map, as seen in Figure 2, that more accurately reflects the morphology and distribution of LiCoO₂ particles compared to the Li-K edge, especially in areas where the thickness is greater than two inelastic mean free paths.

Valence EELS analysis also provides an alternative EELS signature when there is strong overlap between the Li-K edge and other low-loss signatures found in LIB materials. This flexibility, combined with their interpretability in low electron dosage regimes, or large effective sample thicknesses, makes valence EELS analysis an excellent supplementary technique to standard EELS characterization of LIBs.

References:

[1] M. E. Holtz *et al.*, Nano Letters **14** (2014), p. 1453-1459.

[2] M. Boniface *et al.*, Nano Letters **16** (2016), p. 7381-7388.

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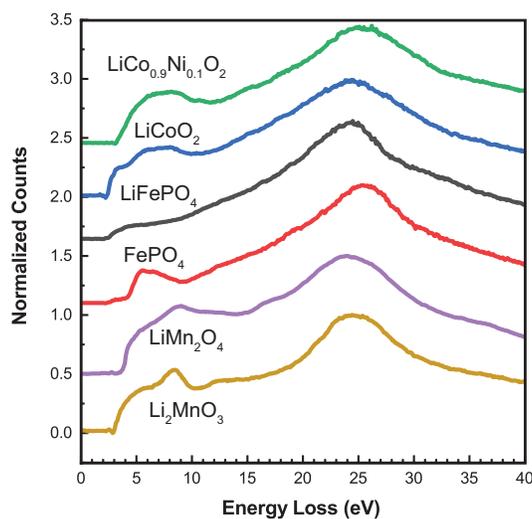


Figure 1. Valence EELS region of several lithium ion battery cathode materials.

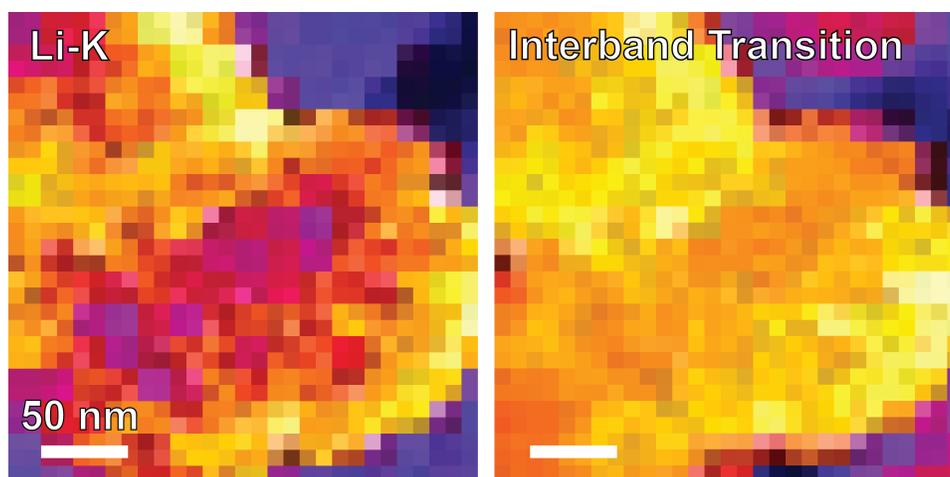


Figure 2. EELS spectrum images of the Li-K edge and 7 eV interband transition region of LiCoO₂, after taking the 2nd derivative of the spectra. Scale bar in both images is 50 nm.