

## Imaging Li Using EFTEM Spectrum Imaging and Multivariate Statistical Analysis

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Much of electrical energy storage technology depends on the transport and storage of Li ions. Understanding the interaction of Li ions with microstructural features during diffusive processes and phase transformations is important to the optimization of battery electrode/electrolyte materials design. A direct observation of how Li is distributed in various electrode and electrolyte material microstructures is challenging, however, because Li is a light element and has no detectable EDS signal. There are many alternative electron and optical microscopy-based approaches that have been used to investigate Li distribution and transport in battery materials. These include (to name a few), electron holography [1], electron diffraction [2], EELS [3, 4], diffraction-contrast imaging [5], and optical microscopy [6].

We will discuss a technique that uses a combination of EFTEM spectrum imaging and multivariate statistical analysis (MSA) to observe the spatial distribution of Li in typical electrode materials. Although some resolution is lost in the EELS spectra obtained from an EFTEM spectrum image, multivariate statistical analysis allows us to discern correlations between features in the low-loss and core-loss regions that can be identified as related to Li content. Figure 1 compares typical EELS spectra from a), as-received  $\text{LiMn}_2\text{O}_4$  and b),  $\text{Mn}_2\text{O}_4$  that has been fabricated by chemically delithiating  $\text{LiMn}_2\text{O}_4$  in a solution of  $\text{NO}_2\text{BF}_4$  in acetonitrile. A visible peak in the O-K edge at approximately 535 eV occurs only in the lithiated material and is seen in conjunction with a Li-K edge feature at 55 eV (the Mn-M edge is too weak to observe in Figure 1 b). The results of a spatial simplicity MSA calculation [7, 8] applied to partially delithiated material are shown in Figure 2 for an EFTEM spectrum image that combined low-loss and core-loss data into one data cube. The spatial simplicity solution shows that the pure spectral components either have both the weak feature at 55 eV in the low-loss spectra and the O-edge pre-peak at 535 eV or neither, which separates the MSA solution into lithiated and delithiated components. The spatial distribution of the delithiated components shown in figure 2 c) (green and cyan) seem to be concentrated at smaller particles and at the near surface regions of the larger particles. This analysis is further complicated by thickness and diffraction effects, but these can be minimized through the use of more rigorous sample preparation and tilted-beam experiments.

### References

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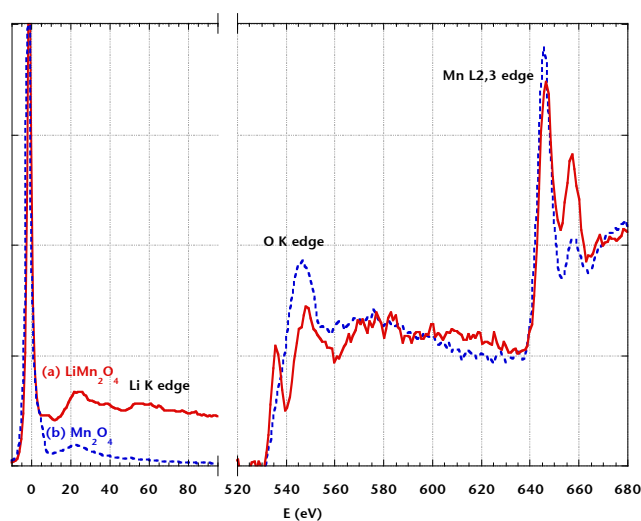


FIG. 1. EELS spectra for (a) as-received  $\text{LiMn}_2\text{O}_4$  and (b), the chemically delithiated form of  $\text{Mn}_2\text{O}_4$ . The O-K edge shows a pre-peak that correlates with the presence of the Li K edge in the  $\text{LiMn}_2\text{O}_4$  material.

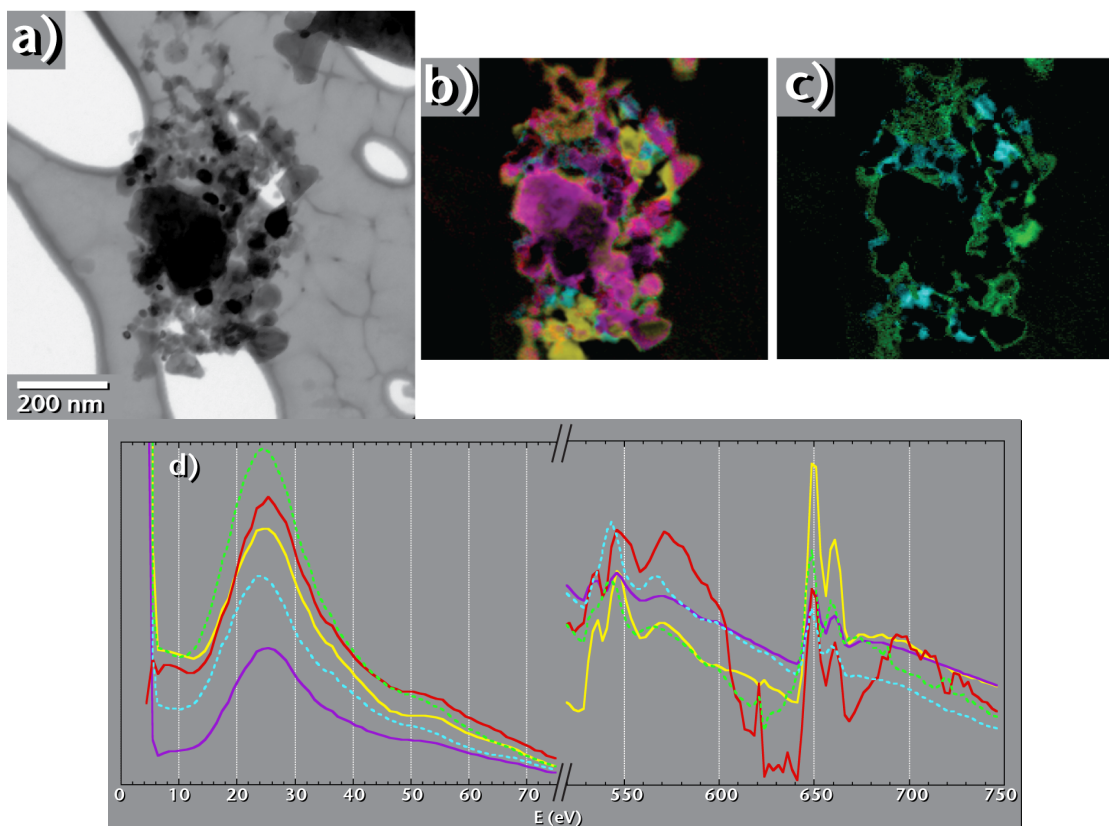


FIG. 2. (a) Zero-loss image of partially delithiated  $\text{LiMn}_2\text{O}_4$  particles. The results of MSA are shown in (b) – (d) with the color distributions in (b) corresponding to their respective spectra in d). Spectra that exhibit the Li K-edge feature also have the pre-peak in the O-K edge (red, yellow, and magenta). In c), only components that are absent of both the Li-K edge and the O pre-peak are shown, and these regions are concentrated at the near surface regions of the particles.