

## Application of Low kV EELS to Problematic Samples

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Electron energy loss spectroscopy (EELS) is an extremely versatile technique that can yield information regarding the composition, chemical state, and electronic state of materials; furthermore, it is especially suitable for detecting low  $Z$  elements [1]. Typically, EELS measurements are conducted at standard TEM/STEM operating conditions (e.g., 200 kV), which can lead to sample damage via radiolysis or knock-on mechanisms. Recent developments have sought to marry the traditional strengths of EELS with additional benefits derived from using much lower accelerating voltages [2-4]. The demonstrated benefits of EELS at 30 kV include reduced delocalization of inelastic scattering, reduced beam diffusion, and reduced knock-on damage [4]. Here we describe several case studies highlighting EELS measurements conducted at 30 kV using the Hitachi SU9000EA UHR SEM/STEM instrument.

Although LaB<sub>6</sub> is a well-known cathode material, when nanostructured by a lithiation-exfoliation method, it becomes reactive and beam sensitive [5]. As a result, this nanomaterial is challenging to characterize using any 200 kV TEM/STEM beam. Under more gentle 30 kV conditions, however, it is possible to image LaB<sub>6</sub> nanosheets as well as conduct EELS measurements, thereby mitigating high-kV effects (Figure 1). The EELS spectrum in Figure 1B shows clear identification of the La N<sub>4,5</sub> and B K edges of LaB<sub>6</sub>. This result suggests that the beam sensitivity of nanostructured LaB<sub>6</sub> may be due to nanoporous boron oxides generated by *in situ* oxidation rather than alternative degradation mechanisms (e.g., lithium boride contamination, carbide formation via *in situ* carbon migration, amorphization-recrystallization) [6].

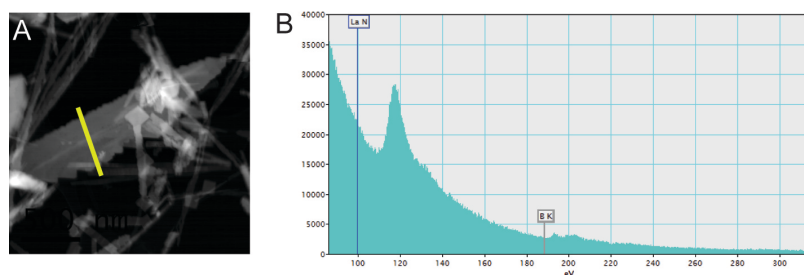
Currently, the use of lithium-rich materials for rechargeable battery cathodes is widespread. However, lithium is a notoriously tricky element to analyze. Figure 2 shows imaging and EELS measurements of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanosheets at 30 kV. The acquired EELS spectra display strong Li-K signals consistent across multiple areas of the sample. Further analysis of such data can provide quantifiable lithium occupation at various sites and details about the electronic structure of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanosheets [7], which are important parameters that influence their behavior under battery operating conditions.

Figure 3 highlights the characterization of another challenging sample, a soil specimen from a climate gradient in Hawaii. Prior work revealed that iron-rich soils along this well-defined gradient contain more carbon that is considerably older and more stable than iron-poor samples [8-9]. EELS measurements can provide insight as to how this carbon is stabilized. Such soil samples are difficult to analyze due to the presence of numerous humic components. As shown in Figure 3B, EELS spectra of iron at spots 2 and 9 are very similar and indicate that it is present as Fe<sup>3+</sup>. However, EELS of oxygen in panel C provides different spectra at the two spots; comparison with literature data suggests that the Fe<sup>3+</sup> at spot 2 exists as ions in an aluminosilicate matrix, whereas Fe<sup>3+</sup> at spot 9 (located on the brighter nanoparticles) is consistent with hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Quantifying the morphology and chemical composition at the single particle level in this way is essential for developing improved models of large-scale soil evolution.

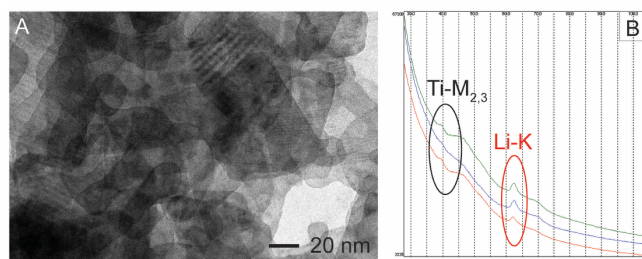
These diverse samples illustrate the utility of low kV EELS in studying problematic samples, whether the reason is sample instability or the detection of challenging low  $Z$  elements. The gentle 30 kV electron beam maintains the fidelity of the sample as well as the EELS data.

## References:

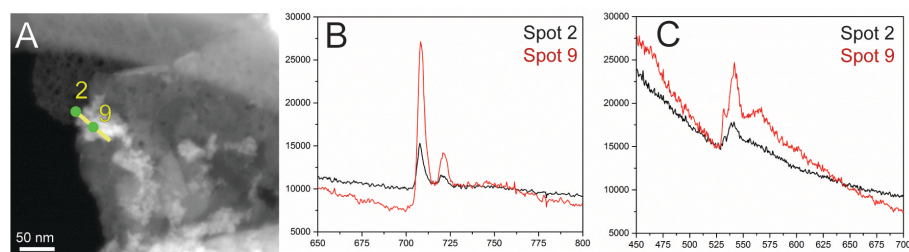
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 [10] Special thanks to Dr. Roshini Ramachandran for preparing the LaB<sub>6</sub> sample, to Mayra Pedraza for preparing the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> sample, and to Prof. Aaron Thompson for providing the soil sample for analysis.



**Figure 1.** (A) Dark field image of nanostructured LaB<sub>6</sub>. (B) EELS spectrum collected at 30 kV from the yellow region indicated in panel A.



**Figure 2.** (A) Bright field image of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanosheets. (B) EELS spectra collected at 30 kV.



**Figure 3.** (A) Dark field image of iron-rich soil particles. (B) EELS spectra monitoring Fe collected at locations along the yellow line in panel A. (C) EELS spectra monitoring O collected at the same locations along the yellow line in panel A.