Application Note

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In Situ EELS and EFTEM Analysis in the Liquid Cell

Introduction

As in situ liquid cell systems for the TEM become more commonplace, a more comprehensive understanding of how the analytical tools on the microscope can be used with a liquid cell is needed. Analysis of samples extending beyond conventional TEM and STEM imaging can provide important information about sample behavior, especially when samples are in their native liquid environment. Electron energy loss spectroscopy (EELS), including energy filtered TEM (EFTEM), is one such analysis tool commonly used by microscopists. This technique provides sample information such as element identification and details about the electronic structure, and can provide quantifiable liquid thickness measurements for liquid cell systems. EELS systems are integrated into a TEM via a post-column filter (GIF by Gatan) or an Omega filter, which is situated in the column just below the objective lens. When an EEL spectrum is generated, electrons from the primary beam interact with electrons near the atomic nucleus (core-loss spectrum), and the electrons in or near the valence shell (low-loss spectrum) of the sample. The electrons are inelastically scattered, and the amount of scatter is detected and quantified by a spectrometer. The EEL signal depends on sample thickness. When samples become increasingly thick scattering also increases, and the signal degrades. Until recently the limitations of EELS analysis within an in situ liquid cell had not been rigorously quantified. Researchers at the National Institute of Standards and Technology (NIST) in Bethesda, MD and in David Muller's group at Cornell University studied how in situ EELS can benefit materials analysis in both spectroscopy and imaging (EFTEM) modes using the Protochips Poseidon liquid cell system. In this application note the capabilities of EELS in liquid is examined, and core and low-loss areas of the EELS spectrum are evaluated as a function of liquid thickness. EFTEM imaging in the low and zero-loss region is also discussed.

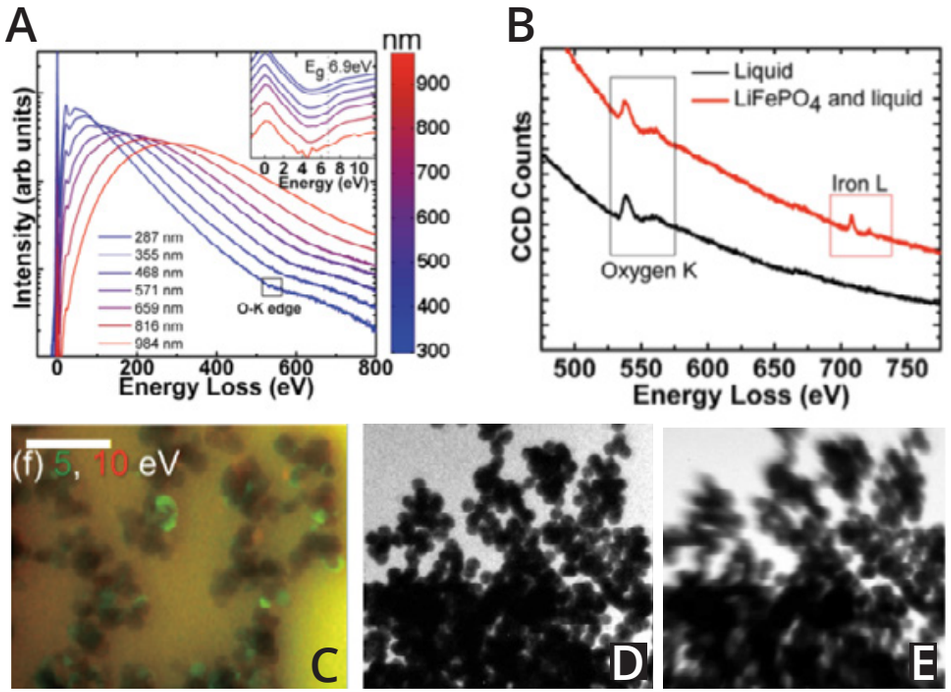

Figure A: A series of EEL spectra as a function of increasing liquid thickness. The oxygen K-edge is only visible in the thinnest liquid layer, highlighted by the box. The inset shows the low-loss spectrum of the same sample. The optical gap of water is visible through thicknesses up to ~650 nm.

Figure B: The core-loss spectra of water and $LiFePO_4$ in water. The liquid layer is ~180 nm in this case, and the oxygen K-edge and iron L-edge is evident.

Figure C: Low-loss EFTEM image of $LiFePO_4$ in water. The red areas indicate Li rich material, and the green area indicates Li poor material. The scale bar is 500 nm.

Figure D: An EFTEM image of 30 nm Au nanoparticles using a 10 eV slit on the zero-loss peak.

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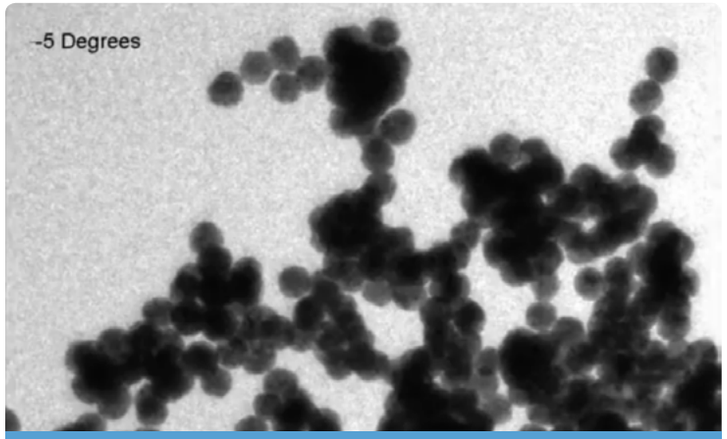
Experiment

For all experiments, two Poseidon E-chips, each with a 50 nm silicon nitride window, were used to contain liquid in the TEM column. EEL spectra and low-loss EFTEM images were taken with an FEI Tecnai F20 by David Muller's lab. The TEM was operated at 200 kV in both conventional TEM and STEM modes, and a Gatan 865 HR-GIF was used for EELS analysis. To evaluate the effects of liquid thickness on the EEL spectrum pure water was used. Zero-loss EFTEM experiments were done using a Philips/FEI CM300FEG operating at 300 kV with a post column Gatan GIF, by Kate Kline and Ian Anderson at NIST. In these experiments agglomerates of 30 nm gold nanoparticles in pure water were imaged.



Click here to view a video of Poseidon tilting within the TEM on YouTube.

Discussion

The researchers in Muller's group found that both meaningful low and core-loss signals can be obtained if the ratio of liquid/sample thickness and inelastic mean free path (t/λ) of the electron in the sample is below a threshold value. The core-loss spectrum is more sensitive to sample thickness because the low-loss electrons can undergo multiple scattering and overwhelm the core-loss signal. In other words, meaningful data can be extracted in the low-loss signal for thicker layers, and meaningful coreloss data can only be obtained from thin liquid layers. An example of this is shown in figure A, where the low and coreloss spectrum of pure water as a function of increasing thickness was measured. The oxygen K-edge appears in only the thinnest liquid layers (< 300 nm, t/λ = ~2.7), and disappears with increasing thickness. However, the optical gap of water, 6.9 eV, was observed in the low-loss spectrum up to liquid thicknesses of ~650 nm (t/λ = ~6.5) (inset). The liquid thicknesses shown in this figure were determined using the equation I=I0exp(t/λ) (Beer's law). Where I is the number of unscattered electrons, determined via the zero-loss peak in the EEL spectrum, and I0 is the number of incident electrons.

A second example of EELS analysis in figure B shows the iron L-edge from a nanoparticle of LiFePO4, and the oxygen K-edge from the sample and liquid. Taking spectra of LiFePO4 in water reveals that with thin enough liquid layers, 180 nm in this case, core-loss signatures are easily identified. A low-loss EFTEM image of the same sample is shown in figure C. In this experiment a 5 eV slit was centered at 5 eV in the EELS signal. At this point the FePO4 signal is strong and highlighted in green. The slit was then centered at 10 eV where the LiFePO4 signal is strong and highlighted in red. An overlay of the images is shown in the figure, so the location of the Li-rich regions can be visualized at the nanometer scale. Energy filtering can provide

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additional benefits when imaging through thick samples. If a small energy selecting slit centered on the zero-loss peak is used, the depth of field is increased, resulting in a crisper image. This effect is analogous to using a small aperture in photography, where a smaller aperture increases the depth of field. An agglomeration of gold nanoparticles in water is imaged in EFTEM mode using a 10 eV slit centered at the zero-loss peak, shown in figure D. The same area is imaged without a slit, and reveals the effect energy filtering has on the depth of field wE. In the EFTEM image substantially more of the image is in focus, although the signal intensity decreases due to the small slit used. EFTEM imaging provides a much clearer image of the structural detail and arrangement of the gold nanoparticle agglomerates than can be obtained directly from the unfiltered image.

Applications

EELS analysis in materials science is a very useful tool in the TEM when applied to *in situ* liquid samples, helping identify elements and map them spatially, as well as provide electronic structure information. This is an especially powerful tool when identifying the behavior of samples in dynamic liquid environments. Material changes can be better identified, and the product of reactions can be better quantified. Contact us to discuss the full range of capabilities of Poseidon. We can be reached at (919) 341-2612 or contact@protochips.com.

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