# Detection of weak ELNES signals using dose-fractionated spectrum imaging combined with direct detection

Andrew Thron[1], Liam Spillane[1], Saleh Gorji[2], Ray Twesten[1]
[1]Gatan Inc., Pleasanton , USA, [2]Gatan GmbH, Unterschleissheim, Germany

Background:
Recent studies showed that mixed Fe-Co oxide nanoparticles could replace more expensive Ir oxide and Ru oxide for the oxygen evolution reaction for water electrolysis [1]. Acquiring spectra at a high resolution is especially advantageous for understanding how the valence state of Fe and Co changes across the nanoparticles and potentially influences their catalytic behavior. EELS combined with STEM has proven effective at studying chemical changes at the sub-nm level [2]. Previous studies systematically characterized how the Fe L2,3 edge changes with changes in local symmetry based on the phase of Fe oxide [3]. The L2,3 edges of the first-row transition metals probe the unoccupied 3d states, which are sensitive to spin-orbit coupling, linking local symmetry changes to oxidation state. However, the transition metal K-edges probe unoccupied 4p states and are more sensitive to nearest neighbor distances, bonding angles, and the onset of the K edge undergoes measurable shifts with changes in oxidation state. Characterizing the Fe K edge at the sub-nm scale could add more profound insight into changes in structure and chemistry.

The cross-section of the transition metal K edges is ~3 orders of magnitude smaller than the corresponding L2,3 edge. This requires increased acquisition times and the likelihood that radiolysis and sample drift will compromise the measurement. It was shown in polymer blends that the performance of the microscope does not limit the resolution of an EELS spectrum image. Instead, the resolution is limited by a critical dose above which the polymer structure changes [4]. Gatan recently implemented new software and hardware tools that acquire and analyze weaker signals without compromising the sample. Using direct detection cameras for EELS on the GIF Continuum increases the detection efficiency needed to collect weaker, higher-energy K-edges, mitigating radiolysis by reducing acquisition times [5]. Upgrades to DigiScan 3 enable continuous in-line drift correction, where features in the simultaneously acquired ADF image are used to monitor drift, reducing latency during the drift measurement. Coupled with the fast, sub-millisecond frame rate of these direct detection cameras, accurate and frequent drift correction is critical in ensuring no spatial blurring of the spectrum image during long acquisition times. Finally, the in-situ spectrum imaging in DigitalMicrograph allows tracking and monitoring of the experiment over time and the total dose to be fractionated over multiple, individually saved passes. This enables integration or removal of passes after acquisition, enabling the enhancement of the SNR or removal of passes that may be compromised by sample damage or contamination.
In this study, we demonstrate why it is critical to combine the sensitivity and speed of direct detection with the ability to fractionate the dose over several passes using in-situ spectrum imaging when acquiring weaker ionization edges. We show how these tools can be utilized to study the spatial resolution limits based on the dose threshold of Fe oxide and mixed Fe-Co oxide nanoparticles. Ultimately, we explore how the material's interaction with the electron beam limits the resolution of the measurement and how this compares to analogous techniques such as scanning XAS.

Methods:
A JEOL F200 with a cold-FEG with a post-column Gatan Continuum Spectrometer was used to acquire EELS spectrum images (SI) at 200 kV. The spectrometer is fitted with single electron

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counting (K3, Gatan) and hybrid pixel thresholding (Stela, Gatan/Dectris) cameras, and were used to collect SI datasets targeting the Fe K edge (7112 eV). DigitalMicrograph's Elemental Quantification tool and concurrent standards were used to study the reduction of the Fe oxide particles as a function of applied dose. The linear-least squares tool in DigitalMicrograph was used to measure the shift in the Fe K-edge across the nanoparticles by fitting Gaussian functions to the pre-peak and main peak after the edge onset.

Results :

An EELS spectrum image acquired from a cluster of Fe¬2O3 nanoparticles is shown in the ADF image in Figure 1a. The spectrum image was acquired using multi-pass spectrum imaging. A step size of 5 nm and a pixel dwell time of 330 µs was used to minimize the total dose per pass while being able to resolve individual particles in the SI. The short pixel dwell time combined with inline drift correction enabled frequent and accurate drift correction to minimize drift artifacts during the measurement. In Figure 1b, an elemental map was created from the integrated intensity of the Fe K-edge, and the smaller particles can be resolved in the cluster. The Fe K-edge ELNES extracted from the Fe¬2O3 particles is plotted in Figure 1c, along with the fitted Gaussian functions of the pre-peak and the main peak of the K-edge. Shifts in the pre-peak and the main peak were measured by mapping the position of the fitted Gaussian in Figure 1e and 1f, respectively. The pre-peak originates from a weak 1s to 3d quadrupole transition. As a result, the SNR is lower than the main peak, producing a larger variability in the fit in Figure 1e. The main peaks in the Fe K ELNES originate from a stronger 1s to 4p dipole transition, resulting in a signal that is an order of magnitude larger than the pre-peak. A shift in the main peak is observed in Figure 1f, from 7130 eV in the smaller particles to 7132 eV in the larger particles. To confirm this trend, further measurements are needed from well-separated particles.

Conclusion:

Detailed analysis of the weaker Fe K-edge is possible across individual particles. However, further experiments are needed to determine why the main peak of the Fe K edge shifts with changes in particle size. In-situ experiments fractionating the dose over several individually acquired passes are needed to confirm that the shift in the main peak is caused by radiolysis. We will apply this workflow to a mixed Fe-Co oxide system to study how the oxidation state changes with the concentration of Fe and Co, by examining changes to the ELNES of the Fe and Co K-edges. Finally, we aim to study how radiolysis limits the spatial resolution of weaker ionization edges.

**Graphic:**

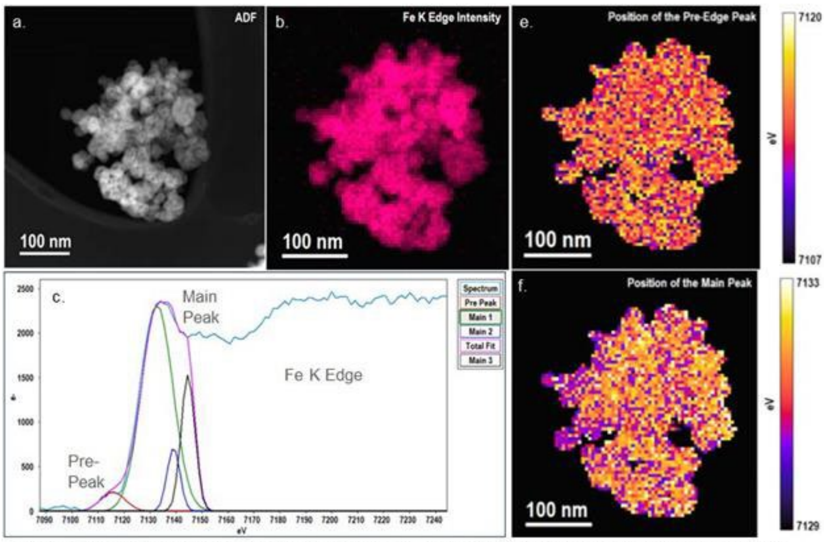


**Figure 1. (a)** ADF image of the $Fe_2O_3$ particle cluster. **(b)** Integrated Fe K Intensity **(c)** Extracted Fe K ELNES with Gaussian functions fitted to the pre-peak and the main peak. Shifts in the **(e)** pre-peak and the **(f)** main peak were observed by plotting the position of the fitted Gaussians.

**Keywords:**

Dose Fractionated EELS, ELNES, Catalyst

**Reference:**

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