Experiment Brief

GIF Continuum with direct detection

Title

Dose fractionation using multi-pass *in-situ* spectrum imaging

Gatan instruments used

GIF Continuum® K3® System

Background

Traditionally, electron energy-loss spectroscopy (EELS) spectrum images were acquired using a single pass with dwell times on the order of 10's to 100's of milliseconds to limit the effect of detector read noise in optically coupled cameras. Drift, sample damage, and contamination were not apparent until several minutes into the acquisition or until it was finished. Multi-pass spectrum imaging (SI) sums several rapidly acquired passes until the desired accumulated dwell time is achieved. This allows for fast feedback on sample integrity and the ability to correct sample drift between frames. Summing multiple passes acquired with the K3 increases the signal-to-noise ratio (SNR) since direct detection is only limited by shot noise. Saving passes separately, rather than summing, allows for the removal of compromised passes post-acquisition and the ability to study the evolution of beam damage. This provides critical feedback for the design of future experiments.

Materials and methods

Commercially available calcium carbonate ($CaCO_3$) is used as a model system as the total dose thresholds for reduction and mass loss are well characterized [1]. The calcium carbonate nanoparticles were dispersed in water and drop-cast onto 25 nm-thick SiN membranes. *In-situ* spectrum imaging was used to save each pass individually. EELS spectrum images were acquired at room temperature (25 °C).

The morphology, composition, and density of the $CaCO_3$ particles were monitored at discrete steps in accumulated dose (Figure 1). Decreases in image contrast and the projected particle area were observed in the simultaneously acquired ADF images. Elemental maps (volumetric density) were created from the C K-edge, O K-edge, and the Ca $L_{2,3}$-edge. The largest changes in the density (a decrease in contrast) were observed in the C and O maps. Changes in density were more subtle in the Ca maps. The thickness maps further supported the decreases in particle density, where the particles' inelastic mean free path (thickness) was observed to decrease with increasing dose. Changes in density started at the edges of the particles and propagated inward. The accelerated mass loss appears to occur in select regions, where a void forms at the edge of the particle and rapidly propagates (highlighted by the blue arrows). This inhomogeneity in void formation is likely due to defects where the threshold for nucleation is lower [2].

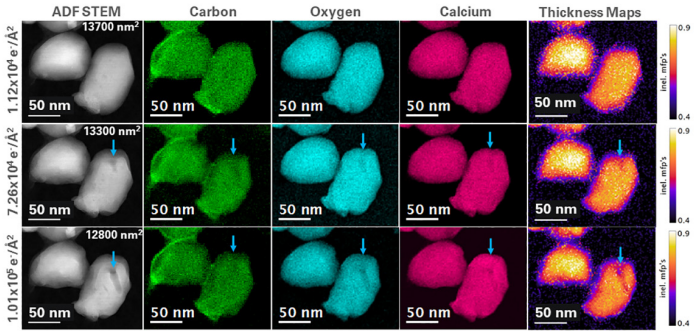

Figure 1. Each row represents a single pass of the SI, extracted at different accumulated doses. Simultaneously acquired ADF images with the projected particle area inset in the image are shown in the far-left column. To the right of the ADF image, are elemental maps of $CaCO_3$ particles created from the C K, O K, and Ca $L_{2,3}$ edges. Relative thickness maps in the far-right column were calculated using the low-loss region of the EELS spectra.

Summary

In-situ multi-pass spectrum imaging, combined with the added sensitivity of the K3, allowed us to characterize changes to the $CaCO_3$ particles during radiolysis. With increasing dose, we observed decreases in the volumetric density of C, Ca, and O in the $CaCO_3$ particles. The most significant change in composition occurred from the removal of C, followed by O. This is consistent with previous studies, which showed $CaCO_3$ nanoparticles decompose into CO_2 and CaO [3]. We can further verify that mass loss occurred by measuring a decrease in the projected area of the particles with increasing dose in the ADF images and a decrease in thickness by calculating the inelastic mean-free path using the low-loss region of the EELS spectra.

References

[1] R. Hooley, A. Brown, R. Brydson Micron 120 (2019) p25-34 doi: 10.1016/j.micron.2019.01.011.

[2] J. Cazaux, Ultramicroscopy 60 (1995) p411-425 doi :10.1016/0304-3991(95)00077-1.

[3] A.W.D. Hills, Chemical Engineering Sciences 23 (1968) pg297-320 doi: 10.1016/0009-2509(68)87002-2.

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