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doi:10.1017/S1431927621009314
Microsc. Microanal. 27 (Suppl 1), 2021

Radiolysis Characterization in Liquid Cell STEM Using Ultra Low-Dose Electron Energy-Loss Spectroscopy

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Liquid-cell experiments are used to study a wide variety of real time chemical reactions such as: nanoparticle growth, battery electrochemistry and catalysis. Understanding electron beam-specimen interactions for liquid phase is critical to the correct interpretation of *in-situ* observations at the micro or nanoscale in order to translate the results and draw meaningful conclusions for macroscopic systems ex-situ.

Electron energy-loss spectroscopy (EELS) performed in the scanning transmission electron microscope (STEM) is a powerful technique for probing local chemistry and electronic structure at high spatial resolution. In cases where high spatial resolution is not an experimental constraint, scanning transmission electron microscopy is uniquely positioned as a method that enables highly controlled or tunable specimen dose. Probe current and probe defocus may be used as free parameters to tune dose rate (figure 1). Precise control of the probe position can then be used to precisely irradiate target regions of interest to nearly the "first electron" dose (~ 0 e-/Å^2). Current generation transmission-mode electron-counting detectors are highly optimized for low dose analysis due to the high detector quantum efficiency (DQE) provided by electron counting and are particularly well suited to low dose analysis due to an inherently low detector point spread function (PSF). The low PSF allows spectral data to be acquired at low spectrometer energy dispersions while maintaining energy resolution. Operating at low energy dispersion maximizes signal collection efficiency.
Here, we use a counting-mode EELS spectrometer (GIF Continuum K3) to acquire time resolved electron energy-loss spectra from carbonate solutions to study early reaction products formed from the interaction of the electron beam and aqueous solution. Radiolysis of carbonate solutions yields several molecular products (CO_2, CO, O_2, H_2) all with characteristic features in the low energy-loss region of the EELS spectrum. Using the sensitive low-loss region and operating at an ultra-low probe current (0.2 pA), this experimental setup has enabled access to dose rates as low as 0.15 e-/Å^2/spectrum.

Initial findings show the formation of three characteristic low-loss peaks at specimen doses as low as 1.0 e/Å^2. Normalized peak intensity was seen to increase up to doses of approximately 10.0 e-/Å^2 with no further significant changes up to doses of 60.0 e-/Å^2 (figure 2). In this presentation, we will expand upon these findings and demonstrate low-dose STEM and temperature dependent EELS as techniques that provide detailed understanding of the different stages of the radiolytic degradation of liquids during i*n-situ* liquid cell experiments. These insights are crucial to limit the impact of radiolysis on the results of liquid cell experiments by developing efficient protection strategies.

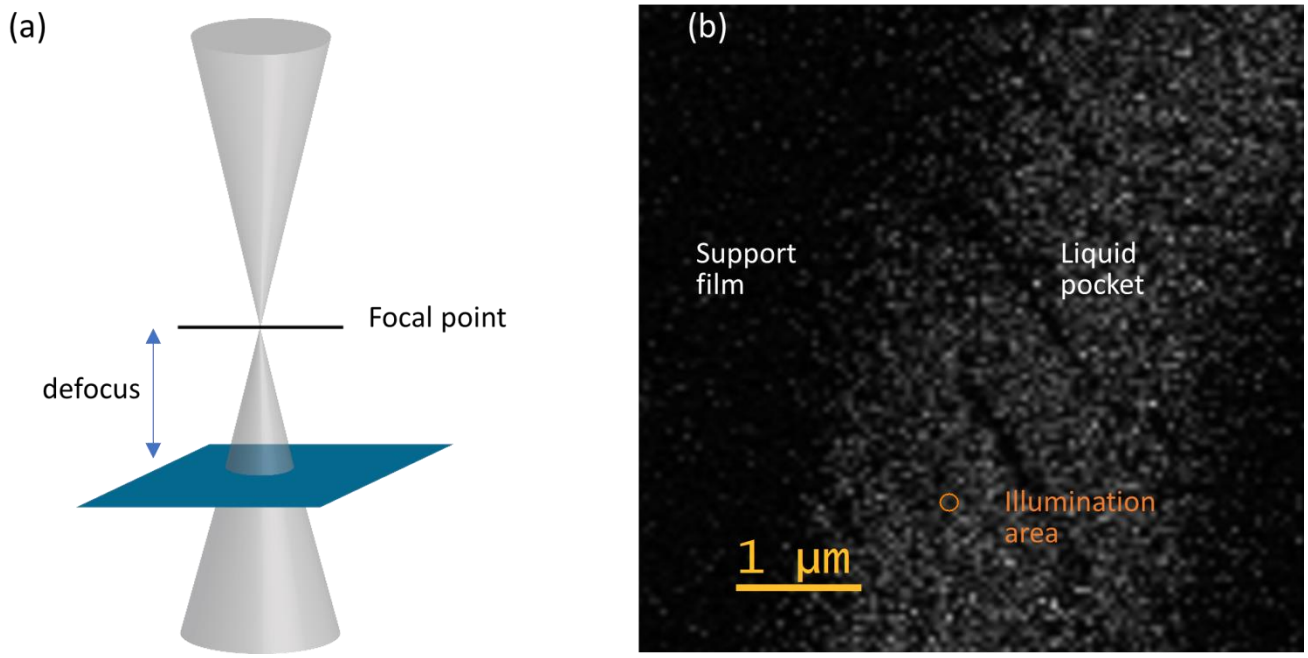

Figure 1. (a) STEM schematic diagram showing effect of probe overfocus on illumination area at specimen position. (b) Example ADF STEM image showing support film and liquid pocket regions from a typical liquid cell specimen. Illumination area shown is 80 nm in diameter.

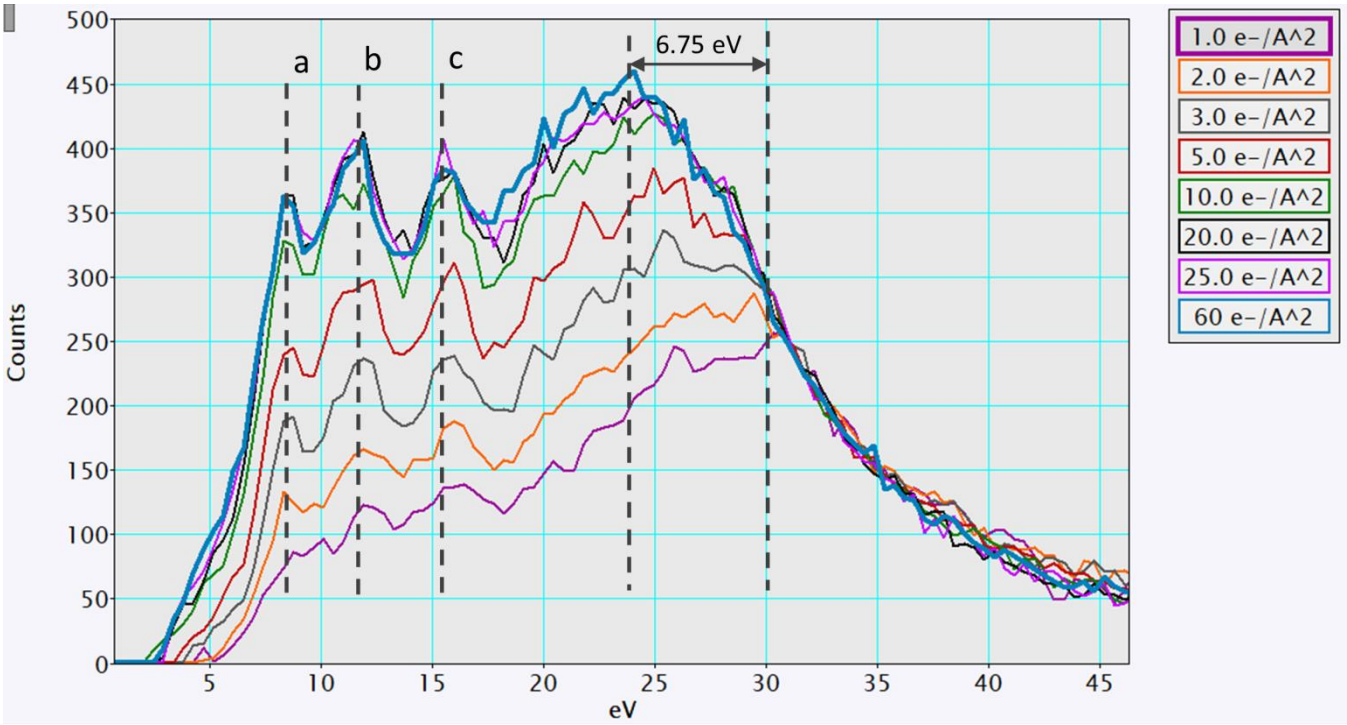

Figure 2. Single scattering distribution (SSD) low-loss spectra from aqueous carbonate solution specimen at accumulated doses of: (1.0, 2.0, 3.0, 5.0, 10.0, 20.0, 25.0, 60) e-/Å2. SSD achieved by Fourier-log deconvolution. SSD spectra were normalized against relative thickness and integral in the 30 – 35 eV energy window. Characteristic peaks a, b and c were found to increase in intensity up to a dose of 10.0 e-/Å2. A shift in plasmon energy of 6.75 eV was also observed.

https://doi.org/10.1017/S1431927621009314 Published online by Cambridge University Press

References

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the KC22ZH program. Work at the Molecular Foundry of Lawrence Berkeley National Laboratory (LBNL) was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.