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doi:10.1017/S1431927620018863
Microsc. Microanal. 26 (Suppl 2), 2020

Stabilizing Fuel Cell Materials Through Cryogenic Cooling for Simultaneous EELS-EDS Analysis

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Hydrogen fuel cell technologies are enjoying a period of renewed interest, especially for heavy duty applications such as long-haul trucking and shipyards. The longer operational lifetimes of these applications place new durability and efficiency demands on the materials used in the fuel cell stack, particularly the catalysts, supports, and proton-conducting polymers used in the membrane electrode assembly (MEA). Rapid materials discovery, characterization and testing is required to keep pace with the changing market demands. Advanced characterization tools are required to establish structure-property relationships and understand degradation pathways, and analytical electron microscopy is ideally suited to span the length scales (sub-nanometer to tens of microns) in the fuel cell MEA. The perfluorosulfonic acid (PFSA) ionomer enabling proton conduction within the electrode has been shown to suffer from electron beam-induced radiolysis under the doses required for 2D spectrum imaging by electron energy loss spectroscopy (EELS) or energy dispersive X-ray spectroscopy (EDS).[1] Although typically stable under standard STEM imaging conditions, metal nanoparticles can also suffer from seldom-reported beam damage artefacts under the high doses required for either electron tomography or spectrum imaging, with the effect increasing with decreasing particle size.[2,3] The small (< 5 nm diameter) Pt-alloy nanoparticle electrocatalysts used in fuel cells are particularly prone to beam damage, making it difficult to quantify the critical Pt-skin structures present over the particle alloy core.[4] The sensitivity of these two fuel cell constituents to electron beam irradiation is demonstrated in Figures 1 and 2 using the play back function in the JEOL Analysis Station software on data obtained on a JEOL NEOARM equipped with two 100 mm2 silicon drift detectors (SDD). Although the system boasts one of the largest solid-angle SDD-EDS systems currently available, fluorine loss and changes in particle morphology are still observed during map acquisition. Simultaneous EELS-EDS acquisition offers an opportunity for improved acquisition efficiency at lower doses. The complementary information found in EELS and EDS spectra for mapping ionomers and alloy particles will be discussed. This includes differences in sensitivity limits, as well thickness effects. Strategies for combining and optimizing the signal from each technique will be discussed, including the use of multivariate statistical analysis on combined EELS/EDS data to improve signal-to-noise and reduce electron dose. Finally, results obtained from recently acquired cryogenic cooling holder designed by HennyZ for stable high-resolution imaging will be presented. Cryogenic cooling has shown to slow the rate of radiolysis in PFSA ionomers, but not sufficiently to map the distribution of thin (< 10 nm) films needed for fuel cell modelling efforts. Cryogenic cooling will be combined with simultaneous EELS-EDS to further push the resolution limits for ionomer mapping. The benefit of cooling on nanoparticle stability will also be quantitatively investigated, as will spatial resolution limits under these conditions.[5]

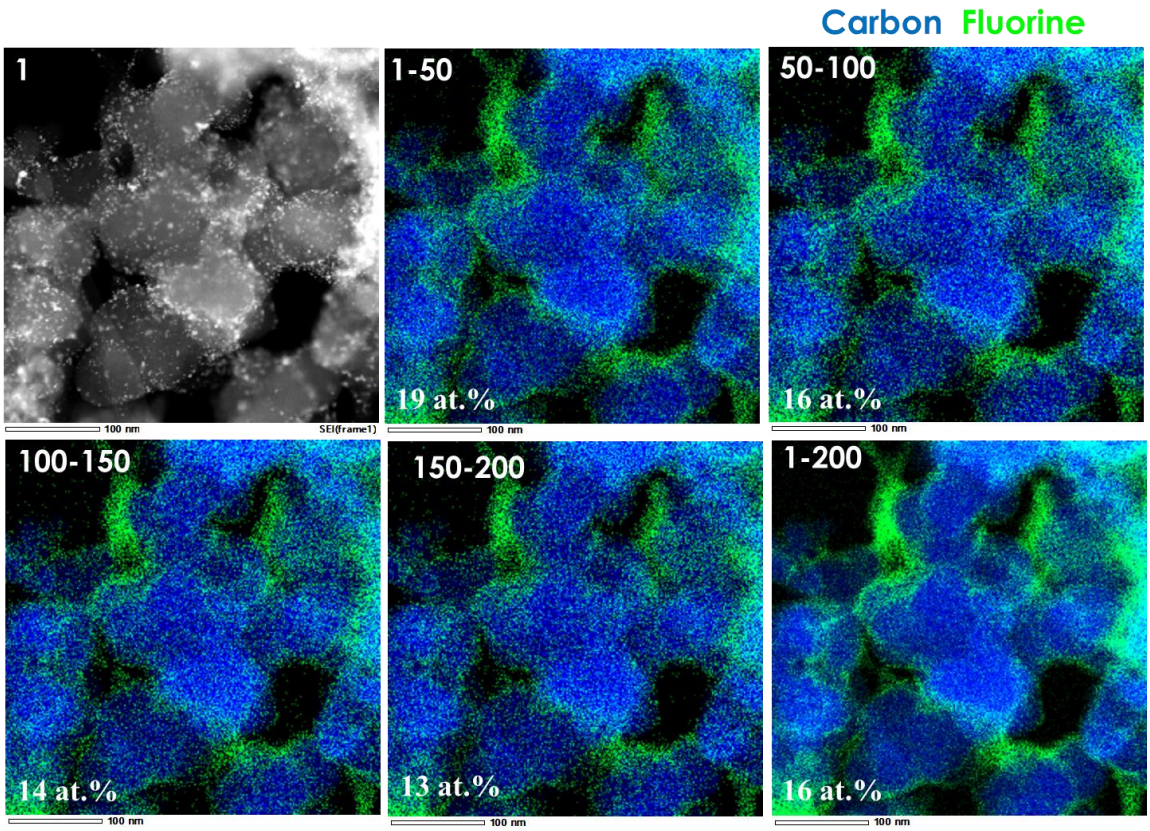
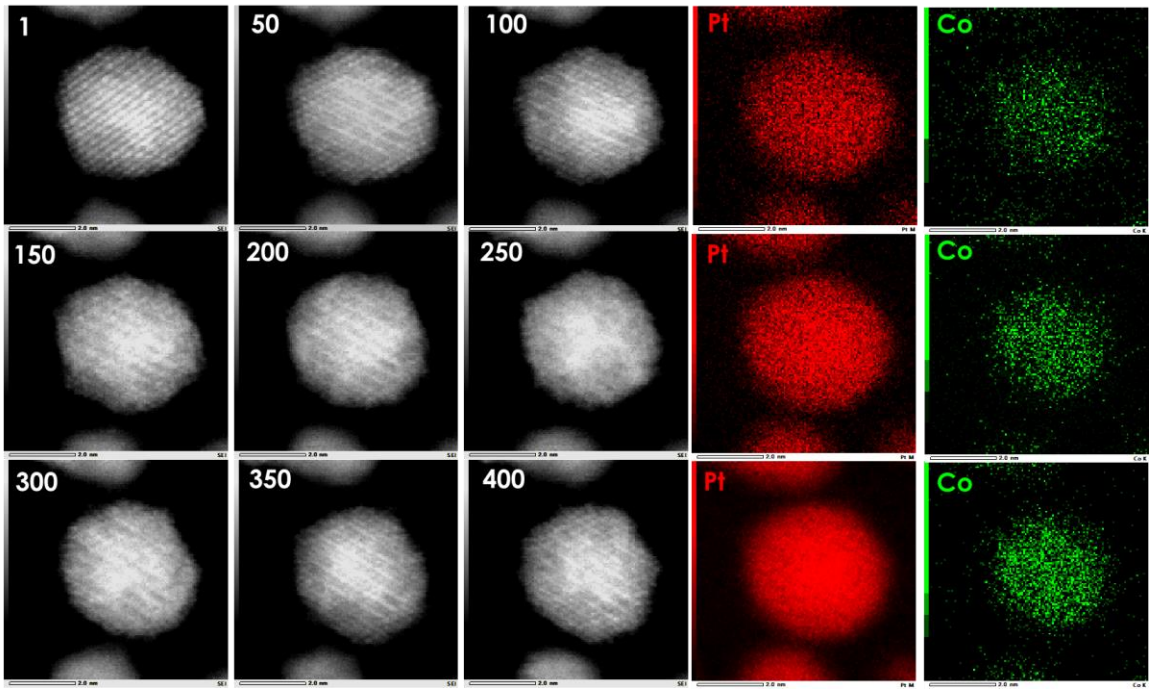


Figure 1. HAADF-STEM image and overlaid STEM-EDS spectrum images for F and C. Text in upper corner indicates range in frames used to generate the maps and lower corner indicates F content in at.%. Acc. Voltage: 80 kV, Pixel Resolution: 1.5 nm, Dose per 50 frames: 2.3x106 e-/nm2



https://doi.org/10.1017/S1431927620018863 Published online by Cambridge University Press

Figure 2. (left) HAADF-STEM images and (right) corresponding STEM-EDS spectrum images of an L10- ordered PtCo nanoparticle. The frame number is indicated in the top left corner of each image, with the Pt and Co spectrum images corresponding to the total signal obtained after 100, 200, and 400 frames. Acc. Voltage: 80 kV, Probe Current: 100 pA, Dose/Frame: 2.4x107 e-/nm2

References

[1] LGA Melo et al., ECS Transactions **80** (2017), p. 275.
[2] E Padgett et al., Journal of the Electrochemical Society **166** (2019), p. F198.
[3] BT Sneed et al., Journal of the Electrochemical Society **165** (2018), p. F3078.
[4] J Li et al., Joule **3** (2019), p. 124.
[5] Research sponsored by the Fuel Cell Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy (DOE). Electron microscopy performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.