

Comparison of electron and X-ray microscopies for characterizing perfluorosulfonic acid ionomer for fuel cell applications

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Optimizing the composition and nano-scale distribution of catalyst layer (CL) components in the electrodes of polymer electrolyte membrane fuel cells (PEM-FC) can maximize power efficiency and durability while minimizing cost. The current design of CL employs carbon support particles with a dispersed catalytic phase of Pt/Pt alloy and a proton conducting perfluorosulfonic acid (PFSA) ionomer. Electron and X-ray microscopies have been essential to understand the nanostructure of PEM-FC cathodes [1,2]. Although its spatial resolution (30 nm) is significantly lower than that of transmission electron microscopes (TEM), Scanning Transmission X-ray Microscopy (STXM) causes significantly less radiation damage, and thus provides more reliable results. The objective of this work is to quantitatively compare damage to PFSA thin films by electrons and X-rays caused by TEM and STXM.

130 nm thin films of Dupont D521, prepared by spin coating from isopropanol/water solution, were mounted on separate SiN_x windows and (each) damaged with controlled exposure to electrons in a 200 kV TEM and to 320 eV photons in STXM. The TEM exposures ($10^3 - 10^5$ e⁻/nm²) were similar to those needed for analytical measurements [2,3]. X-ray absorption spectroscopy, measured in STXM, was used to quantify changes to the F 1s spectra caused by both types of irradiation (**Figure 1**). For the same exposure (areal incident flux, particles per nm²) X-rays cause higher fluorine loss than electrons (Fig. 1a). However, STXM give images and chemical analysis at a significantly lower exposure than electrons (arrows in Fig. 1a). For high exposure, both types of radiation lead to similar chemical and structural changes: rapid decay of the F 1s \rightarrow σ^*_{C-F} transition at 690 eV and fluorine loss (Fig. 1b - photon, 1c - electron exposure).

Thin films of PFSA (~50 nm) were intentionally damaged with electrons in a 200 kV TEM at ambient (298 K) and cryo temperature (93 K). **Figure 2** plots the fractional decrease in the 690 eV peak (Fig. 2a) and the amount of fluorine loss (Fig. 2b) as a function of the exposure. The lowest electron exposure used (100 e⁻/nm²), which is below that needed for TEM imaging using state-of-the-art electron counting cameras [4], resulted in ~25% damage by both metrics. At room temperature (RT) the film ruptures at 2000 e⁻/nm², while the film could sustain higher exposures if exposed at cryo temperature. These results show that using ultra-low exposure TEM imaging methods and cryo-microscopy for morphology investigations causes significant structural and chemical damage to PFSA thin films. The main advantage of STXM over analytical TEM is its ability to get analytically useful results with minimal radiation damage. Methods developed by our group [1] have shown that low dose spectroscopic imaging at 4 energies in STXM can quantitatively map ionomer and carbon support with negligible modification to PFSA, as measured spectroscopically [3].

References

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- [5] The electron microscopy was completed at the Canadian Center for Electron Microscopy supported by NSERC and McMaster University. Research was performed using the ambient-STXM on BL10ID1 at the Canadian Light Source, funded by CFI, and on BL 5.3.2.2 at the Advanced Light Source, funded by DoE BES. Research supported by AFCC, NSERC and the Catalyst Research for Polymer Electrolyte Fuel Cells (CaRPE-FC, Canada) network.

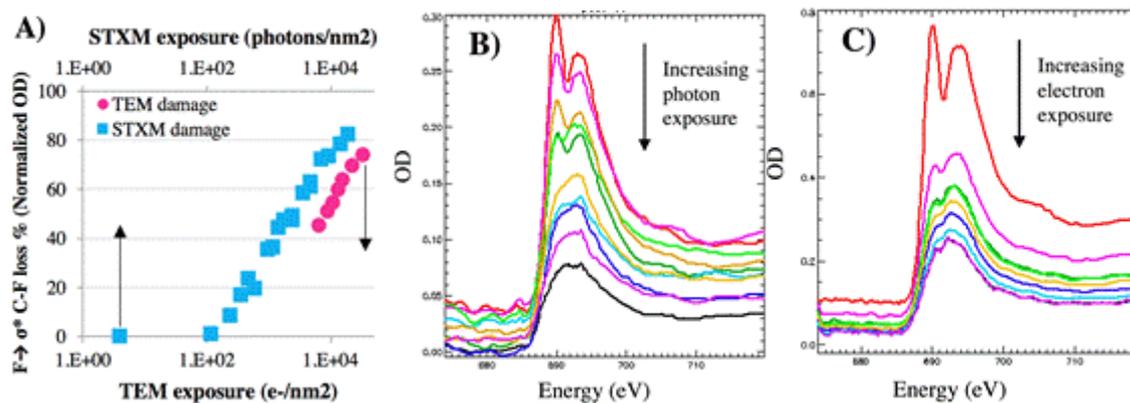


Figure 1 STXM analysis of radiation damage to ~130 nm PFSA films as a function of electron and photon exposure. (A) STXM quantification of fluorine loss from 200 keV electron exposure in TEM (bottom horizontal axis) and 320 eV photon exposure in STXM (top horizontal axis). The arrows indicate minimum exposure for imaging in each method. Changes in the F1s spectrum of PFSA exposed to (B) photons and (C) electrons as a function of increasing exposure.

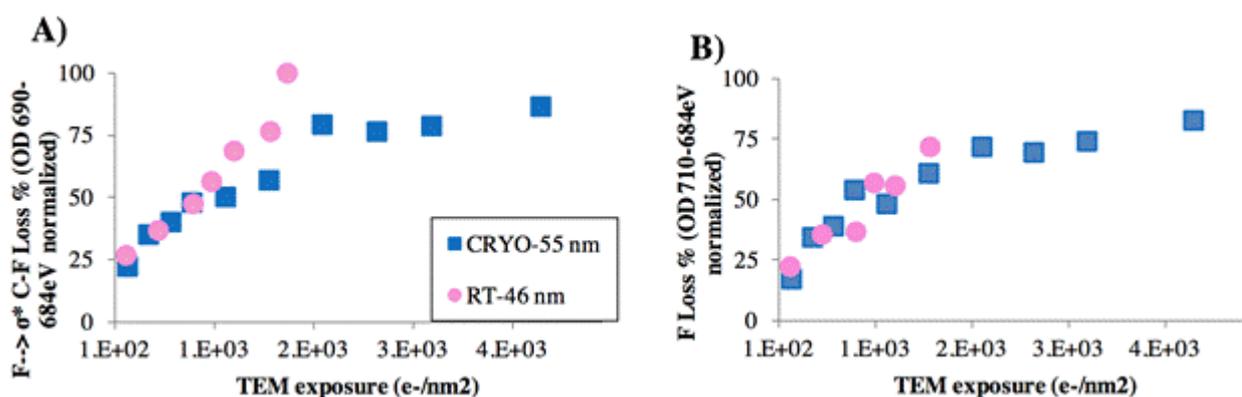


Figure 2 Comparison of chemical changes to thin PFSA films at RT (46 nm) and cryo temperature (55 nm) as a function of electron exposure. (A) loss of F 1s → σ* C-F signal (OD₆₉₀ - OD₆₈₀, normalized to initial signal) and (B) Fluorine mass loss of the same areas in (A).