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Quantification of the critical dose for radiation damage to perfluorosulfonic acid membranes using soft X-ray microscopy

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The rate limiting reaction in polymer electrolyte membrane fuel cells (PEM-FC) occurs in the cathode catalyst layer at the triple-phase boundary between the catalyst and electron conductor (Pt or Pt-alloy on carbon nanoparticles), the proton conductor (perfluorosulfonic acid (PFSA) ionomer) and the gas (transport of O_2 and H_2O through the porous structure of the carbon nanoparticles). The ionomer distribution affects the performance of PEM-FC and its optimization can decrease use of the expensive Pt/Pt-alloy catalyst nanoparticles. Analytical microscopies such as TEM-EELS, TEM-EDX and Scanning Transmission X-Ray Microscopy (STXM) provide a means to analyse ionomer distributions [1-3]. However, radiation damage by ionizing radiation (electron beams or X-rays) limits visualization of the distribution of ionomer at the nanoscale. In order to develop measurement protocols which minimize errors due to damage it is helpful to know the critical dose for radiation damage, which, along with careful evaluation of doses associated with different methods, can lead to more reliable analytical imaging of ionomer in PEM-FC cathodes.

The critical dose is defined for this work as the dose for which the intensity of a spectral feature characteristic of PFSA is reduced by 1/e. Here, we quantify the critical dose for damage by ionizing radiation using the focused soft X-ray beam of STXM. Previous studies [4] have shown that critical doses for high energy TEM electron beams and X-rays are similar if the absorbed doses are correctly evaluated. An activated Catalyst Coated Membrane sample with a 3M PFSA membrane was embedded with epoxy and 100 nm sections were cut with an ultra-microtome and placed on a formvar-coated Cu TEM grid. 9-pad patterns were exposed in uniform regions of the membrane with the focused (~32 nm) X-ray beam using different exposure times and incident photon energies (see **Figure 1)**. Each pad is 600 nm x 600 nm in size. Post patterning images at 292.4 eV (C1s $\rightarrow \sigma^*_{C\text{-}F}$) or 692.6 eV (F1s $\rightarrow \sigma^*_{C\text{-}F}$), as well as full C 1s and F 1s image sequences were used to quantify the spectral changes in each pad and thus the relative damage (see **Figure 2)**. Two different exposure energies were used: 280 eV (pre C 1s edge) and 310 eV (C 1s continuum), chosen to explore possible photon energy dependencies of the critical dose.

The absorbed dose is the amount of energy absorbed by a material divided by the amount of material as explained in [5]. The absorbed dose rate will change if the material loses mass due to damage. Four different analytical methods were used to determine the critical dose. These methods include approaches which use an estimated D_{inf} (analytical signal at infinite dose), those which optimize D_{inf}, and methods which take into account the reduction of the absorbed dose as damage progresses due to mass loss, which is the dominant outcome of radiation damage to ionomer. The first method used an exponential fit to $OD(t) = OD(\infty) + C \exp(-a/a_c)$, where the input values are $OD(t)$ (optical density measured for each pad from the 292.4 eV image taken after damage) and a (absorbed dose), yielding the critical dose, a_c[6]. The second and third methods were as outlined in [5], considering no significant mass loss and mass loss, respectively. The fourth method to calculate critical dose is valid for mass loss cases and was based on the F 1s optical density value at 692.6 eV for each damage pad. The sources of both random and systematic errors for each method differ.

For all four methods and all conditions explored, the derived critical dose values were similar within non-systematic uncertainties, yielding an averaged critical dose of 5±3 MGy, independent of the energy used to create the damage, or the energy used to analyze the damage. This is by far the lowest critical dose reported for polymeric materials to date. The next most sensitive material is polymethyl-methacrylate (PMMA) which has a measured critical dose of 67±10 MGy [5,6]. This quantitative measurement, the first for PFSA to our knowledge, emphasizes the challenges of making analytically meaningful measurements of ionomer spatial distributions, especially at the highest spatial resolution scale, where the dose used increases substantially. Planned extensions of this work to evaluate radiation damage to PFSA under cryo-conditions and with water present in the cathode and membrane will be described [7].

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[7] Measurements made at Advanced Light Source beamline 5.3.2.2 STXM. The ALS is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231. We thank AFCC for supplying the sample. Research supported by NSERC, CFI, Canada Research Chairs and the Catalyst Research for Polymer Electrolyte Fuel Cells (CaRPE-FC) network.

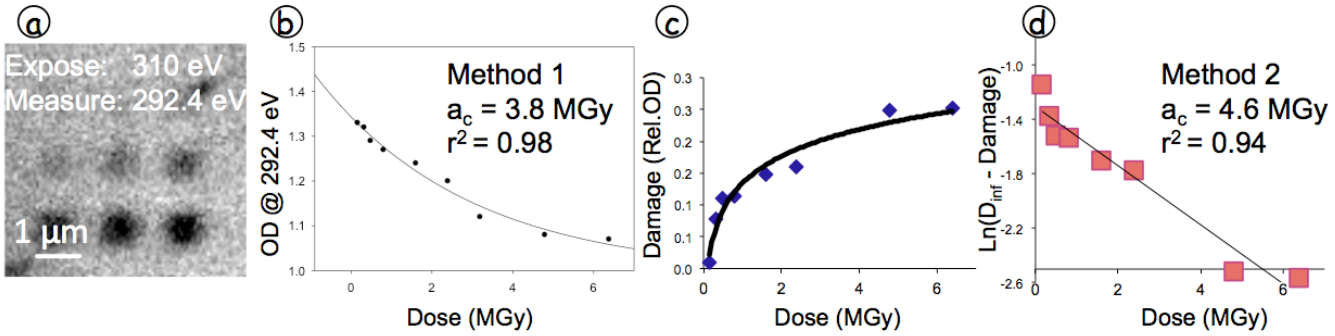

Figure 1 (a) 9-pad pattern created by STXM in PFSA membrane at 310 eV (exposure times of 2.5, 5.0, 7.5, 12.5, 25, 38, 50, 75 and 100 ms) measured at 292.4 eV. b) exponential fit and derived critical dose (a_c) using method 1 c) relative damage in OD as function of dose (assuming no mass loss) – method 2 d) linear fit of $\ln(D_{inf} - D(t))$ as function of dose.

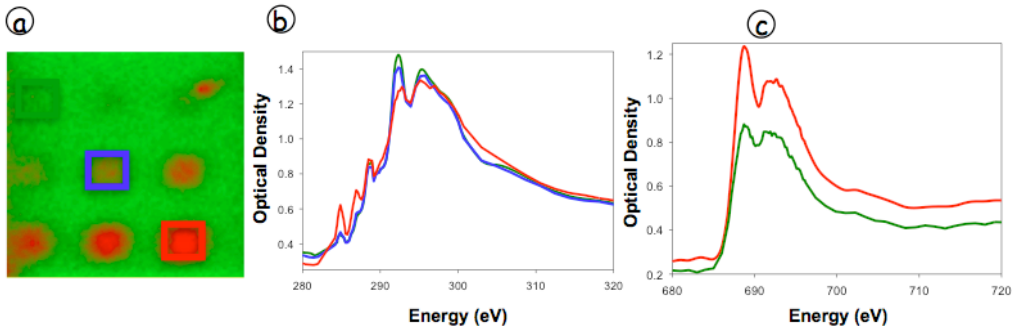

Figure 2 (a) color coded map of undamaged and damaged PFSA derived from full stack fit C 1s stack, (b) C 1s spectra of the 3 pads indicated in (a), (c) F 1s edge spectra for same pads from another area. Mass loss occurs only for F 1s edge.