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Optimizing Soft X-ray Spectromicroscopy for Fuel Cell Studies: X-ray Damage of Ionomer.

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Polymer electrolyte membrane fuel cells (PEM-FC) using H_2 as fuel are entering commercial use for personal automobiles, as a means to reduce greenhouse gas emissions while retaining performance and refueling times similar to ICE-based engines. Further optimization of PEM-FC focuses on reducing the amount of expensive catalyst and increasing reliability. Both factors depend on optimization of the distribution of components in the cathode catalyst layer (CL), particularly the perfluorosulfonic acid (PFSA) proton conduction ionomer. Soft X-ray Scanning Transmission X-ray Microscopy (STXM) at the C 1s and F 1s edges has been shown to be a powerful tool to quantitatively map ionomer in the CL relative to carbon support, Pt catalyst and pores, in both 2D [1] and 3D [2]. However, PFSA is readily damaged. Achieving a quantitative understanding of the damage kinetics and mechanisms is of interest to design STXM analysis protocols that achieve maximum quality with acceptable levels of radiation damage. Accurate, quantitative reference spectra for various forms of PFSA (ionomer and membrane) have been measured [3]. The accuracy of thickness determination by X-ray absorption has been verified though a comparison to film thicknesses determined by UV-spectral reflectance [4]. This paper reports results of soft X-ray damage of PFSA spun cast thin films (50-200 nm) using several irradiation energies, and spectroscopy studies to determine quantitative critical doses and damage mechanisms.

The films were exposed in STXM to X-rays in 3 x 3 arrays of pads each with 10 x 10 pixels, with 60, 120 and 180 nm pixel separation, at variable dwell times. The irradiation beam was defocused to the pixel spacing in each case. The absorbed dose (D, in MGy) was calculated from eqn. 1 [5], where E is energy (eV), Io is incident flux (MHz), t is dwell time (s), s is the beam diameter at the sample (nm), ρ is density in g/cm^3, $OD(E)$ is optical density of the sample at E, $OD1(E)$ is optical density per nm of the material at E (OD/OD1 is the sample thickness), and K is the measured detector efficiency (0.4, 0.6, 0.8 for C, O, F edges). This equation is a simplified form, which ignores sample thinning due to mass loss since the changes in dose due to reduced OD and reduced sample thickness roughly cancel [5]. When evaluating dose-damage relationships, first order kinetics is assumed and different damage phenomena are characterized by a critical dose, a_c, - the dose which decreases (or increases) a spectral feature by 1/e. Damage analysis was performed at specific photon energies sensitive to specific damage channels.

$$D = \frac{6.4x10^5 \cdot E \cdot OD1(E) \cdot I_o\left(1 - e^{-OD(E)}\right) \cdot t}{K \cdot \pi \cdot s^2 \cdot \rho \cdot OD(E)} \qquad \text{(eqn. 1)}$$

Figure 1 plots the C 1s, O 1s and F 1s spectra of a 200 nm PFSA film as a function of dose. After only 20 MGy, there are visible changes. The two major 1s $\rightarrow$ σ*(C-F) peaks in the C 1s and F 1s spectra lose intensity; the F 1s continuum intensity declines, and the broad O 1s peak at 535-540 eV related to the side-chain sulfonate and ether bonds [3], reduces intensity. At doses of 190 MGy, the two σ*(C-F) peaks coalesce into one centred at 295 eV (C 1s) and 692 eV (F 1s), and new C=C bonds (C 1s $\rightarrow$ π* peak at 285 eV) and C=O bonds (peaks at 287 and 532 eV) are formed. Further dosing induces only physical

damage (decreased film thickness). Loss of fluorine is evidenced by reduction of F 1s signal and decrease in the signal below 284 eV where F 1s valence absorption dominates.

Figure 2 plots the critical dose, a_c, of PFSA at 3 photon energies. The influence of the incident photon energy was evaluated by irradiating at 320 and 710 eV, while the influence of O_2 was evaluated by comparing the a_c measured in He with some residual O_2, to that measured in vacuum (active pumping at $2x10^{-4}$ mbar, negligible O_2). Energies of 292.4, 540 and 690 eV are C1s $\rightarrow \sigma^*_{C\text{-}F}$ (CF_2), O1s $\rightarrow \sigma^*_{C\text{-}O}$ (C-O-C) and F1s$\rightarrow \sigma^*_{C\text{-}F}$ (CF_2) transitions, respectively [3]. Damaging the film at 710 eV leads to slightly higher a_c at all 3 energies compared to damage at 320 eV in He. The a_c is expected to be similar at 292.4 and 690 eV considering the transitions are related to the same bonds. The a_c for breaking the ether bond (540 eV) is smaller than a_c for breaking C-F bonds, consistent with a larger sensitivity of the side-chain ether and sulfonate groups to damage, which was also found in membrane degradation studies mimicking fuel cell degradation conditions [6]. Operating with a smaller residual O_2 concentration lowers the a_c at 292.4 and 690 eV to a similar value, which indicates some of the damage processes are catalysed by photo-oxidation [4,7]. Based on these studies, we recommend that quantitative STXM analytical methods for ionomer mapping be carried out in the strict absence of O_2, with less than 20 MGy total dose [8].

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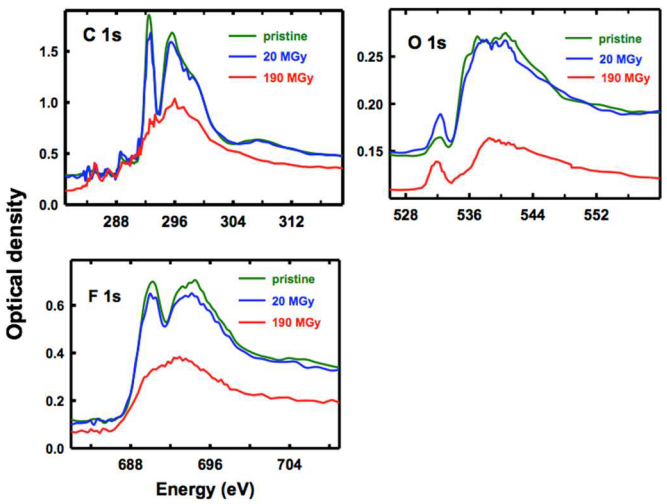

Fig. 1. C 1s, O 1s and F 1s spectra of a pristine 200 nm PFSA (<7 MGy dose) and after exposure at 320 eV to a low dose (20 MGy) and a high dose (190 MGy).

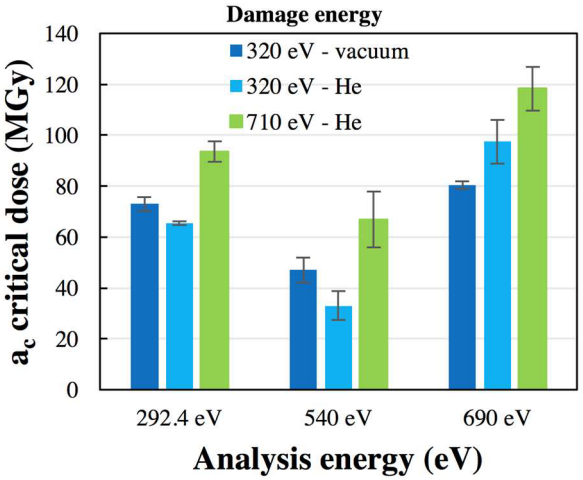

Fig. 2. Critical dose (MGy) of PFSA damaged at 320 eV in vacuum, and 320 and 710 eV under He, derived from an exponential fit to dose-damage data recorded at 292.4 and 690 eV (C-F bonds), 540 eV (sulfonate & ether bonds)

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