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Soft X-ray Scanning Transmission Microscopy Studies of Radiation Damage by Electron, Ion and X-ray Beams

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As the brightness of electron, ion and X-ray probes increases, the dose (energy per unit volume delivered to the sample) typically increases. In many situations it is the accompanying radiation damage rather than the instrument performance that limits focused ion beam sample preparation or meaningful analytical microscopy at high spatial resolution. We are using Scanning Transmission X-ray Microscopy (STXM) in the soft X-ray region for systematic studies of (i) rates of radiation damage, (ii) modifications of sample chemistry and structure, (iii) effect of sample environment (temperature, substrate, solvent, etc) on the damage process. The results of these studies provide insights into how to optimize data acquisition strategies to minimize the impact of radiation damage on analytical microscopy

STXM uses monochromated X-rays focused by a zone plate to ~30 nm (or defocused to a larger spot size to reduce dose rate) to image thin samples (50-200 nm) [1]. X-ray damage is studied quantitatively by first generating patterns of damage with controlled variable dose, then measuring the damage signal and X-ray absorption spectra of the pads. The damage as a function of dose is typically fit to first order kinetics to derive a critical dose. **Fig. 1** presents STXM images measured at the O 1s → π* peak at 532 eV of 9-pad patterns generated by 560 eV X-rays in polymethylmethacrylate (PMMA) at 25 C and -173 C. Fig. 1c plots the optical density (OD) at 532 eV of each pad versus dose for both patterns. The critical dose is 65±5 MGy at 25 C and 110±8 MGy at -173 C indicating less X-ray damage for the same dose under cryo conditions. When the cryo-damaged sample was imaged at -173 C, the 9-pad pattern was not visible except at 532 eV, indicating negligible mass loss. This result is in general agreement with an earlier study [2] indicating cryo cooling is very effective at suppressing mass loss but less effective at preventing chemical changes, such as reduction of the C=O double bond in PMMA.

Quantitative mapping of the spatial distributions of perfluorosulfonic acid (PFSA) ionomer in 2D and 3D is an important target for optimization of electrodes in polymer electrolyte membrane fuel cell (PEM-FC) devices [3]. Previously we showed that STXM was much less damaging than energy dispersive spectroscopy in a scanning transmission electron microscope (STEM-EDS) for quantitative mapping of PFSA in PEM-FC cathodes [4]. Still, it is difficult to avoid X-ray damage when imaging PFSA at 25 C, especially when using tomography. Since cryo-cooling is known to reduce mass loss damage (a major problem for PFSA), damage reduction was a key motivation in the development of the recently commissioned cryo-STXM [5] at the Canadian Light Source (CLS). **Fig. 2** compares images and F 1s spectral characterization of PFSA damaged by 710 eV X-rays with the sample at +25 C and -173 C. In contrast to PMMA, cooling PFSA to near liquid N_2 temperature not only eliminates mass loss, but also dramatically slows the rate of chemical damage to the point where the 9-pad pattern is barely visible at 694 eV, a photon energy very sensitive to degradation of the –(CF2)- repeat units. When the cryo-damaged sample was warmed, the 9-pad pattern was revealed (Fig. 2c) and the extent of damage (Fig. 2f) was very similar to that of the sample damage at 25 C (Fig. 2d). This important result indicates that accurate, quantitative 3D [6] maps of PFSA ionomer in polymer electrolyte membrane fuel cell (PEM-FC) cathodes can be measured with STXM tomography under cryo conditions [5].

The method of preparing PEM-FC and other radiation sensitive samples is also critical. While focused ion beam (FIB) milling is popular for 3D mapping (slice and view^{TM}) and preparing thin sections, radiation sensitive materials such as PFSA are significantly damaged by FIB [7]. Recently the Canadian Centre for Electron Microscopy has acquired a Xe plasma FIB system, which delivers much faster milling rates, less ion implantation, and possibly lower radiation damage. We have used STXM spectromicroscopy to compare Ga and Xe plasma FIBs as to the extent and type of chemical changes induced in an alumina aerogel coated with ZnO [8]. These results show that, indeed, Xe plasma is less damaging, although the extent of damage by Ga FIB can be mitigated by careful dose control and use of Ar^{+} damage removal after generating the milled sample.

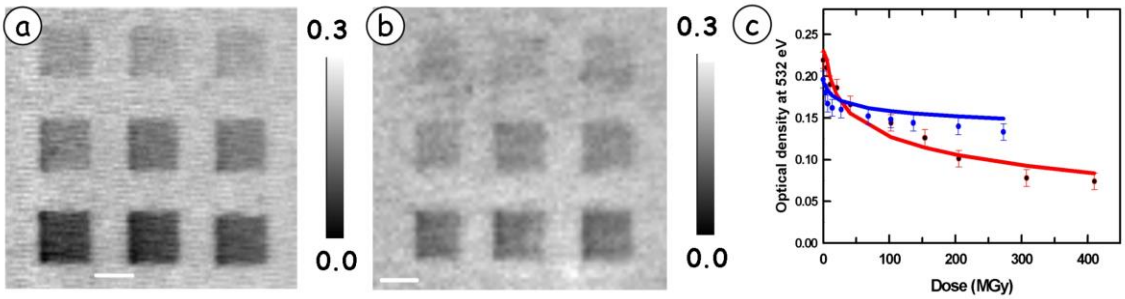

Figure 1. STXM OD images at 532 eV of 9-pad X-ray damage patterns burnt at 560 eV into a PMMA thin film at (a) 25C and (b) -173C. (c) Plot of damage versus dose and first order fit. Scale bar is 1 μm

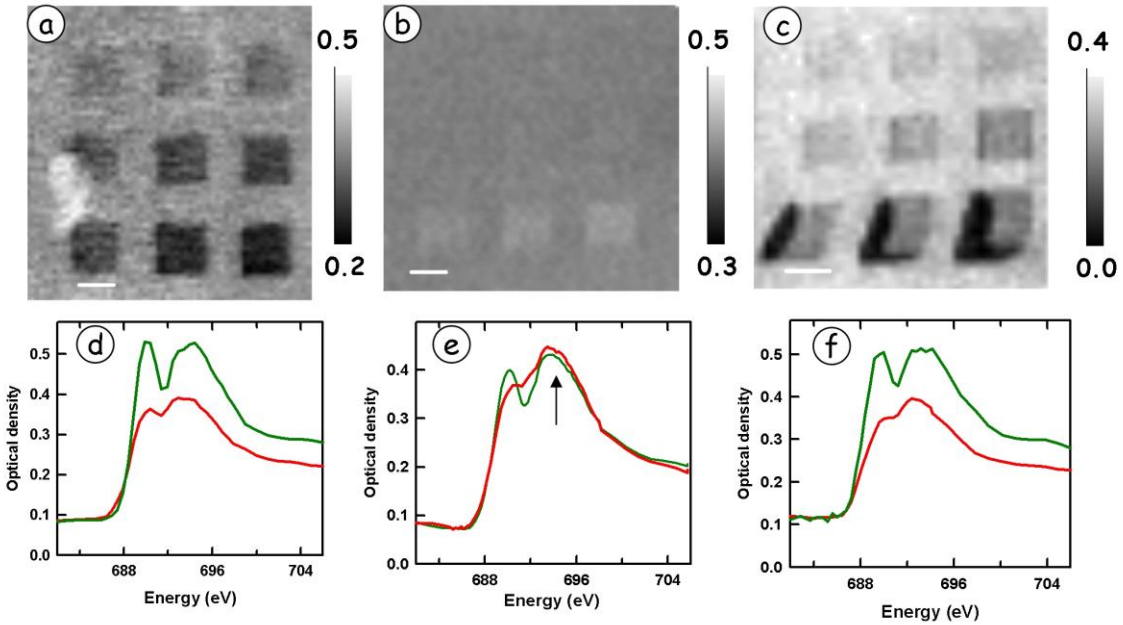

Figure 2. STXM OD images at 694 eV of 9-pad X-ray damage patterns burnt at 710 eV into a PFSA thin film at (a) 25 C and (b) -173 C. The most damaged pad received a dose of 440 MGy in (a) and 640 MGy in (b). (c) OD image at 694 eV of same region in (b) after warming to 25C. F 1s spectra of undamaged PFSA (green) and the most damaged pad (red) for (d) RT damage; (e) pattern generated and measured at -173C; and (f) the cryo-pattern after warm-up. The reversed contrast in (b) is real. Scale bar is 1 μm

References

1. C.J. Jacobsen, X-ray Microscopy (Cambridge, 2019)

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2. A. Putz et al. ECS Transactions 75 (2016)3.
3. L.G.A. Melo, et al., ECS Trans. 80 (2017) 275.
4. A.F.G. Leontowich, et al., Rev. Sci. Inst. 89 (2018) 09374.
5. T. Beetz and C. Jacobsen, J. Syn. Rad 10 (2003) 280.
6. J. Wu et al., J. Power Sources 381 (2018) 72.
7. L.G.A. Melo, et al., J. Power Sources 312 (2016) 23.
8. J. Wu et al., J. Phys. Chem. C 122 (2018) 25374

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