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Characterization of Thin Ionomer Layers

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The presence of perfluorosulfonated ionomers within polymer electrolyte membrane fuel cell (PEMFCs) electrodes plays a critical role in the transport of protons to catalytically active sites. However, the loading and distribution of the ionomer throughout the electrode can also affect mass transport properties for the other reactants and products. Scanning transmission electron microscopy (STEM) is a highly suitable tool for characterizing the distribution of ionomer within PEMFC electrodes [1]. However, it has long been recognized that fluorinated compounds are sensitive to electron beam radiation damage [2]. The high electron doses needed to acquire spectroscopic maps by either energy dispersive X-ray analysis (EDS) or electron energy loss spectroscopy (EELS) can induce severe changes to the ionomer layers [3].

In this work, we begin by exploring the impact of electron beam dose and energy on thin ionomer layers that were deposited on model substrates. Ionomer layers were adsorbed on a PtCoMn nanostructured thin film [4, NSTF]. The fluorine in these thin layers (1-3 nm) was extremely sensitive to the electron beam, such that most F was lost from the ionomer structure before the first EELS spectrum could be obtained (Fig. 1). Ionomer layers at 2 - 40 nm dry thickness were then spin coated onto a saturated 2D array of Pt nanoparticles with 8-10 nm diameter. Since vacuum pressure is another variable controlling damage rate [5], these samples will be studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) after being dosed in a scanning electron microscope at variable pressure (Fig. 2). Finally, thin ionomer layers (5-50 nm dry) were spin coated on special nanoporous Si windows for STEM analysis (Fig 3). EELS spectra were recorded at various electron beam doses using accelerating voltages of 300 and 60 kV, at both room and cryogenic temperatures, to determine the optimal conditions for studying thin ionomer layers.

These optimized imaging and spectroscopy parameters will be applied to actual Pt/C electrode layers to determine the through thickness distribution and compositional uniformity of ionomer films for different electrode coating schemes.

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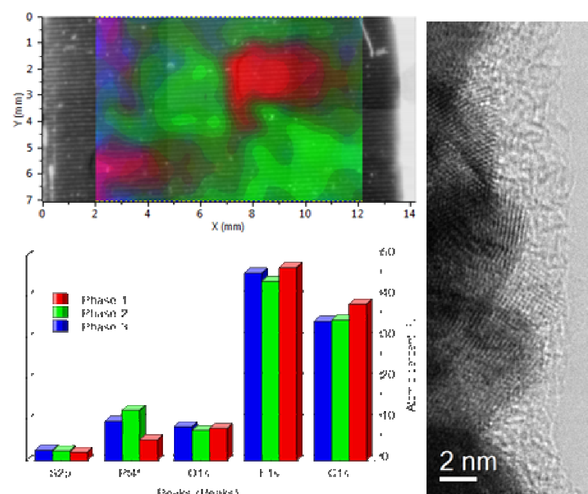

Figure 1. (left) XPS measurement showing compositional uniformity of ionomer distribution on a NSTF decal. (right) Low-voltage STEM of NSTF whisker coated with a thin ionomer layer.

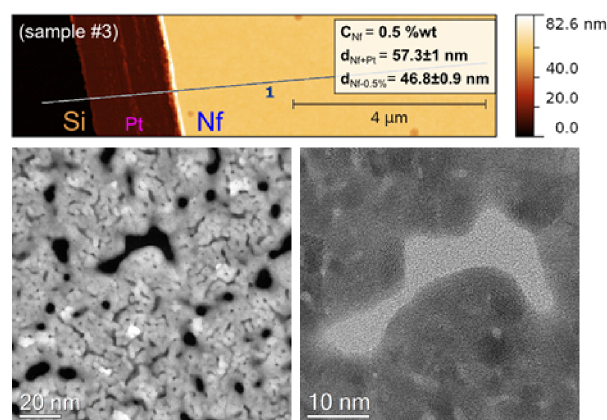

Figure 2. (top) AFM measurement of ionomer thickness on a 2D Pt array grown on a Si substrate. (bottom) STEM images of ionomer layer seen through pores in the 2D Pt array.

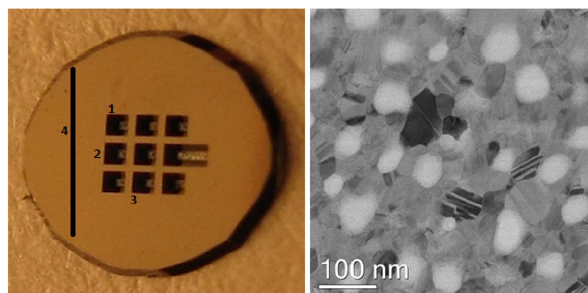

Figure 3. (left) Optical and (right) STEM images of nanoporous Si windows coated by a thin ionomer layer used for beam damage studies.

References

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