

## XPS Analysis of Fuel Cell Membrane Prepared Using an Ultra-Low-Angle-Microtomy Technique

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In recent years, the development of new proton exchange (or polymer electrolyte) membranes (PEM) for PEM fuel cells (FCs) has been a major focus area for the U.S. Department of Energy's Hydrogen, Fuel Cells, and Infrastructure Technologies Program. These new membranes must be stable at higher operating temperature ( $>80^{\circ}\text{C}$ ) and require significantly less humidification, than the current industry standard, Nafion<sup>TM</sup>. A review of alternative polymer systems for PEMFCs, published in 2004, details a variety of strategies [1]. One developmental strategy for new PEM materials having improved performance builds upon Poly(vinylidene fluoride) (PVDF) blended with a polyelectrolyte(PE). Several of the resulting PVDF/PE membranes have shown promise in PEMFC applications and characterization of the materials is ongoing [2]. ORNL has conducted transmission electron microscopy (TEM) of both the blended PVDF/PE and unblended (pure-PVDF) membranes; TEM has provided new insight into the blended microstructures of these membranes, but only limited compositional/chemical information has been measured. The recent addition of a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) to ORNL's materials characterization tools provides a method for quantifying compositional/chemical information about the membranes, such that performance-structure-composition relationships can be established.

Of particular interest is the through-depth compositional uniformity of the membranes. Although the membranes are only 20-30  $\mu\text{m}$  thick, the surface-sensitivity of XPS only provides information about the outer 3-5 nm. Traditional  $\text{Ar}^+$ -ion depth profiling is not possible since even low energy (200-500 eV) Ar ions completely disrupt the polymer structure and chemical bonding. Polyatomic sputter systems developed for etching polymer surfaces without imparting damage are also of little use due to very low sputter rates ( $\sim 0.1$  nm/s). To probe the inner region of the membrane film, an ultra-low-angle microtomy (ULAM) technique, similar to metallographic low-angle lapping, was developed based on reports published by Watts and co-workers [3]. Figure 1 shows how the ULAM-derived taper through a 25  $\mu\text{m}$  thick membrane has extended the cross-section to  $\sim 400$   $\mu\text{m}$ . With this exaggerated cross-section, the 30  $\mu\text{m}$  X-ray spot of the K-Alpha XPS instrument was able to evaluate composition as a function of depth from one face of the membrane to the other. C1s XPS spectra from the top (air-film) and bottom (film-substrate) surfaces of a standard PVDF membrane (produced by tape casting) are compared with a C1s spectrum obtained on the cross-section sample. All spectra taken from the cross-section had the same general appearance as the one shown in Figure 2, indicating that the radical differences seen on the film-substrate surface are extremely thin and a compositional gradient through the membrane does not exist. Indeed, when the film-substrate side was rinsed with distilled water, the resulting C1s spectrum compared favorably with the air-film spectrum. This confirmed that the original C1s spectrum from the film-substrate side was due to a very thin ( $\sim 3$ -5 nm) layer of adsorbed contaminants.

Figure 3 shows XPS mapping results for both C1s and F1s, and confirm that the composition within the membrane cross-section is relatively uniform.

References

- [1] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, and J.E. McGrath, *Chemical Reviews*, 2004, 104 (10), 4587-4612.
- [2] Only results for the unblended (pure) PVDF will be shown since details of the blending process and chemical nature of the polyelectrolyte are considered proprietary. Research supported by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cell, and Infrastructure Technologies Program. Research at the ORNL SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Dept. of Energy.
- [3] S.J. Hinder, C. Lowe, J.T. Maxted, J.F. Watts, *Journal of Materials Science* **40** (2005) 285-293.

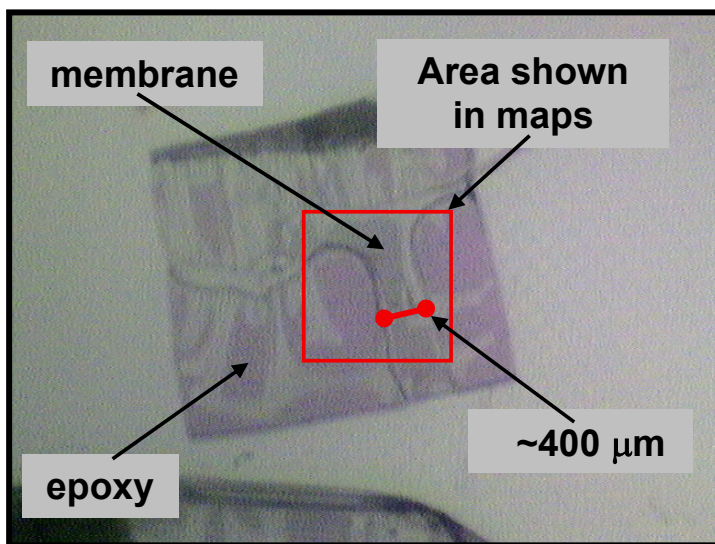


Fig. 1. Optical image of a membrane prepared using ultra-low-angle microtomy. The red box shows the area mapped in Fig. 3.

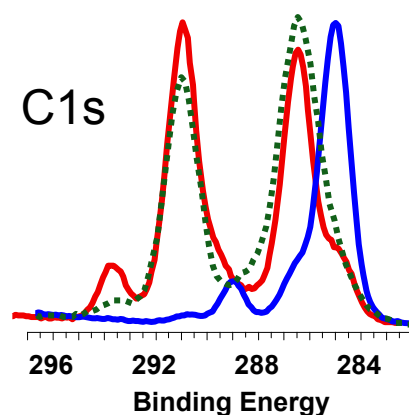


Fig. 2. Comparison of C1s spectra from the air-film (red) and film-substrate (blue) sides and from the cross-section (dashed).

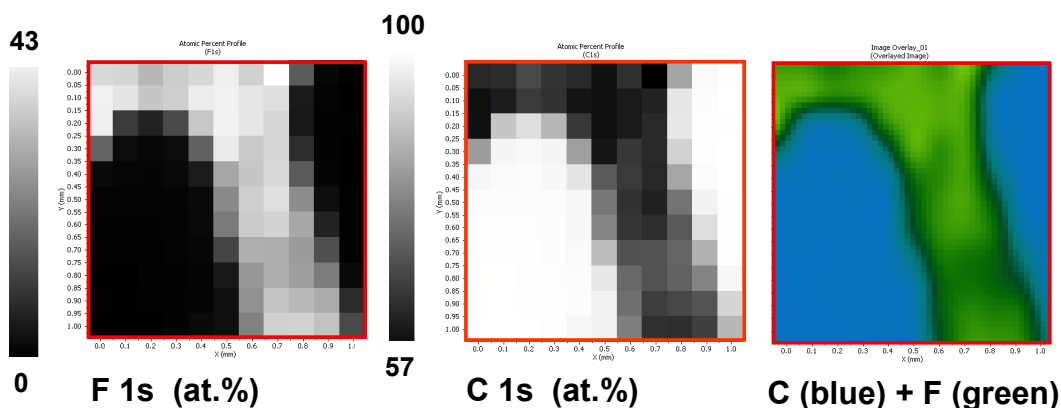


Fig. 3. C 1s and F 1s “snapshots” were taken over an array of 121 points. The data were processed to create maps atom% C and atom% F (gray scale maps). The two maps were overlaid, colored, and smoothed using an interpolation routine.