Membrane Casting
We have modified our existing 16-inch HEPA-filtered web coater (Figure 1.) for continuous casting of dense membranes from optionally-fluorinated, sulfonated polysulfone. These proton exchange membrane polymers are designed to have enhanced methanol barrier properties in fuel cell applications (e.g., relative to Nafion), and use a novel synthetic approach that eliminates the need for post-polymerization sulfonation, while allowing precise control of molecular structure and composition. Both the sodium and acid forms of these polymers have glass transition temperatures ($T_g$) that exceed 220°C. Continuous casting of ‘solvent-free’ dense membranes from solution at reasonable web speeds presents a problem due to the very significant reduction of solvent diffusion rate as solvent, e.g., DMAC, is driven off in the coater oven. Hansen$^2$ has shown that solvent diffusion rates in solutions of ‘rigid polymers’ can decrease orders of magnitude during solvent evaporation, due to reduced plasticization by the declining solvent concentration. Furthermore, the rate of solvent loss is expected to drop dramatically if the glass transition temperature of the solvent-containing film rises to exceed the drying (oven) temperature. To date, our coater modifications have included increased oven temperature via the installation of pre-heaters for incoming air, matching of feed pump size to the target membrane thickness, revised placement of air jets with respect to the web, and the use of non-contacting gauges to measure film thickness with feedback to pump speed. Due to the present scarcity of the experimental membrane polymers, our optimization work has used non-sulfonated Udel P-3500 polysulfone ($T_g \approx 190^\circ C$) with encouraging results re. residual solvent content, gauge control, and membrane homogeneity. Web distortion encountered in earlier work using non-continuous batch coating was not a problem when running continuously with ‘Udel’. Work currently underway includes increasing wattage of a primary oven convection heater, and the use of supplementary heaters. Once polymer synthesis is scaled up, this should permit the continuous casting of commercial quantities of (proton exchange) membranes from high-$T_g$ polymers.

![Figure 1. Continuous Web Coater for Proton Exchange Membranes](image)

Surface Characterization
In parallel with the engineering optimization of membrane manufacturing we have been characterizing the surfaces of proton exchange membranes to help explain how surface chemistry affects membrane performance in fuel cells. For several years we have used a similar method in the study of biomedical polymers$^3$. 
Sum Frequency Generation Study
In this work, Sum Frequency Generation (SFG) was performed on UDEL, BPS 45, and BPS 35 6F30 in air, water, and methanol to learn about the surface chemical structure at each interface. SFG is a surface specific vibrational spectroscopy that has been recently applied to polymer applications. SFG is a versatile technique in that it can be used to probe any surface or interface as long as the beams are not attenuated by the media.

![Figure 2. Spectra of materials in air.](image)

Figure 2. Spectra of materials in air. Figure 2 shows the air spectra for each material. The same peaks are observed for each material; however the relative intensities are quite different. Peaks at 2870 and 2915 cm\(^{-1}\) are associated with the symmetric and asymmetric stretches of methyl groups. The large peak at 2943 cm\(^{-1}\) may be due to residual DMAc solvent. Peaks between 3070 and 3155 cm\(^{-1}\) are assigned to various vibrational modes associated with the phenyl rings. The main conclusion from the air spectra is that UDEL contains a higher concentration of methyl groups at the surface as compared to the BPS materials. Figure 3 compares the spectra for the materials when they are placed in deionized H\(_2\)O. These spectra are very different for each material indicating the surfaces respond differently. UDEL shows similar features as observed in the air spectrum, although a small, broad water peak is superimposed on the UDEL peaks. BPS 45 shows a very small water peak around 3150 cm\(^{-1}\). A huge water peak is observed for the fluorinated BPS 35 6F30. This type of ordered water peak is often associated with an “ice like” water structure. Figure 4 compares the SFG spectra for the three materials in methanol. The

![Figure 3. Spectra of each material in H\(_2\)O](image)

Figure 3. Spectra of each material in H\(_2\)O spectra are dominated by peaks at 2835 and 2945 cm\(^{-1}\) which are assigned to the methyl symmetric and asymmetric stretch of methanol. From the size of the methanol peaks, it appears that methanol is most ordered on UDEL and least ordered on BPS 35 6F30.

These SFG results demonstrate that the addition

![Figure 4. Spectra of materials in Methanol](image)

Figure 4. Spectra of materials in Methanol

of the fluorine groups and sulfonate groups dramatically change the surface structure of the materials when exposed to water or methanol.

Reference: