Proton exchange membrane fuel cells (PEMFC’s) are an emerging energy technology which can be used in a variety of different applications, including automotive, stationary and portable power. Some of the barriers to PEMFC commercialization include high system cost and insufficient durability for certain applications. A factor contributing to both of these barriers is the requirement that the electrolyte membrane at the heart of the fuel cell be kept hydrated during operation. This hydration allows the membrane to have the high proton conductivity required for good fuel cell performance, and it also increases the membrane resistance to chemical degradation and the lifetime of the system. In order to maintain this level of hydration, the incoming reactant gas streams must be kept humidified and the cell temperature must be
controlled to prevent the membrane from drying out. This requires the added expense of humidification equipment and the parasitic power losses associated from its operation. Additional cooling is also required, another added expense. To control cost and maintain system simplicity, the system designs for automotive fuel cells include allowing higher stack temperatures and lower levels of humidification of the incoming reactant gasses than commonly used in current systems. Target operating lifetimes in this application, put forth by the automotive industry and the U. S. Department of Energy, are greater than 5,000 hours and conductivity targets include 0.1 S/cm at 120°C at low (20-40% RH) humidification. Some ionomers with very high acid group content can achieve these conductivity targets, but unfortunately these materials can swell excessively in water leading to poor mechanical properties which compromise fuel cell durability and lifetime. Also, these operating conditions increase the rate of chemical degradation of the membrane and MEA failure, and so these lifetime targets and conductivity targets can not both be met with existing commercially available membranes.

For these reasons, effort is being focused on the development of new ionomers and new membranes for proton exchange membrane fuel cells with improved performance and durability under hot, dry operating conditions. The most common type of polymer used in PEMFCs are perfluorinated, sulfonic acid containing ionomers, or PFSAs. These ionomer have highly acidic acid groups, promoting high proton conductivity, and excellent chemical stability. At 3M, we have been developing new fluorinated ionomers with improved mechanical properties and chemical stability. We have been developing thin, cast membranes from these ionomers with improved performance and durability. These membranes are based on the 3M PFSA, the
structure of which is shown in Figure 1. The acid content or equivalent weight (grams polymer/moles acid) of these polymers is a function of the ratio n/m.

\[
\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H}
\]

\[
(\text{CF}_2\text{CF})_n(\text{CF}_2\text{CF}_2)_m
\]

Figure 1. The chemical structure of the 3M Ionomer.

We have made this polymer at a variety of equivalent weights, ranging from about 1500 to less than 600. The conductivity for a range of different EW membranes made from this ionomer is shown in Figure 2. While the conductivity is higher for the lower EW samples, membranes made from these polymers with EW below about 750 swell excessively in liquid water and below an EW of about 650 the membrane starts to “dissolve”.

Figure 2. Conductivity vs. relative humidity at 80ºC. In-plane measurements were performed using a 4-point conductivity cell.
New polymers and processes for providing membranes with a combination of improved conductivity and durability will be discussed.

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