Proton Exchange Membranes: The View Forward and Back

by Drew Dunwoody and Johna Leddy

The development of proton exchange membrane (PEM) fuel cells is largely tracked by the history of the membranes. Because fuel cells of various types were known prior to PEM technologies, the catalysts, fuels, and oxidants used in PEM fuel cells were reasonably well-established materials. The first PEM systems served as the power plants for the Gemini space missions in the early 1960s. The cells were short-lived because of the oxidative degradation of the membranes (a copolymer of sulfonated polystyrene and divinylbenzene). In the late 1960s, DuPont introduced the fluorocarbon, cation exchange polymer, Nafion®. The history and current development of PEM fuel cells follows the community's appreciation of the advantages and disadvantages of Nafion under different operating conditions.

The separator used in a PEM fuel cell must satisfy many design constraints, as outlined in Table I. The most important challenges for PEM technologies have been ionic conductivity, separation of fuel and oxidant, hydration, and stability. Below, the challenges for the membrane are reviewed as PEM fuel cell technology has evolved to serve different needs.

Table I.
Requirements for a Good Membrane Separator in PEM Fuel Cells[1]

- High ionic (protonic) conductivity but low electronic conductivity
- Low fuel and oxidant permeability
- Limited crossover and solvent transport
- Stability, thermal and oxidative
- Low cost
- Good mechanical properties and easy fabrication of fuel cells

The Promise of Nafion - A Brief, Early History to the 1980s

In the mid 1980s, DuPont (Nafion®), Dow, and Asahi (Aciplex® and Flemion®) perfluorosulfonic acid polymers were viewed as unique and nearly optimal materials to serve as separators in PEM fuel cells. The fluorocarbon sulfonic acid polymers sustain proton conductivities on the order of amperes per centimeter square. The resistivity of Nafion membranes, set by ion transport, is ~ 0.1 S cm^{-1}, a few ohms for the typically 178 µm thick films used in hydrogen PEM fuel cells. The fluorocarbon structure of the polymer was thought to provide chemical stability.

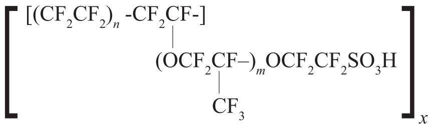
$$\left[\begin{array}{l}[(CF_2CF_2)_n\text{-}CF_2CF\text{-}]\\ \qquad\qquad\qquad (OCF_2CF\text{–})_m OCF_2CF_2SO_3H\\ \qquad\qquad\qquad\quad CF_3\end{array}\right]_x$$

FIG. 1. Structure of Nafion.

The molecular structure of the perfluorosulfonic acid polymers consists of a fluorocarbon backbone with pendant side chains that terminate in sulfonate groups. The structure of Nafion in the protonated form is shown in Fig. 1. For Nafion 1100, the equivalent weight is 1100 g/mol, which is consistent with polymer subunits of *m* equal to 1 and *n* equal to 6 to 7. The structure of the Dow polymers was similar but had a lower equivalent weight, in part, due to the shorter side chains.

The dichotomy of properties associated with the fluorocarbon backbone and the highly ionic sulfonate sites provides unique structures when the polymer is hydrated. The fluorocarbon is a low dielectric material that is correspondingly hydrophobic. Fluorosulfonic acids are typically superacids, and thus highly ionic and hydrophilic. When the membrane is hydrated, the water clusters around sulfonate sites while the fluorocarbon domains tend to segregate from the water domains. This leads to a unique nanostructure within the film. The original structure proposed by Hsu and Gierke,[2,3] based on small angle X-ray scattering studies of silver ions intercalated into a Nafion film, consisted of spherical water filled domains of approximately 5 nm interconnected by narrow channels of 1 nm diameter (see Fig. 2). Although this is a crude approximation of the structure of Nafion, and there is still currently extensive debate as to the structure of the hydrated membrane,[4] this picture suffices as a useful starting point for describing some unique properties of perfluorosulfonic acid polymers. The symposium volume in which Hsu and Gierke's first papers appeared remains an excellent reference on ion exchange membranes, especially Nafion.[3]

One principal advantage of Nafion as a separator is its unique nanostructure. Nafion imbibes water to the extent that hydrated, commercial films contain approximately 30% water based on measured density of approximately 1.8 g/cm^3.[5] This corresponds to a concentration of sulfonic acids in the bulk hydrated polymer of about 1.6 M or about three times that in the water phase. Nafion is superselective in that if the membrane is placed in a solution of electrolyte at concentrations greater than the concentration of exchange sites in the film, the film still strongly rejects anions and extracts cations. Selective cation exchange membranes exclude anions only as long as the concentration of anion exchange sites in the film exceeds the concentration of anions (and cations) in the solu-

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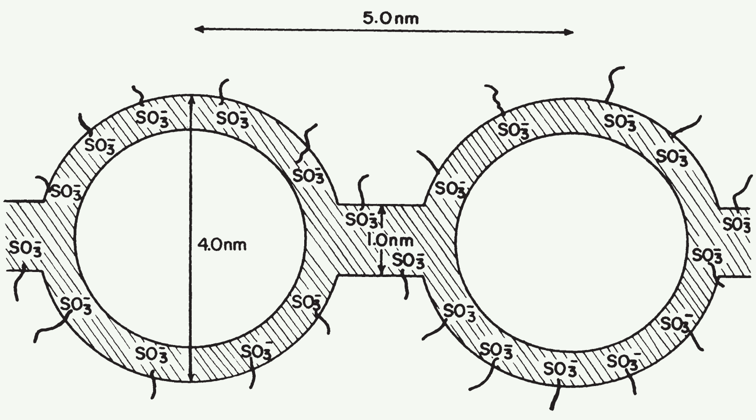

Fig. 2. Cluster network model of Nafion as proposed by Hsu and Gierke. Reprinted from Ref. 2, with permission from Elsevier.

tion. In terms of the Hsu and Gierke model, the membrane is superselective because the high density of sulfonate sites about the narrow interconnecting channels generates sufficient electrostatic repulsion that the solution anions are excluded. The channels coupled with the inverted micellar spheres provide the internal transport pathways that sustain the high protonic conductivity.

Nafion membranes are produced by forming the sulforyl fluoride polymer into sheets and then hydrolyzing to the sulfonate. Once the sulfonate is formed, the membranes swell in various organic solvents, but the material is extremely insoluble. Based on the insolubility and inertness of fluorocarbons, Nafion was thought to be a very stable and robust material. Under pressure and temperature, the sulfonate polymer can be suspended in mixed solvents; these suspensions are used to modify electrodes and are often used in the formation of membrane electrode assemblies of PEM fuel cells to control wetting.

In the mid 1980s, the known liabilities of Nafion in PEM fuel cells were the low glass transition temperature (~105°C) and the cost (currently listed at ~\$700/m^2), largely due to environmental issues associated with the manufacture and disposal of fluorocarbons.

The Realities of Nafion – The 1990s

By the 1990s, concerns about the cost of Nafion were prevalent. But concerns about the limitations that poor oxygen kinetics imposed on PEM fuel cells run on H_2 and either O_2 or air, were increasing. As poor oxygen kinetics is a major challenge for PEM technologies, research has turned to better cathode catalysts and higher temperature PEM systems. Higher temperature systems will improve the efficiency of oxygen reduction. However, the membrane must remain stable and sustain hydration and ionic conductivity at higher temperature. The glass transition temperature of Nafion limits the upper temperature ranges to about 100°C. The useful operating temperature is closer to 80°C because the membrane loses water and thus ionic conductivity at high temperature.

These limitations generated extensive research activity into alternative membranes and composites. The alternative membranes[1] include other perfluorosulfonic membranes, styrene-based systems, poly(arylene ether)s, polyimides, and polyphosphazenes. The challenges for these materials include stability at 120°C and conductivity at 50% relative humidity. Various ionic functional groups have been investigated but the sulfonic acid groups are of high stability and are strongly acidic (*i.e.*, they are good ion conductors). Generally, hydrocarbon linkages to sulfonic acids are more susceptible to oxidation than fluorocarbon bonds.

In parallel with better membranes for hydrogen powered systems, there has been interest in separators for direct reformation fuel cells that use organic fuels. In these cells, the kinetics of the anode dictate system response. The mechanistic complexity of oxidizing organic fuels has limited these systems to lower power output than hydrogen-based systems. The appeals of a liquid fuel are that the fuel can be easily dispensed within the existing infrastructure for octane-based fuels; consumers are familiar with handling liquid fuels; and liquid fuels can be derived from natural gas and biomass. Direct reformation systems have all the membrane requirements of the hydrogen cell plus additional constraints because of interactions between the fuel and membrane. Organic solvents (*i.e.*, fuels) swell Nafion substantially,[2] which causes fabrication problems for the cells. But, more critically, the swollen membrane allows substantial crossover of fuel from the anode to the cathode, thereby reducing cell voltage and poisoning the cathode catalyst. Efforts to modify Nafion have included surface modification of the membrane to reduce crossover (*e.g.*, as with other polymers, metals, and clays and by surface etching); intercalants, such as metals and inorganic salts and oxides, in the membrane to react with permeating organics before they reach the cathode; and formation of composites and blends of Nafion with other polymers. New membranes include fluorinated polymers containing silicon dioxide, fluoropolymers with ether functional groups, and non-fluoropolymers with ether groups and their composites with inorganic oxides. Some success has been achieved but there is little data on long term stability under operationing conditions.

In the 1990s, strong political and social forces impacted the development of PEM fuel cells. In states along the eastern seaboard and in California, regulations were adopted that mandated major auto manufacturers provide low to zero emission vehicles. In 1990, the California Air Resources Board required that a percentage of new vehicles sold must be zero emission: 2% in 1998; 5% in 2001; and 10% in 2003. In 1994, the Partnership for a New Generation of Vehicles (PNGV) was established between the U.S. government and the Big Three auto manufacturers (Daimler Chrysler, Ford, and GM) to develop lower emission vehicles. By 2001, the program and its progeny had expended approximately \$2 B toward that end.

The Current Challenges of Commercially Viable Fuel Cells – The Present

The large injection of funding by the PNGV made fuel cells of more than academic interest and, importantly, provided resources that led to testing for extended periods. The extended testing, interestingly enough, exposed new challenges for commercialization of PEM fuel cells.

Ideally, for oxygen and air cells powered by hydrogen, the reduction of oxygen proceeds by 4 electrons/4 protons to yield water. However, the inefficiencies of oxygen kinetics lead to peroxides by a 2 electron/2 proton process. In fuel cells run for several days, this is not a significant problem. However, in cells run for extended periods and under transient conditions, the peroxides attack the membranes and the catalysts. Membranes, such as Nafion, that are stable for a few weeks under steady state conditions are not stable over a few months under cycling conditions. Given the high stability of fluorocarbons, an organic polymer or composite that will be stable and maintain ion conduction under these more rigorous and commercially appropriate conditions is needed.

Potential Routes to Technological Viability – The Future

The current state of the technology is such that Nafion is an acceptable material for low duty cycle applications. For technologically more demanding systems, such as automotive applications, important membrane issues remain: maintaining ionic conductivity, preventing crossover, and preserving membrane stability. In part, a better cathode catalyst for the hydrogen systems would reduce generation of peroxide. New materials and composites that operate at higher temperatures with higher stability would be useful but are challenging to design. A combination of better cathode catalyst and better membranes may be effective. Perhaps an oxidant other than oxygen is appropriate. Finally, Nafion has remained the material of choice for over three decades because it satisfies some critical requirements for PEM fuel cells. Ultimately, given current catalysts and stack design, Nafion is not sufficiently stable to run fuel cells under heavy duty cycles for protracted periods. Perhaps an alternative embodiment exploits a monomer that can be replaced on a regular basis. For example, an ionomer that is soluble in an organic solvent might be easily flushed from the stack and replaced with fresh ionomer. After all, we are supposed to change the oil in a combustion engine every 3,000 miles! ■

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