

## Chapter 9

# An Overview of Polymer Electrolyte Membranes for Fuel Cell Applications

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While fuel cells have received considerable attention over the last 10 years to 20 years, the history of hydrogen fuel cells dates back to 1838. It would take more than a century before polymers would be implemented as an electrolyte for proton transport (1955) and another 40 years after that before a real renaissance would be sparked that would finally make polymer electrolyte membrane (PEM) fuel cells a conceivable means of electrochemical energy conversion. This chapter covers a brief history of the fuel cell and the use of polymer electrolytes as an ion-transport medium. In addition to an overview of the materials challenges, the various types of polymeric materials being pursued as potential fuel cell membranes are presented. Although this chapter is not an exhaustive review of the literature, it is our hope that it will give the reader an appreciation for the history of PEM fuel cells and the approaches that polymer chemists are taking in order to address the major impediments for wide-spread commercialization of PEM fuel cells.

## Introduction

A fuel cell is an electrochemical device that is capable of converting the stored, chemical energy of a fuel into electrical energy, *i.e.*, electricity, through electrochemical processes. A typical fuel cell consists of three major components including (1, 2):

- 1) a fuel electrode, or anode
- 2) an oxidant electrode, or cathode; and
- 3) an electrolyte.

For a PEM fuel cell, the electrolyte consists of a polymer membrane that is capable of charge transport; a generic scheme is shown in FIGURE 1. In general, the fuel is catalytically oxidized at the anode to produce electrons and ions. While the electrons are diverted to an external circuit to create a current, the positively charged ions are transported through the electrolyte to the cathode where they recombine with the electrons and an oxidant to form exhaust. Fuel cells are typically distinguished by the type of electrolyte used in charge transport. The major classes of fuel cells include: alkaline fuel cells (AFC), solid oxide fuel cells (SOFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), and proton-exchange (or polyelectrolyte) membrane fuel cells (PEMFCs). The latter class, PEMFCs, is the principle subject of the studies presented in this book. It should be noted that some AFCs use polymer membranes and will also be discussed in subsequent chapter(s). Before going into further detail, it is important that the reader have at least a general knowledge of the history of fuel cells and the use of polymers in fuel technology. A detailed historical account of this technological area is beyond the scope of a single introductory chapter on PEMFCs; however, this introduction will serve to give the reader an appreciation for the long history of fuel cell technology. While it is nearly a decade old, Perry and Fuller (3) offer an excellent historical perspective on fuel cell technology in the 20<sup>th</sup> century. Moreover, the Smithsonian Institution is collecting information and developing a website dedicated to the history and workings of fuel cell technology (4).

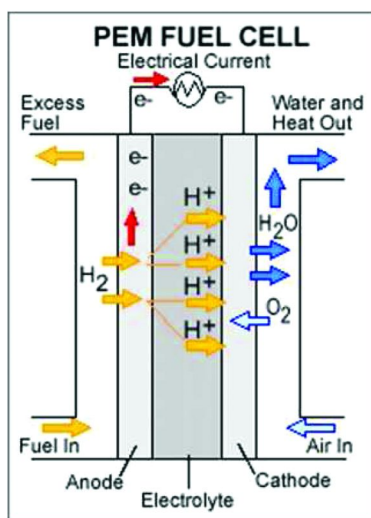


Figure 1. Generic PEM fuel cell schematic (5).

## History of the Fuel Cell

Advances in the understanding of electrochemistry and catalysis in the early 18<sup>th</sup> and 19<sup>th</sup> centuries helped to nurture the discovery of the fuel cell effect and the ultimate invention of the fuel cell (6). The origin of this specific technology, however, can really be credited to the work by Christian Friederich Schönbein (1799-1868) and Sir William Robert Grove (1811-1896). It was the talent and vision of these two scientists that gave the world a technology with significant potential for solving the energy needs of today and tomorrow (3, 7–9).

Schönbein was the first person to report and accurately describe the fuel cell effect in his early 1839 paper entitled “On the Voltaic Polarization of certain Solid and Fluid Substances” in which he reported a current produced through the combination of hydrogen and oxygen, thus the first reported hydrogen fuel cell (10). This publication was followed shortly by an article in which Grove suggested, in a short postscript, that he had found a means to produce electricity through the combination of the constituents of water, that is, hydrogen and oxygen (11).

Despite Schönbein’s early discovery of the fuel cell effect, it is often Sir William Robert Grove to whom credit of the invention of the fuel cell is given. Both men made significant contributions to the understanding of the electrochemistry underlying the fuel cell effect in the early 1840’s leading up to Grove’s 1845 publication that demonstrated the first working 10-cell power generator. An excellent historical account of these events and evidence of the remarkably close and personal relationship that developed between these two men can be found in the book, The Birth of the Fuel Cell by Ulf Bossel (7). Bossel most aptly and succinctly states that to be historically accurate, and fair, one would characterize the events in a way that gives Schönbein the credit for discovery of the fuel cell effect and Grove credit for inventing the fuel cell. In essence, in the years between 1838 and 1845, Schönbein delighted in developing a fundamental understanding of the phenomena giving rise to the effect that he had observed, while Grove put this understanding to use in the development of an energy technology that had, and still has, the potential to revolutionize the way humans produce/convert and consume energy.

Interestingly, it was in 1894 that a scientist named Friedrich Wilhelm Ostwald, later a Nobel Laureate, in his address to the Deutschen Electrochemischen Gesellschaft that was later published as an article in the *Zeitschrift für Elektrotechnik und Elektrochemie* entitled “The Electrochemistry of Today and the Technology of the Future,” spoke about the inefficiency and potential harm of using combustion for producing electricity (12). He saw the potential for storing and producing energy through electrochemical processes, which were quite efficient given the infantile nature of the field at that time. He demanded that mankind must replace the heat engine with electrochemical cells, such as the fuel cell, as a means to convert the stored energy in combustible materials, *i.e.*, coal, into electrical energy. The echoes of Ostwald’s vision can be heard, 117 years later, in the voices of people today who demand that we find alternative, clean, and sustainable means of energy conversion.

## History of PEM Fuel Cells

For the most part, the earliest fuel cells used platinum (Pt) as electrodes and a liquid electrolyte that was usually acidic in nature (*e.g.*, dilute sulfuric acid). In the early work by Schönbein and Grove, the fuel was typically hydrogen with oxygen being the oxidant. However, at the dawn of the 20<sup>th</sup> century, researchers were also pursuing direct-coal fuel cells due to the use of coal as a fuel in combustion engines.

It would not be until the 1950s that polymer materials, or solid-polymer electrolytes, would find their way into a working fuel cell and would be developed and eventually put to use in a technological application. In large part, the development of polyelectrolyte membrane technology was stimulated by the energy needs of space exploration. Because fuel cells operate with relatively high efficiency and are light-weight, they were poised to meet the auxiliary power needs of spacecraft. The first practical fuel cell for this application was invented in 1955 by W. T. Grubb (13–15), a scientist working for General Electric Company, and used an ion exchange (13, 14) resin membrane as the electrolyte. The specific resins used changed in the years from 1959–1967, but ranged from membranes synthesized from the polymerization of phenol-sulfonic acid with formaldehyde, in the early years, to variations of polystyrene sulfonic acid in the mid-to-late 1960s. The patent on this technology, issued in 1959, purported that the fuel cell, using a solid-polymer electrolyte, was capable of operating at room temperature and under atmospheric pressures. The list of properties Grubb ascribed to this cation exchange resin, which gave it the ability to perform well in a fuel cell, would become the target for which decades of polymer chemists since have focused their aim while devising new synthetic routes towards higher performing polymer membranes for fuel cell applications. These attributes include, but are not limited to:

- 1) a good electrolyte (*i.e.*, high ion conductivity)
- 2) a negligible electrical conductivity
- 3) permeable to ions but allow only one type of charge
- 4) resistive to permeation of uncharged gases
- 5) variable membrane area and thickness; and
- 6) good mechanical strength.

Despite their famed use in NASA's Gemini program, these PEMFCs suffered from insufficient proton conductivity, which resulted in poor power output ( $< 100 \text{ mWcm}^{-2}$ ), and poor durability, due to the oxidative instability of the C-H bonds in the polymer chain. To use a term by Costamanga (16, 17), the 'quantum leap' in fuel cell performance and durability hinged on the invention of the perfluorosulfonic acid membrane, Nafion, by E.I. Du Pont de Nemours & Company, Inc. in 1962 (18, 19). Nafion was initially used as a membrane separator in chloralkali cells and it was not until 1966 that Nafion was implemented in an H<sub>2</sub>/O<sub>2</sub> fuel cell. Nafion met the originally-stated criteria for an ideal solid-polymer electrolyte, and it surpassed all other materials in its specific conductivity and its durability – increasing the conductivity by at least a factor

of two and the lifetime by nearly four orders of magnitude – and remains the industry benchmark for PEMFC performance to this day. The specific properties of this material will be discussed in greater detail in later sections.

One would intuit, after such successful demonstrations of the practical use of PEMFC technology, that polymer-based fuel cells would enjoy widespread technological advancements and commercial use as power supplies for any number of applications ranging from portable electronic devices and back-up power stations to fuel cell-powered automobiles. However, this reality did not manifest itself. In fact, if one examines the time-line of patent and publication activity for polymer-based fuel cells (FIGURE 2), there is a surprisingly vast dormancy in activity after the developments of the 1960s and 1970s. In large part, durability and the cost of the membrane materials and the platinum catalyst in the electrodes were, and continue to be, critical factors that inhibited further commercial success.

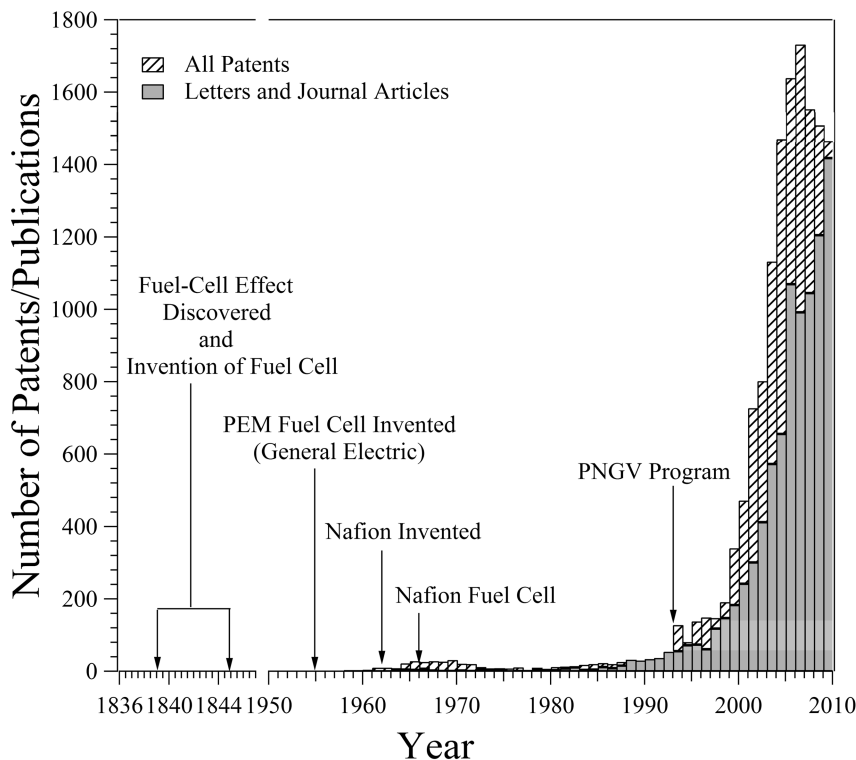


Figure 2. Historical perspective of fuel cell development.

A particularly salient feature of FIGURE 2 is the rapid rise in the number of patents and publications (referencing polymer fuel cells) that occurred in the mid-1990s. There are several factors, both societal and technological, that were

responsible for the genesis of this renaissance in PEMFC technological research. While fuel cell research did not afford any particular prominence during the height of the Energy Crisis of the 1970s, it is likely that means of alternative energy were on the minds of politicians and researchers alike. However, this fact did not stimulate any advancement in fuel cell technology, at least with regards to PEM fuel cells. Undoubtedly, the origins in the rise of PEMFC research activity (circa 1996) can be traced back to the advancements in the fabrication of membrane electrode assemblies (MEA) by researchers at Los Alamos National Laboratory (LANL). Ian Raistrick, Supramaniam Srinivasan, and others developed methods capable of reducing the membrane electrode assembly (MEA) platinum content from  $4 \times 10^{-3} \text{ g cm}^{-2}$  to  $3.5 \times 10^{-4} \text{ g cm}^{-2}$ , a significant advancement in reducing the overall cost of the fuel cell (20, 21). From the mid-1980s to the early 1990s the research team at LANL continued to refine the MEA manufacturing process and made several seminal contributions to understanding the kinetics of the electrochemical processes in PEMFCs, durability testing, and modeling of PEMFC performance.

On the heels of these technological and scientific breakthroughs, the Clinton administration established the Partnership for a New Generation of Vehicles (PNGV) program (22). This large-scale program was a concerted effort sponsored by the United States Federal government and the U.S. Council for Automotive Research (including DaimlerChrysler, Ford, and General Motors (GM)) with a mission to oversee the research and development (R&D) activities for the advancement of state-of-the-art technologies that could lead to increased fuel economy and reduced emissions of a wide range of vehicles. While there were several Federal agencies that participated in the program, the Department of Commerce, Office of the Under Secretary for Technology, was tasked with leading the Federal government's participation. This program was followed by the Bush administration's announcement of the FreedomCAR program in January of 2002. The Department of Energy (DoE) continues to support R&D in the area of fuel cell technology. It is reasonable to infer that these investments helped to spur further technological innovation and development as evidenced by the rapid increase in the number patent and literature publications pertaining to PEMFCs. With this history in mind, several questions come to mind including:

- What is the current state-of-art in membrane technology?
- What are the materials challenges?
- What are the alternative membrane materials?
- What are the future directions?

We hope to offer an overview of these guiding questions in the following sections.

## Membrane Technologies and Challenges

The most cited impediments to world-wide commercialization of PEMFCs in the areas of transportation, stationary, and portable power applications are the high cost and poor durability of PEMFC stacks (23–25). The MEA constitutes

a significant portion of this cost due to the high production cost of the polymer membrane and the use of precious metals, notably platinum, in the catalyst layers (CL). The cost and durability targets for transportation and stationary power applications have been set by the DoE and are shown in TABLE 1. As of 2009 and 2005, respectively, a lifetime of *ca.* 2,500 h has been achieved for transportation (equivalent to *ca.* 75,000 miles) and 20,000 h for station fuel cells. The cost of fuel cell stacks has been reduced drastically over the last decade, dropping from \$275/kW in 2002 to \$51/kW in 2010.

**Table 1. DoE cost and durability performance targets for fuel cell stacks. Goal years in parentheses**

	<u>Cost</u>	<u>Durability/Lifetime</u>
<i>Transportation</i>	\$45/kW (2010); \$30/kW (2015)	>5,000 hrs (2015)
<i>Stationary Power</i>	\$750/kW (2011)	>40,000 hrs (2011)

Researchers are tackling the cost of PEMFCs in a number of ways. The materials used in the catalyst layers (and the catalyst support) and the membranes themselves can be expensive and represent a significant fraction of the cost of a fuel cell stack. Three strategies for reducing the catalyst layer cost that have been identified and are being pursued: 1) reduction of Pt loading (*i.e.*, more efficient use of the catalyst materials), 2) replacing Pt with new, cheaper catalyst materials and alloys (*e.g.*, ruthenium and palladium) and 3) to replace Pt, or other precious metals, with non-precious metal catalysts. In addition, the perfluorosulfonic acid membranes materials typically used can also be expensive because of the chemistry used to synthesize them. For example, a review of solid polymer electrolytes for fuel cells written in 2005 placed the cost of Nafion at \$700 per m<sup>2</sup> (24). The membrane performance targets for transportation applications set by the DoE can be seen in TABLE 2 (26, 27). Polymer chemists are searching for alternative membrane materials that are cheaper to synthesize, but still meet the high performance criteria demanded by the harsh fuel cell operating conditions and that, to date, have been met by perfluorosulfonic acid ionomer-based materials. The various types of membranes are described in a later section.

While durability and cost are identified as two separate challenges facing commercialization of fuel cells, the two factors are actually inter-dependent. While the base cost of the materials is not necessarily a reflection, or related to, the durability of the materials, the overall operating costs of a fuel cell are intimately tied to durability issues. The more often a stack, or stack components, must be replaced, the more expensive it is to operate. Therefore, a more appropriate term might be the *durability-cost* factor of fuel cell commercialization.

**Table 2. DoE technical targets for membranes for transportation applications**

<i>Characteristic</i>	<i>Units</i>	<i>2010 Target</i>	<i>2015 Target</i>
<i>Maximum operating temperature</i>	°C	120	120
<i>Area specific proton resistance at:</i>			
<i>Maximum operating temp and water partial pressures from 40 to 80 kPa</i>	Ohm cm <sup>2</sup>	0.02	0.02
<i>80°C and water partial pressures 25 - 45 kPa</i>	Ohm cm <sup>2</sup>	0.02	0.02
<i>30°C and water partial pressures up to 4 kPa</i>	Ohm cm <sup>2</sup>	0.03	0.03
<i>-20°C</i>	Ohm cm <sup>2</sup>	0.2	0.2
<i>Maximum Oxygen cross-over<sup>a</sup></i>	mA/cm <sup>2</sup>	2	2
<i>Maximum Hydrogen cross-over<sup>a</sup></i>	mA/cm <sup>2</sup>	2	2
<i>Minimum electrical resistance<sup>b</sup></i>	ohm cm <sup>2</sup>	1000	1000
<i>Cost<sup>c</sup></i>	\$/m <sup>2</sup>	20	20
<i>Durability<sup>d</sup></i>			
<i>Mechanical</i>	Cycles w/<10sccm crossover	20,000	20,000
<i>Chemical</i>	Hours	>500	>500

- a) Tested in MEA at 1 atm O<sub>2</sub> or H<sub>2</sub> at nominal stack operating temperature, humidified gases at 0.5V DC.
- b) Measure in humidified N<sub>2</sub>/N<sub>2</sub> at 0.5V DC at 80°C.
- c) Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
- d) Based on MEA chemical stability and metrics and membrane mechanical cycle and metrics.

The durability of the MEA can mean several things. First, one must consider the durability of each component independently and the variety of factors that can lead to degradation. All of the materials in the MEA are subject to chemical, electrochemical, and mechanical degradation processes (23). The catalyst and the catalyst support undergo electrochemical degradation, which can ultimately lead to mechanical failure. Likewise, the membrane lifetime is reduced due to chemical and electrochemical degradation (23–25, 28–30). Ultimately, this molecular-level degradation can lead to mechanical failure of the membrane as well. In addition to the functional segments of the MEA, the durability of other components that are part of fuel cell operations, including gaskets and seals need to be carefully understood.

Another key factor when considering the durability and performance of a PEMFC is the effect of contaminants on performance (23, 30). Again, contamination can occur throughout the MEA and come from the fuel (hydrogen), the oxidant (air), or other components present in the cell stack. At the anode,



impurities in the fuel feed can lead to degradation and low performance. Typical impurities include CO, CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, and CH<sub>4</sub>. At the cathode, NO<sub>x</sub> and SO<sub>x</sub> are the foremost causes of contamination. Lastly, metal ions such as Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Cr<sup>3+</sup> coming from the bipolar plates can leach into the PEM causing chemical and mechanical degradation and failure. The most recent review by Zamel and Li cover these issues in detail (30).

## Polyelectrolyte Membranes for Fuel Cell Applications

A wide variety of polymer types have been developed and studied for application as proton exchange membranes. These materials include, but are not limited to, poly(perfluorosulfonic acid)s, polystyrene derivatives, poly(arylene ether)s, polysulfones, polyimides, and engineered block copolymers (31)–(38). Although different applications for proton exchange fuel cells, *i.e.*, stationary, portable, or automotive power, have specific operational and material requirements, several material properties are key to high performance membranes. In all applications, materials with high proton conductivity, low fuel crossover, good mechanical and chemical stability, and manufacturability are needed for optimal performance. In addition to these requirements, materials must have low enough costs for commercial viability. Anion exchange materials containing ammonium, phosphonium, and sulfonium groups, which are being studied for application in alkaline fuel cells, must also meet analogous requirements as their proton exchange membrane counterparts.

One particularly difficult challenge for PEM materials development is achieving high proton conductivity with low water content. Because of the nature of proton mobility in these materials, there is an inherent tradeoff between water content and conductivity (39). For example, there is a minimum level of hydration to achieve a desirable conductivity (*e.g.*,  $\sigma = 0.1$  S/cm,  $\lambda$  (moles of H<sub>2</sub>O/moles of SO<sub>3</sub>H) = 22). However, maintaining a high water content during fuel cell operation complicates water management issues and associated support systems. These issues are a large part of the motivation to develop high performance anhydrous membrane materials (40). A similar tradeoff between ionic conductivity and methanol permeability is an important issue in the design of materials for direct methanol fuel cells.

A broad overview of the basic material classes used in fuel cell membranes is presented here as an introduction to the development milestones in the area. This section is not an exhaustive review, and the reader is referred to additional resources for more detailed information. These material classes represent a sampling of the range of materials studied for application in PEMFCs. Extensive efforts to modify and improve these base materials continues to drive further development in this field.

### Perfluorosulfonic Acid Ionomers (PFSA)

Nafion, a poly(perfluorosulfonic acid), is the most widely studied proton exchange material; its chemical structure is shown in FIGURE 3. Nafion exhibits

excellent thermal and chemical stability. Nafion consists of a perfluoroethylene backbone with flexible perfluorinated vinyl ether side chains terminated by a sulfonic acid group. Many studies have investigated the molecular-scale structure of this complex material, which contains ionic clusters and crystallites in an amorphous perfluorinated, Teflon-like, matrix (41)–(44). The specific morphology of Nafion can strongly influence its performance characteristics, and the reader is referred to additional information on this subject (35). Similar materials to Nafion have been developed by other chemical manufactures, including Flemion by Asahi Glass, Aciplex by Asahi Chemical, and Aquivion by Solvay Solexis (45, 46).

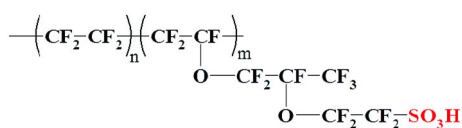


Figure 3. Nafion chemical structure.

Nafion is also available as dispersions in a range of solvents, most commonly in water and alcohol mixtures. These dispersions are used to create thin films of Nafion and in the preparation of catalyst layers in MEAs. The properties of these “re-cast” Nafion materials depend on the preparation conditions and can be significantly different than the commercial melt-processed films (47)–(49). Early work by Moore and Martin showed that recast Nafion material, without thermal annealing, had poor mechanical properties as compared to the melt processed films (50). Ma *et al.* have shown that the molecular conformations of Nafion in dilute dispersions and the morphology of the membranes prepared from these dispersions are strongly influenced by the solvent quality (51). While these studies focused on recast materials of bulk-like thickness, work continues on understanding the properties of thin films created using these dilute dispersions (52).

Despite Nafion’s strengths, the material is expensive and exhibits poor proton conductivity at low water contents and high temperatures, which limits the ideal operating range. Extensive efforts have focused on improving the performance of Nafion, including blends, patterning, nanofiber formation, and the incorporation of moieties, such as zeolites, silica and titanium dioxide, to improve water retention (53)–(55). Reinforced PFSA membranes, such as those developed by Gore Fuel Cell Technologies based on e-PTFE, have been shown to improve the durability of Nafion by up to an order of magnitude and are considered state-of-the-art materials (56, 57). Because of its unique performance characteristics and the extensive studies focused on this material, Nafion is likely to remain the primary benchmark for PEM materials for the foreseeable future. New multiple acid side chain (MASC) polymers with low equivalent weight are being developed by 3M (58). By adding acidic groups to the side chains, the backbone regions of these perfluorinated materials are still able to crystallize and thus maintain mechanical strength. The use of nanofiber supports has also been shown to reduce swelling and increase the mechanical strength of these MASC polymers under hydrated conditions (59). This approach is aimed at developing

materials with enhanced conductivity as compared to Nafion while maintaining mechanical integrity in very low equivalent weight materials.

## Polysulfones and Phosphazenes

Researchers seeking novel materials that are competitive with Nafion have made significant progress in the development of novel hydrocarbon PEMs based on sulfonated aromatic polymers, including polystyrenes, polysulfones, polyimides, polyphosphazenes, poly(arylene-ether)s, and others (34, 60, 61). These hydrocarbon-based materials offer promising routes to high performance PEMs at lower cost than the perfluorinated Nafion.

The most common method for preparing these materials uses electrophilic aromatic sulfonation to modify existing polymers. A classic example of this material class is sulfonated and crosslinked polystyrenes, which were part of the Gemini space program. This post-polymerization modification technique offers limited control over the location and degree of sulfonation, and may create undesired byproducts or degrade the polymer structure. However, the relative simplicity and applicability of this technique have driven many studies focused on understanding the influences of this modification on material properties.

To circumvent the problems associated with post-modification methods, McGrath's research group at Virginia Tech popularized the direct copolymerization of sulfonated monomers (34). Using mono- and di-sulfonated monomers, copolymers could be synthesized in any composition desired. This technique was used to create a wide range of sulfonated poly(arylene ether) materials. The conductivity and water uptake of these materials were shown to be directly related to the degree of sulfonation. Phase separation and significant swelling were observed in materials with high sulfonation levels, thus highlighting the need to balance water uptake and mechanical stability with proton conductivity. The variety of monomers available for this synthetic route has led to many variations in the chemistry of these materials. Because many of the monomers used to create these materials are also available at low prices and easily produced on a commercial scale, these materials offer potentially less expensive proton exchange membranes. Efforts have also been extended to include fluorinated monomers (32).

Another class of PEM materials that offers a wide range of possible macromolecular architectures is polyphosphazenes, which consist of a backbone of alternating phosphorus and nitrogen atoms with side groups attached to each phosphorus atom. The first PEM materials based on polyphosphazene chemistry were from sulfonated poly(aryloxy phosphazenes) (62). Additionally, Allcock *et al.* synthesized phosphonated poly(aryloxy phosphazenes), which showed significantly lower methanol crossover as compared to Nafion (63).

It is important to keep in mind that when comparing the performance characteristics of materials that have significantly different densities, such as hydrocarbon-based and perfluorinated materials, it is often more appropriate to use volume-based parameters, rather than mass-based parameters (64). Kim and Pivovar have developed a methodology for making meaningful comparisons between dramatically different materials. The effects of morphology on proton

conductivity and performance should also be considered in any comparison. Many hydrocarbon polymers show sufficiently high proton conductivities only in materials with high ion-exchange capacities, which exhibit significant water uptake and decreased mechanical strength due to swelling. Improving the dimensional stability and proton conductivity of aromatic polymers are critical issues in the design of new materials.

## Block Copolymers and Blends

It is generally understood that proton transport through ionomers is associated with the ionic network within a material, and the transport properties are intimately related to morphology of this network, *i.e.*, poorly connected ionic domains do not facilitate fast proton transport while materials with an interconnected path through ionic channels can exhibit high conductivities. In many random copolymers and post-sulfonated materials, the size and connectivity of these ionic nanostructures are poorly controlled. One approach to create and control nanophase separation is through the use of block copolymers with concentrated ionic blocks along the polymer backbone (31). This type of structural architecture, with the ionic block facilitating transport and the nonionic block providing mechanical strength, enables the development of specifically engineered materials. By decoupling these performance requirements into different segments of the polymer chain, one can start to unravel how specific molecular structures affect different aspects of the material. Furthermore, by controlling the molecular mass of each component, the size scale of the phase separated regions can be tailored to some degree. Balsara and Beers recently summarized efforts to determine the ideal size and geometry of proton conducting channels; they report that channels with dimensions less than 6 nm in width are ideal for proton transport (65).

While sulfonated block copolymers generally show increases in proton conductivity with IEC and hydration, consistent with other polymer systems, changes in morphology with IEC or hydration can also significantly influence transport and performance properties. A morphological transition from periodic lamellar to a nonperiodic structure in sulfonated poly(styrene-*b*-(ethylene-*r*-butylene)-*b*-styrene) increased proton conductivity by an order of magnitude, as reported by Kim *et al.* (66). This significant increase in proton conductivity was realized by adding methanol to tetrahydrofuran as the casting solvent. Similar changes in conductivity with morphology were reported for sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) (67). Although these non-equilibrium structures are difficult to predict, it is important to develop an understanding of the factors that control these kinetically trapped morphologies due to their strong influence on performance. Through systematic studies on a series of polystyrene sulfonate-*b*-polymethylbutylene (PSS-PMB) block copolymers, Balsara *et al.* have established relationships between morphology, water uptake, and ionic conductivity (68–71).

With aims to harness possible synergistic effects of miscible polymer blends, blended systems have also been studied for application as fuel cell membranes (72). For example, poly(vinylidene fluoride) (PVdF) is miscible under certain conditions with Nafion; however, the addition of PVdF reduces water uptake and

proton conductivity. Song *et al.* demonstrated improved performance of Nafion/PVdF blends by chemical modification of the PVdF phase (73). Studies on other materials such as blends of sulfonated poly(ether ketone ketone) polymers with different ionic exchange capacity showed that the ratio of proton conductivity to water sorption could be optimized. Optimization of the tradeoff between these two factors was attributed to percolative pathways for proton transport, which were created by the co-continuous morphology of the blended system (74, 75).

## Anhydrous Proton Conducting Membranes

Elevated temperature fuel cell operation,  $>120\text{ }^{\circ}\text{C}$ , offers several advantages over lower temperature operation, including: increased tolerance to contaminants such as carbon monoxide, faster electrode kinetics, and streamlined water/heat management (40). However, because water contributes to the network for proton conduction in PEMs, conductivity decays rapidly at temperatures above  $100\text{ }^{\circ}\text{C}$  as the material dehydrates. Two possible ways to resolve this issue are to replace the water with a higher boiling point solvent or to immobilize a proton solvent within the material. Furthermore, membrane stability can also be compromised at high operating temperatures; requiring development of materials with improved high-temperature strength for these applications (23).

One of the most prominent candidates for high-temperature PEM fuel cell applications is phosphoric acid doped polybenzimidazole (PBI) membranes (40). Early development of these materials at Case Western Reserve University in the 1990s showed their promise in fuel cell membrane applications (76). PBI is capable of incorporating large amounts of phosphoric acid from dilute aqueous solutions. Increasing acid concentration in PBI membranes increases conductivity, but also lowers mechanical strength. Wainright *et al.* reported that the mechanical properties of the membrane are no longer sufficient at acid concentrations higher than five acid molecules per polymer repeat unit (76). While early work on these materials incorporated acid molecules by immersing preformed membranes in solutions, more recently, doped PBI films were synthesized using a sol-gel process; these materials showed promising fuel cell performance at temperatures above  $150\text{ }^{\circ}\text{C}$  using a non-humidified feed gas (77). Additionally, this material was shown to give stable operation for  $>1000\text{ h}$ . Some concerns regarding the low temperature performance of these material types question their performance under cold start-up conditions in applications such as transportation. Also, the long term retention of phosphoric acid in such materials also has to be proven under appropriate operating conditions.

Another approach to creating anhydrous proton conducting membranes is to covalently link heterocyclic molecules to polymeric materials. Heterocycles such as imidazole, benzimidazole, and pyrazole are good proton solvents and due to their amphoteric nature and high boiling temperatures, they are suitable replacements for water within a PEM material (78). Because proton transport in these materials is likely facilitated by structural diffusion, flexible spacers are often used to attach these molecules to increase their mobility within the system. Studies on model compounds, including phosphonic acid groups, sulfonic acid groups, and imidazole groups, at low humidity and temperatures from  $120\text{ }^{\circ}\text{C}$

to 160 °C identified phosphonic acid groups as the most suitable additive for improving proton conductivity (79). The high proton conductivity in the dry state of this material was attributed to high degrees of self-dissociation and dynamical hydrogen bonding. A straightforward addition of phosphonic acid into a polymer system is poly(vinylphosphonic acid) (PVPA) (80). Although PVPA exhibits good proton conductivity, it has poor mechanical properties due to its low glass transition temperature; therefore, researchers are continuing along this path by incorporating aromatic groups into the polymer structure to improve material stability needed for practical applications (81, 82).

## Anion Exchange Membranes

The potential advantages of alkaline fuel cells as compared to proton exchange membrane fuel cells have recently generated great interest in anion exchange membranes (AEM)s. In addition to benefits of reduced fuel crossover, improved water management, and a wide range of fuels, perhaps the greatest benefit of alkaline fuel cells is that they have the capability to operate with non-noble metal catalysts (9, 83). The cost savings opportunity associated with using catalysts other than platinum is a significant factor in the drive for development of AEM materials. A recent review categorized the current AEM materials of interest into three classes:

- 1) heterogeneous membranes containing ion-solvating polymers; organic-inorganic membranes
- 2) interpenetrating polymer network membranes, and
- 3) homogeneous membranes (9)

Each material type has specific advantages and disadvantages for application in alkaline fuel cells, and a dominant high performance material, such as Nafion in the case of PEM fuel cells, is not apparent.

One of the most critical issues with the use of AEMs in alkaline fuel cells is chemical stability. Commercially produced AEMs are typically created by radiation-induced grafting and mostly based on crosslinked polystyrene materials (9). Unfortunately, these materials are not highly stable in electrochemical or alkaline environments. Due to the nucleophilicity of the hydroxide anion, the cations present in these materials are susceptible to several degradation mechanisms. Furthermore, the formation of carbonates from CO<sub>2</sub> that may be present during operation can reduce conductivity; however, because there are no mobile cations, the formation of solid precipitate is eliminated by using a membrane instead of a liquid electrolyte. In addition to the development of novel polymers that are resistant to these degradation pathways, several crosslinking strategies have been applied to improve chemical and thermal stability of AEM materials (83).

Understanding the transport behavior of AEM materials is also important in developing optimized materials for this application. Hibbs *et al.* compared the transport properties of AEMs synthesized from chloromethylated polysulfone and PEMs such as sulfonated polyphenylenes and Nafion (84). Although water

mobility was higher in the AEMs—based on water self-diffusion behavior—they exhibited lower conductivity and water permeability than the sulfonated PEMs. The phase-separated morphology of the PEM materials was hypothesized as the reason for the greater conductivity of these materials despite slower local water mobility as compared to the AEMs. Clearly, understanding the influence of morphology on transport and performance characteristics is essential for further development of all material types for fuel cell applications.

## Summary and Outlook

Fuel cells have the potential to become an important large-scale energy conversion technology for a variety of applications including stationary and portable power and transportation. Significant achievements in the development of polymer electrolyte materials and membrane electrode assemblies have greatly improved the viability of this technology at an industrial scale. A wide variety of materials have been studied for application in PEM fuel cells, all with some advantages and disadvantages. One of the most significant road blocks to the commercialization of current PEM fuel cells is cost; however, if production volume discount projections are correct, the price of PEM fuel cells will decrease dramatically as they begin to enter the market in larger quantities. Furthermore, researchers are investigating the design and synthesis of new polymeric materials that can be produced at a lower cost while maintaining the criteria for high performance PEM materials. Durability continues to be another significant issue that is being addressed by researchers by seeking to understand the complex degradation mechanisms of these materials under operational conditions in order to find ways to mitigate failure. Support for continued materials and device development, in addition to support for fuel infrastructure, will be required for fuel cell technologies to reach their full potential.

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