Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation

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Article Outline

Glossary

Three-phase boundary Region in the electrode where protons from the ionomer, electrons from the electrically conducting Pt and/or carbon, and reactant gases meet.

Electrolyte membrane A solid polymer ion-conducting membrane used in the center of the fuel cell membrane electrode assembly. Fuel cell electrocatalyst A catalyst that catalyzes either the oxidation of the fuel or the reduction of oxygen in a fuel cell.

Equivalent weight A measure of the acid content of an ionomer in the units of grams of polymer per mole of acid. Gas diffusion layer A carbon paper or cloth used as a current collector in fuel cells that can allow the passage of reactant gases and product water to and from the electrodes.

Hydrogen oxidation reaction (HOR) Electrochemical oxidation of H_2 at the anode.

Ionomer A copolymer of an ion-containing monomer and a nonionic monomer, typically not soluble in water. Membrane electrode assembly (MEA) An ion-conducting membrane sandwiched between two electrodes, an anode at which fuel oxidation occurs, and a cathode at which oxygen reduction occurs.

Oxygen reduction reaction (ORR) Electrochemical reduction of O_2 at the cathode. Flooding Liquid water collecting within the electrodes or current collectors, impeding the flow of gases to the catalyst surface.

Perfluorinated sulfonic acid-containing polymer (PFSA) A fluorinated sulfonic acid-containing ionomer. The most commonly used polymer in proton-exchange fuel cell membranes today.

Definition of the Subject

Proton-exchange membrane fuel cells (PEMFCs) together with hydrogen represent an important storage and utilization technology for energy generated from renewable sources such as wind, solar, geothermal, or hydroelectric. This is due in part to their high energy density, low operating temperature, rapid start-up, modular design, flexibility of scale (a few watts to hundreds of kilowatts), and the absence of any point-of-use emissions. One barrier to commercialization and widespread acceptance of this technology is cost, a situation fairly common with the introduction of a new technology. Over the past decade, much work has been done, and very significant progress has been made, in bringing down the manufacturing cost of fuel cell systems [1].

Manufacturing processes have been optimized, volumes manufactured have increased, less expensive materials have been demonstrated, system efficiencies and power outputs have been increased, and the amount of precious metal catalyst required to generate a kilowatt of power has been reduced dramatically. All of these features have contributed to significant cost reductions. In the case of the precious metal catalysts, one of the major costs, a fuel cell stack that can generate enough power for an automobile can now be built using less than 30 g of platinum catalyst (about three to four times as much precious metal as is used in vehicles today), and the auto industry target of 10 g per vehicle appears within reach, and fuel cell vehicles are beginning to appear on our roads [2–4].

There is still work to be done. One area where important improvements are currently being made is in developing materials and constructions that address the need of today's PEMFC systems for high levels of humidification during operation. Materials currently used in PEMFCs require water for optimum performance. The electrolyte membranes require a relatively high level of hydration to provide sufficient conductivity for high performance. The electrodes in use also require water, both to provide ionic conductivity within the electrode and between the electrode and the electrolyte, as well as to maintain high electrocatalytic activity for high efficiency.

This thirst for water within the fuel cell requires strict water management, imposing limitations on the system design and adversely affecting manufacturing cost. Reactant gases entering the cell often must be humidified, adding the expense of humidification equipment and the parasitic power loss from its operation. Toyota has overcome these issues in the Mirai fuel cell car where the humidification equipment is eliminated [5]. This is achieved by the use of reinforced membranes that are 1/3 of the thickness of previous PEMs allowing back diffusion of product water from the cathode to the anode. These thinner membranes, when the inlet gases are introduced in counter flow, allow humidification of the inlet air from the water exhaust from the H_2 fuel side across the membrane. In addition, cell temperature must be carefully controlled, as overheating can cause the cells to dry out, and so larger capacity cooling systems or radiators are required. This must be balanced with the fact that excess cooling or over humidification can cause water vapor formed in the electrochemical reaction to liquefy and collect within the electrodes or current collectors, impeding the flow of gases to the electrodes, a phenomenon called flooding. These requirements of careful control of humidification and temperature in fuel cells are not consistent with the need for a robust, inexpensive power source. New materials, including new membrane materials and catalysts that are less dependent on water, are needed to address this limitation.

Introduction

For the last few years, there has been a growing, worldwide public focus on the increasing use of energy. One cannot pick up a newspaper or watch a television news program without being exposed to stories about the growth in the need for energy and the economic and environmental cost of that growth. Concerns about energy cost, energy security, and environmental factors (notably climate change) are driving many toward a shift to cleaner, cheaper, and more sustainable methods of generating and using energy. Much of this discussion has centered on the generation of energy, through the more efficient use of fossil fuels, nuclear energy generation, or renewables such as solar and wind energy. There is also growing recognition that if a movement to more sustainable methods of generating energy is to be made, a change in the way of transporting and storing energy will also be required.

An important area of energy technology that has received attention is the area of energy storage. Advanced batteries, capacitors, pumped hydroelectric, compressed air, flywheels, and other methods of energy storage are being considered [6]. As stated above, many believe that proton-exchange membrane fuel cells (PEMFCs) together with hydrogen represent an important energy storage and utilization technology for a number of application areas to allow the transition

away from fossil fuels. For this reason, significant research and investment in this technology have taken place over the last two decades. PEMFCs are beginning to find use in certain emerging applications, such as backup and primary power supplies for telecommunications, powering material handling fork trucks and providing electricity in remote, off-grid locations. While these represent relatively low volumes of systems in the greater energy market, they are an enabling first step, which is important for the introduction of fuel cells into a marketplace where they must compete with established technologies.

Another application of PEMFCs that has received much media attention and many research dollars over the past few years is transportation. Fuel cell-powered vehicles are now commercially available but still limited to 3000 commercial vehicles sold as of the summer of 2017; they are seen by many as the "end game" for renewable energy-powered vehicles [4]. Hydrogen fuel cells for powering automobiles are attractive for several reasons. Their high energy density can provide driving ranges of 250 miles or more, and compressed hydrogen tanks can be refilled easily in less than 5 min. This allows automakers to provide vehicles with essentially the same functionality as drivers enjoy today. However, the strict limitation on weight and volume in automotive applications, as well as the variation in power requirements during use, mean that these systems must run efficiently and reliably under a wide range of temperatures and humidification levels. The current limitations on temperature and humidification require excessively large cooling systems, or radiators, and humidifiers, which make meeting cost and efficiency targets more difficult.

In addition to the utility of hydrogen for storing energy from renewables such as wind or solar, the conversion of hydrocarbon feedstocks such as renewably derived methane or biomass into hydrogen can be an energy-efficient way of utilizing these resources. Currently, the least expensive route to hydrogen is from the reforming of natural gas, a process that initially produces a mixture of hydrogen gas, water, and carbon dioxide with a high carbon monoxide (CO) content. At the current relatively low temperature of operation of the

PEM fuel cell, 80 °C, CO is a severe poison to the Pt catalyst on the fuel cell anode. It is, therefore, necessary to reduce the CO content of the hydrogen fuel to a few parts per million by use of water gas shift reactors and a final gas cleanup stage that may be a hydrogen-selective membrane, pressure swing adsorption, or a preferential oxidation reactor. Each of these additional unit operations adds expense to the hydrogen production process. If hydrogen from the reforming of biomass is to be cost competitive, then the tolerance for CO on the catalyst must be improved so that less expensive less pure hydrogen can be utilized. One method of doing this is to operate the fuel cell at elevated temperature, e.g., a phosphoric acid fuel cell operating at >180 °C can tolerate a reformed hydrogen fuel containing 2% of CO. The operation of PEM fuel cells at elevated temperatures would, therefore, enable the utilization of biomass-derived hydrogen at a price competitive fuel cost.

For the rate of commercialization of PEMFCs to continue to increase, system costs must continue to decrease. One way to do this is to eliminate the fuel cell temperature and humidification requirements described above, allowing operation over a wide range of temperatures without the need for humidification of the incoming gases. To do this, new materials are needed. These include new ion-conducting materials for membranes and electrodes and new catalysts that can function with less water. This entry will review how these materials function in a PEMFC and some of the approaches to new materials that may overcome the humidification and temperature barriers.

Proton-Exchange Membrane Fuel Cells

A fuel cell is an electrochemical cell that oxidizes a fuel and reduces oxygen to provide electrical energy. It is similar to an engine in that you provide fuel and air to generate energy, but rather than producing heat to produce mechanical energy, it is similar to a battery in that it is an electrochemical cell that produces electricity. The efficiency of electric motors approaches 99%, so this loss is often neglected. A variety of fuels can be used depending on the type of fuel cell. High-temperature fuel cells, such

as solid oxide fuel cells, can use a wider assortment of fuels because the electrocatalysts are more efficient and less prone to poisoning at these higher temperatures, up to 1000 °C. These fuels include hydrogen, alcohols, and hydrocarbons such as methane. Fuel cells that operate at lower temperatures are typically restricted to using fuels that are more easily oxidized, such as hydrogen or methanol. PEMFCs fall into this class. PEMFCs use a polymeric ion exchange membrane as an electrolyte and operate at lower temperatures, typically up to about 80 °C.

A schematic of the cross section of a single cell, often called a *membrane electrode assembly* (MEA), is shown in Fig. 1. The electrolyte membrane is at the center of two porous, catalyst-containing electrodes. The electrodes are typically formed from carbon-supported platinum particles. These carbon particles are held together by a small amount of an ion-conducting polymer, which act as both a binder and an ion conductor, allowing protons to move through the electrode. Newer types of electrode structures that allow for improved catalyst efficiency and durability are being introduced [7]. This three-layer construction is then positioned between two porous gas diffusion layers that also act as current collectors. Hydrogen is supplied to the negative electrode, or anode, and oxygen, usually in the form of air, is supplied to the positive electrode, or cathode. The product water is formed at the cathode.

A PEMFC system typically comprises a fuel cell stack where MEAs are stacked between electrically conductive bipolar plates that have flow fields embedded in them, allowing the reactive gases to be supplied to the catalyst surface and allowing the reactant water to be carried away. The area of the MEA determines the amount of current that can be passed through a cell, and the number of cells in the stack determines the voltage. Together, these define the power the stack is capable of providing.

To allow PEM fuel cells to operate under the hotter, drier conditions required for widespread use in applications such as automobiles, new materials are needed. These include new electrolytes with higher proton conductivity and improved durability at low relative humidity (RH) and at higher temperatures. New electrodes that can provide adequate performance with less water are needed.

Electrolyte Membranes

The electrolyte in a PEMFC, as the name implies, is a proton-exchange membrane, or PEM. It functions by allowing transport of protons from the negative to positive electrode and as a physical barrier to prevent shorting of the electrodes and crossover of the reactant gases. The requirements

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 1 A schematic representation of the cross section of an MEA
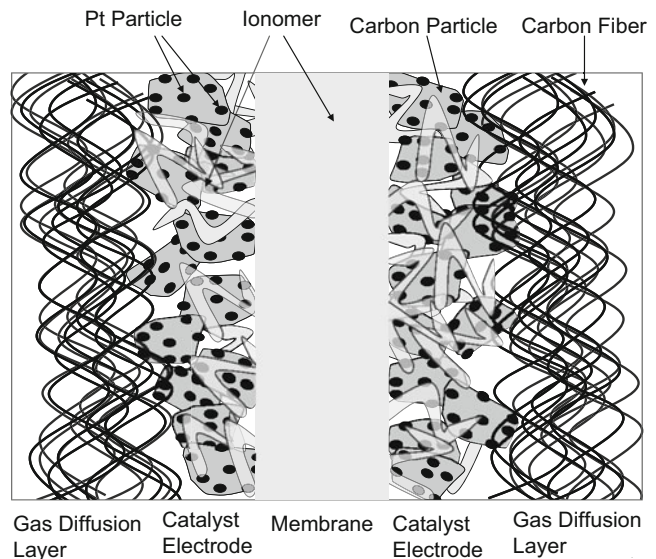
for an electrolyte membrane in a PEMFC typically include the following:

- High proton conductivity
- Low permeability to reactant gases
- Good mechanical properties both dry and equilibrated with water
- Stability toward leaching of components by liquid water
- Excellent chemical stability (hydrolytic and oxidative)
- Reasonable cost
- The ability to form stable intimate interfaces with the electrodes

A variety of types of materials have been used in electrolyte membranes for PEM fuel cells. Most of these fall into two classes: basic polymers that have been imbibed with an acid and polymers with acidic groups attached.

In the first category, the most commonly used polymers for this are polybenzamidazole (PBI) or analogs imbibed with phosphoric acid [8]. This type of membrane was developed at Case Western Reserve University in the mid-1990s [9]. These membranes are known to have good conductivity at very high temperatures, up to 200 °C, and membranes with high phosphoric acid contents and increased conductivity combined with good mechanical properties have been prepared [10]. MEAs comprising such membranes are commercially available from Advent Technologies and Danish Power Systems.

There are drawbacks to using PBI/Phosphoric acid-based membranes in many fuel cell applications. The highly water-soluble phosphoric acid leads to it being easily leached out of the membrane by liquid water, preventing use in applications where the cell could experience higher humidification or lower temperatures. The phosphoric acid also absorbs to the platinum catalyst surface, inhibiting the electrode kinetics, particularly on the oxygen electrode. To overcome this, high levels of expensive platinum catalysts are required for adequate fuel cell performance. It should be stressed that while PBI/Phosphoric acid-based membranes have drawbacks that prevent their widespread use, they are the only commercially available membranes that can be used in the temperature range between about 120 °C and 200 °C.

The majority of PEMs used today are from the second class of polymers, those with pendent acidic groups. Specifically, most polymers currently used in PEMs are typically members of a class of polymers called *ionomers*. An ionomer is a copolymer of a strong acid-containing monomer and a nonionic, neutral monomer [11]. When the neutral monomer is relatively nonpolar, ionomers will adapt a phase-separated morphology, where the ionic groups can bind tightly together into ionic aggregates or clusters. These clusters have a significant impact on the physical properties of the ionomer, often behaving as physical cross-links and stiffening the polymer [12]. A few examples of ionomers of this type are commercially available, such as DuPont's Surlyn™, a copolymer of ethylene and a salt of methacrylic acid, which is used in several applications, including the coating on the outside of golf balls.

In order for the protonated form of an ionomer to be suitable for use in a fuel cell, it must be chemically and mechanically stable enough to survive the chemically aggressive, oxidizing environment of a fuel cell. Oxidizing species such as peroxides can be formed during operation, which attack and chemically degrade the membrane [13]. Simultaneously, the membrane is mechanically stressed from the fluxuations in water content resulting from variations in current density and temperature. These combined can cause the membrane to fail, leading to gases crossing over and catastrophic cell failure. For this reason, ionomers used in fuel cells today fall into two categories of polymers that have sufficient chemical stability and mechanical properties. These are perfluorinated sulfonic acid-containing polymers (PFSAs) and aromatic backbone polymers with pendent sulfonic acid groups.

PFSAs

Perfluorinated sulfonic acid-containing polymers (PFSAs) are the most commonly used membrane materials in fuel cells today. Membranes made from these ionomers provide the benefits of highly acidic pendant acid groups for high proton conductivity, good mechanical properties, excellent

chemical stability, and fairly low cost. The first PFSA used in PEMFCs was DuPont's Nafion™, originally developed in the 1960s for brine electrolysis to produce chlorine [14]. Since then, several other PFSA membranes have been developed and introduced for use in fuel cells [15]. All of these are copolymers of tetrafluoroethylene (TFE) and a sulfonic acid-containing monomer. The chemical structures of some of these polymers are shown in Fig. 2.

When enough acid groups are present in the ionomer, the very hydrophilic sulfonic acid aggregates will absorb water. These hydrated acid groups can provide a continuous, acid-rich, hydrated pathway through the polymer. For PFSAs, in addition to the ionic regions, the TFE segments in the backbone provide another structural feature of the polymer. If the ratio of TFE units to acid-containing monomers is high enough to provide TFE runs of sufficient length (about four or more TFE monomer units), these can crystallize, much like the highly crystalline polymer, polytetrafluoroethylene. These crystallites in the hydrophobic region of the polymer provide significant mechanical stabilization to the membrane. The amount of acid contained in the membrane is typically expressed as *equivalent weight* (EW), the number of grams of polymer required to provide one mole of acidic protons. For traditional PFSAs such as Nafion™, this value is in the range of 1000–1100. This gives a ratio of TFE to acidic monomers of about 5.5–6.5, enough to provide some stabilizing backbone crystallinity. Such polymers have a good combination of proton conductivity and mechanical properties when fully hydrated. Much work has been done over the years to provide a detailed understanding of the structure of PFSAs, and this is still an active area of research. A comprehensive review on the subject has been written by Mauritz and Moore [16] and recently updated by Kusoglu and Weber [17]. A generalized representation of a hydrated PFSA structure is shown in Fig. 3.
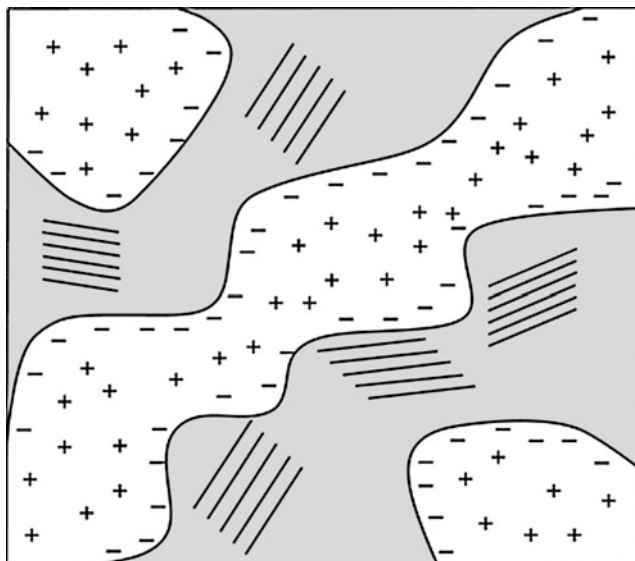

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 2 Structures of some PFSA's. Polymer 1 is available from DuPont (Nafion™), Asahi Glass (Flemion™), and others; Polymer 2 is the short-side-chain ionomer developed at Dow, currently available from Solvacore; and Polymer 3 is the ionomer available from 3 M Company
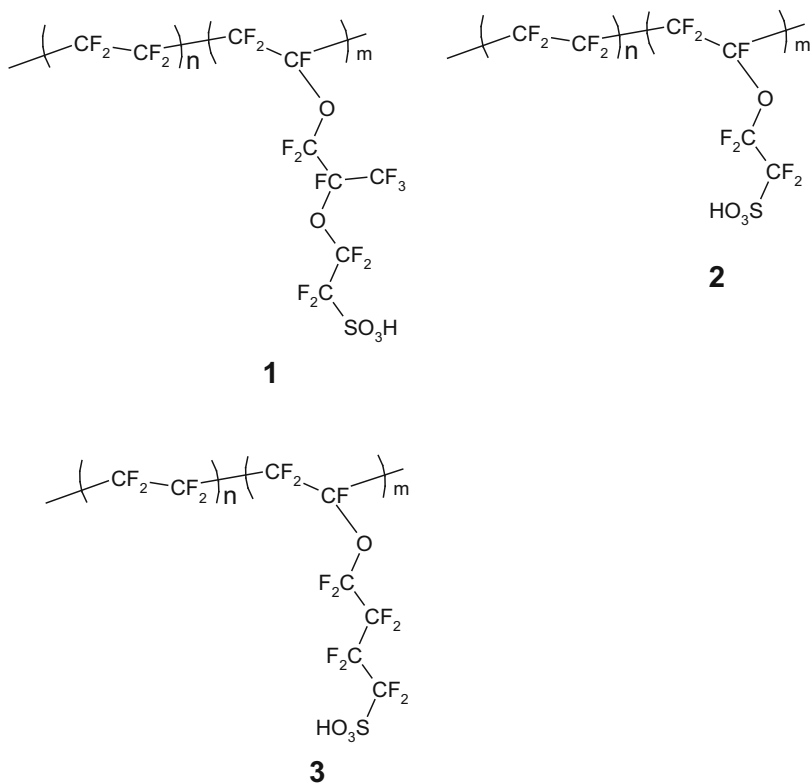
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 3 A general representation of the morphology of a hydrated PFSA. The + represents the hydrated protons, and the – represents the sulfonate groups at the edges of the hydrated region. The parallel lines represent the crystallites formed from the TFE groups of the backbone

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 4 Conductivity vs. relative humidity for several different 3 M Ionomers (Polymer 3) measured by AC impedance spectroscopy at 80 °C
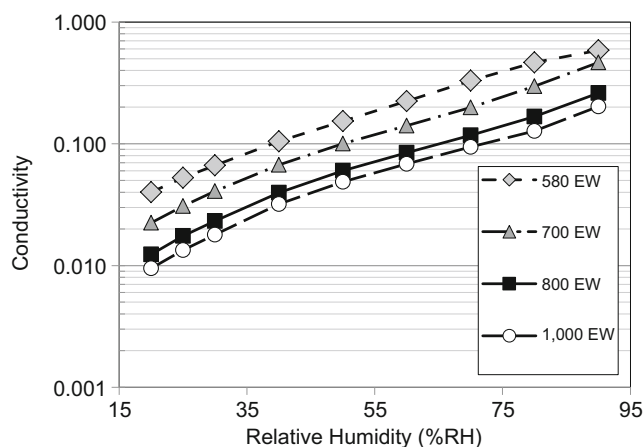

The amount of water present in the hydrated channels of the membrane is a function of the number of sulfonic acid groups present in the membrane and the humidity of the reactant gases [18]. In a typical PFSA membrane, at a given relative humidity, the ratio of water molecules to sulfonic acid groups (referred to as lambda, λ) is fixed. At low %RH, there are a few tightly bound water molecules. As the %RH is increased, more water is absorbed, and these additional water molecules are less tightly bound and more mobile. It is thought that the less tightly bound, more mobile water molecules that are farther from the sulfonic acid groups are more able to contribute to proton transport [19]. When the temperature is increased, or humidity levels in the reactant gases are decreased, the membrane will dry out and the conductivity drops. This represents an increase in the resistance of the cell and causes a loss in efficiency and performance.

One method of maintaining high conductivity with less water is to lower the EW, increasing the concentration of sulfonic acid groups in the membrane.

Figure 4 shows the conductivity as a function of relative humidity for several different EW
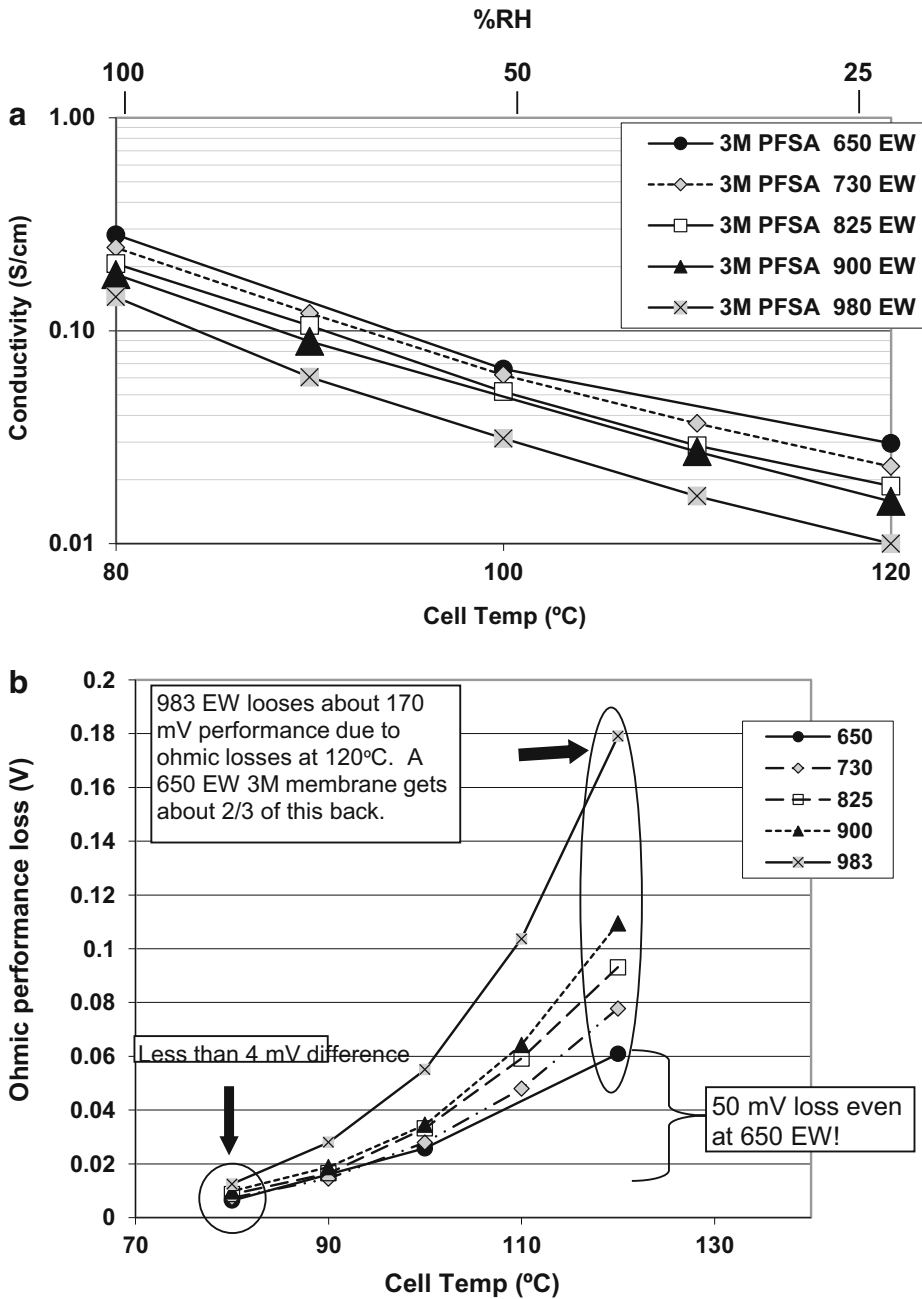
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 5 (**a**) Conductivity of various EW 3 M ionomer membranes (Polymer 3) as a function of temperature in an atmosphere with an 80 °C dewpoint. (**b**) Calculated performance loss due to membrane ohmic losses at 0.6 A/cm² for these membranes at 25 micron thickness

membranes. Lower EW membranes do provide a significant increase although conductivity still drops off at lower relative humidity.

Another way to consider the impact of membrane conductivity on fuel cell performance is shown in Fig. 5. Figure 5a shows the conductivity

of a few different EW membranes as a function of temperature with the atmosphere inside the conductivity cell held at a fixed dew point of 80 °C [20]. When the conductivity cell is at 80 °C, the % RH is 100%. As the temperature of the cell increases, the %RH at a fixed dew point decreases, causing a decrease in the membrane conductivity. This is similar to the situation in some PEMFC applications where the cell temperature may rise, while the humidity level of the incoming gases remains constant. The graph in Fig. 5b uses the same data. Here the conductivity is used to calculate the resistance of a 25 μm membrane, and using Ohms law, that resistance is used to calculate the voltage loss (ohmic loss) one would see in a fuel cell at a 0.6 A/cm^2 current density [20]. This represents the fuel cell performance loss due to the loss of membrane conductivity (certainly not the only performance loss under these conditions!).

At 80 °C, 100% RH, the performance loss is low, about 10 mV. Further, the performance difference between the different EW membranes is also quite low, less than 4 mV. As the temperature increases, the performance losses also increase, and the effect of the different EW ionomers becomes apparent. At 120 °C, the 1000 EW membrane has a large ohmic loss of about 180 mV. This represents a $\geq$ 20% loss in the operating voltage of a typical PEMFC at this current density or about $\geq$15% of the energy contained in the hydrogen fuel being converted to heat. The lower EW membranes do provide a significant improvement, but even at the lowest EW shown here, 650, the ohmic loss is still six times that of the fully humidified cell.

Lowering the EW of the ionomer does seem to provide at least a partial solution to this problem. This suggests the possibility that even lower EW ionomers could allow performance equivalent to the fully hydrated membranes even under these dry conditions. In the case of typical PFSAs, this is not a practical approach. This is due in part to the lack of the backbone crystallites mentioned above. At an EW of below about 700, these polymers do not have enough TFE to provide sufficient backbone crystallinity. This renders the membrane effectively water soluble and thus not useful in most PEMFC applications [21]. The
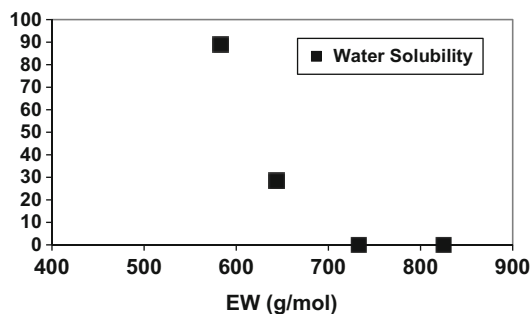
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 6 Water solubility of 3 M ionomers (Polymer 3) as a function of EW. The samples were boiled for 3 h

solubility of the 3 M ionomer as a function of EW is shown in Fig. 6.

PFSA ionomers with lower MW side chains should allow additional crystallinity at a given EW. The Polymer 2, shown in Fig. 2, has a side chain that is 100 MW units lower than the 3 M ionomer, so it may allow a more stable membrane at somewhat lower EW. Otherwise PFSA ionomers need to be supported in a matrix such as e-PTFE to act as very thin membranes with low ASRs.

Non-fluorinated or Hydrocarbon PEMs

A variety of non-fluorinated or partially fluorinated ionomers have been evaluated as alternatives to PFSAs for PEM fuel cells. These are typically sulfonated aromatic hydrocarbon polymers. Examples include sulfonated engineering thermoplastics such as polyimides [22], polyetherketones [23], and polysulfones [24] as well as polyphosphazenes [25] or sulfonated polystyrene grafted to fluoroplastics such as polyvinylidene fluoride [26]. Some of the observed or proposed advantages of these membrane materials include lower cost, increased toughness or improved mechanical properties, and lower permeability to oxygen and fuels [27]. Permeation of oxygen through the membrane is thought to lead to formation of hydrogen peroxide on the hydrogen electrode, contributing to chemical degradation of the membrane [28]. One significant

advantage of hydrocarbon-based ionomers that PFSAs do not have is their inherent synthetic versatility, allowing one to more easily design the polymer structure needed for optimum conductivity, physical and mechanical properties, and chemical stability (of course, this assumes one knows what structure one needs).

Many examples of hydrocarbon ionomers have been prepared by exposing aromatic backbone polymers to sulfonating agents, producing ionomers with sulfonic acid moieties attached to the most electron-rich positions on the aromatic rings. By controlling the degree of sulfonation, ionomers can be prepared by this method with suitable swelling characteristics and high proton conductivity at high relative humidity. It should be pointed out that due to the lower density of hydrocarbon-based polymers compared to fluoropolymers, a lower EW is needed in a hydrocarbon ionomer to provide an equivalent volumetric density of acid groups of a PFSA. Differences in the volumetric density of acid groups are more useful when comparing the conductivity of ionomers based on different classes of polymers [29]. Unfortunately, many studies have shown that randomly sulfonated hydrocarbon ionomers often suffer from lower conductivity at low relative humidity compared to PFSAs [23]. This is likely a consequence of a less favorable microstructure for proton transport as well as the lower acidity of the sulfonic acid groups bound to the aromatic ring (pKa = ca. -2 to -4) compared to the sulfonic acid groups of the PFSA (pKa = ca. -5.5) [23, 30].

Synthetic methods that allow attachment of sulfonic acid groups to more electron-deficient sites on aromatic rings can produce polymers where these groups are not only more acidic but also more stable toward thermal desulfonation [31]. Kreuer and coworkers have prepared such polymers in sulfonated polysulfones with a variety of EWs [32]. The structure is shown as Polymer 4 in Fig. 7. These ionomers have high thermal stability, high conductivity at low levels of hydration, and surprisingly low water solubility. These sulfonated polysulfones are not water soluble at 100 °C at EW values of down to 430. The improved conductivity at low hydration is likely due in part to the low electron density of the aromatic rings of the polysulfone and also possibly due in part to a favorable microstructure for proton transport. To further increase conductivity under very dry conditions, some highly sulfonated hydrocarbon polymers have been shown to have very high proton conductivity, even at low relative humidity. The Kreuer group has also prepared a completely sulphonated polysulfone that is polysulfone with a sulfonic acid group on every aromatic ring (EW = 220). While this ionomer is water soluble, it has conductivity substantially higher than 1100 EW Nafion™, even under dry conditions [34]. Litt and coworkers have prepared highly sulfonated polyphenylenes with one and two sulfonic acid groups per aromatic ring, shown as polymers 5 and 6 in Fig. 7 [33]. The latter has an EW of 118! Both of these ionomers are also water soluble and have very high proton conductivity at low %RH. These ionomers have

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation,
Fig. 7 Structures of some hydrocarbon ionomers. Polymer 4 is from Ref. [31] and Polymers 5 and 6 are from Ref. [33]
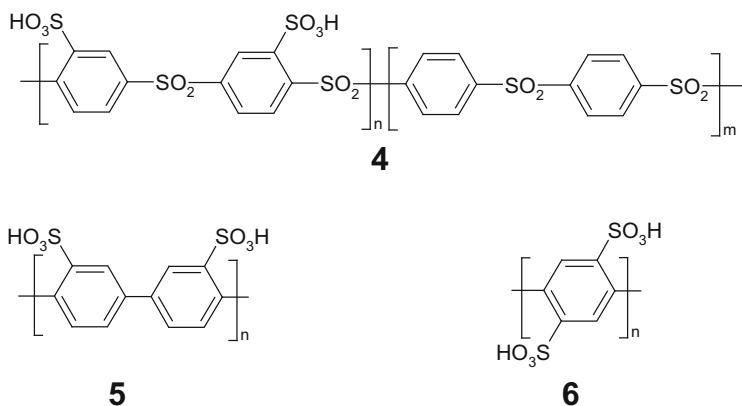
been shown to hold more water at lower %RH than other sulfonic acid-based ionomers. This observation was explained by an increase in the "frozen-in free volume" in these ionomers, that is, that the rod-like morphology of the polymer hindered close packing. Removal of the last few waters of hydration in the voids between these rods would force them closer together into a higher energy state, effectively increasing the heat of vaporization of the bound water molecules.

The studies mentioned above show that through control of the electronic and structural features of hydrocarbon ionomers, increased conductivity can be achieved. However, this is often at the expense of the mechanical stability of the polymer to the point where these materials cannot be used in fuel cells. One potential method of stabilizing these materials is to incorporate them into a stable multiphase or segmented system. A variety of synthetic methods exist that allow generation of different branched or block copolymers, and these have been applied to the synthesis of PEMs [35]. This allows control over the morphology of the phase-separated structures to create interconnected proton-conducting channels that may allow increased proton conductivity. McGrath and coworkers have prepared and evaluated sulfonated multiblock poly arylene ether sulfones with conductivity at low relative humidity equivalent to a Nafion™ membrane [36, 37]. The conductivity has been shown to be a function of the length and the chemistry of both the hydrophilic and the hydrophobic blocks.

Mechanical Stabilization of Low EW Membranes

One way of mechanically stabilizing low EW ionomer membranes is to generate a composite membrane using a porous film as an internal reinforcing structure [38, 39]. A PFSA membrane reinforced with a thin expanded polytetrafluoroethylene layer is available from W.L Gore. Reinforced membranes of this type have been shown to have increased strength and lower in-plane swelling upon hydration, lowering the potential of damage due to stresses generated during fuel cell operation. This should result in increased fuel cell durability [40]. Composite membranes have also been formed by using the porous phase as the conducting phase and filling the pores with a reinforcing phase. Pintauro and coworkers have made membranes using microfibers of sulfonated polyether sulfone filled with an inert filler to provide a membrane with good mechanical properties and proton conductivity when fully hydrated [41]. This group then used low EW PFSA fibers in this process, which gave a membrane with low swelling and very good conductivity at relatively low %RH (0.10 S/cm conductivity at 80 °C and 50% RH, about two to three times higher than a 1100 EW Nafion™ membrane) [42].

Mechanical stabilizing membranes in this way can allow significant stabilization of low EW ionomers. However, since many applications of PEM fuel cells require not only hotter and/or drier operation conditions but also require that the membrane to be insoluble in liquid water (often hot!) at times during operation, there is a limit to how low this method will allow one to go. In order to allow very low EW ionomers to be feasible, a change in the polymer chemistry will also probably be required.

Stabilizing Low EW Membranes Through Chemical Modification of the Ionomer

One possible method of chemically stabilizing low EW ionomers's toward excessive swelling and dissolution in water is to cross-link the ionomer. Many attempts are being made to cross-link low EW ionomers [43–45]. Generally, there are two "regions" in which ionomers can be cross-linked, in the hydrophilic, conducting region, near the acid groups and in the hydrophobic region, near the backbone. In the case of the former, one method that has been studied is forming a bis-sulfonyl imide from two of the pendent sulfonyl halide groups on the ionomer precursor [46]. Bis-sulfonyl imides are known to have highly acidic protogenic hydrogens and excellent chemical stability [47]. This method has the advantage that the
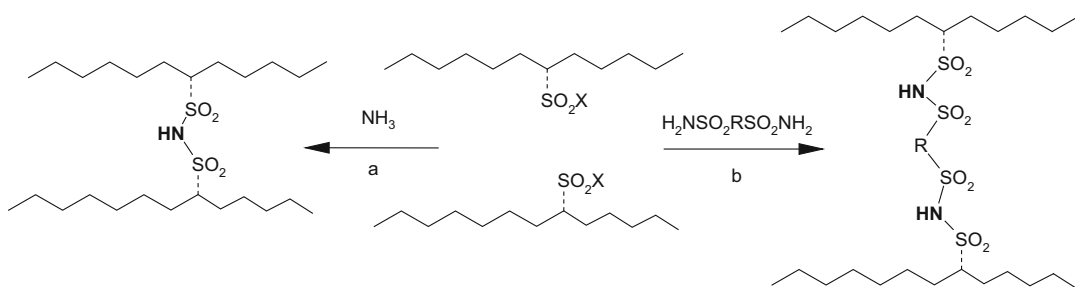
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 8 General method of synthesizing bis-sulfonyl imide containing cross-links from polymers with pendent sulfonyl halide groups
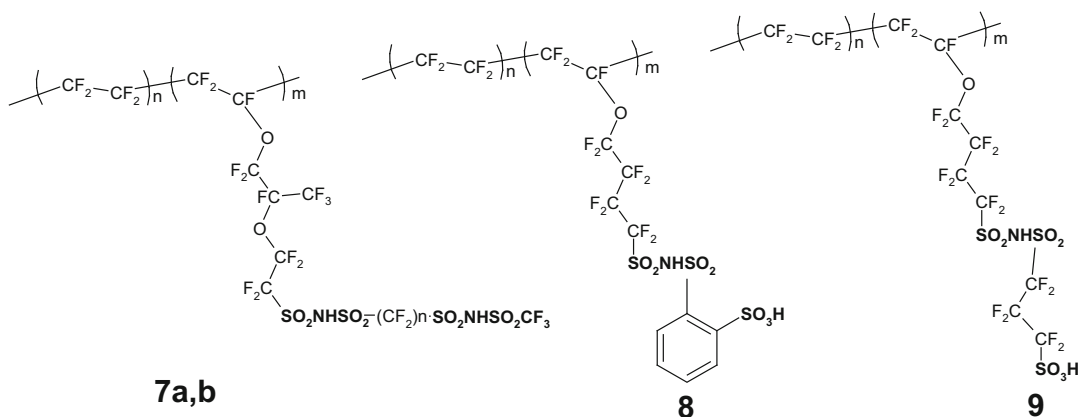
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 9 The structure of three multi-acid side-chain ionomers. Polymer 7a, n = 4, 7b n = 2 are from Ref. [51], Polymers 8 and 9 are from Ref. [53]

cross-links formed have similar acidity to the acid groups consumed. A generalized representation of this method is shown in Fig. 8.

Methods in which the backbone of the polymer can be cross-linked include radiation grafting [48] and through the preparation of a cross-linkable terpolymer by including a reactive third monomer in the polymerization of the ionomer, followed by curing in film form [49–51].

Another approach to providing ionomers with lower EW and suitable mechanical and solubility properties is to have more than one acidic proton per side chain. If the side chain has additional protogenic groups, a low EW ionomer can be prepared having a higher degree of backbone crystallinity and hopefully increased stability toward liquid water. One way to prepare such ionomers is to include a highly acidic bis-sulfonyl

imide acid in the side chain. Such materials were prepared by Desmarteau (Polymers 7a,b) and more recently at 3 M (Polymers 8 and 9) [52–55]. The structures of some of these materials are shown in Fig. 9.

The relationship between the number of TFE units that form the backbone crystallites and EW is shown in Fig. 10. The slope of each line gives the EW of the ionomer/the ratio of TFE units to protons in the polymer, and the intercept is the MW of the acid functional monomer/the number of protons. This shows the utility of having multiple protogenic groups on each side chain in providing polymers having high crystallinity and low EW.

In the case of Polymers 8 and 9, it has been demonstrated that low EW ionomers with higher conductivity, low swelling in boiling water, and good mechanical properties can be prepared [56].

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 10 Plot of EW vs. the number of TFE units in the backbone of selected ionomers
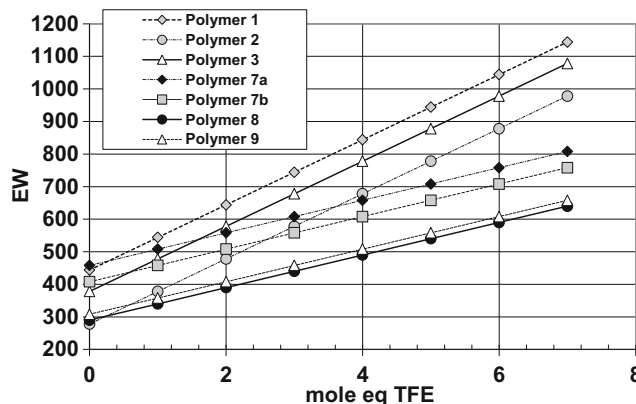
Conductivity Enhancing/Stabilizing Inorganic Additives

Another approach to overcome the inherent deficiencies of ionomers under hot, dry operating conditions has been to investigate the use of inorganic additives to form composites membranes [55]. Three basic functionalities are invoked:

1. Additives that are hygroscopic and designed to retain additional water in the membrane so that no loss of performance is observed when the fuel cell is operated under conditions of reduced RH. If the fuel cell spends significant time under dry operations, these approaches inevitably fail.
2. Additives that have enhanced acidity and can facilitate proton transport and so enhance performance under drier conditions.
3. Additives that are designed to decompose peroxide in situ in the membrane to increase the membrane chemical durability.

A number of additives also have combined functionality.

Probably every common hygroscopic inorganic oxide has at some time been used to prepare a composite membrane for fuel cell use [55]. The perceived benefit of an insoluble inorganic additive is from a surface interaction between the additive particle and the ionomer, and so nanosized individual particles or mesoporous materials into which the ionomer can penetrate have the larger benefit. Larger particles give no additional benefit and simply reduce the EW of the ionomer. The inorganic materials are either preformed before being mixed with the ionomer or are formed in situ, typically by a solgel process. Of the oxides that can be formed in situ, the most commonly used additive has been silica, but it is unstable to acid, and so its suitability for fuel cell operation is questionable [57]. Titania and zirconia composites would appear to have more promise from a stability viewpoint [58], although they have mostly been found to enhance membrane mechanical properties, as ultimately the water in these additives will also be lost on sustained dry operation. Recently improved performance has been observed under drier operation by combining tin oxide with titania [59]. Clays both natural and synthetic have also been used, but again their benefit to fuel cell under RH cycling is also questionable.

More promising are approaches using either acid-functionalized particles [60] or super acidic inorganic materials that are designed to increase proton mobility. Of these, the two most promising are zirconium phophonates and the heteropoly acids (HPAs) [61–63]. The effect of these may simply that they are more hygroscopic, or that the phenomena are simply a proton concentration effect, essentially lowering the equivalent weight. However, as they also lower the activation energy for proton transport, it seems that they also act as an effective proton transport promoter, perhaps more effective than the sulfonic acids.

Figure 11 shows proton conductivity data at 100 °C for the 3 M ionomer doped with various

Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation,
Fig. 11 Proton conductivity at 100 °C for the 3 M ionomer (■) and the 3 M ionomer doped with (◇) 1% HPW, (◆) 5% HPW, (△) 1% HSiW, and (▲) 5% HSiW at 20–100% RH (From Ref. [61])
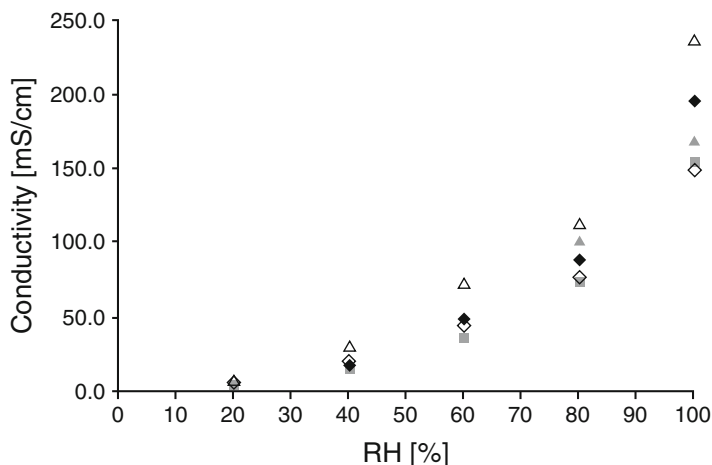
HPAs. Two observations are immediately apparent: (1) that the structure and amount of the additive have a strong influence and (2) that the effect becomes dramatically less as the RH is lowered. Similar results are shown for zirconium phosphonate composites with PFSA ionomer [64].
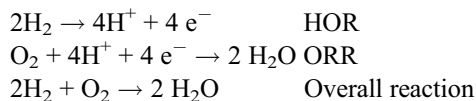
Hydrogen peroxide decomposition catalysts can be added to ionomer membranes in small amounts to slow down the decomposition of the ionomer during fuel cell operation. Additions of cerium and manganese, in both oxide and ionic forms, have been shown to increase the oxidative stability of membranes by orders of magnitude, and fuel cells prepared with such membranes have shown substantial increases in lifetime under aggressive hot and dry operation [65–67]. Unfortunately, these metal ions and oxides can consume ion exchange capacity and negatively impact fuel cell performance.

The ideal additive would enhance proton conductivity and stability. One demonstration of this was in a composite PFSA membrane using Pt nanoparticles supported on titania or silica [68]. The composite membranes when employed in MEAs demonstrated unhumidified fuel cell performance comparable to that of a similar humidified fuel cell. Whether adding Pt to the membrane will help durability or hurt, it is still a matter of some debate [69, 70]. Unfortunately, it is not commercially feasible at this time to add additional Pt to the MEA, and so this approach while novel is not practical. The HPAs are known

peroxide decomposition catalysts, and so these inorganic oxides have been demonstrated to improve performance and decompose peroxide in fuel cells, and if they could be immobilized would present a practical solution to this problem [71].

Electrodes

As stated above, the membrane acts as the proton transporting medium, is an electrical insulator, and separates the reactant gases from direct chemical reaction. On either side of this membrane are placed two electrodes. The anode at which hydrogen is consumed in the hydrogen oxidation reaction (HOR) and the cathode in which oxygen from air is consumed in the oxygen reduction reaction (ORR). The two half-cell reactions and the overall reaction are shown below.

$$2H_2 \rightarrow 4H^+ + 4\,e^- \qquad \text{HOR}$$
$$O_2 + 4H^+ + 4\,e^- \rightarrow 2\,H_2O \quad \text{ORR}$$
$$2H_2 + O_2 \rightarrow 2\,H_2O \qquad \text{Overall reaction}$$

The electrons flow around an external circuit and do work, while the protons pass through the fuel cell membrane. This overall reaction represents the combustion of hydrogen that produces heat, one reason why the membranes function to separate the two reactant gases is critical. Not only would a leak lead to fuel cell inefficiency, but also a hot spot would develop at the site of the leak,

which would result in potential damage to the MEA. Unfortunately, the ORR is not 100% efficient and a $2e^-$, $2H^+$ reaction results in the formation of hydrogen peroxide as shown below:

$$O_2 + 2H^+ + 2\ e^- \rightarrow H_2O_2$$
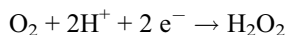
This reaction is currently unavoidable and appears to be favored at hot and dry operating conditions of the fuel cell. The peroxide decomposition forms reactive radials such as hydroxyl, $^\bullet$OH, and peroxyl, $^\bullet$OOH, that cause oxidative degradation of both the fuel cell membrane and catalyst support [72]. Both electrodes currently use Pt or Pt alloys to catalyze both the HOR and ORR reactions. The catalyst particles are typically supported on a high surface area, heat-treated carbon to both increase the effectiveness of the catalyst and to provide a path for the electrons to pass through to the external circuit via the gas diffusion media (which is typically also made of carbon) and the current collecting bipolar plates. In addition, the catalyst particles are coated in ionomer to facilitate proton transport; however, the electrode structure must also be porous to facilitate reactant gas transport. A schematic of a typical PEM MEA is shown in Fig. 1. A boundary condition exists at the catalyst particle where protons from the ionomer, electrons from the electrically conducting Pt and carbon, and reactant gases meet. This is usually referred to as the *three-phase boundary*. The transport of reactants, electrons, and protons must be carefully balanced in terms of the properties, volume, and distribution of each media in order to optimize operation of the fuel cell.

Typically, a good proton conductor is thought to be one where the proton conductivity is ≤ 0.1 S cm^{-1}; however, from the point of view of fuel cell operation, it is the area-specific resistance (ASR) of the MEA that is more important. If one was to consider the MEA as a series of resistances, an anode resistance would be observed, an interfacial resistance between the membrane and the anode, a membrane resistance, an interfacial resistance between the membrane and the cathode, and a cathode resistance. It is assumed here that the resistance of electrical connection between the anode and the current collectors is negligible compared to those described above;

however, this too can be compromised if there is insufficient pressure between the bipolar plates and the gas diffusion media. All of these resistances must be optimized in order to lower the area-specific resistance of the fuel cell. The effect of the resistances or ohmic losses on the overall performance and efficiency of the fuel cell is illustrated in Fig. 5. While a large amount of current work is concerned with optimizing membrane ionomers for hotter and drier operation, little thought has to date been put into optimizing the electrode ionomer, the ionomer catalyst interface, or the catalytic reactions at the anode or cathode for higher temperature, lower RH operation. If the ionomer in the membrane is not well matched and linked to that in the fuel cell electrodes, a large ASR can result. Of course part of the reason for this, until recently, has been the lack of suitable hot, dry ionomers for practical fuel cell testing.

As stated above, in a conventional, fully humidified fuel cell, part of the reactant gas stream is diluted by water vapor, and the cathode suffers from formation of liquid water blocking the pores, or flooding, as the water is being produced in a water-saturated environment. To overcome this problem, hydrophobic fillers such as Teflon ™ may be added to the electrode to facilitate water rejection [73]. These systems have been to a large extent already optimized, and great deal of art pertains to electrode fabrication [74]. One advantage of running a fuel cell hot and dry is that the electrode flooding issue is eliminated. In these fuel cells, there is still water produced on the cathode but possibly not enough to saturate the PFSA polymer in the electrode layer and potentially leaving the anode side of the fuel cell under humidified. However, as it is likely that polymers with low EW will be used for high-temperature operation, back diffusion of water should be increased improving the chance that the anode will not be dried out. With less water in the fuel cell system, freeze issues on start-up in cold climates may also be partially mitigated.

Each of the electrode components is now considered in terms of hot and dry operation, what is known, and what needs to be accomplished to realize these systems.

It is generally thought that as temperature increases so do reaction kinetics. However, the situation in a fuel cell, an electrochemical device, is far more complicated. The reaction mechanism will depend on the surface environment of the catalyst particle and the potential at which the reaction is taking place. The electrode over-potential associated with the ORR represents the largest voltage loss in fully humidified fuel cells, and so it is important that the situation not be exacerbated in running fuel cell under hot and dry conditions. In the kinetically controlled region of the fuel cell operation, the performance can be described by the Tafel equation:

$$E = E_{rev} + b \log i_0 - b \log i$$
$$b = -2.3 \frac{RT}{\alpha nF}$$

where E, E_{rev}, b, i, i_0, n, and α are the electrode potential, reversible potential, Tafel slope, current density, exchange current density, the number of electrons transferred in the rate determining step, and the transfer coefficient, respectively [75, 76]. The first observation is that increasing the fuel cell temperature from 60 to 120 °C while maintaining a constant relative humidity (RH) causes the theoretical opened circuit voltage (OCV) to decrease from 1.22 to 1.14 V due to the increase in water partial pressure [77], and so again it is desirable to operate the fuel cell at reduced RH. The Tafel slope, a measure of the potential loss of the electrode due to reaction kinetics, is the logarithmic decrease in current density with applied voltage. It is therefore desirable to have as small a Tafel slope as possible. The Tafel slope varies with current density as the surface of the platinum varies with voltage. At high-voltage or low current density, the Pt is oxide coated (Temkin adsorption conditions), and the Tafel slope is 60 mV/decade; at lower voltage, higher current density the Pt is oxide-free (Langmuir adsorption conditions), and the Tafel slope is 120 mV/decade. So above 100 °C, the reaction mechanism may change if the surface coverage is compromised by the lack of water. Experimentally it has been shown for a water-saturated electrode that the Tafel slope increases with temperature at high voltage but is invariant at low voltage [78].

There are very few studies of the ORR under hot and dry fuel cell operating conditions. Recently, methods have been devised to separate the mass transport effects from the kinetic effects [79, 80], but none of these have been applied to hot and dry fuel cell operation. These studies showed that, under fully humidified conditions up to 70 °C, oxygen reduction had a tenfold higher specific performance for platinum black at 0.90 V compared to Pt on carbon as has been previously reported in the literature [81]. However, this significant benefit of platinum black is shown to rapidly decrease when the potential is shifted to lower, more fuel cell relevant potentials. This is manifested in the Tafel slope, which decreased from ~360 to ~47 mV/decade in the region where the overpotential was <0.35 V. The effect of hot and dry conditions has been studied in a 5 cm^2 MEA where mass transport and kinetics are difficult to separate [78]. At 120 °C, the Tafel slope is found to increase inversely with RH. It is speculated that this is due to the decrease in ionic conductivity in the electrode. RH can also influence water oxidation to form Pt-OH and Pt-O and thereby change the surface condition of the platinum crystals.

It has been shown that the current exchange density increases up to 70 °C, but there is no data for this above 100 °C; again there is a critical need to measure this under real fuel cell conditions. Much work is being undertaken in precious metal alloy catalysts where Pt is combined with one or more other metals and in non-precious metal catalysts [82]. These new catalytic materials are being studied in aqueous acid or in MEAs at 100% RH; very little data exists on how these materials will behave under hot and dry conditions. In fact the development of new catalyst for fuel cells run under hot and dry conditions may require there optimization outside of aqueous or water-saturated systems.

H_2 can be produced from fossil hydrocarbons such as natural gas or renewable biomass via reforming to produce syn gas (H_2 + carbon monoxide, CO), which can be converted to a H_2-rich

gas via the water gas shift reaction. These processes, while commonplace in chemical engineering practice, do not produce pure H_2; the last 1000 ppm or so of CO must be removed by expensive and/or inefficient unit operations such as partial oxidation, pressure swing adsorption, or membrane technology. The great advantage for the fuel cell electrodes in terms of high-temperature operation is on the anode where the effected of adsorbed contaminants that slow the HOR are mitigated. This allows the anode to operate with H_2 contaminated with increasing levels of CO, a by-product of hydrocarbon reforming. At 80 °C, CO levels as low as 10 ppm can cause significant degradations in performance, but at 130 °C, the fuel cell anode can tolerate 1000 ppm of CO allowing the cost of H_2 produced from hydrocarbons to be dramatically reduced.

The optimum particle size for Pt in the catalyst layer is 3–5 nm [83]. Another issue is that the Pt both agglomerates and suffers from dissolution and re-precipitation. Both processes are expected to increase at higher temperature and result in higher particle sizes, lowering the rate of the ORR [84]. As described above, in a typical electrode, the precious metal catalyst is supported on a carbon support that is susceptible to corrosion. It has been shown that the carbon corrodes rapidly if the electrode is held at relatively high potentials and that the reaction is first order with respect to water vapor. Carbon corrosion obviously increases with temperature and Pt loading, Fig. 12 [85]. Doping carbon with N is expected to increase the durability of the carbon.

Another solution to both the carbon support and the ionomer contact issue is to use a Pt catalyst that has no support and is embedded in the membrane such as the nano-structured thin film (NSTF) catalyst being developed by 3 M [7, 86]. A SEM of the NSTF-Pt catalyst is shown in Fig. 13. In addition to not having a carbon support to corrode, this catalyst system is much less susceptible to Pt dissolution because the small whiskers are coated with a continuous layer of Pt, not Pt nanoparticles, and so behaves more like bulk Pt. MEAs made with these electrodes also produce less F^- in the effluent water coming from the

fuel cell under hot and dry operating conditions, as shown in Fig. 14. The fluoride content in the effluent water coming from the cell is a common diagnostic for the rate of membrane degradation. Materials known to decompose peroxide have also been added to PEM fuel cell catalyst layer such as MnO_2 [87], CeO_2 [66], and HPA [88], and all have shown a decrease in fluoride emission rates of the fuel cell under hot and dry conditions.

Nafion™ and other PFSA ionomers work very well in conventional PEMFC electrodes because they form a thin layer that allows both gas diffusion and proton transport. For this reason, they are still the ionomer of choice in fuel cell electrodes for hot and dry operation, although under these conditions, the PFSA used usually has a much lower EW to increase proton conductivity at the drier conditions. While the approach of adding a lower EW PFSA ionomer works well for hot and dry operating conditions, the increased swelling and hydrophilicity at lower EW leads to serve flooding if the same fuel cell is operated under high RH. As new ionomers for hot and dry operation are developed, they must be capable of extending their proton connectivity into the electrode without a large interfacial loss due to material incompatibility at the boundary of the electrode and membrane. The consequence of a change in ion-conducting material is that proton transport to and from the catalyst layer may be compromised if conventional ionomers are employed. It is true that at the current time, little work has been done to develop new, stable ionomers suitable for high-temperature applications that will also allow high proton conductivity and high gas permeability in the fuel cell electrodes. One may consider using stable, lower EW version of the new ionomers, functionalizing the carbon support with suitable functional groups or developing new ionomers with higher gas permeability for use as binders in the electrode. It may be necessary to completely redesign fuel cell electrodes for high-temperature, low relative humidity operation using materials that are stable to oxidation, enhance the ORR, proton conductivity, and gas permeability, while maintaining suitable electrical conductivity to maintain the three-phase boundary condition during operation.

Fig. 12 Maximum fraction
of carbon consumed as a
function of temperature for
samples with 30–80 wt.%
Pt (From Ref. [83])
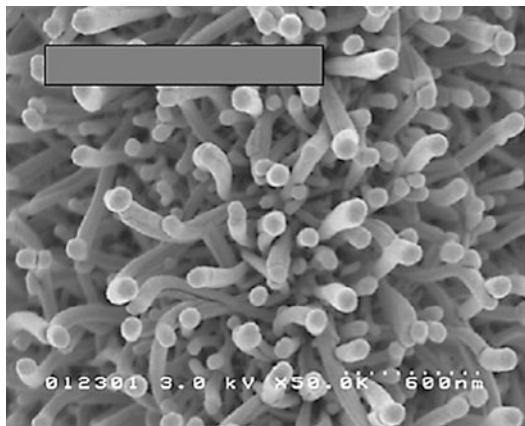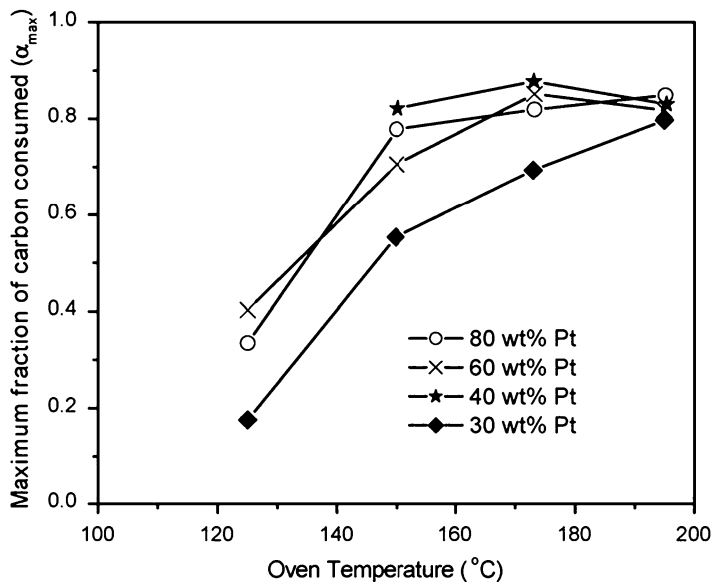
**Proton Exchange Membrane Fuel Cells: High-
Temperature, Low-Humidity Operation,**
Fig. 13 NSTF catalyst as fabricated and before transfer
to a PEM. Plan view at 50,000 X original. The scale bar
indicates 600 nm (From Ref. [7])

Future Directions

This entry is by no means comprehensive. It is
intended to show important examples of the
approaches being taken to address the need for new
materials to allow the robust operation of fuel cells
under hotter and drier conditions than possible today.

At this point, there are no membranes or
ionomers commercially available that will meet
both the performance and durability requirements

outlined above, although much progress has been
made in the development of polymer membranes,
which have improved conductivity and durability
under these conditions. More radical approaches to
the development of new fuel cell electrolytes includ-
ing the development of ionomers with a variety of
different protogenic groups are being explored [89,
90]. Using imidazole, ionic liquids, and other
replacements for water to allow completely dry
operation is also being studied [91–93]. The next
few years should see significant technical advances
and the introduction of improved electrolyte mem-
branes into the marketplace.

Optimization of the electrodes for these fuel
cell systems has just started. Work has been done
on the optimization of electrode structure for oper-
ation under hot, dry conditions but less has been
done to study catalysis under these conditions.
Part of the reason for this is that as stated above,
there are no commercially available polymeric
materials available for the development of new
electrodes studies. It is hoped that until commer-
cially available materials for this application
become available that researchers offer to share
their materials. This will, however, be insufficient
as the ionomers developed for catalyst layers need
different properties than ionomers developed to
act as fuel cell membranes. The other major issue
is that catalysts for fuel cells run under conditions
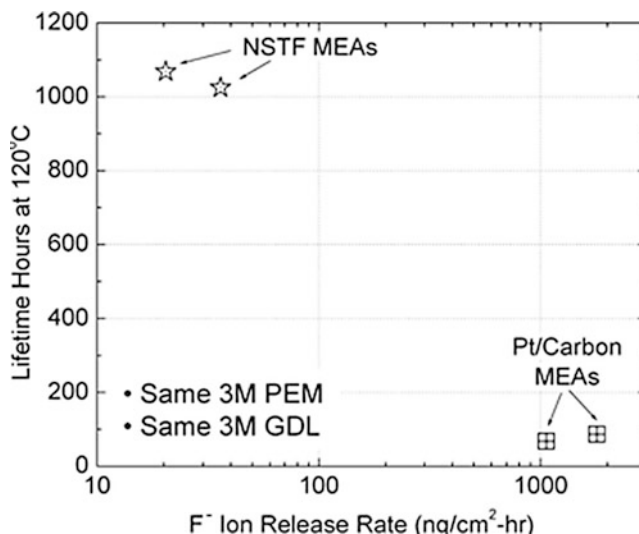
Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation, Fig. 14 Hours of lifetime at 120 °C (before catastrophic failure of the PEM) versus fluoride ion release rates (by IC) for NSTF and Pt/C catalyst -based MEA's having the same type PEM and GDL. 100 cm^2 cells were operated at 0.4 A/cm^2, 120 °C, 300kPa, 61%/84% inlet RH. ECSA and cross-over were measured daily at 75 °C. Total lifetimes were $\sim$ 1800 hours for the NSTF MEA's due to diagnostic testing at 75 °C. End-of-life

of water saturation have been developed using liquid phase electrochemical methods. It will be extremely important that new catalyst for fuel cells to be operated under hot, dry conditions be developed by solid-state electrochemistry. New methods must also be developed so that electrodes containing compatible ionomers can be tested.

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