

The US DOE High Temperature Membrane Program

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Introduction

Membranes used in current Proton Exchange Membrane (PEM) fuel cells require thermal and water management systems to control temperature and keep the membrane humidified. These components increase the weight and volume of the fuel cell system and add complexity. Estimates of the cost of the humidification systems for current membranes range from \$5-\$8/kW, while the thermal management system is estimated to cost \$3-4/kW.(1) These costs must be reduced to meet the DOE transportation fuel cell system cost target of \$30/kW for the complete power train.

The cost and complexity of the thermal and water management systems could be minimized if the fuel cell operated at higher temperatures (up to 120°C) and at lower relative humidity (RH). The heat load for the system can be reduced to ½ and the size to ~ ¼ by increasing the operating temperature to 120°C and decreasing the RH.(2)

Operation at 120°C would also increase the tolerance of fuel cells to CO, which would in-turn reduce the cost of hydrogen from hydrocarbon sources because extraordinary steps would not be necessary to purify the hydrogen. The U.S. Department of Energy has a major effort to develop new membranes that can operate at temperatures up to 120°C without the need for humidification. These membranes must also be able to operate over the full range of conditions expected during automotive operation, including freezing conditions and frequent start-ups and shut downs which are likely to include exposure to liquid water under some conditions. Targets for the membranes are shown in Table 1.

While it is desired that the fuel cell membrane operate without external humidification (an inlet water vapor pressure of 1.5 kPa), the water generated by the fuel cell can be utilized to provide some humidification of the membranes. Under operation, it is believed that recycling product water from the cathode to the inlet air can provide ~25% RH inside a stack operating at 120°C with inlet feeds at a water vapor partial pressure of <1.5 kPa.(3) This reduces the burden for performance with very low water content, but operation at this low RH still remains a major challenge.

Results and Discussion

A variety of strategies are being pursued to provide membranes that can operate at low RH and temperatures up to 120°C, as well as the broad range of other conditions required. Approaches include those that still require water for conduction but reduce the water needed by managing the membrane microstructure and/or increase water retention at high temperature and low RH using hydrophilic additives, and those that do not require water and provide conduction through an alternative mechanism. By pursuing multiple strategies, the chances of success increase. In addition, by tracking the results from these different approaches, we can improve our knowledge of structure-property relationships as they relate to proton conduction in polymer membranes.

Membrane microstructure has been observed to have a substantial effect on conductivity. Several approaches are being pursued to try to control the microstructure in order to increase conductivity at higher temperature and lower RH while maintaining mechanical properties. The first approach attempts to control microstructure by manipulating the polymer structure to control phase segregation between the hydrophilic and hydrophobic portions of the polymer. Some success has been obtained using block co-polymers and varying the sizes of the hydrophilic and hydrophobic domains. With block copolymers McGrath has observed that as the block length increases, the

performance under partially hydrated conditions increases.(4) This suggests the presence of long continuous channels at higher block lengths through which protons can be transported along the sulfonic acid groups and water molecules. Utilizing block copolymers consisting of a hydrophilic macromonomer and a hydrophobic perfluorinated macromonomer, Virginia Tech has prepared a block copolymer that exhibited higher proton conductivity than Nafion® 112 at 80°C at all RH values (30-95%).(4)

Table 1. Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2010 Target	2015 Target
Inlet water vapor partial pressure	kPa	<1.5	<1.5
Oxygen cross-over	mA/cm^2	2	2
Hydrogen cross-over	mA/cm^2	2	2
Membrane conductivity at inlet water vapor partial pressure and: operating temperature 20°C -20°C	Siemens/cm Siemens/cm Siemens/cm	0.10 0.07 0.01	0.10 0.07 0.01
Operating Temperature	°C	≤120	≤120
Area specific resistance	$\text{Ohm}\cdot\text{cm}^2$	0.02	0.02
Cost	$\$/\text{m}^2$	20	20
Durability with cycling at operating temperature <80°C at operating temperature >80°C	Hours Hours	5,000 2,000	5,000 5,000
Unassisted start from low temperature	°C	-40	-40
Thermal cyclability in the presence of water	Yes/no	yes	yes

3M is also investigating modified polymer structures to try to control membrane morphology. 3M has developed a new ionomer with a shorter side chain than standard perfluorosulfonic acid (PFSA) membrane ionomers without the pendant CF_3 group. This structure provides a higher degree of crystallinity and allows for lower equivalent weight membranes with improved mechanical properties and durability under hot, dry conditions. Initial results with these membranes have demonstrated conductivity of over 0.1 S/cm at 120°C and 61.5% RH, and >0.02 S/cm at 120°C and ~25% RH.(5)

Another strategy to control morphology separates the mechanical/structural functions of the membrane from the ion-conducting functions by utilizing composite membranes with a non-conductive polymer support providing the mechanical strength and a low equivalent weight (EW) ionomer providing the conduction. This allows for the use of lower equivalent weight ionomers without paying the penalty of lower mechanical strength and higher swelling inherent in these ionomers. One implementation of this approach is being pursued at Giner. The overall approach is to lower the EW of PFSA ionomers to increase low RH conductivity and support the ionomer with

two- and three-dimensional non-ionic materials. Membranes that are stable in two dimensions are being generated by direct polymerization of low EW PFSA into a 2-dimensional micro-scale honeycomb matrix. The matrix is generated by laser machining. The effects of ionomer EW and support geometry/composition on the PEM composite are being explored. Initial results with the two-dimensional microporous grid are very encouraging, and improvements in conductivity of a factor of 2-3 from that of Nafion® 112 have been observed over the range of RH from 30-80% at 80 and 120°C.(6) A conductivity of ~0.09 S/cm was obtained at 120°C and 50% RH.(6) In addition, the dimensionally stabilized membrane successfully restrained x-y swelling in high acid content PFSA's.

An alternative approach is the use of hydrophilic additives to increase conductivity at higher temperature and low RH. The additives should hold on to water more tightly than the ionomer at high temperature, providing some water for conduction. These hydrophilic surfaces can also play a role in determining the structure of the membrane, providing water-rich surfaces to attract the hydrophilic portions of the ionomer. Recent results at Florida Solar Energy Center have demonstrated improvements in conductivity over Nafion® 112 of about a factor of 2 at 80°C and 25% RH.(7)

FuelCell Energy is pursuing a combination of approaches. The company is utilizing a four-component composite consisting of a co-polymer, a support polymer, a water retention additive and a protonic conductivity enhancer. The main focus of the effort has been on increasing the proton conductivity at 120°C and 25% RH, without decreasing the mechanical properties. The co-polymer provides the basic building block for the membrane. It is an advanced perfluorosulfonic acid with significantly higher conductivity than state-of-the-art polymers. The support polymer is designed to give a stable cluster structure and to enhance mechanical properties. The functionalized additives are designed to retain water at the low RH conditions and to enhance the composite membrane's proton conductivity by providing an alternate proton conduction path. This path is designed to efficiently transport protons at the high temperature as well as subfreezing conditions. Progress to date has led to a membrane with conductivity about a factor of 2 better than Nafion® 112 at 120°C. (8) In addition, the RH dependence appears to be different than that for Nafion®.

While the above approaches have shown improvements in conductivity at low RH, they still rely on water for conduction. An alternative strategy is to try to develop materials that do not rely on water for conduction. Systems utilizing phosphonic acids, heteropolyacids, protic ionic liquids, and heterocyclic bases that do not rely on water for conduction are being investigated. One of the major issues for these systems is that the acid or base aiding proton transport is generally water-soluble. The acid or base must be immobilized for use in transportation applications where condensation of liquid water under some of the operating conditions is inevitable. However, enough mobility must be retained by the active group to be able to participate in proton conduction.

Recent work at LBNL has focused on systems utilizing tethered imidazoles and other heterocyclic bases. The PIs have demonstrated that these systems can be immobilized without significantly affecting the proton conductivity. Their work has indicated that phase separation and polymer morphology are also critical for promotion of fast proton mobility and selectivity in gas transport in this type of membrane. (9)

Membranes based on heteropolyacids are also being pursued. Heteropolyacids have high proton conductivity, even at room temperature. However, they are in general soluble in water. Colorado School of Mines is investigating methods to immobilize heteropolyacids and prepare membranes

from these materials. The PIs have shown conclusively that they can fabricate immobilized HPA systems that are still proton conductors, and have achieved conductivities of >0.1 S/cm at 80°C and 100% RH. (10) Unfortunately, conductivity drops substantially at lower RH.

Conclusions

Membranes with improved conductivity at higher temperature and reduced RH are being developed. Systems which rely on water for conduction can provide better performance than that observed for Nafion® 112, but have not yet been able to reach the DOE goals. Systems with potential for conduction without water are in their early stages of development and show potential.

Acknowledgements

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References

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