Polymeric Membranes for Fuel Cells: Overview and Recent Developments

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Polymeric membranes play a critical role during the generation of electricity in hydrogen/air and direct methanol proton-exchange membrane (PEM) fuel cells. The membrane in such devices performs three roles: (1) it physically separates the anode and cathode to prevent an electrical short circuit, (2) it separates the fuel and oxidant to eliminate a chemical short circuit, and (3) it provides a facile pathway for the flow (transport) of ionic species (protons) from the anode to the cathode. The general requirements for a fuel cell membrane are:

- Low resistance under cell operating conditions (high ionic conductivity with zero electrical conductivity))
- Long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments.
- Good mechanical strength, preferably with resistance to swelling.
- Low gas (oxidant and fuel) cross-over and pinhole free.
- Interfacial compatibility with catalyst layers.
- Low cost.

For H_2/air proton-exchange membrane fuel cells (PEMFC) operation under high relative humidity (RH) conditions at $T \leq 80^{o}C$, perfluorosulfonic acid (PFSA) proton conductors (e.g., Nafion®) are the membrane material of choice due to their high conductivity and chemical/mechanical stability. There are numerous papers in the literature that detail the performance of Nafion-based MEAs in a H_2/air fuel cell. Early studies on DMFCs with liquid methanol feeds operating at 60-80°C utilized, for the most part, Nafion as the proton conducting solid polymer electrolyte because of its prior use and acceptable performance in a PEMFC. Unfortunately, methanol leakage (crossover from the anode to the cathode) through Nafion during DMFC operation is unacceptably high. When methanol contacts the air cathode in a DMFC, it will be oxidize chemically (with oxygen from the cathode feed air) to form CO_2 and water. Methanol oxidation at the cathode has a number of unwanted consequences: (1) There is cathode depolarization (a loss in voltage) due to a mixed potential phenomenon (where two reactions, the electrochemical reduction of O_2 and the chemical oxidation of methanol, occur on the same electrode), (2) CO intermediate, generated on the cathode during the oxidation of methanol, poisons the cathode catalyst, (3) oxygen is consumed during methanol oxidation and is not available for electrochemical reduction, (4) there is excess water generation at the cathode and flooding of the electrode occurs (which will lower the O_2 concentration at catalytic sites), and (5) there is consumption of methanol without electricity generation, thus lowering the overall fuel efficiency of the fuel cell.

There are two major challenges for membrane scientists with regards to proton-exchange membrane fuel cells: (1) PEMFC membranes that conduct protons under high temperature and low humidity conditions and (2) DMFC membranes that are highly conductive but act as barriers to methanol.

PEMFC operation with lightly humidified or dry gases at 120^{o}C would be highly advantageous with regards to heat rejection from a fuel cell stack, compatibility with automotive radiators, catalyst tolerance to CO impurities in the hydrogen gas stream, and faster electrode kinetics. Unfortunately, the conductivity of PFSA membranes drops dramatically at $T > 100^{o}$C under low humidity conditions due to: (i) an insufficient number of membrane-phase water molecules for protons to disassociate from sulfonic acid fixed charge sites, (ii) a loss of percolation pathways for proton movement due to low membrane swelling, and (iii) structural changes in the polymer which cause membrane pores to collapse (the glass transition temperature of Nafion is only about 100^{o}C). At high temperatures and low humidity, PFSA membranes also exhibit a loss in mechanical strength (e.g., creep and pinhole formation), increased gas permeability, and higher rates of oxidative degradation.

For a DMFC, the membrane properties of utmost interest are the proton conductivity and methanol crossover. Ideally, the membrane should be a good proton conductor (with a conductivity > 0.1 S/cm) and a good methanol barrier. Since proton conductivity in polymeric ion-exchange membranes is highly dependent on membrane water content (as noted above for PEMFCs) and since methanol and water are highly miscible, it is difficult to block methanol from absorbing in (and eventually moving through) a hydrated DMFC membrane.

Specific targeted properties of membranes for use in high temperature, low relative humidity PEMFCs and in DMFCs are listed in Table 1, along with references for general procedures as to how the properties are measured.

Table 1 - Targeted Membrane Properties for High Temperature PEMFCs and Low Crossover DMFCs (from ref 1)

Property	**Target Membrane Properties for a PEMFC (H_2/air fuel cell)**	**Target Membrane Properties for a DMFC**	**Methods to Determine the Property**
Proton Conductivity	> 0.1 S/cm at 120°C at 25% RH > 0.03 S/cm at 25°C at 25% RH	Min of 0.01- 0.03 S/cm at 25°C	2 or 4-point methods (ref 2)
Fuel Permeability (H_2 or methanol)	Below 1.0 x 10^{-12} (mole-cm)/(cm^2-s-kPa) At 80°C	Less 9.0 μmole/cm^2-min	GC methods (ref 3) for H_2. Limiting current method (ref 6), CO_2 sensor method (ref 7), or diffusion cell (ref 8) for methanol
O_2 Permeability	Below 4.0 x 10^{-12} (mole-cm)/(cm^2-s-kPa) at 80°C	Below 4.0 x 10^{-12} (mole-cm)/(cm^2-s-kPa) at 80°C	GC methods (ref 3)
Solubility in H_2O	< 1% at 150°C for 24 hr	< 1% at 150°C for 24 hr	Autoclave in H_2O
Swelling in H_2O	<100% H_2O uptake in boiling water	<100% H_2O uptake in boiling water and 1-3 M methanol solutions	Weight-gain meas. (ref 4)
Chemical Stability	Stable in presence of peroxyl species	Stable in presence of peroxyl species	Test with H_2O_2 and/or Fentons reagent (ref 5)
Mechanical Stability	Critical	Critical	Specifications and requirements not yet determined

The Hydrogen, Fuel Cells, and Infrastructure Technologies Program at the U.S. Department of Energy see (http://www.eere.energy.gov/hydrogenandfuelcells/tech_teams.html#targets) has also compiled a list of membrane properties for high T, low relative humidity PEMFC operation. Target goals for membrane properties have been proposed for the next 10 years, as shown in Table 2. Proton conductivity targets at low humidity conditions are particularly ambitious.

With regards to the proton conductivity data in Tables 1 and 2, it is important to note that the membrane resistance loss in a operating PEMFC or DMFC is a function of both the proton conductivity and the membrane thickness (i.e., one can tolerate a low proton conductivity if the membrane is made sufficiently thin). The membrane property parameter that takes into account both film thickness and conductivity is the area-specific (areal) resistance (with units of ohm-cm^2), defined as the ratio of membrane thickness to conductivity. For a water-equilibrated Nafion 117 membrane (approximately 200 μm wet thickness), the areal resistance at 60^{o}C is 0.22 ohm-cm^2. For a high temperature (e.g., 120^{o}C) and low relative humidity (25-50%) PEMFC, the U.S. DOE has established a long-term target of < 0.05 ohm-cm^2 for the areal resistance of the membrane material.

Membrane thickness also plays an important role in DMFC operation. Here one must balance an increase in ohmic loss (due to finite membrane conductivity) with a decrease in methanol crossover as the membrane thickness is increased. If the membrane thickness is too high, ohmic losses dominate and the DMFC power output is low. Similarly, if the membrane is too thin, then methanol crossover will control the output power. This situation is not the case for a PEMFC, where decreasing the membrane thickness improves fuel cell performance (until the membrane becomes so thin that H_2 and/or O_2 gas crossover becomes a concern).

References

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Table 2 - DOE Technical Targets for High Temperature, Low relative Humidity PEMFC Membranes

Characteristic	**Units**	**Calendar Year**			
		2004 Status	**2005**	**2010**	**2015**
Membrane Conductivity at					
Operating Temperature	S/cm	0.1	0.1	0.1	0.1
Room temperature	S/cm	0.07	0.07	0.07	0.07
-20°C	S/cm	0.01	0.01	0.01	0.01
Operating Temperature	°C	≤80	≤120	≤120	≤120
Inlet water vapor partial pressure	kPa	50	25	1.5	1.5
Oxygen crossover[a]	mA/cm^2	5	5	2	2
Hydrogen crossover[a]	mA/cm^2	5	5	2	2
Cost	\$/m^2	65[b]	200	40	40
Durability with cycling					
At operating temp of ≤80°C	hours	1000[c]	2000[d]	5000[d]	5000[d]
At operating temp of >80°C	hours	not available[e]		2000	5000
Low Temperature Survivability	°C	-20	-30	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes	Yes

[a] Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature.
[b] Based on 2004 TIAX Cost Analysis and will be periodically updated.
[c] Durability is being evaluated. Steady-state durability is 9,000 hours.
[d] Includes typical driving cycles.
[e] High temperature membranes are still in a development stage and durability data are not available.