

V.N.4 Proton Exchange Membranes for Next Generation Fuel Cells

Joseph DeSimone (Primary Contact),
Marc Hillmyer[†], Frank Bates[‡]

University of North Carolina at Chapel Hill
CB#3290, 257 Caudill Labs
Chapel Hill, NC 27599-3290
Phone: (919) 962-2166; Fax: (919) 962-5467
E-mail: DeSimone@email.unc.edu

[†] University of Minnesota, Department of Chemistry

[‡] University of Minnesota, Department of Chemical
Engineering and Material Science

DOE Program Officer: Arvind Kini

Phone: (301) 903-3565

E-mail: aravinda.kini@science.doe.gov

Objectives

To develop crosslinked networks of cured liquid precursors (“Liquid Nafion”) with high acid content, which results in high proton conductivity and better performance at low relative humidity than Nafion, and can be molded into high surface area PEMs resulting in higher power density. To develop chemically stable, mechanically robust, high use temperature (>120°C) nanoporous networks from block copolymers. To fabricate a hybrid PEM from the nanoporous polymers and the Liquid Nafion. The nanoporous polymers will provide mechanical and thermal stability while the Liquid Nafion imparts proton conductivity.

Technical Barriers

The liquid precursor approach eases PEM processing and allows for high surface area PEMs, which increases power output within the same geometric volume and allows for the potential miniaturization of fuel cells. Additionally, improved proton conductivity at low relative humidity and operation at high temperatures (>120°C) is imparted. These properties should significantly simplify MEA design and lower cost by reducing cooling requirements and fuel purity requirements (particularly those associated with removing carbon monoxide that poisons the Pt catalyst).

Abstract

Polymer electrolyte membranes (PEMs) for fuel cells have been synthesized from easily processable, 100% curable, low molecular weight, reactive liquid precursors that are photochemically cured into highly proton conductive solid membranes. The liquid

precursor to solid membrane approach alleviates the need for further processing steps, such as melt extrusion or solvent casting. Chemical crosslinking allows for higher ion exchange capacity (IEC), and therefore, higher proton conductivity, without rendering the material water-soluble, which plagues commonly used non-crosslinked polymers. The mechanical strength of the material can easily be adjusted by altering the crosslink density. Fabrication of membrane electrode assemblies (MEAs) from these PEMs has resulted in fuel cells that have outperformed those based on Nafion[®]. Furthermore, the liquid precursor to solid membrane approach enables the fabrication of three-dimensional, patterned PEMs with high fidelity, micron-scale features by using soft lithographic/micromolding techniques. Patterned membranes have provided a larger interfacial area between the membrane and catalyst layer than standard flat PEMs. MEAs composed of the patterned membranes demonstrated higher power densities over that of flat PEMs without an increase in the macroscopic area of fuel cells. This can potentially miniaturize fuel cells and promote their application in portable devices. The liquid precursor approach also facilitates fabrication of composite membranes consisting of chemically, mechanically, and thermally robust nanoporous block copolymers impregnated with Liquid Nafion. The self-assembly of the block copolymers provides a means of controlling the nanoscale geometry of the proton conducting network and the block copolymers can improve mechanical properties, moisture retention, and long term stability of the hybrid membranes. Networks structures with percolating domains that do not require alignment are particularly promising morphologies. Three different strategies are being pursued to fabricate the nanoporous networks: chemical degradation of a minority component from network structures of pentablock copolymers, chemical degradation of the minority component of a crosslinked diblock copolymer adopting the double gyroid morphology, and solvent extraction of homopolymer from a multiply continuous microemulsion of homopolymer and multiblock copolymers. All three strategies offer the potential for mechanically robust and chemically stable nanoporous materials that can be filled with Liquid Nafion and used at temperatures above 120°C.

Progress Report

Polymer electrolyte membranes (PEMs) for fuel cells have been synthesized from easily processable, 100% curable, low molecular weight, reactive liquid precursors that are photochemically cured into highly proton conductive solid membranes. The thermal stability of these materials has been determined by

thermal gravimetric analysis (TGA), and they display a thermal decomposition temperature of 290°C in the acid form and 322°C in the sodium salt form. Successive fluorination via elemental fluorine gas results in higher thermal degradation temperatures (359°C in the sodium form). Both the fluorinated and non-fluorinated cases demonstrate stability at the target operating temperature range. The mechanical properties of the PEM materials were characterized by stress-strain measurements. The membranes become stronger as the IEC is increased. As the IEC increases from 0.53 to 1.82 meq/g, the moduli increase from 15 to 126 MPa. Water sorption and dimensional change were also studied as a function of IEC. In liquid water and over the same IEC range, the water uptake increased from 14 to 121 wt% and dimensional change increased from 9 to 44%. Water uptake studies were also performed in water vapor. At 100% RH, the water uptake varied from 13 to 50 wt%. Proton conductivity studies were also completed. The highest IEC (1.82 meq/g) studied has a conductivity of 0.254 S/cm in liquid water, which is almost 3 times higher than that of Nafion[®]. A very reliable house made apparatus was developed to measure proton conductivity at various temperatures and RHs with the capability of simultaneously measuring six samples. Membranes with IECs of 1.11 and 1.5 meq/g had higher IECs than Nafion[®] at all RHs and temperatures between 25 and 80°C. To investigate the effect of the highly proton conductive PEMs on fuel cell performance, MEAs were prepared. MEAs from liquid precursor PEMs outperformed Nafion[®] 117 despite the use of electrodes specifically designed for Nafion[®] and Nafion[®] 117 being thinner (175 versus 190 μm).¹

The mechanical integrity of the material has been adjusted by increasing the crosslink density by decreasing the molecular weight of the cure site macromonomer. By decreasing the molecular weight of the cure site macromonomer from 4,000 g/mol to 1,000 g/mol, the modulus increased from 55 to 108 MPa at an IEC of 0.83. Dimensional change of membranes with similar IEC decreased from 42% to 28% as crosslink density increased in this manner.

The liquid precursor to PEM approach has realized the fabrication of high surface area patterned PEM with unprecedented levels of morphological control (verified by SEM) through the use of micromolding/imprint lithography techniques. Fuel cell tests have confirmed an increased performance compared to flat membranes. When the cell potential is greater than 0.5V, the MEA performance was found to be closely proportional to the surface area of the PEM membranes, with higher surface area PEMs displaying better performance. At a current density of 360 mA/cm², the MEA made from a flat PEM displayed a power density of 127 mW/cm² compared to the 204 mW/cm² provided by the highest surface area PEM studied.¹

The highly fluorinated nature of the liquid precursors allows for easy impregnation of ePTFE films (verified by SEM) to form composite membranes. An ePTFE composite membrane has demonstrated higher proton conductivity than a non-composite membrane of similar IEC. Fuel cell performance looks promising even at low RH, and an increase in maximum MEA operating temperature has been observed. Long-term durability of membranes is also expected to be greatly increased.²

While the ePTFE composite membrane demonstrates the feasibility of the hybrid approach, it does not provide a means of controlling the nanoscale structure of the proton conducting channels. Block copolymer self-assembly provides a means of manipulating the structure on the nanometer length scale. Multiply continuous network morphologies are particularly attractive because they do not require any difficult or expensive alignment procedures. A well-defined nanoporous network of chemically, mechanically, and thermally robust polymer used in conjunction with Liquid Nafion could prove to be an exceptional hybrid PEM. Three strategies for fabricating these nanoporous structures are currently being pursued.

The first strategy focuses on pentablock copolymers. Three network morphologies have been identified over relatively large composition ranges in poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) triblock copolymers.³ While the multiply continuous domains make these morphologies attractive for membrane applications, the ISO triblocks are very brittle materials. The mechanical properties would improve significantly if these network morphologies could be obtained in poly(ethylene oxide-*b*-styrene-*b*-isoprene-*b*-styrene-*b*-ethylene oxide) (OSISO) pentablocks because the rubbery polyisoprene domain would be pinned at both ends by glassy polystyrene. The OSISO pentablock is thermodynamically similar to the ISO triblock because it has the same interaction parameters and required interfaces, making it reasonable to expect the existence of network phases in the pentablock system. A strategy utilizing the novel functional organolithium 3-triisopropylsilyloxy-1-propyllithium has been developed to synthesize well defined OSISO pentablocks.⁴ The orthorhombic network phase identified in the ISO triblocks has been identified in the OSISO pentablocks, the first such identification in a symmetric pentablock system. The pentablock network has mechanical properties far superior to the triblock networks, with a strain at break of 100-150% and a tensile stress of 5-6 MPa whereas the brittle triblocks crumbled upon loading into the tensile testing apparatus. This vast improvement validates the strategy of using the pentablock architecture.

The second strategy seeks to utilize diblock copolymers containing a modified polystyrene

block. The intrinsic brittleness and relatively low use temperature (<95°C) of widely-studied nanoporous polystyrene limits its utility as a material for PEMs. Polydicyclopentadiene (PDCPD) synthesized via ring-opening metathesis polymerization (ROMP) has shown promising mechanical properties with a modulus up to 2 GPa and tensile strength of about 50 MPa. PDCPD can be incorporated into the polystyrene matrix using a metathesis crosslinking reaction to improve the thermal and mechanical properties of nanoporous polystyrene monoliths. A new norbornene-functional block copolymer poly(norbornylstyrene-*s*-styrene)-*b*-polylactide has been synthesized. DCPD, which preferentially locates in the PNSS domain, was blended with metathesis catalyst and PNSS-PLA diblock copolymer that adopted a cylindrical morphology. The PLA cylinders were aligned and the PNSS matrix was crosslinked by simple heating. The PLA was chemically degraded to yield a solvent-resistant nanoporous monoliths with cylindrical channels, as confirmed by both SAXS and SEM. The resulting monoliths were thermally stable to temperature exceeding 120°C, a significant improvement compared to polystyrene. Preliminary tensile testing indicates crosslinked blends exhibited mechanical properties along the PLA cylindrical axis similar to PDCPD and that tensile strength and modulus decreased slightly following PLA degradation (1.5 GPa before PLA etching, 0.8 GPa after), excellent tensile strength (90 MPa before PLA etching, 60 MPa after), and modest elongation (strain at break of 11% before and after PLA etching).

The third strategy seeks to utilize a methodology for preparing a nanoporous material with an isotropic, three-dimensionally continuous pore structure from a polymeric bicontinuous microemulsion that was recently developed.⁵ A polymeric microemulsion was obtained by the judicious blending of immiscible polystyrene and polyisoprene with poly(styrene-*b*-isoprene) diblock copolymer. Crosslinking of the polyisoprene and the subsequent extraction of the polystyrene homopolymer led to the formation of a brittle isotropic nanoporous material with a resulting porosity on the order of 50%. A bicontinuous microemulsion of polyolefin block copolymers and homopolymers comprised of glassy poly(cyclohexylethylene) (C), elastomeric poly(ethylene-*alt*-propylene) (P), and semicrystalline poly(ethylene) (E) could provide a nanoporous material with the chemical, mechanical, and thermal robustness required for PEMs. Monodisperse CEC, CECECP, and P were synthesized by sequential anionic polymerization of styrene, butadiene, and isoprene followed by catalytic hydrogenation over a silica-supported Pt/Re catalyst. Ternary blends of CEC, CECECP, and P were prepared along the isopleth where CEC and P are mixed in equal volumes in an effort to locate the composition window of the bicontinuous

microemulsion phase. The two components of such a microemulsion would be the mechanically robust CEC/CECEC multiblock copolymers and the extractable P homopolymer. Preliminary small-angle x-ray scattering and rheology data are consistent with the existence of a microemulsion.

Future Directions

The morphology of the Liquid Nafion materials will be characterized via a combination of light scattering techniques and microscopy. Future efforts will also focus on making thinner and more robust membranes. Conditions for fluorination of high IEC membranes will be optimized and the use of low molecular weight crosslinkers will be studied as an alternative way to improve mechanical properties. ePTFE composite membranes will be analyzed with regards to operating temperature.

The pentablock strategy has improved mechanical robustness relative to triblocks and will now focus on improving chemical and thermal stability (upper use temperature of ~140°C) by shifting to pentablocks containing a degradable block along with CPC triblocks instead of SIS triblocks. Synthesis of these pentablocks with compositions that could yield multiply continuous network morphologies is currently underway. The diblock strategy will focus on generating robust cocontinuous nanoporous thin films by synthesizing PNSS-PLA diblocks that adopt the gyroid, and not cylindrical, morphology. The microemulsion strategy will focus on characterizing the current blends using TEM and SAXS in the hopes of definitively identifying a microemulsion. Once mechanically robust materials are generated using these strategies, the pores will be filled with Liquid Nafion that will be crosslinked to yield hybrid PEMs.

References

1. Zhou, Zhilian; Dominey, Raymond N.; Rolland, Jason P.; Maynor, Benjamin W.; Pandya, Ashish A.; DeSimone, Joseph M. *Journal of the American Chemical Society* **2006**, *128*, 12963-12972.
2. Liu, Wen; Ruth, Kathy; Rusch, Greg. *J. New Mat. Electrochem. Systems* **2001**, *4*, 227-231.
3. Epps, T. H.; Cochran, E. W.; Bailey, T. S.; Waletzko, R. S.; Hardy, C. M.; Bates, F. S. *Macromolecules* **2004**, *37*, 8325-8341.
4. Meuler, Adam J.; Mahanthappa, Mahesh K.; Hillmyer, Marc A.; Bates, Frank S. *Macromolecules* **2007**, *40*, 760-762.
5. Zhou, N.; Bates, F.S.; Lodge, T.P. *Nano Letters* **2006**, *6*, 2354.

Publications (Including Patents) Acknowledging the Grant or Contract

1. Zhou, Zhilian; Dominey, Raymond N.; Rolland, Jason P.; Maynor, Benjamin W.; Pandya, Ashish A.; DeSimone, Joseph M. "Molded, High Surface Area Polymer Electrolyte Membranes from Cured Liquid Precursors." *Journal of the American Chemical Society* **2006**, *128*, 12963-12972.
2. Meuler, Adam J.; Mahanthappa, Mahesh K.; Hillmyer, Marc A.; Bates, Frank S. "Synthesis of Monodisperse α -Hydroxypoly(styrene) in Hydrocarbon Media Using a Functional Organolithium." *Macromolecules* **2007**, *40*, 760-762.