

V.G.19 Improved Membrane Materials for PEM Fuel Cell Applications*

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Technical Barriers

This project addresses technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is focused on fundamental studies of PFSA membrane durability. Insights gained from these investigations will be applied toward design and synthesis of PEMs that will allow the following DOE 2010 targets to be met:

- Durability: 5,000 hrs (transportation); 40,000 hrs (stationary)
- Cost: \$20/m² (Alternative materials)
- Performance: 0.1 S/cm at 120°C and 50% relative humidity (RH)

Objectives

- Improve low temperature proton exchange membranes (PEMs) by identifying technological variations that prevent membrane failure by chemical/mechanical degradation.
- Pursue research avenues that elucidate failure mechanisms and suggest remedies that yield membranes meeting or exceeding a lifetime of 40,000-hr operation with 10% degradation in performance.
- Identify characterization tools that interrogate chemical, morphological and physical property changes of perfluorosulfonic acid (PFSA) membranes subjected to accelerated chemical degradation.
- Investigate membrane and membrane electrode assembly (MEA) processing parameters that influence performance and chemical durability.
- Exploit dielectric spectroscopy to identify/probe molecular motions impacted by degradation and relate to polymer structure.
- Collect and integrate critical structure-property information in order to develop methods that lead to significant improvements in the durability and performance of PEM fuel cell membrane materials.

Accomplishments

- Solution-processed Nafion[®] membranes with mixed tetrabutyl ammonium and Na⁺ ions were used to produce membrane electrode assemblies and fuel cell testing revealed that performance and power density increase with increase of tetrabutyl ammonium content used during the casting step.
- Broadband dielectric spectroscopy (DS) was demonstrated to be a powerful technique in analyzing macromolecular motions in membranes over a vast range of time and distance scales, and how hydration and chemical degradation influences these motions.
- Real time drying experiments with DS of acid form Nafion[®] revealed a shift in macromolecular dynamics which is relevant in the context of membrane desiccation at high temperatures.
- The α relaxation was shown to be associated with the acid side chains as they transition from being in static to dynamic aggregates while the β relaxation is the backbone-related glass transition.
- Fenton-degraded membranes have slower T_g -related motions which was attributed to an a shift in Nafion[®] average molecular weight.
- Durability of Nafion[®] was improved by enhancing its mechanical and barrier properties via in situ grown titania sol gel networks.



Introduction

A Nafion[®] solution processing method involving mixed counterions was developed to produce MEAs. Fuel cell testing of these materials was conducted to establish performance and power density characteristics. Processes for membrane-in situ growth of hydrophilic inorganic oxide nanoparticle growth via sol-gel chemistry were explored. The effect of in situ grown titania networks on performance and durability was investigated. The potential of using broadband dielectric spectroscopy to identify molecular motions in Nafion[®], to monitor changes in these motions at low humidification at high temperatures, and to detect changes in these motions with chemical degradation in fuel cells, was assessed.

Approach

The following characterization techniques were applied to analyze structure/property changes of membranes subjected to accelerated chemical degradation. Morphology was investigated using transmission electron microscopy, scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy, atomic force microscopy, small angle X-ray scattering, and side-angle X-ray diffraction. Chemical composition and inorganic oxide bonding structure were elucidated using ¹⁹F and ²³Na solid-state nuclear magnetic resonance and Fourier transform infrared spectroscopic methods. Tensile testing and dynamic mechanical analysis were used to monitor changes in mechanical properties and thermal transitions with membrane modification and degradation. DS was employed to monitor changes in chemical microstructure and morphology caused by degradation. Proton conductivity measurements and determination of water diffusion by pulsed field gradient spin echo nuclear magnetic resonance experiments were used to study molecular transport properties.

Results (Highlights)

Figure 1 indicates how solvent and casting temperature affects solubility of H⁺ solution-processed membranes. For each solvent used, percent solubility of all solution-processed membranes decreased with increasing casting temperature.

Mechanical properties of membranes at 80°C and 100% RH were tested in a custom design environmental chamber and sparger. After mounting, the samples were conditioned for 2 hrs in a 100% RH nitrogen stream at 80°C. After such conditioning, the crosshead position was slowly adjusted until a 0.1 N tension was detected. The crosshead position was then locked and the 100%

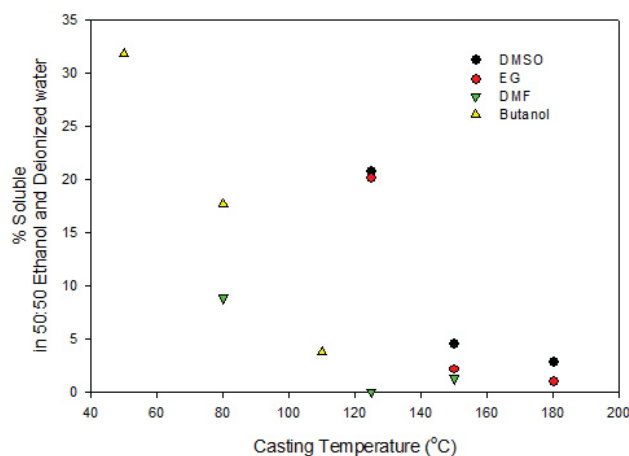


FIGURE 1. Percent solubility of solution-processed H⁺ form Nafion[®] using various solvents and casting temperatures.

humidified N₂ stream switched to dry N₂ at the same flow rate. This change of circulating gas stream causes the membrane to dehydrate and the sample attempts to regain its un-swollen length. Since the clamps are locked at the swollen length they have a contractile force exerted on them. These resistive forces were monitored for 2 hrs after the humidity drop and Figure 2 shows stresses developed for two Nafion[®] and two Nafion[®]/titania membranes measured for 2 hrs after the humidity drop.

Stress-time profiles for two Nafion[®] controls peak at around 1.56 MPa and 1.89 MPa. The profiles for both samples are similar and both yield after reaching a critical stress. Due to low modulus and lack of cross-linking or reinforcement in this unfilled membrane, it is unable to withstand the contractile stress developed and yields perhaps through chain slippage through entanglements. In strong comparison, the composite membrane resists the dimensional constraint. For both composite samples, at ~70 min the stress reaches peak values of 8.4 and 8.6 MPa and remains fairly constant during the experiment. The in situ grown titanium oxide quasi-networks provide good membrane reinforcement and prevent yielding due to humidity change.

Damage surface morphology of the clamped Nafion[®] and Nafion[®]/titania membranes subjected to this RH drop was inspected using SEM and is shown in Figure 3. The unfilled Nafion[®] membrane shows significant signs of yielding. The entire width of the membrane shows cavities and stretching/orientation indicating failure propagation. On the contrary, the Nafion[®]/titania membrane does not show such cooperative failure. There are isolated cavities but mechanical integrity is greatly improved relative to the unmodified membrane. These morphological results and interpretations are highly supported by the contractile stress vs. time curves in Figure 3 that show a significantly greater resistance offered by the composite.

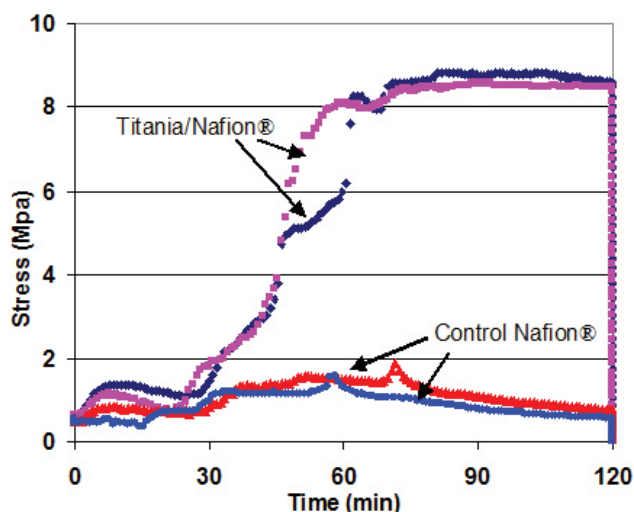


FIGURE 2. Contractile stress development with RH drop for Nafion[®] controls and Nafion[®] membranes incorporating sol-gel-derived titania.



FIGURE 3. SEM micrograph of Nafion[®] (bottom) and Nafion[®]/titania (top) membrane after contractile stress buildup vs. time at constant strain experiments with drop in RH.

Polarization curves of the Nafion[®]/titania and Nafion[®] control membranes in a fuel cell before and after an open circuit voltage (OCV) test are in Figure 4. Performance of the titania-incorporated Nafion[®] membrane is extremely poor compared to that of the pure Nafion[®] membrane. Based on low water uptake and low proton conductivity, this poor performance is not unexpected. However, the performance of the Nafion[®]/titania membrane is unchanged after the OCV test compared to a huge drop in performance of the Nafion[®] membrane. The unmodified Nafion[®] membrane, due to poor dimensional stability and poor mechanical properties, yields under stresses developed due to RH and temperature changes. Weak regions

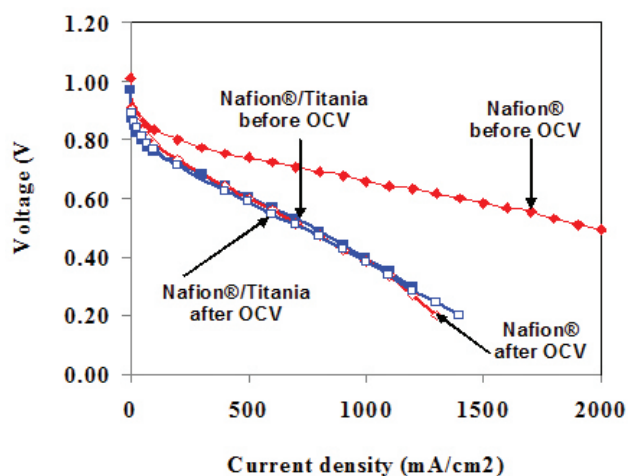


FIGURE 4. Polarization curves for Nafion[®] and Nafion[®]/titania membranes before and after OCV at 80°C, 75% RH.

may serve as easy paths for gas diffusion, offering less resistance due to thickness reduction. Periodic swelling/de-swelling stresses induced during fuel cell operation will lead to further membrane weakening and increase fuel crossover. Crossover produces hydrogen peroxide which on decomposition forms reactive hydroxyl radicals which degrade polymer chains. Thus, mechanically weak regions, after experiencing microscopic material hysteresis owing to periodic stresses, and attack from hydroxyl radicals, may eventually form pinholes.

For the Nafion[®]/titania membrane, the inorganic reinforcement significantly improves dimensional stability and increases initial elastic modulus which helps resist physical stresses. Also, the network imparts better fuel gas barrier properties reducing chemical degradation due to crossover.

Conclusions and Future Directions

- With increasing casting temperatures, membrane extractable reduced for the solvent used.
- The titania modified Nafion[®] microstructure can better withstand humidity changes and exhibits less physical degradation than unmodified Nafion[®].
- However, the fuel cell performance of the titania modified membrane is less than that of the unmodified Nafion[®] membrane presumably due to low water uptake, restricted side chain mobility and increased tortuosity that impedes proton transport.
- After accelerated chemical degradation under OCV conditions, unmodified Nafion[®] shows significant performance loss whereas Nafion[®]/titania performance shows no performance loss. This indicates that such an inorganic modification imparts physical and chemical durability to Nafion[®]. At the least, this effort represents a model study

of how Nafion® can be modified for improved durability in fuel cells.

Special Recognitions & Awards/Patents Issued

1. K.A. Mauritz received Outstanding School of College and Science and Technology Researcher Award, University of Southern Mississippi, 2007, largely for his work in fuel cell membrane modification and characterization.

FY 2008 Publications/Presentations

Publications

1. Mauritz, K.A.; Hassan, M.K. "Nanophase Separated Perfluorinated Ionomers as Sol-Gel Polymerization Templates for Functional Inorganic Oxide Nanoparticles" *Polymer Reviews* 2007, 47, 543.
2. Rhoades, D.W.; Hassan, M.K.; Osborn, S.J.; Moore, R.B.; Mauritz, K.A. "Broadband Dielectric Spectroscopic Characterization of Nafion® Chemical Degradation." *J. Power Sources* 2007, 172, 72.
3. Page, K.A.; Jarrett, W.; Moore, R.B. "Variable Temperature ¹⁹F Solid-State NMR Study of the Effect of Electrostatic Interactions on Thermally-Stimulated Molecular Motions in Perfluorosulfonate Ionomers," *J. Polym. Sci., Part B: Polym. Phys.*, Accepted, in press 2007.
4. Hassan, M.K.; Mauritz, K.A. "Broadband Dielectric Spectroscopic Studies of Nafion® Silicate Nanocomposite Membranes" *PMSE Prepr.* 2008, 98, 891.
5. Hassan, M.K.; Mauritz, K.A. "Nafion® Silicate Hybrid Membranes Via Dibutyltin Dilaurate-Catalyzed in Situ Sol-Gel Processes" *PMSE Prepr.* 2008, 98, 740.
6. Hassan, M.K.; Rhoades, D.W., Osborn, S.J.; Moore, R.B.; Mauritz, K.A. "Chain Dynamics of Nafion® Films Neutralized with Tetrabutyl Ammonium Counterions as Investigated by Broadband Dielectric Spectroscopy" *Amer. Chem. Soc., Div. Fuel Chem. Prepr.* 2008, 53, 533.

Presentations

1. K.A. Mauritz: "Organic-Inorganic Nanocomposite Fuel Cell Membranes." ACS Symposium on Organic/Inorganic Hybrid Materials II, Ventura Beach, CA, 2-5 Mar 08. Invited.
2. K.A. Mauritz, "Model studies of the characterization of the durability of Nafion® membranes and Nafion/inorganic oxide nanocomposite membranes." Materials Research Society Meeting, San Francisco, 5 Mar 08. Invited.
3. K.A. Mauritz, "Characterization of the durability of Nafion membranes and Nafion/inorganic oxide nanocomposite membranes." Illinois Institute of Technology, 7 May 08. Invited.

4. Hassan, M.K.; Mauritz, K.A. "Broadband Dielectric Spectroscopic Studies of Nafion® Silicate Nanocomposite Membranes" *Amer. Chem. Soc. Spring Meet, New Orleans*, 10 Apr 2008.
5. Hassan, M.K.; Mauritz, K.A. "Nafion® Silicate Hybrid Membranes Via Dibutyltin Dilaurate-Catalyzed in Situ Sol-Gel Processes" *Amer. Chem. Soc. Spring Meet, New Orleans*, 9 Apr 2008.
6. Hassan, M.K.; Rhoades, D.W., Osborn, S.J.; Moore, R.B.; Mauritz, K.A. "Chain Dynamics of Nafion® Films Neutralized with Tetrabutyl Ammonium Counterions as Investigated by Broadband Dielectric Spectroscopy" *Amer. Chem. Soc. Spring Meet, New Orleans*, 10 Apr 2008.
7. K.A. Mauritz "Characterization of Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Simon Fraser University, Vancouver, BC, 11 Dec 07.
8. K.A. Mauritz, "Characterization of the Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Chemical Sciences Division Seminar, Oak Ridge National Labs, 4 Jun 07.
9. K.A. Mauritz, "Characterization of the Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Plenary Speaker, 2007 National Graduate Polymer Research Conference, U. Tennessee, 6 Jun 07.
10. Patil, Y., Mauritz, K.A. "Inorganic Modification of Nafion® for elevated temperature fuel cell operation." *Am. Chem. Soc. Fall Natl. Meet, 2007, Boston*.