

V.M.7 Improved Membrane Materials for PEM Fuel Cell Applications*

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Contract Number: DE-FG36-06GO86065

Project Start Date: June 1, 2006
Project End Date: November 30, 2007

*Congressionally directed project

Objectives

- General: Lifetime improvements of low temperature proton exchange membranes 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.

Technical Barriers

This project addresses technical barriers from the Fuel Cells section 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 polymer electrolyte membranes (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 ambient to 120°C;
0.01 S/cm -20°C

Accomplishments

- Solution-processed Nafion[®] membranes with mixed tetrabutylammonium and Na⁺ ions were used to produce MEAs and fuel cell testing revealed that performance and power density increase with increase of tetrabutylammonium 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 chemical degradation influences these motions.
- Real time drying experiments with DS of acid from 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 α relaxation is the backbone-related glass transition.
- Fenton-degraded membranes have slower T_g-related motions which was attributed to a shift in Nafion[®] average molecular weight.
- Hydrophilic inorganic oxide nanostructures were grown, molecule-by-molecule in Nafion[®] using *in situ* sol-gel processes and nanocomposite structure and properties were elucidated.



Introduction

These studies were directed toward producing superior MEAs, understanding the mechanism of membrane degradation within the context of durability and modifying Nafion[®] membranes for higher temperature operation.

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. The potential of using broadband dielectric spectroscopy to identify the 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. Processes for the membrane *in situ* growth of hydrophilic inorganic oxide nanoparticle growth via sol-gel chemistry were explored.

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 (TEM), scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), small angle X-ray scattering analysis (SAXS), and wide-angle X-ray diffraction (WAXD). Chemical composition and inorganic oxide bonding structure was elucidated using ¹⁹F and ²³Na solid-state nuclear magnetic resonance (SSNMR) and Fourier transform infrared (FTIR) spectroscopic methods. Tensile testing and dynamic mechanical analysis were used to monitor changes in mechanical properties and thermal transitions with membrane modification and degradation. Dielectric spectroscopy 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 (NMR) experiments were used to study molecular transport properties.

Results

Solution-processed 2 mil thick Nafion[®] membranes with mixed tetrabutylammonium and Na⁺ ions were used to produce MEAs and studied under fuel cell conditions. Figure 1 shows fuel cell performance and power density curves of membranes with different compositions after a 12 h activation period where the load was constant at 0.5 V. Fuel cell testing studies revealed that performance and power density increase with increase of tetrabutylammonium content used during the casting

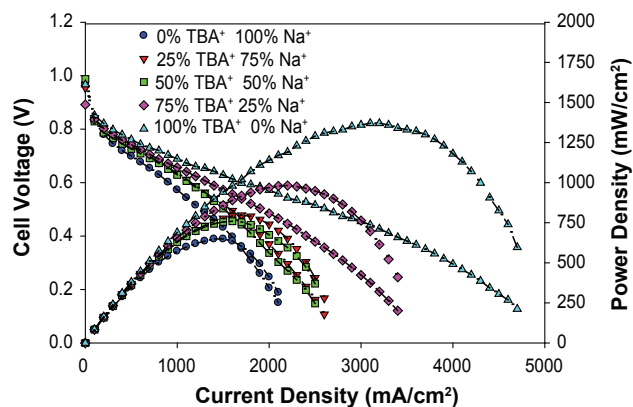


FIGURE 1. Solution Processed Nafion[®] Membranes (180°C), 2 mil thick, 1,100 EW with mixed TBA⁺ and Na⁺ counterions, reacidified in 4M sulfuric acid in methanol; 5 cm² cell; Pt loading=0.5 mg/cm² on anode and cathode (decal method); H₂/O₂ stoich. =1.5/2; T_{cell}=60°C, T_{anode humidifier}=70°C (100% RH), T_{cathode humidifier}=55°C (80% RH)

step. The membrane solution processed with 100% tetrabutyl ammonium (TBA⁺) is able to produce a maximum power density almost 1,400 mW/cm² at 3,500 mA/cm² and fuel cell potential of 0.5 V at 2,800 mA/cm². The ability to increase fuel cell performance of solution-processed Nafion[®] membranes by using different counterions may be a step in understanding the morphology of solution-processed Nafion[®] membranes.

The longstanding question of how small unknown quantities of water affect the physical properties of Nafion[®] was addressed. *In situ* testing methods were established to monitor moisture levels between specimens in the interest of reproducibility and an accurate/reproducible method to control moisture content was developed. Real-time drying experiments of Nafion[®] revealed a shift in macromolecular dynamics and these results are relevant in the context of membrane hydration at high temperatures.

In parallel with dynamic mechanical analysis (DMA) studies, DS studies showed that the α relaxation is 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. Membranes degraded for 75 h in Fenton's reagent have slower T_g-related motions which is attributed to increase in average polymer molecular weight (MW) as the low MW fraction leaches out of the membrane and Fe⁺² ions complex with sulfonate groups.

The β relaxation does not follow Arrhenius behavior as log β_{max} vs. 1/T curves are nonlinear (Figure 2). Curves for films degraded for 75 h followed by HCl wash shift to longer relaxation times showing that degradation restricts chain motions by shifting the distribution of Nafion[®] MW.

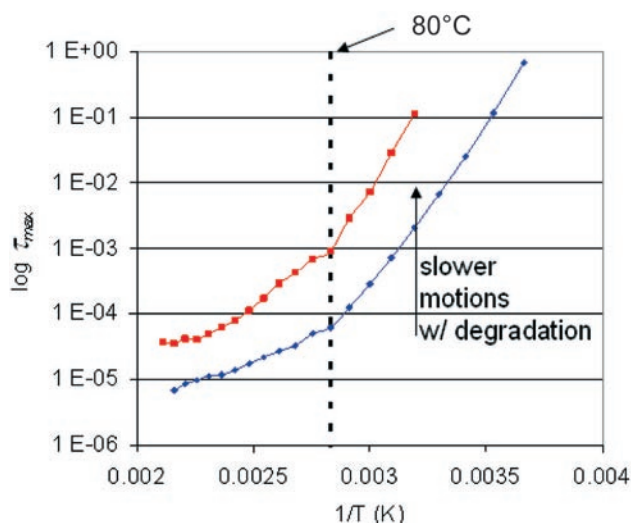


FIGURE 2. Log τ_{\max} vs. $1/T$ for Non-Degraded Films (lower) and 75 h Degraded Films Cleaned with HCl (no Fe^{2+} present) after Degradation (upper)

Successful *in situ* molecule-by-molecule growth of hydrophilic inorganic oxide nanostructures was affected in Nafion[®], using sol-gel processes, to impart good high temperature performance. Bonding structures within nanoparticles were determined using FTIR spectroscopy. Silicates formed by tetraethylorthosilicate do not hinder conductivity whereas those formed by triethoxysilane do. Sol-gel-derived zirconia, alumina and titania all reduce membrane proton conductivity, perhaps by shielding SO_3H groups from proton hopping or simply by introducing transport tortuosity.

Conclusions and Future Directions

- Solution-processed Nafion[®] membranes with mixed tetrabutylammonium and Na^+ counterions were used to produce membrane/electrode assemblies; fuel cell tests revealed that performance and power density increase with increase in TBA^+ content.
- Broadband dielectric spectroscopy uncovered chain dynamics in membranes at low degrees of hydration and the results are relevant with respect to high temperature fuel cell operation.
- Macromolecular chain motions in membranes degraded in Fenton's reagent become slower because of a shift in molecular weight distribution.
- Inorganic oxide nanostructures were incorporated in Nafion[®] membranes to enhance hydration and characterized for bonding structure and properties.
- Fuel cell testing of the effect of various MEA processing procedures on durability and performance will be conducted.
- Dynamic mechanical relaxations will be correlated with fuel cell performance.

- Effect of alkylammonium counterion catalyst inks on three phase interface in MEA will be studied.
- Mechanical aspects of membrane durability (chemical degradation, RH cycling) will be assessed using stress relaxation, creep and nanoindentation techniques.
- Nafion/[inorganic oxide] membranes:
 - The stability of inorganic nanoparticles as exposed to fuel cell environmental factors will be determined.
 - The potential of using silicate nanoparticle surface functional groups to act as $\bullet\text{OH}$ scavengers will be explored.
 - Metal ions will be inserted into silicate quasi-networks as structure modifiers and to enhance membrane hydrophilicity.

FY 2007 Publications/Presentations

Publications

1. 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*. In press, 2007.
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2. Rhoades, D.W.; Mauritz, K. A.; Peusch, D. "Dielectric Spectroscopic Analysis of Amine Modified Nafion[®] Precursor Films". *Amer. Chem. Soc. PMSE Prepr.* 2006, 95, 952.

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5. Mauritz, K.A. "Characterization of the Durability of Nafion Membranes and Nafion/Inorganic Oxide Nanocomposite Membranes". Dept. Chemical Engineering, Colorado School of Mines, Golden CO, 13 Oct 06.
6. K.A. Mauritz, Dielectric Spectroscopy as a Probe of Molecular Motions in, and Chemical Degradation of Nafion and Hydrocarbon Fuel Cell Membranes. Asilomar Conference on Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Pacific Grove, CA, 18–21 Feb 2007.
7. S.J. Osborn, 2007 Spring AIChE Meeting, Houston, TX. "Analysis of the Physical and Chemical Stability of Cast Nafion[®] Membranes with Respect to Methanol Solubility and Radical Attack", April 26, 2007.
8. K.A. Mauritz and Mohammad, Hassan, "Broadband Dielectric Spectroscopy Characterization of Chemical Degradation in Nafion[®]/Silicate Nanocomposite Membranes." AIChE Meet, Houston, TX, 26 Apr 07.
9. K.A. Mauritz and Mohammad Hassan, "Characterization of the Durability of Nafion Membranes and Nafion/Inorganic Oxide Nanocomposite Membranes." AIChE Meet., Houston, TX, 26 Apr 2007.
10. 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.
11. 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
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15. "Probing the Molecular and Morphological Origins of Relaxations in Perfluorosulfonate Ionomers", Drexel University, Department of Chemical and Biological Engineering, Philadelphia, PA, September 29, 2006.
16. "Manipulating the Glass Transition of Nafion[®]: Membrane Properties and PEMFC Performance," Plenary Lecture at the 2006 Fall ACS Meeting, Div. Fuel Chem., San Francisco, CA, September 11.