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 dessication 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 35F 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 pulse 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 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 Tg –related motions which is attributed to increase in average polymer molecular weight (MW) as the low MW fraction leaches out of the membrane and Fe2+ ions complex with sulfonate groups.

The β relaxation does not follow Arrhenius behavior as log βmax 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.
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$_3$H 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 OH scavengers will be explored.
  - Metal ions will be inserted into silicate quasienetworks as structure modifiers and to enhance membrane hydrophilicity.

FY 2007 Publications/Presentations

Publications


Presentations


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.