

VII.B.11 Hydrocarbon Membrane

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Objectives

- Improve the fuel cell operating performance at low relative humidity (RH) and elevated temperature by designing a polymer electrolyte membrane (PEM) that can operate more efficiently at these conditions
- Improve the efficiency of hydrocarbon-based PEM materials by utilizing alternative electrolyte within the catalyst structures
- Improve overall PEM fuel cell operating efficiency

Technical Barriers

This project addresses the following 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. Electrode Performance
- D. Thermal, Air, and Water Management
- F. Fuel Cell Power System Integration

Technical Targets

This research task addresses several technical challenges and barriers as outlined in the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) Multi-Year Research, Development and Demonstration Plan (MYRDDP). The technical tasks addressed by this research project are crosscutting and consequently include fundamental research needs in the areas of high temperature membranes for distributed power applications; advanced membrane R&D; membrane electrode assembly (MEA) materials, components, and processes; advanced MEA meeting 2010 targets; direct methanol fuel cells; and fuel cell cold start. This research effort is directed at developing a hydrocarbon-based PEM material with low humidity and low- to high-temperature PEM conductivity (<25% RH and >80 mS/cm). The desired PEM will have low gas permeability (hydrogen and oxygen crossover) while maintaining good electrical and mechanical properties with a low-cost hydrocarbon membrane. Research in this area will investigate new approaches and materials for the development of electrode structures that have good adhesion between new membranes and catalyst layers, as well as studying the relationships between ionomer content, type, electrode structure, water and gas transport, proton conductivity, and fuel cell performance. The expected outcome and significance of this research plan is the development of a structure-property-performance relationship based upon this fundamental research project for PEM and MEA design and operation. This work will directly contribute to the achievement of the goals and targets set by the Department of Energy's HFCIT Program by advancing fuel cells with PEMs and MEAs that have improved humidity-insensitive conductivity, enhanced durability, lower cost, and improved fuel cell performance and will contribute in the realization of a hydrogen-based economy.

Approach

- Design alternative PEM hydrocarbon membranes with improved fuel cell performance at low RH and elevated temperature
- Utilize controlled polymer morphology to improve low-RH fuel cell activity
- Develop catalyst coating approaches to integrate Nafion[®]-based electrodes with the hydrocarbon-based PEM
- Investigate and design methods to improve the interface between hydrocarbon membranes and Nafion-based anode and cathode electrodes
- Investigate use of hydrocarbon-based electrolytes for replacement of Nafion in the anode and cathode electrodes for reduction in interfacial resistance and improved fuel cell performance

Accomplishments

- Demonstrated a relationship between ion exchange capacity (IEC) and H₂ crossover, and demonstrated existence of an area with optimal IEC and fuel cell performance as well as minimized hydrogen and oxygen crossover
- Demonstrated that thinner membranes can be used without significant reactant crossover
- Demonstrated improved proton conductivity over Nafion at 50% RH
- Over a 2-month period, we have been able to demonstrate better performance than Nafion at modest RH and temperature
- Successfully synthesized and demonstrated performance of hydrogen fuel cell based upon Sandia's hydrocarbon-based PEM
- Characterized hydrocarbon membrane via differential scanning calorimetry, thermal gravimetric analysis, dynamic mechanical analysis, infra-red spectroscopy, water-uptake, IEC, tensile strength, and elemental analysis.
- Demonstrated hydrocarbon membrane performance with a MEA with Nafion and Sandia's hydrocarbon membrane within the electrode structure at a total catalyst loading of less than 0.5 mg/cm²
- Demonstrated that hydrocarbon membranes have a H₂ and O₂ crossover current of 5 mA/cm² at a temperature of 80°C

Future Directions

- Continue the evaluation of hydrocarbon membrane and its use in a fuel cell
- Continue to develop improved MEA fabrication protocols
- Investigate the effects of thermal cycling and water content on internal membrane stresses, and determine the impact of these stresses on PEM mechanical stability
- Continue to evaluate high-temperature, low-humidity, fuel cell PEM properties
- Develop a non-Nafion based MEA technology
- Investigate viscoelastic mechanisms associated with PEM thinning, conductivity degradation, and transport changes in PEM and MEA
- Investigate alternative proton conduction groups for low-humidity, high-temperature fuel cell operation
- Investigate the effect of low-temperature fuel cell start-up on PEM properties

Introduction

The cost and performance limitations of current perfluorinated polymer electrolyte membranes (PEM) such as Nafion have hindered large-scale commercialization and market penetration of polymer electrolyte membrane fuel cells (PEMFC) in mobile and stationary systems. This has sparked a worldwide research effort to design alternative PEM materials with high ionic conductivity, thermal stability to allow operation at temperatures over 100°C, chemical stability to strong acid proton conductors, oxidative stability, good processability, and excellent barrier properties to fuels (e.g., methanol, oxygen, etc.). One common approach has been to sulfonate existing thermoplastics such as polystyrene, polyetherketones, and polyethersulfones. This has generated PEMs with lower costs and some materials with improved thermal stability, but generally lower ionic conductivities at comparable ion exchange capacities than Nafion. However, many of these thermoplastic-based PEMs are more susceptible to oxidative or acid catalyzed degradation than Nafion. Utilizing a purely aromatic polymer, such as poly(phenylene)s, provides a route to potentially improve the oxidative and acid catalyzed degradation stability of PEMs due to the inherent thermochemical stability of such materials. In addition to chemical stability, high molecular weights are necessary for these aromatic polymers to ensure polymer chain entanglements that are responsible for producing physically robust PEM films that can be processed into membrane electrode assemblies that survive within a PEMFC. We have generated sulfonated poly(phenylene) that provides a very promising solution to producing PEMs with high molecular weights, good hydrogen fuel cell performance, and improved operating temperature capabilities. These material traits are consistent with the goals of developing a low-relative-humidity PEM that can operate at elevated temperatures.

Approach

The following approach is being used to achieve the objective of developing a fuel cell stack with a polymer electrolyte membrane that has high material durability, manufacturability, and low cost. The ideal physical properties of this alternative hydrocarbon PEM include the ability to operate at

low humidity and low to elevated temperatures and the physical integrity to survive material stresses during cycling (-40°C to 120°C and shut-down to start-up). These properties are believed to be critical in the development of a low-humidity PEM material. Current PEM materials utilize sulfonic acid moieties for proton conduction, but these acid moieties require water to facilitate proper solvation and dissociation that are necessary for proton conduction. One goal of an alternative PEM material is to operate at a low RH and dynamic temperature ranges (-30°C to 120°C) in order to have the fuel cell stack operate at atmospheric pressure. The development of a PEM material that requires little to no water for proton conduction is the primary goal of this work. Developing such a PEM material is recognized to have significant impact on water management in a fuel cell; it would reduce the overall weight, enable better heat management, and reduce the cost of the fuel cell stack. This research task is divided into several subtasks to address fundamental material research needs in the areas of hydrocarbon PEM development. These research areas include PEM development, addressing the catalyst-membrane integration challenges with hydrocarbon-based PEMs, tailoring gas and liquid transport within the MEA catalyst layer, and the development of alternative electrolytes in order to create a compatible interface between the MEA and the PEM to minimize interfacial resistance and maximize fuel cell performance.

We will also explore approaches for mitigating structural changes in the PEM and MEA due to viscoelastic flow caused by water plasticized membranes, which causes membrane thinning; MEA-PEM cracking and pinholes; the interface between the PEM and catalyst layer; and freezing water that contributes to premature MEA and fuel cell stack failures. Future Sandia PEM materials will be functionalized with phosphonic acid and imidazole groups to improve proton conduction characteristics at low- to zero-humidity conditions with polymer blends, random and block ionomers. An additional advantage of utilizing a blend is that ionic interactions can be used to stabilize acid groups, and these interactions can be used to force self-assembly of the PEM such that more efficient proton conduction can occur within the final PEM structure. This optimized PEM structure is believed

to be necessary for better utilization of water present and proton conductive groups that also minimize PEM swelling.

Results

The hydrogen fuel cell performance of the sulfonated Diels-Alder polyphenylene (SDAPP) series of materials was investigated to evaluate its potential as a fuel cell membrane. In order to evaluate the potential of the SDAPP materials, it was necessary to form an MEA. MEAs were formed based on standard ink hand painting techniques developed at Los Alamos National Laboratory and the decal method. The ink process involves creating a colloidal suspension of Pt/Pt-alloy catalyst in water, isopropanol, and Nafion1100 solution. The final target composition was varied to investigate the impact of ionomer loading in the electrode catalyst layers on fuel cell performance. Electrodes were applied to the PEM by painting multiple layers of the catalyst ink suspension with a paintbrush to achieve the target catalyst loading, or the decal method was utilized to create the MEA. The final MEA was assembled into a Fuel Cell Technologies 500-mm² test cell and tested using ETEK LT-1400W 18 mil thick gas diffusion layers at the anode and cathodes. A 120A Fuel Cell Technologies test unit equipped with high-frequency impedance was used to evaluate all samples. This test unit has the capability to measure the bulk proton conductivity of the PEM, follow changes in high-frequency resistance (HFR) due to membrane dry-out or electrode failure, and assess the role of interfacial resistance due to poor adherence between the PEM and the electrode composite. Figure 1 displays the performance of the SDAPP series as a function of conductivity or IEC within a hydrogen fuel cell operating at 375 K (100°C) and 100% RH with 240 kPa (20 psig) backpressure on the anode and cathode, and reactant flow rates of H₂ at 3.21e⁻⁷ kg/s (200 SCCM), and O₂ at 1.19e⁻⁵ kg/s (500 SCCM). Results from this work show that with increasing IEC there is a significant improvement in fuel cell power output, and there appears to be a transition in HFR from SDAPP1 to SDAPP2 to lower values or increasing proton conductivity, but there was not a significant change in HFR when increasing the IEC from 1.4 to 1.8 as seen in SDAPP2 and SDAPP3. As shown in this figure, a large HFR (0.82 Ω*cm²) is observed for

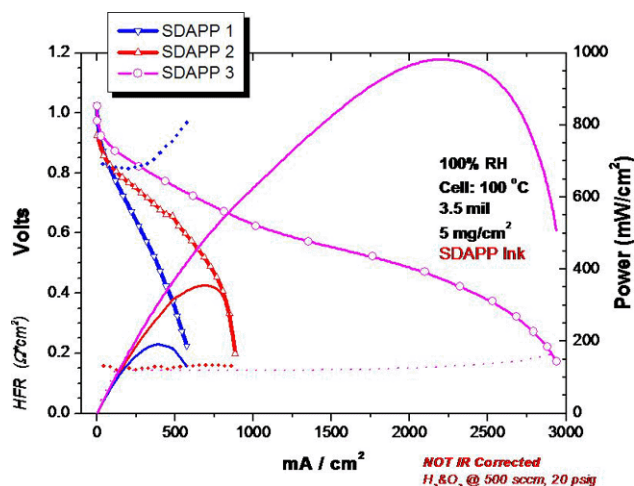


Figure 1. Hydrogen fuel cell performance as a function of IEC represented by SDAPP1 (0.94 IEC), SDAPP2 (1.4 IEC), and SDAPP3 (1.8 IEC). Hydrogen fuel cell conditions are 100°C and 100% RH with 20 psig backpressure, 200 sccm H₂, and 500 sccm O₂ with a membrane thickness of 3.5 mil.

SDAPP1 that quickly increases with increasing current density. This behavior is attributed to membrane dehydration due to electro-osmotic drag that also results in a loss in proton conductivity. Overall, this sample has an inadequate concentration of sulfonic acid groups necessary for good proton conductivity and fuel cell performance. Increasing the concentration of sulfonic acid groups from an IEC of 0.98 to 1.4 results in a dramatic increase in fuel cell performance, as demonstrated with SDAPP2 (350 mW/cm²) versus SDAPP1 (175 mW/cm²). This increase in IEC also results in a significantly low HFR (0.15 Ω*cm²) that is constant throughout the fuel cell test. This performance improvement is attributed to the increase in proton conductive carriers (sulfonic acid groups) and better electrode adherence to the PEM. Maximum fuel cell performance was observed for SDAPP3 that also had a low HFR throughout the test (0.15 Ω*cm²). The power density of this sample reached 980 mW/cm² at 2900 mA/cm², which is 2.8 times greater than that of SDAPP2 and 5.6 times greater than that of SDAPP1. This dramatic improvement in fuel cell performance resulting from increasing the IEC from 0.98 to 1.8 appears to suggest a percolation effect with regard to performance. In fact, the transition appears to be centered between an IEC of 1.4 and 1.8. While

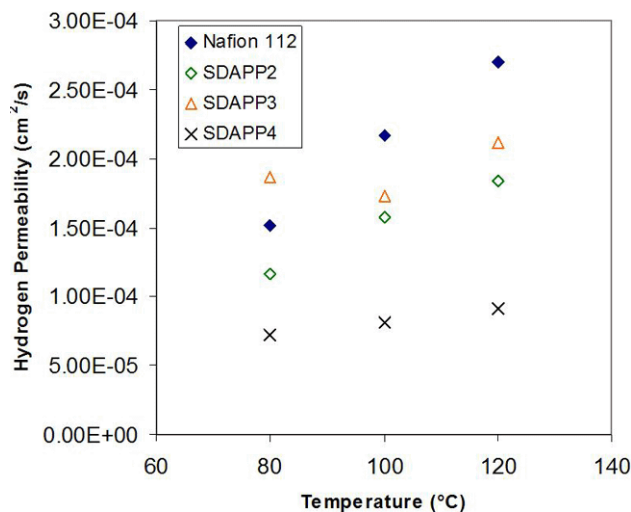


Figure 2. SDAPP membranes show lower crossover currents and permeability than N112, especially at higher temperatures.

SDAPP4 was not tested, it is expected to result in further fuel cell power density improvements over SDAPP3. Results from this work reveal good fuel cell performance at 100°C and 100% RH, which indicates that it is possible to use an alternative electrolyte in the catalyst electrode structure. Further work should be done in this area to maximize the performance of this alternative electrolyte.

Figure 2 is a comparison of the SDAPP2 (IEC 1.4), SDAPP3 (IEC 1.8), SDAPP4 (IEC 2.2), and Nafion112 hydrogen permeability as a function of temperature (253 K to 393 K). The normalized hydrogen flux is represented as cm^2/s , and from this work there appears to be an optimal IEC for this SDAPP material that minimizes hydrogen crossover. The general trend from this work is that at lower IEC values there is not a dramatic change in hydrogen crossover, but by increasing the IEC to 2.2, there is a significant drop in hydrogen gas crossover. Additional experimental studies in this area need to be completed to further validate these results. However, this demonstrates the general need to optimize the IEC for power output but also to balance the changing rates of oxygen and hydrogen crossover that will occur with alternative hydrocarbon-based PEMs.

The high-temperature performance of SDAPP4 was evaluated versus Nafion112 to test its potential as a high-temperature fuel cell membrane. The film

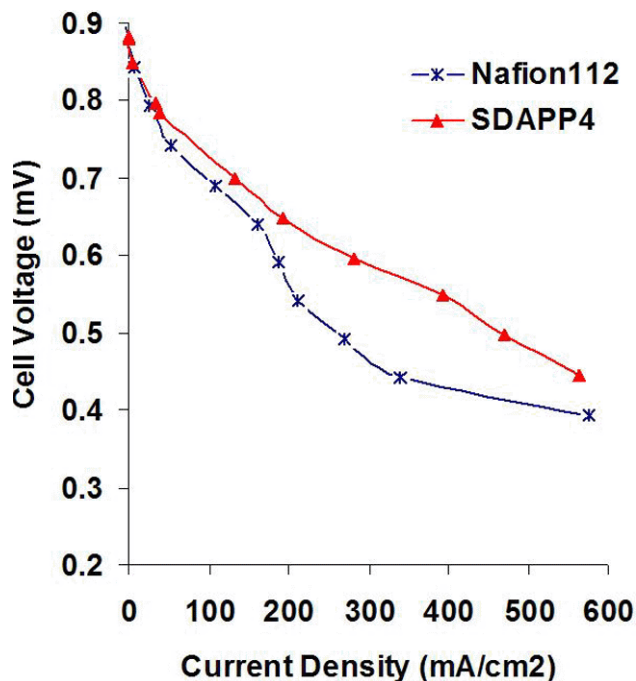


Figure 3. Hydrogen fuel cell performance at 120°C and 50% RH, 20 psig backpressure, 200 sccm H_2 , and 500 sccm air, based upon SDAPP4 with a thickness of 3 mil versus Nafion112. A DAE electrolyte was used within the SDAPP4 anode and cathode electrode structures.

thicknesses of SDAPP4 and Nafion112 were 7.62×10^{-2} mm and 5.08×10^{-2} mm (3 mil and 2 mil), respectively, as measured in the dry state for both samples. A catalyst loading of $0.4 \text{ mg}/\text{cm}^2$ was applied to both the anode and cathode by hand painting, as previously described, utilizing DeNora 20 wt% Pt on XC-72 for both the anode and cathode electrodes. Fuel cell operating conditions were 393 K (120°C) at 50% relative humidity with pure hydrogen flowing at $3.21 \times 10^{-7} \text{ kg}/\text{s}$ (250 SCCM) and air flowing at $1.07 \times 10^{-5} \text{ kg}/\text{s}$ (500 SCCM) throughout the test. The SDAPP MEA had an ether version of SDAPP in the electrode, while Nafion1100 was used with the Nafion112 MEA. The results of this study are shown in Figure 3 and show that the performance of SDAPP4 is promising when compared to Nafion, which is also thinner than the SDAPP4 MEA sample. Even though the Nafion sample is 50% thinner than the SDAPP4 MEA, which should result in better performance at higher currents, the thicker SDAPP4 sample still out-performed the Nafion112 MEA. While this result shows promise for the SDAPP materials, significant work needs to be completed to

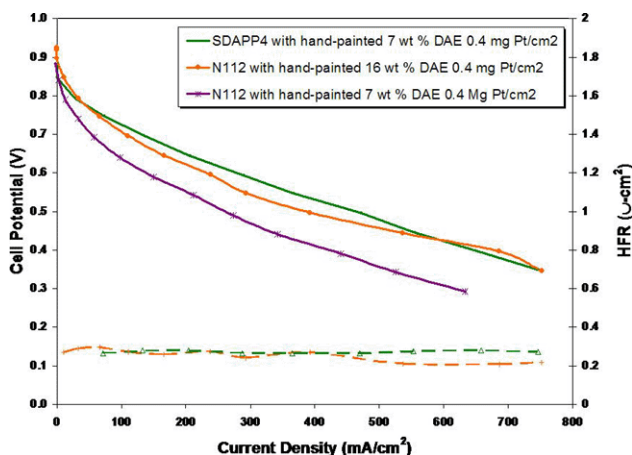


Figure 4. Hydrogen fuel cell performance at 120°C and 50% RH, 20 psig backpressure, 200 sccm H₂, and 500 sccm air, based upon SDAPP with a thickness of 3 mil. Purple and orange lines are Nafion112 with DAE in the catalyst layers. The green line is SDAPP4 with DAE in the catalyst layers.

optimize the electrode structure and evaluate the role of thickness on the fuel cell performance at these very challenging fuel cell conditions. Based upon these results, further work is warranted to examine the potential of these materials as a replacement for Nafion.

In order to understand the advantages of using an alternative electrolyte in the catalyst structure, Nafion112 was used as the PEM while Diels-Alder ether (DAE) was used as the electrolyte within the cathode and anode electrode structures. Figure 4 shows the fuel cell performance of a hydrogen fuel cell operating at 393 K and 50% RH. The observations and trends for this system were that with increasing DAE in the Nafion-based MEA, there was an increase in fuel cell performance from 7 wt% DAE to 16 wt% DAE. When a SDAPP4 MEA was created with 7 wt% DAE within the electrode structure, there was an improvement in performance over Nafion112 at both DAE loadings. This preliminary work suggests the potential to optimize a SDAPP with a hydrocarbon or DAE electrolyte in the catalyst electrode structure to arrive at improved high-temperature and low-RH fuel cell operation. Additional work must be done at lower temperatures and at varying RH to understand the fundamentals of reactant mass transport, electrolyte

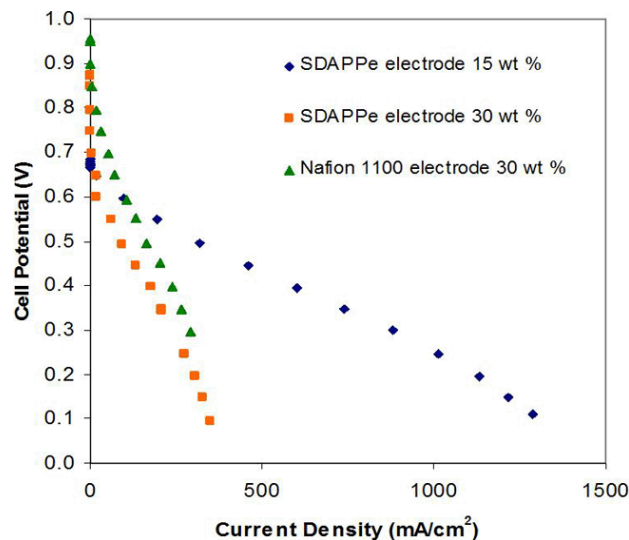


Figure 5. Hydrogen fuel cell performance at 80°C, 50% RH, 20 psig backpressure, 200 sccm H₂, and 500 sccm air, based upon SDAPP with a thickness of 1 mil. Catalyst layers with greater ionomer binder contents show large activation and transport losses at low RH.

proton conductivity, and the relationship of these factors to fuel cell performance.

Figure 5 shows the initial attempts to begin to evaluate the impact of alternative electrolytes in the electrode structure at lower temperatures and low RH within a hydrogen fuel cell operating at 80°C and 50% RH. In this figure, we are examining the performance of Nafion112 versus SDAPP4 at nearly the same equivalent thickness (3.048×10^{-2} mm/1.2 mil versus 2.54×10^{-2} mm/1.0 mil) for an optimized Nafion112 system versus SDAPP at two different SDAPPe loadings. It has been well established that 30 wt% Nafion within the electrode structure is ideal for a hydrogen cell using 20 wt% Pt/C. Operating the fuel cell under these conditions shows that having a lower SDAPPe loading in the electrode (15 wt%) results in improved hydrogen fuel cell performance compared to a fully optimized Nafion MEA at 50% RH and 80°C. This work suggests that there may be an opportunity to develop MEAs based solely on a hydrocarbon-based PEM that have better performance than Nafion at low RH. Additional work will be done in the future to corroborate these findings, but based on these preliminary results, there appears to be an opportunity to improve the hydrogen fuel cell performance at these challenging conditions.

Further characterization of the catalyst layers of the MEA is warranted to understand the relationship between gas and water transport within the electrode and overall electrode porosity. Future work will look at the role of changes in mass transport as well as fuel cell performance optimization with alternative electrolyte inks for improved interfaces between the PEM and electrode.

Conclusions

The first-generation poly(phenylene) synthesized via Diels-Alder condensation resulted in polyelectrolytes that could be post sulfonated in a controllable manner with chlorosulfonic acid. The aryl backbone resulted in a tough rigid-rod material, indicated by its high glass transition temperature and inherently high thermochemical stability. This type of high glass transition temperature material possesses physical properties that are attractive in high-temperature fuel cell applications. In addition, the backbone stiffness does not negatively affect membrane properties such as water uptake (21% to 137%) and proton conductivity (13 to 123 mS/cm) with IECs that are typically employed with sulfonated aromatic polymers (0.98 to 2.2 meq/g). The resultant polymers could be solution cast into robust, creaseable films. Results at hydrogen fuel cell operating conditions of 25% RH and 100°C demonstrated that this first-generation material performed better than Nafion of equivalent thickness and electrode structure. Future strategies during this project are directed at enhancing the conductivity under partially dry conditions by controlling the polymer morphology, improving the electrode structure with our hydrocarbon-based electrodes, and consideration of other organic moieties for proton conduction as well as organic-inorganic composite PEM materials.

FY 2005 Publications/Presentations

1. Electrochemical Society, Las Vegas Nevada Meeting 6/12/05 – 6/16/05

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