V.G.1 Development of a Novel Proton Conducting Membrane and a CFD Multi-Phase Porous Flow Model for PEM Fuel Cells

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Objectives

- Development of a novel proton conducting membrane capable of conducting protons at low relative humidity (RH), withstanding temperatures in excess of 110°C and electrically insulating.
- Quantify extent of membrane performance enhancement compared to peer materials available in the market place.
- Reduce material cost and develop simple manufacturing processes.
- Improve durability, dimensional stability and thermal stability.
- Development of a computational fluid dynamics (CFD) multiphase porous flow model to understand thermal and water-transport phenomena in a single proton exchange membrane (PEM) fuel cell as well as PEM fuel cell stacks.

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) Performance
(E) System Thermal and Water Management

Technical Targets

This project is conducting fundamental studies to develop a new class of PEM materials capable of conducting protons at low RH. The multiphase CFD model will help to understand underlying physics related to water and thermal management in PEM fuel cells. Insights gained from these studies will be applied toward the design and manufacturing of advanced membrane materials that meet the following DOE 2010 membrane materials targets:

- Cost: \$20/m^2
- Conductivity at operating temperature (≤120°C): 0.1 S/cm
- RH range: ≤50%
- Area specific resistance: 0.02 Ohm/cm^2
- Durability with cycling: at operating temperature (≤80°C) – 5,000 hours
- Multiphase CFD porous flow model for designing improved water and thermal management strategies

Accomplishments

- Developed inexpensive membrane materials and designed simple manufacturing process capable of producing proton conducting membrane materials at a cost 60% below the DOE targets for 2010.
- Increased proton conductivity: average seven times increase in proton conductivity compared to peer materials (Nafion® 212) at 80°C.
- Reduced resistance: 71% lower resistance per unit area than peer (Nafion® 212) materials at 80°C.
- Reduced induction time: induction time (time required to start proton transfer) is 70% lower than Nafion® 212.
- Low membrane water content: the membrane conducts protons at low water content i.e. at low relative humidity compared to peer materials (Nafion® 212) at 80°C.
- Developed and simulated multiphase porous flow model for CFD analysis of a single PEM fuel cell.
- Improved prediction: two-phase flow model predicts fuel cell's water and thermal management phenomena better than a single-phase model.

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Introduction

The essential requirements of PEMs for fuel cell applications include following: (i) high proton conductivity, (ii) minimal thickness (to minimize resistance resulting in fuel cell's ohmic drop), (iii) high thermal stability, (iv) excellent mechanical properties (strength, flexibility, and processability), (v) excellent chemical stability, (vi) low water drag, (vii) rapid adjustment of fast kinetics for electrode reactions, (viii) low or minimal gas permeability, and finally (ix) low cost and high availability. Currently, a benchmark commercially produced and widely used PEM for fuel cell applications is Nafion® [1]. Nafion® has a number of limitations such as an operating temperature range of 50°C~90°C [2] undesirable gas permeability - on the order of 10^{-6} cm^2/s [3], which results in decreased fuel cell performance, limited operational hydration range [2-3] and high cost, \$800 per m^2 [1-3]. Additionally, Nafion® (polymer membrane) is easily degraded under high power and during on/off cycling. As such, polymer membranes need considerable improvement. Another concern is to thoroughly understand the water production and proton conduction mechanisms to minimize cathode electrode flooding and to ensure proper membrane hydration.

In this project, using patented [4] polymer surface modification technology, a novel approach to the design and fabrication of PEMs has been developed whereby a non-structural polymer fabricated for proton exchange capacity is bound to an inert polymer matrix. This fabrication technique separates the proton exchange and structural requirements of the PEM allowing greater flexibility in proton exchange membrane design. To benchmark the performance of the membranes, we developed a theoretical model [5] to quantify several physical quantities such as proton exchange capacity (conductivity), resistance, induction time, and membrane water content. The results suggest a new route to fabricate cost-effective PEMs for fuel cell applications wherein one may focus more on the proton exchange capacity of the membrane allowing the structural properties of the membrane to be considered separately. To understand water and thermal management phenomena in an operational PEM fuel cell, we developed a multi-phase CFD model and simulated it using a finite element method for an operational single PEM fuel cell. The CFD results show the two-phase model gives better cell prediction than a single-phase model.

Approach

- Use an inert, robust, mechanically and dimensionally stable polymer mesh that may be chemically modified on the surface to render it adhesive or chemically reactive.
- Use patented technology to prepare a proton exchange polymer media that has been designed primarily to have high proton exchange capability.
- Cast the proton exchange polymer media onto the robust polymer support to prepare the hybrid proton exchange membrane.
- Use mathematical model with an efficient and simple experimental method of testing the proton exchange characteristics of the new PEMs.
- Alter the composition of the proton exchange polymer media to optimize proton transport.
- Compare the performance of new PEM materials with the peer materials such as Nafion® 212.
- Use finite element-based computer software (COMSOL) for CFD analysis of thermal and water management of a unit fuel cell as well as fuel cell stacks.

Results

In the past year, the main focus was utilization of a patented polymer surface modification technology [4] and exploration of synthetic routes that allowed selective addition of chemical species to the polyethylene regions of the ethylene-tetrafluoroethylene (ETFE) mesh. We developed an inexpensive, benign water-borne process for the attachment of the styrene-acrylonitrile-vinylsulfate (SAS) polymer matrices to the ETFE mesh allowing greater flexibility in design by separating the proton exchange and structural requirements of the PEM. To measure membrane properties at the laboratory-based manufacturing stage, we formulated a rigorous mathematical model [5] based on electrokinetics and diffusion mechanism. Some properties of new SAS membranes and Nafion® 212 were validated by both theoretical model and experimental results.

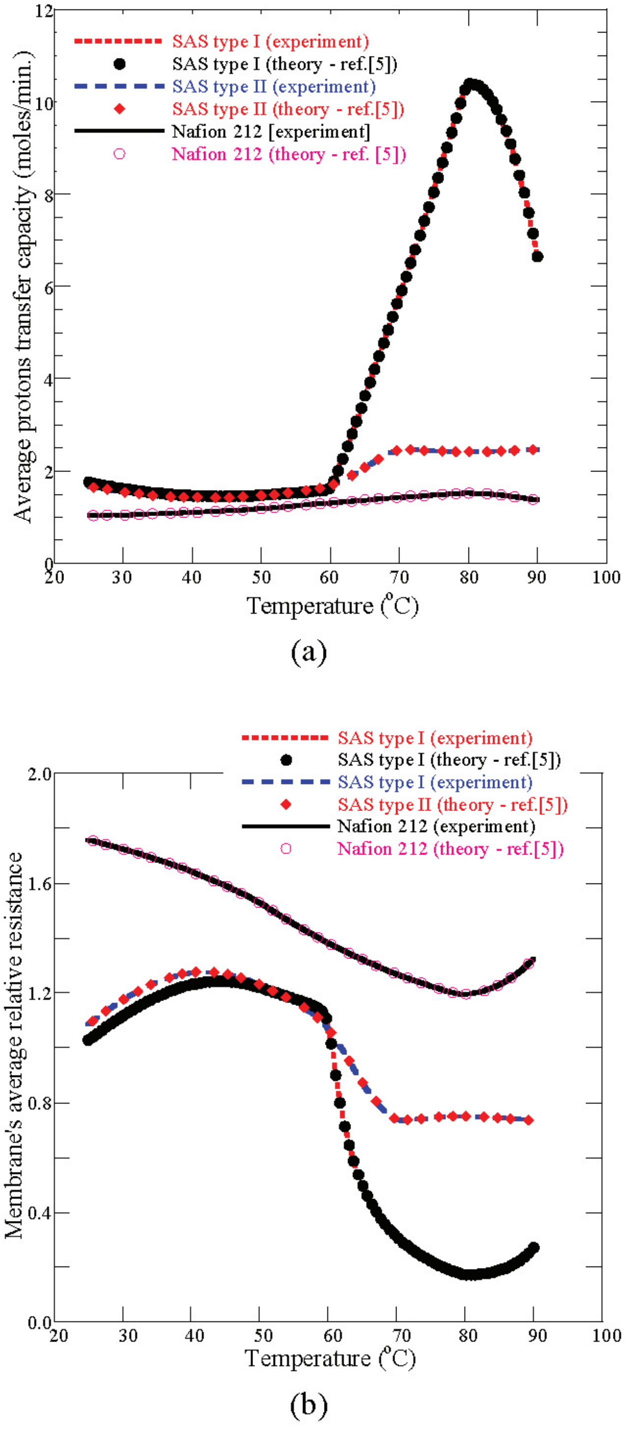
After the Fiscal Year 2007 annual report, the membrane characterization continued at the laboratory but the efforts were mainly directed towards durability testing keeping in mind the operational PEM fuel cell environment. The water and thermal management issues of an operational single PEM fuel cell were also taken into account by simulating a two-phase CFD model developed earlier (reported in quarterly report in 2007 and 2008).

To confirm the stability of the SAS membrane's performance under fuel cells operating conditions, the membranes were immersed into water at different temperatures for four hours and then re-evaluated their proton transfer capacity. The proton transfer capacity and relative resistance for each of the SAS membranes and Nafion® 212 were then determined in the range of 25°C to 90°C in order to judge the membrane conductivity at different temperatures. The experimental procedures (developed and reported in last year) were followed to accomplish this. The standard deviation from the mean values of proton transfer capacity was ±2% (minimum 5 trials each).

Figure 1a presents the average proton transfer capacity and relative resistance for each of the membranes examined at different temperatures. Average proton transfer capacity was determined using the average slope calculated from the proton transfer phase profiles (calculation procedures reported last year) in water cell at 80°C. From Figure 1a we see that the average proton transfer rate of SAS type I membrane is 10.5 moles per minute compared to 1.5 moles per minute for Nafion® 212. This implies that the SAS type I membrane has 7 times faster average protons transfer rate than Nafion® 212 membrane under the test conditions utilized in this study. As we can see from Figure 1a, there is an excellent agreement between the experimental and theoretical results.

Figure 1b represents average relative resistance among membranes at different temperatures. The average relative resistance of membrane is calculated based on the average proton transfer capacity and the time required for each individual membrane to allow a specific amount of protons to pass through it [5]. Comparing results presented in Figure 1b, it can be seen that at 25°C, the average relative resistance of Nafion® 212 membrane is 65% higher and at 80°C the average relative resistance is about 80% higher than the SAS type I membrane. Since low membrane resistance is a requirement for the enhancement of low temperature PEM fuel cells performance, SAS type I membrane shows a promise to perform better than Nafion® 212 membrane. The membrane resistance has a great impact on the performance of low temperature proton exchange membrane fuel cells since high membrane resistance causes a drop of fuel cell's overall Ohmic voltage [3]. From figure 1b, it may be seen that among the membranes reported in this study, the SAS type I membrane had the lowest resistance and the Nafion® 212 membrane the highest resistance at different temperatures. Once again, the experimental results are in excellent agreement with the results obtained from the theoretical model [5] as can be seen from Figure 1b.

Figure 2a provides the average time required for one mole of protons to pass through the membrane per minute at different temperatures. As before, both experimental and theoretical results are presented in Figure 2a. The average time was calculated by using the starting and ending times of proton transfer at different temperatures. Both SAS type membranes took less average time to transfer a mole of protons compared to Nafion® 212 membrane. At 25°C SAS type I membrane took 70% less average time whereas at 80°C it took 85% less average time than the peer Nafion® 212 membrane.



(a)

(b)

FIGURE 1. Comparison of average: (a) proton transfer capacity and (b) relative resistance among different membranes. Both experimental and theoretical results are presented.

This implies that both SAS type membranes are able to transfer protons at a higher rate than Nafion® 212.

The swelling characteristics of the SAS membranes were determined by water uptake measurement. The

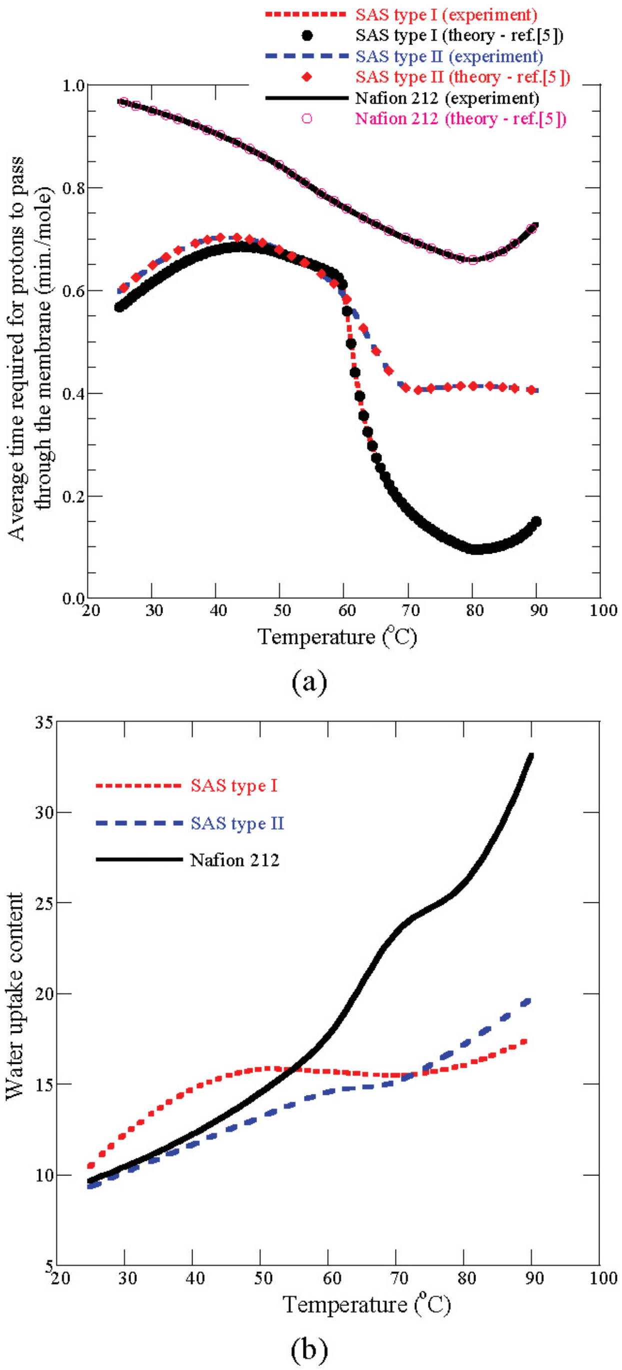


FIGURE 2. Comparison of: (a) induction time and (b) water content among different membranes.

water uptake content was calculated using the following relationship:

$$\text{water uptake content, } w(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

where W_{dry} and W_{wet} are the weights of the wet and dried membrane samples, respectively. Figure 2b shows the water uptake content among membranes at different temperatures. From Figure 2b, we see that the water uptake content for Nafion® 212 membrane is very high around 34 and increased almost linearly with increasing temperature compared to SAS type membranes around 17~20 at 80°C. This implies that to conduct proton transfer efficiently through the Nafion® 212 membrane requires higher amount of water presence (i.e. higher humidity level) as compared to SAS type membranes. It appeared that SAS type membranes are capable of transferring protons efficiently at low water content i.e. at low humidity level than Nafion® 212. The dependence of the liquid water uptake on preceding dehydration conditions could have significant implications for the use of membranes in PEM fuel cells [3]. For example, in one common mode of fabrication of membrane-electrode assemblies (MEAs), the membrane and electrodes are hot-pressed together at higher temperature (e. g. at 120°C). During this process, all water is lost from the membrane and the subsequent operating temperature to which the membrane will be exposed (e.g. 80°C) could result in incomplete rehydration. If less water is taken up by the membrane thus treated, a decrease in the maximum attainable conductivity will occur since the conductivity depends strongly on membrane water content and hence on the membrane's relative humidity (RH). Thus, the increased water uptake by the Nafion® 212 membrane following high temperature dehydration (by hot-pressing during MEAs manufacture) could be a disadvantage in fuel cell operations in low humidity range. A rigorous RH cycle measurement will be studied in the near future to verify the performance of these membranes in terms of conductivity, resistance, temperature, RH and other parametric conditions.

To improve understanding regarding water and thermal management phenomena in an operational PEM fuel cell, we simulated a two-phase CFD model (developed last year and reported in the quarterly report in 2007 and 2008) using a finite element method for an operational single PEM fuel cell. Figure 3a represents the resulting gas-velocity (gas phase) distribution in the cathode gas channel. The applied pressure difference of 25 Pa between inlet and outlet resulted in a maximum gas velocity of approximately 2 m/s. A typical laminar flow profile is present in the straight sections of the cathode gas channel. In the curved sections, on the other hand, the gas velocity distribution is asymmetric, resulting in an asymmetric concentration of gas distribution there. We studied the water production at the cathode by plotting the water fraction (liquid phase) in the gas channel as shown in Figure 3b. We can see clearly from Figure 3b that the water fraction increases significantly in the cathode electrode. It reaches a maximum value of 0.74 in the corner at the top of the Figure 3b. It is probably because of the fact that water droplets would start forming in this region. To avoid this problem, in the design we should decrease the inlet

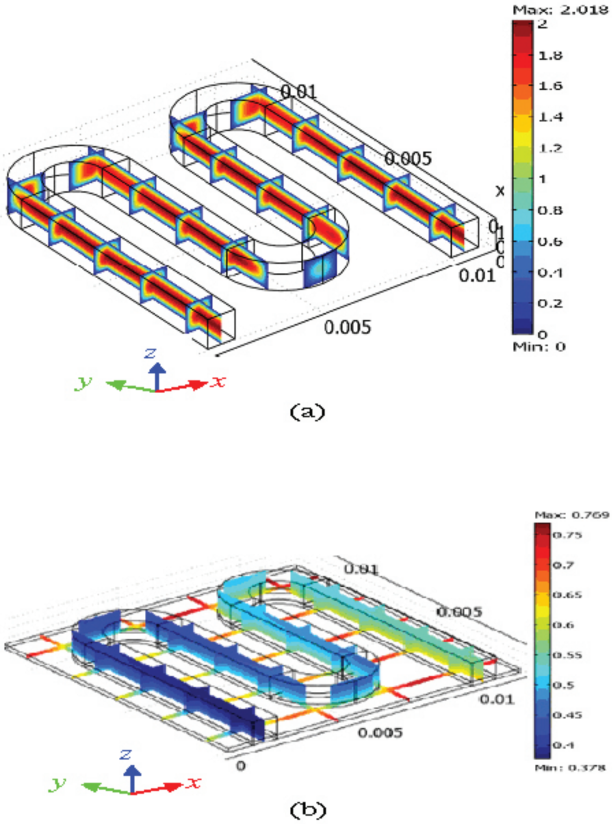


FIGURE 3. (a) Gas-velocity (gas phase) distribution in the gas channel for a 25 Pa pressure drop between the inlet and outlet. (b) Weight fraction of liquid phase (water) in the cathode gas channel.

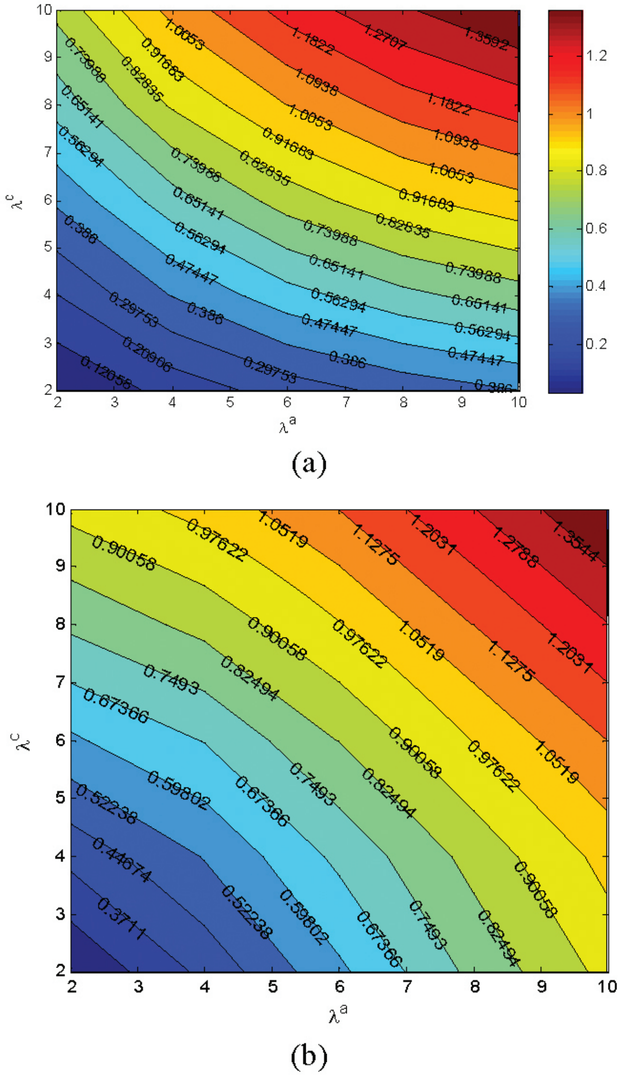


FIGURE 4. Current density distribution across the membrane at 80°C. I^a and I^c denotes the membrane water content at the anode and cathode side of the membrane respectively. (a) Single phase model [6] and (b) two-phase model.

water fraction (i.e. less humid gas) and increase the thickness of the gas diffusion layer.

For improving CFD model predictions especially for an operational PEM fuel cell environment, we simulated both a single-phase CFD model [6] and our two-phase CFD model using finite element analysis tools. Figure 4 represents the current density distribution across the membrane at 80°C for different anode and cathode side membrane humidification. Both single phase (Figure 4a) and two-phase model (Figure 4b) simulations are presented in Figure 4. We can see significant improvement in current density predictions in two-phase model (Figure 4b) compared to single phase model (Figure 4a), especially at low membrane water content. The predictions obtained from two-phase flow model (Figure 4b) will be beneficial to improve air-breathing fuel cell designs.

Conclusions and Future Directions

From FY 2007 to current-date has resulted in a great knowledge expansion regarding manufacturing processes of new PEM materials, laboratory-based testing of membrane properties and multiphase CFD analysis of operational single fuel cell. We now understand the manufacturing process of new materials and the performance validation protocols in quantitative terms at least at laboratory-based manufacturing stage. We have a good understanding of the polymer chemistry, thermodynamics and electro-kinetics. We also gained insight into the water and thermal management issues through multiphase CFD analysis. This information is critical to developing new membrane materials for fuel cell applications where chemical treatment, polymer casting, and performance evaluations are of the utmost importance. This year we intend to continue evaluation of membrane properties using industry-standard characterization protocols which will help us to review the new membrane materials in further details and begin to study water and thermal management phenomena in fuel cell stacks.

Although the DOE deliverables of our project up-to-date have been achieved, the following membrane attributes are necessary to further evaluate the membrane performance:

- Refining manufacturing process to reduce the cost and use of low cost raw materials.
- Characterization of membrane properties such as conductivity, resistivity, and thermal stability over the entire temperature and humidity range (e.g., operation up to 120°C) using industry standard protocols.
- Implement CFD two-phase porous flow model in single fuel cell as well as fuel cell stacks for improvement of water and thermal management design strategies.

FY 2008 Publications/Presentations/Patents

1. Susanta K. Das, Panini Kolavennu, J. Hedrick, Beholz, L., Ali R. Zand and K. J. Berry, Synthesis and Characterization of a Composite Membrane for Polymer Electrolyte Fuel Cell, *Journal of Fuel Cell Science and Technology*, 2008 (Accepted – in press).

2. Susanta K. Das, L. Beholz, J. Hedrick, Ali R. Zand, and K. J. Berry, Synthesis and Performance Validation of a Polymer Mesh Supported Proton Exchange Membrane for Fuel Cell Applications, *Journal of Electrochemical Society*, 2008 (submitted).

3. Susanta K. Das, Antonio R. and K. J. Berry, Experimental Evaluation of CO Poisoning on the Performance of a High Temperature PEM Fuel Cell Stack, *Journal of Electrochemical Society*, 2008 (submitted).

4. Panini Kolavennu, Susanta K. Das, and K. J. Berry, Control Oriented Model for Enhancement of Membrane Hydration of PEM Fuel Cell Stacks, *J. Power Sources*, 2008 (In Preparation).

5. Susanta K. Das, Antonio Reis, Etim U. Ubong and K. Joel Berry, Experimental evaluation of CO poisoning of an Air-Breathing High Temperature PEM Fuel Cell Stack, *Proc. ASME 6th International Fuel Cell Science, Engineering & Technology Conference, held on June 16-18, Denver, Colorado, USA, Cell, Stack and System Experiments*, Paper No. 65239, p. 1-5 (2008).

6. Panini Kolavennu, Susanta K. Das and K. Joel Berry, On-board Hydrogen for High Temperature PEM Fuel Cell Stack by Methane and Methanol Steam Reforming, *Proc. ASME 6th International Fuel Cell Science, Engineering & Technology Conference, held on June 16-18, Denver, Colorado, USA, Fuel Processing and Storage*, Paper No. 65213, p. 1-5 (2008).

7. Susanta K. Das and K. J. Berry, CFD Analysis of a Two-Phase Flow Model for a Low Temperature Proton Exchange Membrane Fuel Cell, *Proc. ASME 6th International Fuel Cell Science, Engineering & Technology Conference, held on June 16-18, Denver, Colorado, USA, Cell, Stack and System Modeling*, Paper No. 65212, 1-10 (2008).

8. Etim U. Ubong, Susanta K. Das, Antonio Reis and K. J. Berry, Experimental Performance Evaluation of a High Temperature PEM Fuel Cell at Different Temperatures and Pressures, *Proc. ASME 6th International Fuel Cell Science, Engineering & Technology Conference, held on June 16-18, Denver, Colorado, USA, Cell, Stack and System Modeling*, Paper No. 65177, 1-6 (2008).

Patent Applications

1. Susanta K. Das, Jayesh Kavathe, Panini Kolavennu and K. Joel Berry, Novel design of fuel cell bipolar plate for optimal uniform delivery of reactant gases and efficient water removal, US Patent Application, 2008 (Under Process - pending).

2. Susanta K. Das, Jayesh Kavathe and K. Joel berry, Novel stack design and assembly of high temperature PEM fuel cell, US Patent Application, 2008 (Under Process - pending).

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5. Susanta K. Das and K. Joel Berry, Two-cell theory to measure membrane resistance based on proton flow: Theory development and experimental validation, *Journal of Power Sources*, 173, 909 (2007).

6. T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, "Polymer electrolyte fuel cell model," *J. Electrochem. Soc.*, **138**, 2334 (1991).