

# V.D.15 Development of Novel PEM Membrane and Multi-Phase CFD Modeling of PEM Fuel Cell\*

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\*Congressionally directed project

- (C) Durability
- (E) 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 the underlying physics related to water and thermal management in PEM fuel cells. If successful, 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<sup>2</sup>
- Conductivity at operating temperature ( $\leq 120^{\circ}\text{C}$ ): 0.1 S/cm
- Humidity range:  $\leq 50\%$
- Area specific resistance: 0.02 Ohm/cm<sup>2</sup>
- Durability with cycling: at operating temperature ( $\leq 80^{\circ}\text{C}$ ) – 5,000 hours
- Multiphase CFD porous flow model for designing improved water and thermal management strategies

## Objectives

- Develop novel proton conducting membrane capable of conducting protons at low relative humidity (RH), withstanding temperatures in excess of  $110^{\circ}\text{C}$  and providing electrical insulation.
- Quantify extent of membrane performance enhancement compared to peer materials available in the market place.
- Reduce materials cost and develop simple manufacturing processes.
- Improve durability, dimensional stability, and thermal stability.
- Develop 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.

## 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) Performance
- (B) Cost

## Accomplishments

- Identified inexpensive membrane materials and developed simple manufacturing process capable of producing proton conducting membrane materials at a cost 60% below the DOE targets for 2010.
- Increased Proton Conductivity: In-house laboratory test shows that average 10 times increase in proton conductivity compared to peer materials (Nafion<sup>®</sup> 212) at  $80^{\circ}\text{C}$  (results presented in the last year DOE report). Though the third party (BekkTech) test results presented below show a lower conductivity than the in-house lab test, an updated version of our membrane sample is presently under testing at BekkTech to validate our lab test results. The updated results from BekkTech will be included in the final DOE report to be submitted soon.
- Reduced Resistance: An in-house laboratory test shows 71% lower resistance per unit area than peer (Nafion<sup>®</sup> 212) materials at  $80^{\circ}\text{C}$  (results reported to DOE last year).
- Reduced Induction Time: Induction time (time required to start proton transfer) is 70% lower than Nafion<sup>®</sup> 212.

- Low Membrane Water Content: Membrane able to conduct protons at low water content i.e. at low RH 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: Using two-phase CFD model results we developed a three dimensional (3D) control strategy for improved prediction of fuel cell stack performance while meeting the power demand.



## Introduction

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<sup>2</sup>/s [3], which results in decreased fuel cell performance, limited operational hydration range [2-3] and high cost, \$800 per m<sup>2</sup> [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. The essential requirements of PEMs for fuel cell applications include the 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.

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 finite element methods for an operational single PEM fuel cell. Using two-phase CFD model results we developed a 3D control strategy for improved prediction of fuel cell stack performance while meeting the necessary power demand.

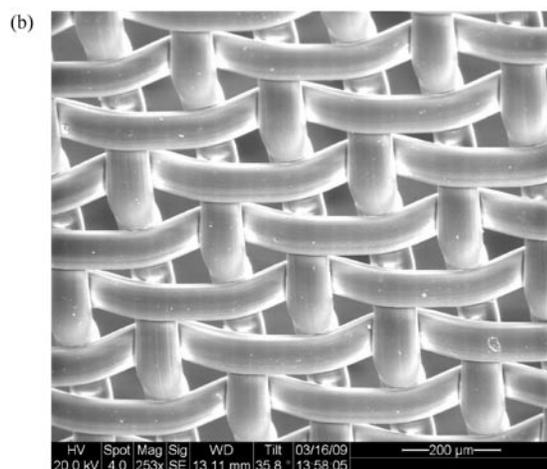
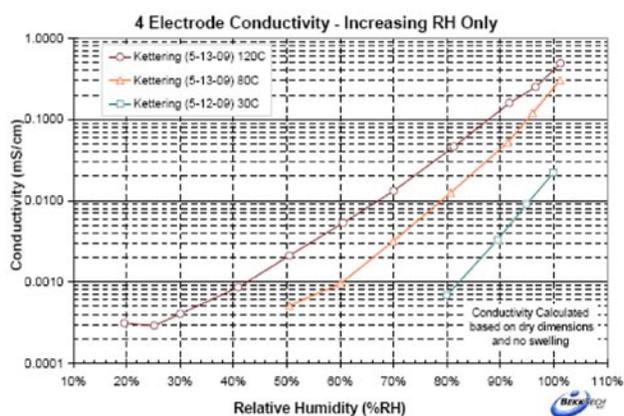
## Approach

- 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.
- 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.
- Validate multiphase CFD model results with the results published in the literature for a single PEM fuel cell.
- Using two-phase CFD model results, develop a 3D control strategy for improved prediction of fuel cell stack performance in order to meet the power demand.

## Results

During the past year, the main focus has been the validation of membrane performance both at the laboratory scale and using industry-standard testing protocols. We sent our membrane samples to the BekkTech testing service, an industry-standard membrane sample testing service provider and obtained preliminary results regarding the membrane conductivity, resistivity, thickness measurements and RH cycling at 30°C, 80°C and 120°C. We analyzed the BekkTech test results and made necessary modifications. The efforts were mainly directed towards preparation of membrane samples in order to accommodate performance enhancement required in the operational PEM fuel cell environment. The entire process is currently underway. The water and thermal management issues of an operational single PEM fuel cell were also taken into account by validating the multi-phase CFD model with the results published in the literature. Using the two-phase CFD results, we developed and tested a 3D control strategy on a 5 kW PEM fuel cell stack (reported in quarterly report in 2009).

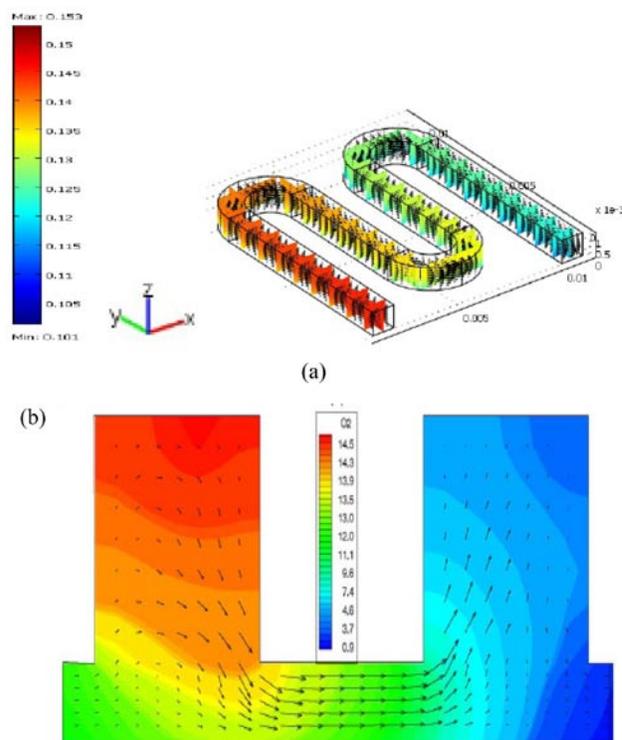
Figure 1a represents the 4-electrode conductivity versus RH at 30°C, 80°C and 120°C. From Figure 1a, we can see that our PEM membranes are able to



**FIGURE 1.** (a) 4-electrode conductivity test of our developed styrene-acrylonitrile-vinylsulfate type membrane with different relative humidity at 30°C, 80°C and 120°C. (b) SEM image of a styrene-acrylic acid-vinylsulfonate membrane – produced at Kettering facility.

conduct protons at different RH levels but required further improvement in terms of proton conductivity at reduced humidity conditions. Figure 1b represents the scanning electron microscope (SEM) image of our PEM membrane which shows the presence of proton conductive media on the inert mesh we used for mechanical and chemical stability of the membrane.

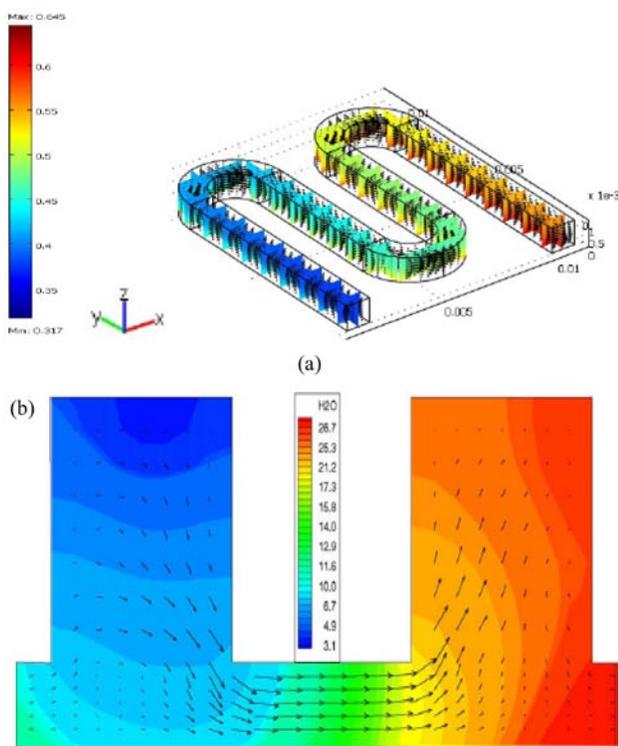
The water and thermal management issues of an operational PEM fuel cell are critical to enhancing cell performance because electrode flooding and membrane dehydration results in degradation of cell performance. For better understanding, we compared results of our multiphase porous flow model with the results available in the literature. Figure 2 presents the distribution of  $O_2$  concentration in the cathode channel obtained using our multiphase porous flow model simulation (Figure 2a) with those obtained (Figure 2b) by Wang and Wang [6]. The color bar represents the concentration from highest (red) to lowest (blue) and the black arrows denote cathode gas velocity. As seen



**FIGURE 2.** Concentration distribution of gas phase ( $O_2$ ) in the cathode channel. (a) 3D simulation of cathode with present multiphase model, (b) two dimensional (2D) model simulation of Wang and Wang [6] – two adjacent channels including bending regions of the serpentine channel. Black arrow indicates cathode gas velocity inside the channel.

from Figure 2, the  $O_2$  concentration at the cathode inlet is the highest since fresh humidified air is supplied at the cathode. The  $O_2$  concentration decreases along the gas channel from inlet to outlet due to the electrochemical oxygen reduction reaction (ORR) which results in water formation at the cathode. The depletion of  $O_2$  along the cathode electrode is due to the electrochemical reaction which resulted in water production at the cathode. From Figure 2, we see a substantial amount of oxygen depletion in the regions far away from the inlet gas channel which resulted in the high current density. Comparing Figures 2a and 2b we see that the  $O_2$  depletion trends along the gas channel are similar or comparable in terms of color bars. Thus we obtained a qualitative agreement between our multiphase flow model and that of the results reported by Wang and Wang [6]. In Figure 2b, we see a higher amount of  $O_2$  concentration (see the values at the color bar, Figure 2b) at the inlet because of the requirements of maintaining the balance of the anode/cathode gas ratio. In our simulation, we only simulated the PEM fuel cell cathode. Addition of the anode portion into our simulation will be considered in the next step.

Figure 3 presents the concentration distribution of liquid phase ( $H_2O$ ) in the cathode channel obtained



**FIGURE 3.** Concentration distribution of liquid phase (water) in the cathode channel. (a) 3D simulation of cathode with present multiphase model, (b) 2D model simulation of Wang and Wang [6] – two adjacent channels including bending regions of the serpentine channel. Black arrow indicates cathode gas velocity inside the channel.

using our multiphase porous flow model simulation (Figure 3a) with those obtained (Figure 3b) by Wang and Wang [6]. The color bar represents the concentration from highest (red) to lowest (blue) and the black arrow denotes cathode gas velocity. From Figure 3, we see that the concentration of liquid phase (water) at the cathode inlet is the lowest since humidified air, which has small water vapor content only (no liquid water), is supplied at the cathode. The liquid phase concentration is increasing along the gas channel from the inlet to the outlet due to the ORR over the cathode electrode to produce liquid phase (water). The depletion of  $O_2$  along the cathode electrode produced liquid water through the electrochemical reaction at the cathode. Hence the liquid phase concentration increased along the gas channel. From Figure 3, we see that the liquid phase concentration increases substantially in larger amount in the regions far away from the inlet gas channel. Comparing Figures 3a and 3b, we see that the trend of increasing liquid phase concentration along the gas channel is similar. This indicates a qualitative agreement between our multiphase flow model and that of the results reported by Wang and Wang [6], although in Figure 3b we see a higher concentration of liquid phase water (see the values at the color bar, Figure 3b) at the outlet because of the requirements of maintaining the

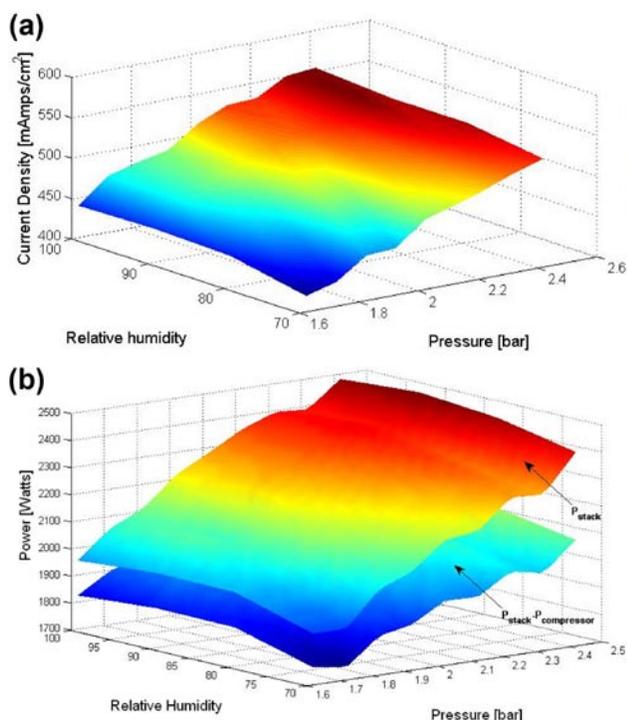
balance of the anode/cathode gas ratio. A higher supply of reactant gases which increases the reaction rate results in higher liquid phase concentration. The liquid phase concentration increases along the far end of the channel due to the production of liquid water through the electro-chemical reaction. In our simulation, we only simulated the PEM fuel cell cathode. Addition of the anode portion into our simulation will be considered in the next step. The parametric values used in the simulation for the results presented in Figures 2 and 3 are listed in tables in [6-7]. The predictions obtained from the two-phase flow model (Figures 2a and 3a) will be beneficial to improve PEM fuel cell designs.

**Implementation of Control Algorithm:** Using the multi-phase CFD model results given in Figures 2 and 3, a 3D surface map of RH, pressure at the cathode and current density at different voltages of the PEM fuel cell stack was developed and tested for a 5 kW stack. Figure 4a shows the surface map for a voltage of 0.7 V. At this voltage, the current density varies from 440-550 mA/cm<sup>2</sup> depending on cell conditions (RH, pressure, etc.). Using the current density, we can calculate the stack power from the following equation:

$$P_{stack} = I_{stack} * n * V_{op} * A \quad (1)$$

where  $P_{stack}$  = total stack power,  $I_{stack}$  = stack current,  $V_{op}$  = cell operating voltage,  $n$  = number of cells in the stack and  $A$  = cross sectional area of the fuel cell. This gives us the range of power at which we can operate the fuel cell stack at this voltage. For different voltages, we can calculate the power and we can obtain a lookup table for the power demand with operating voltage. On the green-light test stand at Kettering Center for Fuel Cell Systems and Powertrain Integrations, the fuel and oxidant gases were supplied at a higher pressure. The energy needed for compression has to be supplied by the fuel cell itself. To obtain the power demand for the compressor, CHEMCAD simulation software was used to calculate the power based on the anode and cathode flow rates and compression ratios. By subtracting the compressor power from the fuel cell stack power we can obtain the net power that can be provided by the fuel cell stack. Figure 4b shows both the stack power and net power for a cell voltage of 0.7 V. Based on the net power, we can develop a lookup table between the operating voltage and power demand. So, for a particular power demand we can calculate the optimum operating pressure and humidity. The feed forward control strategy developed here calculates this optimum operating point and sends it as an input to the fuel cell stack. The steps followed to obtain the optimum operating points are:

- Determine the power demand.
- Calculate the appropriate operating voltage ( $V_{op}$ ) based on the range of power demand from the lookup table.



**FIGURE 4.** (a) Surface map of the variation of current density with pressure and relative humidity at a constant voltage of 0.7 Volts for 5 kW stack. (b) Surface map of stack power and the net power that can be provided by the stack at a voltage of 0.7 Volts for 5 kW stack.

- From the surface map for net power at the selected voltage, calculate the minimum pressure  $P_{r_{op}}$  and RH ( $RH_{op}$ ) at which you can get the required power demand.
- From the surface map we can calculate the corresponding  $P_{stack}$  for the selected operating pressure and RH ( $P_{r_{op}}, RH_{op}$ ).
- Calculate  $I_{stack}$  from  $P_{stack}$  using equation 1 and send  $I_{stack}, P_{r_{op}}, RH_{op}$  as input to the system.

For a gas of known or desired humidity, we can calculate the pressure to operate the fuel cell stack from the 3D surface map of current density, humidity, and pressure as shown in Figure 4a. Then the pressure can be used in a feed forward control algorithm to meet the power requirement. As such, we can operate the fuel cell stack with a humidity driven power management strategy. For a gas of known humidity, for example 90%, the control algorithm was modified to search along a particular RH.

## Conclusions and Future Directions

The past year has resulted in a great knowledge expansion regarding manufacturing processes of new PEM materials, laboratory-based and industry-standard

testing of membrane properties and multiphase CFD analysis of operational PEM fuel cells. We now understand the manufacturing process of new materials and the performance validation protocols in quantitative terms at least at the laboratory-based manufacturing stage. We have a good understanding of the polymer chemistry, thermodynamics and electro-kinetics. This information is critical to develop new membrane materials for fuel cell applications where chemical treatment, polymer casting, and performance evaluations are of the utmost importance. We also gained insight into the water and thermal management issues in the PEM fuel cell through multiphase CFD analysis. This year we intend to submit a final project report after finishing the evaluation of membrane properties using industry-standard characterization protocols which will help us to finalize the membrane materials with detailed membrane manufacturing process. We also will finalize the water and thermal management phenomena study in a PEM fuel cell.

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

- Refining the manufacturing process to reduce the cost and use of low cost raw materials.
- Characterizing 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.
- Implementing CFD multi-phase porous flow model in a single fuel cell as well as fuel cells stack for improvement of water and thermal management design strategies.

## Special Recognitions/Patents Issued

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, U.S. Patent Application, 2009 (Under Process - pending).
2. Susanta K. Das, Jayesh Kavathe and K. Joel berry, Novel stack design and assembly of high temperature PEM fuel cell, U.S. Patent Application, 2009 (Under Process - pending).

## FY 2009 Publications/Presentations

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*, vol. 6, p. 011021-1~011021-6 (2009).

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 Power Sources*, 2009 (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 Power Sources*, 2009 (in press- online available).
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*, 2009 (In Preparation).

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