

V.F.1 Fuel Cell Research at the University of South Carolina*

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Objectives

- Project 1-Non-Carbon Supported Catalysts
 - Develop novel materials (e.g., Nb-doped) for improved corrosion resistance of catalyst supports.
- Project 2-Hydrogen Quality
 - Develop a fundamental understanding of performance and durability losses induced by fuel contaminants.
- Project 3-Gaskets for Proton Exchange Membrane Fuel Cells (PEMFCs)
 - Develop a fundamental understanding of the degradation mechanisms of existing gaskets and the performance of improved lower-cost materials.
- Project 4-Acid Loss in PBI-type High Temperature Membranes
 - Develop a fundamental understanding of acid loss and acid transport mechanisms.
 - Predict performance and lifetime as a function of load cycle.

Technical Barriers

These projects address the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

TABLE 1. Technical Targets

Characteristic	Units	2010/2015 Stack Targets	USC Project # and 2007 Status
Electrochemical Area Loss	%	<40	Project 1 - started
Electrocatalysts Support Loss	mV after 100 hours @ 1.2V	<30	Project 1 - started
Mass Activity	A/mg Pt @ 900 mV _{IR-free}	0.44	Project 1 - started
Specific Activity	μA/cm ² @ 900 mV _{IR-free}	720	Project 1 - started
Tolerance to Fuel Contaminants	various		Project 2 - started
Seal/Gasket Life	hours	> 5,000 for transportation	Project 3 - started
Durability @ <10% Rated Power Degradation (Stationary)	hours	40,000	Project 4 - started

Accomplishments

- Project 1: Nb-doped TiO₂ non-carbon supports have been synthesized with reasonable conductivity and surface area. Electrode characterization is in progress.
- Project 2: Computational fluid dynamics software has been used to predict distributions for lab-cell designs. New designs are proposed to minimize temperature gradients and to increase uniformity of current density.
- Project 3: Seal materials selected and six companies engaged in reviewing results of accelerated tests.
- Project 4: Experiments designed with Plug Power.



Introduction

Fuel cell research at the University of South Carolina (USC) funded under this contract involves four projects. The first project, “Non-Carbon Supported Catalysts” (Dr. John Weidner), focuses on improved catalyst supports and seeks to develop novel materials that are more corrosion resistant. This corrosion behavior is critical during transient operation and during start-up and shutdown. This project is leveraged with recent, peer-reviewed, supplemental funding from the National Science Foundation (NSF) for use in the NSF Industry/University Cooperative Research Center for Fuel Cells (CFC) at USC. The second project “Hydrogen Quality,” (Dr. Jean St-Pierre) will support sub-team #1 in the cross-project effort on H₂ quality. We will adapt the methods employed in previous work on reformat for stationary systems to the issue of hydrogen fuel quality as it relates to transportation needs. We will perform experiments and develop models that describe performance losses associated with CO, NH₃, and H₂S contaminants in the hydrogen fuel. As part of this project USC and Oak Ridge National Laboratory (ORNL) will explore, in a collaborative effort, the usefulness of a techniques developed at ORNL to measure differences in the extent of contaminates adsorption with a spatially resolved mass spectrometer.

The third project, “Gaskets for PEMFCs” (Dr. Y.J. (Bill) Chao), will complement industrial sponsorship of Project 25C in the NSF Industry/University Cooperative Research CFC at USC. There, we have found some materials that give relatively good initial performance and minimal long-term stress relaxation but their raw material cost is higher than that desired by stack and component suppliers. Our goal here is to obtain a fundamental understanding of the degradation mechanisms of existing gasket and seal materials in a PEMFC environment. We seek to explain the interactions of chemical and mechanical stresses that decrease the long-term durability of both existing and new sealing materials. The fourth project, “Modeling the Acid Loss in PBI-type High Temperature Membranes,” (Dr. Sirivatch Shimpalee) will support the development of stationary fuel cells, but the fundamental studies of acid transport should have applications as new high-temperature membranes are developed for transportation and other early market fuel cells. We will work with Plug Power, Inc., to develop a model that allows for long-term prediction of acid loss from PBI-type high temperature membranes.

Approach

Project 1 has six tasks: (1) development of high surface area titania-based non-carbon supports and the preparation of electrodes through deposition of catalysts and formation of electrodes on these supports, (2)

characterization of the developed supports and catalysts through the use of surface analysis and spectroscopy methods, (3) electrochemical characterization, (4) corrosion studies; (5) stability analysis of loaded catalysts and supports, and (6) industrial interaction and presentations. Project 2 has seven tasks: (1) group contaminants by probable mechanism (i.e., adsorption, reactive, or transportable through the membrane electrode assembly), (2) study the temperature distributions in laboratory cells, (3) design and perform experiments to analyze the mechanisms, (4) predict long-term effects, (5) explore with ORNL the use of spatially resolved mass spectroscopy, (6) interact with the H₂ Quality team, and (7) publish and present results.

Project 3 has six tasks: (1) select commercially available seal materials, (2) age seal materials in simulated and accelerated fuel cell environments, with and without stress deformation, (3) characterize the chemical stability, (4) characterize the mechanical stability, (5) develop accelerated life testing procedures, and (6) interact with industry through the NSF CFC and the U.S. Fuel Cell Council. Project 4 has three tasks: (1) exercise the existing computer code to determine model limitations, to compare with existing data, and to propose experiments to improve the model, (2) perform experiments and modify model to account for transient behavior during start-up and to improve the model, and (3) disseminate the results through presentations and publications.

Results

It is well known that CO, one of the contaminants of interest to the H₂ Quality team [1], adsorbs on the Pt anode catalysts and can be oxidized electrochemically under certain overpotentials. This adsorption depends on the local temperature of the membrane electrode assembly (MEA) and the local overpotential of the anode. Thus, as laboratory cells are used to verify mechanistic models and to determine adsorption model parameters, it is important to characterize the extent of uniformity of these laboratory-scale cells. Task 2 of Project 2 studied the distributions and the uniformity of current density, temperature, overpotential, and MEA water content. These distributions were determined as a function of flow-field geometry and particular attention was given to the concept of a cell composed with a series of straight parallel channels. All simulations were performed with commercially available computational fluid dynamics software designed for PEMFCs, based on a finite volume technique solver, STAR-CD 3.24.000, and an add-on tool with electrochemical subroutines, *es-pemfc* 2.2, were used to solve the fully coupled governing equations [2]. Automotive conditions were used as: cell and inlet temperatures of 353 K; relative humidity on anode of 75%; relative humidity on cathode of 0%; stoichiometry = 1.3 for anode and 2.0

for cathode; hydrogen/air feeds and outlet pressures of 274 kPa.

Figure 1 shows a conventional straight-channel cell, and an idealized straight-channel cell. The straight channel configuration was chosen to investigate “conventional thinking” that a series of parallel straight channels will lead to more uniform temperature and current density distributions. Thus, the ideal cell has equal velocities in each channel. The argument is that, in the limit of infinite stoichiometry, the straight flow will produce data with minimal variation so that estimated parameters from these data correspond to a well-defined cell temperature with minimum variance. The relaxation of infinite stoichiometry to a stoichiometry corresponding to an automotive condition of 1.3/2.0 (anode H_2 /cathode air) will yield a distribution in temperature even in the ideal cell as discussed below. However, this distribution should be the same for each channel and variations along a serpentine path due to bends in the channels will not confound the data.

The conventional straight channel cell has co-flow of the fuel and air. The manifold channels for the inlet and exit are 0.8 mm in width and 1.0 mm in height. The gas diffusion layer (GDL) thickness is 250 μm with a porosity of 0.7, a thermal conductivity of 0.213 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The GDL thermal conductivity is 0.147 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. There are 44 channels of width 0.8 mm and height 1.0 mm and the inlet velocity of the fuel and

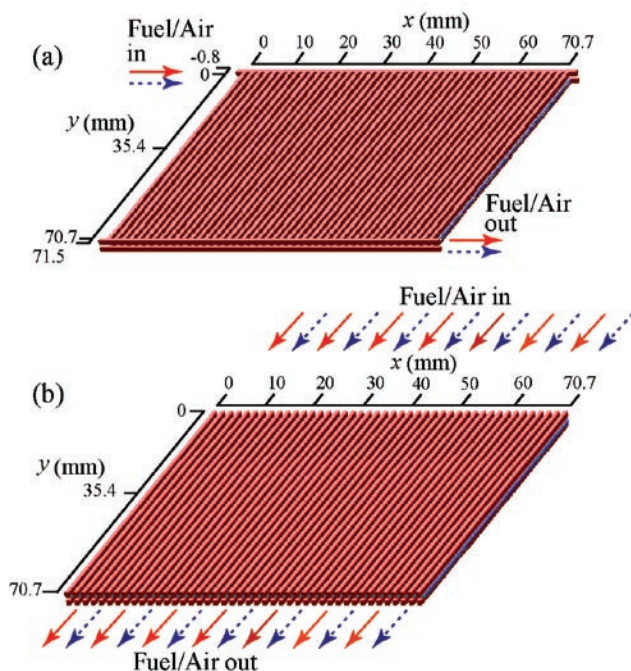


FIGURE 1. Geometry of 50 cm^2 Straight Parallel-Channel PEMFC: (a) Conventional Cell; (b) Ideal Cell

air at 0.6 A/cm^2 are 0.311 and 0.992 m/s corresponding to Reynolds numbers of 18 and 59, respectively. Other information can be found in references 3-5 which are being prepared for submission to referred journals. For the conventional cell, there are differences in the velocity profiles in each channel across the X-direction as a natural result of the reacting flow and the physical boundary conditions, which induce pressure drops and constrain the flow at the exit. These velocity differences yield the distribution of current density shown in Figure 2 for an average current density of 0.6 A/cm^2 . In Figure 2, the largest area corresponds to a current density of 0.1 A/cm^2 because there are higher velocities through the first 5-7 channels to the channels and the inlet manifold being the same height and width.

These large non-uniformities can be decreased with proper adjustment of the size of the manifolds, the direction of flow, and the location of the entrance and exits relative to their respective manifolds. This optimized geometry is shown in Figure 3. Note that the anode bipolar plate has a smaller exit manifold than the cathode, which would require an additional 8.0 mm of material so that the plates have the same overall dimensions. Figure 4 shows that the current density distributions resulting from this optimized cell are very similar to the ideal cell. There is a slight amount of sinusoidal distribution across the optimal cell at about 80% of the distance from the inlets. These slight “waves” on the optimal cell are influenced but the no-slip boundary conditions at the edge of the plates. The current is also larger at the exit due to a gradual increase in membrane water content from the dry inlet cathode conditions. The temperature distributions, which will be critical for analysis of the isotherms for CO adsorption, follow the distributions of the current density. Although not shown, predictions for serpentine flow field were

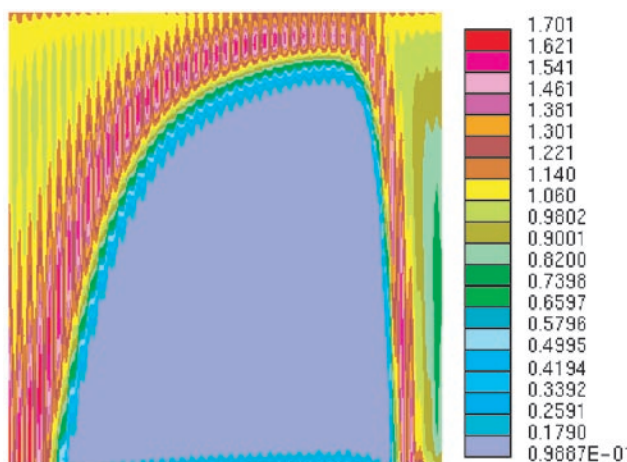


FIGURE 2. Current Density Distributions of 50 cm^2 Conventional Cell for Automotive Conditions at 0.6 A/cm^2

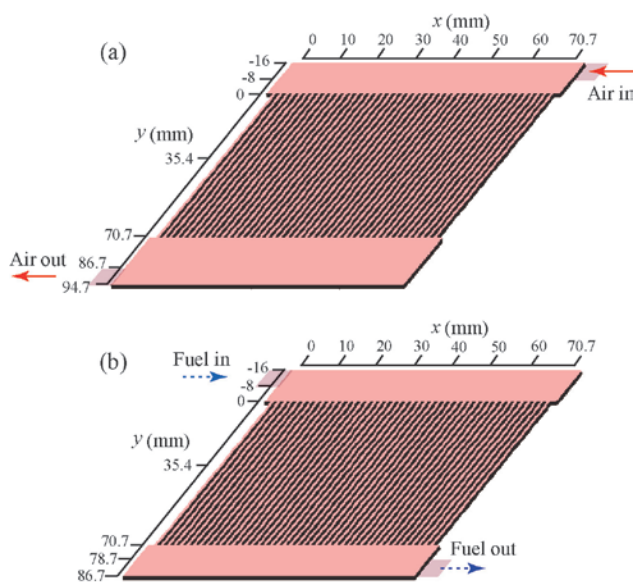


FIGURE 3. Geometry of 50 cm² Optimized Parallel Channel PEMFC: (a) Cathode Bipolar Plate (b) Anode Bipolar Plate

also performed as reported in Table 2. This serpentine cell had a single channel for flow on each side with channel widths of 1 mm and heights of 2 mm and the path consisted of 33 bends.

Table 2 summarizes the results and statistics for non-uniformity for two average current densities. Table 2 shows the cell voltage, the differences between highest and the lowest current densities (i.e., Δi), the average water content (i.e., λ), the average temperature (i.e., T_{avg}), and the difference between the highest and the lowest temperature ΔT as well as the standard deviations of current density and temperature at 0.6 A/cm². We computed the standard deviations at the higher current density to understand better this non-uniformity. As shown at 0.2 A/cm², the cell voltage of the conventional cell is 0.06 V less than the other three flow field designs. For the conventional cell operated at 0.2 A/cm², we also observed a highly non-uniform current similar to that shown in Figure 2 and this yields a difference in current density of 0.446 A/cm². The low average cell temperature is also due to the large area of low current density (labeled 0.1 A/cm² in Figure 2) even for a cell with 353 K inlet temperature. Note that because the air and hydrogen enter at the same location, albeit opposite sides of the MEA, the average water content is much larger than the other three designs at 0.2 A/cm². When the current density is increased to 0.6 A/cm² the conventional cell has a difference of 0.16 V compared to the other three and this is reflective of the non-uniformity shown in Figure 2. The standard deviations indicate that the conventional cell has a difference of almost 4 K from its average, which is still 4 K above the cell temperature of 353 K.

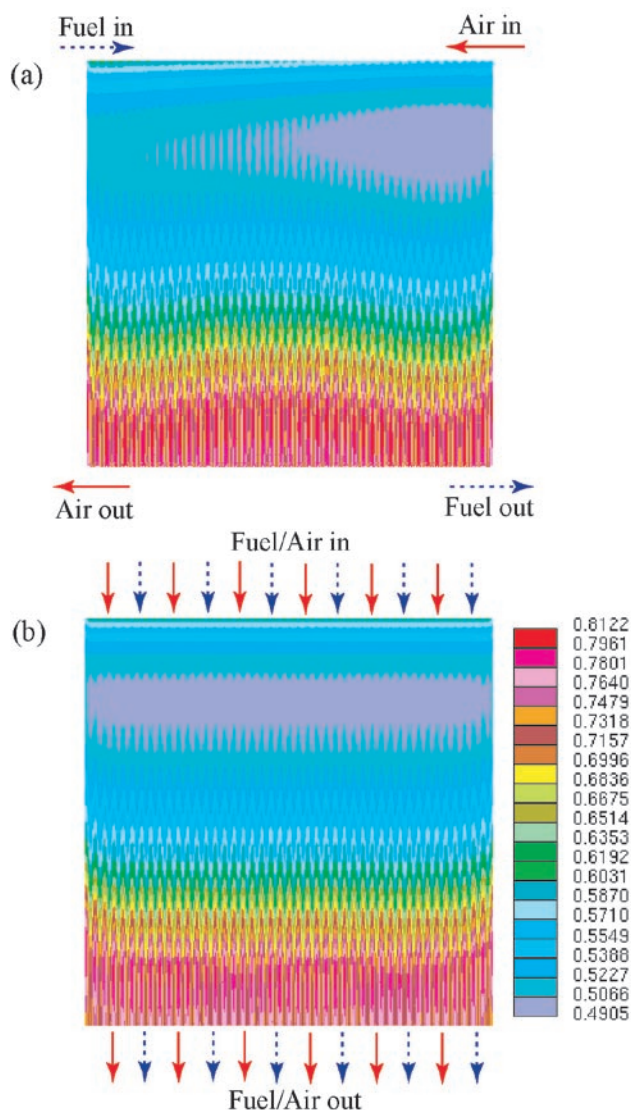


FIGURE 4. Current Density Distributions of 50 cm² of (a) Optimal Cell and (b) Ideal Cell for Automotive Conditions at 0.6 A/cm²

TABLE 2. Summary of Simulated Results for PEMFCs to Illustrate Differences in Uniformity for Different Designs

Cell type	$i_{avg} = 0.2 \text{ Acm}^{-2}$				
	V^{cell} (V)	Δi (Acm ⁻²)	λ_{avg}	T_{avg} (K)	ΔT (K)
Serpentine	0.712	0.056	6.25	354.3	2.4
Ideal	0.713	0.041	7.25	353.9	0.8
Optimum	0.713	0.034	6.77	353.9	0.8
Conventional	0.661	0.446	11.6	344.0	2.9

TABLE 2. Summary of Simulated Results for PEMFCs to Illustrate Differences in Uniformity for Different Designs (Continued)

Cell type	$i_{avg} = 0.6 \text{ Acm}^{-2}$				
	V^{cell} (V)	σ (Acm^{-2})	λ_{avg}	T_{avg} (K)	σ (K)
Serpentine	0.561	0.091	4.45	357.5	1.5
Ideal	0.566	0.097	5.15	356.4	1.0
Optimum	0.563	0.097	4.97	356.4	1.0
Conventional	0.405	0.537	9.57	357.3	3.9

Conclusions and Future Directions

The extent of uniformity with a straight parallel channel was quantified and an optimum cell has been designed that showed uniform flow profiles, and symmetric current density and temperature distributions similar to ideal cell. This design method should be used if the H₂ quality experiments dictate higher flowrates or different stoichiometry. The non-uniform flow profiles, which lead to the non-uniform current density distributions, were mainly caused by different channel velocities. These velocities within each cell change with the extent of electrochemical reaction and thus optimization such as those shown above must be performed with software that includes the electrochemical reactions (i.e., use reactive flow conditions rather than cold flow calculations).

Future work will follow the tasks in the Approach section.

References

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