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14. ABSTRACT Previous work in this research demonstrated the feasibility of fabrication of proton exchange membrane (PEM) fuel cell bipolar plates by an indirect selective laser sintering (SLS) route. Properties of the SLS bipolar plate, such as flexural strength, corrosion resistance and gas impermeability, etc. are quite promising and satisfactory. However, initial results showed that there was still room for the improvement in electrical conductivity. The first objective here is to investigate the potential methods that are capable of improving the electrical conductivity of SLS bipolar plates. Strategies investigated in an effort to increase the electrical conductivity were: (1) infiltration of brown parts with conductive polymer (2) addition of a liquid phenolic infiltration/re-curing step prior to final sealing and (3) reduction of glassy carbon resistivity by curing process parameter control. The other main objectives are (a) to simulate the performance of PEM fuel cells via computational fluid dynamics (CFD), and (b) develop a fuel cell testbed for experimentation. These complimentary objectives provide a basis to investigate, quickly and efficiently, novel designs for better PEMFC bipolar plates.

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Fiscal Year 2005 Summary Report

Laser-Based Fuel Cell Manufacturing for Thermal Management

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Project Attributes.

- Number of graduate students supported ≥ 25% of full time: 4
- Number of undergraduate students supported: 2

Summary of Objectives

Previous work in this research demonstrated the feasibility of fabrication of proton exchange membrane (PEM) fuel cell bipolar plates by an indirect selective laser sintering (SLS) route. Properties of the SLS bipolar plate, such as flexural strength, corrosion resistance and gas impermeability, etc. are quite promising and satisfactory. However, initial results showed that there was still room for the improvement in electrical conductivity. The first objective here is to investigate the potential methods that are capable of improving the electrical conductivity of SLS bipolar plates. Strategies investigated in an effort to increase the electrical conductivity were: (1) infiltration of brown parts with conductive polymer (2) addition of a liquid phenolic infiltration/re-curing step prior to final sealing and (3) reduction of glassy carbon resistivity by curing process parameter control. The other main objectives are (a) to simulate the performance of PEM fuel cells via computational fluid dynamics (CFD), and (b) develop a fuel cell testbed for experimentation. These complimentary objectives provide a basis to investigate, quickly and efficiently, novel designs for better PEMFC bipolar plates.

Summary of Technical Progress

Infiltration with Conducting Epoxy Resin

Infiltration with epoxy resin is one of the steps in the previously reported fabrication process. This necessary step was taken to make the porous brown part gas impermeable. It showed that with an adequate viscosity, epoxy resin was able to penetrate into the pore channels inside the part making it impermeable upon curing. However, our attention at this point was focused on searching for an infiltrant capable of improving the electrical conductivity as well as sealing the porous part. Based on an extensive literature survey, it is realized that epoxy resin containing carbon black makes up the greater portion of conductive epoxy resins available since this additive is the most cost effective; even though some other fillers such as copper, silver and carbon fibril, etc. are available.

Electrically conductive compounds made of an insulating polymer matrix and conducting particles have been extensively used in antistatic materials, electromagnetic shielding and liquid crystal display (LCD) industries. The electrical conductivity of such composites depends significantly on the concentration of the conducting phase and the extent of its continuity. Various mechanisms have been proposed to describe the electrically conducting behavior in polymeric composite materials, among which percolation theory and the quantum mechanical tunneling effect are two popular models to illustrate the electron transport process. The law of percolation theory states that a critical concentration or volume fraction, referred to as percolation threshold, of conductive filler is necessary to initiate the electrical conductivity in polymeric composite materials. The material behaves as an insulator when the filler concentration is too low to form a connecting network of conductive sites. On the other hand, the material undergoes a sharp transition from nonconductor to conductor when the filler concentration is above the percolation threshold, allowing electrons to tunnel through or jump between closely distributed filler sites.

To assess the feasibility of electrical conductivity improvement on SLS bipolar plate by using conducting epoxy resin infiltration, we would like to first know the maximum achievable electrical conductivity value a cured conducting epoxy resin can have. A commercially available epoxy resin and hardener obtained from System Three Resins, Inc. were mixed with carbon black powder purchased from Alfa Aesar Company. The epoxy was Clear Coat Epoxy Resin mixed with the hardener in a ratio of 2:1. The carbon black powder has an average particle size of 0.042 micron and a specific surface area of 75 m^2/g. Ten cups of carbon black loaded epoxy resins were prepared and cured overnight in an oven to form ten solid samples. The carbon black loading level for each sample was 1, 2, 3, 5, 7, 10, 12, 15, 20 and 25 volume percent, respectively. Each cured solid sample was then cut into four 3 mm by 3mm by 30 mm test specimens, making a total of 40 specimens, for electrical resistivity testing according to ASTM D257 specifications. This four point probe technique measures electrical resistivity by applying a constant current over the test specimen and measuring the voltage drop across the specified distance. The electrical resistivity can subsequently be calculated by following Equation (1):

$$\gamma = \frac{\Delta V(t)(w)}{I(L)} \tag{1}$$

where γ is electrical resistivity, ΔV is voltage drop across a prescribed distance, t is specimen thickness, w is specimen width, L is the distance over which ΔV is measured and I is applied constant current. A Keithley 224 Programmable Current Source and

Keithley 181 Nanovoltmeter were used to perform the tests. Figure 1 shows the average resistivity value for cured conducting epoxy resin versus its carbon black loading.

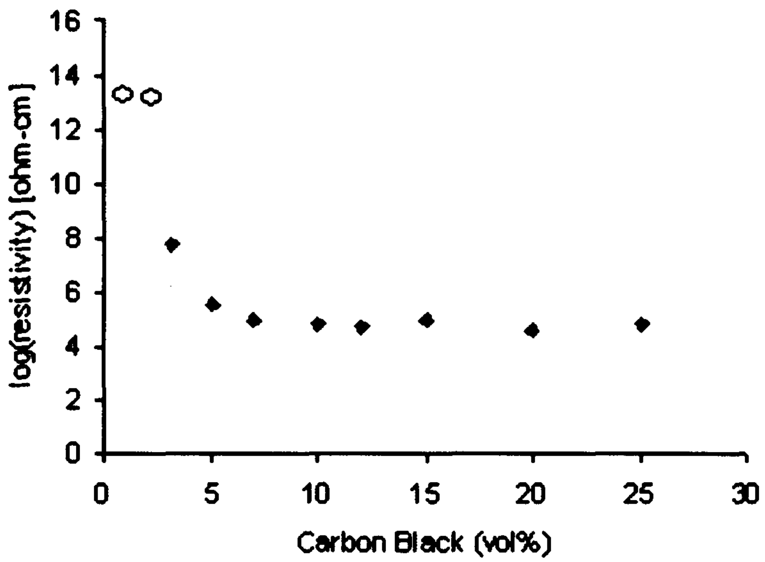

Figure 1. Resistivity of CB-filled epoxy resin versus CB content.
The first two circle points are predicted values.

As can be noticed from the plot, the electrical resistivity curve is expected to drop dramatically from nonconductive to conductive behavior over a narrow range of carbon black loading due to the development of a network of closely-seated CB particles. The predicted very high electrical resistivity for 1 and 2 vol % CB specimens was not obtained due to the limits of our equipment. More importantly, the minimum resistivity achieved is around 10^5 Ω-cm, which is equivalent to a maximum electrical conductivity value of 10^{-5} S/cm when CB loading is roughly above 8 vol. %. However, the outcome is not promising for our application since it is far below our current conductivity value and does not seem to help in the overall conductivity improvement to a value of over 100 S/cm. What was even more disappointing is that the fine carbon black powder tends to agglomerate easily in the CB-filled epoxy resins and largely increase the resin viscosity. High resin viscosity and CB agglomeration can block CB powders from flowing into pores of the porous plate and limit the performance of infiltration. It is apparent, at this point, that infiltration of conducting epoxy resin will not be workable for the conductivity improvement of our SLS plates. Even many commercially available conducting epoxy resins exhibit much higher values of conductivity; most of them are in the form of "paste" instead of what is required here, a low viscosity infiltrant.

Liquid Phenolic Infiltration/Re-Curing

The electrical conductivity of powder metallurgy parts is affected by many variables, such as impurity, pore shape, and connectivity, etc, and one of the most significant factors is the amount of pores presented in the solids. Many models for thermal and electrical conductivity, based on theoretical or semi-empirical results, have been reported. From these models, it is obvious that electrical conductivity increases as the percentage of porosity is reduced while the part becomes denser. This trend brought up the idea for improving electrical conductivity of SLS bipolar plate by increasing the glassy carbon residue level so as to replace portion of the porosity space that is originally occupied by the non-conducting epoxy resin when final epoxy sealing is completed.

Phenolic resin was previously chosen as one of the constituents along with graphite particles to make up the powder mixture for the requirements of this application. It is selected here as the intermediate infiltrant to elevate the carbon residue level when recuring process is executed. The phenolic resin GP5546 PARAC Powdered Phenolic Resin was obtained from Georgia Pacific Resins, Inc. and was dissolved in acetone at a temperature of 50 °C by using a magnetic stirrer for 30 minutes. The phenolic infiltrant was made of 60 vol. % of powdered phenolic resin and 40 vol. % of acetone for the first infiltration and the phenolic infiltrated brown part was placed back in the high temperature furnace for recuring. The recuring process was performed under inert gas atmosphere as the furnace chamber was filled with research grade argon gas from PraxAir Inc. The temperature profile for the recuring cycle started at room temperature and went up to 800 °C with a 1 °C/min heating ramp rate and was held for 1 hour before cooling back to room temperature naturally. The recured brown part was less porous compared to brown parts that did not receive such treatment. Electrical conductivity was improved to an average value of 108 S/cm. Following the same strategy, a second phenolic infiltration/recuring step was performed in an attempt to further increase the conductivity. The phenolic infiltrant was modified to a composition of 45 vol. % of powdered phenolic resin and 55 vol. % of acetone for reduced viscosity. The same temperature profile was implemented for the second time recuring process and the final electrical conductivity was increased to an averaging value of 117 S/cm. Figure 2 shows a bar chart for electrical conductivity with respect to each fabrication step. As can be seen, there is a 35% boost in electrical conductivity when the first phenolic infiltration/recuring step is employed and another 8.3% increase when the second phenolic infiltration/recuring step is done. The reduced rate in electrical conductivity improvement implies that less glassy carbon residues are deposited each time inside the brown part since the corresponding amount of porosity is lessened.

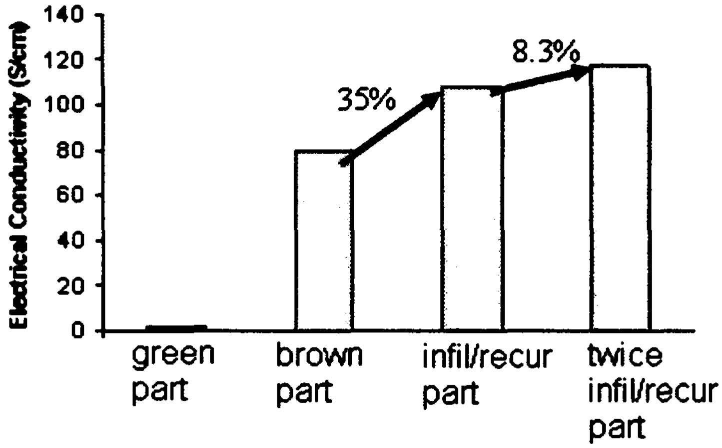

Figure 2. Electrical conductivity improvement of SLS bipolar plate with respect to corresponding fabrication step.

Curing Process Parameter Control

The brown part is composed of graphite particles and glassy carbon produced from carbonization of phenolic resin, and both ingredients contribute to its final conductivity. If the conductivity of glassy carbon were able to be significantly improved, it might be able to benefit the overall conductivity of brown part supposing that the conductivity of graphite particles is constant. Bhatia et al. explored the variation of some physical properties of carbonized phenolic resin when increasing the curing temperature, one of which gives the relationship between its electrical resistivity and curing temperature as shown in Figure 3. It is evident from the curve that the electrical conductivity of pyrolyzed phenolic falls drastically in the range of 600° C to 800° C, beyond which the rate of fall in resistivity decreases gradually.

To examine the extent of the effect of conductivity increase from glassy carbon, the peak dwell temperature for brown part formation was raised from the original 800° C to 1000° C and electrical conductivity values were measured by using the four point probe technique described previously. Results showed, unfortunately, that the electrical conductivity of brown part does not exhibit significant improvement from the increase in final curing temperature. This may be attributed to the fact that only a relatively small portion of glassy carbon exists in the composition and the most critical factor dominating the electrical conductivity in powder sintered parts is its porosity level. Electrical conductivity of powder sintered parts normally follows a power law and is a strong function of porosity level inside the part.

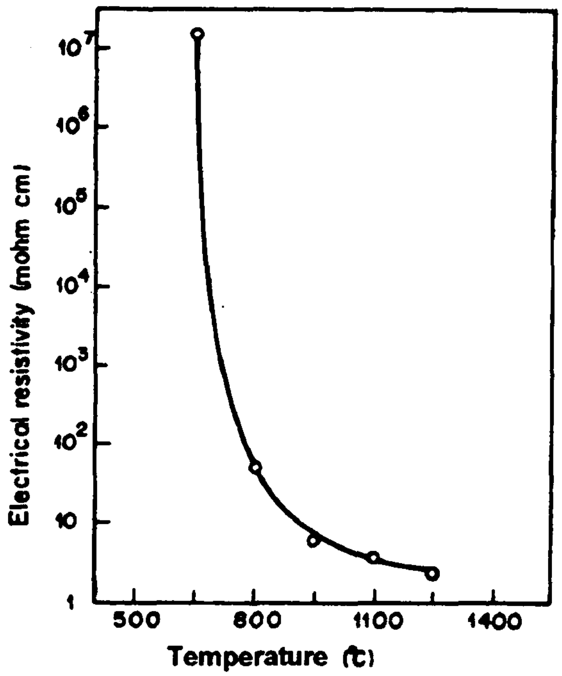

Figure 3. Variation of electrical resistivity of cured phenolic resin versus temperature. (From Bhatia et al.)

Conclusions

Three potential strategies were examined to ascertain the most appropriate method for improving the electrical conductivity of SLS bipolar plates. Inclusion of liquid phenolic infiltration/recuring steps to the fabrication route proved to be the most effective solution among others. This method is very similar to the way people used to make carbon/carbon or carbon/graphite composite materials where multiple cycles of thermosetting resin impregnation and curing are performed to form a gas-tight matrix. For our special application of fabrication of SLS PEM fuel cell bipolar plates, however, simply one or two times of liquid phenolic infiltration/recuring step are necessary to meet the electrical conductivity target value, especially when considering the lengthy and costly polymer pyrolysis process. The treated part is subsequently infiltrated with liquid epoxy resin to seal its surfaces. One other possible way to improve the electrical conductivity is chemical vapor infiltration (CVI) of carbon from hydrocarbon gaseous precursors into porous SLS brown parts. This technique is potentially capable of creating a hermetic skin on the plate surfaces as well as improving electrical conductivity due to the addition of elemental carbon.

Simulation of PEM Fuel Cell

With the ability to rapidly fabricate PEM fuel cell bipolar plates by the established indirect SLS process, the flow field design for bipolar plates will benefit significantly since the performance of various bipolar plates can then not only be assessed numerically but also verified experimentally in a prompt manner. Several CFD software packages such as CFX, PHOENICS, FLUENT, FLOW3D and STAR-CD, etc are commercially available. All of which listed above use finite volume method to discretize the governing equations. In this study, the FLUENT 6.2 code, which is accessible from the Dell Precision 530 workstations in the High Performance Computing (HPC) laboratory of Department of Mechanical Engineering at the University of Texas at Austin, was used to perform the numerical calculations. To ensure and allow the high-powered mathematical calculations, each computer in HPC laboratory is equipped with two 1.8 GHz Pentium Xeon processors, 1GB of SDRAM and runs under SuSE Linux operating system. The FLUENT code is a general purpose CFD software package capable of solving general CFD problems in either two dimensions or three dimensions. One of the outstanding features of FLUENT is that it allows users to customize the code through a special option, called User Defined Function (UDF), to fit the particular modeling needs. For PEM fuel cell simulations, equations related to electrochemical reactions and various source and sink terms, etc. can be written in the C programming language and grouped as UDFs. These UDFs can then be hooked to the FLUENT solver using a graphical user interface panel to perform the specific-purpose calculations.

Alternatively, a special license for PEM fuel cell modeling was purchased from Fluent Inc. The license allows users to access the PEM fuel cell module implemented as a toolbox within the framework of original FLUENT code. The FLUENT PEM fuel cell toolbox is actually composed of many User Defined Functions that are incorporated into the fuel cell model developed by Fluent Inc. The model is a multi-phase mixture model and is capable of predicting local current density distribution, local voltage distribution, temperature distribution and species concentration, etc. in either a single PEM fuel cell or fuel cell stacks. Up to date, we have simulated several types of bipolar plate flow channel design such as single parallel serpentine flow channel, multiple-parallel serpentine flow channel and interdigitated flow channel etc. by using this CFD model. Figure 4 through Figure 9 demonstrate the simulation results of the most basic flow field pattern design, single parallel serpentine flow channel, for PEM fuel cell bipolar plates.

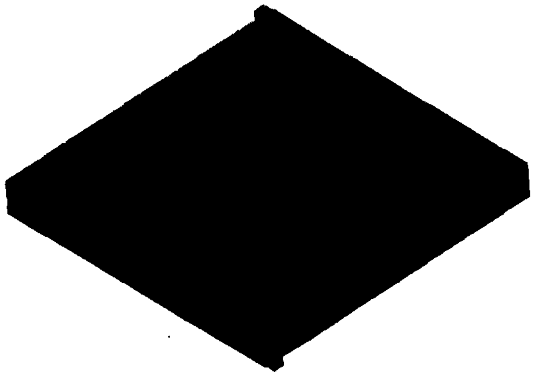

Figure 4. Single parallel serpentine flow channel design. The CAD model is created using AutoCad and is imported to Gambit, which is the preprocessor of FLUENT, for generating the meshes. The meshed model is then imported to FLUENT for CFD analysis.

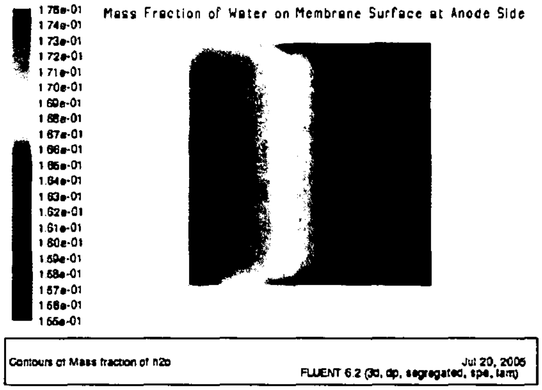

Figure 5. Distribution of mass fraction of water on membrane surface at anode side. The anode side membrane surface suffers from dehydration from gas inlet to outlet during operation.

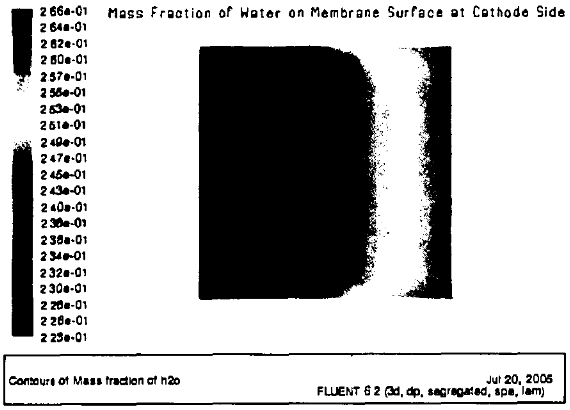

Figure 6. Distribution of mass fraction of water on membrane surface at cathode side is totally opposite to that at anode side. This can be explained by the cathode side half cell reaction.

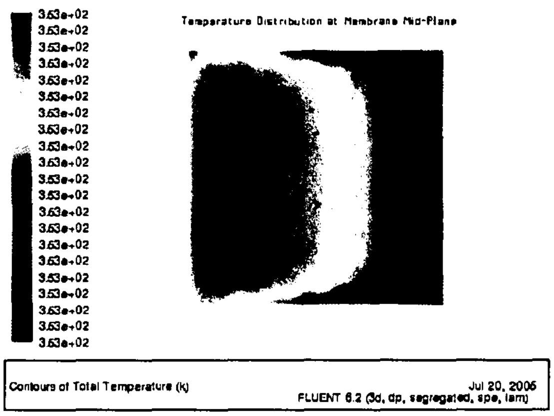

Figure 7. Temperature decreases from gas inlet to outlet at membrane mid-plane. This can be attributed to the slower reactions taking place near the end of flow channel due to depletion of reactant gases.

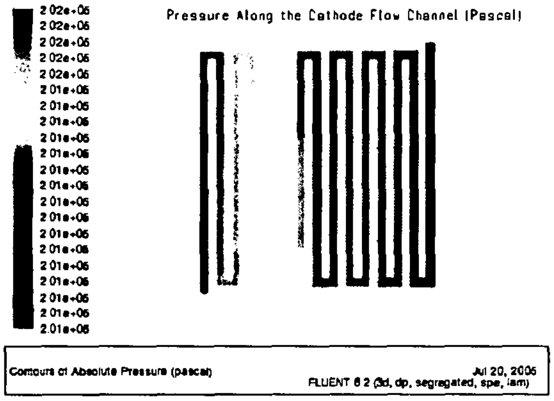

Figure 8. Pressure decreases from gas inlet to outlet in the flow channel. More advanced flow channel design can reduce high pressure gradient in the flow channels.

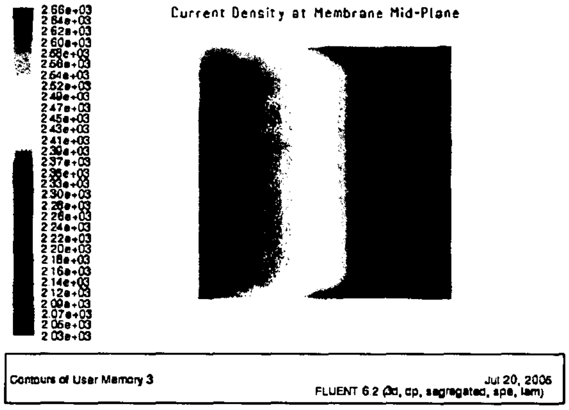

Figure 9. Current density distribution at cell voltage of 0.7V and gas pressure of 2atm is shown. Pressure gradient, water depletion or flooding and flow velocity all contribute to the uneven current density distribution.

Recommendations and Future Work

Based on the CFD model, simulation of the operation of PEM fuel cells is able to provide more in-depth information on fuel cell performance that is not possible to be obtained simply through experimentation. Simulation results such as current density distribution, temperature distribution, reactant gas usage distribution and water content distribution etc. can be graphically analyzed and more importantly, their relationships to bipolar plate flow channel configurations can be established. Improved design and prompt experimental validation of fuel cell bipolar plates are thus possible through the combination of computer simulation and established indirect SLS process. Additionally, two of the proposed novel bipolar plate designs are presented in Figure 10. A bipolar plate testing apparatus is also being designed and constructed to experimentally evaluate the thermal management and flow field properties for the purpose of verifying the model and plate designs. The testing apparatus is expected to be capable of evaluating the plate heat transfer properties, flow fields fluid properties, and fuel cell stack performance during operation.

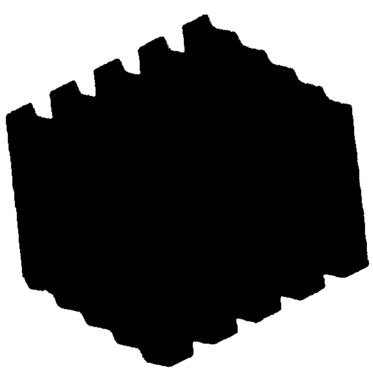

Figure 10(a). Rippled bipolar plate designed to increase active surface area.

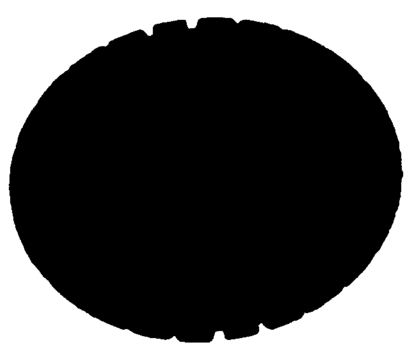

Figure 10(b). Toroidal fuel cell stack design to optimize overall stack dimension.

List of Publications

S. Chen, D. Bourell, "Fabrication of PEM Fuel Cell Bipolar Plate by Indirect Selective Laser Sintering", *Trends in Materials and Manufacturing Technology and Powder Metallurgy R&D in Transportation Industry*, the 134th TMS symposium, San Francisco, California, Feb. 13-17, 2005.

D. Bourell, R. Evans, S. Chen and S. Barrow, "Rapid Manufacturing Using Infiltration Selective Laser Sintering", *Rapid Prototyping and Manufacturing*, Dearborn, Michigan, May 10-12, 2005.

S. Chen, D. Bourell, and K. Wood, "Improvement of Electrical Conductivity of SLS PEM Fuel Cell Bipolar Plates", *Proceedings of the 16th Solid Freeform Fabrication Symposium*, Austin, Texas, Aug. 1-3, 2004.

Recent Graduate Students Supported by ONR

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