VI.5 Adaptive Process Controls and Ultrasonics for High-Temperature PEM MEA Manufacture

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Fiscal Year (FY) 2011 Objectives

The high level objective of the proposed work is to enable cost-effective, high-volume manufacture of high- (160-180°C) and low-temperature (<100°C) proton exchange membrane fuel cell (PEMFC) membrane electrode assemblies (MEAs) by:

- Achieving greater uniformity and performance of high-temperature MEAs through the application of adaptive process control (APC) combined with effective in situ property sensing to the MEA pressing process.
- Greatly reducing MEA pressing cycle time through the development of novel, robust ultrasonic bonding processes.

Technical Barriers

This project addresses the following Manufacturing R&D technical barriers in the Manufacturing R&D section (3.5.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes

(F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section (3.5.7) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2**: Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- **Milestone 3**: Demonstrate sensors in pilot scale applications for manufacturing MEAs. (4Q, 2013)
- **Milestone 4**: Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

FY 2011 Accomplishments

- Added APC capability to Rensselaer's MEA thermal bonding station.
- Designed, built, and tested temperature-controlled stack hardware, servo press, and fuel cell test stand that can handle one MEA and short stacks of 5 and 10 high-temperature MEAs (50 cm^2 active area) bonded using thermal pressing and APC or ultrasonics.
- Designed, built and tested thermal and ultrasonic bonding tools, component assembly and laser cutting fixtures, and single cell test hardware for thermal pressing, ultrasonic bonding, and characterization of larger scale high-temperature MEAs (140 cm^2).
- Found that heat treatment (to boil off excess water), low pressing pressure, low anvil support backer stiffness, and high booster amplitude were optimal process parameters for ultrasonic bonding of high-temperature MEAs.
- Created a vibration model coupled with thermal finite element analysis (FEA) model to accurately predict transient temperatures through MEA thickness during ultrasonic bonding.
- Found that current heat treatment time can be reduced as much as 50% without adversely affecting performance, membrane thickness and acid concentration in the MEA.
- Designed, built, and tested thermal and ultrasonic bonding tools, component assembly and laser-cutting fixtures, and single cell test hardware for low-temperature (Nafion®) MEAs (10 cm^2 active area).
- Found that MEAs sealed ultrasonically with optimized process parameters exhibit excellent stability (no cell voltage degradation and minimal cell internal resistance change) under extreme start/stop operating conditions over a period of 200 hours.

- New cost model predictions between Phase I and Phase II based on actual experimental data include lower cost reductions for implementing APC (29% vs. 38%) but higher reductions for implementing ultrasonics (90% vs. 84%).

Introduction

To realize the tremendous potential that fuel cell technology has to improve the world's environment and reduce our dependence on fossil fuels, it is essential that high volume, high quality manufacturing technologies are developed in parallel with the materials and designs for MEAs, stacks, and the other stack components, which is currently not the case. There are currently three main barriers to the development of high volume fuel cell manufacturing. First, the current practice involving extensive testing and burn-in of components and stacks will not allow the industry to achieve the necessary cost targets and throughput for stacks, components, and systems. Second, for the current process used to press low-temperature (e.g. Nafion®) MEAs used in both PEMFCs and direct methanol fuel cells, it is common to thermally press for as long as 1½-5 minutes. Even the pressing process for high-temperature (polybenzimidizole, or PBI) MEAs, while much shorter than for Nafion®-based MEAs at about one minute, is still too long for high volume manufacture. Third is the variability of MEA performance. The component materials, including gas diffusion layer or gas diffusion electrode (GDE), membranes or catalyst-coated membrane, and gasketing materials all exhibit variations in key properties such as thickness, porosity, catalyst loading, and water or acid content and concentration. Yet, it is common practice to employ a fixed combination of pressing process parameter values (time, temperature and pressure), regardless of these variations. As a result, MEAs exhibit variations in physical and performance related properties.

The research being conducted in this project will help reduce all three of these barriers by reducing the unit process cycle time for MEA pressing by the use of ultrasonic sealing, and by minimizing the variability in performance of MEAs produced using adaptive process control. This will in turn help lead to the reduction or elimination of the practice of burn-in testing of fuel cell stacks. All of these benefits will contribute to a reduction in manufacturing costs for MEAs.

Approach

The current state of practice in MEA manufacturing calls for the application of fixed pressing process parameters (time, temperature, and pressure), even though there are significant variations in incoming material properties of the membrane and electrodes including thickness, mechanical properties, and acid/water content. MEA manufacturers need to better understand the relationships among those incoming material properties, the manufacturing process parameters, the resulting MEA physical and electrochemical properties, and the eventual electrical performance of the MEA in a stack.

We plan to address the problems associated with different methods of pressing high-temperature MEAs, specifically PBI with phosphoric acid as the electrolyte, by applying APC techniques and ultrasonics, and pressing low-temperature MEAs, specifically Nafion®-based, by applying ultrasonics. Through extensive experimentation and testing, we will develop analytical and empirical models of the relationships among incoming component material properties, the manufacturing process parameters, the resulting MEA properties, and the performance of the MEA in a stack. With the knowledge gained and new hardware designs, we will then attempt to identify one or more key properties (e.g., alternating current [AC] impedance, electrochemical capacitance) of the MEA that can be measured in situ during the thermal or ultrasonic pressing process, and then correlate these properties to the eventual physical and electrochemical performance of the MEA in a stack. If we are successful in identifying such an in situ measurement(s), adaptive control algorithms along with integrated process parameter and MEA performance sensing capabilities will be developed to allow us to vary the thermal and ultrasonic pressing process parameters in real time in order to achieve optimal uniformity of MEA performance.

We anticipate that the APC and processing techniques being investigated can be applied equally well, with certain modifications, to the pressing of both high-temperature and low-temperature MEAs, although the focus of this work to date has been on the former because of our extensive experience with these materials and the enhanced performance they offer (e.g., high operating temperature, no water management issues, high CO and H_2S tolerance). Our research is not application specific as the results may be applied to a broad range of fuel cell applications.

Results

APC: The application of APC to the experimental manufacturing of high-temperature PEMFCs has been an on-going effort. Experiments have been conducted to determine the best sensing method to correlate real-time electrical characteristics to eventual performance for MEAs made by thermal pressing. Using in situ alternating current (AC) impedance measurements, we are able to determine when the electrochemical cell has been formed by observing the drastic change in reactance. Our experimentation points to this change, specifically when the impedance reaches a minimum, as being the indicator of the completion of the manufacturing process.

In our current work, we apply the instrumentation method to our manufacturing process and complete the cycle when the impedance (sensed with a 1 kHz milliohmmeter) becomes a minimum. In preliminary tests,

we have found that the cycle time is reduced significantly. Our continuing experimentation will determine how much of an improvement will be made to the uniformity of performance of the cells produced using this method.

MEA Performance Evaluation Via Stack Testing: High-temperature MEAs (with 50 cm^2 active area) produced using APC and ultrasonics will be tested in single cell test fixtures and the performance of the MEAs will be compared to those tested during the Phase I experimentation. MEAs will also be tested in short stacks of 5 and 10 cells to determine cell to cell performance variations (e.g., voltage, temperature). Uniformity of MEAs produced by thermal pressing with APC and by ultrasonics will be compared to those produced by thermal pressing alone.

FIGURE 1. Fuel cell stack for testing 50 cm^2 MEAs produced using thermal pressing, thermal pressing with APC, and ultrasonics.

We have completed the design and fabrication of the stack that will be used for this investigation, as shown in Figure 1. It is be highly instrumented so that we will be able to identify individual cell performance (impedance, voltage, temperature) and also stack performance.

A serious experimental issue that was identified and corrected involved leaching of phosphoric acid into the porous graphite bipolar plates during testing. The solution was to procure POCO graphite plates that are first machined and then subjected to a post surface sintering process to completely seal surfaces.

The current experimental schedule will test single baseline MEAs (i.e. made by thermal pressing only), then a 5-cell stack, and finally a 10-cell stack test to validate the hardware. After stack performance is validated, the performance of thermally bonded MEAs with APC and ultrasonic MEAs will be tested in stacks.

Large-Scale MEA Testing: Tooling for thermal and ultrasonically bonding large scale MEAs has been designed, built and tested. The ultrasonic and thermal press tooling including registration fixtures is shown in Figures 2a and 2b, respectively. An MEA with 140 cm^2 active area was specially designed for this task, because the size is similar to those used in automotive applications and it was the maximum size that could be accommodated by ultrasonic horns commercially available from Branson Ultrasonics Corporation, a project collaborator. Laser cutting fixtures and a carrier frames were also designed and built. MEAs have already been fabricated using thermal and ultrasonic bonding. Performance testing of thermally and ultrasonically bonded large-scale MEAs are on-going.

Ultrasonic Bonding Process Optimization and Process Modeling: Optimal process parameters were determined for ultrasonic bonding of high temperature MEAs. Since heat treatment (i.e. boiling off excess water using an oven) was identified as the most significant process parameter in a previous designed experiment and statistical analysis (Phase I), all membranes were heat treated while the other process parameters – membrane thickness, anvil support backer stiffness, sealing pressure, and energy flux - were

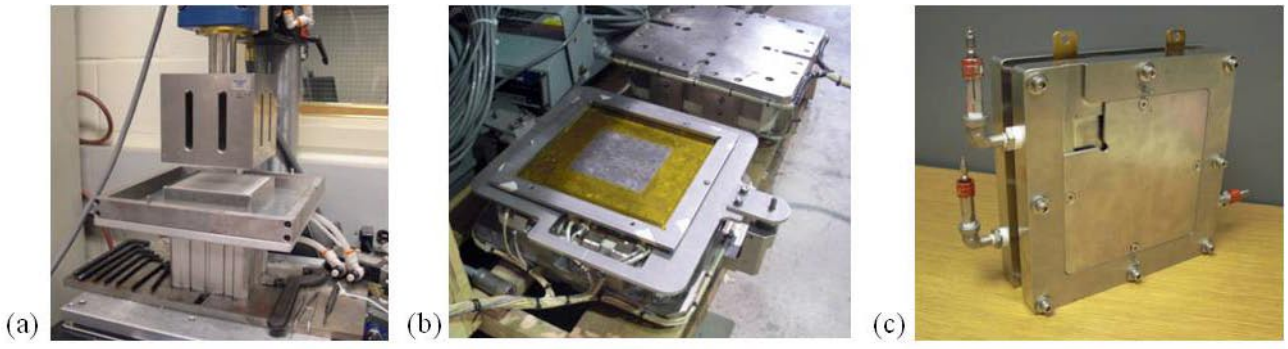

FIGURE 2. (a) Ultrasonic tooling, (b) thermal press tooling and (c) single-cell test fixture for large-scale MEAs (140 cm^2)

systematically varied in a two-level, full-factorial (2^4) experimental design with two replicates. Testing including creating a pole curve and measuring cell resistance after a 16-hour incubation period required for the hydrolysis and vaporization reactions to reach equilibrium. Specifically, current density at two voltages (0.4 and 0.6 V) and cell resistance were measured as output variables. In addition to heat treatment, process conditions for making optimal performing MEAs included low pressing pressure, low anvil support backer stiffness, and high booster amplitude based on analysis of variance. A comparison of polarization curves between the manufacturer's baseline thermally pressed MEA and an MEA fabricated with optimal ultrasonic process parameters is shown in Figure 3.

The MEA ultrasonic bonding process is being modeled using a combination of vibration and FEA theory. The vibrational model – masses coupled in series with a spring and spring/damper in parallel for each of the three layers (GDE, membrane, GDE) – currently contains six degrees of freedom. Model input is a high frequency (20 kHz) and low amplitude (20 μm) vibrational signal along with a constant preload (pressing pressure) from the ultrasonic horn. Because of the extreme ratio of the model spring stiffness to the model mass, the natural frequencies are very high. This necessitates the use of a stiff computational solver. Currently, the model is still being refined to balance model accuracy with computational time. Heat dissipated by the dampers in real time is used in a COMSOL FEA transient thermal analysis with internal heat generation at each of the MEA material interfaces (GDE/membrane × 2). Because of the symmetry of the model and the fact that the heating is assumed to be uniform, the COMSOL model is now two-dimensional, rather than three-dimensional. A one-dimensional model was found not to give as clear of a visualization of the heating process.

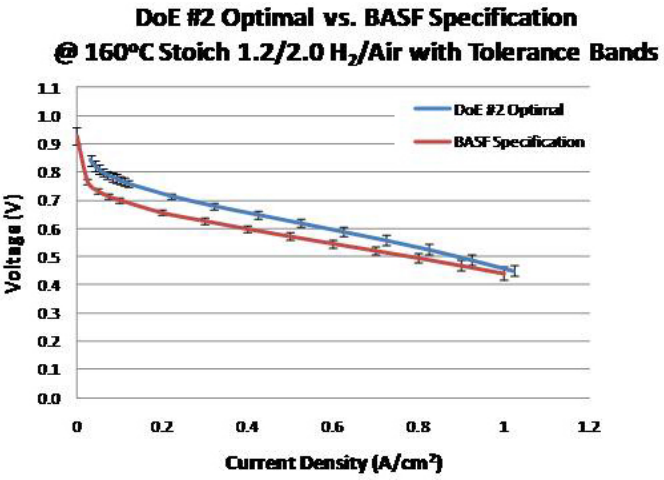

FIGURE 3. Polarization curve of optimal ultrasonically bonded MEA with superior performance as compared to the BASF specification.

Using experimentally derived stiffness and damping values for each layer of the MEA (no fudge factors), the model closely matches thermocouple temperatures measured through the MEA thickness during ultrasonic bonding.

Heat Treatment Optimization: A 2-factor, 3-level, 2-replicate design of experiment was designed for the MEAs with oven temperature and soak time as the variables. Single cell evaluation of the heat-treated MEAs was performed after an 18-hour burn-in period at 200 mA/cm^2 followed by polarization curve measurements at 160°C. The single cell performance of the heat-treated, ultrasonically sealed MEAs was measured along with membrane thickness and acid concentration. Statistical analysis showed that the middle and low temperature and their corresponding heat treatment duration were all significant. More importantly, heat treatment duration beyond the lowest level (15 min) provided no performance benefit.

Ultrasonic Bonding of Low Temperature MEAs: Low-temperature MEAs with 10 cm^2 active area have been successfully sealed using a 20 kHz ultrasonic machine and by thermal pressing. With ultrasonic bonding, the MEA is built carefully by hand, ensuring alignment between the two electrodes, on a piece of Kapton. A second layer of Kapton is placed on top of the assembly to protect the ultrasonic horn, and it is placed on a smooth anvil in the ultrasonic sealer. The ultrasonic welding setup is shown in Figure 4a. Finally, registration holes for alignment in the single cell test hardeware are laser-cut into the oversized Nafion® membrane. An ultrasonically welded MEA is shown in Figure 4b.

Testing of the low-temperature MEAs is planned so that those that are ultrasonically bonded can be compared to thermally pressed baseline MEAs. The bonding process on the ultrasonic setup will be optimized by varying the sealing pressure and energy flux and evaluating the performance. Various techniques and "recipes" to produce thermally pressed MEAs will be explored to maximize the baseline performance.

Durability Testing of Ultrasonically Bonded MEAs: Accelerated durability testing of the high-temperature MEAs (50 cm^2) was performed using test protocols designed to simulate real life operating conditions. The accelerated durability testing protocols involved fuel cell startup/shutdown, load cycling and thermal cycling processes performed over 200 hours. MEAs sealed ultrasonically with optimized process parameters exhibited excellent stability, i.e. no cell voltage degradation and minimal cell internal resistance change, during the 200-hour tests. The authors believe that the ultrasonic sealing technique combined with accelerated durability testing will be vital to the development of high volume fuel cell manufacturing

Conclusions and Future Directions

We are encouraged by the performance of ultrasonically bonded high temperature MEA performance made using

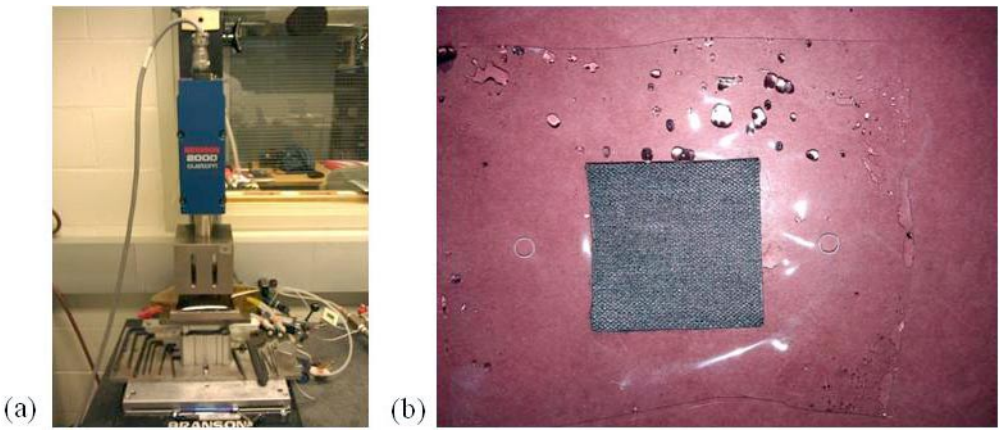

FIGURE 4. (a) Ultrasonic setup used to bond low-temperature MEAs and (b) resulting MEA after laser cutting alignment holes.

optimized process parameters based on single-cell testing after standard incubation and accelerated durability testing. Performance to date has been at least equal to baseline data provided by the manufacturer for thermally bonded MEAs. APC offers a way to minimize cycle time and improve the consistency of thermally pressed MEAs, although cycle times will still be at least an order of magnitude longer than for ultrasonic bonding. Likewise, cost model predictions based on actual experimental data include a 29% reduction by implementing APC and 90% by implementing ultrasonics. The entire research team is prepared to test the performance of 50 cm^2 high temperature MEAs made by standard thermal pressing, APC, and ultrasonic bonding in short stacks and monitor individual cell characteristics. We are also prepared to test and compare larger scale (140 cm^2) high temperature MEAs made using the same three bonding methods. Finally, the team is prepared to compare the performance of small (10 cm^2) low-temperature MEAs made by thermal pressing and ultrasonic bonding. Major activities planned for the remainder of Phase II include:

- Showing how MEAs made by thermal pressing with APC and ultrasonic bonding perform in short stacks compared to those made by conventional thermal pressing.
- Showing how the ultrasonic bonding process scales by comparing the performance of larger scale MEAs (ultrasonically and thermally bonded) to that of standard size MEAs.
- Continue refining the ultrasonic bonding models, validate with experimental data, and demonstrate how such a model would be used for process design and optimization.
- Showing how ultrasonic bonding works for low-temperature MEAs and identifying significant process parameters.

Patents Issued

1. Snelson, T., Puffer, R., Pyzza, J., Walczyk, D. and Krishnan, L., "Method for the production of an electrochemical cell," *U.S. and International Patents Pending*, 2011.

FY 2011 Publications/Presentations

1. Guglielmo, D., Snelson, T. and Walczyk, D., "Modeling Ultrasonic Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," *Proceedings of the ASME 9th Fuel Cell Science, Engineering and Technology Conference*, Washington, DC, Aug. 7–10, 2011, Paper # ESFuelCell2011-54427.

2. Pyzza, J., W. Sisson, W. and Puffer, R., "Manufacturing Implementation of Ultrasonic Sealing of Membrane electrode assemblies for high temperature PEM fuel cells" *Proceedings of the ASME 9th Fuel Cell Science, Engineering and Technology Conference*, Washington, DC, Aug. 7–10, 2011, Paper # ESFuelCell2011-54441.

3. Pyzza, J., "Implementation of Ultrasonic Welders in Automated High Temperature PEM Fuel Cell Membrane Electrode Assembly Manufacturing," *M.S. Thesis*, Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY, 2011.

4. Snelson, T., "Ultrasonic Sealing of PEM Fuel Cell Membrane Electrode Assemblies," Ph.D. Thesis, Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY, 2011.

5. Puffer, R. and Walczyk, D., "Adaptive Process Controls and Ultrasonics for High Temperature PEM MEA Manufacture," *Fuel Cell Tech Team Meeting (USCAR)*, Southfield, MI, March 16, 2011.

6. Krishnan, L., Snelson, T., Walczyk, D. and Puffer, R., "Effect of Heat Treatment Process Parameters on Polybenzimidazole-based Membrane Electrode Assemblies," *Journal of Fuel Cell Science and Technology* (in review).

7. Krishnan, L., Snelson, T., Walczyk, D. and Puffer, R., "Durability Studies of Ultrasonically Sealed Membrane Electrode Assemblies for High Temperature PEMFCs," *Journal of Fuel Cell Science and Technology* (in review).

8. Snelson, T., Pyzza, J., Krishnan, L., Walczyk, D. and Puffer, R., "Ultrasonic Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," *Journal of Fuel Cell Science and Technology* (in review).