VI.3 Adaptive Process Controls and Ultrasonics for High-Temperature PEM MEA Manufacture

Fiscal Year (FY) 2012 Objectives

- Conduct experiments to determine the feasibility and benefits of using ultrasonics for bonding low-temperature (Nafion®) membrane electrode assemblies (MEAs).
- Test and evaluate the performance of ultrasonically and thermally bonded high-temperature polymer electrolyte membrane fuel cell (PEMFC) MEAs (160-180°C) in 5- and 10-cell short stacks to (1) investigate the compatibility of the bonding process with cell stacks and (2) increase testing throughput to support simultaneous testing of cells fabricated with similar conditions.
- Test and evaluate the performance of ultrasonically and thermally bonded MEAs with larger active area (140 cm²) and compare with the 'standard' MEA size (45 cm²).
- Investigate the causes of excessive variation in ultrasonically and thermally bonded high-temperature MEAs using more diagnostics applied during the entire fabrication and cell build process.
- Perform a cost analysis that compares roll-to-roll manufacturing and discrete manufacturing (current) approaches for high-temperature MEAs.
- Develop guidelines and analytical models that allow manufacturing engineers to design/specify tooling and determine optimal process parameters for bonding high-temperature PEM MEAs using ultrasonics.

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 R&D 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 2012 Accomplishments

- Found that performance of ultrasonically bonded low-temperature MEAs is sensitive to electrode composition and structure.
- Optimized the thermal and ultrasonic bonding processes for low-temperature MEAs, i.e., consisting of Nafion® 115 and commercial (Fuel Cell Earth) electrodes, using designed experiments and analysis of variance (ANOVA) to estimate main effects of the bonding process.
- Characterized performance loss of low-temperature MEAs between ultrasonic and thermal bonding, high and low catalyst loading gas diffusion electrodes (GDEs), and conditioned and dry membrane conditions.
- Stack for high-temperature MEAs with composite bipolar plates was developed and qualified as having insignificant impact on cell performance.
VI. Manufacturing R&D

- Stack utilized for high-throughput, simultaneous high-temperature MEA cell testing.
- Demonstrated consistent cell performance for thermally and ultrasonically bonded high-temperature MEAs in stack and single-cell testing.
- Completed dynamic modeling of ultrasonic bonding process with mixed results related to model versus experimental temperature measurement of membrane/electrode interfaces.
- Polarization (voltage/current, V/I) curves for larger high-temperature MEAs (140 cm²) that were ultrasonically and thermally bonded showed similar performance, but both types initially performed below the BASF fuel cell specification for MEAs with 45 cm² active area.
- Redesigned MEA flow field plate made from composite material instead of graphite helped improve V/I performance, and new polarization curves were obtained.
- Demonstrated that the performance of MEAs bonded in 2 seconds using an ultrasonic bonding method is the same as MEAs bonded in 30 seconds using the traditional thermal bonding method.
- Developed cyclic voltammetry-based quality control methods to detect shorted MEAs and the degree of bonding between the electrodes and the membrane. The methods can be applied during manufacturing prior to cell build.
- Demonstrated using X-ray diffraction that ultrasonic bonding does not induce catalyst coarsening.
- Implemented a suite of diagnostic tests to detect variations in catalyst loading, catalyst crystallite size, MEA fabrication, cell performance, and specific processes within operating cells.
- Obtained data suggesting the possibility of a 6X reduction in MEA thermal bonding and annealing cycle times to increase manufacturing throughput on existing production equipment.
- By using ultrasonic bonding instead of thermal bonding, experimentally demonstrated 96% energy and 93% cycle time reductions with 45-cm² high-temperature MEAs, and 98% energy and 94% cycle time reductions with 10-cm² low-temperature MEAs.

Introduction

To realize the tremendous potential of fuel cell technology, high-volume, high-quality manufacturing technologies must be 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 for both PEMFCs and direct methanol fuel cells, it is common to thermally press for as long as 1 1/2 - 5 minutes. Even the pressing process for high-temperature (polybenzimidizole, or PBI) MEAs, although 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 (GDL) or GDE membranes or catalyst-coated membranes, 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 component variations, which leads to MEAs that exhibit different 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 bonding, and by minimizing the variability in performance of MEAs produced using advanced diagnostics to gain insight into how process conditions and variables affect performance. This will in turn help to 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. The specific research tasks addressed during FY 2012 include applying ultrasonic bonding to low-temperature MEAs, demonstrating the performance of ultrasonically and thermally bonded high-temperature MEAs in 10-cell stacks, continued development of an ultrasonic bonding process model, demonstrating ultrasonic bonding process scale up from 45 to 140 cm² active area MEAs, and using advanced diagnostics to fully understand and improve the high-temperature MEA ultrasonic bonding process.

Approach

Low-Temperature MEA Bonding – Through extensive R&D efforts, commercially available low-temperature PEMFC electrodes have been optimized by their manufacturers for thermal pressing, but not for ultrasonic pressing. Hence, four different GDEs (two commercially available and two custom made) were compared using conditioned and unconditioned Nafion® membrane for both ultrasonic and thermal bonding. A pilot study determined the ranges of energy and pressure required for ultrasonic bonding. Two-way ANOVA estimated main effects and interaction of process parameters for ultrasonic and thermal process optimization based on performance data collected.
from fuel cell testing. Finally, additional diagnostic techniques including impedance spectroscopy, cyclic voltammetry and flow sensitivity were used to compare performance losses between optimized ultrasonic and thermally bonded MEAs. Electrode catalyst loading and membrane preconditioning were also studied. A duplicate array of MEAs was sent to the National Renewable Energy Laboratory (NREL) for third party testing to verify results and conduct additional performance characterization incapable at RPI.

High-Temperature MEA Stack Testing – A new stack architecture was developed in computer-aided design software, prototyped at the 5-cell scale, and then expanded to 10 cells. Each cell was monitored for performance versus current, temperature, reactant composition and time. The cell-to-cell variation was then analyzed and compared to variation observed when testing individual cells to determine if the ultrasonic bonding process had an adverse effect on performance in stacks, and to validate the stack architecture for simultaneous testing of cells. Thermal management was performed through a combination of end plate heaters and one cooling plate (with internal air cooling manifold) located between cells 5 and 6. The end plate heaters were used to bring the stack up to operating temperature and the cooling plate was used in conjunction with natural convection to maintain operating temperature once reasonable currents were drawn.

Ultrasonic Bonding Modeling – Work on modeling of the ultrasonic bonding process continued with a different approach to solving the system of ordinary differential equations (ODEs) necessary to describe the system behavior. Solving eight simultaneous ODEs, especially with terms several orders-of-magnitude apart in value, proved to be too computationally intensive to complete. Instead, a method for solving the system of ODEs symbolically was found, which allowed the resultant output to be computed directly. Additionally, the model now contains eight degrees of freedom (previously six). The two additional degrees are used to mimic present sinusoidal displacement input from the ultrasonic welder.

Testing of Scaled-Up MEAs – Not knowing if ultrasonic bonding would produce functional scaled-up MEAs, ultrasonically and thermally pressed MEAs with 140 cm² active area were produced for comparison. These MEAs were produced using larger tooling, but with parameters used for the 45-cm² MEAs scaled proportionally. Likewise, the ultrasonically bonded MEAs were produced with proportionally scaled energy flux and force. All scaled-up MEAs underwent V/I curve testing using similar test conditions as before. Because the overall performance was worse than the manufacturer specifications, the flow field plates were redesigned to minimize losses. V/I curves were also taken using these flow field plates and results were compared to that of the smaller MEAs.

Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding – Ultrasonic bonding of PBI MEAs was studied to reduce the cycle time required for bonding MEAs and increase manufacturing throughput. The fuel cell performance of MEAs fabricated using ultrasonic bonding was compared to thermally bonded MEAs. Measuring properties of the incoming electrodes such as catalyst loading and crystallite size and also defining variance in critical parameters associated with MEA fabrication and cell testing helped eliminate sources of noise in cell performance caused by the MEA fabrication and testing after initial cell performance results exhibited variation. Diagnostic test techniques were developed to detect electronic shorts and measure the degree of electrode/membrane bonding. These methods were applied at various stages of cell production including post bonding, annealing, and cell build. The diagnostic testing allowed fabrication issues to be isolated prior to cell assembly and improved the understanding of changes in performance related attributes of the MEAs during fabrication. The assembled cells were tested through a protocol of V/I curves and electrochemical diagnostic tests to allow performance differences to be ascribed to specific physical processes within the cells. A complete suite of test capabilities was developed for critical parameters related to characteristics of the catalyst, MEA fabrication cell assembly, and cell performance. This suite of tests will allow the effect of changes in manufacturing parameters, MEAs components, and cell hardware design to be accessed in the future.

Results

Low-Temperature MEA Bonding – Composition of the GDE is a major factor in performance of ultrasonically bonded MEAs. Different GDL materials are adversely affected by the ultrasonic vibrations resulting in irreversible mechanical deformation of the structure. Both lower catalyst-loaded, custom-made RPI GDEs (0.16 and 0.33 mg Pt/cm²) outperformed commercial Fuel Cell Earth GDE (0.5 mg Pt/cm² reported loading) in ultrasonic MEAs. Performance of thermally bonded MEAs was much more consistent across the various GDEs.

The ultrasonic optimization study tested two factors (energy level and sealing pressure) with three and two levels, respectively. Performance data at three operating current densities (0.4, 0.6, and 0.8 A/cm²) are used for the ANOVA. Two-way ANOVA estimates no main effects of energy flux or sealing pressure in ultrasonic bonding, and there is no statistically significant interaction effect either. This suggests that the ultrasonic bonding process is robust as the variance in performance cannot be explained by variation in the manufacturing process parameters. Optimized ultrasonic bonding conditions are found to be 9.0 J/mm² energy fluence and 3.0 MPa bonding pressure. The thermal press optimization study used two factors (temperature and sealing pressure) of three levels each. Hold time and all
other manufacturing parameters were kept constant. Two-way ANOVA estimates temperature to be a main effect on performance, with performance improving with increasing bonding temperature. No main effect of sealing pressure and no interaction effect are estimated from the statistical analysis. Optimized thermal pressing parameters of 170°C and 2.0 N/mm² produced the best MEA performance.

Ultrasonic MEA performance was comparable to thermal at all current densities operating on H₂/O₂ and low current densities on H₂/Air but quickly degraded at higher current densities on air due to increased diffusion resistance. Figure 1 compares V/I curves of optimized ultrasonic and thermally bonded MEAs made using conditioned membrane and high (0.36 mg Pt/cm²) loaded electrodes. Infrared correction of the performance voltages show that the 7 mV improvement measured on ultrasonic MEAs is attributable to decreased membrane impedance as a result of thinner final MEA thicknesses seen from ultrasounds. Studies in the literature show that membrane preconditioning improves ionic conductivity and performance [1,2]. Conditioned Nafion® measured nearly 20% reduced membrane impedance and increased performance by 0.35 and 16 mV at 0.6 A/cm² operating conditioned for ultrasonically bonded high- and low-loaded (0.16 mg Pt/cm²) MEAs, respectively. Doubling the catalyst loading from 0.16 to 0.33 mg Pt/cm² for ultrasonic MEAs resulted in a performance improvement of 26 mV for dry, unconditioned membrane and 12 mV for conditioned membrane while increasing electrochemical surface area by 65%.

High-Temperature MEA Stack Testing – The stack architecture was proven as an effective tool by validating the temperature distribution and cell voltage distribution at various operating points. Temperature distribution data for a 5-cell stack operating at 0.2 A/cm² showed less than 5°C variation in temperature between MEAs.

A separate test of cell performance versus temperature was performed for a single cell running at multiple constant currents and varying temperatures. It was found that the voltage sensitivity to temperature was in the range of 0.9–1.3 mV/°C. This implies a stack temperature distribution induced voltage distribution as high as 6.5 mV. Further, each cell in the stack is monitored for voltage and temperature and temperature induced voltage variation can be accounted for during analysis.

Once the stack architecture and hardware was proven to have a minimal and predictable impact on individual cell performance, testing of ultrasonically and thermally bonded cells was performed. Ultrasonically bonded and thermally bonded MEAs were built in groups of 10 and run through similar testing routines. The difference in performance was found to be negligible, as shown in Figure 2.

Ultrasonic Bonding Modeling – The model was able to predict the bonding temperatures of 45-cm² MEAs within about 10°C at the top membrane/electrode interface (i.e. closest to vibrating horn) but significantly over predicted the bottom interface. Validity of the finite element analysis model thermal boundary conditions between the stationary anvil and bottom electrode needs to be investigated.

Testing of Scaled-Up MEAs – The larger 140-cm² MEAs were manufactured by hand and V/I curves were taken. A comparison of V/I curves (see Figure 3) shows that the thermally bonded and ultrasonically bonded MEAs were matched in performance; however neither one matched the performance of the BASF specification [3]. We suspect that this is due to a sub-optimal flowfield plate design and other potential performance losses that are currently being investigated.

Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding – The overall cell performance measured while testing 45-cm² single cells was not impacted by the MEA bonding method; however, the MEA bonding method did influence specific performance characteristics of the cells. At a standard operating current density of 0.2 A/cm², the

![Figure 1](link)

**FIGURE 1.** Optimized ultrasonic and thermally bonded low-temperature MEAs tested on both H₂/O₂ and H₂/Air

![Figure 2](link)

**FIGURE 2.** Average and standard deviation ("std") of 10-cell stack performance for ultrasonically and thermally bonded MEAs in a 10-cell stack (1.2 stoichiometry H₂/2 stoichiometry O₂ and air).
average cell voltage for ultrasonically bonded and thermally bonded MEAs was 0.668 V and 0.671 V, respectively. The average cell voltages at 0.2 A/cm² were based on five replicates with standard deviations of 0.004 mV for ultrasonically bonded cells and 0.005 mV for thermally bonded cells. Although the cell voltage at 0.2 A/cm² was independent of bonding process, specific performance attributes may be affected by the bonding process. The oxygen gain at 0.6 A/cm², which is used as a metric of transport losses at higher current densities, was 0.88 mV for ultrasonically bonded cells and 0.127 mV for thermally bonded cells. The catalytic current measured on oxygen at 0.85 volts was 0.13 mA for ultrasonically bonded cells and 0.15 mA for thermally bonded cells. Further testing would be required to truly link the deviations in specific performance attributes to bonding method.

A diagnostic test method based on cyclic voltammetry (CV) was developed to detect MEA quality control issues during MEA manufacturing. The method allows rejected MEAs to be detected prior to assembling the MEAs into stacks and cells and provides insight into the effect of manufacturing processes on the MEAs. One quality control issue detected with the technique was the presence of electronically shorted cells. Evaluating CV data plot of current as a function of voltage for an electronically shorted and a normal cell following cell build, the presence of an electronic short is indicated by a high slope on the plot of current as a function of voltage. In other words, a cell showing a higher slope failed to operate properly during fuel cell testing.

A parameter related to the electrochemically active catalyst area can be extracted from the cyclic voltammetry data. The width of the CV plots or current at zero volts provides a measurement of the electrochemical capacitance which is proportional to the catalyst area wetted with electrolyte. Figure 4 plots the cyclic voltammetry data for ultrasonic and thermally bonded cells following bonding and annealing. It can be seen that the capacitance following ultrasonic bonding is significantly lower following thermal bonding of MEAs. However, the capacitance values following annealing are independent of the bonding process. This suggests that area of contact between electrolyte and catalyst (i.e. degree of bonding) is lower follow ultrasonic bonding but that after annealing the degree of bonding is normalized. As previously mentioned, the cell performance was the same for ultrasonic and thermally bonded MEAs.

As a result of the apparent wide latitude in the degree of MEA bonding which ultimately produced a normal functioning cell, it was hypothesized that the thermal bonding time could be reduced without negatively affecting cell performance provided the cells were annealed. The annealing time was also varied. A single combination of reduced thermal bonding and annealing times is highlighted to suggest the possibility to increase manufacturing throughput by shortening the cycle times of the existing processes. Average V/I curves for cells bonded for 30 seconds and annealed for 30 minutes (standard conditions) and cells bonded for 5 seconds and annealed for 5 minutes (6X reduction in cycle time) were plotted. Each curve V/I curve is the average of five cells tested simultaneously in a 10-cell stack. The positions of the MEAs manufactured with normal and reduced cycle time manufacturing parameters were alternated up the length of the 10-cell stack to remove cell positioning basis from the data set. The performance was the same at the standard operating current density of 0.2 A/cm² but the faster cycle time conditions performed better at
higher current densities. These results indicate the possibility of improving manufacturing throughput with existing equipment and processes.

The platinum catalyst crystallite size was estimated before and after electrodes were ultrasonically bonded to see if ultrasonic bonding caused coarsening of platinum crystallites. The Scherrer formula was used to calculate the platinum crystallite size from the full width at half maximum of the platinum (111) peak. The data indicate that the platinum crystallite size did not increase during ultrasonic bonding.

Conclusions and Future Directions

- **Low-Temperature MEA Bonding** – GDL structure and mechanical properties are sensitive to ultrasonic vibrations resulting in performance effects. After ultrasonic and thermal bonding processes were optimized, no main or interaction effects were estimated in ultrasonics, while bonding temperature is estimated to be a main effect for thermal pressing. Ultrasonically bonded MEA performance was equal to thermally pressed MEAs at all H₂/O₂ and low H₂/Air operating current densities. However, ultrasonics increases diffusion resistance compared to thermal bonding resulting in poor performance for H₂/Air.

No future work is planned for DOE regarding ultrasonic bonding of low-temperature MEAs. Performance testing results will be compiled from NREL and used to support and/or improve conclusions made about ultrasonic bonding.

- **High-Temperature MEA Stack Testing** – The stack hardware will be utilized to increase the rate at which testing of high-temperature MEAs can be performed. Future testing will focus on optimization of the bonding and treatment conditions and also determining why cell performance in a stack is better than that of a single cell.

- **Ultrasonic Bonding Modeling** – The model does not predict temperatures exactly, especially for the membrane/electrode interface farthest from the vibrating horn. The validity of thermal boundary conditions used in the model will need to be investigated.

- **Testing of Scaled-Up MEAs** – Since ultrasonic and thermally bonded MEAs are matched in performance, it can be concluded that the ultrasonic bonding process is effective in producing functional MEAs. However, since the performance of either using the new flow field plates does not match the BASF Fuel Cell specification and testing conditions are identical to those used for the 45-cm² MEAs, the testing protocol and hardware needs to be investigated to determine if other causes of performance error can be determined. A hardware redesign may be necessary.

- **Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding**
  - The performance of PBI-phosphoric fuel cells is not strongly affected by the degree ultrasonic and thermal bonding of the MEA assuming an annealing step is preformed following bonding.
  - The wide manufacturing latitude during bonding of PBI/phosphoric acid MEAs supports the possible implementation of a variety of new bonding methods such as ultrasonic bonding and significant reductions in thermal bonding time.
  - CV-based quality control methods are a valuable tool for accessing MEA bond formation and detecting electronic shorts in MEAs.
  - Ultrasonic bonding times on the order of 1-2 seconds can adequately bond MEAs prior to annealing.
  - Early data indicate that anneal times can be reduced from 30 to 5 minutes and traditional thermal pressing times can be reduced from 30 seconds to 5 seconds without negatively impacting performance.

- Diagnostic testing will be used to understand the dependence of MEA bond formation of time during hot pressing and annealing steps.
- The effect of faster cycle time annealing processes on anode performance needs to be defined.
- The applicability of ultrasonic bonding to paper GDLs and larger active areas will be studied.

Special Recognitions & Awards/Patents Issued


FY 2012 Publications/Presentations


References

