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

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Overall Objectives

- Significantly reduce pressing cycle time for high-temperature polymer electrolyte membrane (PEM) membrane electrode assembly (MEA) through the development of novel, robust ultrasonic bonding processes (also demonstrate for low-temperature [<100°C] PEM MEAs).
- Achieve greater manufacturing uniformity and performance through (a) an investigation into the causes of excessive variation in ultrasonically and thermally bonded MEAs using more diagnostics applied during the entire fabrication and cell build process, and (b) development of rapid, yet simple quality control measurement techniques for use by industry.

Fiscal Year (FY) 2013 Objectives

- Test ultrasonically and thermally bonded high-temperature MEAs, the latter with and without adaptive process control applied, in 5- and 10-cell short stacks.
- Test ultrasonically and thermally bonded MEAs with larger active area (140 cm^2) to obtain statistically significant performance data for comparison with the 'standard' 45-cm^2 MEA size.
- 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 that allow manufacturing engineers to design/specify tooling (horn, anvil, registration fixture) 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 Office Multi-Year Research, Development, and Demonstration Plan:

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

(K) Low Levels of Quality Control

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 Office Multi-Year Research, Development, and Demonstration Plan:

- 1.1: Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- 6.3: Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2014)

FY 2013 Accomplishments

The major accomplishments for FY 2013 are as follows:

- Successfully demonstrated operation of ultrasonically and thermally bonded MEAs in a 10-cell stack for efficient multi-cell testing and also correlated performance differences to stack conditions.
- Demonstrated that thermal bonding times for high-temperature MEAs can be drastically reduced from 30 to 5 seconds provided cells are annealed for at least

five minutes. MEA bonding strength was measured using peel testing and electrochemical capacitance measurement.

- Demonstrated that ultrasonically and thermally bonded MEAs with 140-cm^2 active area had equal performance.
- Ultrasonically bonded 605-cm^2 MEAs using the new large area 15 kHz welder, successfully demonstrated cell operation using BASF testing hardware, and demonstrated that performance exceeded that of equivalent thermally pressed cells.
- Demonstrated that cyclic voltammetry (CV) with ambient air and at room temperature can be used to measure shorts and the degree of electrode-to-membrane bonding in a MEA.
- Finished first draft of a design guide for manufacturing engineers to use when designing an ultrasonic or thermal bonding system for high- and low-temperature PEM 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 laminate low-temperature (e.g., Nafion®) MEAs for both PEM fuel cells 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 polybenzimidazole/phosphoric acid (PBI/PA) 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 or gas diffusion electrode, membrane 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 component variations, which leads to MEAs that exhibit different physical and performance-related properties.

APPROACH

The research being conducted for this project will help reduce the barriers to the development of high-volume fuel cell manufacturing 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 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.

High-Temperature MEA Stack Testing – A new stack architecture for testing up to ten 45-cm^2 high-temperature PEM fuel cell MEAs was designed, fabricated, debugged, and thoroughly tested. Each cell can be monitored for performance versus current, temperature, reactant composition, and time. The cell-to-cell variation is then analyzed and compared to variation observed when testing individual cells to determine if (1) the ultrasonic bonding process had an adverse effect on performance in stacks, and (2) defective cells detected using CV show up as poor performing cells during stack testing.

Testing of Scaled-Up MEAs – Not knowing if ultrasonic bonding would produce functional scaled-up MEAs (i.e., 140 cm^2), thermally pressed MEAs were produced for comparison. These MEAs were produced using larger tooling, but with parameters used for the 45-cm^2 MEAs scaled proportionally. Likewise, the ultrasonically bonded MEAs were produced with proportionally scaled energy flux and force. All scaled-up MEAs underwent voltage/current curve testing using similar test conditions as before.

Even larger high-temperature MEAs with 605 cm^2 active area were ultrasonically bonded using a new custom-designed 15-kHz press and associated tooling (horn and anvil) designed and fabricated at Rensselaer. The resulting MEAs were tested by BASF and compared to baseline performance.

Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding for Quality Control – Single defective fuel cells configured electronically in series in a fuel cell stack can require stack disassembly and cell replacement, resulting in wasted manufacturing resources and a risk of damaging additional cells. As a result, Rensselaer has developed a diagnostic technique capable of detecting defective fuel cells prior to stack assembly; specifically, the technique detects electronically shorted MEAs and poorly bonded MEAs prior to stack assembly. Such defects are detected using cyclic voltammetry, which can measure a current proportional to the degree of bonding and electronic shorting. The measurement time for this technique is on the order of 1-10 seconds—fast enough to be used in production-scale MEA manufacturing. The measurement is acquired at room temperature with ambient air exposed simultaneously

to both fuel cell electrodes on either side of the MEA, thereby simplifying the design of the test fixture. A range of simulated shorts and degrees of MEA bonding were tested using the CV technique. The voltage scanning rate was varied to characterize the effect of scan rate on the sensitivity of defect detection.

Advanced diagnostics were also used to validate the result that the manufacturing latitude is wide during MEA bonding as long as cells are annealed. MEA peel strength, capacitance, and cell performance were measured for MEAs fabricated with a range of bonding and annealing conditions.

Design Guide – Rensselaer is developing a comprehensive design guide that will allow manufacturing engineers to design/specify tooling (horn, anvil, registration fixture) and determine optimal process parameters for bonding high-temperature PEM MEAs using ultrasonics.

RESULTS

High-Temperature MEA Stack Testing – A stack consisting of five thermally bonded and five ultrasonically bonded MEAs was fabricated and tested. The stacks were constructed with the MEAs alternating, i.e., the odd cells were thermally pressed and the even were ultrasonically sealed. As shown in Figure 1, there was no significant difference in performance between cells when the stack was operated on H_2/O_2, but the H_2/air shows a very clear division between the odd and even numbered cells, which corresponds to a performance difference between the thermally bonded (slightly better) and ultrasonically bonded (slightly worse) MEAs. Same thickness gasketing was used for ultrasonically and thermally bonded MEAs.

Because of differences in starting thickness (ultrasonic were slightly thicker due to lower processing pressure), actual post lamination thickness compression for the mixed stack was 17% for the ultrasonic MEAs and 35% for the thermal MEAs. Hence, poorer ultrasonic MEA performance on air (21% O_2 concentration) is attributable to higher in-stack compression, which results in higher cathode gas diffusion media resistance and mass transport losses.

MEAs have been prepared for use in a simulation of the use of the air-air CV approach to manufacturing inspection of MEA active area and cross-shorting. Ten MEAs have been ultrasonically bonded, with one MEA having a partial short caused by membrane misalignment.

Testing of Scaled-Up MEAs – Fabrication of the larger 140-cm^2 cells required a redesigned ultrasonic press combined with a 15-kHz system. The original C-Frame-style press from Branson used for all previous research visually flexed when placed under loads required for 45-cm^2 cells. An H-Frame press, required for any larger MEAs, was brought on-line late in the fourth quarter of 2012, with debug continuing into the first quarter of 2013. The press was designed to maintain parallelism of the ultrasonic horn (top) and anvil (bottom) during loading. Tooling alignment is obtained through the use of matching spherical dome and

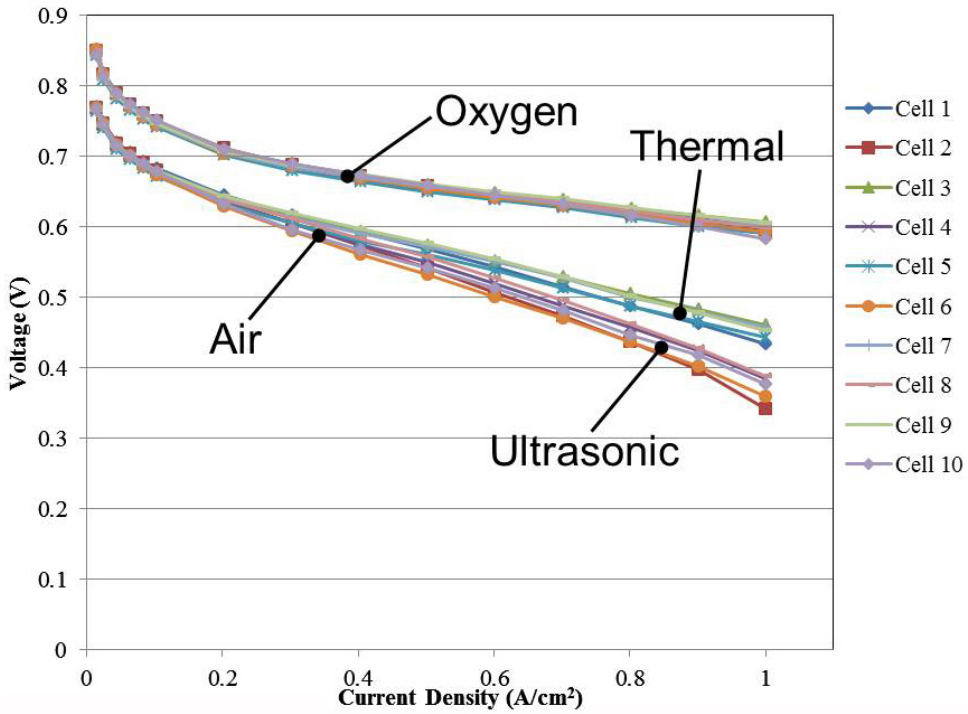

FIGURE 1. H_2/air polarization curve for stack with five each of thermal and ultrasonic MEAs.

seat supporting the bottom tooling. The large surface area of the geometry distributes high loads without damaging the structure.

Two small pneumatic guide cylinders (50-mm bore) are used to move the lower tooling into place, followed by a large load cylinder below (8-inch bore) to supply lamination force/pressure. The combined loads of the main and guide cylinders are capable of generating up to 5,600 lb_f at 100 psi, or 10,000 lb_f at 200 psi pressures. Lamination loads (at the MEA) range from 45-100 psi, thus requiring up to 9,400 lb_f to laminate a 605-cm^2 MEA, which is the maximum size envisioned for this press.

Thermally and ultrasonically bonded MEAs with 140-cm^2 active area had previously been shown to have negligible deviation. Due to improvements made to the custom-designed testing hardware, the polarization curve for the 140-cm^2 MEAs is approaching that of the baseline 45-cm^2 MEA, as shown in Figure 2 (thermally bonded 140-cm^2 MEA curve shown). Elevated ohmic losses are believed to be caused by insufficient current collector thickness and poor electrical interface between current collector and bipolar plate.

As further proof that the 140-cm^2 test hardware was responsible for the lower performance shown in Figure 2, MEAs with 605-cm^2 active area, the largest to date, were bonded ultrasonically using the 15-kHz machine, tested by project collaborator BASF Fuel Cell using their own test hardware, and performance was compared to thermally pressed MEAs made by BASF. The performance of the ultrasonically bonded MEAs was actually better than that of the thermally bonded ones, as shown in Figure 3.

Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding for Quality Control – Electronically shorted MEAs were successfully detected between 1-10 seconds (depending on scanning rate) prior to cell operation using the aforementioned CV technique as compared to 30-60 seconds using an ohmmeter (traditional method). Interestingly, the degree of MEA bonding could be detected but did not correlate to fuel cell performance for the PBI/phosphoric acid fuel cells tested.

Although the electrochemical capacitance provides an indication of interfacial contact area between the PA electrolyte and the electrocatalyst, which directly impacts cell performance, the electrochemical capacitance measured after thermal bonding did not correlate to cell performance. It is thought that additional acid permeation occurs during cell build and operation, increasing the surface area of catalyst in contact with electrolyte for cells which were bonded to a lesser extent during thermal bonding. Although electrochemical capacitance measurement following MEA thermal bonding does not indicate performance for PBI/PA fuel cells, the authors believe it may for PEM fuel cells and warrants future investigation.

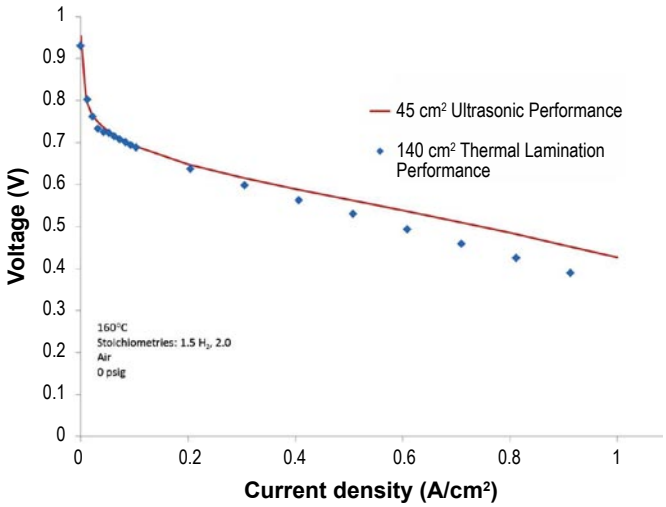

FIGURE 2. 140-cm^2 thermally laminated MEA performance compared to a baseline 45-cm^2 ultrasonic MEA.

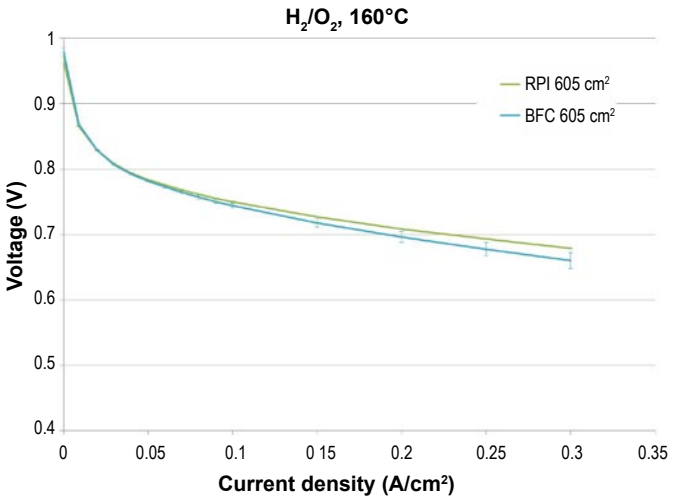

FIGURE 3. Comparison of 605-cm^2 ultrasonically bonded MEA to BASF Fuel Cell thermally bonded MEA.

This CV quality control technique may have value during manufacturing to ensure that electrodes, subgaskets (if used), and membrane comprising an MEA have been structurally unitized after the thermal bonding operation. Adequate MEA bonding, measured as minimum mechanical bond strength (e.g., shear lap or peel), is important from a manufacturing perspective, since MEAs are sold individually to customers and are handled extensively during fuel cell stack assembly. Although not the focus of this work, electrochemical capacitance measurement may provide a non-destructive measurement which could be correlated to mechanical bond strength.

The 15-kHz tooling was used to refine ultrasonic lamination of MEAs using a paper gas diffusion electrode

provided by BASF Fuel Cell. Process optimization resulted in very little performance deviation of ultrasonic lamination samples versus thermally laminated samples. A number of critical performance metrics of cells built with ultrasonically and thermally laminated MEAs are shown in Figure 4 for a relative comparison of the thermal and ultrasonic bonding processes. The chart shows the ratio of ultrasonic to thermal performance for each metric of interest. Gray bars indicate essentially equal performance. Green is substantially better. Red is somewhat worse. Performance is essentially the same for these samples, indicating that further process optimization is not necessary.

The effect of MEA thermal bonding and annealing time on electrochemically active anode catalyst area was studied to determine if reductions in the cycle time of these processes were likely to reduce the anode electrode performance when operating on reformate. MEAs were fabricated with standard thermal bonding and annealing times (30 seconds bonding and 30 minutes annealing) and with reduced cycle times (5 seconds bonding and no annealing). Reducing the thermal bonding time to 5 seconds and eliminating the annealing process step did not decrease the electrochemically active anode catalyst area relative to MEAs fabricated with standard processing conditions. It was also found that the electrochemically active cathode catalyst area and fuel cell performance were not affected by the reduction in bonding time and elimination of the annealing step. However, previous research reported in 2012 indicated other possible benefits to the annealing process such as normalization of MEA thickness and an increase in the mechanical bond strength between the electrodes. This research along with the results obtained through 2012 points toward the possibility of increasing the throughput of PBI/PA fuel cell manufacturing without negatively impacting performance by shortening the cycle times of existing processes.

CONCLUSIONS AND FUTURE DIRECTIONS

High-Temperature MEA Stack Testing – The stack can be used to quickly determine whether changes in processes or process parameters have any significant effect on performance. Using a single-cell testing fixture instead of the 10-cell stack, it would take ten times longer to gather enough data to be able to draw correlations between changes in MEA fabrication.

Parts will be run through the air-air CV test, in which CV will be applied at ambient conditions, with anode and cathode electrodes exposed to air. The test has been shown to have high sensitivity to electrical shorting and also reveals inadequate electrochemical interfaces or lack of electrochemically active surface area. After initial CV testing, the MEAs will be run through the standard thermal treatment (for PBI MEAs) and then a second round of air-air CV followed by functional testing as a 10-cell stack. Results from both CVs and stack testing will be compared to demonstrate relevance of the air-air CV as a manufacturing inspection method.

Testing of Scaled-Up MEAs – Equivalent performance was demonstrated for ultrasonically and thermally bonded MEAs with 140-cm^2 active area, although both were slightly below baseline performance of smaller MEAs due to non-optimized testing hardware. Conversely, performance of ultrasonically bonded 605-cm^2 MEAs was actually better than same-sized thermally bonded MEAs made by BASF Fuel Cell. The overall conclusion is that ultrasonic bonding provides at least equivalent performance to thermal bonding for a wide range of MEA sizes.

Applying Advanced Diagnostics to PBI MEA Ultrasonic Bonding for Quality Control

- The air-air, room temperature CV technique is a rapid diagnostic method (<10 sec) that can be used to identify

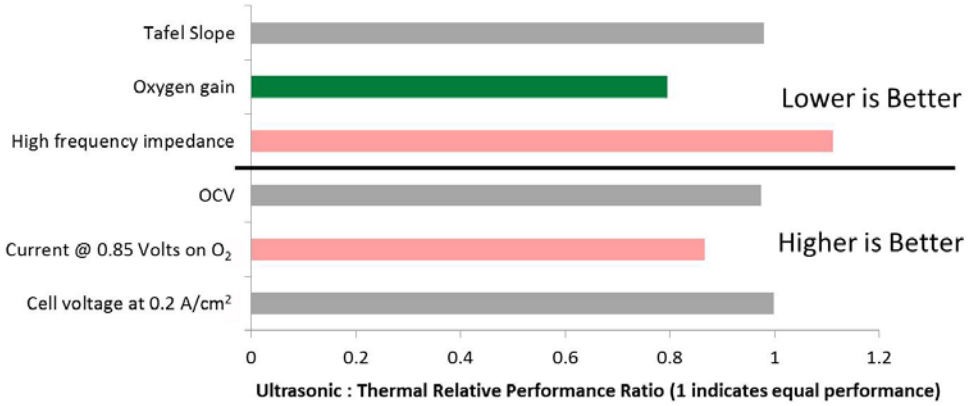

FIGURE 4. Relative performance of cells built with ultrasonically and thermally laminated MEAs. A value of one indicates equal performance. Lower scores are better for Tafel slope, oxygen gain, and high frequency impedance. Higher scores are better for the open circuit voltage (OCV), current at 0.85 V, and cell voltage at 0.2 A/cm^2.

MEA short circuits due to manufacturing defects and possibly the degree of electrode-to-membrane bonding.

- Advanced diagnostics have shown that performance of ultrasonically and thermally bonded MEAs using a new paper gas diffusion electrode is essentially the same.
- Annealing and bonding time were found to have little or no effect on anode or cathode surface area by taking CV measurements of the hydrogen oxidation peak area for MEAs fabricated with normal and reduced bonding and annealing cycle times. It is considered highly likely that the thermal bonding and annealing processes used by our commercial partners can be shortened significantly.

Expanded Cost Analysis – The cost analysis is on-going and will be completed in the third quarter of 2013.

Design Guide – A first draft of the design guide is currently under revision.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Buelte, S., Walczyk, D., and Sweeney, I., "Effect of MEA Bonding Technique on Fuel Cell Performance and Platinum Crystallite Size," *Journal of Fuel Cell Science and Technology* (Accepted for Publication).

2. Beck, J., Walczyk, D., Buelte, S., Hoffman, C., "Comparison of Performance Losses between Ultrasonic and Thermal Bonding of Membrane Electrode Assemblies in PEM Fuel Cells," *Journal of Fuel Cell Science and Technology,* Vol. 10, No. 4, June 2013, 041004 (10 pages).

3. Beck, J., Walczyk, D., Hoffman, C., Buelte, S., "Ultrasonic Bonding of Membrane Electrode Assemblies for Low Temperature PEM Fuel Cells," *Journal of Fuel Cell Science and Technology*, Vol. 9, No. 5, Oct. 2012, 051005 (8 pages).

4. Beck, J., Walczyk, D., Hoffman, C., and Buelte, S., "Ultrasonic Bonding of Membrane Electrode Assemblies for Low Temperature PEM Fuel Cells," *Proceedings of the ASME 2012 10th Fuel Cell Science, Engineering and Technology Conference* (FuelCell2012), Paper # FuelCell2012-91308, July 23-26, 2012, San Diego, CA, USA.