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

Raymond H. Puffer, Jr. (Primary Contact), Daniel Walczyk
Center for Automation Technologies and Systems (CATS)
Rensselaer Polytechnic Institute
Suite CII8011
110 8th Street
Troy, NY 12180
Phone: (518) 276-8990
E-mail: puffer@rpi.edu

DOE Technology Development Manager: Pete Devlin
Phone: (202) 586-4905
E-mail: Peter.Devlin@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954
E-mail: Jesse.Adams@do.doe.gov

Subcontractor:
Arizona State University, Tempe, AZ

Project Start Date: September 1, 2008
Project End Date: June 30, 2012

Objectives

The high level objective of the proposed work is to enable cost-effective, high-volume manufacture of high-temperature proton exchange membrane (PEM) membrane electrode assemblies (MEAs) by:

- achieving greater uniformity and performance of high-temperature MEAs by the application of adaptive process controls (APC) combined with effective in situ property sensing to the MEA pressing process; and
- greatly reducing MEA pressing cycle time through the development of novel, robust ultrasonic bonding processes for high-temperature (160-180°C) PEM MEAs.

Technical Barriers

This project addresses the following Manufacturing R&D technical barriers 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 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)

Accomplishments

- Validated COMSOL[1] models of both thermal and ultrasonic pressing thermal processes.
- Completed promising initial experiments on the use of alternating current (AC) impedance measurement for adaptive process control of the thermal sealing process, resulting in MEA performance that exceeds specifications.
- Demonstrated major reductions in sealing process cycle time (~90%) and energy consumption (~95%) with the use of ultrasonics.
- MEAs sealed ultrasonically demonstrate a significant (~30 mv) improvement in activation losses when compared to thermally sealed MEAs.
- Initial durability tests of ultrasonically sealed MEAs show no measureable degradation after a 190-hour standard test protocol with 25 start-stop cycles.
- Manufacturing cost models show the potential for significant cost reductions by the use of both ultrasonics (84%) and adaptive process controls (38%) for MEA sealing.
- Submitted 10 publications and conference presentations.

✧ ✧ ✧ ✧ ✧

[1] Multiphysics modeling and engineering simulation software

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 call 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 PEM fuel cell and direct methanol fuel cell 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 of about one minute, is still too long for high-volume manufacture. Third is the variability of MEA performance. The component materials, including gas diffusion layers or gas diffusion electrodes, 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 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 in-coming 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, particularly PBI with phosphoric acid as the electrolyte, by applying APC techniques and 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 (such as electrochemical impedance spectroscopy response, porosity, spring constant, or AC impedance) 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 will be 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

We are now in the second year of our research project, and have achieved significant results in all areas of investigation.

We have completed our initial designed experiments of ultrasonic sealing of high-temperature MEAs, and with the use of analysis of variance we have identified the main affects of process parameters on MEA performance. The most dominate process parameter has been identified as the post sealing heat treatment of MEAs in order to eliminate excess water and to achieve a stable acid content and thickness of the MEAs. Using a 95% confidence level criterion we have also identified the anvil backer stiffness, booster amplitude, and applied pressure as having a significant affect on MEA performance. Figure 1 shows representative polarization curves for ultrasonically sealed MEAs, compared to the specification polarization curve provided by BASF Fuel Cell. Initially we were concerned by the steeper slope of the curves in the ohmic loss region. However,

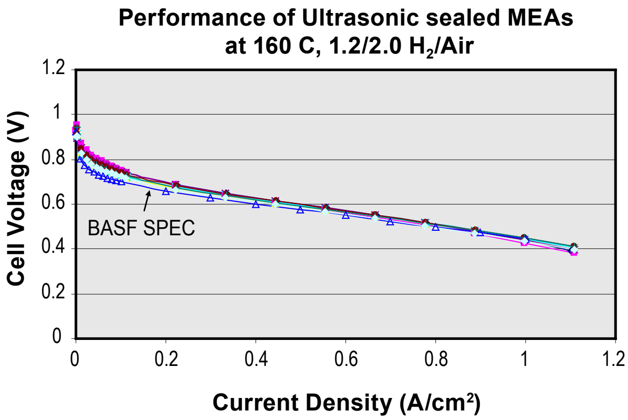

FIGURE 1. Performance Curves for Ultrasonically Sealed MEAs

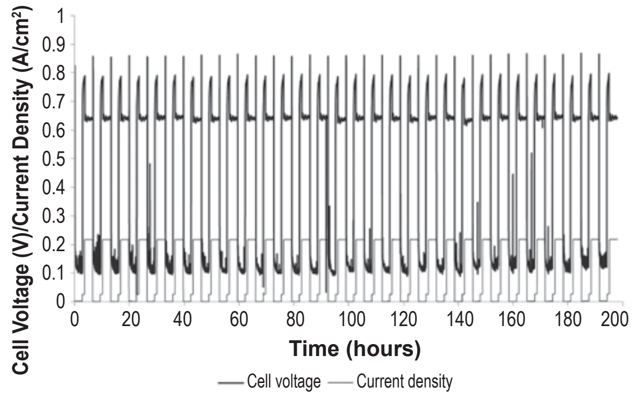

FIGURE 2. Plot of Cell Voltage and Current Density During Accelerated Durability Test

by working with BASF scientists we have confirmed that this is, in fact, the result of the higher contact resistance of the current collectors in our test cells, and the resistance of the flow field plates made of a different graphite material. Of more importance, however, is the fact that all MEAs produced using ultrasonic sealing demonstrates a significant improvement in the activation region of the curve, with a 30 mv improvement being typical. We believe that this is the result of the ultrasonic process resulting in a higher acid content and retention of the acid in the membrane and at the reaction sites in the catalyst layer rather than in the gas diffusion layer. Titration tests have confirmed the higher acid content of ultrasonically sealed MEAs compared to thermally sealed MEAs.

In order to assess whether or not ultrasonic sealing of MEAs may have an adverse affect on MEA durability we have conducted accelerated durability tests on three ultrasonically sealed MEAs. The test protocol used was the standard durability test protocol used by BASF Fuel Cell, consisting of 190 hours of testing during which 25 start-stop cycles were performed, including thermal cycling, load cycling, and reactant shut-off. Figure 2 shows the plot of cell voltage and current density for one such test. In all cases there was no measurable degradation in performance over the test duration. Typically, if there would be a durability problem with an MEA it would be manifested within the first 100 hours of an accelerated durability test.

We have been investigating the potential of applying adaptive process control techniques to the thermal sealing process, coupled with in situ sensing of properties of the MEA during the sealing process that can be correlated to MEA performance. One sensing technique being investigated involves sensing the AC impedance of the MEA during sealing. Figure 3 shows plots of the real value of complex impedance, and also the corresponding phase angle. While we have been unable to correlate the impedance value with MEA performance we have been successful in correlating the

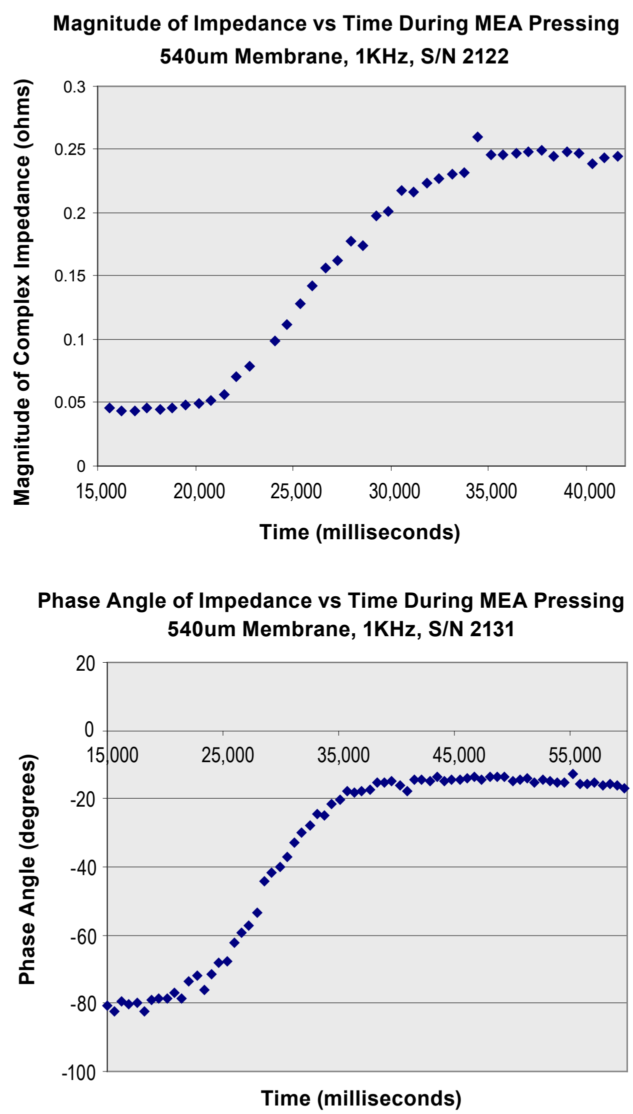

FIGURE 3. Plots of AC Impedance and Phase Angle during Thermal Pressing of High-Temperature MEA

phase angle of the AC impedance to MEA performance. Using a "man-in-the-loop" technique we were able to use the phase angle measurement to control the sealing process duration based on the time to achieve a target phase angle value, with the objective of achieving more uniform MEA performance. With this technique we were able to produce MEAs that all met or exceeded the BASF performance specification, with an average 60% reduction in cycle time. Next we will implement an automated control scheme on the precision press and then evaluate uniformity of MEA performance.

Our efforts at modeling of the relationships among MEA component materials, manufacturing process parameters, and performance of the resulting MEAs are showing good preliminary results. We have developed thermal models of both the ultrasonic sealing process and the conventional thermal sealing process using COMSOL. Figure 4 shows plots of the temperature distribution within MEAs during ultrasonic sealing, on the top, and thermal sealing, on the bottom. These models have been experimentally verified using miniature thermocouples embedded between each layer of the MEAs during pressing. It is important to note that the two processes are significantly different in that thermal sealing adds heat from the outside in, while ultrasonic sealing generates heat from within the MEA at the interfaces between material layers. This explains why ultrasonic sealing is a much more efficient and effective process at raising the materials to the required critical process temperature. We have also completed preliminary compression models of both thermal and ultrasonic pressing. These models help us to understand exactly what happens to the acid and water during the pressing process. In the future the thermal and compression models will be coupled to better describe the pressing process and how it affects MEA performance.

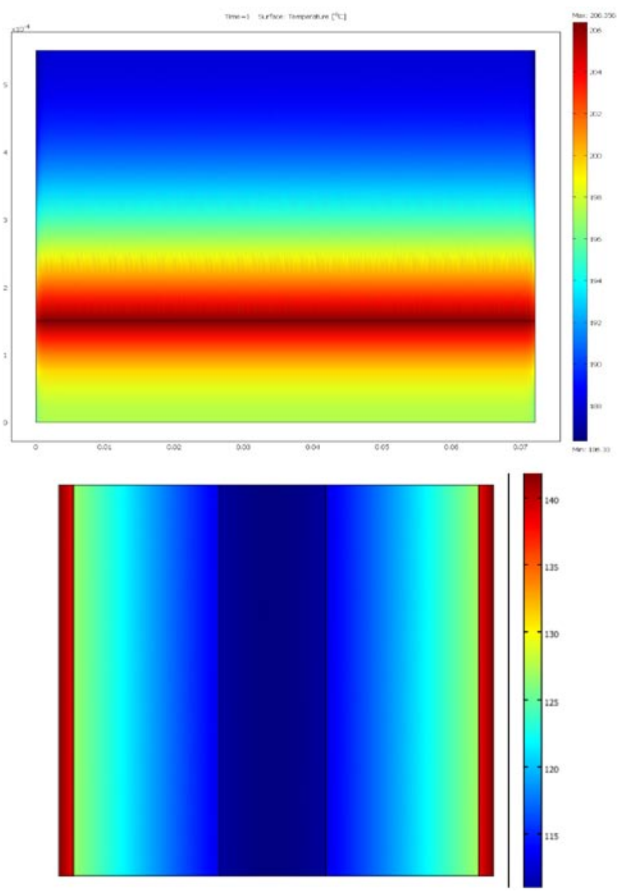

FIGURE 4. Results of COMSOL Models Showing the Temperature Distribution in Ultrasonic and Thermal Pressing of MEAs

During Phase I we completed a detailed manufacturing cost analysis that included the following cost factors: capital depreciation, tooling, space, labor, chilled water, heating, ventilation and cooling, maintenance, electricity, and waste disposal. We did not include MEA materials costs in the analysis, nor did we consider any secondary cost savings that might result, such as reduced costs of stack rework due to greater uniformity of MEA performance. The results of our analysis indicate that the use of adaptive process controls for thermal sealing may result in a 38% process cost savings, and the use of ultrasonic sealing may result in an 84% process cost saving. During Phase II we will update this cost analysis prior to our Phase II milestone review.

During the past year we have successfully passed our Phase I milestone review and have been approved to continue into our Phase II research project.

Conclusions and Future Directions

We are very encouraged by the results we have achieved during the past year. We have found the use of ultrasonic sealing to be a very robust process with the potential to significantly reduce unit process cycle time, improve MEA performance, reduce MEA failure rates, and achieve substantial manufacturing cost reductions. Our investigations into the use of adaptive process control to achieve more uniform MEA performance and shorter pressing times is likewise very encouraging. The Phase I manufacturing cost analysis has shown the potential to significantly reduce manufacturing costs for high-temperature PEM MEAs.

Major activities planned for the remainder of Phase II include:

- Completion of our post sealing heat treatment process optimization design of experiments for both thermal and ultrasonic sealed MEAs.
- Continue modeling of the relationships among incoming MEA properties, manufacturing process parameters, and MEA performance.
- Full factorial process optimization designed experiments for ultrasonic sealing.

- Designed experiment for ultrasonic sealing of low-temperature PEM MEAs.
- Cell level testing of MEAs produced using optimized process parameters.
- Continue durability testing of ultrasonically sealed MEAs.
- Implementation of automated adaptive process control on a commercial precision thermal seal press.
- Continue to seek additional properties that can be measured in situ and that correlate to MEA performance.
- Initiation of stack level testing of MEAs.
- Coordinate low-temperature MEA testing support by National Renewable Energy Laboratory personnel.
- Update of manufacturing cost analysis and comparison with our Phase II cost targets.

FY 2010 Publications/Presentations

Conference Papers/Presentations

1. Snelson, T. and Pyzza, J., "Ultrasonic Bonding of PEM Fuel Cell Membrane Electrode Assemblies," Advanced Energy 2009 Conference, Hyatt Regency Long Island, Hauppauge, NY, Nov. 18–19, 2009.

2. Walczyk, D., "The Performance of Thermally and Ultrasonically Welded Membrane Electrode Assemblies for Low-Temperature PEM Fuel Cells," 2009 ASME International Conference on Manufacturing Science and Engineering (MSEC), West Lafayette, IN, Oct. 4–7, 2009.

3. D. Share, L. Krishnan, D. Walczyk, D. Lesperence, R. Puffer, "Thermal Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," Proceedings of the ASME 8th International Fuel Cell Science, Engineering and Technology Conference, Brooklyn, NY, June 14-16, 2010.

4. T. Snelson, J. Pyzza, R. Puffer, D. Walczyk, "Ultrasonic Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," Proceedings of the ASME 8th International Fuel Cell Science, Engineering and Technology Conference, Brooklyn, NY, June 14-16, 2010.

5. D. Share, D. Lesperence, D. Walczyk, R. Puffer, "Cold Pressing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," Proceedings of the ASME 8th International Fuel Cell Science, Engineering and Technology Conference, Brooklyn, NY, June 14-16, 2010.

6. J. Gullotta, D. Share, L. Krishnan, R. Puffer, D. Walczyk, "Adaptive Process Control and In-situ Diagnostics for High Temperature PEM MEA Manufacturing," Proceedings of the ASME 8th International Fuel Cell Science, Engineering and Technology Conference, Brooklyn, NY, June 14-16, 2010.

7. L. Krishnan, T. Snelson, D. Walczyk, R. Puffer, "Durability Studies of PBI-based Membrane Electrode Assemblies for High-Temperature PEMFCs," Proceedings of the 6th Annual IEEE Conference on Automation Science and Engineering.

Journal Articles (in review)

1. Walczyk, D., Share, D., Krishnan, L., Snelson, T., Lesperence, D. and Puffer, R., "The Performance of Thermally and Ultrasonically Welded Membrane Electrode Assemblies for Low-Temperature PEM Fuel Cells," ASME Journal of Fuel Cell Science and Technology.

Journal Articles (in preparation)

1. Share, D., Walczyk, D., Krishnan, L., Lesperence, D. and Puffer, R., "Hot and Cold Pressing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," to be submitted to the ASME Journal of Fuel Cell Science and Technology.

2. Snelson, T., Walczyk, D., Pyzza, J. and Puffer, R., "Ultrasonic Sealing of Membrane Electrode Assemblies for High-Temperature PEM Fuel Cells," to be submitted to the ASME Journal of Fuel Cell Science and Technology.