VI.6 Adaptive Process Controls and Ultrasonics for High Temperature PEM MEA Manufacture

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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 technical barriers from the Manufacturing section (3.5.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) 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 Fuel Cell Manufacturing section of the HFCIT 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

- Completed unplanned but promising experimentation on the use of ultrasonics for pressing of low-temperature (Nafion®) MEAs.
- Submitted two publications for review based on early unplanned experimentation and testing of low-temperature MEAs produced with both thermal pressing and ultrasonic pressing.
- Completed modifications of commercial ultrasonic press and construction of custom tooling for the needs of our experimentation.
- Completed a working model for manufacturing cost analysis of high-temperature MEA assembly.
- Completed testing of the first high-temperature PEM MEA produced with both ultrasonic welding and sealing.

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Introduction

To realize the tremendous potential that fuel cell (FC) 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 FC manufacturing.

The first major barrier is that 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. It is not uncommon for stacks to undergo burn-in and qualification testing for as long as 24 hours or more. The costs of the test equipment, space, and personnel to execute these tests are a major barrier to the wide-spread adoption of FC technologies. FC researchers and industry must develop the materials, designs, and manufacturing processes necessary to totally eliminate the practice of 100% burn-in testing.

The second major barrier to high-volume FC production is the current processes used to press MEAs. For low-temperature (e.g. Nafion®) MEAs used in both PEMFCs and direct methanol (DM)FCs, it is common to thermally press for as long as 1½-5 minutes. While this process cycle time may be acceptable for prototype level testing and manufacturing, it is totally incompatible with economical high-volume manufacturing. Even the pressing process for high-temperature (polybenzimidizole, or PBI) MEAs, while much shorter than for Nafion®-based MEAs at less than one minute, is still too long for high-volume manufacture. It is also common for assembly of a single PEMFC stack to take as long as an entire day. MEA manufacturing unit process cycle times must be measured in milliseconds, or at most a few seconds, and stack assembly unit process cycle times must be measured in seconds or minutes, not hours.

The third major barrier impeding economical, high-volume FC production is the variability of MEA performance. The component materials, including gas diffusion layers (GDL) or gas diffusion electrodes (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 variations. As a result, MEAs exhibit variations in physical and performance related properties. Even though these MEAs may all perform acceptably in a single cell test fixture, when combined in a stack the variations in MEA properties may result in individual cells failing the performance test. As a consequence, stacks must frequently be disassembled and reassembled with replacement components or component locations re-ordered.

Although there are numerous manufacturing issues with other PEMFC and DMFC components that comprise a stack including (but not limited to) catalyst coating of GDL or membrane and bipolar plate manufacturing, one of, if not the main bottleneck to cost-effective, high-volume FC production is arguably MEA pressing.

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 plan to 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 direct current resistance) 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 research and development 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 FC applications.

Results

We are in the first year of this multi-year research project. Our initial activities were focused on establishing and documenting experimental procedures

and MEA testing protocols, and the validation of those protocols by means of comparison of test results with baseline MEAs produced by our BASF partner. This has been successfully completed.

In order to gain experience with all of the experimental equipment we conducted an unplanned series of tests of low-temperature (Nafion® 117 membrane and BASF Fuel Cell 250EWALT electrodes with 0.25 mg/cm^2 catalyst loading) MEAs produced with both thermal and ultrasonic pressing. Thermal press parameters were taken from various suggested values in the literature. The process parameters of time, temperature and pressure for thermally pressed MEAs and energy, pressure, amplitude, and time for ultrasonically pressed MEAs were not optimized. The resulting MEAs were tested under the following conditions:

- Startup consisted of 1 hr burn-in at 23°C and 0.2 A/cm^2 with cathode and anode humidification at 35°C.
- H_2 and air flow rates were both 100 ml/min.
- Polarization curve taken at 30°C operating temperature.
- Operating temperature was then raised to 80°C with anode and cathode humidifiers at 85°C.
- Second polarization curve taken after running at 0.2 A/cm^2 for several minutes.

For the thermal pressed MEAs the following observations were made:

- Increased sealing time resulted in a slight improvement in MEA performance at 30°C but essentially no improvement at 80°C.
- The middle sealing temperature (140°C) yielded optimum MEA performance at both 30°C and 80°C.
- The middle sealing pressure (50 kg/cm^2) yielded the optimum MEA performance at both 30°C and 80°C.

For the ultrasonically pressed MEAs we observed that high sealing pressure yielded the best MEA performance at 30°C, while there was little difference in MEA performance at 80°C.

As a comparison, for our very limited tests the thermal pressed MEA performed better at 80°C, while the ultrasonically sealed MEA performed better at 30°C.

The major portion of our research during Fiscal Year 2009 has focused on investigating the feasibility of the novel ultrasonic bonding of MEA materials to significantly reduce unit process cycle times, achieve a major reduction in energy consumption, and reduce the cost of manufacturing high-temperature PEM MEAs. Among the many major challenges that are being addressed are:

- What are the best ultrasonic horn materials and design?
- What are the optimal anvil materials and design?
- What are the limits on allowable power/energy to prevent material damage?
- What are the best methods for process controls (e.g. energy mode, collapse mode, absolute mode)?
- How to meet dimensional tolerance requirements?
- Is it possible to meet the target cycle time of <1 sec?
- Are there any feasible rapid (ms level) sensing modes for use in the application of adaptive process controls for ultrasonic pressing?

Currently the bonding (welding) of electrodes to sub-gaskets for high-temperature PEM MEAs is performed in a heated press with a cycle time of about 1 minute. As a result of our investigation we have demonstrated that a unit process cycle time of less than one second is possible, and the resulting weld has a pull strength equal to or greater than that of a thermal weld. Of particular note, the energy consumed by ultrasonic welding is less than 5% of the energy consumed by thermal welding. We plan to conduct a full factorial design of experiments to optimize the weld process parameters.

The more challenging process for ultrasonics is the sealing of the electrodes to the PBI membrane. Figure 1 shows the experimental tooling (horn and anvil) being used in our investigations. Figure 2 shows a destructive test of an ultrasonic seal. The very good bond between the GDE and PBI membrane can be clearly seen in this photo. Figure 3 shows a 50 cm^2 MEA design used in all of our design of experiments for both thermal and ultrasonic sealed MEAs. We have produced and tested our first high-temperature PEM MEA using ultrasonics for both welding and sealing. Figure 4 shows

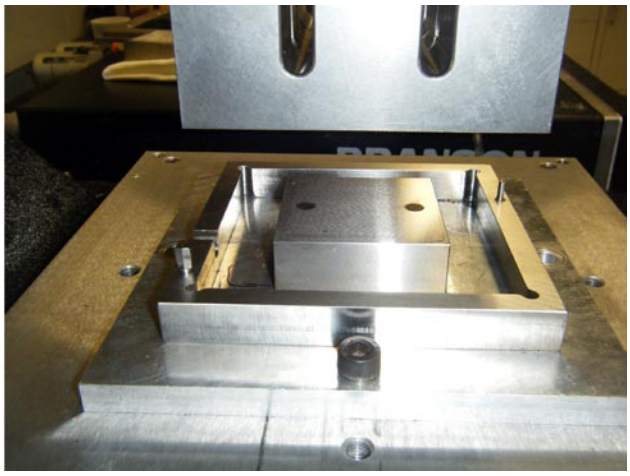

FIGURE 1. Experimental Seal Tooling for Ultrasonic Sealing of MEAs

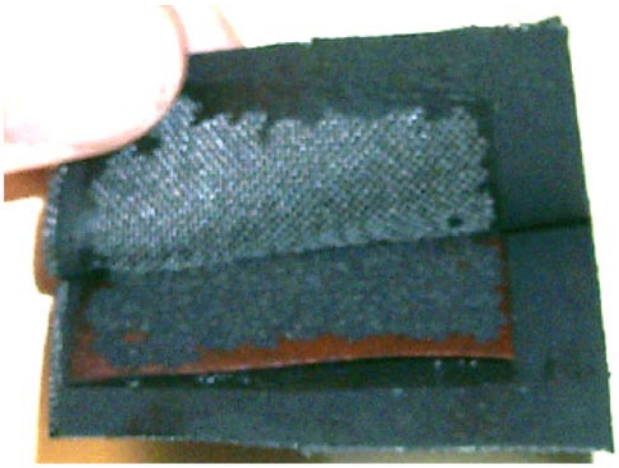

FIGURE 2. Destructive Test of GDE-PBI Membrane Ultrasonic Seal

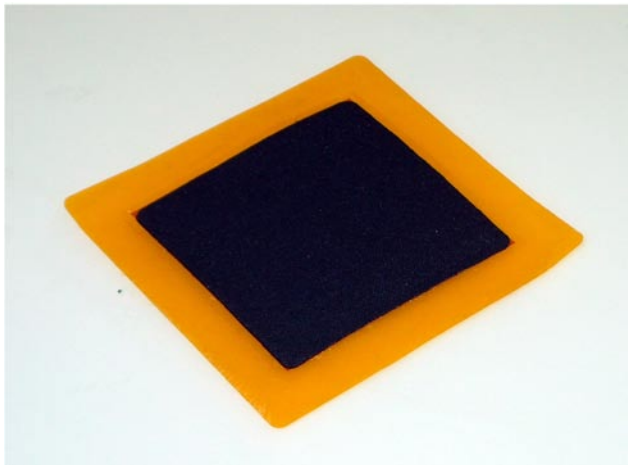

FIGURE 3. Standard 50 cm^2 MEA used for Design of Experiments

the polarization curve for this MEA, tested with both H_2–O_2 and H_2–Air, operated at 160°C. Also shown is the baseline specification performance from BASF Fuel Cell for their thermal pressed MEA operating with H_2–air at 160°C. As can be seen the ultrasonic sealed MEA operating with hydrogen and oxygen performs well, while the MEA operating with hydrogen and air shows greater losses in both the ohmic loss and the mass transport loss regions of the curve. This is likely caused by damage done to the catalyst layer by the ultrasonic sealing process. It should be noted, however, that we have not yet completed our design of experiments and have not tried to optimize the ultrasonic sealing process parameters. Of equal interest, however, is the fact that the activation losses for the ultrasonic sealed MEA are significantly less than for the baseline MEA. If this holds true for other ultrasonic sealed MEAs this could be a major advantage of the use of ultrasonic sealing.

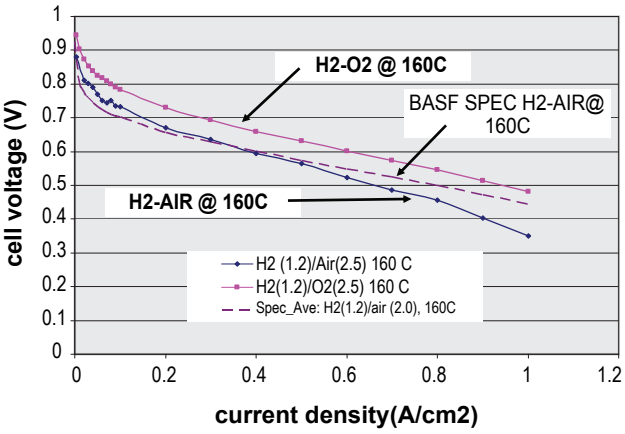

FIGURE 4. Performance Curve for Ultrasonically Welded and Sealed MEA

Conclusions and Future Directions

Although the results are very preliminary and we have not completed our design of experiments we are very encouraged by the performance we have achieved with our first ultrasonic-sealed high-temperature PEM MEA. We are optimistic that we will succeed in achieving a major reduction in unit process cycle time for MEA pressing, and a corresponding major reduction in energy consumed by this critical MEA manufacturing process. We may also realize an unexpected improvement in activation loss, if our initial test is an indication of an inherent benefit for ultrasonic sealing.

Major activities planned for the remainder of Phase I include:

- Completion of our design of experiments for both thermal and ultrasonic-sealed MEAs.
- Modeling of the relationships among incoming MEA properties, manufacturing process parameters, and MEA performance.
- Investigation of various in situ sensing modes that might be used for feedback control during the sealing process.
- Design and experimentation of adaptive process control techniques.
- Cell level testing of MEAs produced using optimized process parameters.
- Completion of manufacturing cost analysis and establishment of cost targets for Phase II.

FY 2009 Publications/Presentations

- Walczyk, D., Share, D., Krishnan, L., Snelson, T., Puffer, R., "The Performance of Thermally and Ultrasonically Sealed Membrane Electrode Assemblies of Low Temperature PEM Fuel Cells," Accepted for publication in *Proceedings of the*

ASME International Manufacturing Science and Engineering Conference (MSEC) 2009.

- Walczyk, D., Share, D., Krishnan, L., Snelson, T., Puffer, R., "The Performance of Thermally and Ultrasonically Sealed Membrane Electrode Assemblies of Low Temperature PEM Fuel Cells," Submitted for review in the *ASME Journal of Fuel Cell Science and Technology.*