VI.8 MEA Manufacturing R&D Using Drop-On-Demand Technology

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Project Start Date: June 1, 2010
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

- Evaluate membrane electrode assembly (MEA) fabrication process and compare catalyst printing and coating process.
- Critically evaluate inkjet or "drop-on-demand" printing technology to meet the criteria specified in the above objective.

Technical Barriers

This project addresses the following technical barriers from 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 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Develop fabrication and assembly processes for polymer electrolyte membrane automotive fuel cell that meets cost of \$30/kW. (4Q, 2015)

FY 2011 Accomplishments

- Technical analysis of printing coating fabrication process completed and report to DOE in final draft.
- Developed printhead control algorithms suitable for printing of thin films.
- Thin film printing station constructed and has undergone initial testing and calibration. Will be brought on line soon.
- Demonstrated that MEAs prepared by inkjet fabrication have comparable performance to commercially available MEAs. Needs optimization.

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Introduction

One of the primary DOE goals for use of proton exchange membrane fuel cells (PEMFCs) as power plants in transportation includes the reduction of manufacturing costs to below \$30/kW. Today's low-volume, actual cost is greater than \$1,000/kW and the high-volume manufacturing cost, based upon current manufacturing process, is extrapolated to be less than \$300/kW [1-3]. New manufacturing processes are needed and must be able to:

- Adapt to the transition from low-volume specialty to the high-volume automotive markets,
- Rapidly incorporate advances in PEMFC technology, and
- Accommodate both small and large production runs.

Approach

Digital fabrication, in combination with unique catalyst-layer ink formulations, will eliminate or simplify many of the currently necessary, but slow and cumbersome, pre- and post-deposition processing steps. In earlier work [4] we have shown that for the digital fabrication process that:

- No hot-press/lamination is needed to ensure catalyst layer adhesion to the membrane,
- Wastage of membrane and catalyst materials are minimized,
- Catalyst utilization can be enhanced with XY and Z gradations in composition,
- The hydrogen form of the membrane can be directly used and no chemical transformation to the sodium form is needed, and
- Digital fabrication is highly adaptable in an evolving technology scenario.

It is the goal of the project to understand fully the implications of digital fabrication on processing, design prototype digital fabrication facilities to test production methods, provide a basis for quantitative cost comparison with current fabrication technology, integrate the fabrication with the rest of PEMFC stack assembly and develop design criteria for a pilot plant manufacturing line based upon digital fabrication. The project digital-fabrication approach will lead to a higher quality product with improved performance, fabricated by a simpler and more cost-effective production process. Digital fabrication will be an agile and versatile means of production, and will provide a viable route to meeting DOE production targets for PEMFC-based power plants.

Results

Analysis of Catalyst Layer Printing and Coating Technologies

A review of the advantages and disadvantages of printing and coating technologies in the fabrication of catalyst coated membranes was conducted [5-7]. This included direct contact methods such as offset and flexographic printing, ink spreading systems such as the myriad forms of roll coating, doctor blading and slot die coating and Gravure printing. Noncontact methods include aerosol and airless spraying as well as piezoelectric and thermal inkjet processes were also considered.

Process deposition speed is not the only requirement to be considered in the manufacturing process and may be of minor importance especially for an emerging industry. The criteria for evaluation of the catalyst coating process were 1) ink development complexity, 2) suitability to long, medium and short production runs, 3) coating speed and adaptability, 4) ability "patch" coat, 5) ability to grade catalyst layer composition, and 6) coating thickness and variability.

In comparison of the various techniques slot die, Gravure and inkjet printing provide the best characteristics for at least some scalability in comparison to the other techniques discussed:

- Each of these three methods conserves expensive catalyst and membrane material.
- Each has highly variable speeds although slot die coating quality has a stronger dependence on speed.
- Inkjet coating is easier to integrate into a process line whereas slot die and Gravure process will constrain if not dominate the process line design.
- Slot die coating cannot be used to grade coatings.
- Slot die coating provides a relatively thick single pass coating.
- Gravure printing is not well suited to lab scale and small job scale production.
- A combination of digital and continuous inkjet printing provides scalability from the lab- to automotive-scale.

Requirements of Thin Film Inkjet Printing

Inkjet printing technology is focused at printing words or images for which surface reflectivity is the most important physical criteria. Further continuous films are not required and half toning and dithering are used to achieve color and gray scale but often leave distinct significant portions of the substrate without an ink deposit. The properties are not compatible with thin film structures that must have uniform or graded but continuous structure over many centimeters. Further a printed layer of a given composition may have to interface with an under or over lying layer of different composition.

To address this issue we developed a unique print algorithm that was implemented for the 2x25 printhead pattern of a HP-26 print cartridge. The algorithm ensures that:

- All jets are used evenly to prevent clogging,
- No single pixel is printed more than once,
- The jet patterns are "woven" to prevent vertical and horizontal banding,
- The algorithm can be adapted to a particular printhead jet pattern, and
- Successive prints can be offset slightly to ensure uniformity.

A printer was fabricated to allow testing of printing parameters in future work – see the following. The printer was based upon two HP-26 inkjet cartridges and is capable of depositing up to four inks although only one ink systems have been tested to date. The system uses a Microchip PIC24J256GB110 microprocessor to control XYZ table movements and individual jet firing and communication with a universal serial bus (USB) storage device. MATLAB was used to implement the algorithm discussed above, and convolute the print pattern with an image pattern. The file output from this is stored on the USB device in a simple form ready for microprocessor implementation. Figure 1 shows an approximately 10 μm thick film of yittria-stabilized zirconia (YSZ) printed with this experimental printer. YSZ suspensions were used for initial testing as the suspensions are very stable and the average particle size is two orders of magnitude smaller than the jet orifice size.

We previously had worked closely with Hewlett-Packard and used their experimental print facilities for initial work. However we did not have permission to sufficiently modify those instruments to allow close control of humidity and substrate temperature. The new printer, although less sophisticated, will allow better examination of the printing process.

Printhead Reliability

Printheads after many thousands (if not millions) of firing cycles are subject to clogging by the presence of minute quantities of large particles. We conducted two tests using identical printheads with 20 and 28 μm diameter jets. The 20 μm jets failed due to clogging after only a few hundred cycles while the 28 μm jets did not fail during

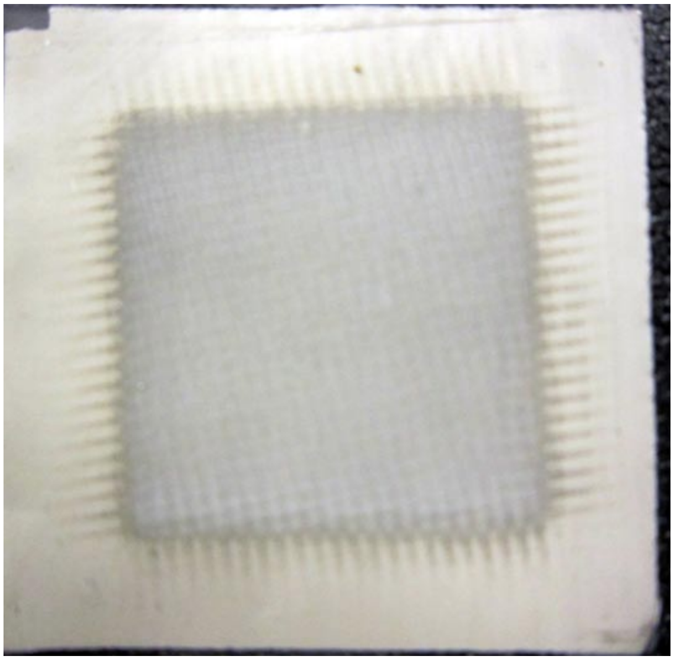

FIGURE 1. Photograph of an Approximately 10 µm Thick YSZ Film

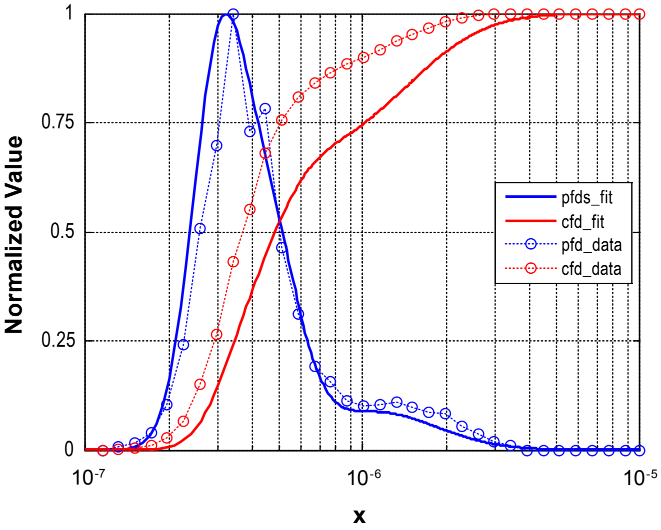

FIGURE 2. Normalized Particle Size Distribution and Log Normal Fits of Catalyst Inks

experimental use. Figure 2 shows the normalized particle size distribution of our catalyst inks as well as the log normal fits to these data. Note the presence of a large shoulder at about 1.5 µm off the main peak at about 0.3 µm. These peaks are much smaller than the 20 and 28 µm jet diameters yet the 20 µm jets clogged while the 28 µm jets did not clog. The log normal fit to the data was used to estimate the distribution of very large particles in a suspension that could not in reality be detected by particle size analysis. As shown in Figure 3, the probability of clogging after 1,000 fires is

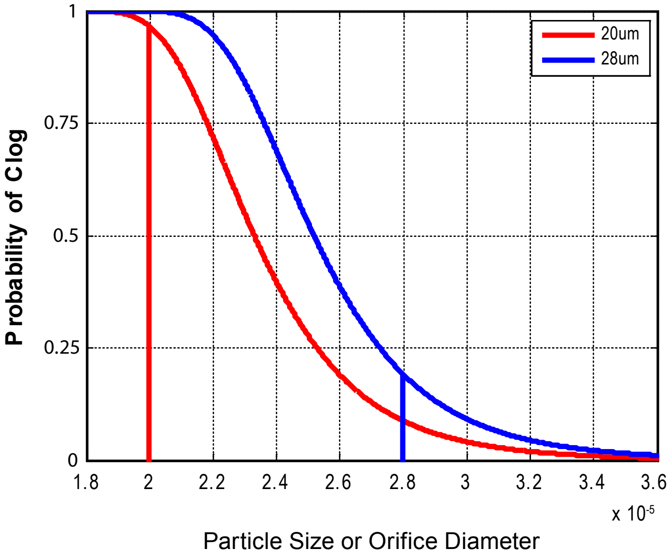

FIGURE 3. Probability of Clogging after 1,000 Fires for 20 µm and 28 µm Jet Orifices

98% for a 20 µm jet while that for a 28% jet is only 25%. By eliminating the large shoulder through appropriate filtering, the probability of clogging can be substantially reduced but this work demonstrates the need to carefully consider ink stability and to prevent particle aggregation before use.

Comparison of Commercial and Inkjet Printed Electrodes

To realistically compare catalyst coated membranes fabricated by different processes we adapted standard performance tests into a series of 15 electrochemical tests that allowed comparison of performance under a wide variety of conditions including back pressure up to 15 psig, O_2 vs. air, different cathode and anode relative humidities and stoichiometries. Shown in Figure 4 are current-voltage curves, taken with air at the cathode and at 0 and 15 psig backpressure, for a digitally fabricated MEA and one purchased from Ion Power. Both had 0.2 mg/cm^2 of platinum. The Ion Power electrode was distinctly better but not so much better that the difference can be attributed to the fabrication method. It may well be that difference in electrode composition may be more important. We note that, with O_2 at the cathode, the inkjet fabricated electrodes outperformed the Ion Power electrodes.

Conclusions

- Technical analysis of printing and coating processes completed and report in final draft.
- Defined algorithms suitable for printing of thin films.
- Thin film printing station constructed and has undergone initial testing and calibration. Will be brought on line soon.

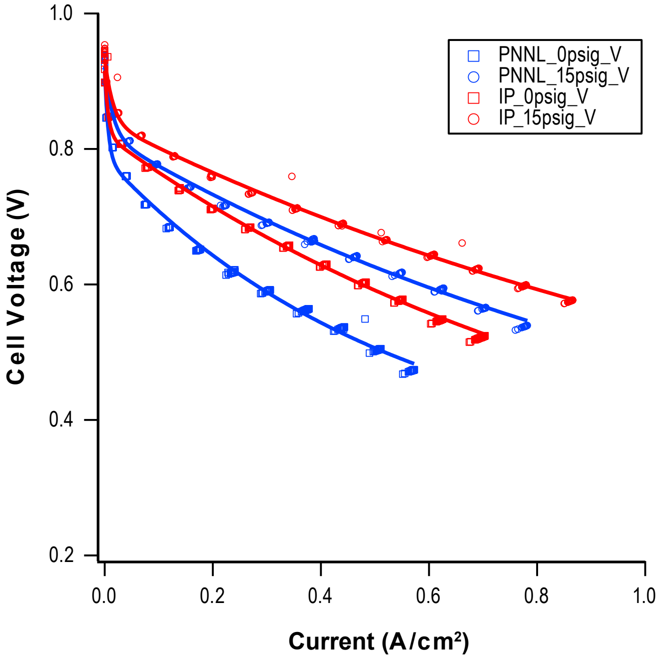

FIGURE 4. Comparison of in-house digitally fabricated MEAs with commercially produced MEAs. Results shown are for air at the cathode and at 0 and 15 PSIG backpressure.

- Demonstrated that MEAs prepared by inkjet fabrication have comparable performance to commercially available MEAs. Needs optimization.

Future Directions

- Develop catalyst-compatible inks that prevent particle aggregation and jet clogging.
- Optimize ink composition (ionomer, carbon, catalyst ratio).
- Determine optimal printing conditions - relative humidity, substrate temperature.
- Quantify relationship of substrate wettability to thin film uniformity.
- Determine maximum single pass thickness.
- Quantify development needs for continuous inkjet fabrication.

FY 2011 Publications/Presentations

1. "Approaches to Manufacturing of MEAs for PEM fuel Cells", Peter C. Rieke, Silas A. Towne, Report to DOE. In final draft.

2. "MEA Manufacturing R&D Using Drop-on-Demand Technology", Peter C. Rieke, Silas A. Towne, DOE Hydrogen Program Annual Merit Review, Washington, DC, May 2011.

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3. E.J. Carlson, P. Kopf, J. Sinha, S. Sriramulu, Y. Yang, Cost Analysis of PEM Fuel Cell Subcontract Report, NREL/SR-560-39104 2005.

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7. Kipphan, Helmut, Handbook of print media: technologies and production methods. Springer, 2001.