VI.2 Digital Fabrication of Catalyst Coated Membranes

Peter C. Rieke, Ph.D. (Primary Contact),
Silas A. Towne
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99354
Phone: (509) 375-2833; Fax: (509) 375-2186
E-mail: peter.rieke@pnl.gov

DOE Technology Development Manager:
Pete Devlin
Phone: (202) 586-4905; Fax: (202) 586-9811
E-mail: Peter.Devlin@ee.doe.gov

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Objectives

- Demonstrate basic process steps in digital fabrication of catalyst-coated membranes (CCMs) and membrane electrode assemblies (MEAs):
  - Ink formulation and delivery with industry standard print heads.
  - Catalyst layer quality and mechanical durability.
  - Electrochemical utility.
- Define advantages and disadvantages of digital fabrication:
  - Reduce large run MEA fabrication cost.
  - Versatile and agile process line.
  - Integration of new technology.
- Identify unique advantages of digitally fabricated CCM:
  - Z gradation in composition – pore, catalyst, ionomer distribution.
  - Variable catalyst loading in XY plane.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section (3.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

(B) Manual Stack Assembly

(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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

M36 Select manufacturing technologies to be developed for producing electrolysis membrane assemblies. (2Q, 2008)

M37 Develop specific technical targets for continuous fabrication of electrolysis membrane assemblies. (4Q, 2008)

M39 Develop pilot scale, high-volume manufacturing processes for membrane assemblies. (4Q, 2010)

M40 Demonstrate pilot scale, high-volume manufacturing processes for membrane assemblies. (4Q, 2012)

Accomplishments

- Demonstrated feasibility of digital fabrication by successfully fabricating and testing CCMs in single cells.
- Characterized CCM printing process including evaluation of substrate handling methods; characterization of print layer thickness, adhesion, uniformity; and demonstration of control of catalyst layer composition in Z and demonstrate fabrication of large area CCMs.
- Evaluated implications of digital fabrications (DF) on process line design and economics including comparison of processing methods, evaluation of process line throughput needs, and determination of means of integration with stack and system assembly steps and qualitative identification of potential process cost saving.

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Introduction

The MEA and the CCM are at the heart of a proton exchange membrane (PEM) fuel cell. In large-scale automotive applications this component must be manufactured with minimal cost, high reliability and at speeds sufficient to match the fuel cell stack assembly process. In addition the automotive industry must “qualify” a production process as being able to meet the above criteria. Once qualification occurs it is substantially more difficult to adopt new fabrication technologies and/or technical advances as they arise. In the short- to medium-term, it is cheaper to go with a known but potentially more expensive process than switch to a new process with many unknowns. Currently, the automotive industry is not committed to a particular MEA or CCM fabrication method and is actively exploring new methods that may have significant cost, quality or speed advantages.

This project has explored the initial feasibility of using printing technology (DF) to fabricate CCMs. Two key technical obstacles were 1) the formation of stable colloidal suspensions (inks) without large particle that could clog print heads and 2) the mechanical manipulation or handling of Nafion® membranes before, during and after the printing process. The CCMs were demonstrated to perform at least as well as commercially prepared membranes. However the primary advantage of DF is the ability to eliminate almost all pre- and post-deposition chemical washes and elimination of any hot press steps.

Approach

The approach of this project was to first demonstrate the feasibility of digital fabrication including ink development, demonstration of CCM printing and validation of electrochemical performance. This demonstrated the essential steps for DF of CCMs. In addition, the adhesion of the catalyst layer to the membrane was, in the as printed condition, impervious to all but rough scraping as well as long-term sonication in acid, methanol and water.

The next phase of the project was to evaluate the printing process with emphasis on controlling the swellability of Nafion® during printing, obtaining uniform catalyst layers of sufficient thickness and demonstrating the ability to control the composition in the Z and XY directions. It was also desirable to demonstrate printing on large membranes up to 500 cm^2.

Finally we qualitatively evaluated the implications of DF on process line design and economics and compared the DF process with the more conventional decal transfer process. Key were the simplification of the process line, the ability to meet throughput needs and integration of DF with stack and system assembly steps.

Results

Figure 1 shows the Z direction uniformity of an approximately 15 μm catalyst layer printed on a Nafion® membrane. The layer was uniform to much less than 1 μm over the sample examined. In the XY plane of the CCM, the catalyst layer was, under some circumstances, visibly irregular. Irregularity could be attributed to clogging of individual print jets and to too rapid of a printing speed for the volume of ink delivered.

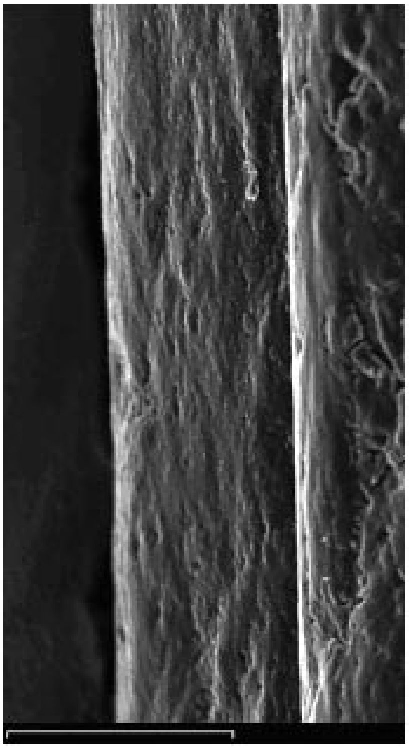

FIGURE 1. Scanning electron micrograph of a DF catalyst layer (center of picture) on a Nafion® membrane (right of pictures). The scale bar is 20 um.

Jet clogging is dependent upon ink composition, drying of ink at the jet orifice and the presence of humectants in the ink. Clogging was primarily a function of open air drying between prints. Most printers have a sealed docking station that prevents this drying. However the print facility that Hewlett-Packard designed for print protocol testing, did not have such a port and we were careful to not let the heads stand idle for more than approximately 10 minutes. We do not believe that jet clogging due to drying will present an ultimate technical barrier to printing CCM although on-line means of detecting jet function may be beneficial.

In addition, jets can readily clog if the ink colloid suspension has any number of particles of approximately the same size or larger than the jet orifice. Properly suspended solutions were essential and a procedure was devised that provided for an ink with a "shelf-life" of many days. Colloid stability is critical in printers, such as with inexpensive consumer printers, where the inks may sit unused for weeks if not months. In a large-scale industrial application, inks could be prepared on an as needed basis and used within a few hours or days of preparation. However, given the high cost of the ink as well as the membrane, jet clogging is an expensive failure mechanism and quality control of the ink during preparation and just prior to printing will be necessary.

Figure 2 shows a power curve for two CCMs with one prepared in our laboratory by printing techniques with 0.2 mg Pt/cm^2 and the other commercially purchased with 0.3 mg Pt/cm^2. The DF-CCM was slightly better than the commercially prepared CCM. Given the substantially lower platinum content of the DF sample the performance difference is significant. In this case the CCM with lower catalyst loading gave better results. The peak power for these membranes was less than that reported in the literature under optimal operating conditions and less than reported by the commercial vendor for the membrane tested. We attribute the low power to test stand limitations and are working to improve the quality of our test stand.

Figure 3 is a photograph of a large CCM in the process of being printed. The objective in these experiments was to demonstrate that DF can accommodate the fabrication of large MEAs (up to 500 cm^2) as would be used by the automotive industry and also to understand how to manipulate the membrane before, during and after printing. After some experimentation with various clamping methods, we determined that, in ambient humidity, the membrane required solid physical clamping to maintain a flat substrate suitable for printing. An acrylic clamp was constructed and used to clamp damp Nafion® membrane. Seven mil thick membranes were able to withstand the tensile forces set up during drying in ambient humidity. Two mil membranes were however susceptible to tearing at the clamp edges. Ultimately a membrane 320 cm^2 was fixed in the clamp and was more than sufficiently flat to achieve good quality prints. No visible wrinkling occurred upon rewetting of the membrane either with sprayed on water or from water contained in the ink. However, the area of the printed catalyst layer (both sides) was limited to 180 cm^2 by the physical design of the print head which in this case prevented close approach to the clamp edges. From our examination of a wide variety of commercial print heads, most modern print heads will require less than about 5 mm of side clearance. In this work, the fixture used to hold the print head presented the greatest clearance problem. Design criteria for new membrane clamp and print head fixtures were developed form these results. By comparing print speeds of commercial high speed four color printers we estimated that approximately 20-30 printers would be required to print CCMs for 500,000 vehicles/year with 70 kW power plants. The critical and limiting step does not appear to be the actual printing step but the membrane handling process.

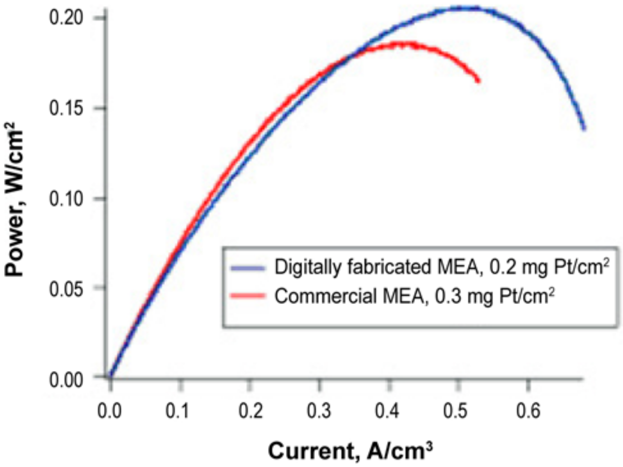

FIGURE 2. Power curves for commercially available and digitally fabricated CCMs.

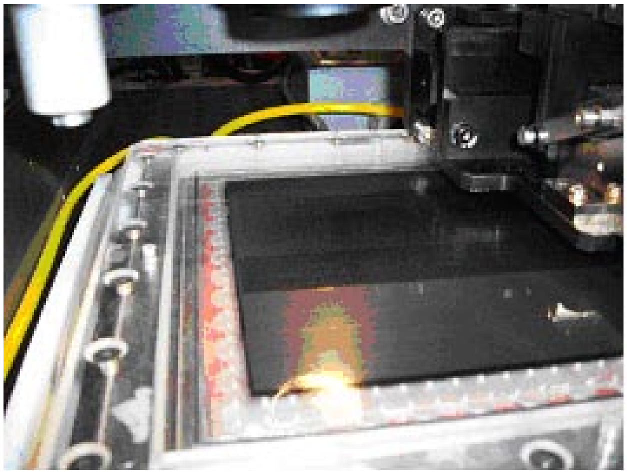

FIGURE 3. Photograph of the printer depositing catalyst layer over a 180 cm^2 area on a membrane with an exposed area of 320 cm^2.

Conclusions and Future Directions

- DF simplifies the fabrication process by eliminating hot press or lamination steps and does not require chemical transformations. The catalyst layer exhibits strong adhesion to the membrane and cannot be removed by boiling in water and solvents and cannot be easily removed mechanically.
- DF is capable of printing large continuous areas with sufficient speed to meet or match stack assembly needs and can do so in an on-demand fashion without compromising quality or consistency.
- The electrochemical performance was comparable to commercial MEAs and given DF's ability to optimize the catalyst loading it may be possible to further improve performance or reduce catalyst loading.

FY 2009 Publications/Presentations

1. *Invention Report – Advantages of ink-jet printing for the fabrication of PEM fuel cell membrane electrode assemblies.* Inventors: Vish Vishwanathan, Silas Towne, Jim Holbery, Peter Rieke.

2. *Invention Report – Formulation of an ink for ink-jet printing of PEM fuel cell membraneelectrode assemblies.* Inventors: Silas Towne, Vish Vishwanathan, Jim Holbery, Peter Rieke.

3. Invention Report – *In-situ 3D Mapping of Fuel Utilization, Gas Flow and Water Flooding in Manifolds and Gas Diffusion Layers of an Operating PEM Fuel Cell Using Hyperpolarized 3He or 129Xe Magnetic Resonance Imaging* Inventors: Kevin Minard Li-Qiong Wang, Paul Majors, Vish Vishwanathan, Silas Towne, Jim Holbery, Peter Rieke, Rick Jacob.