Digital Fabrication of Catalyst Coated Membranes

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MF_07_Rieke

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Pacific Northwest
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Overview

Timeline

- Project start date: 2007
- Project end date: 2009
- Percent complete:100%

Barriers

- **A.** Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- **B.** Manual Stack Assembly
- **F.** Low Levels of Quality Control and Inflexible Processes

Budget

- **Total: $ 315K**
- **FY07: $ 40K**
- **FY08: $ 200K**
- **FY09: $ 75K**

Partners

- Lead Organization:
  - Pacific Northwest National Laboratory
- Collaborators
  - Hewlett-Packard
  - General Motors
  - ImTech

Relevance-Objectives

- Demonstrate Basic Process Steps in Digital Fabrication of CCMs & MEAs
  - Ink formulation and delivery with industry standard print heads
  - Catalyst layer quality and mechanical durability
  - Electrochemical utility
- Define Advantages & 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.

Relevance-Barriers

- **A.** Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
  - Transition from hand lay-up to short-run automated fabrication to dedicated production line.
  - Design of agile and versatile production methods
    - Accommodate small and large volume runs
    - Accommodate substrate, size and catalyst composition needs.
    - Rapidly integrate R&D advances in MEA fabrication
  - Optimization of dedicated single product production lines
- **B.** Manual Stack Assembly
  - Integration of CCM fabrication into automated assembly line
- **F.** Low Levels of Quality Control and Inflexible Processes
  - Adaptation of print industry quality control process to MEA fabrication

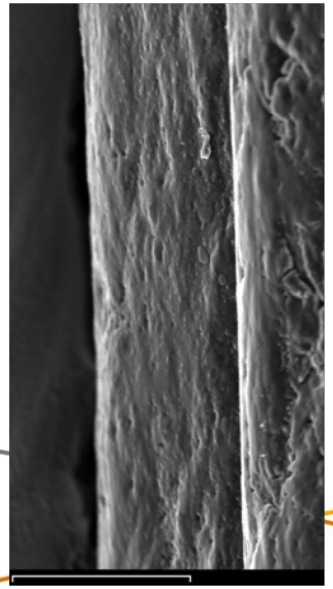
Approach

- Demonstrate feasibility of digital fabrication
  - Ink development
  - Printing demonstration
  - Validate Electrochemical Performance
  - **Milestone: CCMs successfully fabricated and tested in single cells**
- Characterize CCM printing process
  - Evaluate substrate handling methods
  - Print layer thickness, adhesion, uniformity
  - Control catalyst layer composition in Z and XY directions
  - Demonstrate large area CCM fabrication
  - On-line, real-time quality control
  - **Milestone: 4 of 5 print processes characterized**
- Evaluate implications of DF on process line design & economics
  - Changes in process line steps
  - Process line throughput needs.
  - Integration with stack and system assembly steps
  - Identify potential process cost saving and research needs
  - **Milestone: Process line design qualitatively outlined**

Technical Progress

Demonstrate feasibility of digital fabrication

- Ink compositions developed with Pt supported on carbon and PFSA ionomer.
- Dispersion methods developed resulting in ~5 day stability
- HP's TIPS system used to test Ink – Print head compatibility.
  - No large particles
  - No aggregation of particles.
  - Humectants need to prevent nozzle clogging

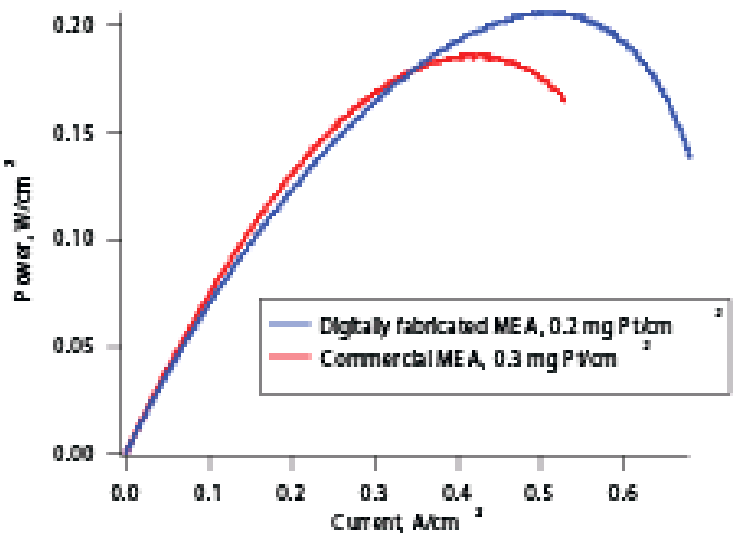


- 10 cm2 CCM fabricated with HP printing equipment
- Very good adhesion of catalyst layer on Nafion®.
- Good uniformity in Z direction
- Uniformity in XY plane dependent on print conditions
- Membrane and Ionomer in H+ form.
- No hot press required.
- Significant processing advantage

Technical Progress

Demonstrate feasibility of digital fabrication (Cont.)

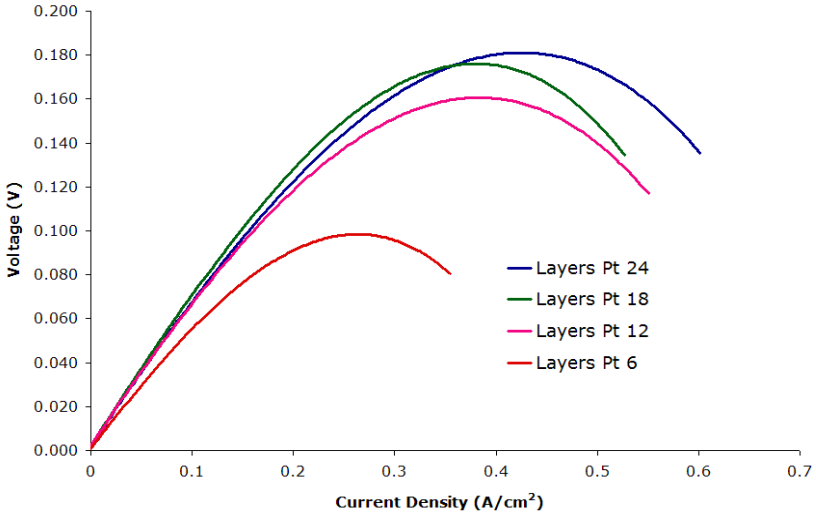
- Electrochemical Viability
  - Digitally fabricated CCM slightly better than commercial CCMs
  - Improvement needed in cell design and operation
  - DF does not adversely impact electrochemical properties

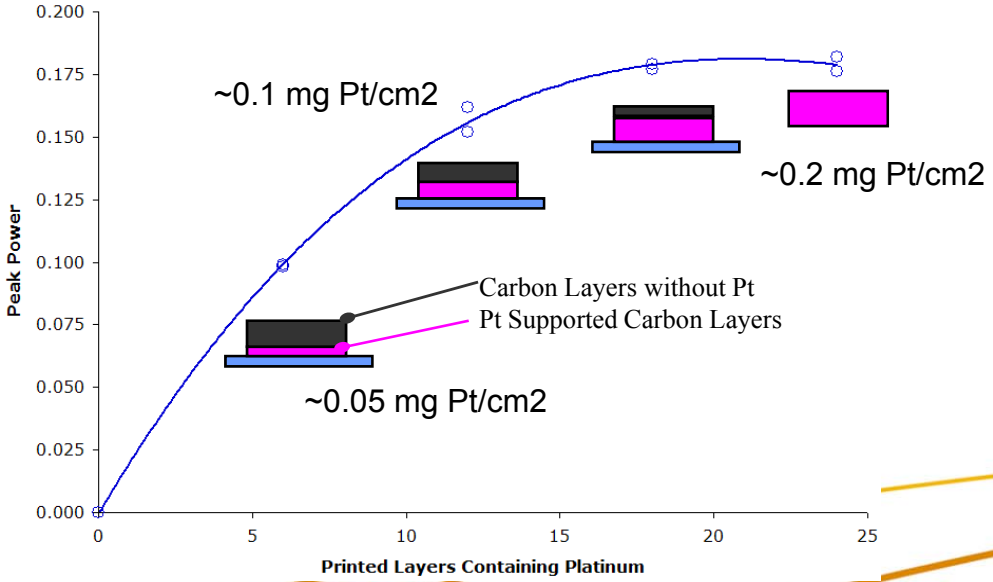


Technical Progress

Characterize CCM printing process

.1 mg Pt loading ~ 90% peak power as 0.2 mg Pt loading



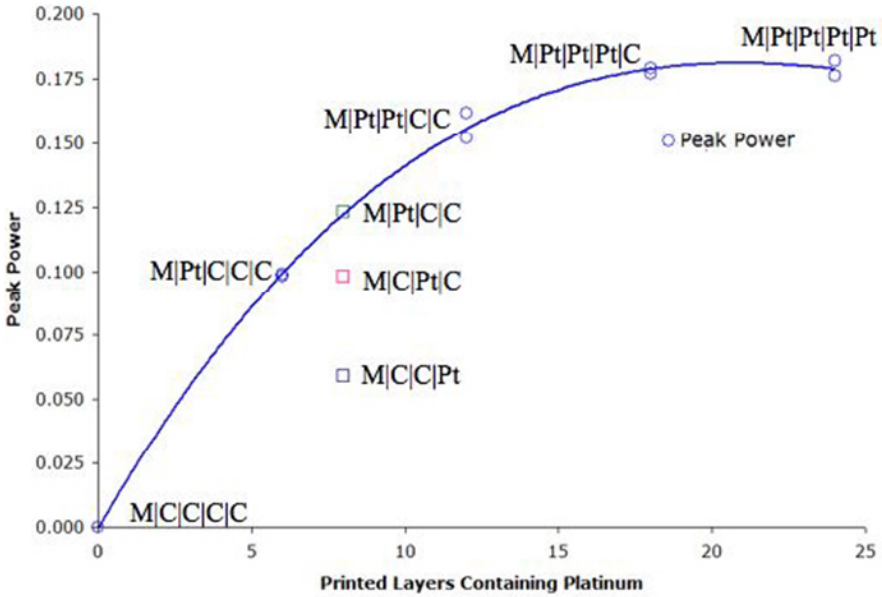


DoD fabrication allows precise optimization of Pt distribution leading to low Pt loading and reduced MEA costs.

Technical Progress

Characterize CCM printing process (Cont.)

- Electrode structure and composition varied using different inks
- Pt supported on XC-72 and XC-72 printed in various layer.
- Pt near the membrane interface is most active.

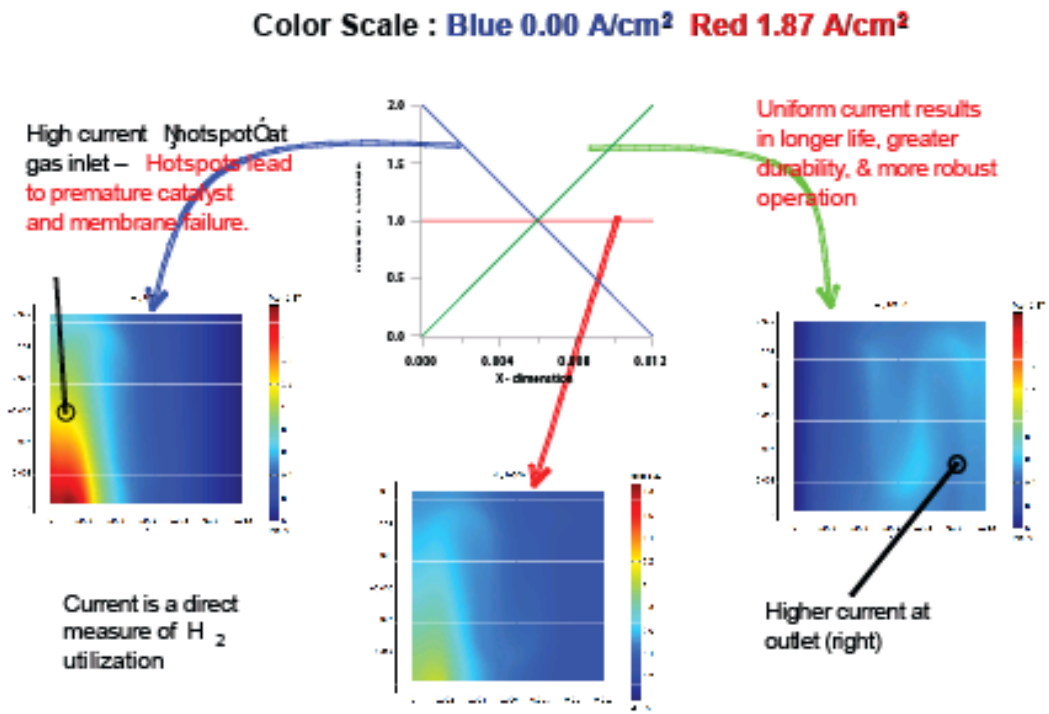


Digital Fabrication is a unique tool for building new electrode architectures

Technical Progress

Characterize CCM printing process (Cont.)

- Finite Element Modeling
- Gradation of catalyst loading impacts current distribution
- Total current not significantly different

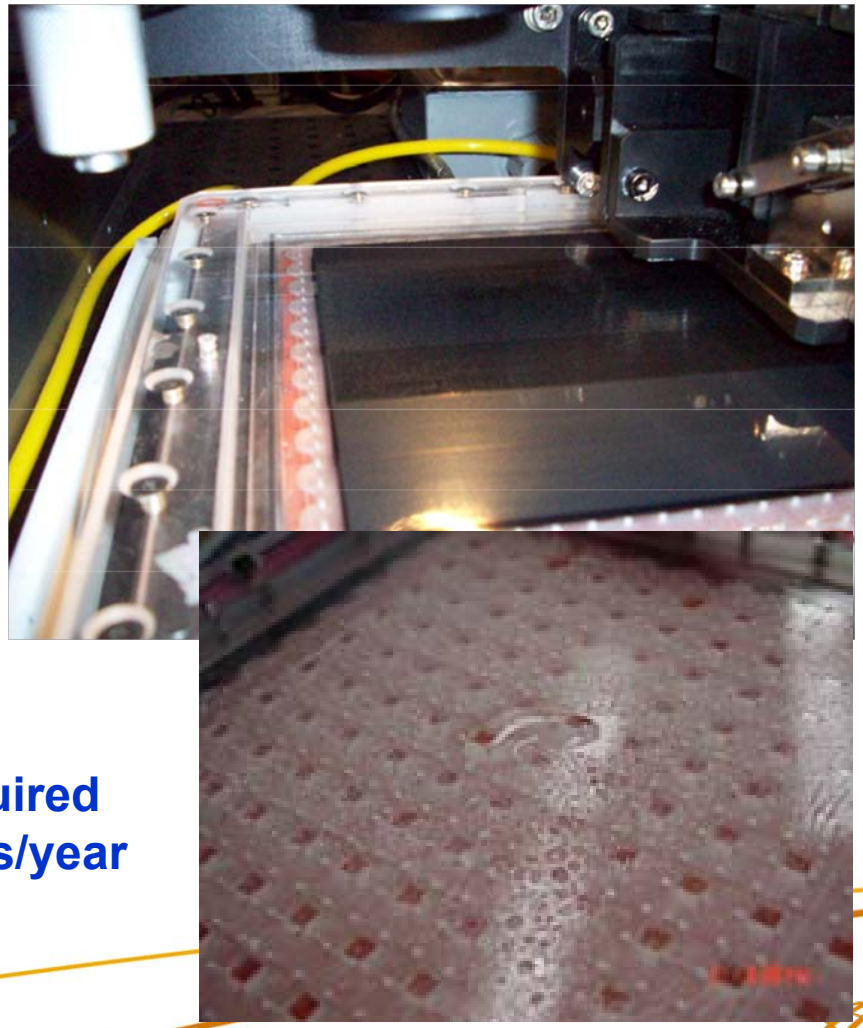


Catalyst stability, water distribution, thermal gradients may be controlled through optimization of catalyst distribution.

Technical Progress

Characterize CCM printing process (Cont.)

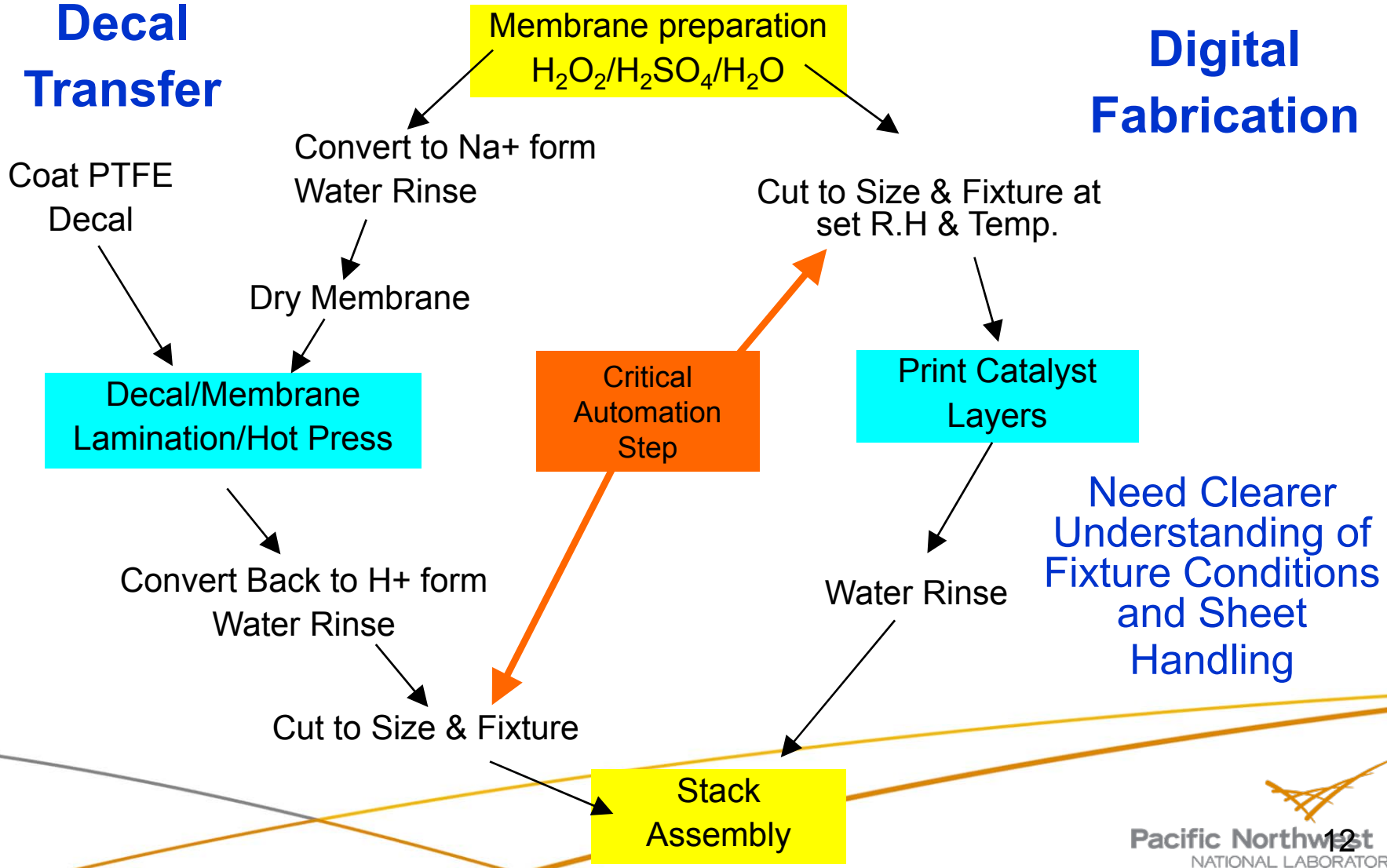
- Demonstrated Printing on Large Area 7 mil membrane
  - 320 cm^2 membrane
  - 180 cm^2 print area
- Print head and fixture collision prevent full area printing
- Water in ink did not significantly swell membrane
- Printing of almost any size & shape should be feasible
- 2 mil membrane cannot withstand tensile forces developed during fixturing



Approximately 20-30 printers required to print CCMs for 500,000 vehicles/year with 70 kW power plants

Technical Progress

DF process line design



Need Clearer Understanding of Fixture Conditions and Sheet Handling

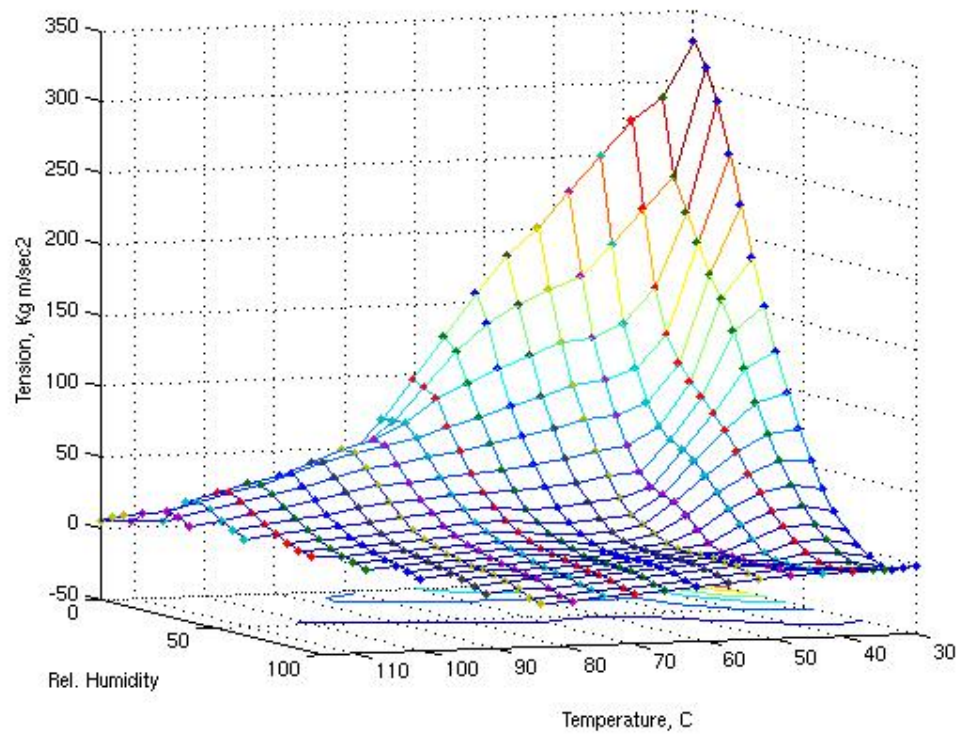
Technical Progress

DF Process Line design (Cont.)

$$E = \frac{(F/A)}{(dl_E / l^0)}$$

$$l = l^0 + dl_E = l^* + dl_S + dl_E$$

- Dimensional changes due to swelling and elasticity
- Proper choice of temperature and humidity when fixing membrane can reduce stresses during printing and cell assembly.



F. Bauer, S. Denneler, M. Willert-Porada, *Influence of Temperature and Humidity on the Mechanical Properties of Nafion® 117 Polymer Electrolyte Membrane,* J. Polymer Science, B, 43 (2005) 786.

Collaborations

- External Collaborations
  - Hewlett-Packard.
    - PNNL is a beta test site for the TIPS printing system. TIPS is used to develop inks.
    - HP also opened their laboratory and allowed us to use their state-of-the-art printing systems.
    - Manufacturing Proposal Partner
  - General Motors
    - Detailed discussions of advantages and limitation of digital fabrication of Catalyst Coated Membranes
    - Manufacturing Proposal Partner
  - ImTech
    - Preliminary design of a print facility for CCM fabrication

Proposed Future Work

- **Process Analysis**
  - Comparison of thermal, piezo and continuous print head technologies
  - Procedures and conditions for handling of PFSA membrane substrate during the printing
- **Process Design Feasibility And Scalability**
  - Design and test of a highly versatile laboratory-scale print-facility
  - Development of inks compatible with the fuel-cell fabrication process that will meet the cell and stack performance criteria
  - Detailed examination of the behavior of ink formulas in print heads and optimization of the print head operating parameters
  - Pre-/post-processing and scalability analysis and integration of the DF process into existing cell, stack and power plant assembly lines.
- **Product Demonstration And Qualification**
  - Screening of electrochemical properties in small (~10 cm2) cell
  - Single cell testing & electrochemical characterization of medium (40-50 cm2) and large scale (>300 cm2
- **Novel CCM Architectures**
  - Optimization of the platinum content and XY & Z placement for enhanced durability and electrochemical performance.
- **Pilot Plant Design And Cost Analysis**
  - Produce design criteria and specifications for a pilot plant facility
  - Quantitatively compare fabrication costs of DF with existing current technology.

Note: Proposed work will be conducted under a new program with contracts under negotiation with DOE

Mandatory Summary Slide

- Digital Fabrication Simplifies Fabrication Process
  - No hot press or lamination steps
  - Fewer chemical transformations
  - On-Demand fabrication
    - No storage of CCM
    - Match of assembly and CCM fabrication through put
- Electrochemical Performance Comparable to Commercial MEAs
  - Better single cell test stand and procedures have been developed
- DF unique in ability to optimize catalyst layer architecture
  - Reduce platinum loading
  - Enhanced durability
  - Better inherent water management