MEA Manufacturing R&D Using Drop-on-Demand Technology

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MN009

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Overview

Timeline

- Project start date: June 1, 2010
- Project end date: Sept., 31 2011
- Percent complete: *60%*

Barriers

- Barriers addressed
  - Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
  - Low Levels of Quality Control and Inflexible Processes

Budget

- Total project funding
  - DOE share: $ 325,000
- Funding received in FY10:
  $ 125,000
- Funding for FY11:
  $ 200,000

Partners

- Pacific Northwest National Lab
- Informal Collaborators
  - Hewlett Packard
  - General Motors

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Relevance-

Problem Statement

Currently the many individual fuel cell companies each fabricate

- a few stacks per day
- of highly variable design
- with many different end applications
- at a cost ~100X greater than automotive industry targets
- at a volume ~100X smaller than automotive industry targets

Industry is moving from the so-called 5 and 7 layer MEAs to ones with fully integrated seals and gas diffusion layers.

This integration will drive reorganization of the MEA fabrication process. Critical step is the transition from Roll-to-Roll processing compatible with the incoming materials (e.g. rolls of membrane material) to Piece-by-Piece processing required for automated MEA insertion into the stack assembly.

Production line must be highly versatile and adaptable to changes in product design or technical advances in catalyst, membrane, seal and GDL materials.

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Relevance-

Project Objectives

- Evaluate MEA fabrication and catalyst coating technologies that will:
  - Transition the industry from low volume to high volume production using a scalable fabrication technology
  - Allow a single fabrication line to handle multiple MEA sizes, shapes and compositions
  - Rapidly accommodate new technology as it develops
  - Reduce the number of fabrication steps
  - Provide for highly consistent and repeatable catalyst coating at small, medium and large scale production runs.
  - Minimize waste of membrane and catalyst material

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Relevance-

Project Approach

- Critically evaluate inkjet or “drop-on-demand” (DoD) printing technology to meet the criteria specified in the previous slide
  - Determine if DoD provides for fewer or shorter fabrication steps.
    - No hot press is needed for film under 20 μm.
  - Determine any conflicting requirements of the ink formulation in printability and catalytic activity.
    - Additives required for printability may inhibit catalytic activity
    - Stable and jettable ink compositions may not be easily formulated or produce catalyst layers with the desired ratios of carbon, catalyst, ionomer and porosity.
    - Particle size distribution and stability may cause print head clogging
  - Determine printing conditions for uniform or graded catalyst layer compositions
    - Substrate temperatures
    - Print chamber humidity

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Tech. Progress 1 – Analysis of Catalyst Layer Printing & Coating Technologies

Comparison Criteria

- Compatibility of ink formulation and printing technology
- Wastage of catalyst and membrane
- Speed range and compatibility with other fabrication steps
- Single layer thickness (and multilayer gradation)
- Potential for "Patch" deposition (>1 cm areas)
- Ability for fine scale (<0.1 mm) deposition and patterning
- Amenability to Large, Medium and Small scale production
- Rapidity of line set-up and modification
- Roll-to-Roll versus Piece-by-Piece processing

Speed is not the most critical issue. Many processes are:

1) Too fast compared to other fabrication steps
2) Line speed cannot be easily varied
3) Line speed is dependent on ink formulation

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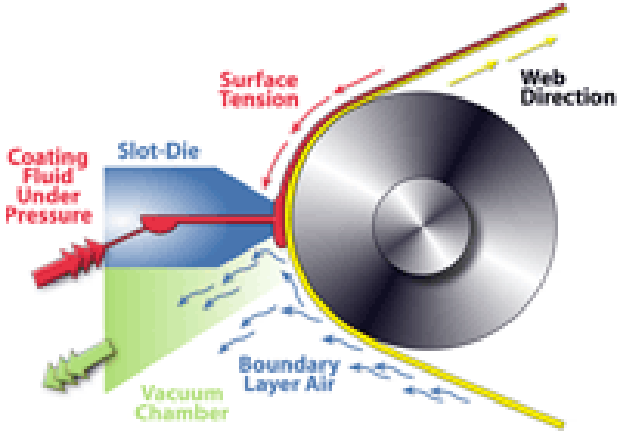
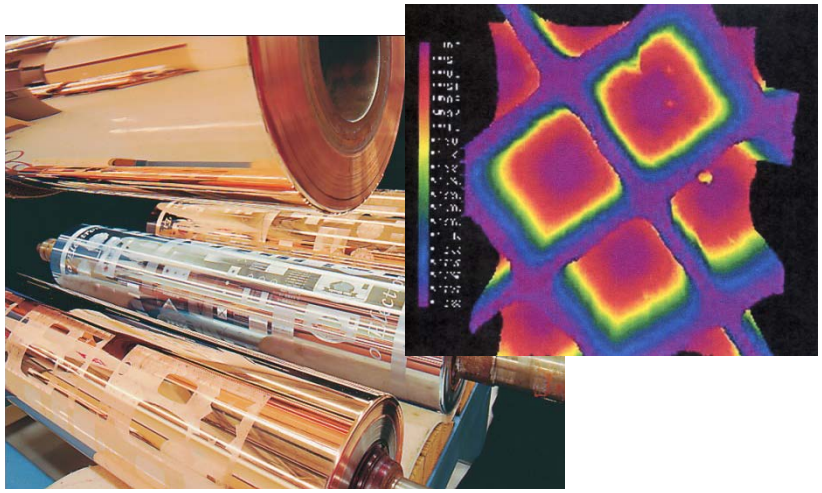
Tech. Progress 2 –

5 Advantageous Coating Technologies

- Slot-Die Coating
  - Uniform patch coating
  - Single thicknesses of ~20-100 µm.
  - 0-10 m/min



Schematic of a slot-die coater. Courtesy of Frontier Industrial Tech., Inc.



Gravure rolls with detail of etched ink cell. Courtesy of Daetwyler R&D Corp

- Gravure Printing
  - Patch coating & pattern printing
  - Single thicknesses of ~1-5 µm.
  - >100 m/min
  - Gravure roll image fabrication requires special equipment

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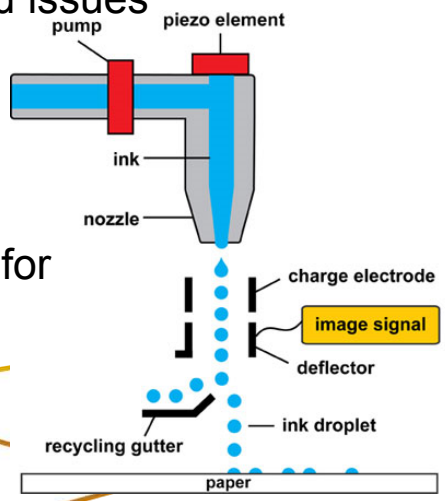
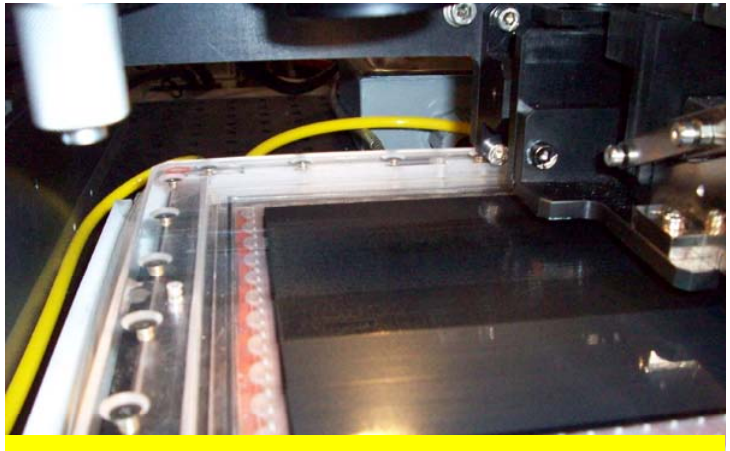
Tech. Progress 3 –

5 Advantageous Coating Technologies

- Spray gun
  - Simple ink formulation
  - Single thicknesses of ~1-10 µm.
  - Uniformity problems
  - Total mass deposited variable
  - 0-1 m/min
  - High catalyst wastage due to overspray
- Continuous Ink Jet printing
  - Eliminates printhead issues
  - Single thicknesses of ~1/2 - 20 µm.
  - 0-10 m/min
  - Rapid set-up
  - Not well developed for industrial materials applications





Printing of catalyst layer on 320 cm2 Nafion membrane

- Ink Jet printing
  - Ink formulation and print head compatibility issues
  - Single thicknesses of ~1/2 - 2 µm.
  - 0-10 m/min
  - Rapid set-up
  - Simple patterning and gradation

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Tech. Progress 4 –
Potential Path to Large Volume Fabrication

Use standard inkjet print technology for low to medium size runs where adaptability and versatility are most important. Graduate to continuous inkjet as processes and compositions become set and volumes increase.

Advantages

1) Little or no wastage of catalyst or membrane
2) Line speed highly adaptable to match other fabrication steps
3) Inks formulated for standard inkjet transferable to continuous inkjet
4) Highly adaptable to new technology
5) Relatively low capital cost
6) High inherent quality control and reproducibility
7) Piece-by-Piece and Roll-to-Roll processing

Development Needs

1) Continuous inkjet not well developed for large scale fabrication
2) Printing algorithms and printheads developed for image applications not thin film applications
3) Ink formulation limitation and requirements need better understanding
4) Printing conditions (e.g. T and RH) need defining

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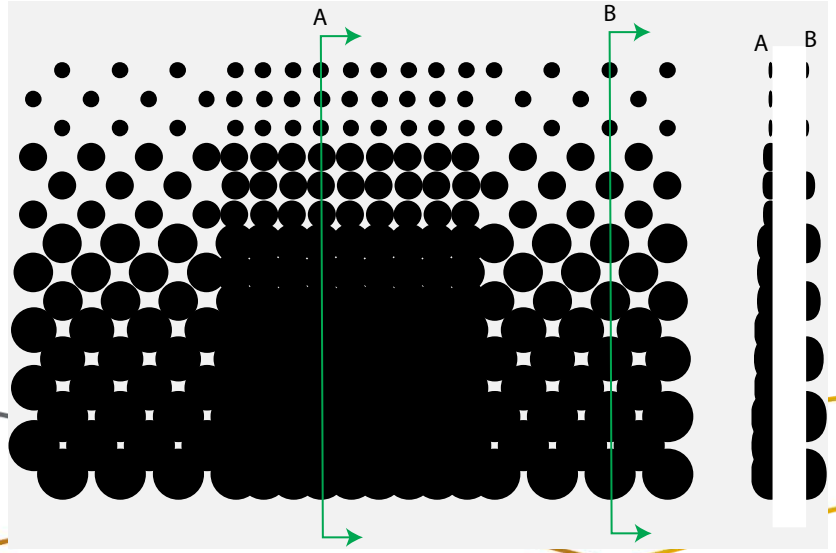
Tech. Progress 5 –

Requirements of Thin Film Inkjet Printing

Images are not thin films

- Images
  - A light reflective surface. Thickness is not critical
  - Half-toning or dithering achieves gray scales and colors but does not always fill printed space



- Thin film
  - Has bulk properties. Thickness IS critical
  - Films must usually be of uniform thickness and composition over large dimensions.
  - Interface with other materials critical.

High density and large drop size are required to form a thin film. Spreading of drop on substrate and contact angle are critical parameters

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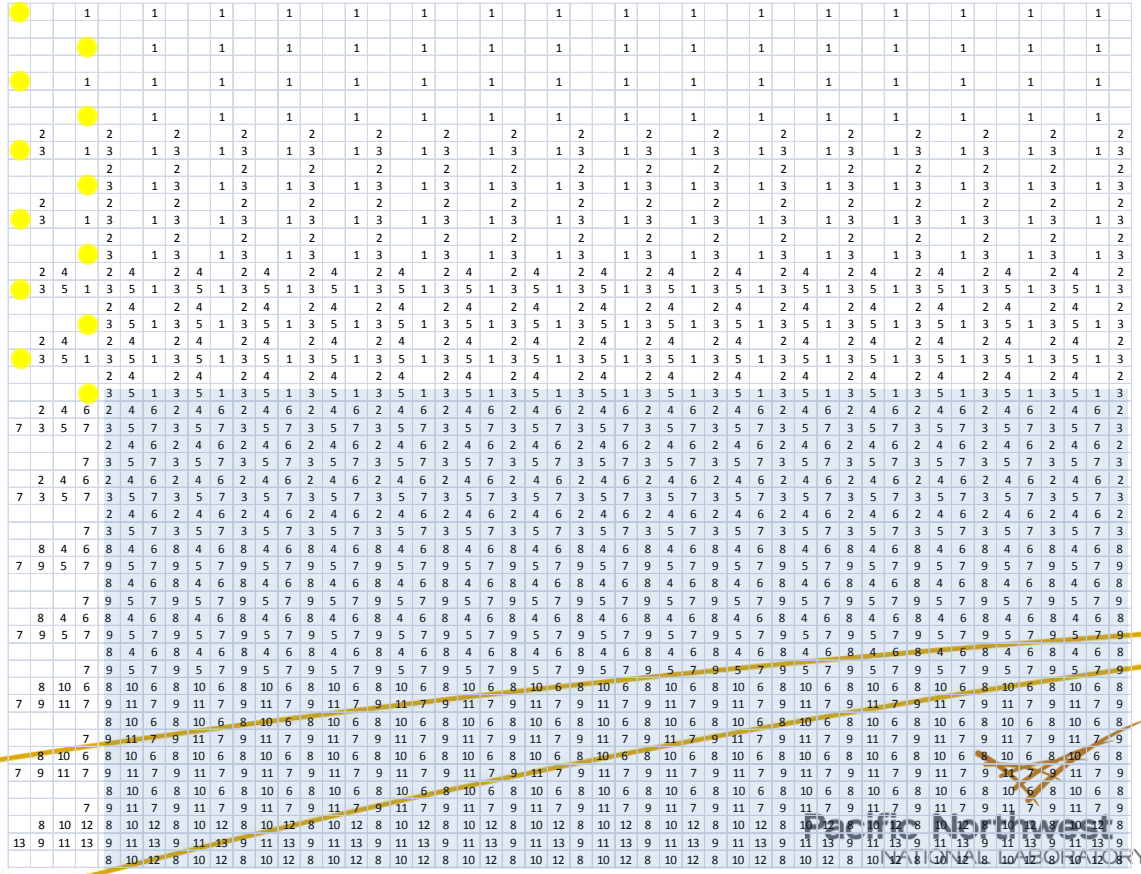
Tech. Progress 6 –
Requirements of Thin Film Inkjet Printing

Print Algorithms

- All jets should be used evenly to prevent clogging
- Jet pattern should be “woven” to prevent vertical and horizontal banding
- Special algorithms are needed at image edges to fill space
- Each printhead jet pattern requires a separate algorithm

Print algorithm for a 2x12 Jet printhead
1st position of jet head shown in yellow
Full print area shaded in blue
Numbers designate the nth pass

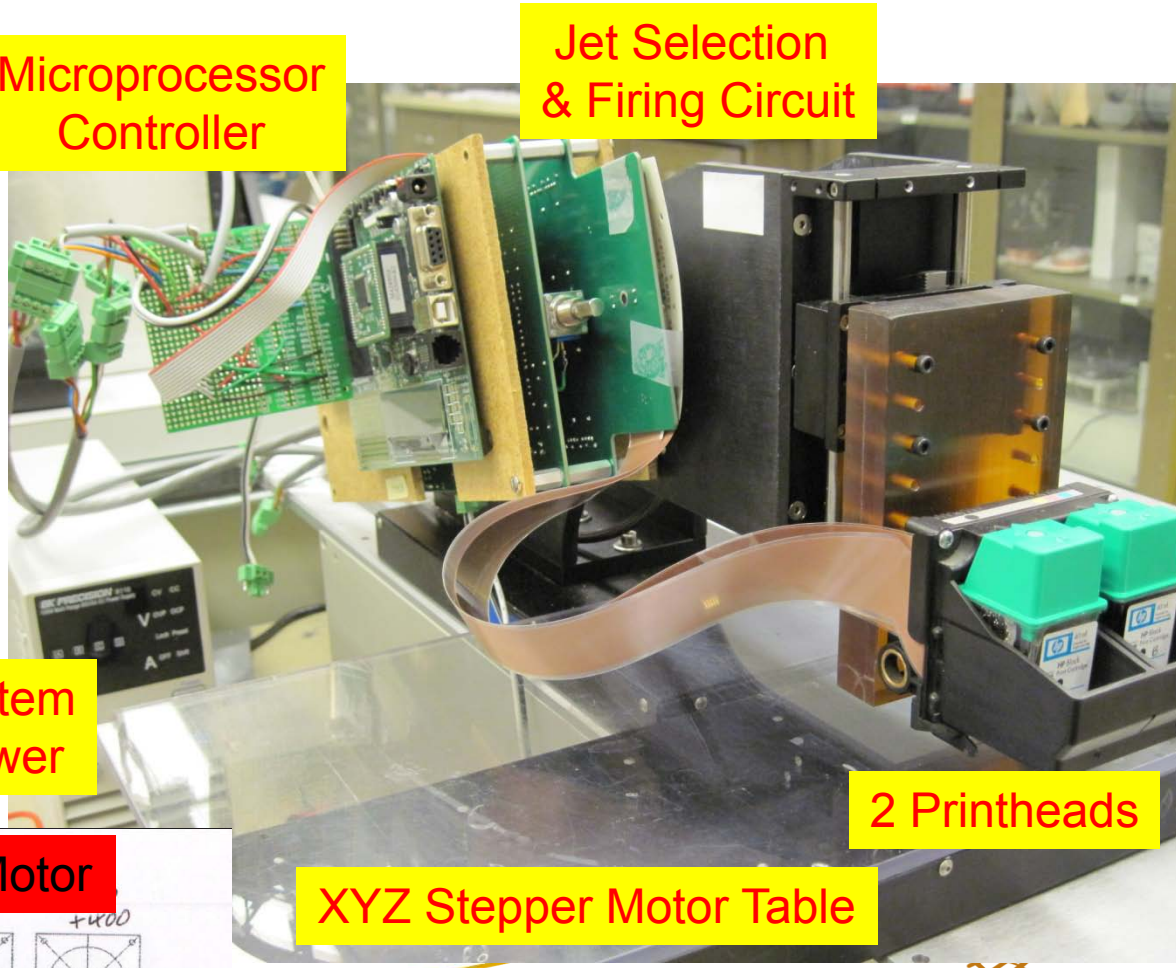


Tech. Progress 7 –

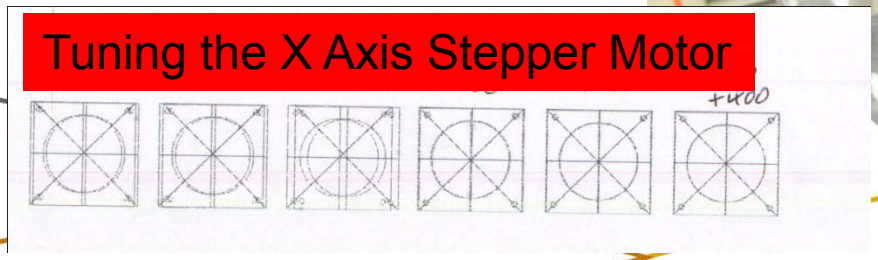
Requirements of Thin Film Inkjet Printing

Specialized printer constructed

- Jets are large to prevent clogging
- Two print heads allow graded ink compositions
- Print algorithm developed for ink cartridge
- Printer completing testing
- Environmental controls being constructed

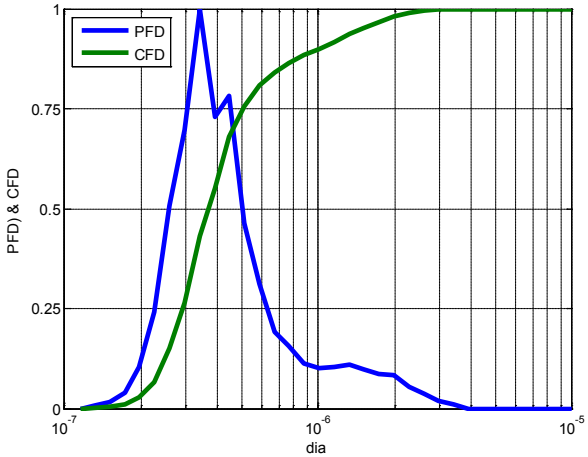


Tuning the X Axis Stepper Motor

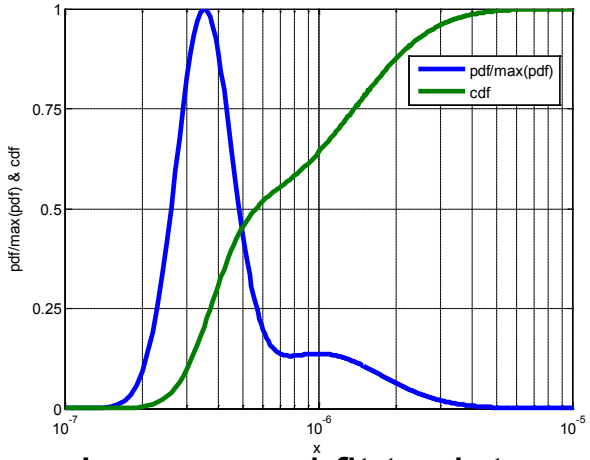


Tech. Progress 8 –
Printhead Reliability

- Two identical printheads with different jet orifice sizes (28 µm & 20 µm)
- Larger orifice size did not fail while smaller size failed rapidly
- Particle size distribution show aggregates at about 1 µm.



Normalized particle size distribution



Log normal fit to data using two particle size distributions.

Particles much larger than can be measured exist in the ink with a very small but significant probability

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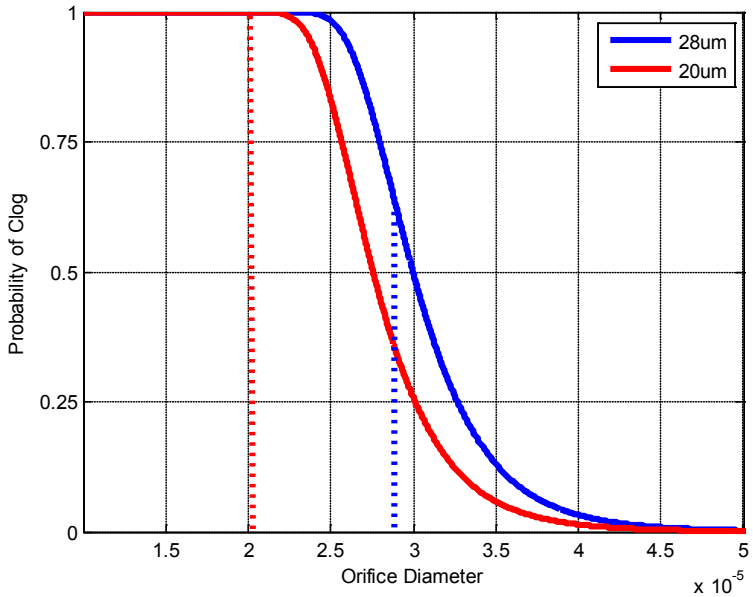
Tech. Progress 9 –
Printhead Reliability

- Particles far from the peak particle size cannot be quantitatively measured
- A log normal distribution fit to data can predict concentration of large particles that might clog a print jet.

Conclusion: Prevention of aggregation even to a very small degree is critical in ensuring printhead reliability



- Figure shows the probability of clogging after 1000 fires.
- Vertical lines denote the actual orifice diameters. RED 20 µm and BLUE 28 µum
- 20 µm orifice has 100% probability of clogging by a 20 µm or larger particle
- 28 µm orifice has a 60% probability of clogging by a 28 µm or larger particle

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Tech. Progress 10 –
Test Protocol Development

- Rapid comparison of MEAs under wide selection of operating parameters
  - Humidification of the cathode
  - Humidification of cathode and anode
  - Preliminary evaluation of durability and reproducibility.
- Leak tests performed before electrochemical tests.

				Anode			Cathode		
Test #	Rep	Time (min)	Voltage	O2	Stoic.	R.H.	Stoic.	R.H.	PSIG
1	1	60	0.6	O2	5	100	7	100	0
2		20	0.7	O2	5	100	7	100	0
3		20	0.5	O2	5	100	7	100	0
4		hold	0.6	O2	5	100	7	100	0
5	2	20 mV/sec	1.0 to 0.3	O2	8	100	10	100	0
6	1	20 mV/sec	1.0 to 0.3	O2	8	100	10	100	15
7	2	20 mV/sec	1.0 to 0.3	Air	2	100	4	100	0
8	1	20 mV/sec	1.0 to 0.3	Air	2	100	4	100	15
9	2	20 mV/sec	1.0 to 0.3	Air	1.2	100	2	100	0
10	2	20 mV/sec	1.0 to 0.3	Air	2	100	4	65	0
11	2	20 mV/sec	1.0 to 0.3	Air	2	100	4	25	0
12	1	20 mV/sec	1.0 to 0.3	Air	2	100	4	100	0
13	2	20 mV/sec	1.0 to 0.3	Air	2	65	4	65	0
14	2	20 mV/sec	1.0 to 0.3	Air	2	25	4	25	0
15	1	20 mV/sec	1.0 to 0.3	O2	2	25	4	25	0

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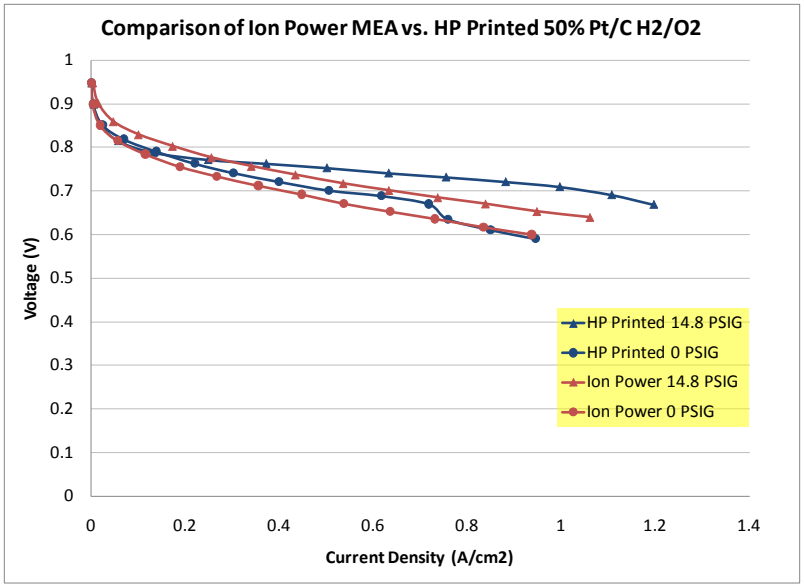
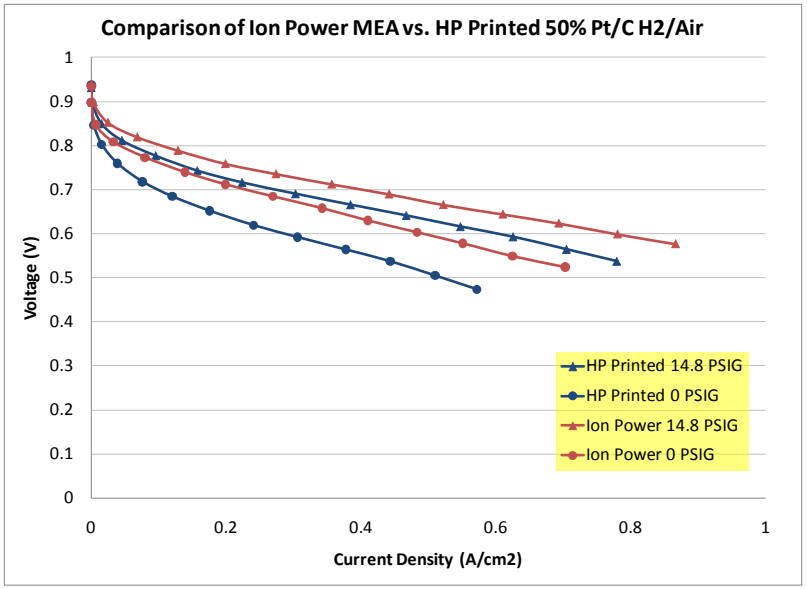
Tech. Progress 11 – Comparison of Commercial and DoD Fabricated MEAs

0.2 mg Pt/cm^2





- DoD MEA better in O_2 (left) while Ion Power better in air (right)
- Difference possibly due to ink composition (more ionomer &/or less porosity in DoD) and not fabrication method.
- But DoD fabrication is not distinctly worse

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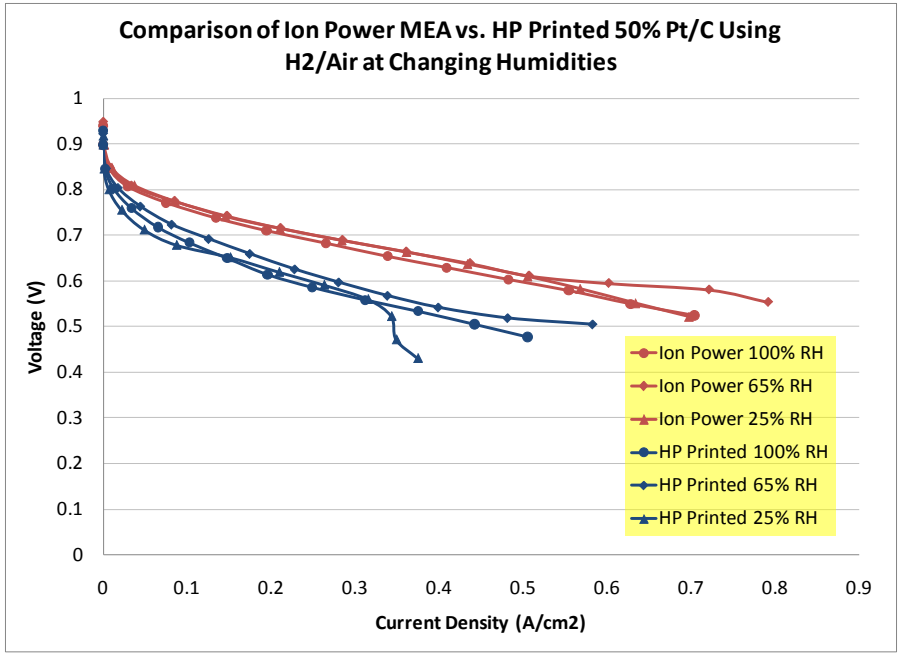
Tech. Progress 12 – Comparison of Commercial and DoD Fabricated MEAs



After 3 days of testing at 0 PSIG

- Both MEAs do better at 65% RH
- Previous slide shows results after 8 hrs of testing.
- DoD MEA gets noticeably worse.
- Know little about Ion Power ink composition and fabrication details
- Cannot make direct comparison of fabrication methods

Conclusion: DoD as a fabrication technique will require optimization but it is not distinctly inferior

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Collaborations

- This project grew out of collaboration with General Motors and Hewlett Packard and was selected for funding starting in 2009. Because of economic conditions, the industrial partners were forced to withdraw.
- Hewlett Packard continues to provide support by allowing PNNL to use their experimental print facilities.

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Proposed Future Work

- Printhead reliability – Develop catalyst compatible ink stabilizers that prevent particle aggregation, prevent jet clogging and give longer shelf life.
- Explore relationship of ink composition (ionomer, carbon, catalyst ratio) to performance using test protocol developed in this work.
- Determine optimal printing conditions:
  - Relative Humidity
  - Substrate temperature
  - Membrane hydration
- Quantify relationship of substrate wettability to thin film uniformity.
- Determine maximum single pass thickness.
- Quantify development needs for continuous inkjet fabrication.

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Mandatory Summary Slide

- Technical analysis of printing coating fabrication process completed and report to DOE 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.
- Demonstrated that MEAs prepared by DoD fabrication have comparable performance to commercially available MEAs. Needs optimization.

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