

Technical Assistance to Developers

**Tommy Rockward (PI), Rod Borup(PI), Eric Brosha, Piotr Zelenay,
Fernando Garzon, Yu Seung Kim, R. Mukundan, Gang Wu, Hoon
Chung, K. Rau**

**The U.S. Department of Energy 2014 Hydrogen and Fuel Cells
Program and Vehicle Technologies Office Annual Merit Review
and Peer Evaluation Meeting**

**June 16-20, 2014
Washington D.C.**

**Project ID:
FC052**

Overview

Timeline

- Project start date: 10/1/05
- Project end date:
 - Project continuation and direction determined annually by DOE

Budget

- Total project funding: **NA**
 - DOE share: 100%
 - Contractor share: 0%
- Funding received in FY13: \$300K
- Total funding planned for FY14: \$450K

Barriers

- Barriers addressed
 - Sharing technical assistance to developers
 - A. Durability
 - B. Cost
 - C. Electrode performance

Partners/Collaborators

- Fuel Cell Tech Team Rep
- Support Working groups
 - Durability WG
 - Mass Transport WG
- GM
- Ford
- NIST
- Argonne National Lab
- Advent Technologies
- Cal State University-Northridge
- Impact Coatings
- Pajarito Powders

Relevance/Approach for Technical Assistance

This task supports Los Alamos technical assistance to fuel-cell component and system developers as directed by the DOE. This task includes testing of materials and participation in the further development and validation of single cell test protocols. This task also covers technical assistance to Durability Working Groups, the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE *Driving Research and Innovation for Vehicle efficiency and Energy sustainability* (U.S. DRIVE) Fuel Cell Technology Team. This assistance includes making technical experts available to DOE and the Fuel Cell Tech Team as questions arise, focused single cell testing to support the development of targets and test protocols, and regular participation in working group and review meetings. **Assistance available by Request and DOE Approval. Nancy Garland, Ph. D:** Nancy.Garland@ee.doe.gov

2014 Outline of Work-scope

- Fuel Cell Tech Team Rep
- Support Working groups
 - Durability WG
 - Mass Transport WG
- GM Humidifier/Water Transport membrane durability
- Ford
- Argonne non-PGM support
- Advent Technologies
- Cal St. Northridge
- Impact Coatings

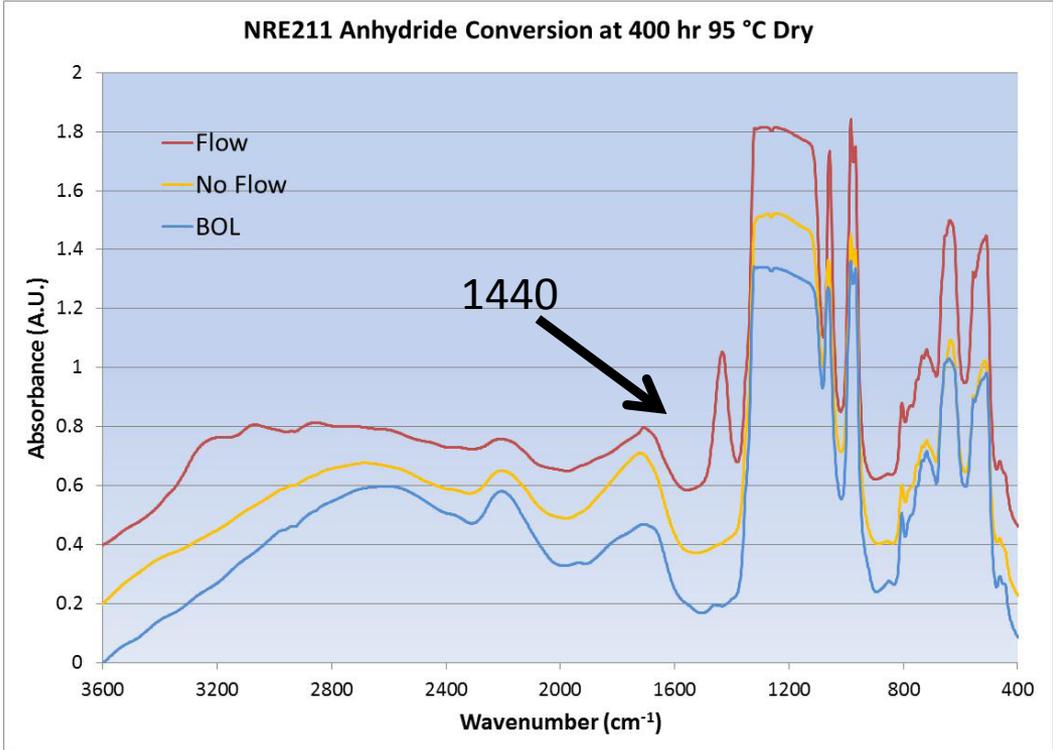
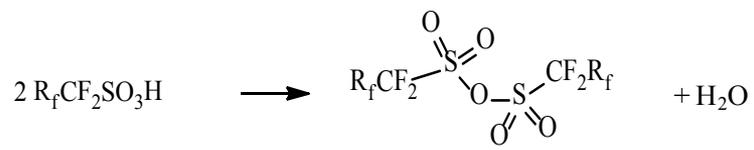
Approach:

General Motors: Degradation of Perfluorosulfonic Acid Membrane Water Permeance via Formation of Sulfonic Acid Anhydrides

Task: During in-situ and ex-situ testing, water transference values of PFSA-based membranes can degrade significantly over operating time. Define causes for degradation and relative degradation rates.

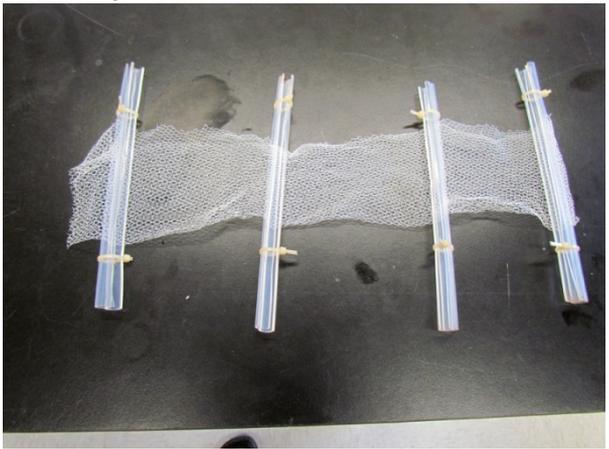
LANL Investigators: Rod Borup and Karen Rau
Ford Motor Co: Shawn Clapham, **Frank D. Coms**, Timothy Fuller, Lijun Zou

The degradation is associated with a crosslinking of sulfonic acid groups to form sulfonic acid anhydrides.

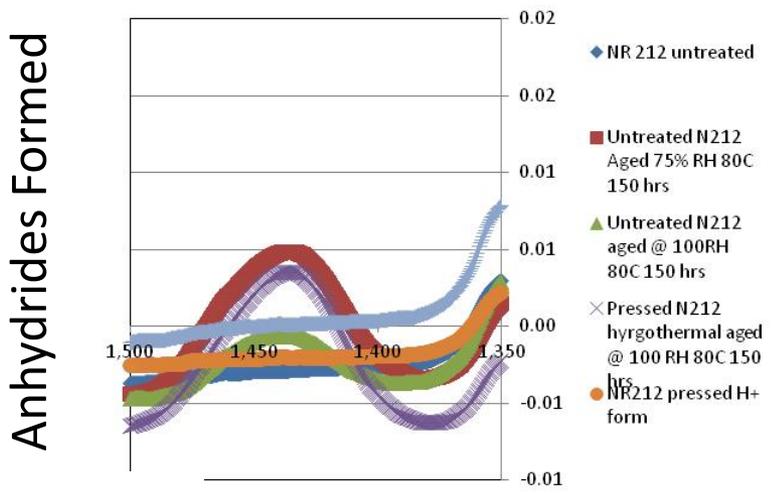
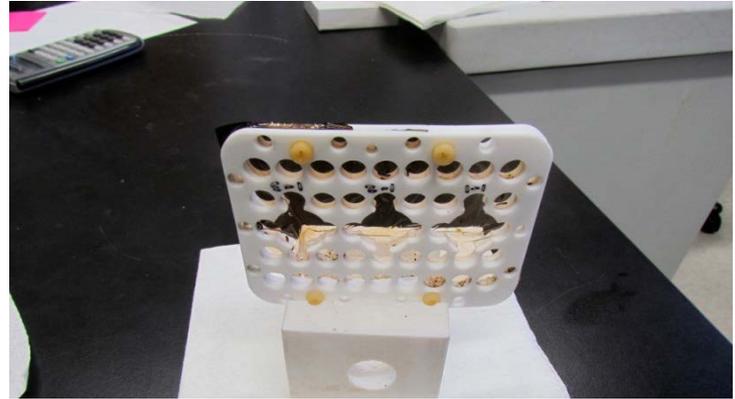


Degradation of Perfluorosulfonic Acid Membrane Water Permeance via Formation of Sulfonic Acid Anhydrides

- Sample Holder #1
 - Nylon® Mesh and Teflon® Tubing



- Sample Holder #2
 - Teflon® matrix
 - Easy analysis without handling membranes



- Anhydrides formed with Nylon® sample holder
- No anhydrides form with Teflon® sample holder
- Nylons are susceptible to hydrolysis, especially by strong acids
 - The products of hydrolysis are a carboxylic acid and a primary amine
- Evidence suggests that surface anhydrides are formed from interactions with a type of impurity, (e.g. air or sample holder)

Catalyst Development

We would appreciate assistance with sputtering (and we agree with your definition of sputtering below) of Pt onto powder substrates. Because many of the candidate powder substrates have been chosen for their stability under fuel cell cathode conditions, they also tend to have low surface energies. This means that Pt wetting of the substrates is best facilitated at elevated temperature ($> 350^{\circ}\text{C}$) and with slower deposition rates. At present, we have experimented with systems that tend to encounter difficulties with providing for both agitation/fluidization of the powder and providing the high temperature environment.

MPL Modifications

For laser MPL modifications, we are interested in two particular types of characterization: pore structure measurements and thermal conductivity measurements. The former may include tortuosity, connectivity of pores, and pore size distributions with MIP. Thermal conductivity measurements would address both through-plane and in-plane directions, as well as bulk and contact thermal resistances.

Bipolar Plates

General assistance with developing next generation bipolar plates. Details will have to be worked out.

Humidifier Design

The Fuel Cell Balance of Plant group in Ford Motor Company would like the Technical Assistance Developers Team at Los Alamos National Laboratory to help investigate the properties of a new humidifier design. The humidifier design is approximately *one-half the volume* and *one-third the cost* compared to existing designs implemented in vehicle fleets without sacrificing performance. The humidifier still relies on the transport of water across an internal membrane/material to accomplish an exchange of water from the moist cathode stack exhaust to the drier air supply leaving the compressor. Los Alamos National Laboratory has performed water transport degradation studies on membranes to understand the mechanisms and causes for decreased performance (permeance) over time. The operation of this humidifier and the behavior of the materials that comprise it are different and have not been employed in fuel cell applications before; understanding the material properties and the degradation mechanisms are necessary to improve designs, predict lifetime behaviors, and develop test procedures for determining the degradation of the transfer rates of the membranes due variations of conditions during operation, i.e. temperature, age, air quality, mechanical stresses, *etc.* This project would utilize some of the same techniques presented in the 2013 DOE Hydrogen and Fuel Cells Program and Vehicles Technologies Program Annual Merit Review in May 2013, and require the development of new testing methods and investigations.

Ford Motor Co – Work Scope for Catalyst Development

Task: Assist Ford's efforts to deposit metal and metal oxide catalyst materials onto carbon supports using our vacuum deposition capabilities.

LANL Investigators: Eric Brosha and Rod Borup
Ford Motor Co: Kerrie Garth and Jun Yang

Status:

- Held several conference calls to discuss details of customer needs and LANL's role
- Timeline discussed was 1-2 months to obtain targets and make test depositions with 2-3 months reasonable for implementing and testing new methods for elevated T and particle agitation to improve coating uniformity
- Customer is presently putting together a statement of work defining roles for Ford and LANL and to define project objectives.
- LANL's vacuum deposition system is active

Ford Motor Co: Metal/Ceramic Coatings

Interest expressed in the preparation of non-corroding surfaces.

- Requirement for multi-layer deposition of materials without exposure to atmosphere

LANL presently has 3 options / systems depending on specifics of deposition requirements.

- part size/geometry, desired temperature, desired film thicknesses

- 1) Multi-hearth electron beam evaporation system
- 2) Multi-gun RF Magnetron sputtering system
- recently upgraded to with new MAK guns
- 3) Multi-target, on-axis sputtering system (room temperature depositions, single gun / 3 target



(1)



(2)

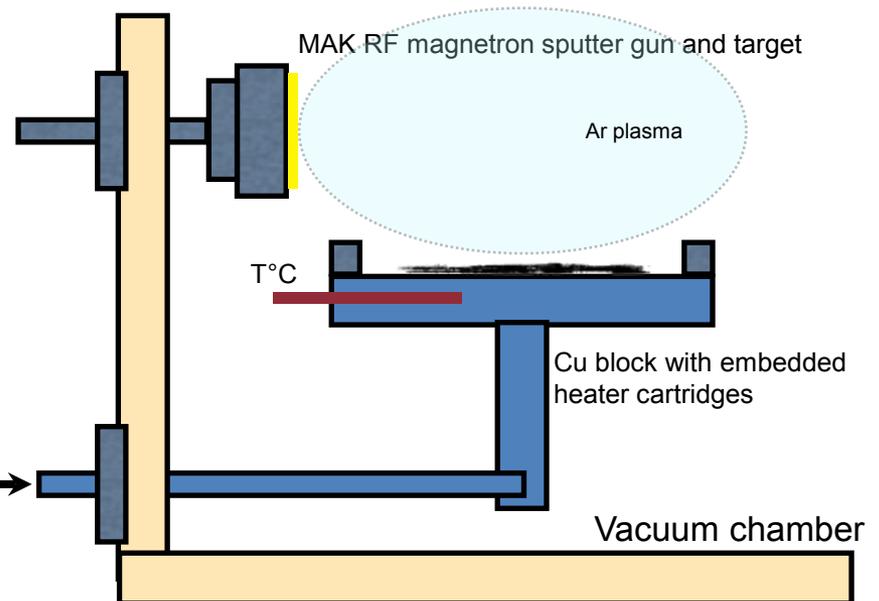


(3)

New Evaporation Methods for PEMFC Catalyst Synthesis

- LANL developed a new method for catalyst dispersion/deposition onto a variety of support materials in collaboration with Ford Motor Co.
- Uniform coverage of catalyst using RF magnetron sputtering with active agitation of support using injection of acoustic energy with support at elevated temperature to enhance catalyst support interaction.
- Uniform coating of surface of support at desired temperature for novel catalyst alloys that do not appreciably wet surface of the support.
- Resonance frequency of injected sound waves may be precisely controlled and tailored to adjusted to control degree of movement of support particles during catalyst sputtering.
- Temperature may be controlled with heater elements embedded into resonance platform or under-mounted BN heater.

Goal: uniform coverage of support material with catalyst. Injection of sound waves to promote translational and rotational movement of particles during sputter evaporation.



ANL's non-PGM Catalyst Evaluation: Tasks

Task: Collaboration underway with ANL for non-PGM catalyst evaluation and MEA preparation

LANL Investigators: **Piotr Zelenay, Gang Wu, Hoon Chung**

ANL: Di-Jai Liu

Status:

Conduct RDE study

- Measure Half-wave potentials of non-PGM catalyst.

- Compare ANL's non-PGM catalyst with state of the art ORR electro-catalysis.

Perform MEA/single cell study

- Test MEAs from ANL and LANL made in-house MEAs using ANL's materials

- Test with various ionomer to catalyst ratio to optimize MEA performance

- Measure open circuit voltages (OCV) of ANL's catalyst prepared by LANL scientists

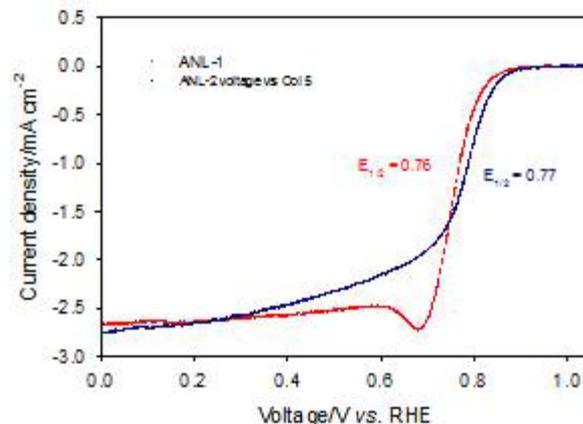
 - one-bar hydrogen/oxygen pressures at 80 °C.

- Measure cell current density at 0.80 V.

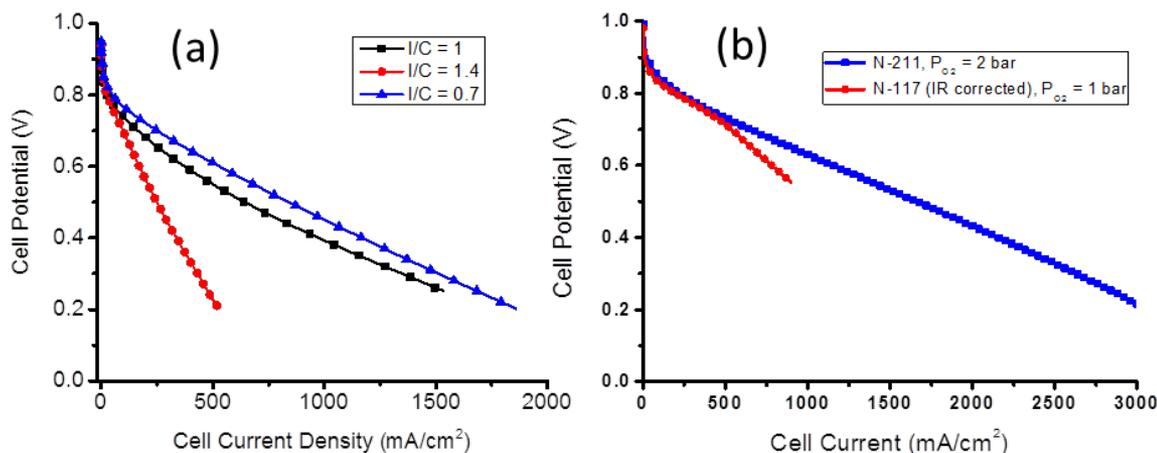
Accomplishments:

ANL's non-PGM Catalyst Evaluation

- ✓ Performed RDE study on materials
 - Measured half-wave potentials of ~ 0.76 V and 0.77 V.
 - Performance was measured to be close to the half-wave potential value of 0.80 V, which represents non-PGM state-of-the-art ORR electro-catalysis.
- ✓ MEA/single cell study
 - Tested 13 MEAs; 8 LANL prepared
 - Varying I/C ratio to optimize performance
 - MEAs prepared using catalysts demonstrate high open circuit voltages (OCV), highest value ~ 0.96 V at one-bar hydrogen/oxygen pressures at 80°C .
 - Cell current density at 0.80 V, up to a value of 80 mA/cm^2 .



Linear sweep voltammograms in an RDE for ANL-1 and ANL-2 catalysts.



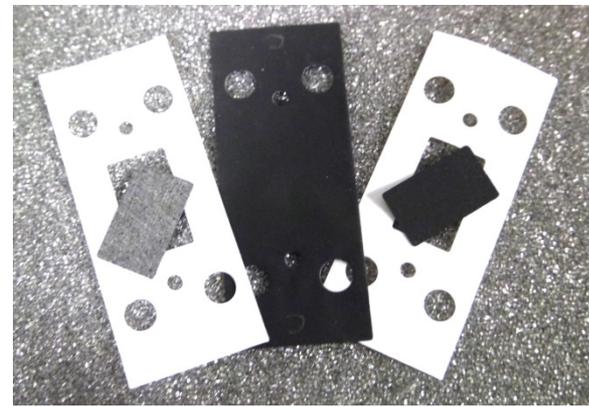
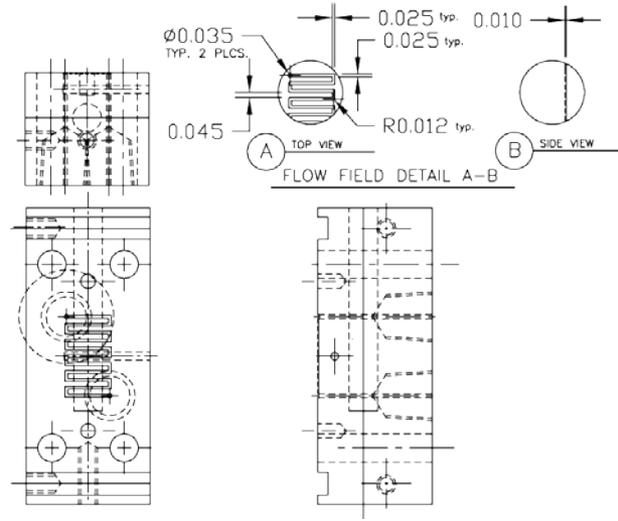
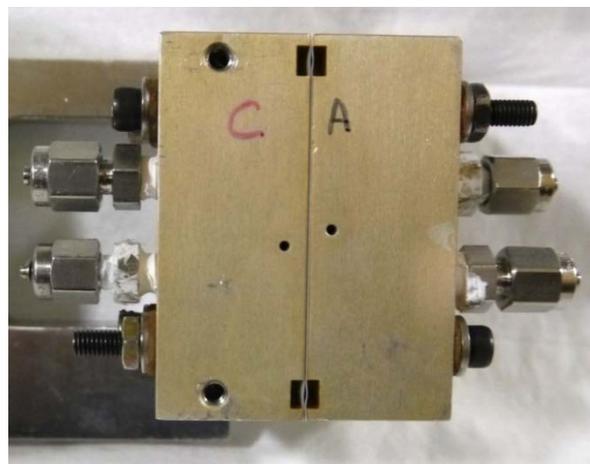
(a) Polarization curves for three representative MEAs with different ionomer-to-catalyst ratios tested at LANL; conditions: $P_{\text{H}_2} = P_{\text{O}_2} = 1$ bar (10.5 psig backpressure, accounting for the altitude of Los Alamos; 7300 feet), $T = 80^\circ\text{C}$, cathode loading 4 mg/cm^2 , Nafion[®] 212. (b) Polarization curves for two representative MEAs previously tested at ANL; conditions for blue curve: $P_{\text{H}_2} = P_{\text{O}_2} = 2$ bar (24 psig back pressure), $T = 80^\circ\text{C}$, cathode loading 3 mg/cm^2 , $I/C = 1.5$, Nafion[®] 211, no iR -correction; conditions for red curve: $P_{\text{H}_2} = P_{\text{O}_2} = 1$ bar (10 psig backpressure), $T = 80^\circ\text{C}$, cathode loading 2 mg/cm^2 , Nafion[®] 117, iR -corrected.

Approach: NIST: Using LANL Standard High Resolution Fuel Cell to measure sub 10 μm

Task: Assist in fuel cell hardware to enable higher resolution (approaching 1 micron) water measurement in operating fuel cells. Provide hardware suitable for external users.

LANL Investigators: **Dusan Spernjak, R. Mukunan, and R. Borup**
NIST: Dan Hussey and David Jacobson

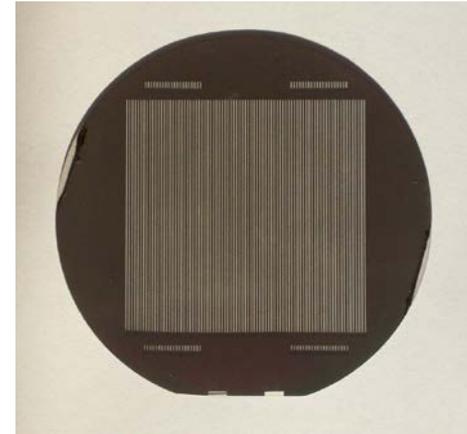
- Robust design (LANL)
 - Lots of use with neutron imaging
 - Easy to build, good performance
 - MEA can be cut from existing 50 cm² soft goods
- High resolution fuel cells
 - Porous metal foam flow fields
 - No non-uniformities from rectangular flow fields
- Gauge block spacer
 - Avoids wedge improves plane parallel



High resolution MEA water content

Grating Path Towards 1 μm Spatial Resolution

- Technique is established
 - Demonstration performed
 - Image reconstruction software developed
 - Performed two fuel cell high resolution test using different acquisition schemes
- Grating fabrication:
 - Silicon transmits neutrons and Gadolinium is a strong neutron absorber
 - Original fabrication methods did not provide a successful candidate for a grating
 - New approach to fabrication to get 10 μm of Gd
 - Thick Gd films are highly stressed
 - Multilayer approach with strike layers between Gd films will hopefully improve GD thickness
 - Current grating period is too large resulting in long image acquisition time

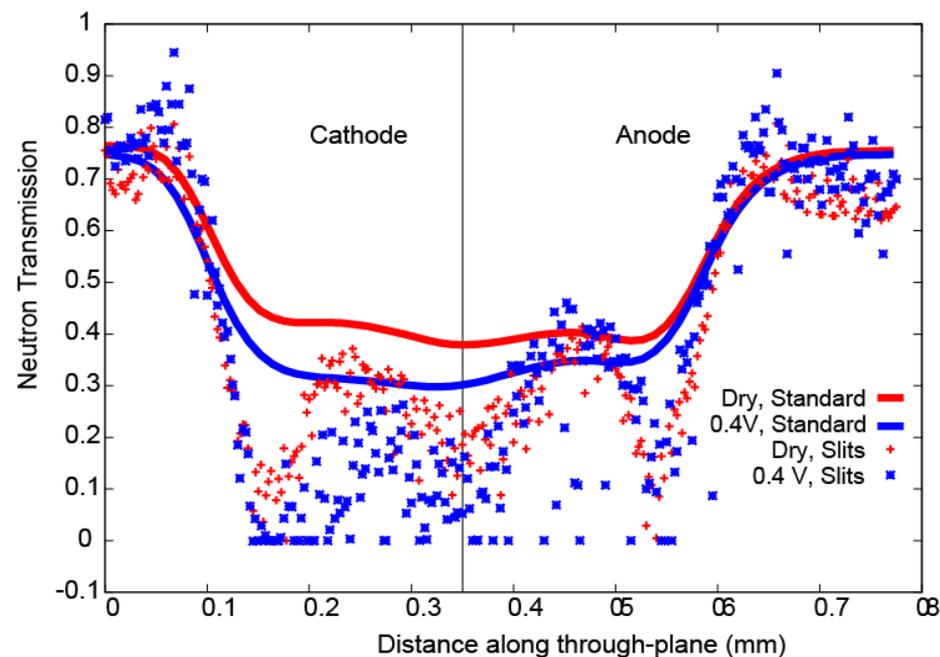
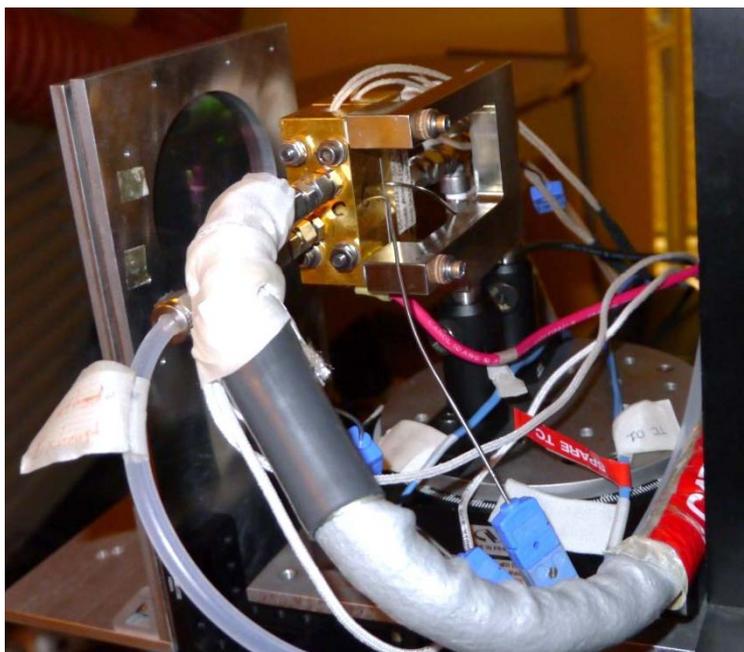


Accomplishments:

High resolution MEA water content:

First results sub 10 μm

- Used two gratings with $\sim 3\ \mu\text{m}$ of Gd, that allowed us to create a small ($5\ \mu\text{m}$) opening
- Line profiles show clearly sharper features and demonstrate need for better signal-to-noise



Line profiles from standard imaging with resolution 25 μm compared to slit method for a dry fuel cell and during operation at 0.4 V (about 2 A/cm^2)

Advent Technologies, Inc.

Task: Validate performance of high temperature MEAs and provide detailed characterizations

- Advent performed test and provided results using with their in-house testing protocol
- Advent requested LANL to validate their findings and provide feedback

LANL Investigators: Tommy Rockward and Rod Borup

Advent Technologies: Nikos Triantafyllopoulos

Status:

- Held several conference calls to discuss details of customer needs and LANL's role
- Received materials (Dec '13) from customer
- Completed modification of FC test stands (i.e. incorporated two automated peristaltic pumps for higher operating temperature humidification scheme).
- Performed several measurements on MEA (i.e. H_2 /Air, H_2 /O₂, AC impedance)

Accomplishments:

Advent Technologies, Inc.

✓ Automated liquid feed

LANL Scientists completed:

- ✓ Test stand modifications by implementing new automated liquid feed
- ✓ Agreed on testing protocol
- ✓ Began evaluating Advent MEAs

✓ Developed List of Experiments:

• Polarization Curves

- (i) Typical IV-plots using H_2/O_2 and H_2/Air
- (ii) IV-plots with 0.5, 2 and 5% CO (continuous flow)
- (iii) IV-plots with 5, 15 and 30% humidity (30 min between changing humidity for steady state)
- (iv) IV-plots with 2% CO and 5, 15 and 30% humidity

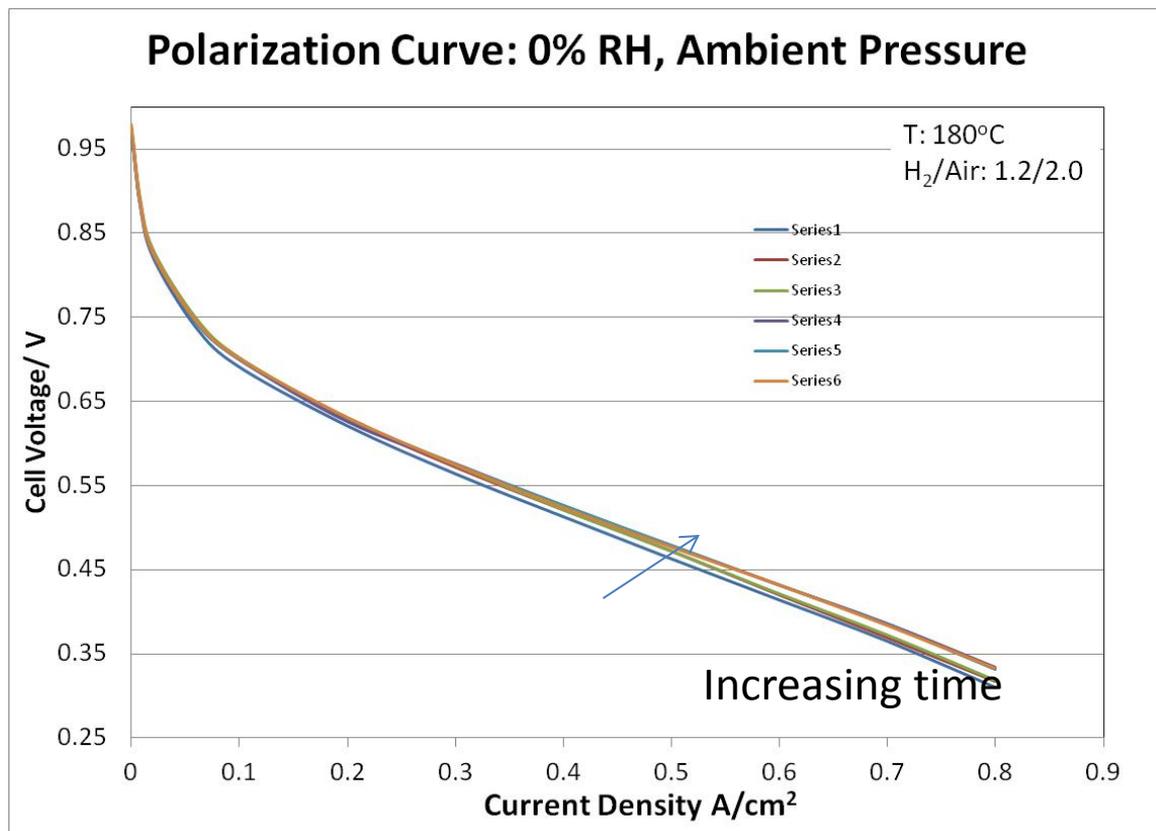
• Additional measurements

- (i) Accelerating cycling tests (membrane, catalyst)
- (ii) Cross over measurements
- (iii) EIS measurements during testing (same conditions as previous)
- (iv) Cyclic Voltammetry (N_2/H_2 , 50-1000-50 mV, 20 mV/sec, 10 cycles, measurements with dry and humidified gases)



Accomplishments:

Advent MEA: H₂/Air Polarization Curve Sample ID: 539-25-10-13



Tests Conditions:

Cell Temp: 180°C

Back Pressure: Ambient

Rel Hum.: 0 % (by-pass)

H₂/Air: 1.2/2.0 stoich

Delay: 30 sec/pt

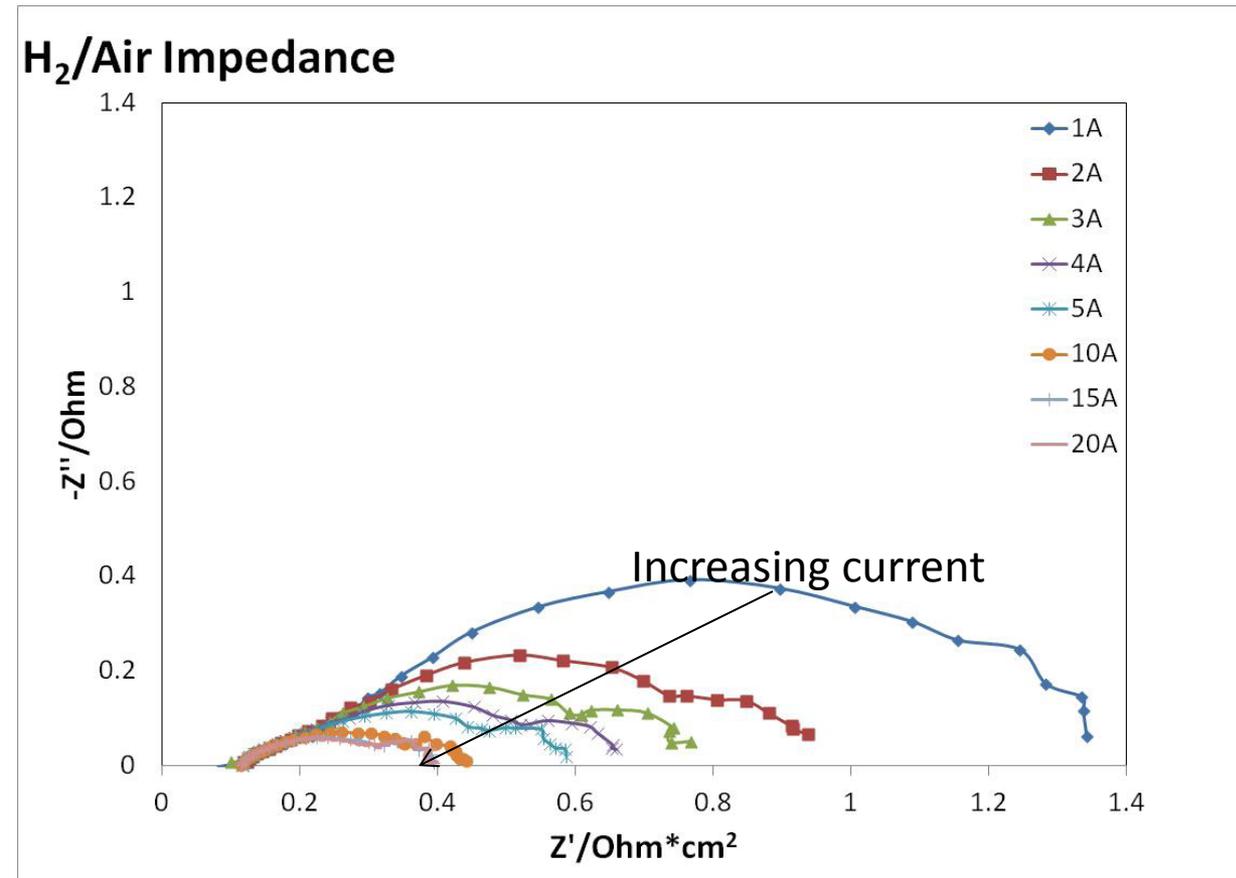
20 min between Series 1, 2, and 3
18hr delay
20 min between series 4, 5, and 6

Improvement observed over time...
This may suggest a longer break-in
is needed...

Initial Results: Lower but comparable to Advent's Pol Curves

Accomplishments:

Advent MEA: H₂/Air Impedance Sample ID: 539-25-10-13



Sample Info:

Cell Size: 25 cm²

Catalyst: 30% Pt/C

A/C: 1.47 mg/cm²

Tests Conditions:

Cell Temp: 180°C

Back Pressure: Ambient

Rel Hum.: 0 % (by-pass)

H₂/Air: 1.2/2.0 stoich

As current increases:

No increase in MTR at the elevated temps; the water formation doesn't inhibit gas access to catalyst

Speculation: Kinetic limitations and/or proton transport w/n catalyst layer

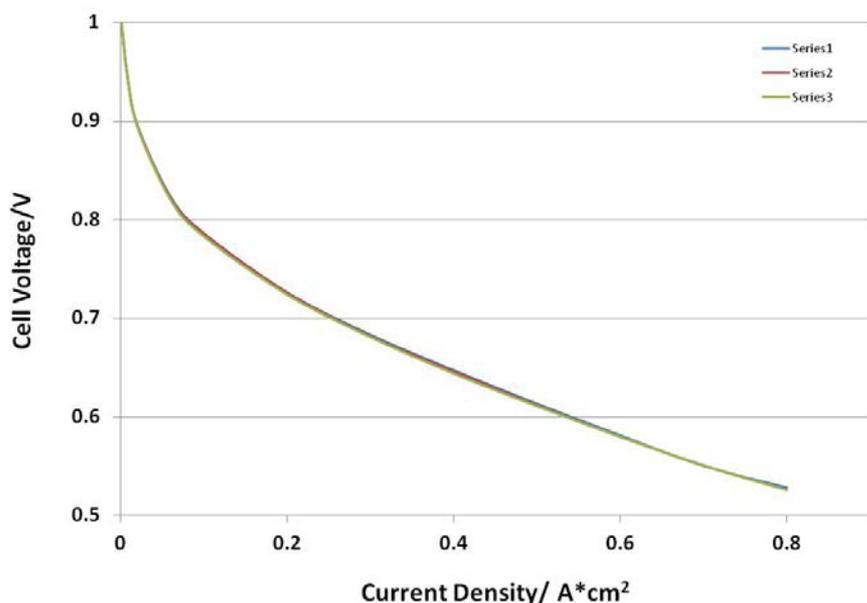
Experiments on-going

Accomplishments:

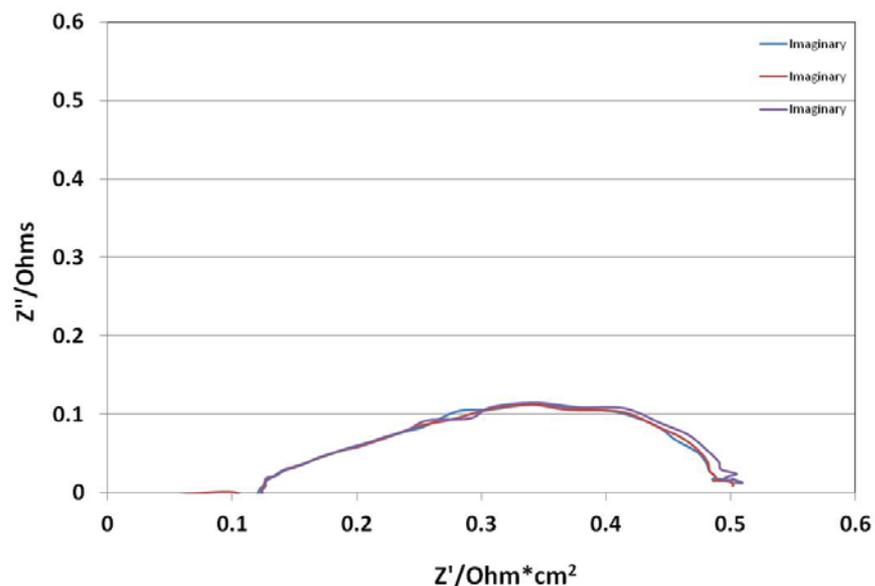
Advent MEA: H₂/O₂ Polarization Curve & AC Impedance Sample ID: 539-25-10-13

Test conditions were identical to H₂/air results but measured in the presence of pure O₂.

Polarization Curves with Oxygen



H₂/O₂ Impedance @ 5A



Similar experiments were run with O₂. Results were also comparable to Advent's. Results shown here were measured after an extended break-in period; the VI curves were identical.

Cal State Univ-Northridge

Task: Investigate the impact of hydrophobic flow plates on FC performance

- Previously completed a study with quad-serpentine flow fields (treated vs non-treated)
- Performed testing on inter-digitated flow fields plates

LANL Investigators: Tommy Rockward, Dusan Spornjak, and Jacob Valdez
Cal State Univ-Northridge: Abhijit Mukherjee

Treated flow-field plate with wax coatings
Completed FC tests with non-treated plate on inter-digitated flow fields at multiple relative humidifications.

Plain bipolar plate (graphite).



Treated bipolar plate.



Hydrophobic treatment was removed from the lands by sanding to minimize contact resistance.

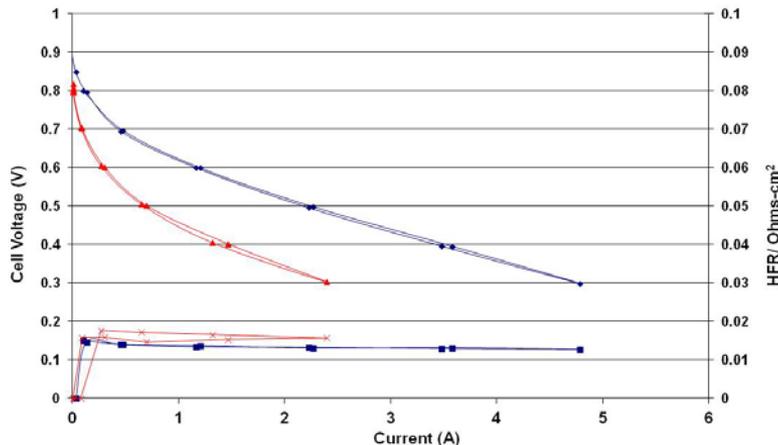
Fuel Cell Technologies and Pajarito Powders

- **Task: Troubleshoot test stands to determine the cause of performance differences on non-PGM MEAs**
 - Performance variations observed between test stands
 - Irreversible performance loss surfaces

LANL Investigators: Tommy Rockward

Pajarito Powders: Barr Halevi

Interlaboratory VIR Comparison:
Station 1 vs Station 2



Initial tests confirmed a substantial difference between test stations.

These differences are those that surface when there are:

- variations in air quality,
- de-ionized water,
- And/or humidification schemes.

Yet another possibility is test stand history:
...previously used for contamination studies?

Impact Coatings

- **Task: Evaluate fuel cell performance of novel metal bipolar plates**

LANL Investigators: Tommy Rockward, R. Borup

Impact Coatings: Mattias Samuelsson

Finalized NDA on 9/2/2013 (~ 4 months May- Sept)

Statement of Work

- Bipolar plate materials for PEM Fuel Cells, metallic bipolar plates and coatings, proper testing methodology for metallic bipolar plates for PEM Fuel Cells and post-characterization of metal plates, and fuel cell components to determine relative durability and performance of metal bipolar plates, relevant to SE 0501667-0, A CONTACT ELEMENT AND A CONTACT ARRANGEMENT; EP 1685626, COATINGS OF $M(n+1)AX(n)$ MATERIAL FOR ELECTRICAL CONTACT ELEMENTS
- 6 coated plates received Feb 2014.

Accomplishments/Status:

- ✓ XRF elemental mapping performed on samples for initial baseline
- Awaiting testing hardware from Impact Coatings

Future Work with Collaborators

- Ford Motor Co
 - Test newly developed sputtering system
 - Begin pore structure measurements & thermal conductivity measurements of laser MPL modifications
- ANL non-PGM
 - Complete testing on ANL materials and report on findings
- Advent Technologies. Inc
 - Complete High Temp MEA tests with Pt/C and start testing with Pt-Co/C.
 - Incorporate additional BOL and EOL diagnostics
- Impact Coatings
 - Perform accelerated stress tests on bi-polar plates
 - Examine materials using XRF mapping (post-testing)
- Fuel Cell Technologies and Pajarito Powders
 - Baseline materials at LANL and then test at Pajarito Powders
- Northeastern University- Boston, MA
 - Evaluate non-PGM materials for ORR electro-catalysis
- Continue interactions with DOE Working Groups
 - Durability and Mass Transport Working Groups
- Participate on DOE/USCAR U.S. DRIVE Fuel Cell Tech Team
- Provide technical assistance to developers as requested by DOE and report on results to DOE and the U.S. DRIVE Fuel Cell Tech Team

Reviewer's Excerpts

... This work was high quality characterization of fuel cell components as pertain to hydrating and water handling. This is important for the DOE for assuring performance and durability objectives. Not much innovation so progress is not directly impacted by this work but indirectly as progress depends on innovation of collaborators being served and the feedback these collaborators get from this work. Supporting the efforts of developers with unique equipment and expertise is an important role that National Labs are very well suited for.

We agree with this comment and appreciate it. We believe this project is an excellent opportunity for our team to help solve problems by various developers.

Personnel and equipment availability to DOE contractors who need this assistance to perform their work and who cannot fund these DOE-funded facilities or only need conditional assistance is an excellent idea and the interaction with working groups to advertise this capability is a very positive feature of this work.

We agree

LANL has successfully addressed several technical issues identified by DOE and other PIs. Apparatus and procedures have been developed as needed.

Most work was characterization to support others. Not much innovation.

The intent of this project is to support DOE and fuel cell developers with the state-of-the-art capabilities, and the long-term experience of the LANL staff. Thus, for this project, the vast majority of innovation should come from the work being done by the developers, unless LANL is asked to develop a new technique to support a project.

Through Technical Assistance to Developers -LANL :

➤ leverages their scientific expertise along with state-of-the-art facilities to address various technical issues,

➤ engages each customer with a detailed account of their findings, and

➤ provides feedback where necessary.

LANL scientists gratefully acknowledges the Fuel Cell Technologies Office, *Technology Development Manager*:
Nancy Garland, Ph.D.

2014 Milestones

1	Q1	12/31/2013	Regular	Provide testing support on non-PGM catalysts for Argonne on an as-needed basis.	NA
2	Q2	3/31/2014	Regular	Submit report on investigation of the initiation of anhydride formation in water transport membranes caused by impurity or air/water.	NA
3	Q3	6/30/2014	Regular	Participate on DOE/USCAR U.S. DRIVE Fuel Cell Tech Team with at least 90% attendance (in person or on phone).	NA
4	Q4	9/30/2014	Go/No-Go	Provide technical assistance to developers as requested by DOE and report on results to DOE and the U.S. DRIVE Fuel Cell Tech Team	Evaluate demand and value of task by peer review at the DOE FCTO AMR.

Experiments Complete

Experiments Complete

On-going

On-going