Technical Assistance to Developers

LANL Fuel Cell Team
Rod Borup and Tommy Rockward (PIs)

The U.S. Department of Energy 2015 Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting

June 8, 2015
Arlington,VA

Project ID: FC052

Overview

Timeline

- Project start date: 10/1/06
- Project end date:
  - Project continuation and direction determined annually by DOE

Barriers

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

Budget

- Funding received in FY14:

  $450 K
- Total funding planned for FY15:
  $532 K*

*Includes support for KIER CRADA and interactions with CEA

Partners/Collaborators

- See List

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 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 Technical 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

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FY15 Assistance Work-Scope

- Ion Power (Steve Grot)
  - Performance verification and characterization of stratified electrode layers
  - Performance verification of GDE-supported ionomer membrane
- Ford
  - Bipolar Plate
  - Catalyst development
- CEA (Commissariat à l'énergie atomique et aux énergies)
  - MEA Testing protocols and characterization
- KIER (Korean Institute for Energy Research)
  - Preparation of Ionomer Dispersion, microelectrode measurements
- Pajarito Powders
  - MEA support
- UC Merced (Abel Chuang)
  - Provided NIST hardware for high resolution imaging and sample mounting

FY15 Assistance Work-Scope

- IUPUI (Jian Xie)
  - Novel catalyst/MEA architecture, Pt/Graphene-PBI catalysts (30% Pt/PBI-Graphene)
- Argonne National Laboratory
  - Vojislav Stamenkovic: Nanoframe Catalyst Testing
  - Debbie Myers: Planned: XCT of MEAs for MEA project
- Impact Coatings
  - Verify performance of metal bipolar plates
- Amalyst
  - Non-Pt Anode Catalyst (verify performance, durability)
- Protocol development with DOE/Fuel Cell Tech Team
  - Un-mitigated Shut-down/Start-up
- Fuel Cell Tech Team Rep
- Support Working Groups
  - Durability WG
  - Mass Transport WG

Milestones

Project Plan

Milestone	Original Planned End Date
Fuel Cell Tech Team Participation	12/31/2014 complete
Catalyst synthesis support to developer - provide novel alloy supported catalysts in quantity sufficient for single cell testing	3/31/2014 complete
Measure HOR, ORR and chronoamperometry of Pt in 6 ionomer dispersions	6/30/2015 On-going
We will closely work with particular industrial contacts in an effort to validate their findings, limited to no more than 6 samples with nominal duplication of fuel cell polarization curves; within 20 mV up to 0.2 A/cm2	9/30/2015 On-going

Approach:

LANL/Amalyst

Task: Perform fuel cell tests on two different catalyst materials, verifying performance and durability

LANL Investigators: **T. Rockward and R. Borup**
Amalyst: Chris Gibbs

We will receive two sample versions of catalyst powder for fuel cells. These catalysts uses different kinds of carbon for support.
1. 40 wt% metal material on Vulcan® (AMCAT H2),
2.40 wt% metal material on Ketjen EC300 (AMCAT H2)

Status:

- Held several conference calls
- Agreed upon a test plan
- Completed a MTA - awaiting legal signatures

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Approach:

LANL/ IUPUI

Task: Perform fuel cell tests on Pt/PBI-Graphene catalysts, verifying performance and durability

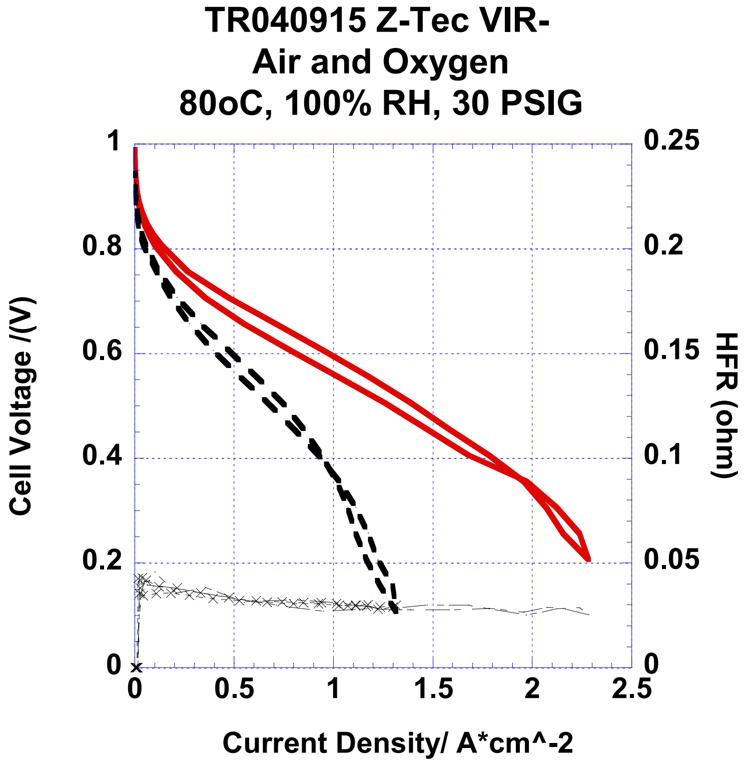
LANL Investigators: **T. Rockward and R. Borup**
IUPUI: Jian Xie

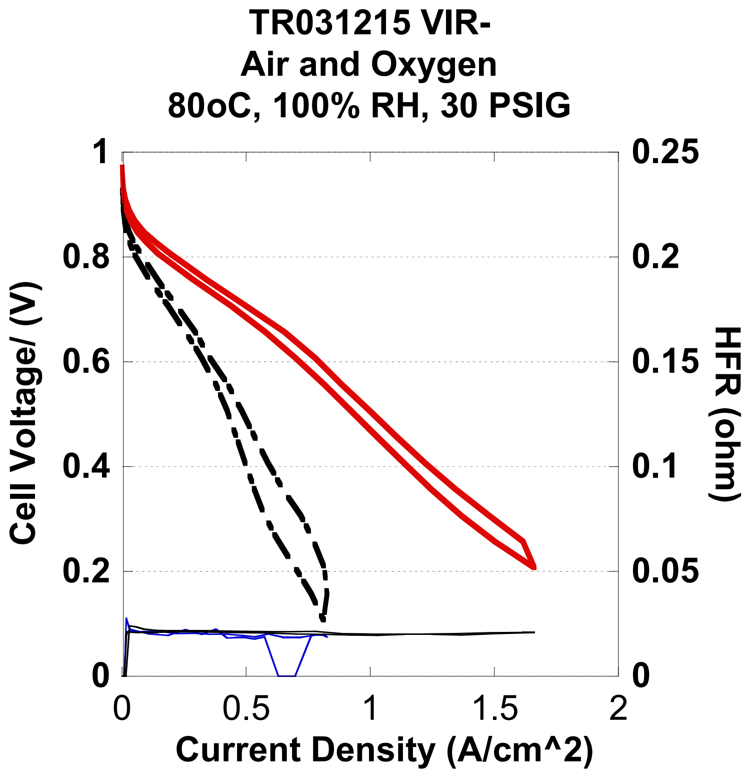
Status:

- IUPUI has synthesized Pt/PBI-Graphene catalysts.
- The catalyst is 30% Pt/PBI-Graphene.
- Currently they are fabricating MEAs (5 cm^2) with 0.1 mg Pt loading (cathode).
- LANL will perform BOT diagnostics, Performance Curves, and EOT diagnostics.
- LANL will provide a report after tests are completed.

Accomplishments:

IUPUI: Performance Curves using PBI/Graphene





- LANL performed fuel cell tests on two different samples to confirm IUPUI results.
- Results performed at LANL slightly better.

Approach:

Argonne National Laboratory

Tasks:

1: Perform XCT of MEAs for MEA project

2: To prepare novel catalyst for making MEAs and verify performance in a fuel cell. (Nanoframe Catalyst)

LANL Investigators: **T. Rockward, R. Mukundan, and R. Borup**
ANL: Debbie Myers and Vojislav Stamenkovic

- Received 8 catalyst samples
- Pre-treated all samples and prepared catalyst ink
  - More sample would allow repeat tests
- Made MEAs and tested for performance and mass activity
- New MEAs to be made with thicker/reinforced membrane to increase survivability during the break-in procedure
- Tests are on-going to obtain surface area, hydrogen cross over, and impedance spectra.

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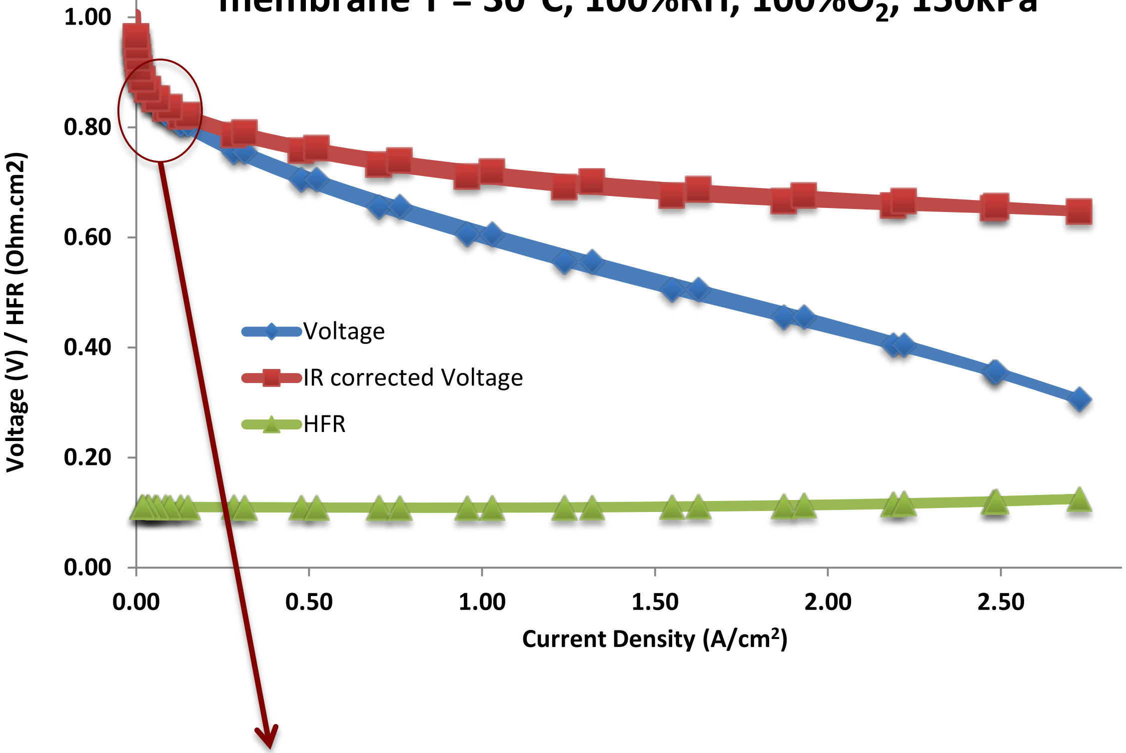
Accomplishments:

Polarization Curves in Oxygen
Mass activity @ 0.9V IR-free Polarization Curve Compared

Nanoframe (0.15mg.Pt/cm²) on DuPont™ XL membrane T = 30°C, 100%RH, 100%O$_2$, 150kPa



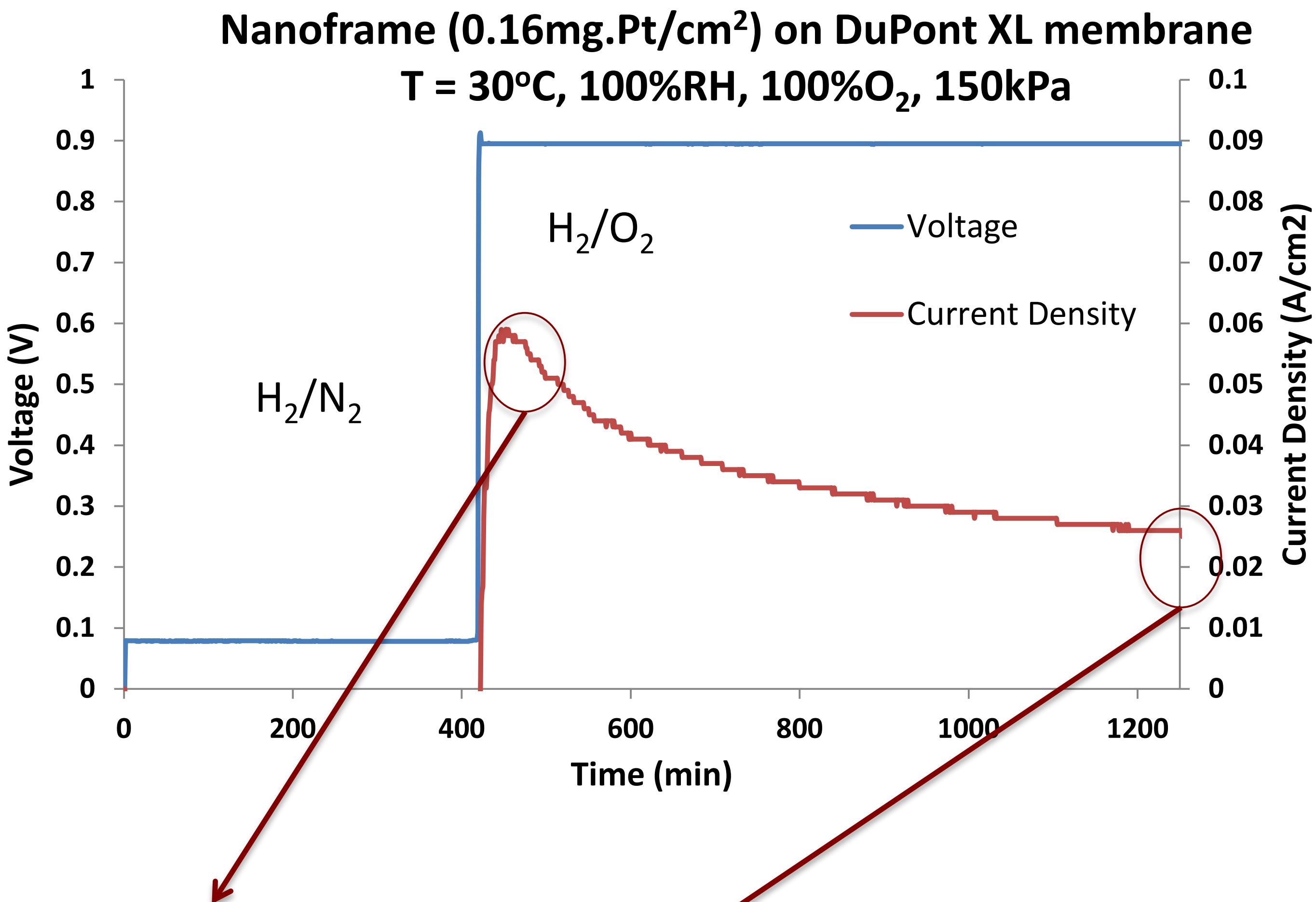
Mass activity = 0.09A/mg$_{Pt}$ (Down) and 0.11 A/mg$_{Pt}$ (Up)

80 °C Catalyst	$i^{*(0.9\ V)}_{m(T,p_{O_2},p_{H_2})}$ (A/mg$_{Pt}$)
47% Pt/C (TKK)	0.13
47% Pt/C (TKK)	0.08
47% Pt/C (TKK)	0.11
47% Pt/Vu (JM)	0.08
Not specified	0.25
20% Pt/Vu (E-TEK)	0.11
20% Pt/Vu (E-TEK)	0.06
20% Pt/Vu	0.06
20% Pt/Vu	0.02
20% Pt/Vu	0.01
20% Pt/Vu	0.01

K. C. Neyerlin, W. Gu, J. Jorne and H. A. Gasteiger, *J. Electrochem. Soc.*, **153 (10)**, A1955-A1963 (2006)

✓ Mass activity of Nanoframe catalyst @ 30 °C in an un-optimized MEA comparable to highest reported mass activity @ 80 °C of Pt catalyst

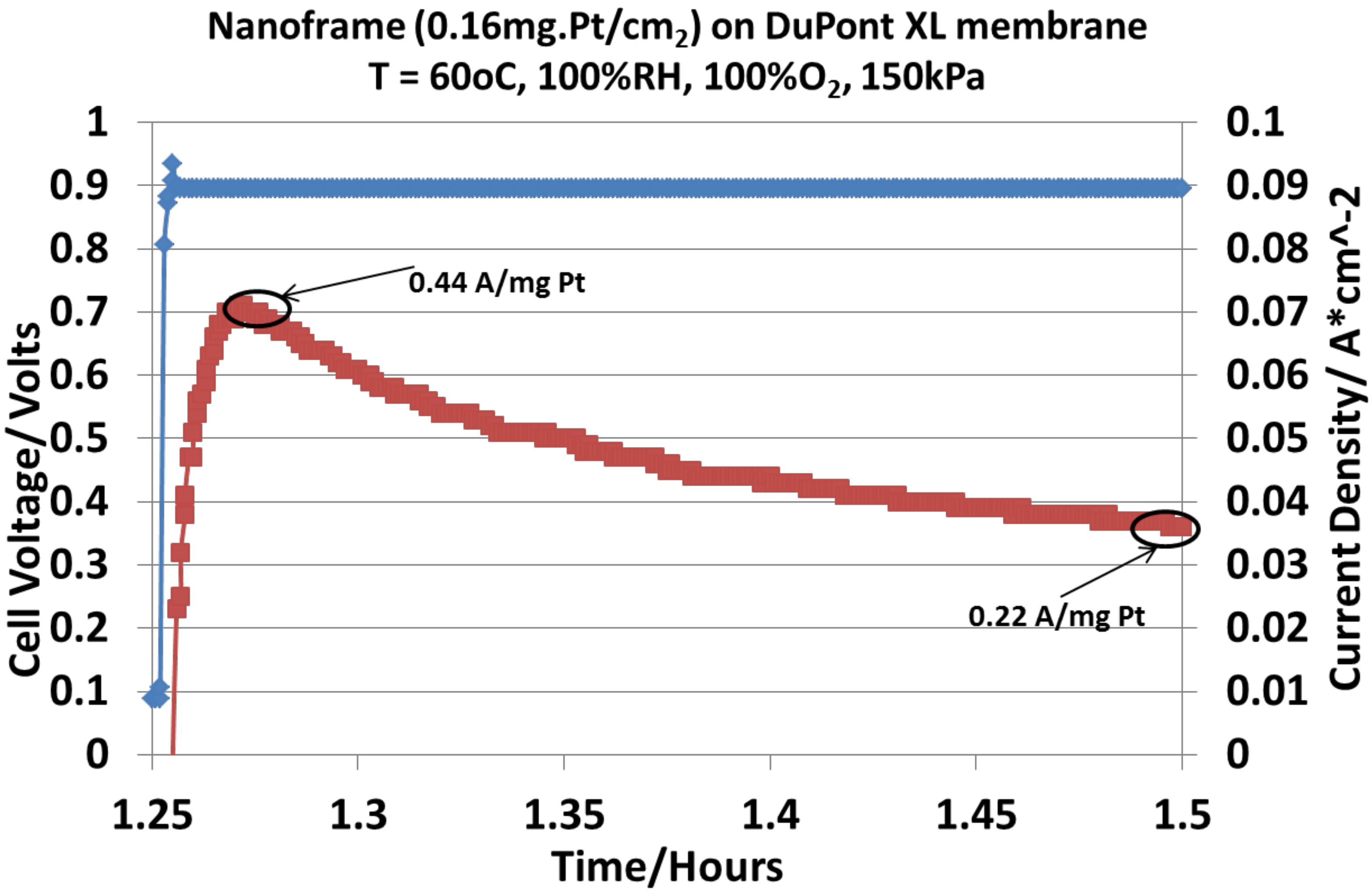
Accomplishments: Mass activity @ 0.9V IR-free 30°C



Mass activity = 0.39A/mg_{Pt} (Peak) and 0.17 A/mg_{Pt} (Steady state)

✓ Peak mass activity at 30°C of reduced Nanoframe catalyst in an un-optimized MEA is comparable to DOE target of 0.44 A/mg_{Pt}.

Mass activity @ 0.9V IR-free 60^{o}C

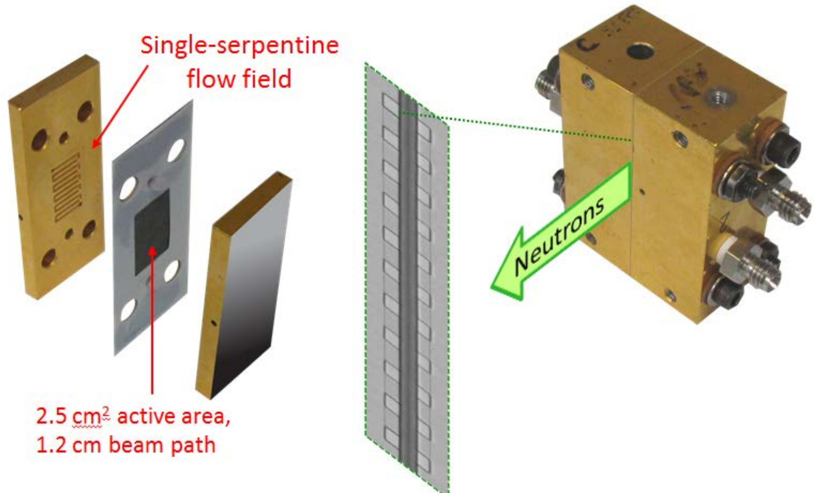


- ✓ **Nanoframe catalyst** in an un-optimized **MEA momentarily meets DOE target of 0.44 A/mg$_{Pt}$.**
- ✓ **Tests are on-going at 80^{o}C**

Approach:

Improved LANL Design of Fuel Cell Hardware for High Resolution Neutron Imaging

Task: Assist in fuel cell hardware design and testing to enable higher resolution water measurement in operating fuel cells (potentially approaching 1 micron).
Provide fabricated hardware as well as design details and technical drawings to external users.



- **Several generations of LANL-designed fuel cell assemblies**
- **Special design features to enable high-resolution neutron imaging**
- Invar holder to minimize movements due to thermal expansion

Metal foam flow field (Nuvera/LANL design)

Remove land/channel variations;
Good for membrane studies

Single-serpentine cell (Macor® spacers)

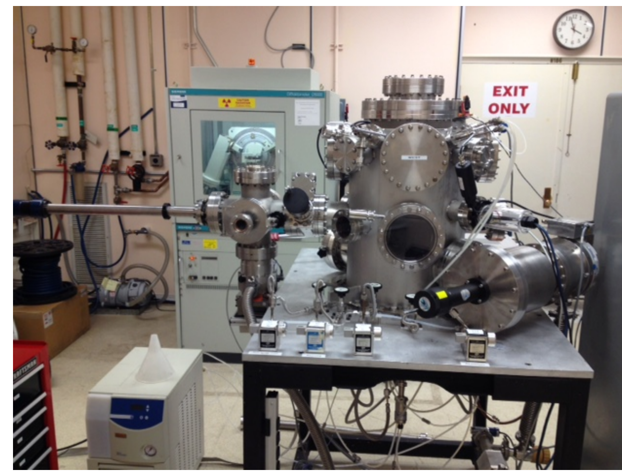
Improved alignment/parallel plates.
Good for GDL and catalyst layer studies.

Parallel channels (internal manifolds, Macor® spacers)

Improved alignment/parallel plates.
Good for differential cell studies.

Approach:

Ford Motors Co.– Metal / Ceramic coatings



Ford Motor Co. contacted LANL to pursue metal – ceramic coatings of fuel cell components.

Interest expressed in the preparation of non-corroding surfaces.

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

LANL now has 4 options / systems depending on specifics of deposition requirements.

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

1) Multi-hearth electron beam evaporation system
2) Multi-gun RF Magnetron sputtering system
   - recently upgraded with new MAK guns
3) Multi-target, on-axis sputtering system (room temperature depositions, single gun / 3 targets)
4) Newly acquired 5 gun system for reactive sputtering and multilayers > than 3 materials.

Ford

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Accomplishments:

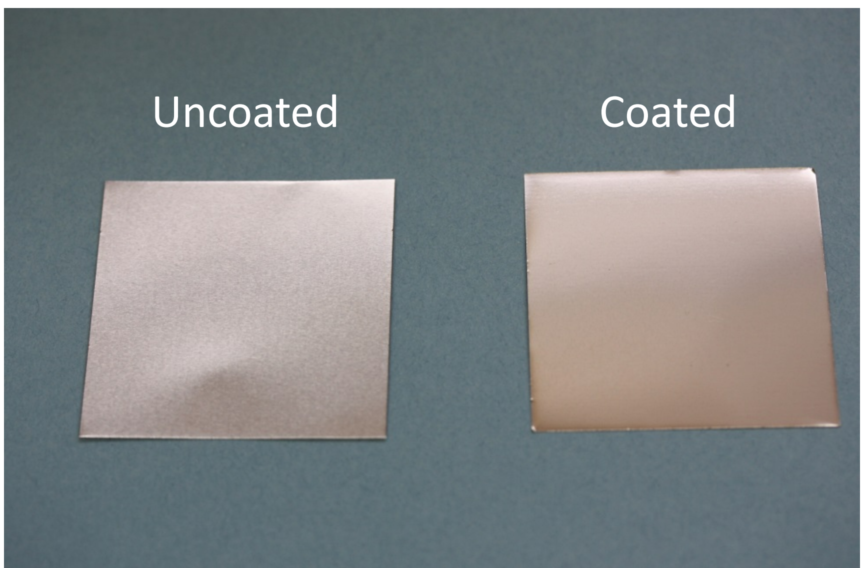
Bi-Polar Plate work for Ford

- Ford sent stainless steel coupons to test performance of coatings.
  - 316 and 304 series stainless (March 2014)
- 1st round : deposit metal bi-metal multilayers
  - Use multi-target sputter system to switch between targets without breaking vacuum.
  - Use existing system calibration rates for this system.
  - Work was performed on this task concurrent with new NDA.
- Characterized properties of support material.
- Tested several cleaning, surface pretreatment methods.

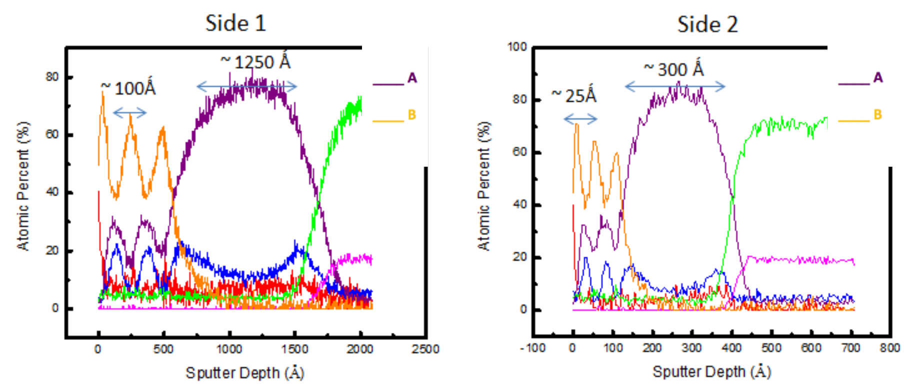
Accomplishments:

Bi-Polar Plate work for Ford

- Cleaned and prepared stainless coupons
- Prepared 14 samples on both 316 and 304 stainless steel
- Ford looked at thicknesses using Auger spectroscopy and confirmed previous sputter rates too high to achieve desired tolerances.
- Recalibrated sputter rates and repeated multi-layer sequence (QTR 1, FY15).



LANL BPP S2 Baseline



Thickness of layer A is substantially greater on side 1. Recalibration of sputter rates required.

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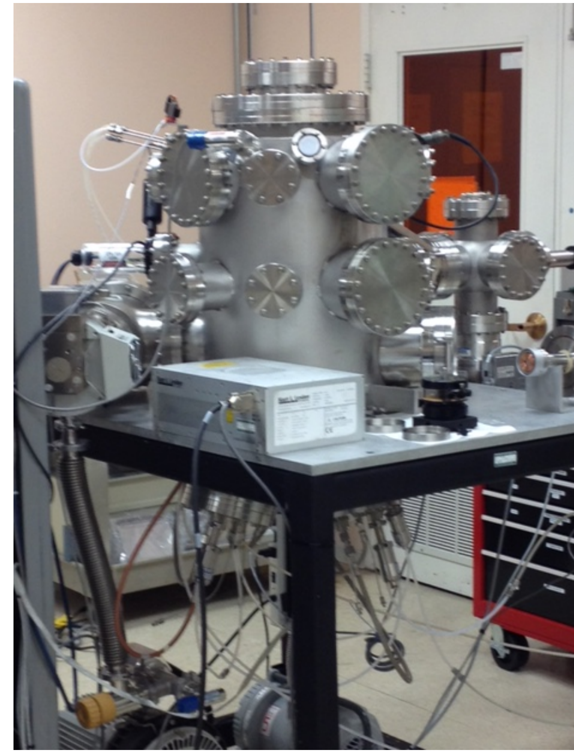
Accomplishments:

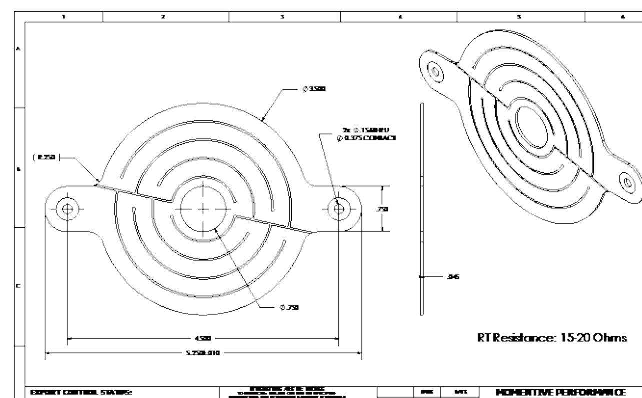
Bi-Polar Plate work for Ford

- Prepared additional Sequence #1 multilayers and delivered to Ford Motor Co. in December 2014.
  - Used new sputter system calibration.
  - Awaiting thickness analysis results from Ford.
- Began preparation of inverted multilayer series configuration, Sequence #2.
- Delivered a total of 14 samples to Ford by end of calendar year plus extra samples that remained at LANL.
- QTR 2, FY15: Ford requested a series of 21 different configurations of bi-metal multilayers on stainless steel.
- Fundamental Parameters (FP) thin film XRF analysis method created to quantify metal loadings before transfer to Ford.
- As of start of QTR 3/FY15, 8 samples in the series completed with all samples due to be finished by end of QTR3.

Accomplishments: Catalyst Support Coating

- Working with Kerrie Gath on this part of the project.
- Added work scope to new Bilateral NDA with Mark Ricketts.
- Prepared Chladni plate hardware and tested concept with alumina and carbon powders outside vacuum system.
- Acquired dedicated vacuum system from TA-46 location and moved system to TA-3.
  - Installed power, water requirements and tested vacuum system.
  - Acquired new 2” Pt target for new 2” MAK RF Sputter gun (from ceramic supports FC project) to be dedicated to this work.
- Received special BN heater to accommodate Chladni plate and attachment to acoustic motor - worked with MOMENTIVE Corp. to fabricate.
- Received support material from Ford. Performed high precision TGA / MS experiments to characterize and determine pre-sputter treatments.
- **Present status of work:** Construction finished, break-in of new target and vacuum testing started. Sample tower construction complete. Presently making electrical pass-throughs testing Chladni driver in vacuum. Testing heat shield to protect acoustic motor from IR radiation.





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Ford

Approach:

Ion Power, Inc.

Tasks:

- Characterize textured MEAs using X-ray Tomography, SEM, and XRF
- Evaluate fuel cell performance and durability
  - *Ion Power is switching to a lower cost transfer substrate, which leads to a stratified catalyst layer on the so-called textured MEAs*
  - *Perform X-Ray Tomography to characterize the stratification level (density variations vs surface texture)*
  - *Run fuel cell performance comparisons between the baseline IP CCM (without stratified catalyst layer) and the textured IP CCM (with stratified catalyst layer)*

- Characterize Kapton®-framed, ionomer-coated GDEs using imaging and Accelerated Stress Tests to verify performance and durability as a low-cost MEA option
  - *Conduct performance testing*
  - *RH cycling, and RH cycling in air to measure durability without any reinforcement.*

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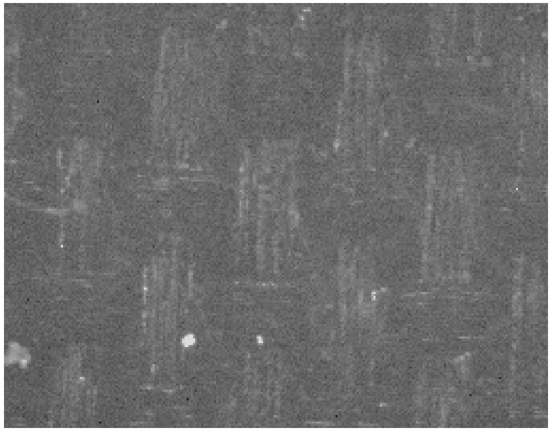
Accomplishments:

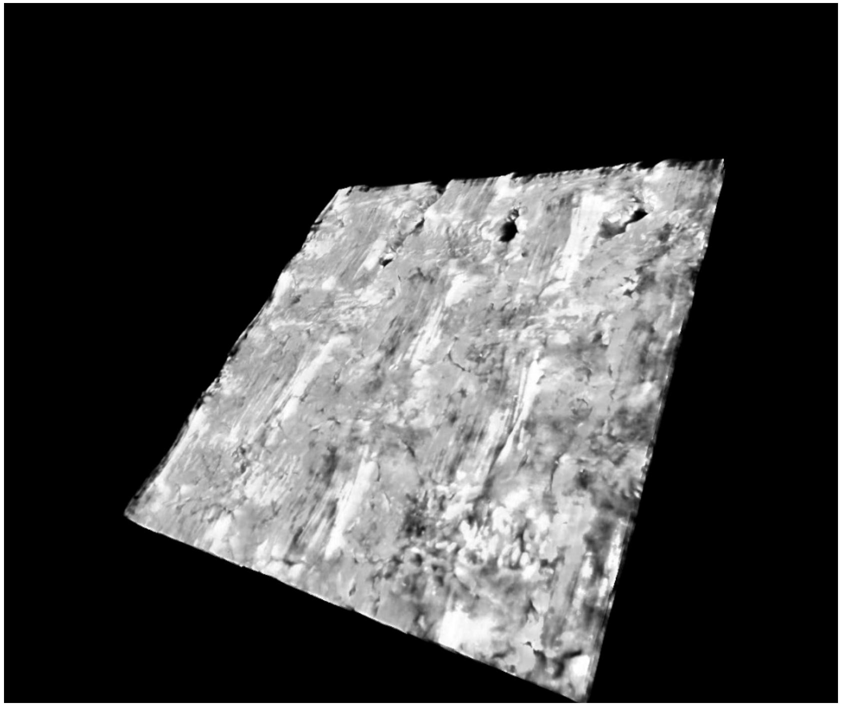
Ion Power Textured MEAs

X-Ray Tomography, SEM and XRF



Optical image showing texture in the catalyst layer

Overall loading Pt/cm^2 uniform, identical to baseline MEA



Tomography results show stratified catalyst layer (textured MEA) which is consistent with observations from optical/SEM images.

Pt Loading = 0.3 mg.$_{Pt}$/cm^2

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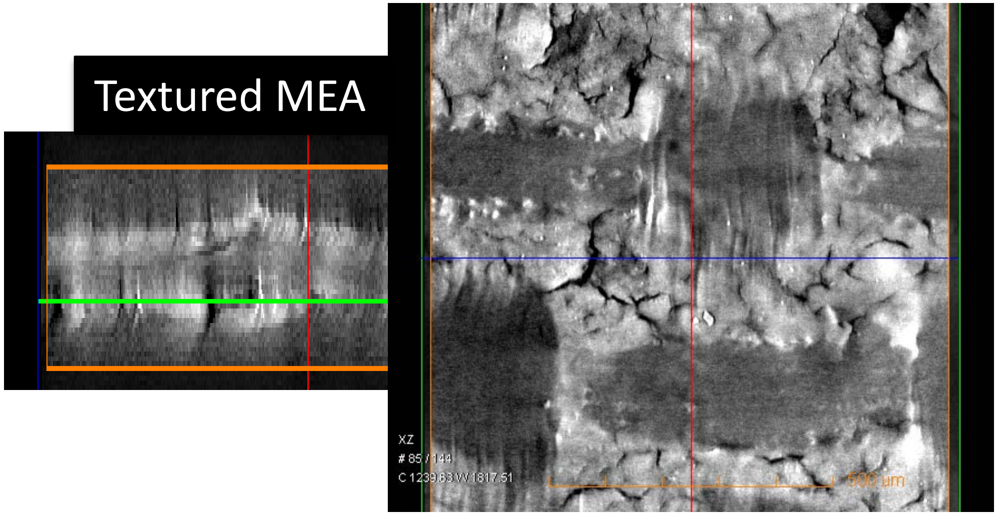
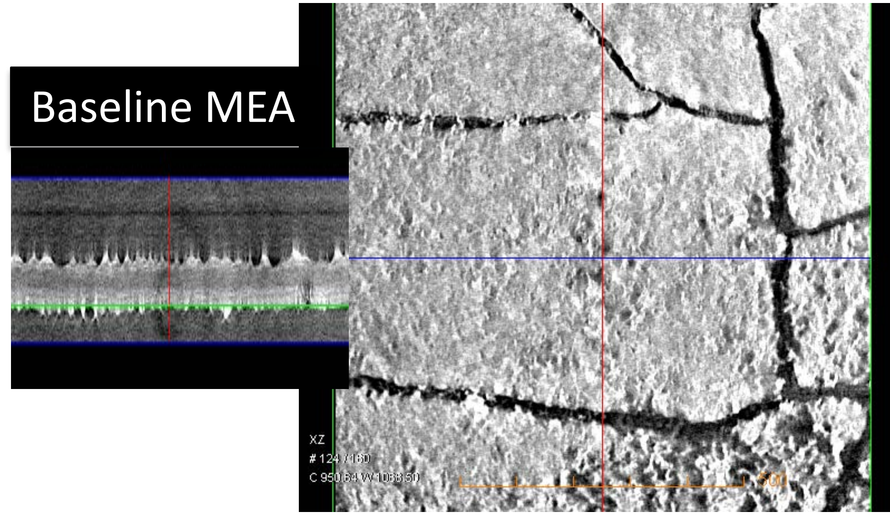
Accomplishments:

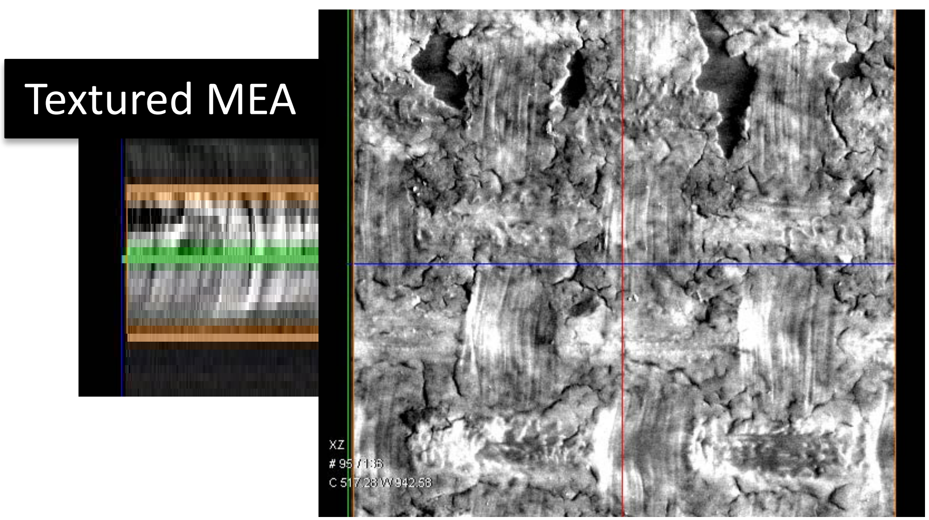
Ion Power MEAs:
MEA Cross-sections from tomography

XCT of stratified catalyst layers



XCT of baseline catalyst layers





X-Ray tomography comparison of stratified catalyst layers (textured, wavy MEA) compared to the baseline MEA fabrication (no texturing or waviness).

Visible density variations in the stratified catalyst layer correspond to optical texturing.

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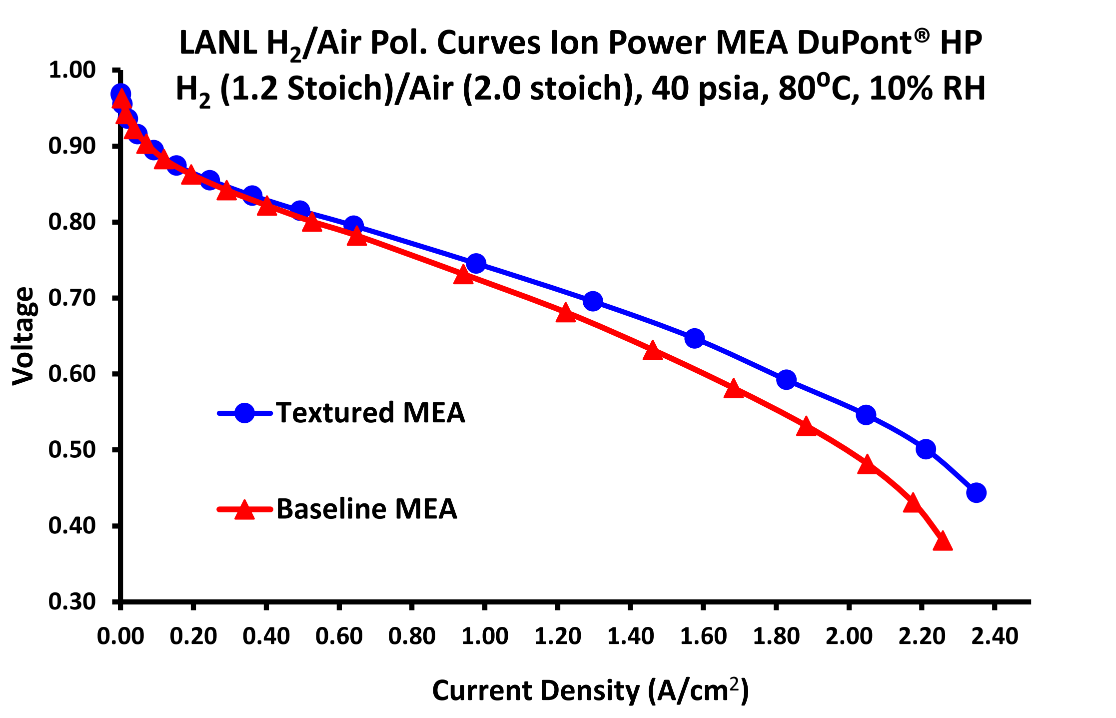
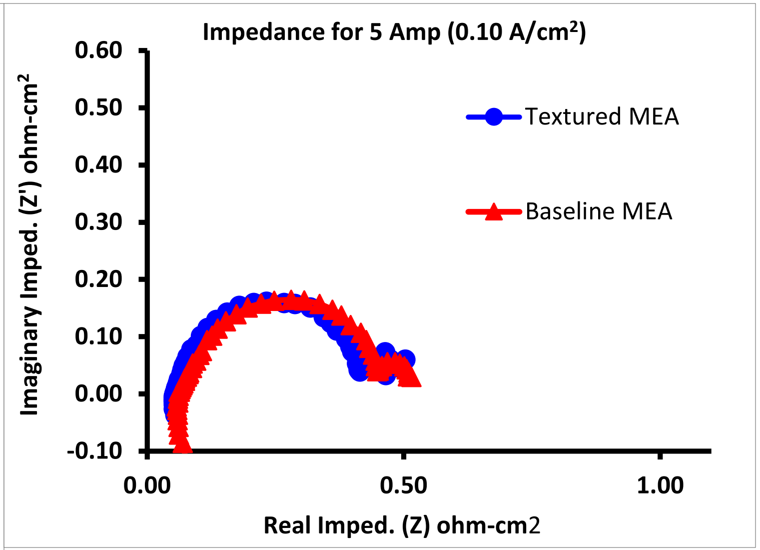
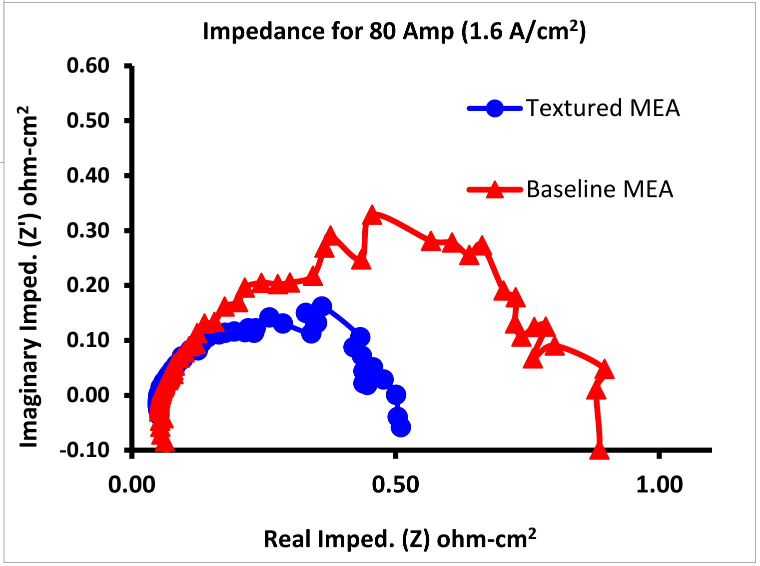
Accomplishments: Ion Power MEA Process Comparison – VI Performance







VIs indicate **textured MEAs** perform better than baseline MEAs at the higher current densities.

Impedance measurements confirm lower mass transport losses in textured MEAs while the kinetic region of both MEAs are identical.

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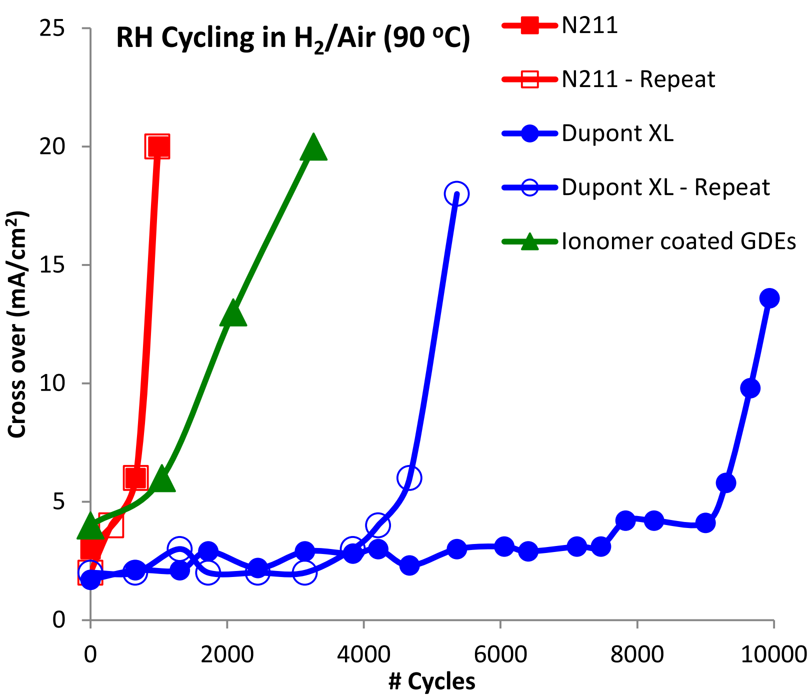
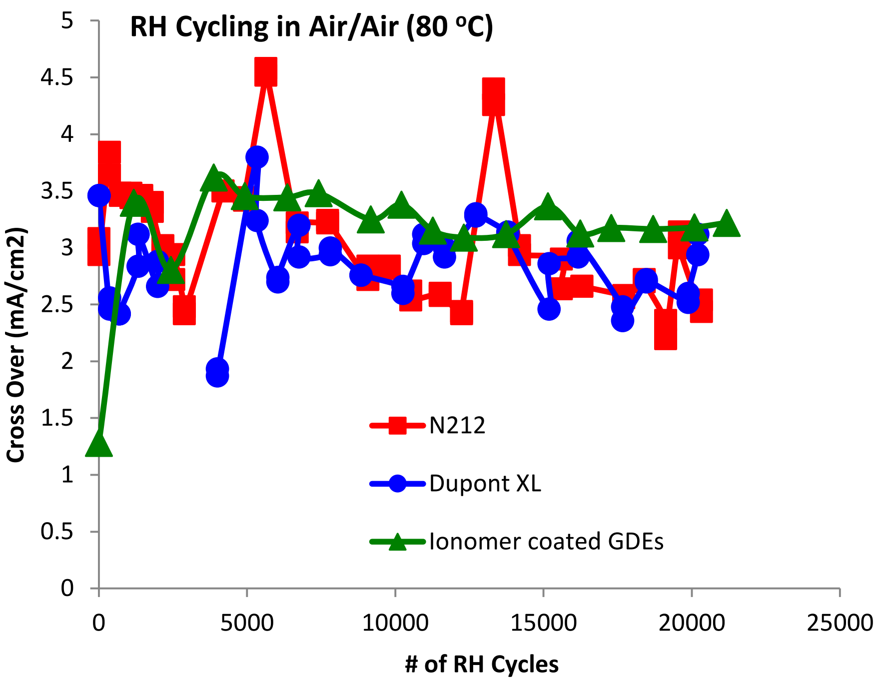
Accomplishments: Ion Power MEA using Ionomer coated GDEs





- Performance under H_2/Air RH cycling is better than N211 but inferior to chemically stabilized DuPont™ XL
  - No Chemical Stabilization in Ionomer coated GDEs.
- Excellent durability during RH cycling test recommended by FCTT

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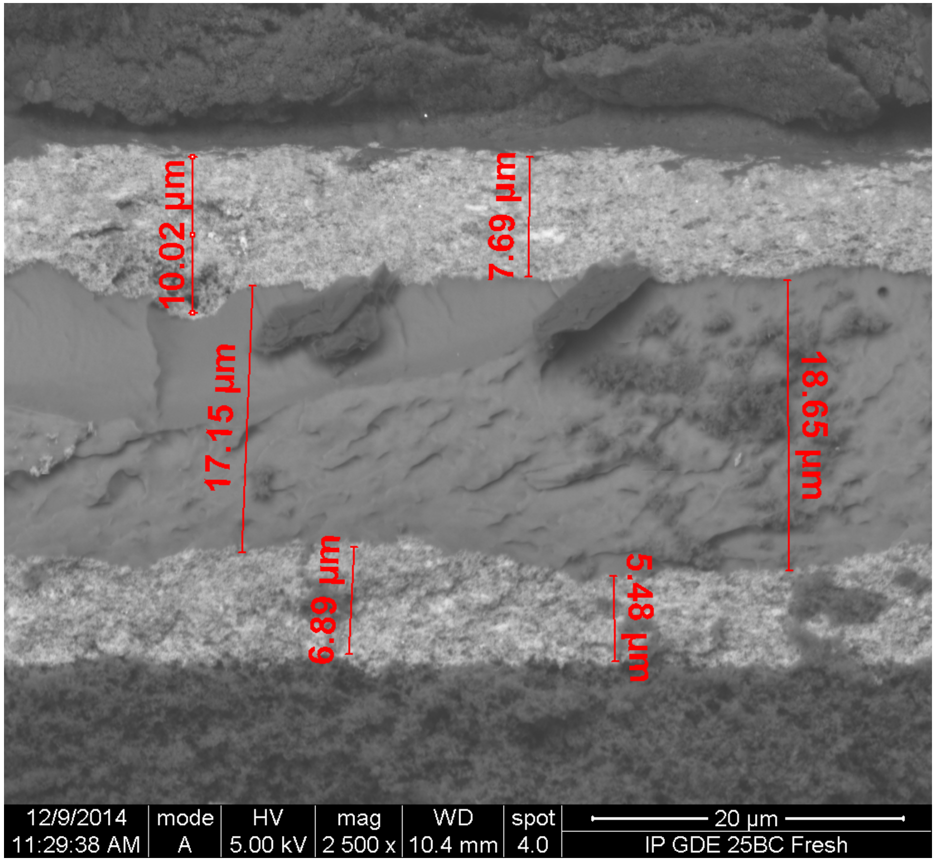
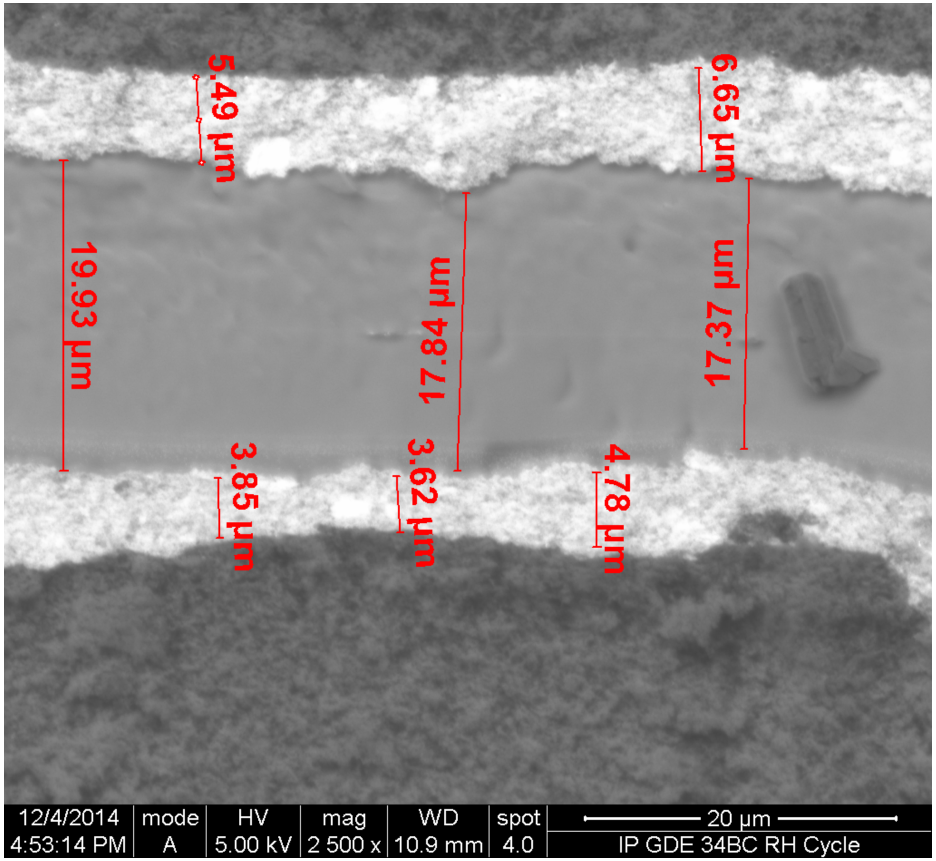
Accomplishments:

SEM X-Sections – Kapton® Framed Ionomer coated MEAs

Fresh



After RH/OCV Testing



- Little to no global thinning of ionomer layer observed
- Mechanical structural defects not observed
- Failure probably due to localized effect

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Approach:

LANL-KIER (Korea) Collaborations

Collaboration objective

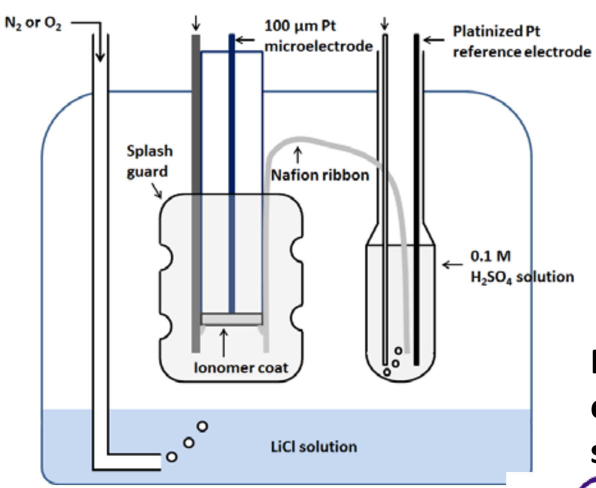
Understand Interfacial Behavior at the Pt Catalyst-Ionomer Interface in PEMFC Electrode

Focused area

LANL (PI: Yu Seung Kim)	**KIER** (PI: Sung Dae Yim)
❑ Microelectrode/RDE studies (FY14-16); ❑ Neutron scattering analysis (FY15) ❑ Fuel cell testing (FY15-16)	
❑ Hydrocarbon and perfluorinated ionomer preparation (FY14) ❑ MEA durability analysis (FY15-2016)	❑ Pore structure-controlled catalyst supports (FY15) ❑ Control of electrode structure by catalyst supports (FY15-2016)

Major collaboration activities

- ***Kick-off meeting and visits**: Dr. Kim's visit to KIER (June 9-12, 2014); Dr. Yim's visit to LANL (July 31-August 4, 2014)*
- ***Material preparation**: Perfluorinated ionomer dispersion in water (completed and shipped 3 times to KIER); Hydrocarbon ionomer dispersion in water (completed and shipped to KIER)*
- ***Microelectrode/RDE experiments**: Instruments set-up was completed both at LANL and KIER (Sep. 2014)*



Micro-electrode set-up

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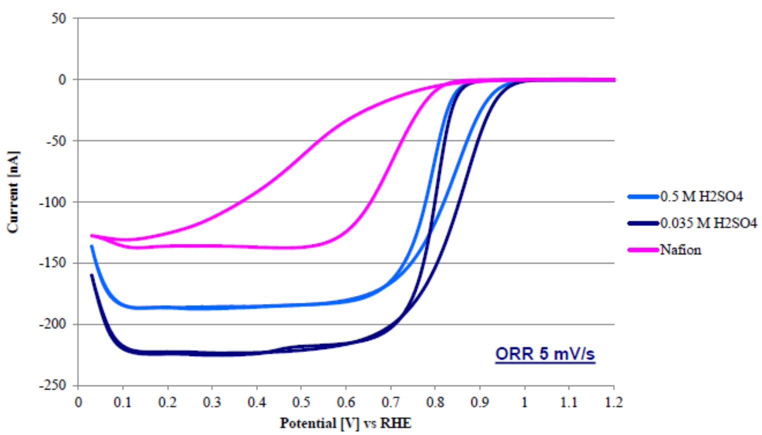
Accomplishments: Effect of Electrolyte Structure on Pt ORR Activity

Comparison of Pt ORR activity in H_2SO_4 and Nafion® solutions*



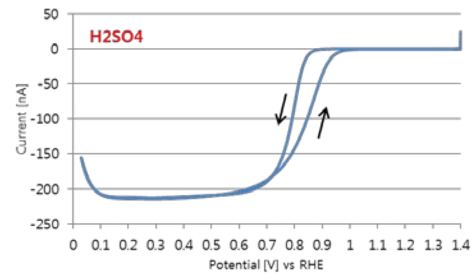
	0. 5 M H2SO4	0.035 M H2SO4	Nafion Solution
Half wave potential	0.827 V	0.844 V	0.700 V
Onset Potential	1.095 V	1.065 V	0.921 V

- ❑ Pt ORR behavior in Nafion® solution is much inferior to those in H_2SO_4 solution and shows substantial hysteresis
- ❑ The hysteresis seems to be related with perfluorinated sidechain structure (further study is required)

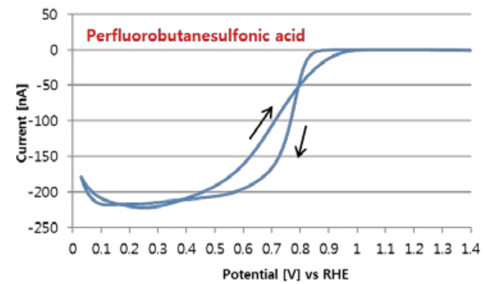
* 0.035M Nafion® in pure water is prepared from LANL method (US 7981319)

Effect of molecular structure on ORR hysteresis

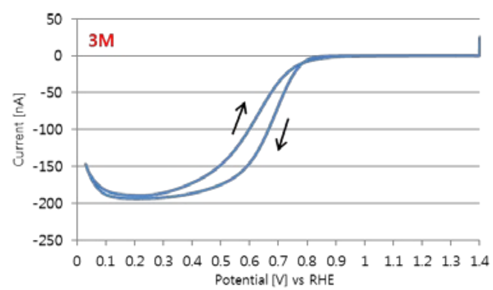
Number of sidechain molecules



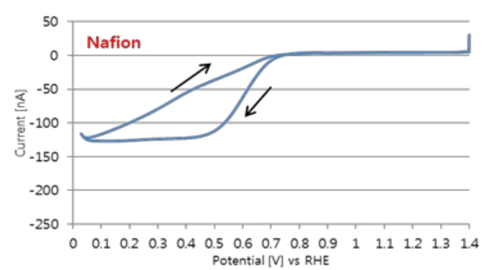
1 (one H)



4 three CF_2 and one CF_3



5 one O and four CF_2



7 Four CF_2, two O and one $CFCF_3$

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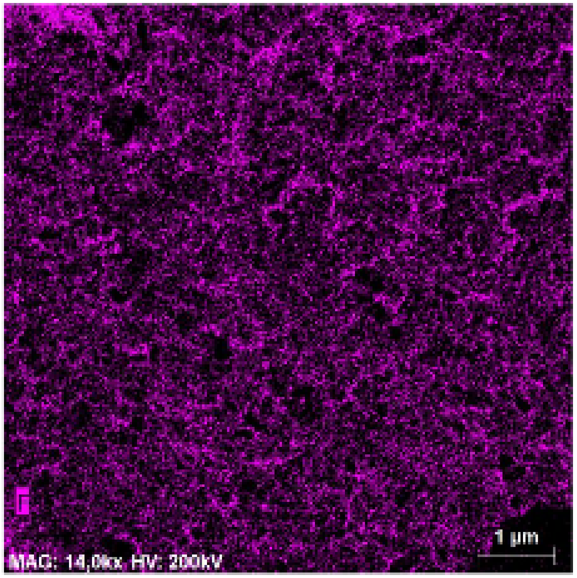
MEA Characterization With CEA - Ionomer Mapping

Ionomer Content Comparison in Aged MEAs

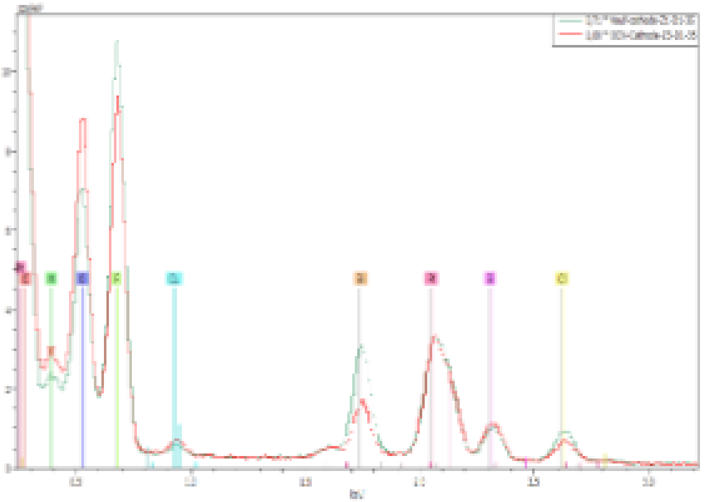
Comparison of the F at.% relative to Pt in fresh cathode and OCV MEA cathode

Fresh MEA

at. % : F: 88 - Pt: 12

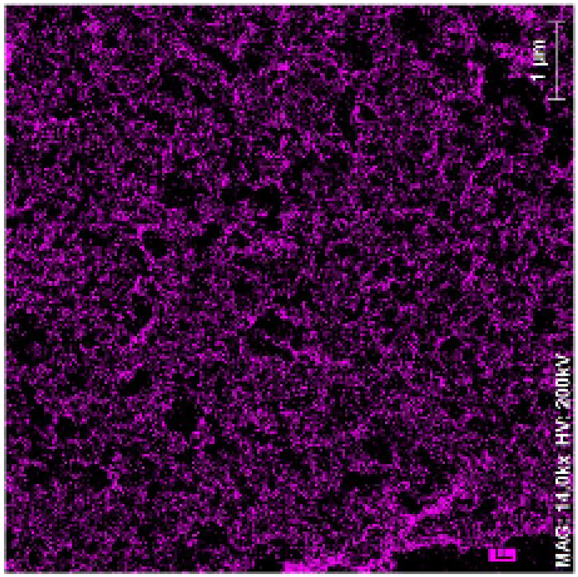


Comparison of the 2 spectra extracted from the 2 cartographies (fresh and OCV)



OCV MEA

at. % : F: 87 - Pt: 13



In OCV aged MEA, there is only a maximum of 3% less of F compared the fresh MEA (3/85=3%) .
This difference is in the F at% incertitude measurement (%F measurement in TEM sample strongly depends on the TEM specimen thickness due to F X-Ray absorption and also decreases with electron irradiation).

We did not observed any significative F content difference between the fresh and OCV MEA

DE LA RECHERCHE À L'INDUSTRIE cea

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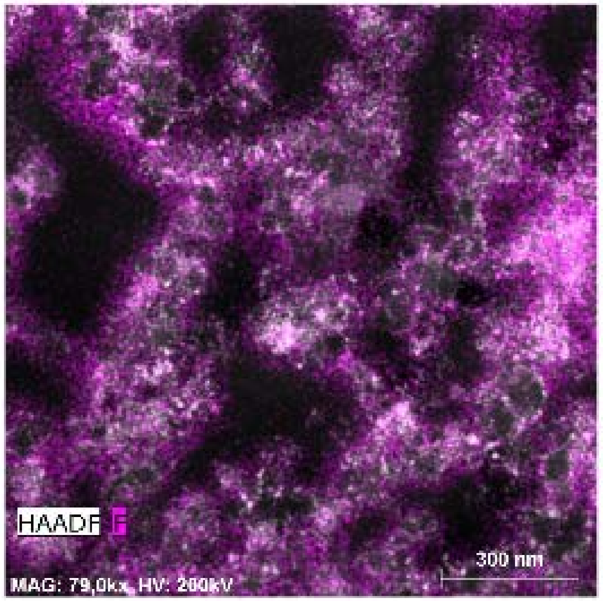
MEA Characterization With CEA - Ionomer Mapping

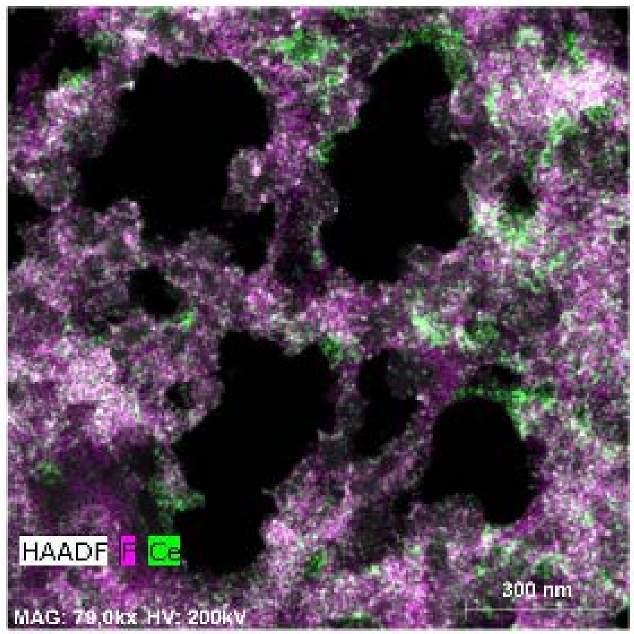
OCV MEA cathode

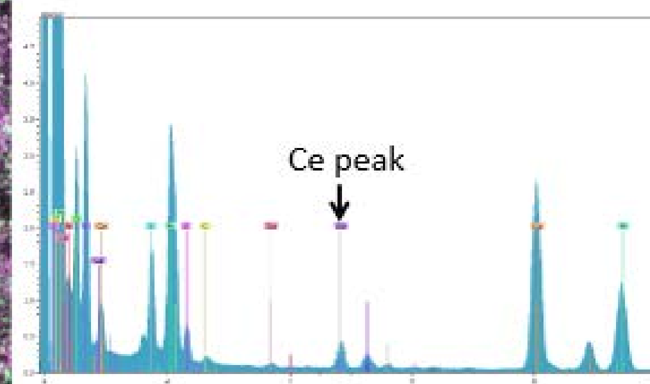
Fluor elemental X-EDS map

We can see the Nafion layer (in pink) around the Pt/C particles



In some zones (only where there is no resin – why ??) Ce (in green) is observed inside the Nafion layer





- Interesting localized interactions of Cerium and catalyst/ionomer
  - Cerium localized where sample didn't 'wet' with epoxy
  - Where epoxy wets are likely the more hydrophobic regions
  - Thus where cerium is localized are the more hydrophilic regions

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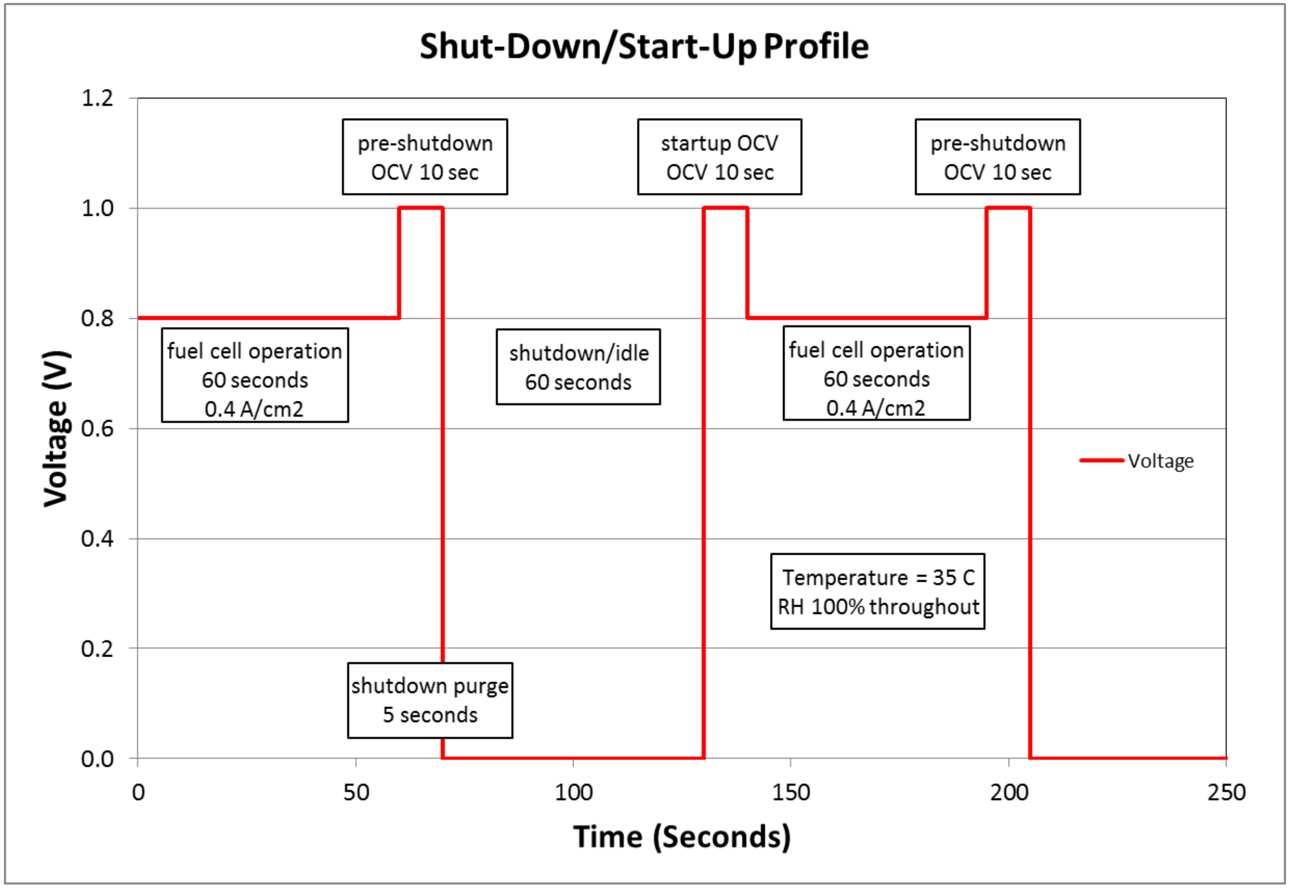
Developed Protocol to Define Un-Mitigated Shut-down/Start-up Durability with DOE FCTT



Characterization performed at: 0, 500, 1000, 1500, 2000, 4000, 5000 cycles

Targets:

(< 5% change in voltage at 1.2 A/cm^2)

Guidelines:

After removal of reversible losses:

(< 20% change in ECSA)

(< 5% change in HFR at 0.02 and 1.2A/cm^2)

(< 10% change in LFR at 0.02 and 1.2A/cm^2)

On-Going and Future Work with Collaborators:

- Ford Motor Co.
  - Presently making electrical pass-throughs testing Chladni driver in vacuum. Testing heat shield to protect acoustic motor from IR radiation.
- Amalyst
  - Non-Pt Anode catalyst (verify performance, durability)
  - **Awaiting legal agreement**
- IUPUI (Jian Xie)
  - Novel catalyst/MEA architecture
  - Pt/Graphene-PBI catalysts (30% Pt/PBI-Graphene)
  - Received 0.1 mg Pt loading (cathode) - 5 cm^2 MEA
  - **Continue Testing MEAs**
- ANL - Debbie Myers
  - XCT of MEAs for MEA project
  - **exploring agreement from Johnson Matthey on ANL's side**
- Impact Coatings
  - Verify performance of metal bipolar plates
  - **Received one version of hardware; need revised version for fuel cell testing**
- ANL - Vojislav Stamenkovic
  - **Continue Nanoframe Catalyst Testing**
- Participate on the DOE/USCAR U.S. DRIVE Fuel Cell Tech Team Rep
- Continue to support DOE Working groups
  - Durability WG
  - Mass Transport WG
- Provide technical assistance to developers as requested by DOE and report on the results to DOE and the US DRIVE Tech Team

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