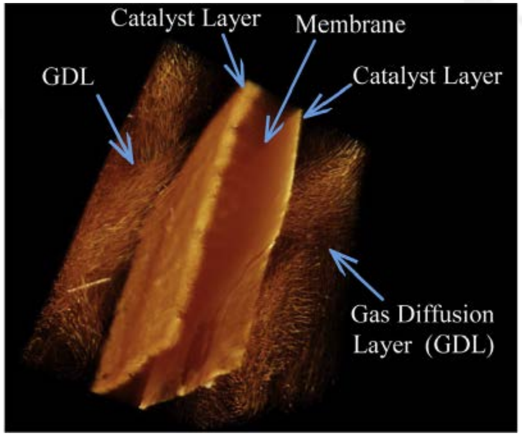
Technical Assistance to Developers

LANL Fuel Cell Team

Rod Borup and Tommy Rockward (PIs)



The U.S. Department of Energy
2016 Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting

June 8, 2016
Washington, D.C.

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 FY15: $532 K
- Funding received in FY16: $550* K

*Includes $100k for Direct support to DOE by J. Spendelow

Partners/Collaborators

- See list on slide 4

Outline

- Partners/Collaborators List
- Relevance/Approach
- FY 16 Work-Scope
- Milestones
- Approach/Accomplishments per Customer
- Summary
- On-Going Collaborations/Future Direction
- Acknowledgements

Partners/Collaborators

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

ElectroChem, Inc.

Ford

Ion Power

Amalyst

NISSAN GROUP OF NORTH AMERICA

NISSAN

PAJARITO POWDER FUEL CELL CATALYSTS

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

IUPUI

Argonne NATIONAL LABORATORY

JM Johnson Matthey

USDRIVE

DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

Relevance/Approach

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 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

FY16 Assistance Work-Scope

- Ford Motor Co.
  - Bipolar Plate
  - Catalyst development
- Pajarito Powder
  - Non-PGM MEA testing
- IUPUI (Indiana University-Purdue University Indianapolis)
  - Novel catalyst/MEA architecture
  - Test several families of MEAs
- Amalyst
  - Non-Pt Anode Catalyst (verify performance, durability)
- Nissan
  - Novel MEA analysis for Nissan by 3D XCT
- Savannah River National Laboratory (SRNL)
  - Testing and validation of non-PGM
- ElectroChem, Inc.
  - ElectroChem EFC-IFF-50 Fuel Cell Stack Validation
- DOE/U.S. DRIVE Fuel Cell Tech Team Representative
- Support Working groups
  - Durability WG
  - Mass Transport WG
- ANL/JMFC
  - 3D imaging of MEA samples

Milestones

Milestone Name/Description	Date	Type
Finish Evaluation of Amalyst non-Pt Anode catalyst	12/31/2015	Quarterly Progress Measure (Regular)
Analysis of novel MEAs for Nissan (3D XCT, electrochemical impedance)	6/30/2016	Quarterly Progress Measure (Regular)
Advanced characterization by 3D imaging for ANL/JMFC project of MEA samples	3/31/2016	Quarterly Progress Measure (Regular)
Fuel Cell Tech Team participation with minimum of six tech team meetings in person and reports on results of tech assistance to developers.	9/30/2016	Annual Milestone (Regular)

Approach: Amalyst non-Pt Anode Catalyst

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

Two versions of catalyst powder for fuel cells.

These catalysts use different kinds of carbon for support.

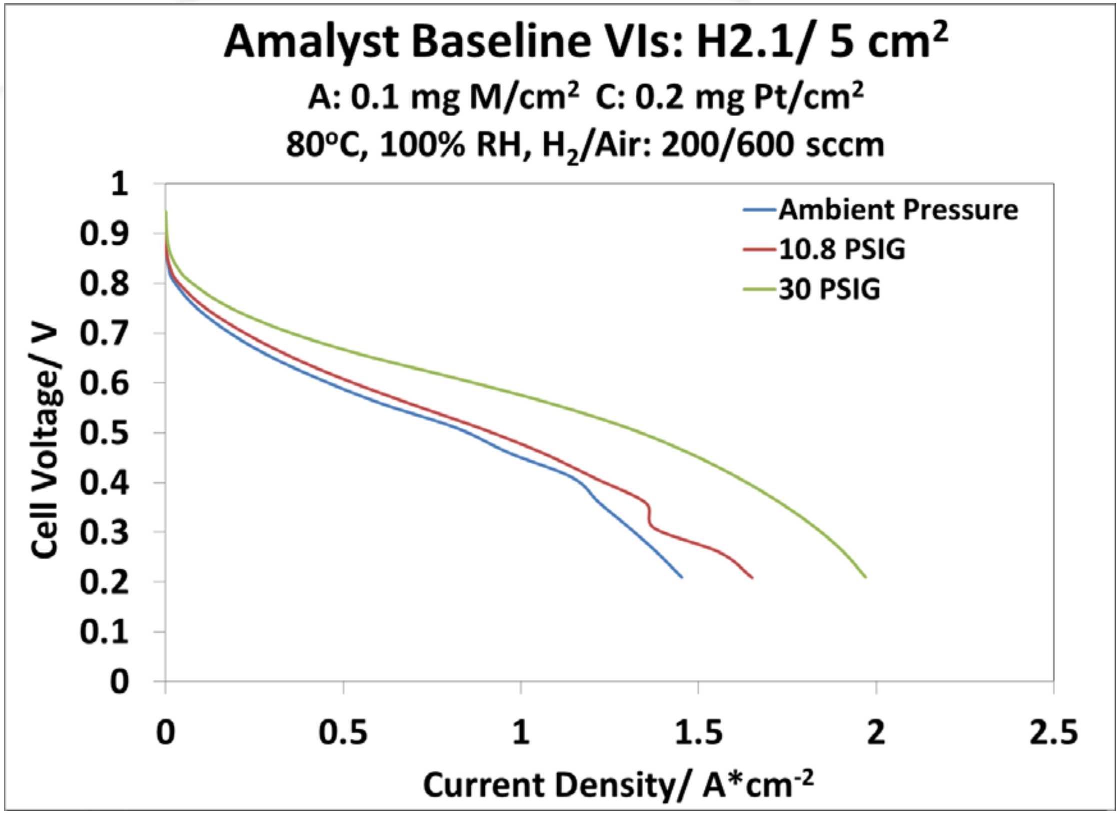
1. 40 wt% metal material on Vulcan (AMCAT H2),
2. 40 wt% metal material on Ketjen EC300 (AMCAT H2) (Received)

Test Plan:

1. **Prepare catalyst ink**
2. **Make membrane electrode assemblies**
3. **Performance test in an operating fuel cell**
4. **Performance test with 2 ppm Carbon Monoxide in H_2**

Results: Amalyst Catalyst VIs

Ketjen EC300 (AMCAT H2)

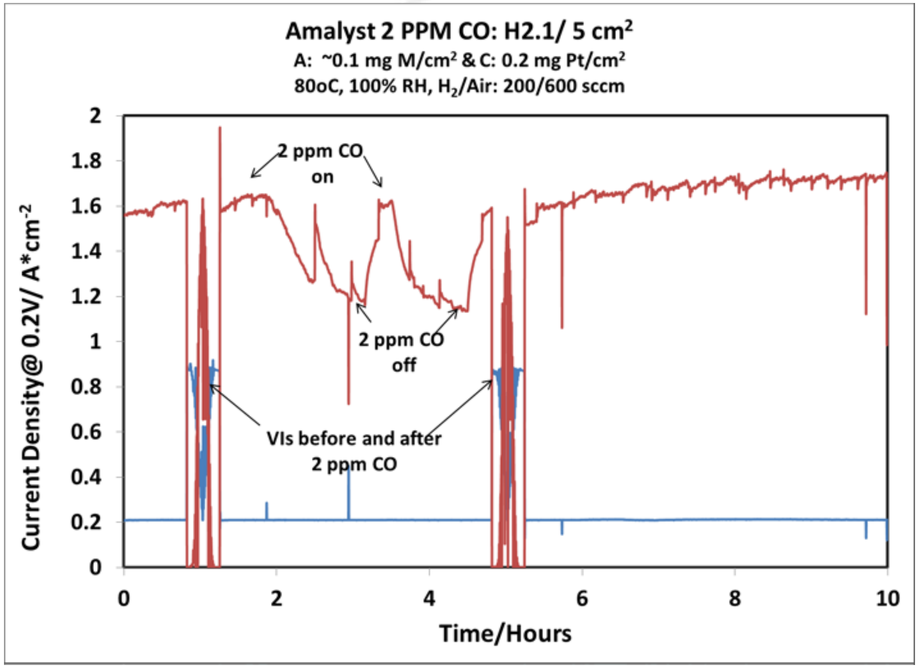


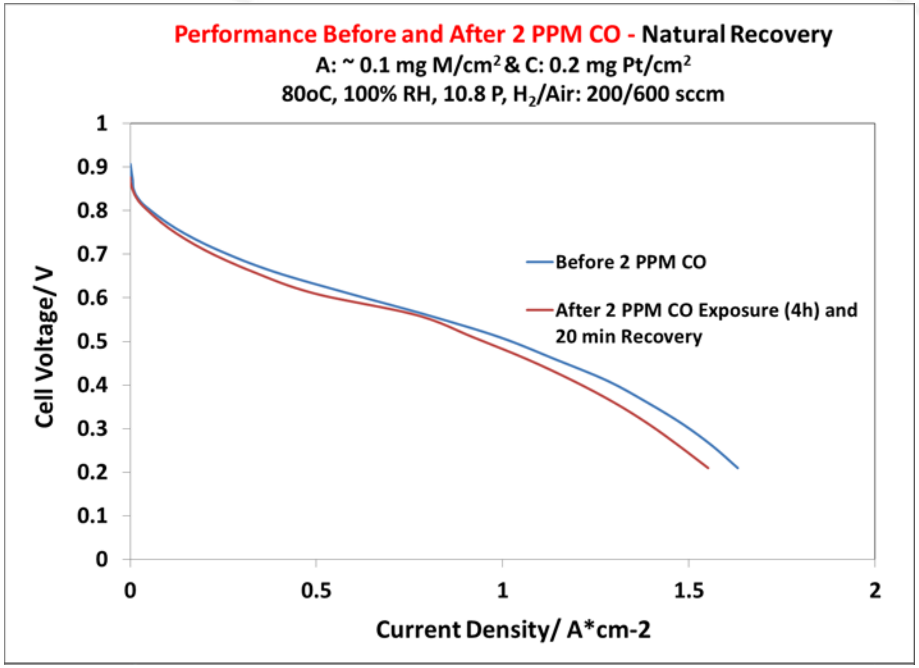
- **Fuel cell results are shown for an MEA made with LANL typical 'Pt Catalyst Ink Formulation'. Improvement possible with modified ink formulation**

Anode: ~ **0.1 mg M/cm²**, Cathode: 0.20 mg Pt/cm² 80°C, 100% RH

Results: Amalyst Catalyst: CO Effects

Ketjen EC300 (AMCAT H2)



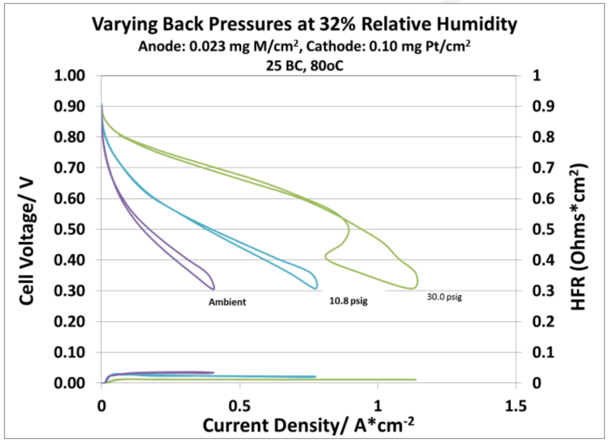


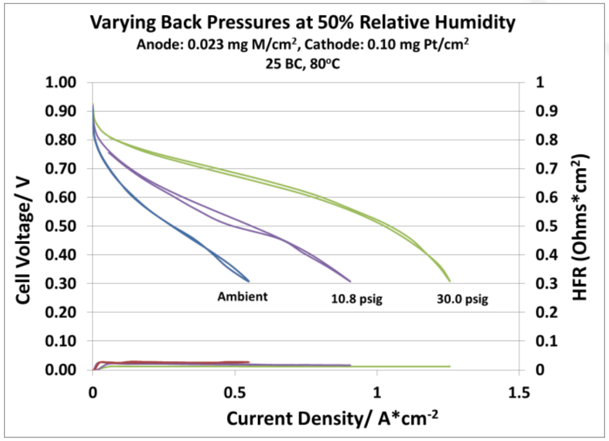
- **Fuel cell exposed to 2 ppm CO/H_2 for a total of 4 hours**
- **Performance Recovery observed after returning to clean H_2**
- **VIR shows marginal losses after 2 ppm CO and recovery**

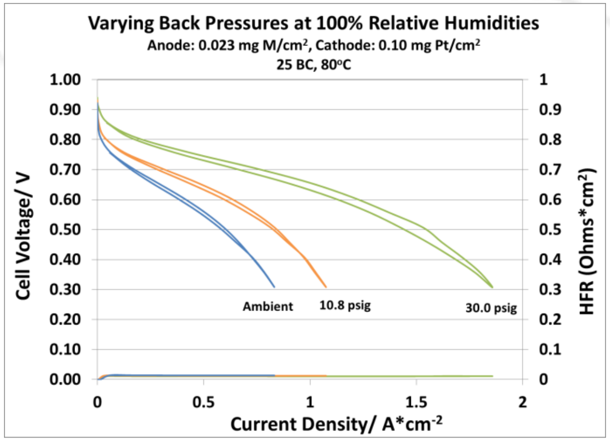
Anode: ~ **0.1 mg M/cm²** , Cathode: 0.20 mg Pt/cm² 80°C, 100% RH

Results: Amalyst non-Pt Anode Catalyst

Ketjen EC300 (AMCAT H2)







5 cm^2, H_2/Air: 200/600 sccm

- **Prepared MEAs with LANL decal method**
- **Verified metal loading by XRF**
- **Performance measured as a function of varying back pressures (ambient, 150 kPa,**
- **and 30 psig for three different RHs (32%, 50%, 100%).**
- **FC performance excellent with ultra low loadings and comparable to platinum**

Loadings aligned with 2015 DOE targets for Platinum
Anode: ~**0.025 M/cm^2** , Cathode: 0.10 mg Pt/cm^2

Approach: Indiana University–Purdue University Indianapolis

Task:
Perform fuel cell tests on Pt/PBI-Graphene, Pt-Amine, Pt-SO_3-H, and a family of PtNi catalysts verifying performance and durability

Potential Advantages:
Examining supports with the ability to stabilize Pt for a more durable catalyst

Status

1. IUPUI provided MEAs for the above series of catalyst
2. **Completed** Pt/PBI Graphene Series
3. PtNi materials received and test are **on-going**
4. Co-authoring two papers

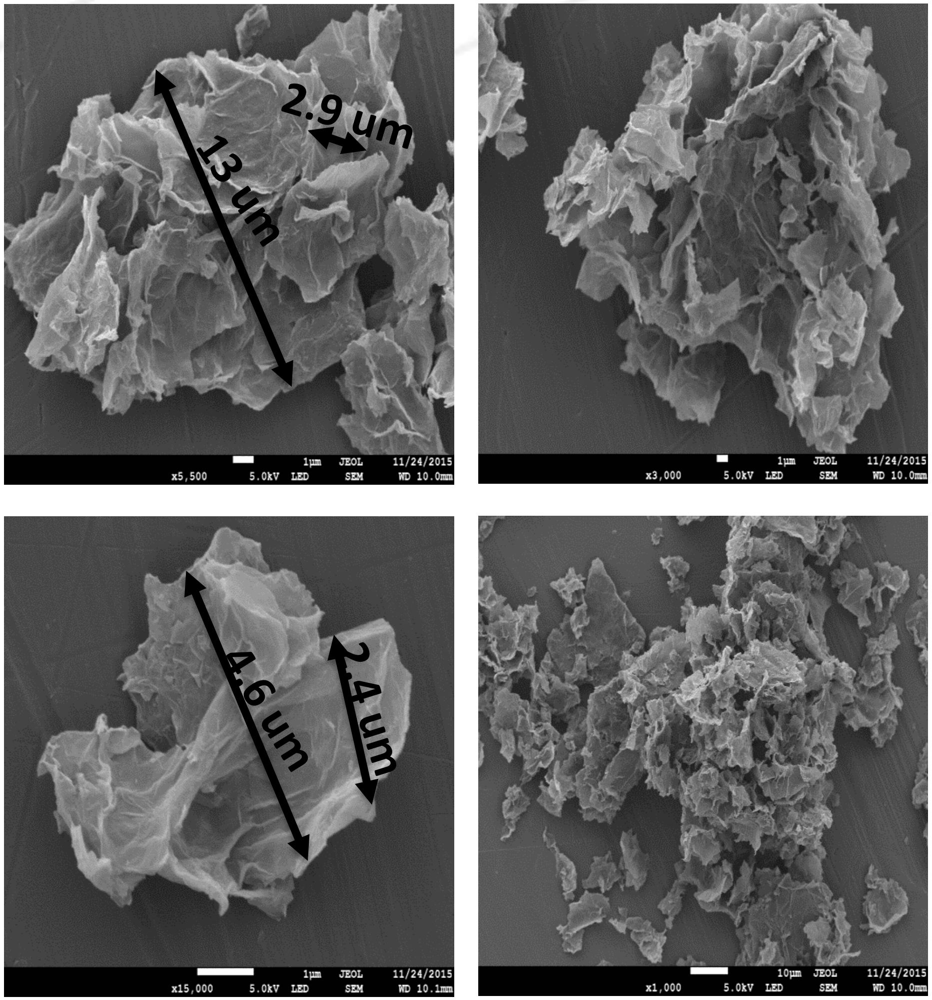
(Two Abstracts submitted to Electrochemical Society Meeting)

Overcoming Challenges with Graphene Supports

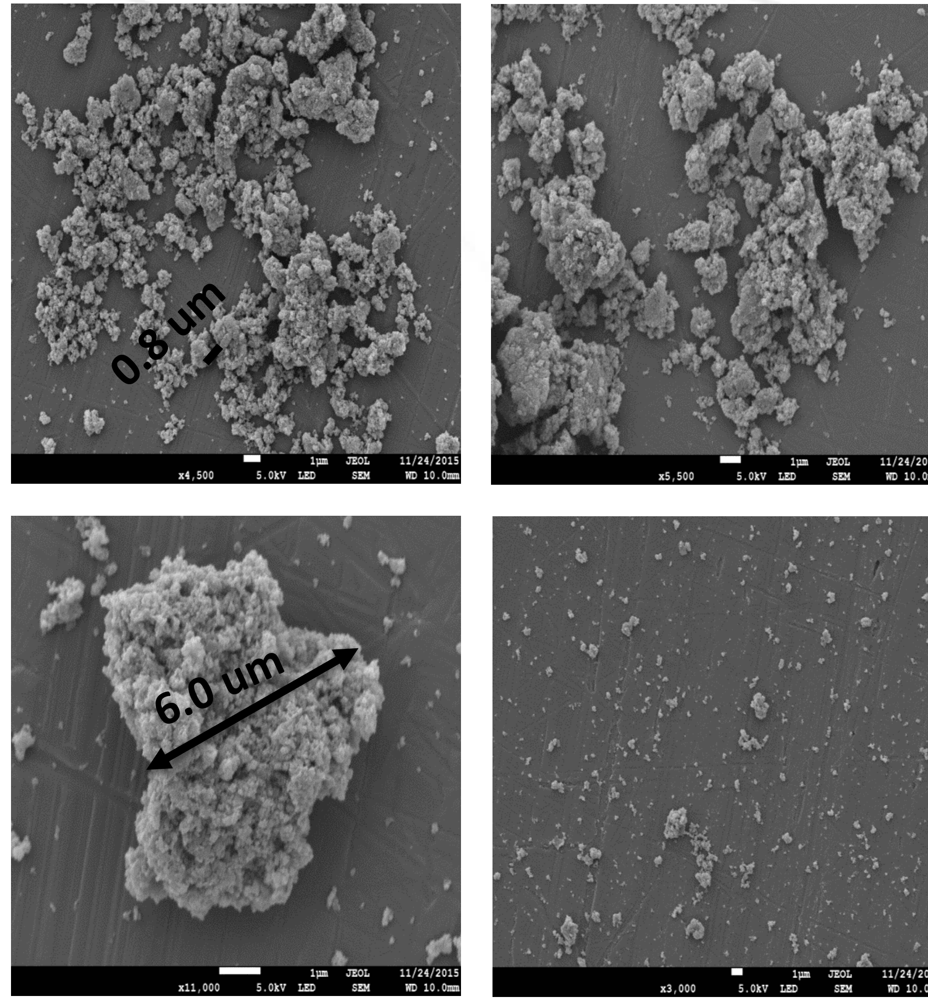
Challenges	Approach	Relevance
Graphene is hydrophobic Poor ionomer/catalyst interface Difficult to create uniform dispersion of PGM nanoparticles on graphene substrate Hard to establish interaction of PGM nanoparticles with graphene	**Functionalize** graphene to reduce hydrophobicity	By overcoming the these challenges, the hopes are for improvements in Performance and Durability of PEFC MEAs
Layering of graphene sheets Inhibits gas access to active sites Lowers ECSA	Introduce **spacers** to prevent layering of graphene sheets	
Defects of graphene at the edges Facilitates carbon corrosion Region where support becomes unstable	**Seal the edges** of graphene to reduce defects	

IUPUI's Results: SEM of Pt/PBI Graphene Materials

Approach: Improving mass transport by reducing the spacing between the graphene layers.



Pt/PBI-graphene



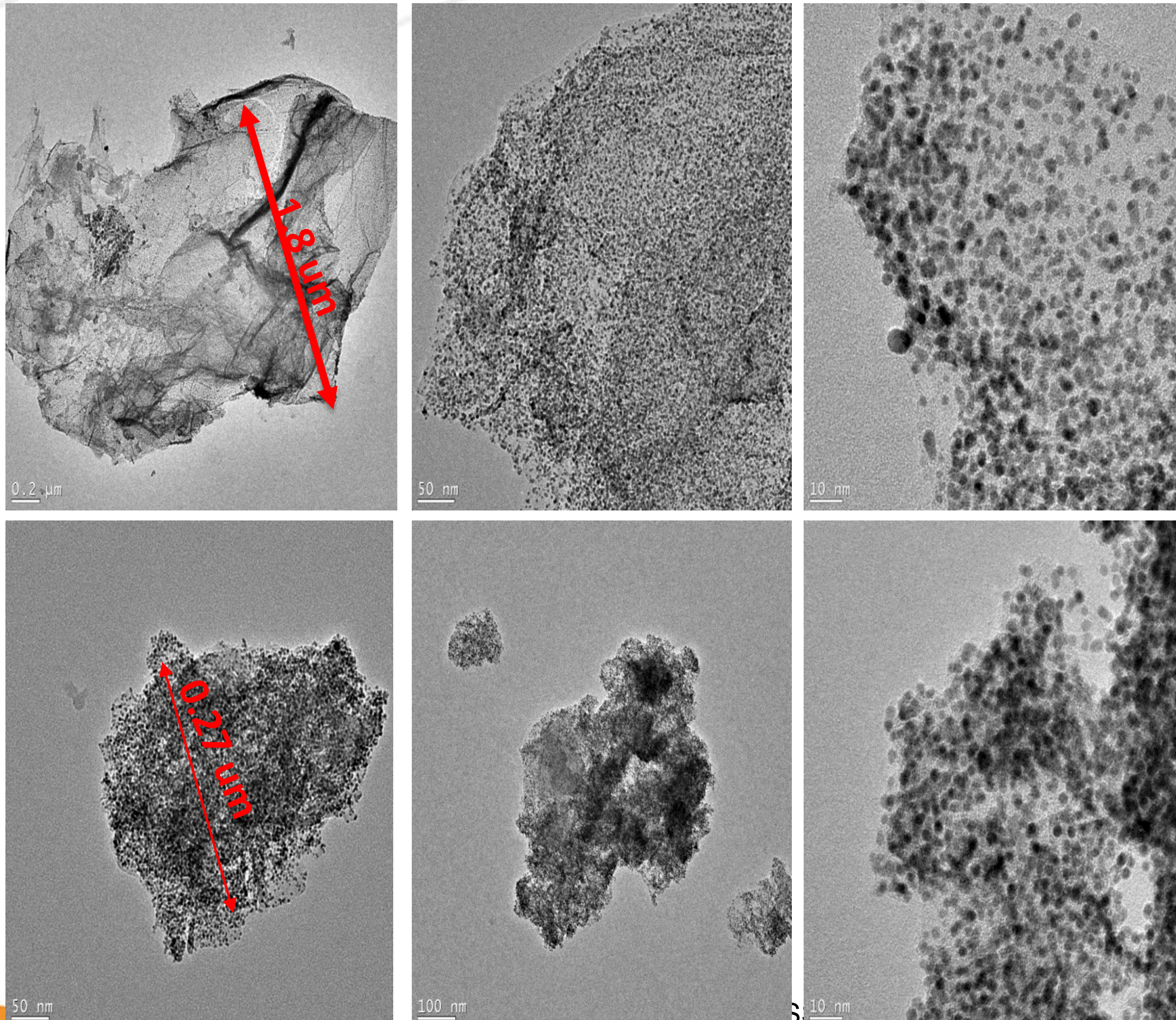
Pt/PBI-nanographene

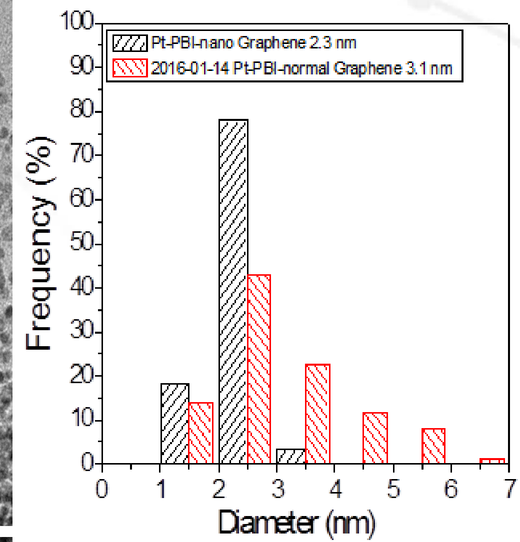
IUPUI's Results: TEM of Pt/PBI Graphene Materials

F-NG shows smaller and better Pt nanoparticle distribution

Pt/PBI-graphene(30wt %)

Pt/PBI-nanographene(50wt%)



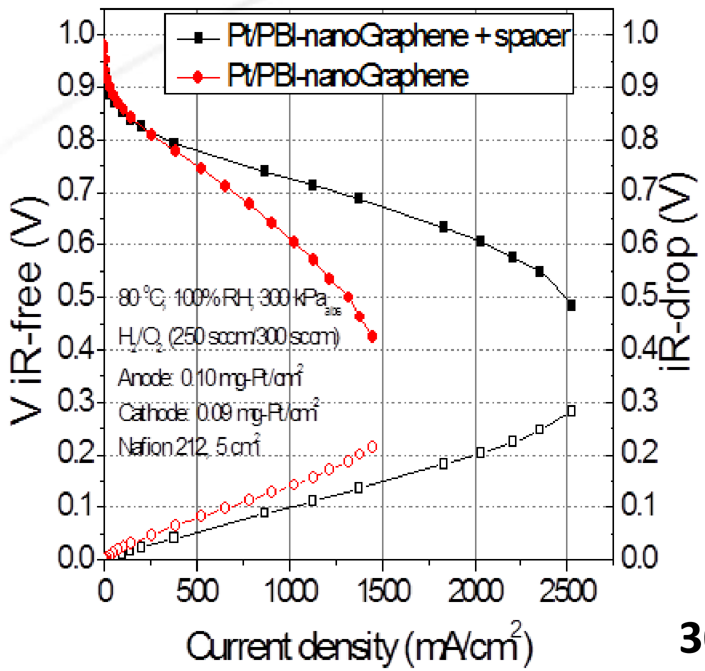


Particle size uniformity in nanographene sample shows ~80% (2.3nm) particles, while the normal graphene has a large distribution of particle sizes.

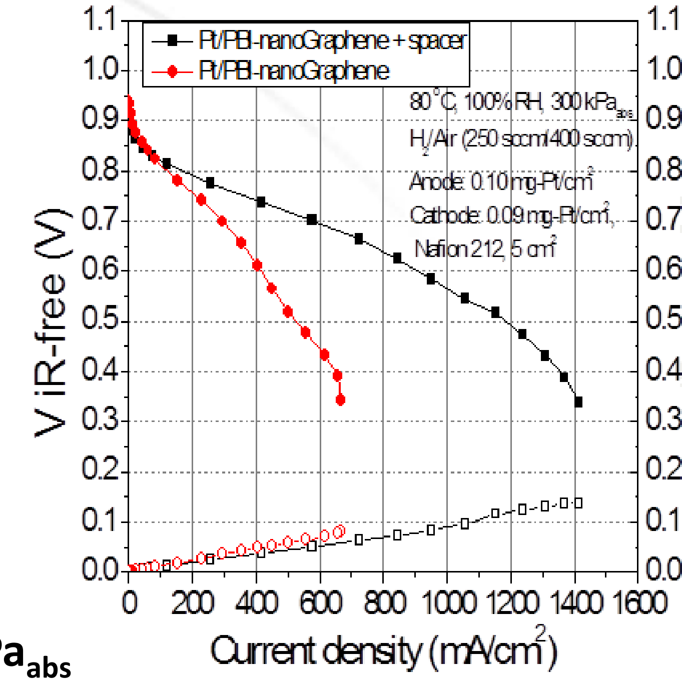
Results: The Impact of Spacers on Pt/PBI-Nanographene

BOL performance

H_2/O_2



H_2/Air



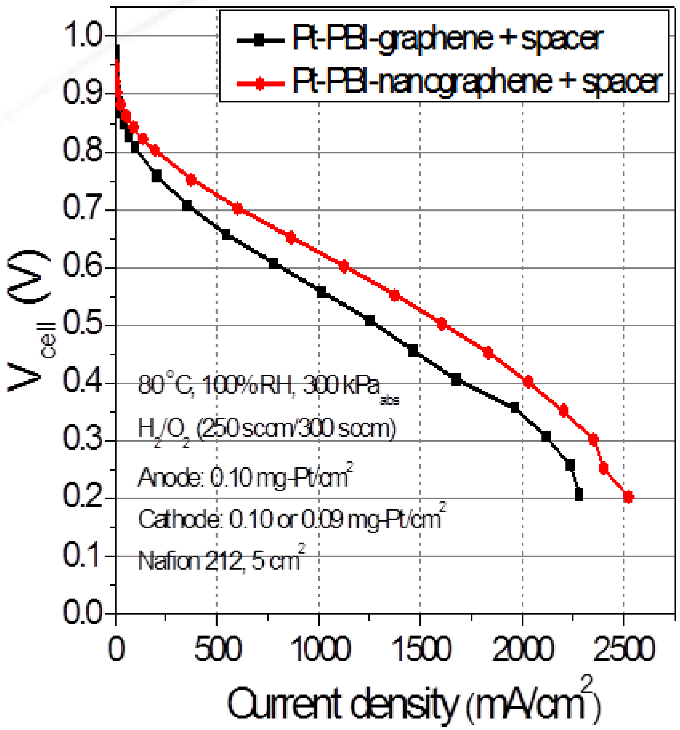
300 kPa_{abs}

The addition of spacers between the graphene sheets shows significant **improvements at the larger current densities**, particularly in the mass transport region. This may be due to the spacers producing a more open-type structure with pores and channels formed to allow good mass transport.

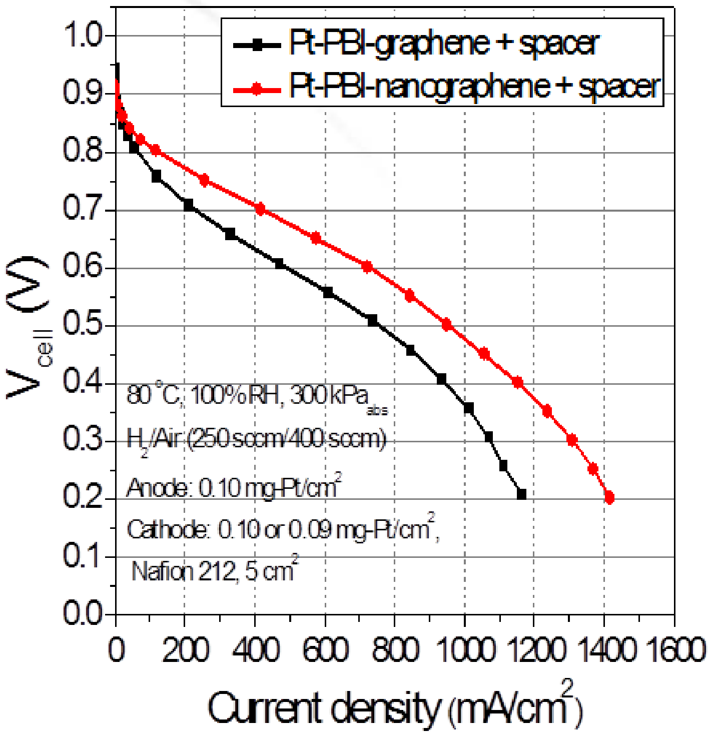
Results: Performance of Nanographene vs. Graphene with Spacers

BOL performance

H_2/O_2



H_2/Air



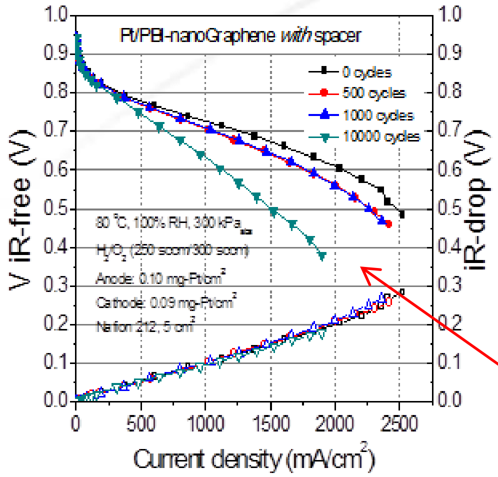
Nano-graphene effectively shortens the length of pore and channels within graphenes which inherently leads to improved mass transport.

Results: Support Durability of Pt/PBI-nanoGraphene + spacer

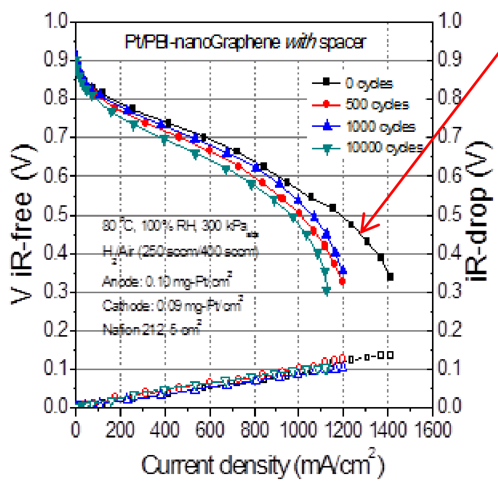
Polarization curve:

T: 80 °C, 300 kPa, 100% RH

H_2/O_2



H_2/Air



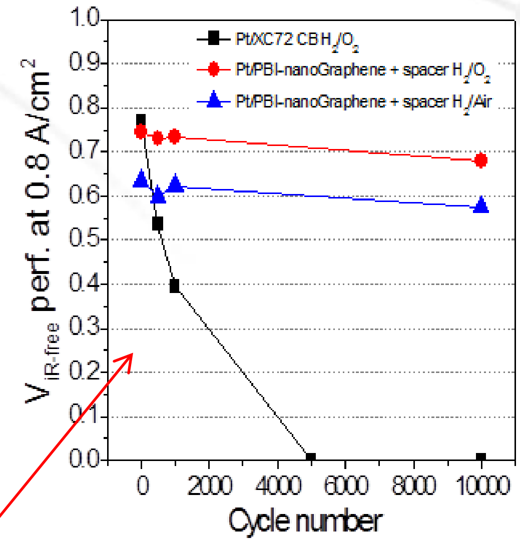
DOE AST protocols:

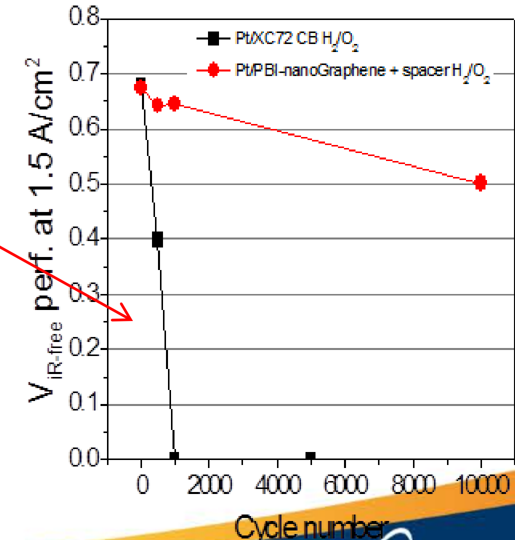
Triangle sweep: 500 mV/s from 1.0 V-1.5 V, H_2/N_2, 80 °C, ambient P, 100% RH.

1. VIs show larger losses in MTR as the number of cycles increase. This is possibly due to issues with the spacers.

2. V_{loss} curve shows Graphene supports more stable than XC72 during the AST cycles.

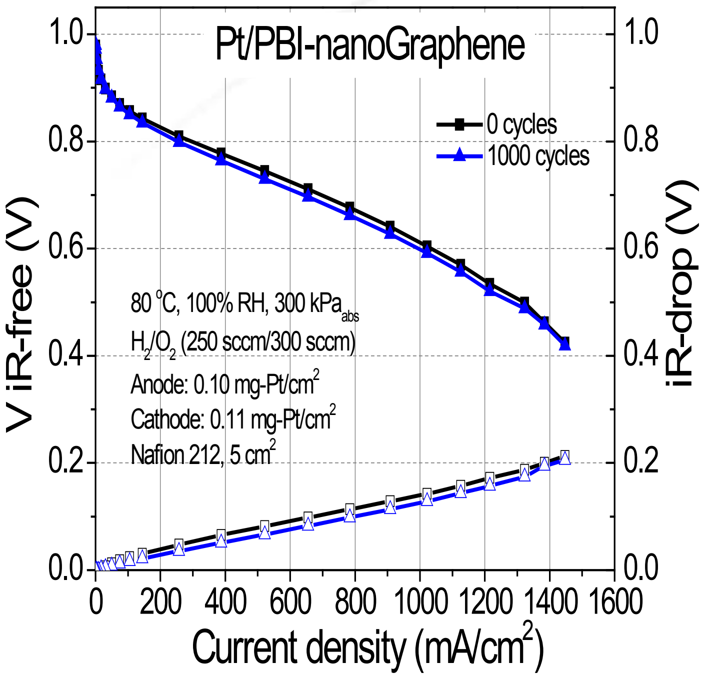
V_{loss} up to 10K Cycles





Results: Comparison of Support Durability of ***Pt/PBI-nanoGraphene*** ***and*** ***Pt/XC72 Carbon Black***

Pt/PBI-nanoGraphene



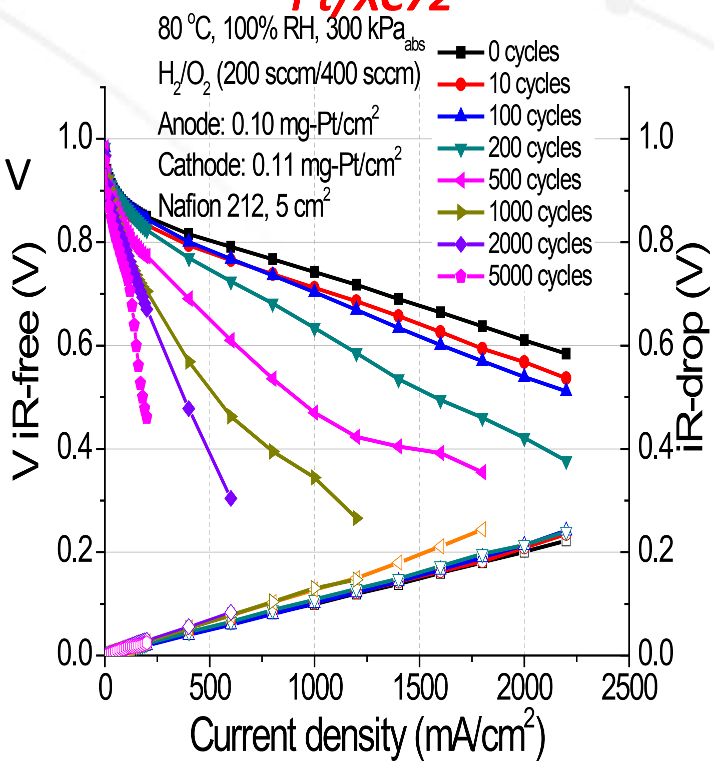
DOE AST protocols:

Triangle sweep cycle: 500 mV/s between 1.0 V and 1.5 V, 1000 or 5000 cycles, H_2/N_2, 80 °C, atmosphere, 100% RH.

Polarization curve:

H_2/O_2, 80 °C, **300Kpa**, 100% RH

Pt/XC72



Results for both H_2 and oxygen show Pt/PBI nanoGraphene durable to 1000 voltage cycles.

Significant decay observed in H_2/Air polarization curve after 5000 cycles.

IUPUI: Summary Table (300 kPa_{abs} back pressure)

Metric	Units	Pt/PBI-NanoG + spacer	Pt/PBI-nanoG	Pt/PBI-G + spacer	Pt/XC72	2020 DOE target
Initial Mass Activity	A/mg_{PGM} @ 900 $mV_{iR\text{-}free}$	0.24	0.26	0.13	0.16	≥0.44
PGM total content (Power Density)	g_{PGM}/kW (rated)	0.38	0.64	0.62	0.50	≤0.125
PGM total loading	mg_{PGM}/cm^2_{geo}	0.19	0.21	0.20	0.21	≤0.125
Support stability (1.0 V to 1.5 V cycling 0.5 V/s, 10000 cycles)						
Loss in catalyst activity	% loss after 5k cycles	25% (10k cycles) (0.18 A/mg_{PGM})	No loss (1k cycles) (0.26 A/mg_{PGM})	No loss (5k cycles) (0.14 A/mg_{PGM})	68% (5k cycles) (0.05 A/mg_{PGM}	≤40%
Loss in ECSA	% loss after 5k cycles	81% (10k cycles) (52→10 m^2/g-Pt)	-	56% (5k cycles) (25→11 m^2/g-Pt)	80%	≤40%
Potential loss at 1.5 A/cm^2	Potential loss (mV)	173 (10k cycles)	N/A	110 (5k cycles)	No activity	≤30mV
Catalyst stability (0.6 V to 1.0 V cycling 0.05 V/s, 30000 cycles)						
Loss in catalyst activity	% loss after 30k cycles	-		-	-	≤40%
Loss in ECSA	% loss after 30k cycles	-		-	-	≤40%
Potential loss at 0.8 A/cm^2	Potential loss (mV)	-		-	-	≤30mV

Analysis of Nano-Fiber MEAs Using X-Ray Tomography

NISSAN GROUP OF NORTH AMERICA

Tasks

Investigate the integrity/stability of the nano-fiber structure using high resolution imaging (1-2 microns).

NISSAN provided two samples:

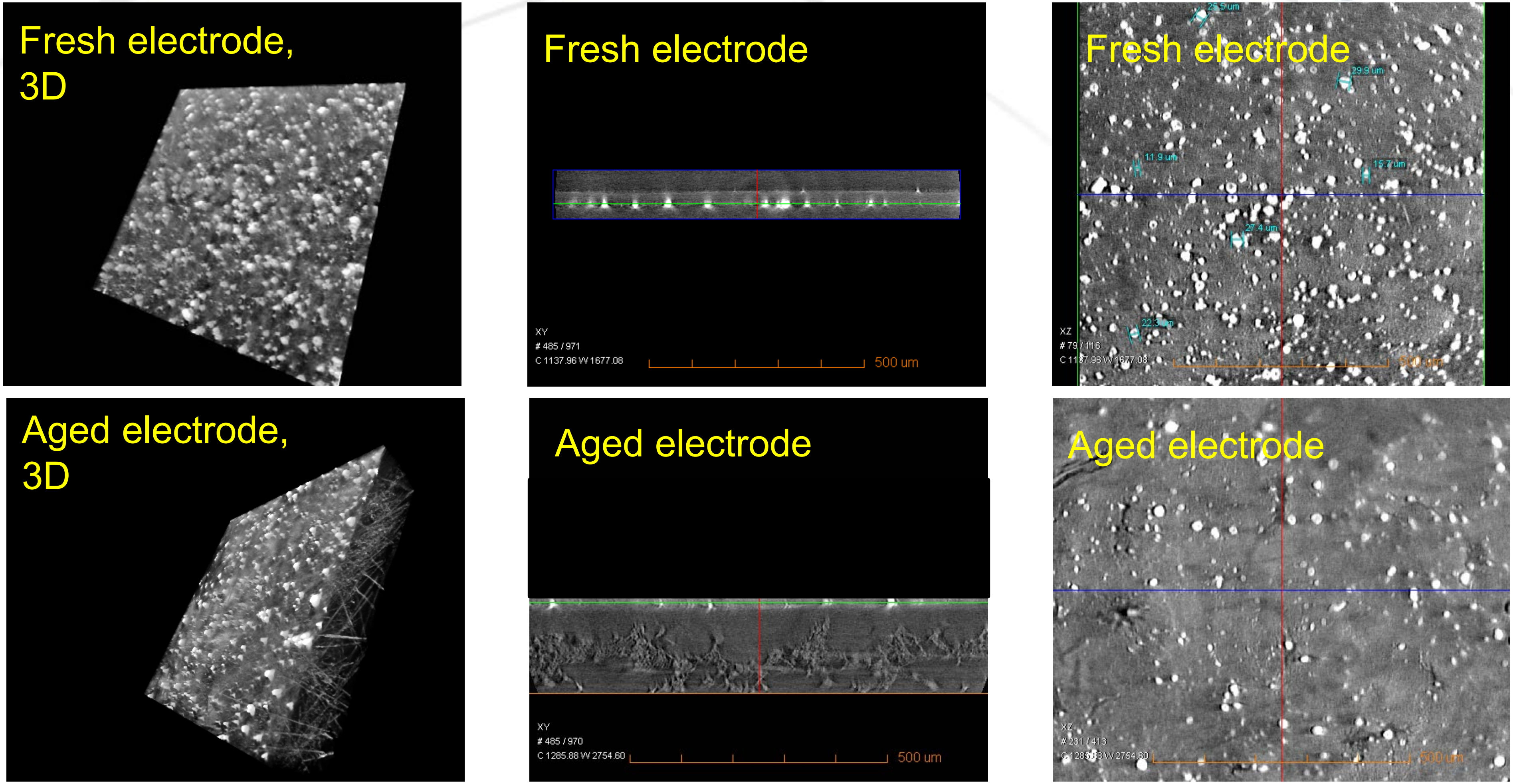
1. A fresh half CCM with a nanofiber electrode on one side.
2. An aged nano-fiber MEA after carbon corrosion AST.

Approach

The aged MEA was subjected to a start-stop cycle similar to the AST 1.0 to 1.5 V triangular wave sweep for 1000 cycles. LANL will provide a report that includes high resolution images and movies of these samples.

NISSAN GROUP OF NORTH AMERICA

Results of Nano-Fiber MEAs: Fresh vs Aged

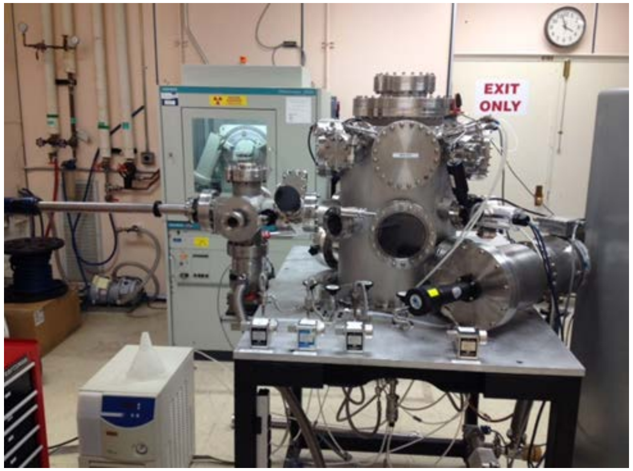


X-Ray micro-tomography reveals only minimal changes in the electrode structure after MEA was aged for 1000 voltage cycles.

Novel Catalyst Support Coating

Tasks/Challenges

Use of novel techniques for preparation of non-corroding surfaces.



Multi-layer deposition system

Approach

Use a multi-layer deposition of materials without exposure to atmosphere

Accomplishments/ Status

Built and tested sample tower for heating

Added Residual Gas Analyzer (RGA),mass spectrometer for measuring surface contaminants

Performed ~8 depositions and characterized each, sent Ford 3 samples. (XRD, SEM, and EDAX)

Enhancing the Surface of Metal Bi-Polar Plates

Tasks/Challenges

Use of novel techniques for metal – ceramic coatings of fuel cell components.

Approach

4 options /customizable Sputtering systems:

1) Multi-hearth electron beam evaporation system
2) Multi-gun RF Magnetron system
3) Multi-target, on-axis system
4) 5 gun system for multilayers > than 3 materials.

Accomplishments/ Status

Performed over 100 depositions
42 samples delivered


Approach: Pajarito Powder Non-PGM Catalyst

Tasks

Perform test on non-PGM Materials, testing for performance and durability using DOE Accelerated Stress Tests

Approach

Pajarito Powder will prepare MEAs with non-PGM catalyst

LANL will verify performance In an operating fuel cell

LANL will subject the MEAs to two different ASTs:

Accomplishments/ Status

LANL received 10 samples

Test completed on 3 samples using both versions of the AST

Results reported to Pajarito Powder

DOE AST protocols:
Triangle sweep: 500 mV/s from 1.0 V-1.5 V, H_2/N_2, 80 °C, ambient P, 100% RH.

DOE AST protocols:
Square wave: from 0.6 V to 0.95 V, for 3 sec each H_2/N_2, 80 °C, ambient P, 100% RH.

Approach: Savannah River National Laboratory

Problem to be addressed

Investigate high potential redox active species present in select non-PGM FC electro-catalysts for the oxygen reduction reaction (ORR) in acidic medium.

Scope of Work

SRNL is currently conducting a study to investigate the electrochemistry of a catalyst prepared by SRNL from a metallic organic framework (MOF) that displays high ORR activity and a high potential redox couple measured during potential cycling. This study focuses on the redox couple present in the cyclic voltammogram and the species' possible role in the ORR, either directly as a part of the ORR mechanism, or indirectly through the formation of the active site. SRNL's initial electrochemical results show the absence of a correlation between the redox couple potential in the CV and the onset potential for the ORR. This is in contrast to literature reports that indicate a relationship between the high potential redox couple, thought to be $Fe{-}N_4$ or Fe based, and the active site for the ORR.

Approach: Savannah River National Laboratory

Objective

LANL to perform an electrochemical characterization similar to SRNL's study, using catalysts synthesized using different materials and methodologies. Results produced will be compared to LANL's high activity catalysts.

Tasks

The electrochemical response using techniques such as cyclic voltammetry, and RDE will be measured in multiple electrolytes (perchloric acid, sulfuric acid). $E_{1/2}$ values for the redox potential couple will be measured and compared between the two electrolytes. $E_{1/2}$ values will also be compared to the ORR onset potential to determine if there is a correlation.

SRNL will synthesize a series of MOF catalysts with varying iron content. These catalysts will be characterized electrochemically by SRNL and the results will be shared with LANL.

SRNL and LANL will compare and discuss the electrochemical results for SRNL's MOF catalysts and LANL's catalysts. Determine additional scope if needed to conclude study, but not to exceed the confines of the Technical Assistance to Developers project.

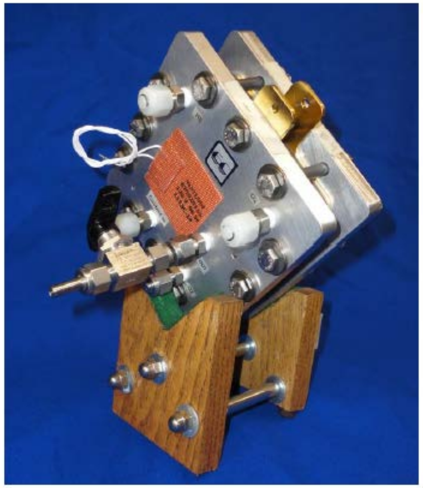
Approach: ElectroChem, Inc. Stack Testing

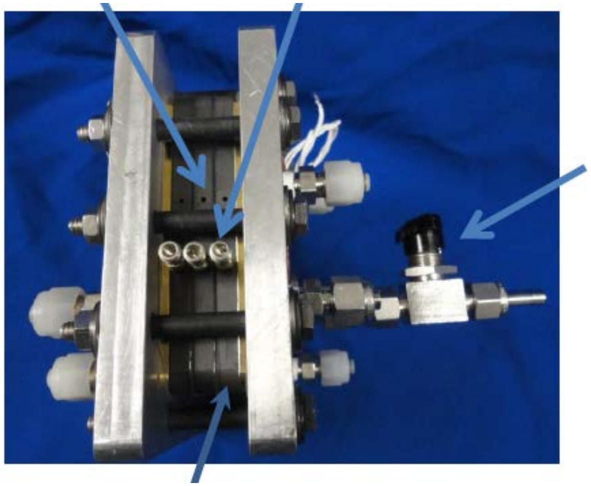
Objective

Evaluate ElectroChem's two cell stack for hydrogen/air application. Provide feedback regarding any needed improvements that can be implemented to assist in its commercial development.

Goal

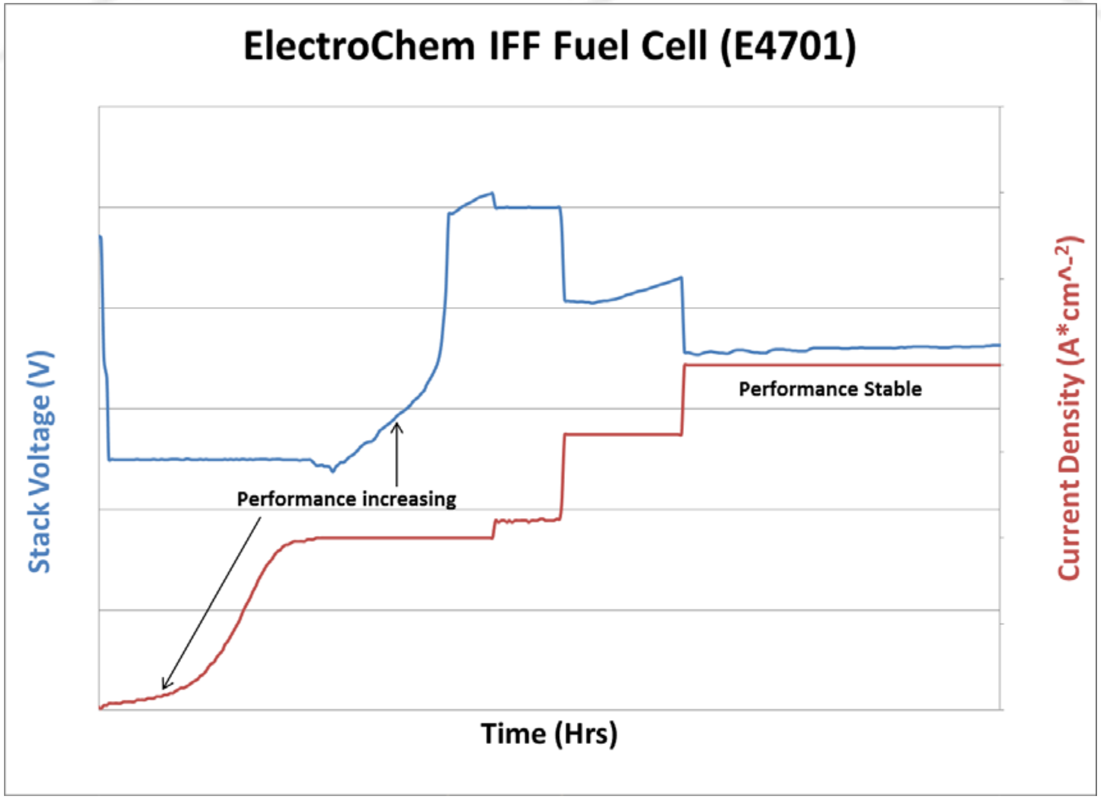
To verify performance of stack built for other purposes





EFC-IFF-50 Fuel Cell Setup

Results: ElectroChem, Inc. Stack Testing



Next Step:
LANL will re-test the IFF stack using an agreed upon pre-conditioning Step.

Initial test results were obtained by pre-conditioning the stack using H_2/O_2 and without any humidification. We observed an increase in performance at the onset before attempting to validate performance. After discussing the results we determined the stack experienced hydration problems.

On-Going Work/Future Collaborators:

- Ford Motor Co.
  - complete the test matrix of bi-polar plate multi-layer passivation samples
  - Optimize coating catalyst supports with metals deposited using LANL acoustic agitation approach developed in FY15 and tested in FY16.
- Amalyst
  - Non-Pt Anode catalyst (verify performance, durability)
- Indiana University –Purdue University Indianapolis
  - Investigating Novel catalyst/MEA architecture
  - Continue testing PtNi MEAs
- SRNL
  - Non-PGM testing of MOF catalyst
- ElectroChem, Inc.
  - Stack testing and validation
- Pajarito Powder
  - Continue testing MEA samples with DOE ASTs
- Participate on the DOE/USCAR U.S. DRIVE Fuel Cell Tech Team
- 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**

Summary

- Ford Motor Co.
  - ❖Designed and built new tower to accommodate acoustic motor and depositions at elevated temperatures. Novel method moves catalyst support particles in plasma - both rotation and translation - during deposition from single target. Provisions to accommodate more than one target for FY17.
- Amalyst
  - ❖Completed test Non-Pt Anode catalyst (verify performance, durability)
  - ❖Test results were discussed and disseminated
- Indiana University –Purdue University Indianapolis
  - ❖ Completed Pt/PBI catalysts tests
  - ❖ Completed tests of Novel catalyst/MEA architecture using Pt/C
  - ❖Tests of PtNi catalysts are on-going
- Nissan
  - Provide high resolution tomography images and movies
- SRNL
  - ❖Discussed and developed work scope for the Non-PGM of MOF catalyst
- ElectroChem, Inc.
  - ❖Stack test of EFC-IFF-50 Fuel Cell performed
  - ❖Diagnostics on proper stack hydration techniques are on-going
- Pajarito Powder
  - ❖Tested 3 different samples using two different Accelerated Stress tests

Acknowledgements

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