Technical Assistance to Developers

The U.S. Department of Energy 2017
Hydrogen and Fuel Cells Program
and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting

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

June 04, 2017
Los Alamos, NM

Project ID: FC052

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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 FY16: $550 K**
- **Funding received in FY17: $450 K**

Partners/Collaborators

- **See list on slide 4**

Outline

- Partners/Collaborators List
- Relevance/Approach
- FY 17 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

Ford

Ucla

Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

THE UNIVERSITY of TENNESSEE KNOXVILLE

Argonne NATIONAL LABORATORY

BERKELEY LAB

NIST National Institute of Standards and Technology U.S. Department of Commerce

THE UNIVERSITY of NEW MEXICO

ALLEN UNIVERSITY 1870

Benedict College

NPL National Physical Laboratory

FLORIDA A&M UNIVERSITY
FLORIDA AGRICULTURAL AND MECHANICAL UNIVERSITY

MOREHOUSE COLLEGE

PRAIRIE VIEW A&M UNIVERSITY

TENNESSEE STATE UNIVERSITY

SOUTHERN UNIVERSITY AND AGRICULTURAL & MECHANICAL COLLEGE

TUSKEGEE UNIVERSITY

Blue-O Technology Inc.
Since 2008

UNIVERSITY of HAWAI'I SYSTEM

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 <u>as directed by the DOE</u>. This task includes:

- **Testing and validation of materials**
- **Participation in the further development and validation of single cell test protocols.**
- **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.**
- **Providing technical experts available to DOE and the Fuel Cell Tech Team**

Assistance available by Request and DOE Approval.

Nancy Garland, Ph.D.: Nancy.Garland@ee.doe.gov

FY17 Assistance Work-Scope

- Ford Motor Co.
  - Bipolar Plate
  - Catalyst development
- Blue-O-Technology
  - Catalyst testing of Pt, PtM, and Pt/TiO_2
  - Catalyst Performance and Durability
  - Investigate novel support materials
- UCLA
  - Catalyst Testing of Mo-doped Pt_3Ni
  - MEA Performance and Durability using ASTs
- Savannah River National Laboratory (SRNL)
  - Testing and validation of PGM-free
- NIST
  - Neutron imaging hardware
- Univ of Tenn
  - Neutron Imaging hardware
- Univ of Hawaii
  - Neutron Imaging hardware
- LANL Fuel Cell Short Course
- National Physics Laboratory
- DOE/U.S. DRIVE Fuel Cell Tech Team Representative
- Support Working groups
  - Durability WG
  - Mass Transport WG

Milestones

Milestone Name/Description	Date	Type
SRNL/Pajarito Powder: Quantitative comparison of ORR Activity and cyclic voltammogram redox peaks of different PGM-Free catalysts defining what correlation exists from minimum two sets of externally provided PGM-Free catalysts (Savannah River National Lab-SRNL, Pajarito Powder)	12/31/2016	Quarterly Progress Measure (Regular)
Ford: Provide Ford a sufficient quantity (200 mg) of reactively sputter deposited Niobium oxide layers onto Ford-provided substrates for catalyst support synthesis for Ford electrochemical evaluation of NbO_x intermediate layer.	6/30/2017	Annual Milestone (Regular)
FCTT: Fuel Cell Tech Team participation with minimum of six tech team meetings in person and reports on results of tech assistance to developers.	3/31/2017	Quarterly Progress Measure (Regular)
Multiple Industry/Academia: Hold annual fuel cell training workshop for Industrial and Academic participants (FY16 participants included UNM, ANL, ORNL, LBNL, Allen University, Morehouse College….); reports on results of tech assistance to developers.	9/30/2017	Quarterly Progress Measure (Regular)

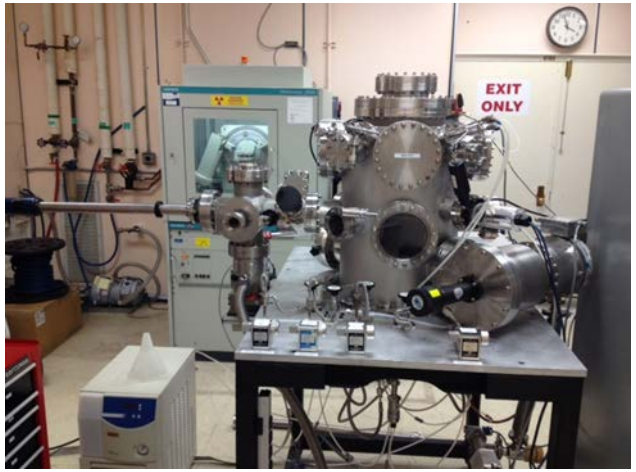
Novel Catalyst Support Coating

Tasks/Challenges

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

Approach

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



Multi-layer deposition system

Milestone Achieved:

Delivered 8 catalyst samples

Enhancing the Surface of Metal Bipolar Plates

Tasks/Challenges

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

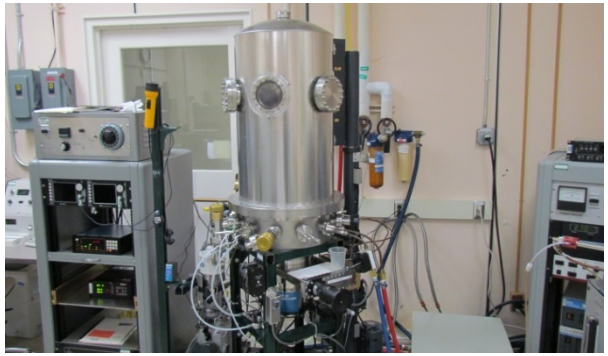
Perform multi-layer coating by PVD

Deliver desired thickness of coatings

Approach

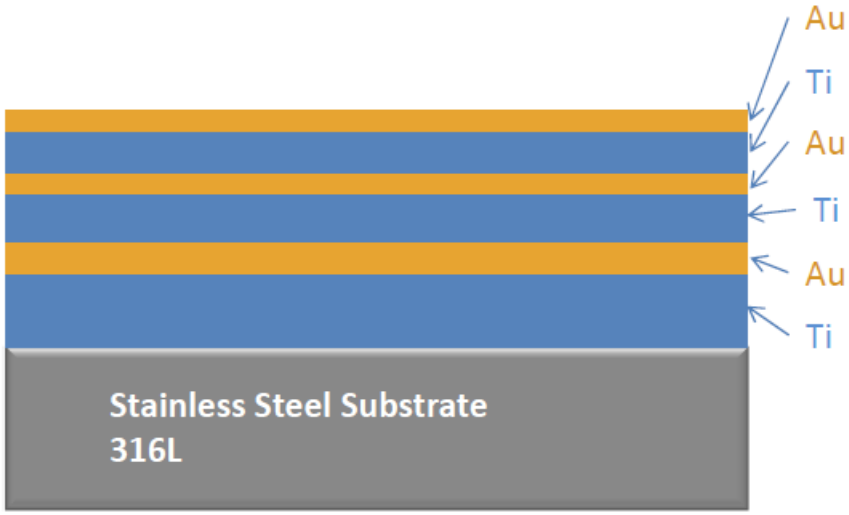
4 options /customizable Sputtering systems:

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.



Multilayer Ti/Au Coating

- Lower amount of precious metals
- Improve durability

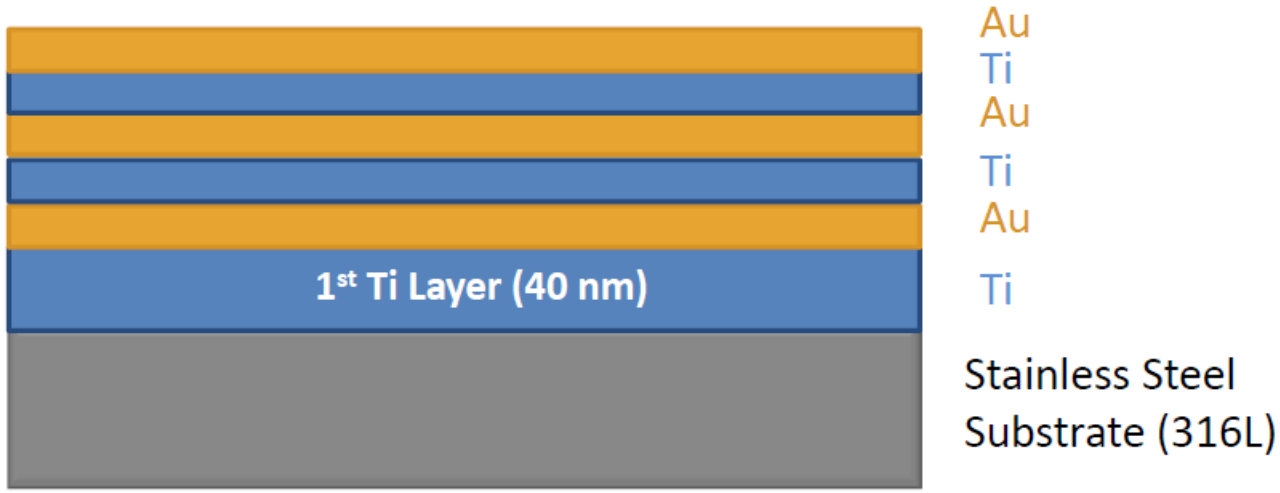


Schematic representation of the multilayer coating by PVD at LANL.
Titanium acts as a corrosion barrier to the SS316L substrate and as an adhesion layer for the Au. Layering promotes immobility of Au.

R. Borup and T. Rockward, Technical Assistance to Developers (Project ID:FC052), LANL, USDOE 2015 Annual Merit Review, June 8, 2015, Arlington, VA

***PRIME ECS Meeting: Multi-Layer Thin Film Coatings on Bipolar Metal Plates for PEMFC, Kerrie K. Gath, Mark Ricketts, Jun Yang, Chunchuan Xu, and Shinichi Hirano, Fuel Cell Research/R&A Ford Motor Company, Oct 2016**

Multilayer Ti/Au Coating – Test Samples



Samples provide by LANL:

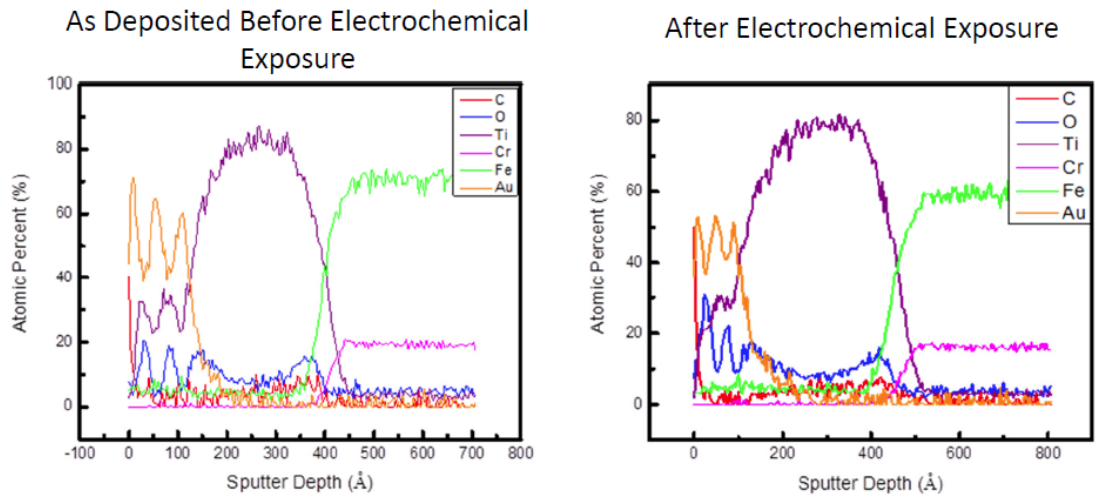
XRF for each substrate type and each side. Each run included a 316 and 304 stainless coupon and both sides were coated.

134 depositions this FY not including calibration runs

20 samples delivered

Enhancing the Surface of Metal Bi-Polar Plates

Test Results – AES Cross-Section Profiles



***PRIME ECS Meeting: Multi-Layer Thin Film Coatings on Bipolar Metal Plates for PEMFC, Kerrie K. Gath, Mark Ricketts, Jun Yang, Chunchuan Xu, and Shinichi Hirano, Fuel Cell Research/R&A Ford Motor Company, Oct 2016**

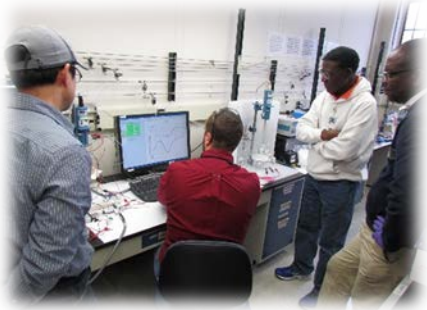
AES depth profile of multi-layer coating structure on the stainless steel substrate (316L), before and after the corrosion tests. Please note that these are two separate specimens (nominally the same) as AES is a destructive test.

LANL deposition table:

Run#	Ti Thickness	Au Thickness	Au Layers
22	A	X	X1
23	B	Y	X1
24	C	Y	X1
25	A	Z	X1
26	A	Z	X2

Fuel Cell Short Course FY17

LANL staff hosted a 3 day hands-on Fuel Cell course that captures basic electrochemistry to advanced characterization techniques. Participants were engaged in all aspects fuel cell science.



Participants in LANL Fuel Cell Short Course

Argonne NATIONAL LABORATORY

THE UNIVERSITY of NEW MEXICO

Benedict College

ALLEN UNIVERSITY 1870

BERKELEY LAB

PRAIRIE VIEW A&M UNIVERSITY

TUSKEGEE UNIVERSITY

MOREHOUSE COLLEGE

FLORIDA A&M UNIVERSITY
FLORIDA AGRICULTURAL AND MECHANICAL UNIVERSITY

SOUTHERN UNIVERSITY AND AGRICULTURAL & MECHANICAL COLLEGE

TENNESSEE STATE UNIVERSITY

Feb. 21-23, 2017

University of California-Los Angeles

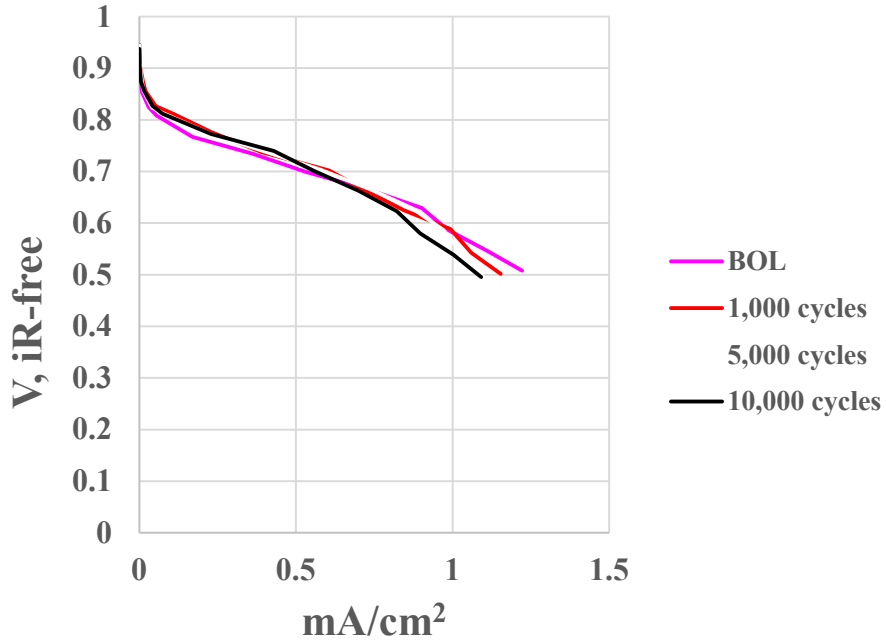
Objective:

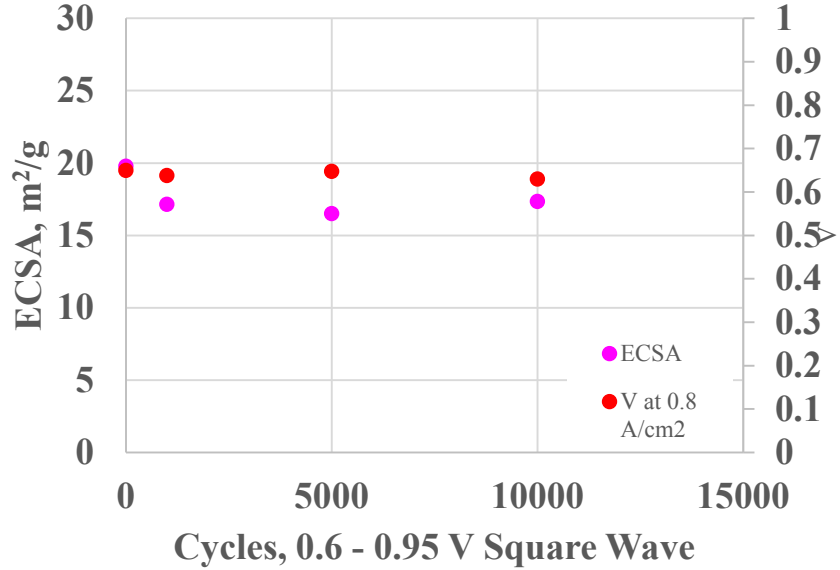
UCLA has reported high RDE activity with Mo-doped Pt_3Ni octahedra catalysts (Huang et al., Science 348 (2015) 1230-1234). LANL will test catalyst for performance and durability.

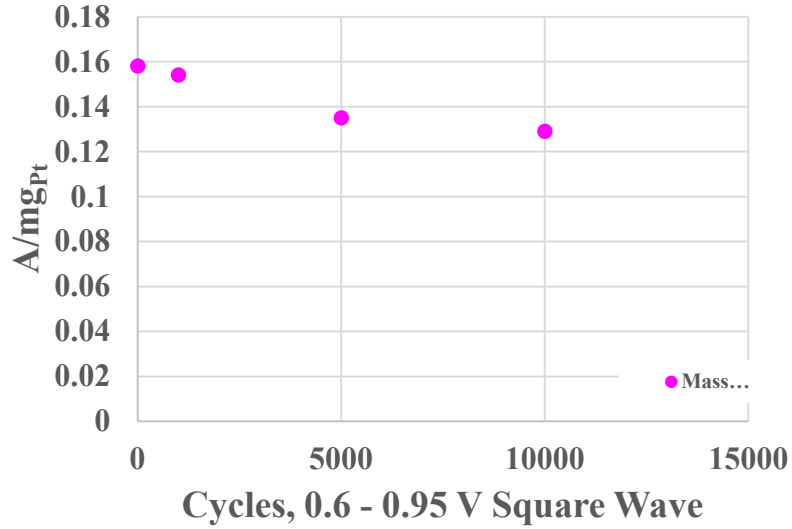
Tasks:

- **Prepare Catalyst Inks and make MEAs**
- **Conduct performance and durability tests of catalysts in an operating fuel cell**
- **Prepare data, discuss results and disseminate**

University of California-Los Angeles







Polarization curves does not show significant losses at10,000 V-cycles.

ECSA remains stable throughout testing

Voltage at 0.8 V after cycles decreased 20 mV

DOE targets require 30,000 cycles

University of California-Los Angeles

Status:

LANL performed initial MEA performance and durability testing for 10,000 cycles (future work: full 30,000 cycle test)

Results after 10,000 cycles:

- **18% loss in mass activity (target: 40% loss after 30,000 cycles)**
- **12% loss in ECSA (target: 40% loss after 30,000 cycles)**
- **20 mV loss in performance at 0.8 A/cm^2 (target: 30 mV loss after 30,000 cycles)**

Testing is on-going to determine whether or not these materials meet current DOE targets.

Blue-O Technology, Inc.

Objective:

To test novel catalyst for performance and durability and investigate the stability of a different support.

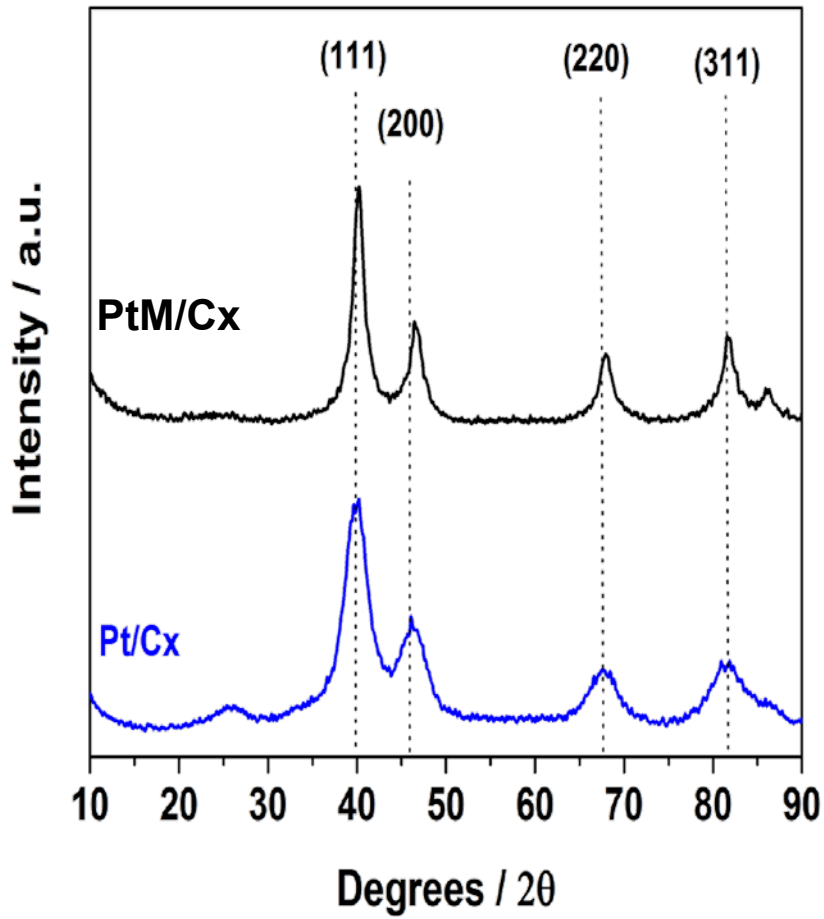
Tasks:

- **LANL will characterize 4 different catalyst samples with various techniques, such as : XRD, XRF, SEM, etc.**
- **Perform electrochemical characterization using RDE to test for activity**
- **Prepare catalyst inks and make MEAs for fuel cell testing**
- **Performance and durability testing of catalyst/support**
- **LANL will compile data and summarize finding.**

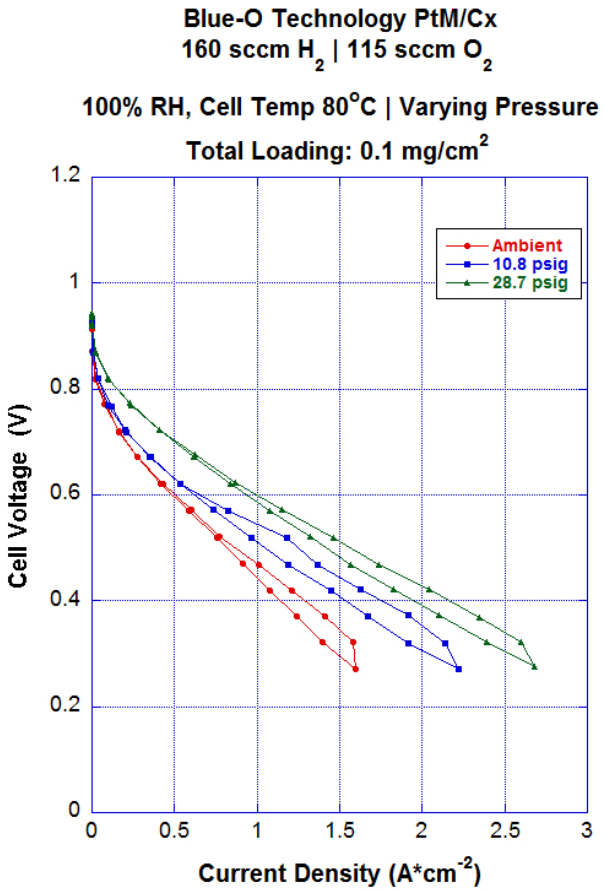
Characterization by X-ray diffraction

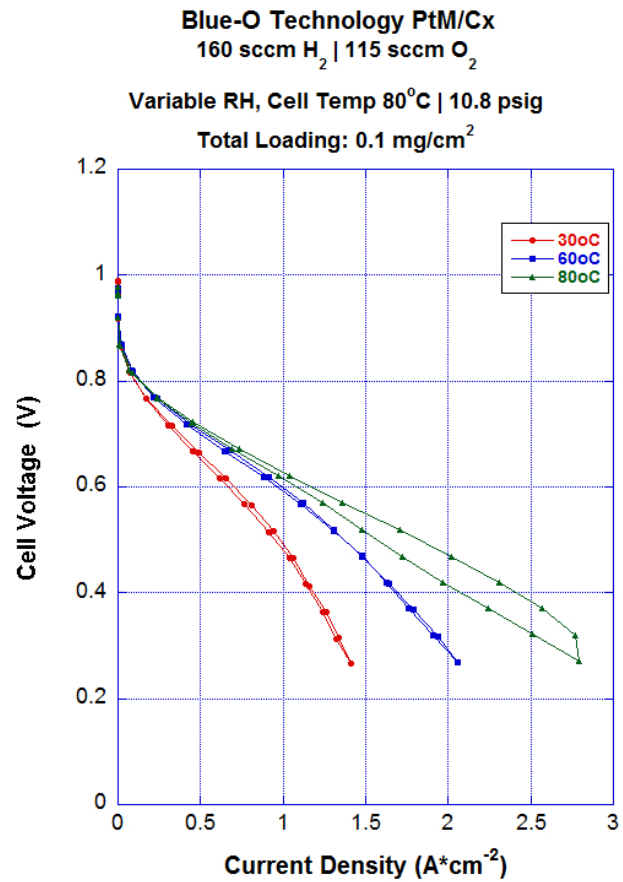
- XRD was performed on the following catalysts
  - Pt/Cx - B62013-3
    - Average crystallite size: 2.5 nm
  - PtM/Cx - B81415
    - Average crystallite size: 4.6 nm

Other comments:
- Well defined structure
- Uniformity in crystallite size
- Carbon visible around 26°



Blue-O Technology Inc.
Since 2008





Initial test results were performed on MEAs with un-optimized I:C ratios.

Performance at ultra-low Pt loading show promise.

Total Pt loading < 0.1 mg/cm^2

Approach: Savannah River National Laboratory

Problem to be addressed

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

Scope of Work

SRNL and LANL are currently conducting a study to investigate the electrochemistry of a Fe-N-C catalysts. This study focuses on the redox couple present in the cyclic voltammogram and whether or not it correlates to ORR performance. SRNL's initial electrochemical results show the absence of a correlation between the redox couple potential in the CV and the ORR activity. This is in contrast to literature reports that indicate a relationship between the high potential redox couple, thought to be Fe based, and the active site for the ORR.

Approach: Savannah River National Laboratory

Objective

LANL and SRNL will perform an electrochemical characterization using two different PGM-free catalysts synthesized in-house. Results produced will be used to determine if a correlation between redox potentials and ORR activity exists. Such a finding would be useful in improving the understanding of the mechanisms that govern electrochemical activity.

Tasks

Synthesize Fe-N-C catalysts.

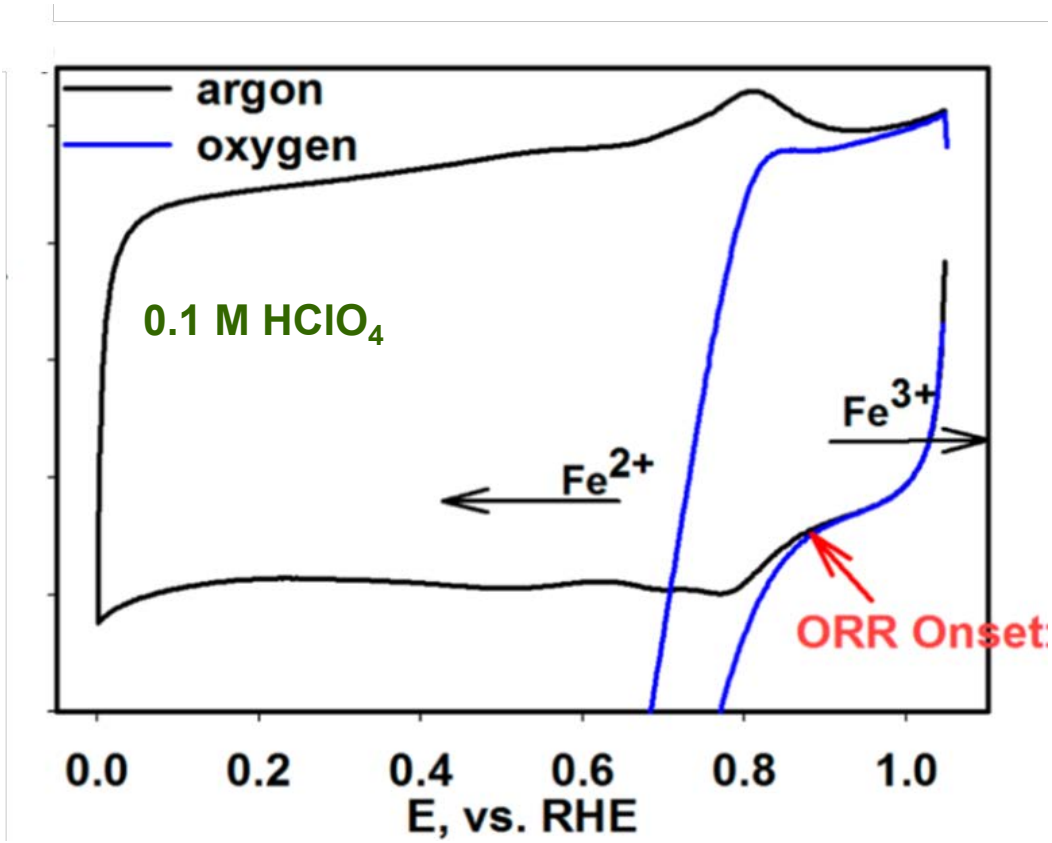
Test the electrochemical response of these catalyst using cyclic voltammetry and RDE with various ratios of perchloric acid and sulfuric acid electrolytes.

$E_{1/2}$ values for the redox potential couple will be measured and compared between the various electrolytes.

SRNL and LANL will compare and discuss the electrochemical results.

Redox Potential *vs*. ORR Activity

Supposition: there is a correlation between redox peak potential and ORR

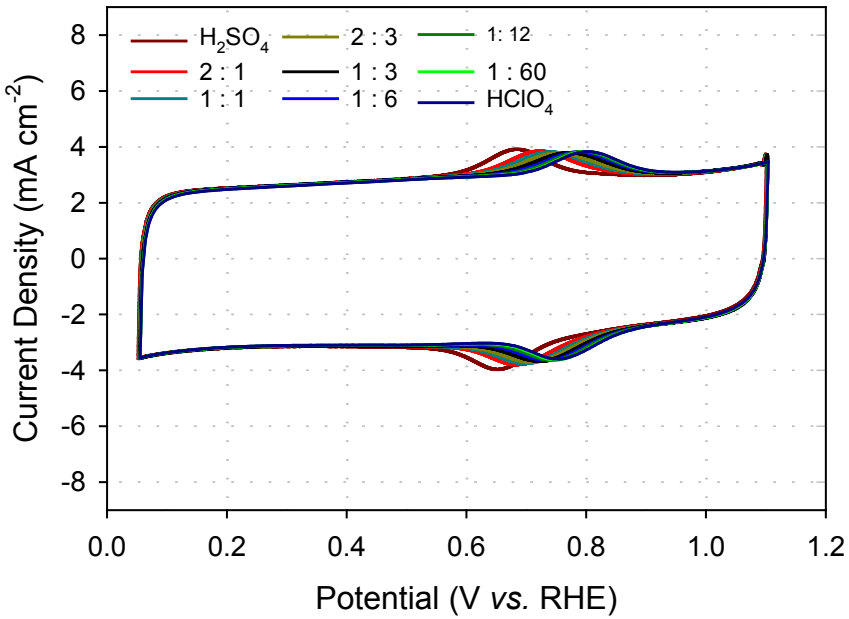


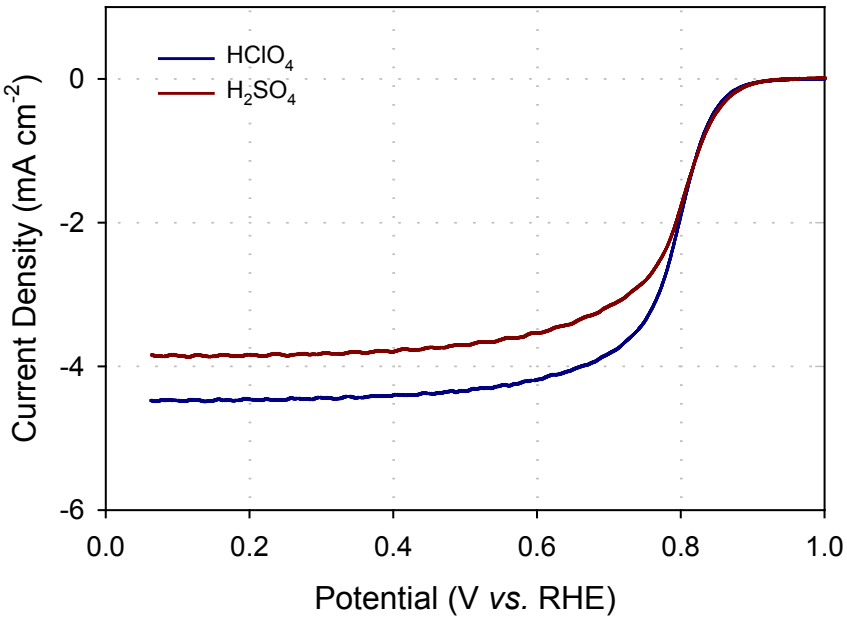
Tylus et al., *J. Phys. Chem. C*, 118, 8999 (2014)

Los Alamos NATIONAL LABORATORY

Redox Potential *vs.* ORR Activity: SRNL Fe-N-C Catalyst

CV: 0.62 mg cm^{-2} **N_2 saturated acid concentration: 0.5 M**; 0 rpm; 25ºC; Hg/$HgSO_4$ reference electrode; graphite counter electrode; linear scan voltammetry: 50 mV/s
ORR: 0.6 mg cm^{-2}; **O_2 saturated acid concentration: 0.5 M** ; 900 rpm; 25ºC; Hg/$HgSO_4$ reference electrode; graphite counter electrode; linear scan voltammetry: 5 mV/sec





Left graph shows a family of CVs for different mixtures of H_2SO_4 and $HClO_4$ yielding different redox potentials of the Fe-based catalyst.

Right graph compares ORR for H_2SO_4 and $HClO_4$. The onset potentials and kinetic region activity are identical.

Redox peaks showing no correlation to ORR performance for SRNL Fe-N-C PGM-free catalyst

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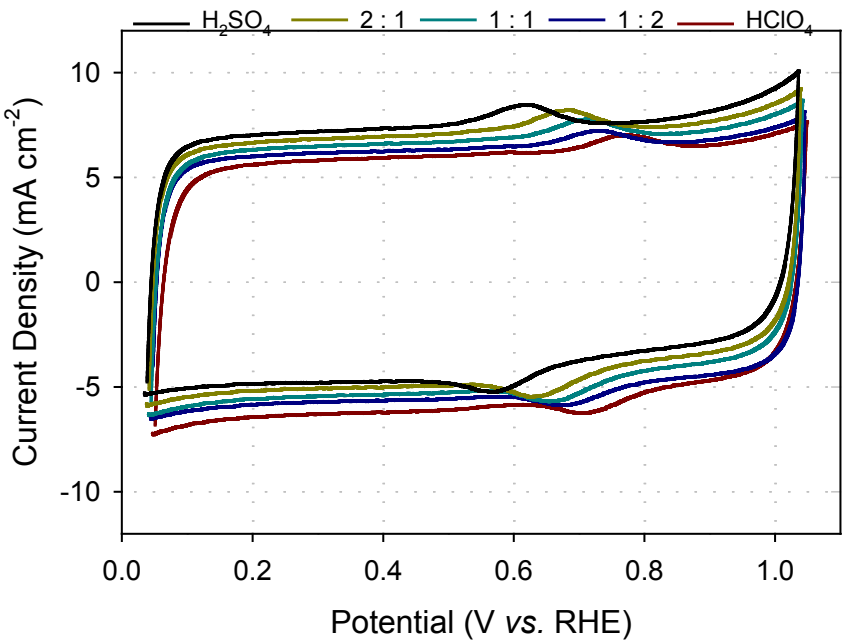
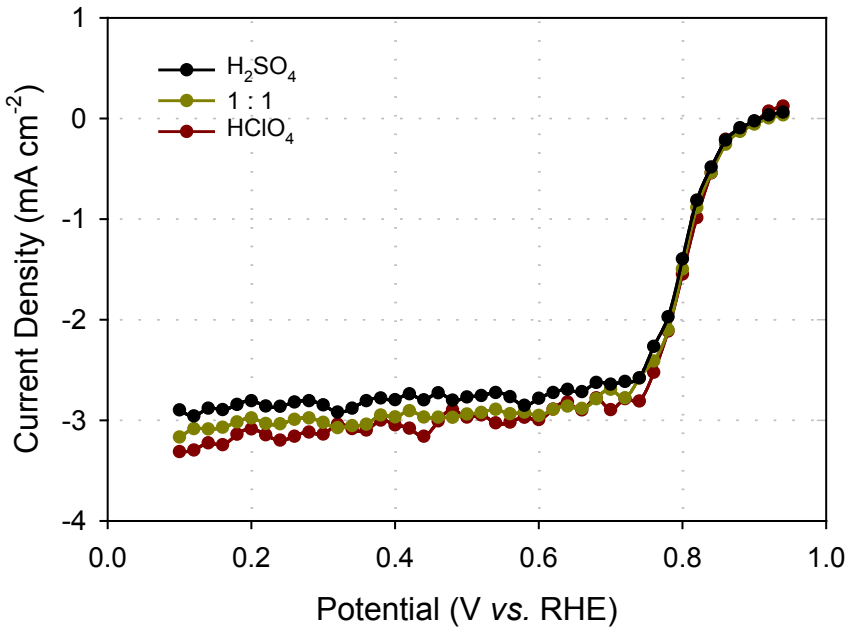
Redox Potential *vs*. ORR Activity: LANL Fe-N-C Catalyst

CV: 0.6 mg cm^{-2} **N_2 saturated acid concentration: 0.5 M**; 0 rpm; 25ºC; Hg/$HgSO_4$ reference electrode; graphite counter electrode; linear scan voltammetry: 50 mV/sec
ORR: 0.6 mg cm^{-2}; **O_2 saturated acid concentration: 0.5 M** ; 900 rpm; 25ºC; Hg/$HgSO_4$ reference electrode; graphite counter electrode; steady-state potential program: 20 mV steps, 20 s/step





Left graph shows a family of CVs for different mixtures of H_2SO_4 and $HClO_4$ yielding different redox potentials.

Right graph compares ORR for H_2SO_4, $HClO_4$, and a 50% Mixture of the two. The onset potentials and activity in the kinetic region are identical.

Redox peaks showing no correlation to ORR performance for LANL Fe-N-C PGM-free catalyst

Los Alamos NATIONAL LABORATORY

On-Going Work/Future Collaborators:

- UCLA Catalysts
  - Continue to perform testing of Mo-doped Pt_3Ni octahedra catalysts
- Blue-O-Technology
  - Complete catalyst testing of Pt, Pt, and Pt/TiO_2
  - Catalyst Performance and Durability
  - Investigate novel support materials
- ElectroChem, Inc.
  - Stack testing and validation (awaiting stack)
- SRNL
  - Compete results with PGM-free testing to solidify finding: Redox potentials vs. ORR activity
- NIST, Univ. of Hawaii, Univ. of Tennessee-Knoxville
  - Provide neutron imaging hardware and guidance on its usage
- 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.
  - Provided 8 catalysts samples
  - Performed approx. 134 depositions for multi-layering metal plates
- UCLA Catalysts
  - Performed initial testing of Mo-doped Pt_3Ni octahedra catalysts (10,000 cycles)
- Blue-O-Technology
  - Prepared catalyst inks and MEAs
  - Conducted initial performance tests in fuel cell: Pressure and Temperature dependence, Air vs Oxygen Polarization curves
  - XRD showed well defined catalyst structures
- ElectroChem, Inc.
  - Stack testing and validation (awaiting stack)
- SRNL
  - Independent tests results did correlate: Redox potentials vs. ORR activity
- NIST, Univ. of Hawaii, Univ. of Tennessee-Knoxville
  - Provided neutron imaging hardware and guidance on its usage
- Participate on the DOE/USCAR U.S. DRIVE Fuel Cell Tech Team
- Continue to support DOE Working groups
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Presentations and Publications

Le Xin, Yu Kang, Fan Yang, Aytekin Uzunoglu, Tommy Rockward, Paulo Jorge Ferreira, Rod L. Borup, Jan Ilavsky, Lia Stanciu, Jian Xie, Novel Catalyst-Layer Structures with Rationally Designed Catalyst/Ionomer Interfaces and Pore Structures Aided By Catalyst Functionalization, 2016/9/1, Meeting Abstracts, The Electrochemical Society

Le Xin, Fan Yang, Aytekin Uzunoglu, Tommy Rockward, Rod L. Borup, Lia Stanciu, Jian Xie, Highly Stable Hierarchical Polybenzimidazole (PBI) Grafted Graphene/Nanographene Hybrids As Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells, 2016/9/1, Meeting Abstracts, The Electrochemical Society

Jacob S. Spendelow, Luis Castanheira, Gareth Hinds, Tommy Rockward, David A. Langlois, Rangachary Mukundan, Rod L. Borup, Measurement of Local Electrode Potentials in an Operating PEMFC Exposed to Contaminants 2016/9/1, Meeting Abstracts, The Electrochemical Society

Xin, Le; Yang, Fan; Qiu, Yang; Uzunoglu, Aytekin; Rockward, Tommy; Borup, Rodney L.; Stanciu, Lia A.; Li, Wenzhen; Xie, Jian, Polybenzimidazole (PBI) Functionalized Nanographene as Highly Stable Catalyst Support for Polymer Electrolyte Membrane Fuel Cells (PEMFCs)
Journal of the Electrochemical Society (2016), 163(10), F1228-F1236

Kerrie K. Gath, Mark Ricketts, Jun Yang, Chunchuan Xu, and Shinichi Hirano, Multi-Layer Thin Film Coatings on Bipolar Metal Plates for PEMFC, 2016/9/1, Meeting Abstracts, The Electrochemical Society

Acknowledgements

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