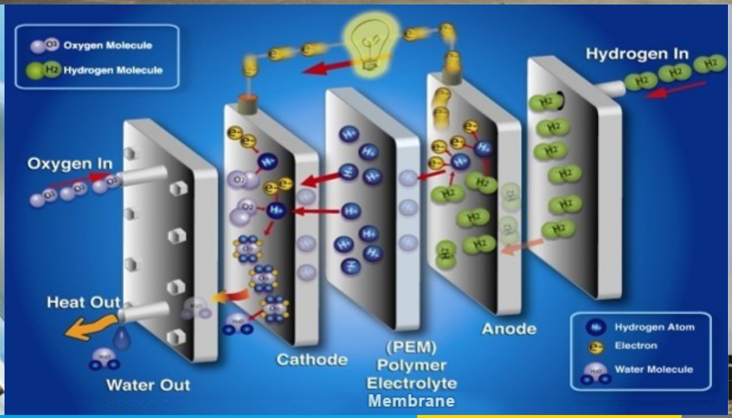
U.S. Department of Energy
Fuel Cell Technologies Office

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







ElectroCat: DOE's Approach to PGM-Free Catalyst and Electrode R&D

21St International Conference on Solid State Ionics
Padua, Italy
June 19, 2017

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Fuel Cell Technologies Office
U.S. Department of Energy

The ElectroCat (Electrocatalysis) Consortium

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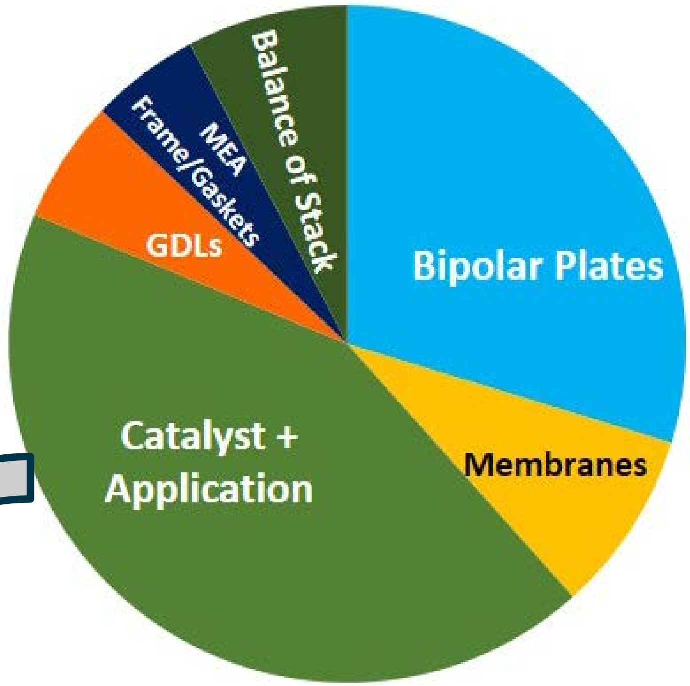
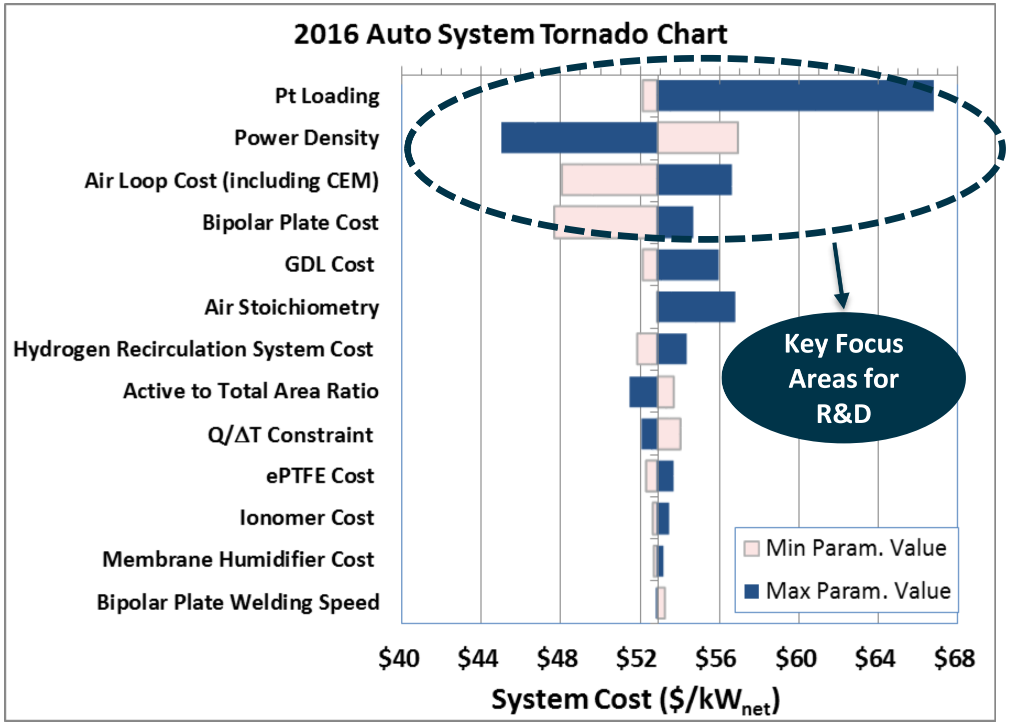
Accelerating the development of PGM-free electrocatalysts for next-generation fuel cells

Analysis Guides Fuel Cell R&D Focus Areas

PEMFC Stack Cost Breakdown*



Sensitivity Analysis



***Catalyst cost** is projected to be the largest single component of the cost of a PEMFC manufactured at high volume.*

Catalyst cost is high because of the need to include PGM metals like Pt.

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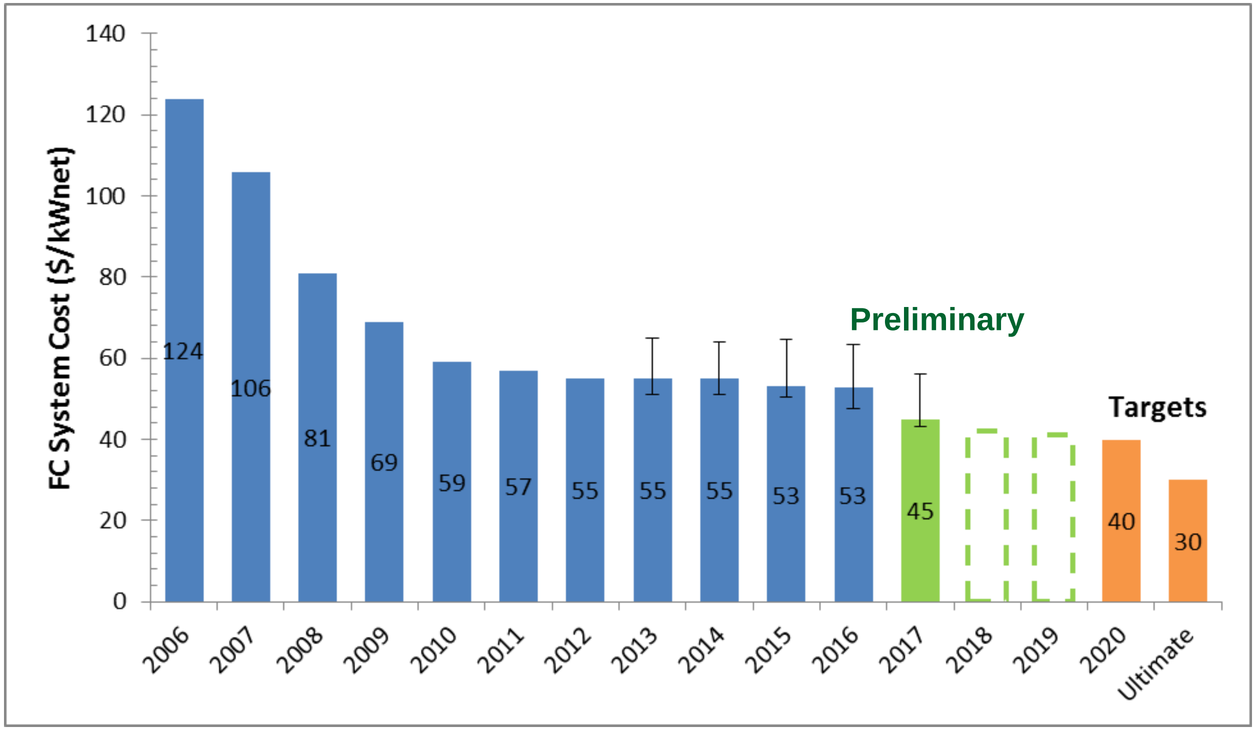
*@ 500,000 systems/year

Fuel Cell Cost Improvements

Fuel Cell Cost Status

- **$53/kW*** for 500,000 units/year
- **$59/kW*** for 100,000 units/year
- **$230/kW†** for currently commercialized technology at 1,000 units/year



Preliminary values for 2017 fuel cell transportation system cost at volumes of 500,000 and 100,000 units/year are $45/kW and $50/kW, respectively.

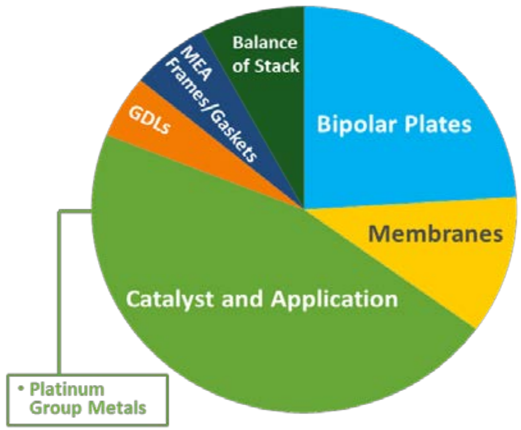
** SA Inc., bottom-up analysis of model system manufacturing cost, high volume manufacturing with next-gen lab technology*
† SA Inc., bottom-up analysis of model system based on commercially available FCEVs

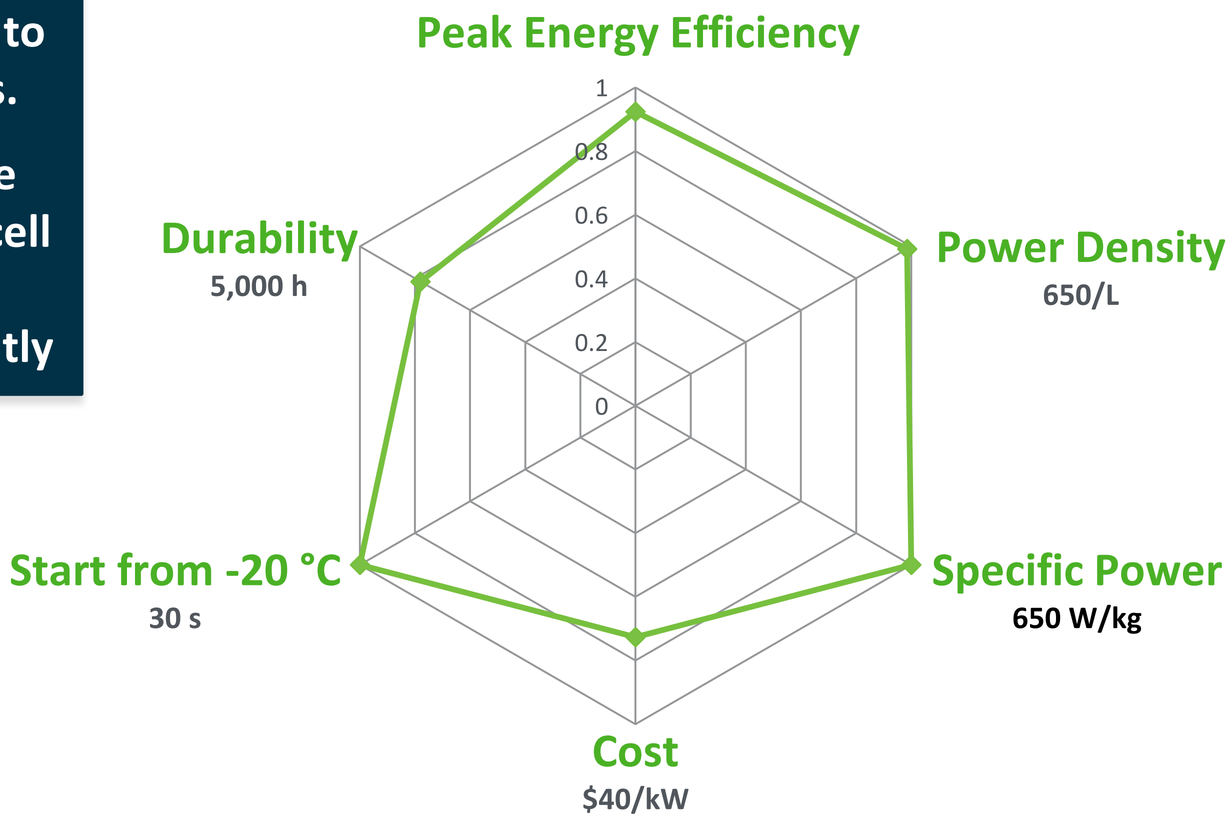
https://www.hydrogen.energy.gov/pdfs/16020_fuel_cell_system_cost_2016.pdf

Problem Statement

Fuel cell system targets set to be competitive with ICEVs.

Durability and cost are the primary challenges to fuel cell commercialization and must be met concurrently





PGM-free catalysts lag behind platinum in efficiency, durability, cost, and ease of integration into membrane electrode assemblies.

Approach: Performance Targets

Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Platinum group metal total content (both electrodes)	g / kW (rated, gross) @ 150 kPa (abs)	0.16	0.125
Platinum group metal (pgm) total loading (both electrodes)	mg PGM / cm^2 electrode area	0.13	0.125
Mass activity	A / mg PGM @ 900 $mV_{iR\text{-}free}$	>0.5	0.44
Loss in initial catalytic activity	% mass activity loss	66	<40
Loss in performance at 0.8 A/cm^2	mV	13	<30
Electro catalyst support stability	% mass activity loss	41	<40
Loss in performance at 1.5 A/cm^2	mV	65	<30
PGM-free catalyst activity	**A / cm^2 @ 900 $mV_{IR\text{-}free}$**	**0.016**	**>0.044**

PGM-free containing MEAs need to meet DOE performance and durability targets

PGM-free activity target equivalent to PGM activity target:

$$0.44\ A/mg_{PGM} \times 0.1\ mg_{PGM}/cm^2_{(electrode\ area)} \rightarrow 0.044\ A/cm^2$$

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FCTO MYRDD Plan - Section 4.4 Fuel Cells, DOE 2016

Strategy: Research Priorities

Materials Discovery & Development	**Catalysts** for oxygen reduction in low-temperature PEMFCs and PAFCs
	Catalysts for oxygen reduction and hydrogen oxidation in AMFCs
	Development of **electrodes and MEAs** that are compatible with PGM-free catalysts
Tool Development	Optimization of **atomic-scale** and **meso-scale models** of catalyst activity to predict macro-scale behavior
	High-throughput techniques for catalyst synthesis
	High-throughput techniques for characterization of catalysts, electrodes, and MEAs
	Aggregation of data in an easily searchable, public database to facilitate the development of catalyst materials and MEAs

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ElectroCat Capabilities Overview

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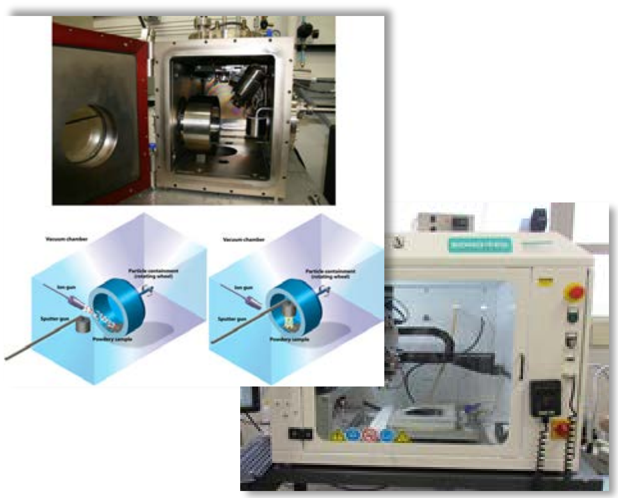
Los Alamos National Laboratory · Argonne National Laboratory · Oak Ridge National Laboratory · NREL National Renewable Energy Laboratory

➢ **Comprising 27 world-class capabilities and expertise in:**

- ***Catalyst synthesis, characterization, processing, and manufacturing***
- ***High-throughput, combinatorial techniques***
- ***Advanced computational tools***

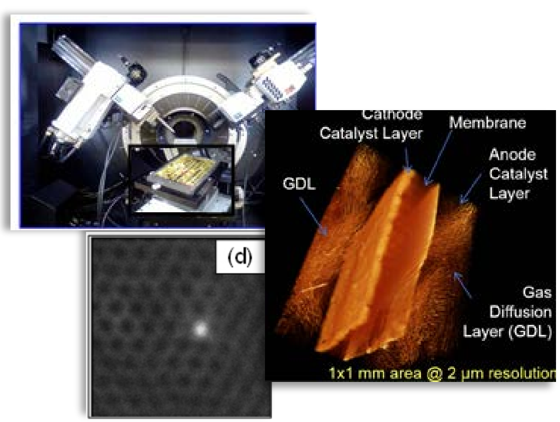
Synthesis, processing and manufacturing

- ✓ High surface area catalysts
- ✓ Planar model systems synthesis
- ✓ Fabrication of electrodes and membrane electrode assemblies



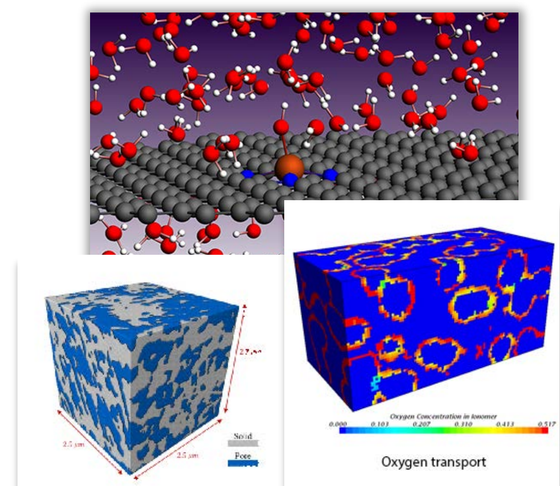
Characterization and Synthesis

- ✓ Materials Characterization
- ✓ Electrode/Cell Characterization & Diagnostics
- ✓ Model Systems Characterization



Computation, Modeling & Data Management

- ✓ Modeling structure-function relationships
- ✓ Methods and models to characterize behavior
- ✓ Systems for handling and correlating data



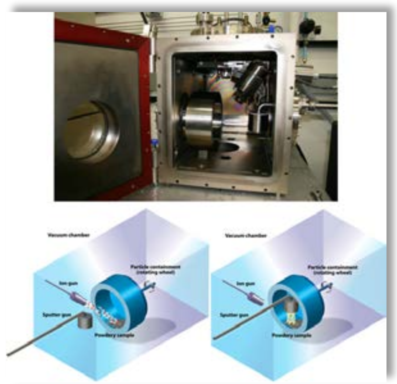
Synthesis, Processing and Manufacturing Capabilities

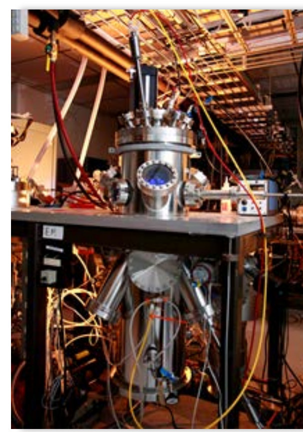
High Surface Area Catalysts

- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- Sputter Deposition of Thin Films and High Surface Area Catalysts (ORNL)
- Powder Sputter and Implant System (NREL)
- High-throughput Synthesis of PGM-free Catalysts and Electrodes (ANL)

Model Systems Synthesis

- Controlled Functionalization of Model Catalysts (LANL)
- Sputter Deposition of Thin Films and High Surface Area Catalysts (ORNL)
- High-throughput (HT) Thin Film Fabrication and Characterization (NREL)





Fuel Cell Fabrication

- Membrane-Electrode Assembly Fabrication (LANL)
- High-throughput Synthesis of PGM-free Catalysts and Electrodes (ANL)
- High-throughput Approaches to Scaling PGM-free Electrodes (NREL)
- Manufacturing Porous Electrodes (ORNL)

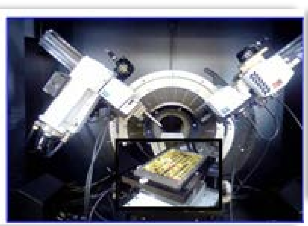
Characterization and Testing Capabilities

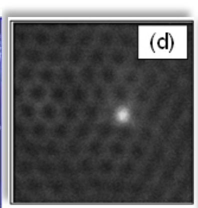
Materials Characterization

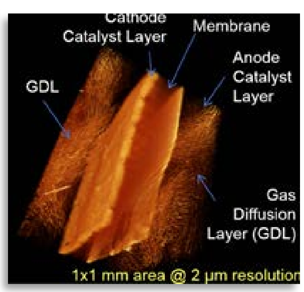
- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- X-Ray Characterization Techniques (LANL)
- X-Ray Photoelectron Spectroscopy (ORNL)
- Electron Tomography (ORNL)
- Analytical Electron Microscopy (ORNL)
- In situ Electron Microscopy (ORNL)
- Structure/Composition-Function Relationships and Active Sites (ANL)
- In situ and Operando Atomic, Nano-, and Micro-structure Characterization (ANL)
- Combinatorial Hydrodynamic Screening of PGM-free Catalyst Activity and Stability (ANL)
- High-throughput Characterization of PGM-free Catalysts and Electrodes (ANL)

Electrode and Cell Characterization

- Operando Differential Cell Measurements of Electrochemical Kinetics and Transport (NREL)
- PGM-free Catalyst Synthesis, Analytical Characterization, and Electrochemical and Fuel Cell Testing (LANL)
- Electrode Microstructure Characterization and Simulation (ANL)
- Electron Tomography (ORNL)
- Analytical Electron Microscopy (ORNL)
- In situ and Operando Atomic, Nano-, and Micro-structure Characterization (ANL)
- Segmented Cell System Optimized for R&D Combinatorial Studies (NREL)
- In situ Fluoride and Carbon Dioxide Emission Measurements (LANL)
- Segmented Cell and Neutron Imaging (LANL)
- High-throughput Characterization of PGM-free Catalysts and Electrodes (ANL)







Model Systems Characterization

- Controlled Functionalization of Model Catalysts (LANL)
- X-Ray Photoelectron Spectroscopy (ORNL)
- High-throughput (HT) Thin Film Fabrication and Characterization (NREL)

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Computation, Modeling & Data Management

Catalyst Modeling

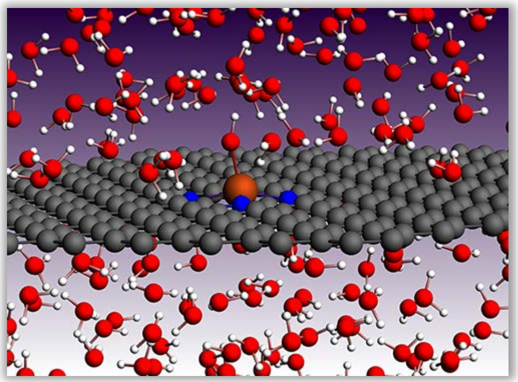
- Multi-scale Modeling
- Rational Design of PGM-free Catalysts (LANL)

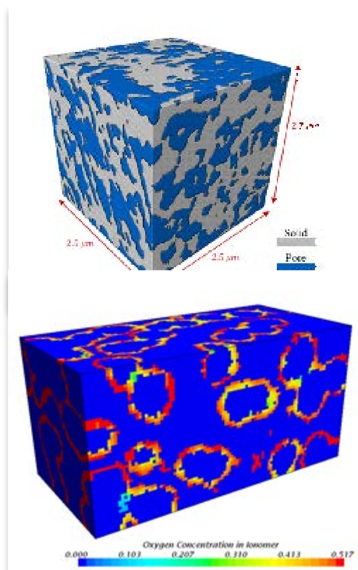
Electrode/Fuel Cell Performance Modeling

- Electrode Microstructure Characterization and Simulation (ANL)
- Modeling Kinetic and Transport Processes in PGM-free Electrodes (ANL)

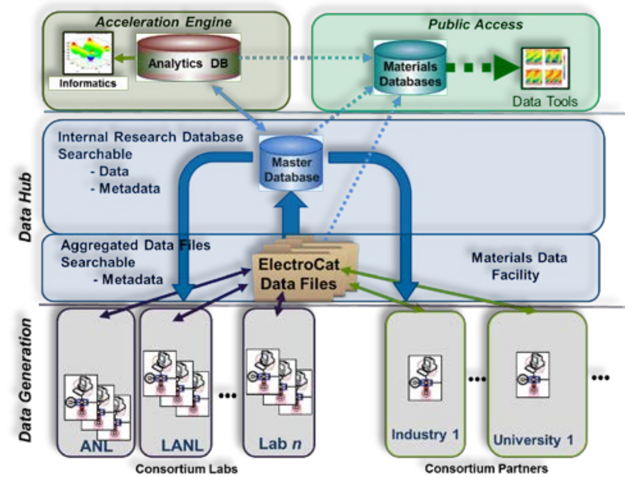
Data Management

- Experimental and Computational Materials Data Infrastructure (NREL)
- Materials Data Facility and Globus (ANL)





Oxygen transport



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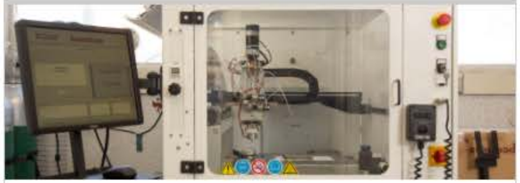
Capabilities



Synthesis, Processing & Manufacturing

ElectroCat has numerous techniques available for synthesis and post-synthesis processing of PGM-free catalysts in high-surface-area form or as planar model systems, and fabrication of electrode layers and membrane electrode assemblies.

High Surface Area Catalysts

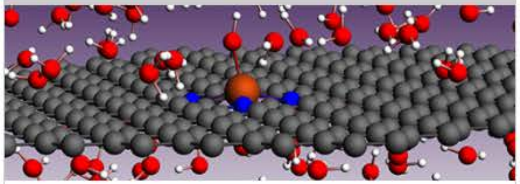
Synthesis of PGM-free catalysts using methods such as tuning of precursor solution chemistry, spray-pyrolysis,

Characterization & Testing

ElectroCat has a wide array of capabilities characterize the composition, structure, and performance of high-surface-area PGM-free catalyst powders, catalyst-ionomer inks, electrode layers, membrane electrode assemblies, and thin film model catalysts.

Materials Characterization

Instruments and expertise to characterize the elemental composition, phase composition, atomic structure, surface area, particle size and pore size distributions,



Computation, Modeling & Data Management

ElectroCat's experimental synthesis and characterization efforts are guided and complemented by computational and modeling capabilities at the catalyst, electrode, and membrane electrode assembly levels, as well as by data management expertise.

Catalyst Modeling

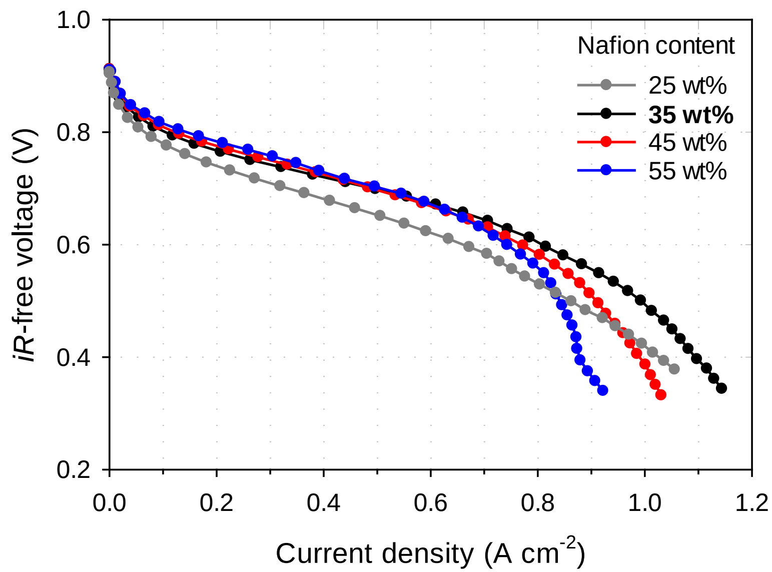
Modeling structure-function relationships, including active site identification and modeling of structural

ElectroCat Technical Accomplishments

Performance Improvement

- Improved PGM-free H_2-air as-measured performance **by 25%** versus 2016 status by using Zn as a pore-forming component in the (CM+PANI)-Fe-C catalyst synthesis and by optimizing electrode ionomer content

Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.8 mg cm^{-2} catalyst loading, air, 200 sccm, 1.0 bar air partial pressure; **Membrane:** Nafion®, 211; **Cell:** 5 cm^2, 80 °C



- Increased ORR activity for atomically-dispersed Fe-N-C catalyst **by 20 mV** at $E_{½}$

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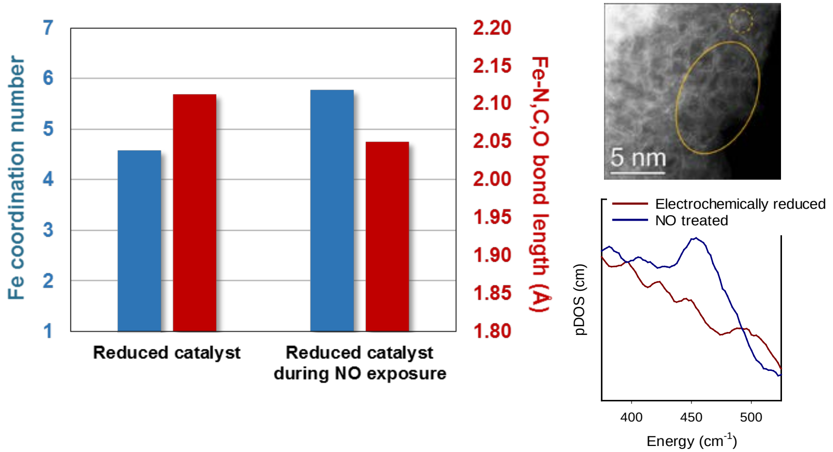
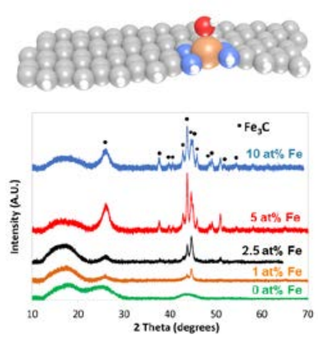
Characterization

- Obtained **direct microscopic and spectroscopic evidence** of a majority of **Fe sites being on the surface** and **atomically dispersed in (AD)Fe-N-C**

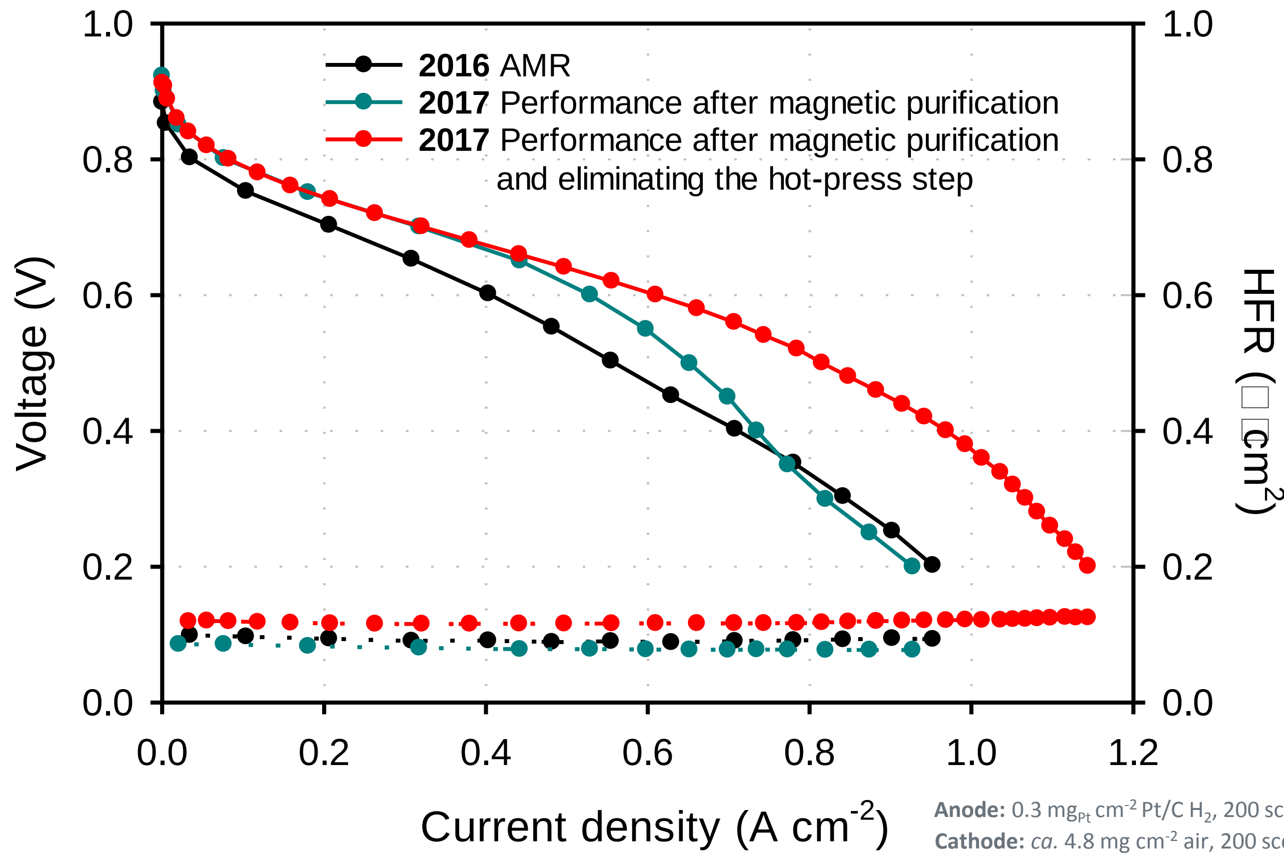


High-Throughput (HT)

- Used **HT software to calculate durability descriptor** for PGM-free cathode catalysts
- Used **HT robotic system to synthesize and characterize** 40 variations of (AD)Fe-N-C



Fuel Cell Performance of (CM+PANI)-Fe-C(Zn) Catalyst



Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.8 mg cm^{-2} air, 200 sccm, 1.0 bar air partial pressure; **Membrane:** Nafion®,211; **Cell:** 5 cm^2, 80 °C

Improved fuel cell performance in both kinetic and mass transport region reaching a current density of 93 mA/cm² (120 mA/cm² at 0.80 $V_{iR\text{-free}}$)

- **Kinetic region** - increasing micropore surface area by Zn evaporation and removal of magnetic Fe species
- **Mass transport region** - removed hot pressing step

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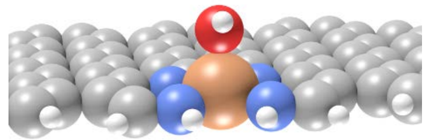
Durability Descriptor Calculation Automation (DDCA)

(1) Input Structure:

*FeN_4(*OH) - ZZ edge*



(2) Structure Relaxed

ORR Activity Calculations

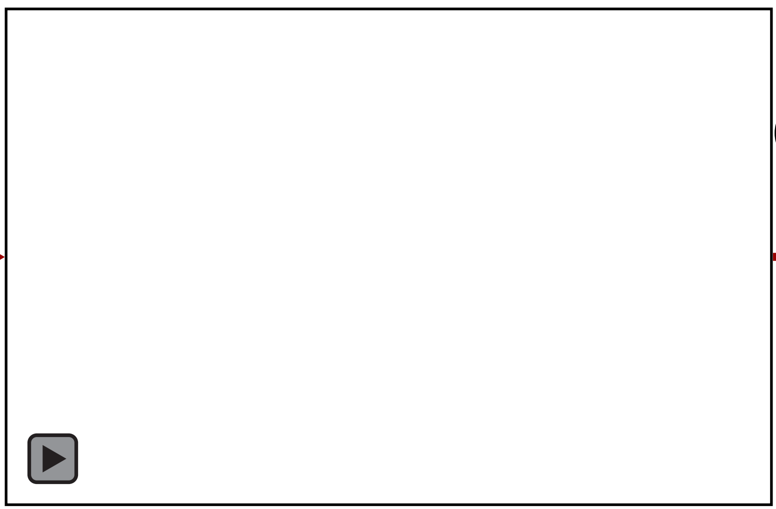
(3) DDCA Setup Script:
input of atoms and energy ranges to test

$$T_{max} = \frac{2ME\left(E + 2mc^2\right)}{\left(M+m\right)^2 c^2 + 2ME} \qquad v_{max} = \sqrt{\frac{2T_{max}}{M}}$$

Zobelli, *et al.*, *PRB* **75**, 245402 (2007)

(4) *Ab-initio* Molecular Dynamics (AIMD) Simulations
(100 fs)

(5) DDCA Visualization Script:
generate movies of AIMD calculations in automated fashion



70 kV e^- impacting N of FeN_4 complex at ZZ edge

(6) DDCA Analysis Script:
determine KODTE for each atom

pymatgen ASE

(7) Durability Descriptor for Input Structure

Successful automation of setup, calculation/submission, visualization, and durability descriptor analysis

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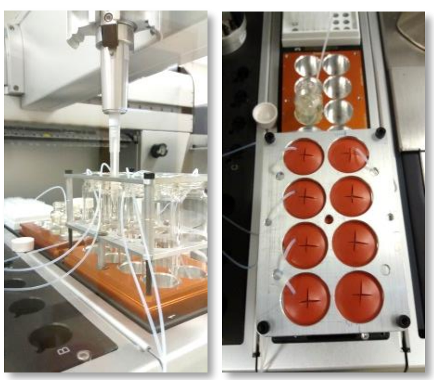
High-throughput Synthesis and Characterization

Utilized Argonne's robotic system to explore catalyst composition and heat treatment effects using simultaneous pyrolysis, high-throughput structural characterization using XRD and XAFS, and a multi-channel flow double electrode cell for ORR activity characterization.

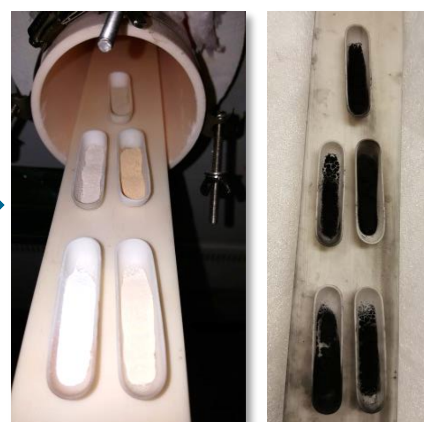
Parameters varied to obtain 40 unique samples based on (AD)Fe-N-C catalyst:

- ✓ Fe-to-Zn ratio: 0, 1, 2.5, 5, and 7.5 at% Fe in precursors
- ✓ Fe salts: sulfate, nitrate, acetate
- ✓ Heat-treatment temperatures: 900, 1000, 1100°C

Precursor synthesis: CM Protégé Robot

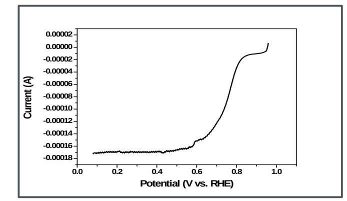


Heat Treatment

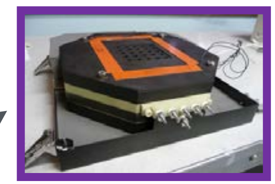


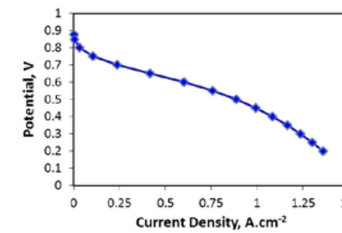
Characterization

ORR Activity

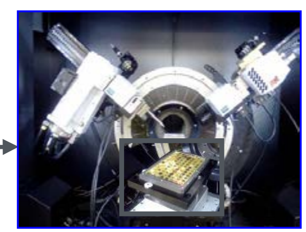


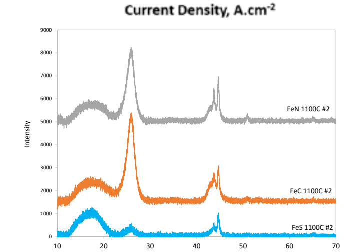
MEA Performance



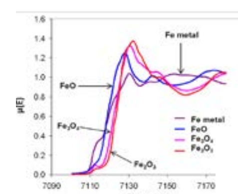


Phase Composition





Atomic Structure



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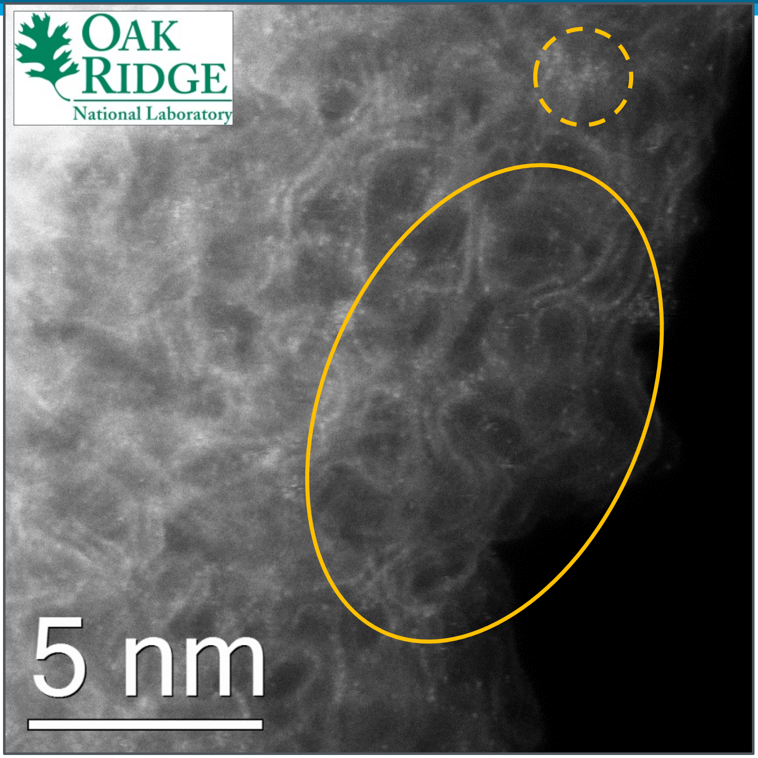
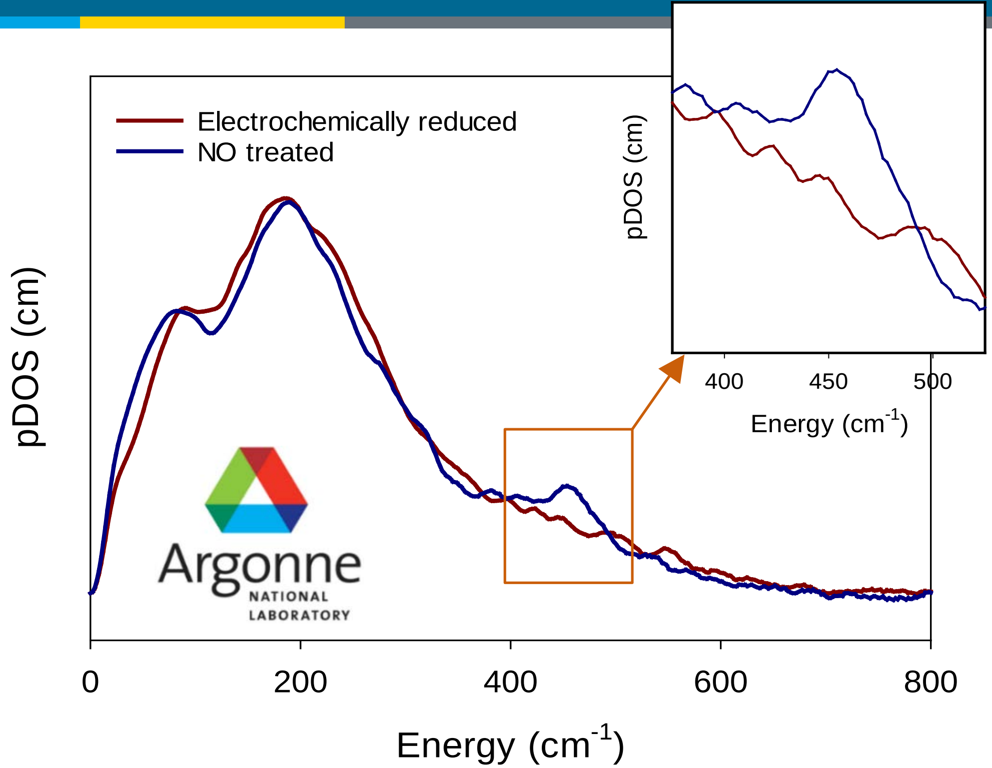
Direct Detection of Fe Sites on (AD)^{57}Fe-N-C





- ^{57}Fe-enriched catalyst demonstrating the same properties as non-enriched catalyst: atomically dispersed iron seen (solid yellow line), with some Fe-clustering (dashed yellow line)
- Nuclear resonance vibrational spectroscopy (NRVS) used with NO as a molecular probe (an O_2 analog) to detect iron sites on (AD)^{57}Fe-N-C catalyst; vibrational feature for NO-treated catalyst at a frequency of 450 cm^{-1}, likely corresponding to the Fe-NO bond stretch (assignment pending)

Direct evidence of the presence of Fe sites on the surface of a PGM-free catalyst!

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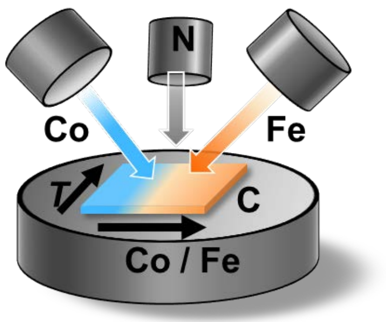
Los Alamos National Laboratory

Capability Development: Model System Synthesis & Characterization

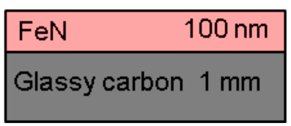
Capability: Combinatorial Synthesis and Spatially-Resolved Characterization

PVD Synthesis

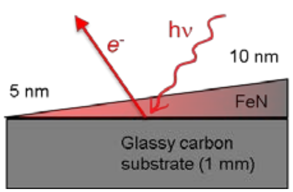


Purpose: Elucidate the nature of ORR active sites and discover materials with enhanced ORR activity using PGM-free thin films with well-controlled composition and structure

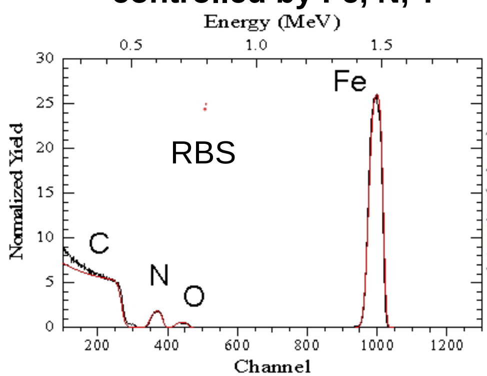
Thick film to determine deposition conditions



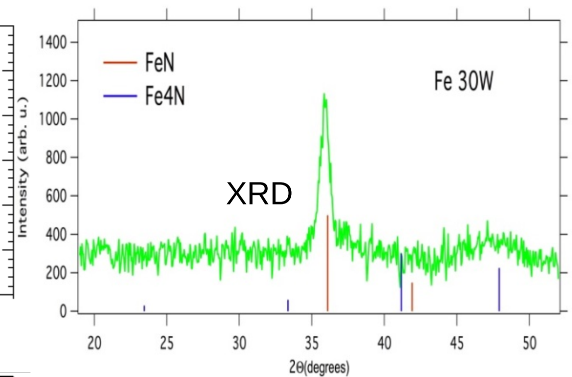
FeN/C interface by thin film deposition

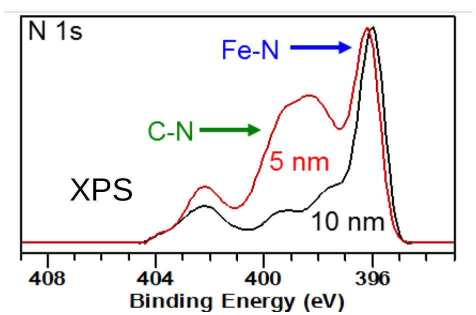


Fe-N composition controlled by Fe, N, T



Tetrahedral FeN formed





- Fe-N bonds present in FeN thin films
- C-N bonds formed at FeN/C interface
- Formation of FeN_4 moiety in carbon matrix likely

Summary: Demonstrated first Fe-C-N model systems with composition similar to active catalysts

Next step: Perform RDE testing of ORR activity to assess catalytic performance of the model systems

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NREL NATIONAL RENEWABLE ENERGY LABORATORY

Technology Transfer and Agreements (TT/A)

Non-Disclosure Agreement (NDA) → Information Disclosure

Intellectual Property Management Plan → IP Protection

Sponsored Research Agreements (CRADAs and SPPs) → Collaboration

Licensing and Material Transfer Agreements (MTAs)

↓

Access / Freedom to Operate

Industry Engagement Plan (IEP) finalized and agreed upon

Multi-Laboratory Non-Disclosure Agreement (NDA) executed

Intellectual Property Management Plan (IPMP) in process

CRADA Template – complete; previously agreed upon format; available for use

Material Transfer Agreement (MTA) – in process

Argonne NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY

ElectroCat FY17 FOA Projects Announced

Carnegie Mellon University

Advanced PGM-free Cathode Engineering for High Power Density and Durability

Pacific Northwest National Laboratory

Highly Active and Durable PGM-free ORR Electrocatalysts through the Synergy of Active Sites

Giner, Inc.

Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells

Greenway Energy, LLC

PGM-free Engineered Framework Nano-Structure Catalysts

Save the Dates!

National Hydrogen & Fuel Cell Day | 10·08

Participate in social media using
#HydrogenNow #FuelCellsNow

H2@Scale Session at the Fuel Cell Seminar
November
Long Beach, LA

AMR and Industry Expo
June 2018 (to be confirmed soon)
Washington, DC

Thank You

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Backup Slides

Future Work

- **Consortium Development**
  - ✓ Incorporate collaborators from DE-FOA-0001647 into ElectroCat and coordinate activities of all ElectroCat partners;
  - ✓ Update ElectroCat website with information from FOA projects, status of capabilities, publications;
  - ✓ Implement capabilities to mint DOIs and other identifiers with persistent landing pages for datasets and to support automated data capture and publication;
  - ✓ Document ElectroCat Data Sources: **(i)** formats, **(ii)** associated metadata, **(iii)** sharing needs, and **(iv)** dataset comparison or integration needs;
  - ✓ Execute intellectual property management plan and material transfer agreements.
- **Performance and Durability Improvement**
  - ✓ Advance activity of atomically dispersed catalysts by maximizing concentration and accessibility of active centers through **(i)** the development of novel synthesis approaches, **(ii)** optimization of hierarchical pore-size and ionomer distribution, and **(iii)** decreasing electrode tortuosity
  - ✓ Explore (AD)Fe-N-C parameter space for improved performance and durability using high-throughput activity, durability, and performance testing of 40 materials synthesized to date
  - ✓ Determine primary factors governing the durability of PGM-free catalysts, concentrating predominantly on homogenous and thus easier to study materials
  - ✓ Further develop surface-specific methods for the ORR active-site determination

Any proposed future work is subject to change based on funding levels

Remaining Challenges and Barriers

- Oxygen reduction reaction activity of PGM-free ORR catalysts in continued need of further improvement to reduce cathode thickness and lower cost of other stack components
- Insufficient long-term stability and performance durability under steady-state and load-cycling conditions
- Limited understanding of the ORR mechanism, nature of the ORR active site and mechanism of catalyst degradation preventing rational design of next-generation PGM-free catalysts
- Low volumetric density of active sites
- Electrode design and component integration to provide adequate ionic, electronic, and mass transport to and from active sites
- Replacement of Fe in catalyst with another PGM-free transition metal not catalyzing hydroperoxy radical formation and ionomer degradation
- Integration with existing automotive fuel cell stack and system technology