ElectroCat
Electrocatalysis Consortium

Summary of ElectroCat Experimental Capabilities

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Argonne National Laboratory
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U.S. Department of Energy | Energy Efficiency & Renewable Energy

ElectroCat Workshop, Argonne National Laboratory – July 26, 2016

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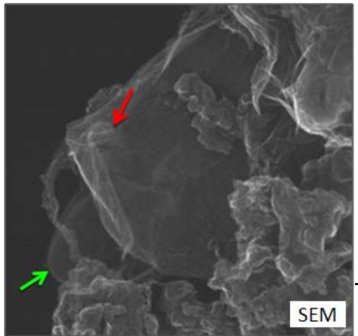
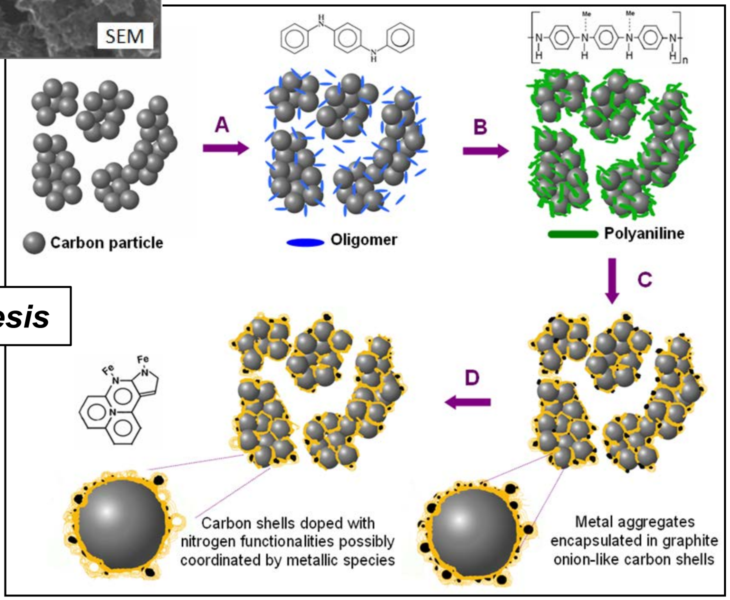
Synthesis of PGM-free Catalysts

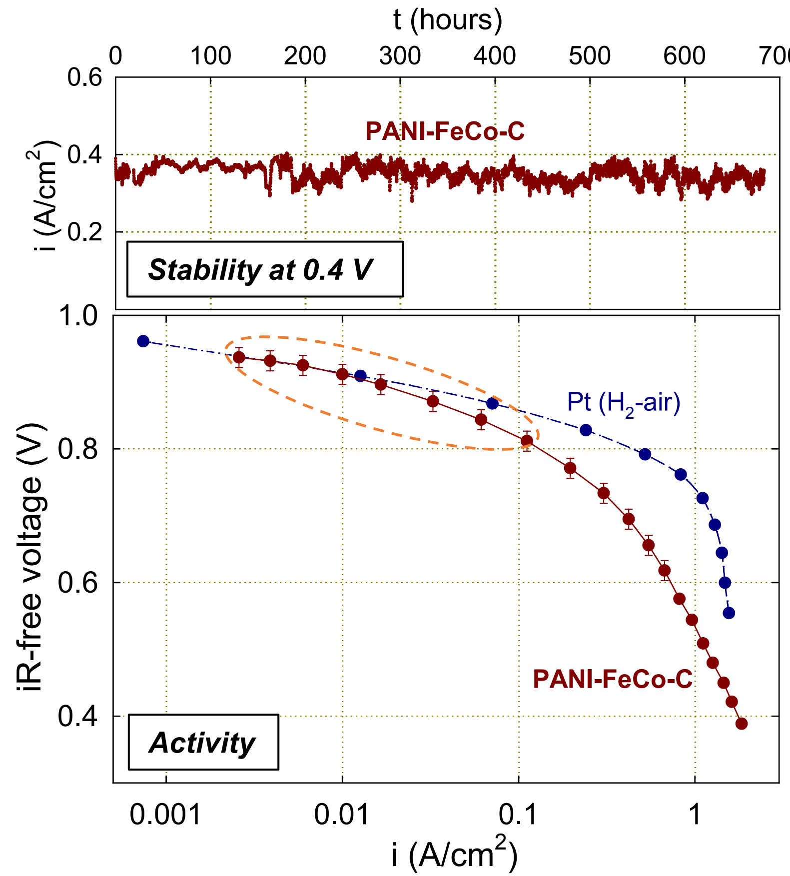


Catalyst SEM: *Layered-graphene sheet marked with green arrow; FeCo- nanoparticle shown with a red arrow.*

G. Wu *et al.*, *Science*, **332**, 443, 2011

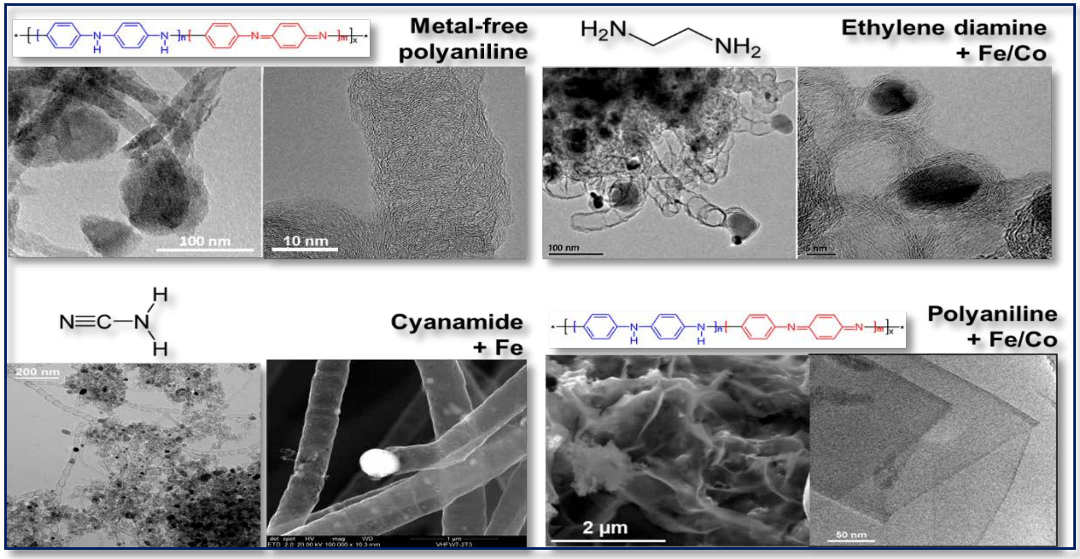
The Synthesis



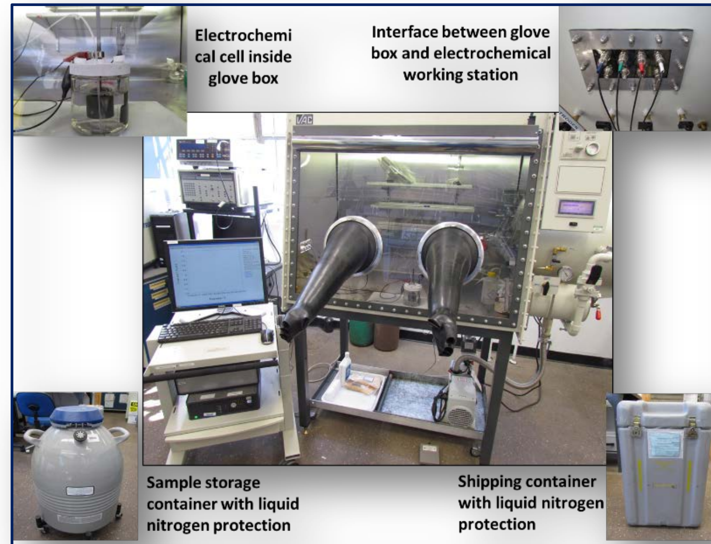


- PGM-free catalyst development, spanning nearly 15 years; lately, focusing on catalysts obtained by high-temperature treatment of transition-metal, nitrogen, and carbon precursors
- PANI-family of catalysts, combining high activity and selectivity with promising stability and low cost; recent dual nitrogen-precursor approach, *e.g.*, PANI-CM-Fe-C catalyst, allowing for significant enhancement in power density of air-operated fuel cell

Synthesis of PGM-free Catalysts



LANL's PGM-free Nanostructured Carbon Catalysts



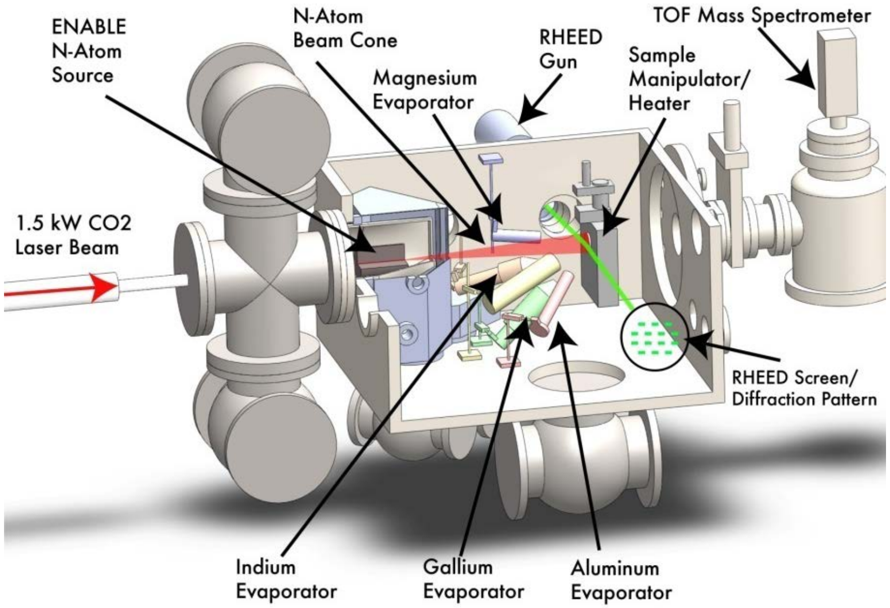
Oxygen-free wet glove box connected to potentiostat

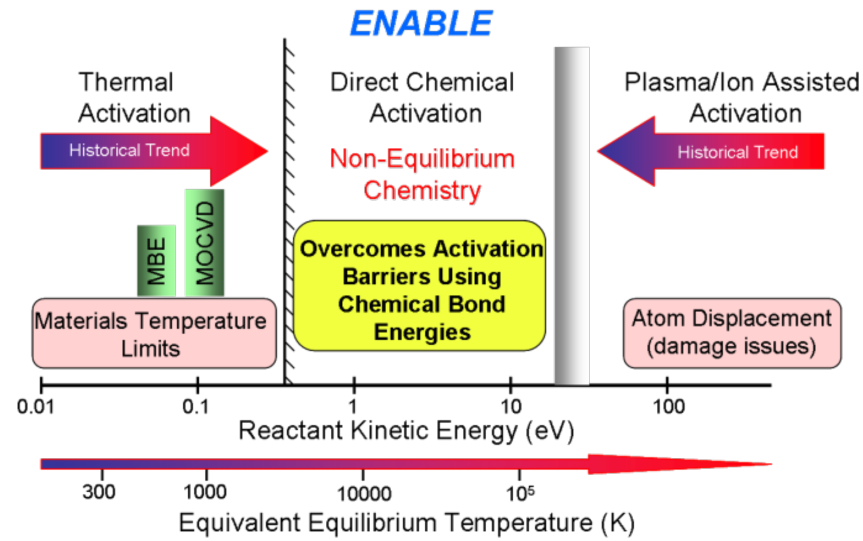
Freeze dryer

High-energy ball mill

- Low- and high-temperature chemical synthesis
- Synthesis by ultrasonic-spray pyrolysis
- Polymer-assisted deposition (bulk powders, thin films)
- Electrospinning, freeze-drying, ball milling
- Multiple batch and plug-flow hydrothermal reactions
- Catalyst modification in O_2-free wet glove box
- Electron beam evaporation; RF magnetron sputtering
- Rapid expansion synthesis of ceramic supports
- Controlled synthesis of carbon nanostructures, such as graphene and carbon nanotubes (found to enhance the performance and activity of PGM-free catalysts)

Controlled Functionalization of Model Catalysts

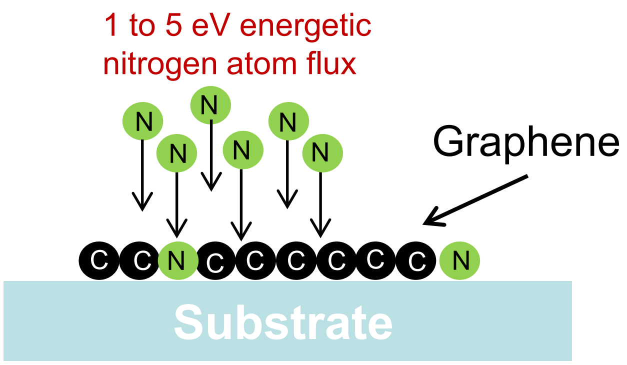




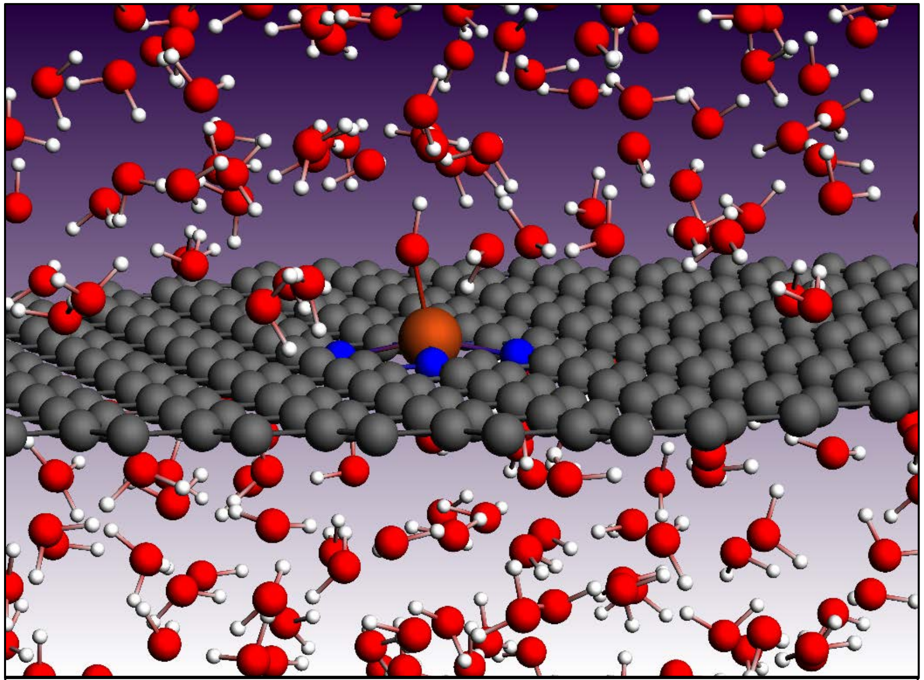
Advantages:

- Substrate can be directly functionalized (N- or O-doped) without inducing defects or degrading structural integrity
- Control of substrate temperature and neutral atom energy for selective functionalization
- High nitrogen incorporation fraction (up to ~9 at.% observed) with few-minute exposure
- Scalable platform capable of processing large volumes
- No toxic chemical precursors

Energetic neutral atom beam lithography/epitaxy (ENABLE) assisted surface chemistry



Multi-scale Modeling for Rational Design of PGM-free Catalysts



Example of Fe-N_4 (orange-blue) active site structure embedded in graphene (gray) with bound *OH (red/white) intermediate surrounded by an H_2O solvation environment.

Quantum chemical modeling tools for studying structure-to-function relationships, by providing fundamental information on:

- Relative stability
- Reaction pathways and associated potential determining steps
- Effects of ligands and poisons
- Kinetics of structural degradation

Tools:

- Density functional theory (DFT)
- *Ab initio* molecular dynamics (AIMD)
- Density functional tight binding (DFTB)
- Reactive force field based molecular dynamics (ReaxFF)
- Higher time/length scale models, *e.g.* Lattice-Boltzmann

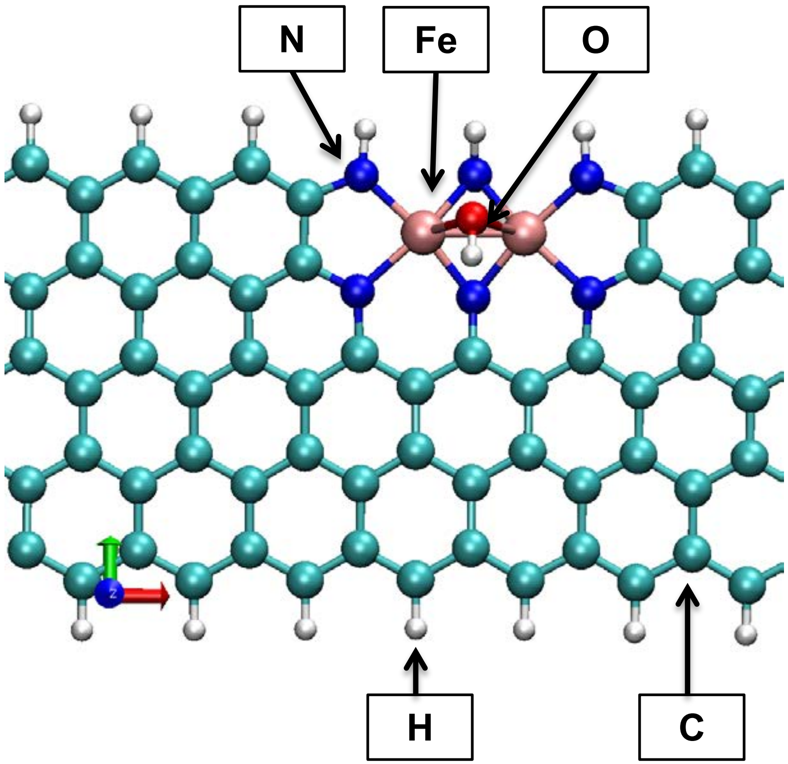
✓ *1024 core (extendable) dedicated HPC computational cluster running state of the art quantum chemistry codes (VASP, ADF, Gaussian, LAMMPS)*

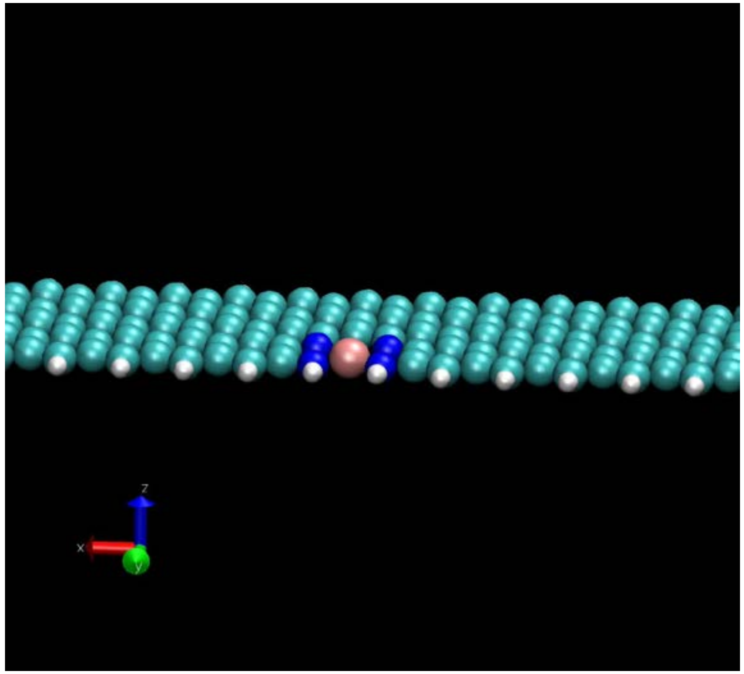
✓ *LANL Institutional Supercomputing providing millions of CPU hours*

✓ *Leverage tools developed by Materials Genome Initiative and LANL's unique computational capabilities*

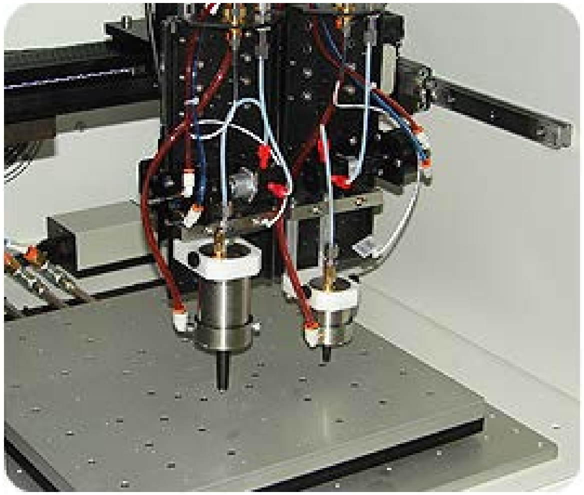
Theoretical High-Throughput Approach to Active Site Problem

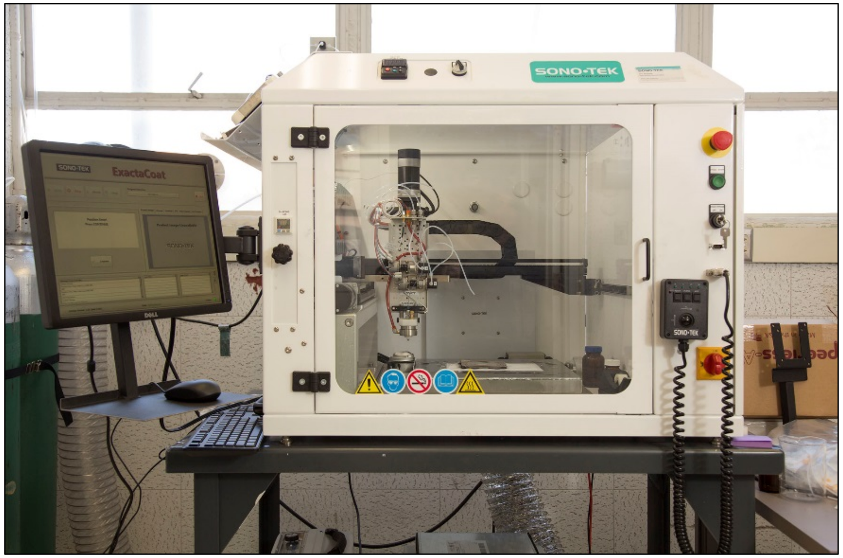
- Developed **high-throughput approach** for screening PGM-free active site structures for relative stability and ORR activity by *ab initio* / quantum chemistry methods; generation of structure-to-function library:
  - ✓ *OH binding energy successfully utilized for down-selecting structures
  - ✓ Formation energy as function of chemical potential used for relative stability determination
- Improved automation and validation of durability descriptors combined to co-optimize active-site structure activity and durability and extend previously generated structure-to-function activity and stability library





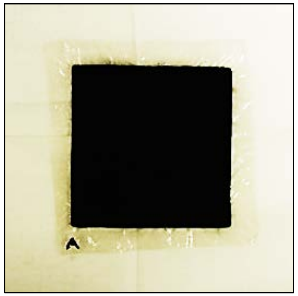
MEA Fabrication





- Preparation of high-quality electrodes with consistent properties and performance of key importance in fuel cell research
- Sono-tek ExactaCoat Ultrasonic Coating System allowing for the preparation of PGM-based and PGM-free electrodes
- Advantages of ultrasonic spray coating:
  - ✓ *Quick and efficient preparation of electrodes in a wide range of sizes*
  - ✓ *Customizable spray patterns*
  - ✓ *Excellent reproducibility of physical and electrochemical properties*
  - ✓ *Minimized catalyst waste*

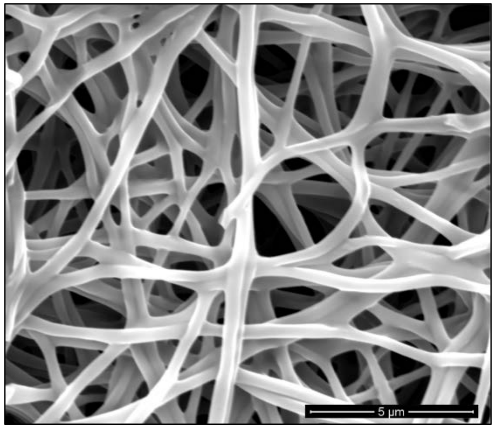
Sprayed Gas Diffusion Layer

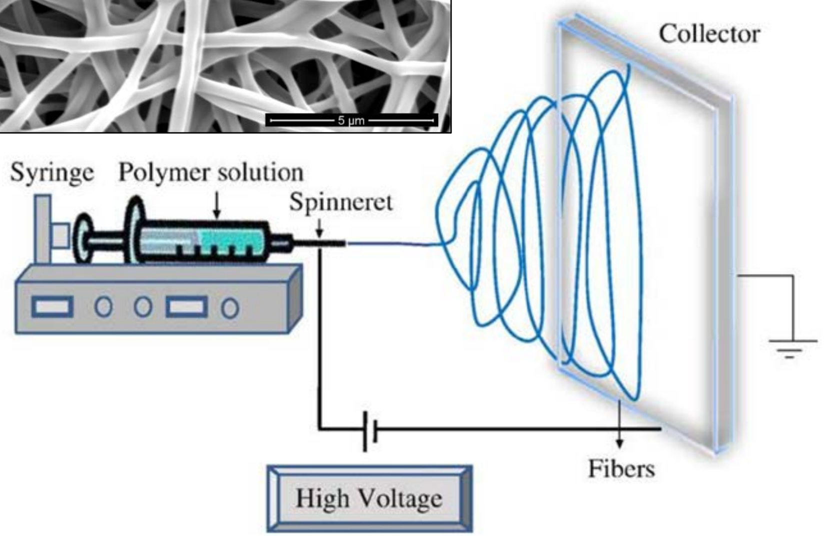


Sprayed Catalyst-Coated Membrane

MEA Fabrication

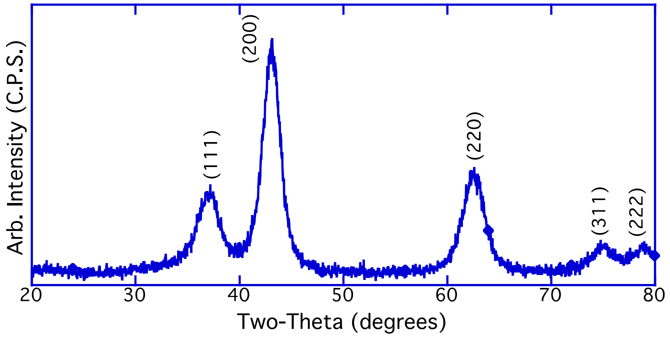
Electrospinning for Unique PGM-free Catalyst Morphology





Robust precursor nano networks formed from electrospun ionomer nanofibers, heat-treated in a thermoplastic form to achieve **fiber linking** and **fusion**.

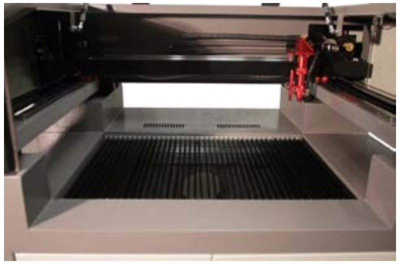
Ultrasonic Freeze Dried for Synthesis



XRD of 3.3 nm particles of MgNiO catalyst obtained from acetates of Mg and Ni

New Laser Cutting System

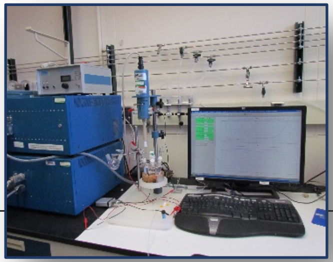
100 W laser cutter for GDL, MEA, gasket and sublayer trimming, as well as modifying GDL porosity and hydrophilicity



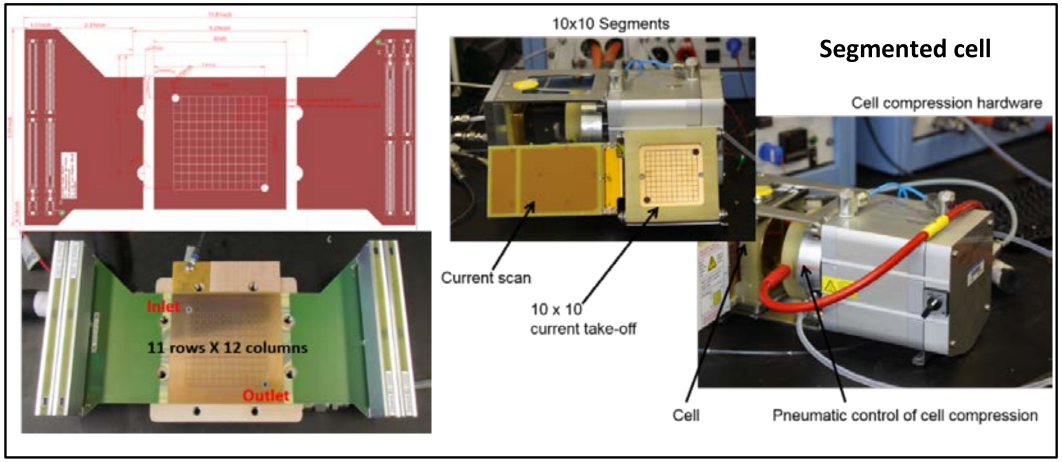
Electrochemical and Fuel Cell Testing

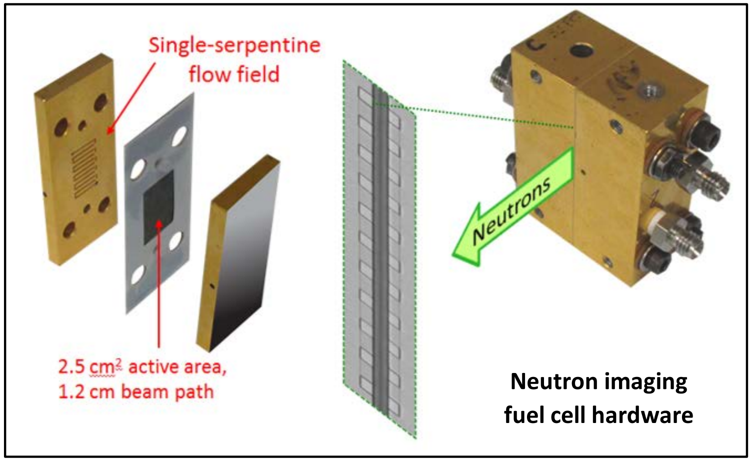
- ✓ ***40 automated fuel cell test stations***
- ✓ ***Stations manifolded for operation on various fuels; startup/shutdown and drive-cycle testing; RH tracking and cycling, temperature cycling, etc.***
- ✓ ***AC impedance capabilities***
- ✓ ***High-power potentiostats for in situ electrode testing***
- ✓ ***Estimated replacement cost of test equipment in excess of $15M***

- Unique combination of electrochemical and fuel cell test stations for PGM-free catalyst development
- Electrochemical cells used to determine PGM-free catalyst activity and selectivity
- Significant single-cell testing capabilities (2 cm^2, 5 cm^2, 25 cm^2, 50 cm^2 cells) for component evaluation in support of internal and external projects
- Design and fabrication of MEAs and electrodes using standard and novel materials, including PGM-free catalysts, high-temperature and alkaline membranes, *etc.*
- Development of protocols, codes and standards; validation and verification of test protocols; accelerated stress tests (ASTs), durability protocols, impurity effects and testing



Advanced Fuel Cell Characterization



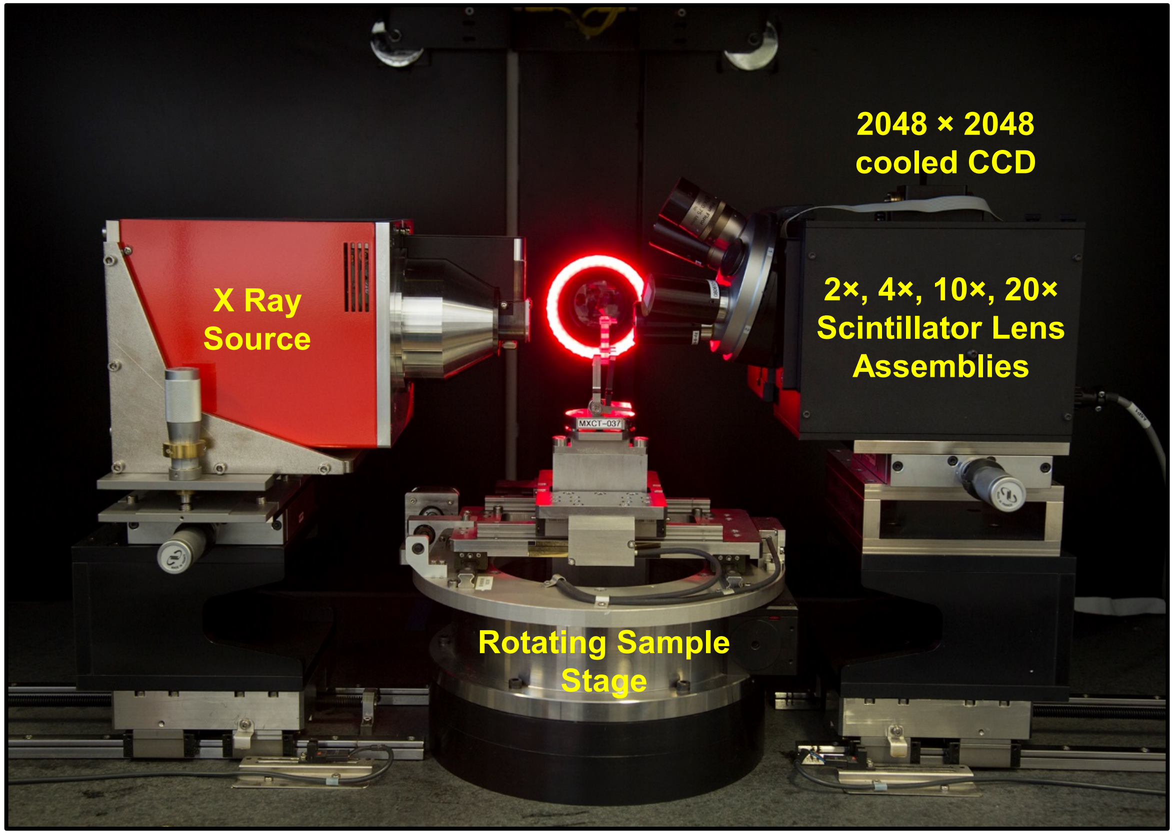


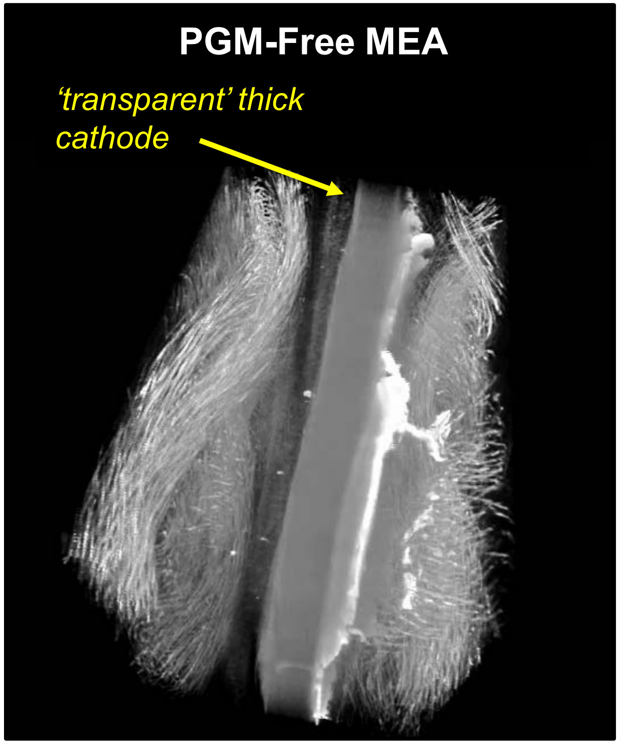
Fuel cell diagnostic tools, designed on site, for different studies of PGM-free electrodes, including mass transport optimization, water and thermal management, and flow field design and validation:

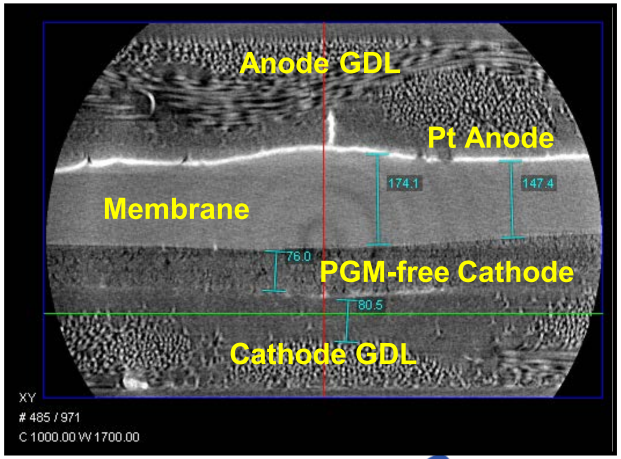
- ✓ *Two high-resolution segmented cells for measurements of current and temperature distributions;*
- ✓ *LANL-upgraded high-resolution neutron imaging fuel cell hardware*

- Segmented cell hardware composed of 132 for current distribution and 66 segments for temperature distribution; operation up to 10 A per segment possible thanks to current boosters
- Fuel cell assemblies dedicated to water management studies using the NIST neutron source
- Latest re-designs involving (a) Invar holder to minimize movements due to thermal expansion, (b) parallel channels for differential studies, (c) single-serpentine cells for GDL/catalyst studies, and (d) metal-foam flow fields for membrane studies (in collaboration with Nuvera).

X-ray Characterization

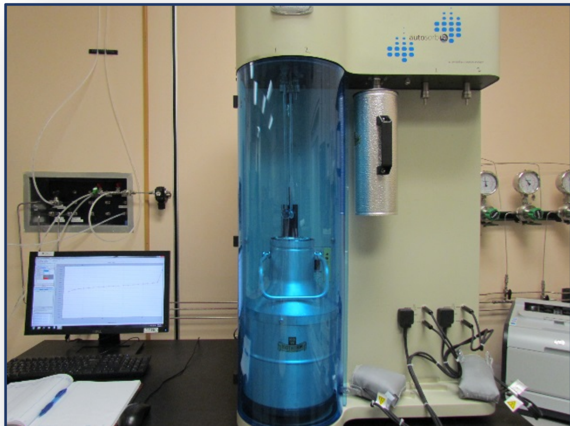






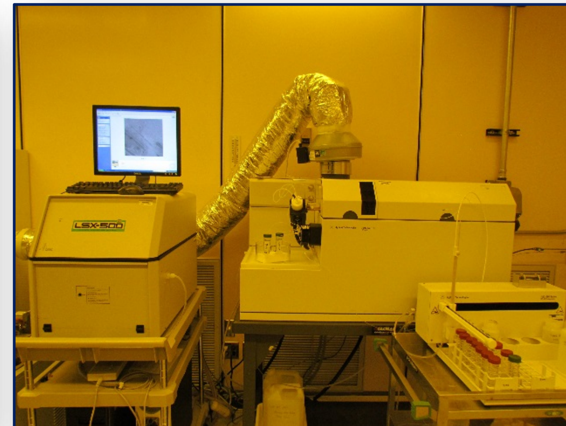
- Non-destructive technique for 3D-imaging of complete three- and five-layer MEAs
- Especially suitable for typically thick PGM-free cathode layers; complementary to neutron techniques for water distribution studies

Analytical Techniques & Fluoride and CO_2 Measurement Set-up

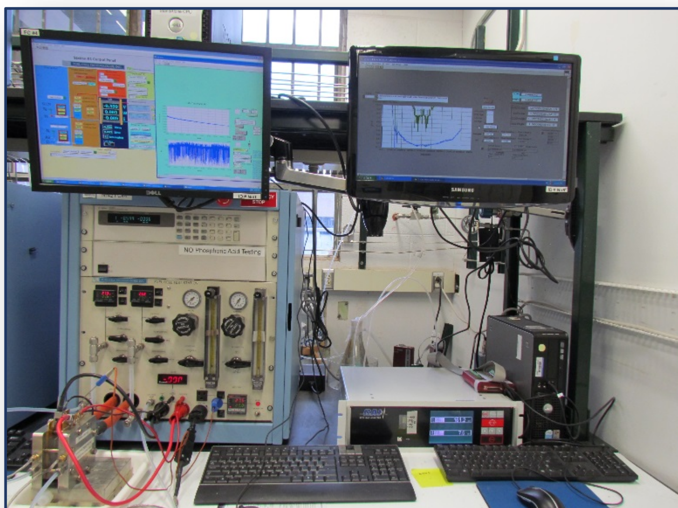


Surface area and pore-size analyzer

Mercury porosimetry



ICP-MS with laser ablation



In situ **fluoride (F^-) and carbon dioxide (CO_2) emission measurement**

- Essential techniques for PGM-free catalysts analysis:
  - ✓ *Surface area and pore-size analyzer for determination of the effect of pore structure and BET surface area performance of PGM-free catalysts;*
  - ✓ *Mercury porosimetry for determining distribution of micro-pores by way of mercury intrusion;*
  - ✓ *Inductive coupled plasma mass spectrometry (ICP-MS) with a laser ablation capable of detecting ppt levels of metals in PGM-free catalyst powder samples.*
- In-house designed and built system for simultaneous determination of CO_2 and F^- emissions using non-dispersive infrared (NDIR) detector and ion chromatography, respectively.

The Most Essential Capability: Research Team

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Argonne's Role in ElectroCat and Capability Overview

- Mission: Expedite the development of PGM-free catalysts and electrodes for FC systems
- Approach: Develop the necessary high-throughput (HT) experimental, HT computational, and material development capabilities and make those capabilities available to industry and academic partners
- Argonne's role: Development, optimization, and implementation of combinatorial and high-throughput materials synthesis, characterization, electrode fabrication, and evaluation methodologies
- Key to realizing the full time-saving benefits of HT: Every step in the process needs to be HT
- Existing Argonne capabilities/equipment:
  - Materials synthesis: Robotic systems and parallel reactors, magnetron sputtering, chemical vapor deposition
  - Materials characterization: HT-XRD, EXAFS, X-ray scattering, particle size analyzer, ultra-high vacuum techniques, rotating disk electrode-ICP-MS
  - Materials evaluation: Multi-channel flow double electrode cells and multi-channel potentiostats, rotating disk electrode, combinatorial 25 electrode fuel cell (NuVant)
  - Electrode fabrication: Robotic powder and liquid dispensing, dynamic light scattering, X-ray scattering
  - Electrode characterization/evaluation:
    - Robotic conductivity measurements, combinatorial fuel cell/multi-channel potentiostat, X-ray nano-tomography, EXAFS, X-ray scattering
    - Cell performance modeling and voltage loss analysis; simulations of electrode structure and electrode transport modeling

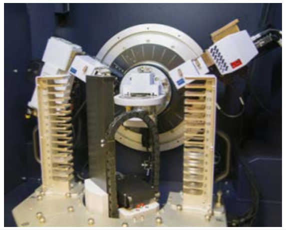
ANL's Commercially-Purchased High-Throughput Equipment

Synthesis/Fabrication

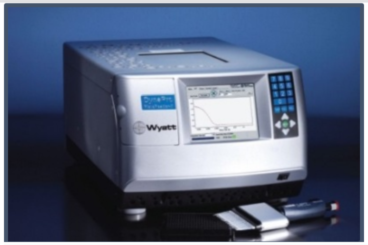
Robotic System – Air Sensitive Synthesis

Robotic System – non-Air Sensitive Synthesis

Characterization



X-ray Diffractometer

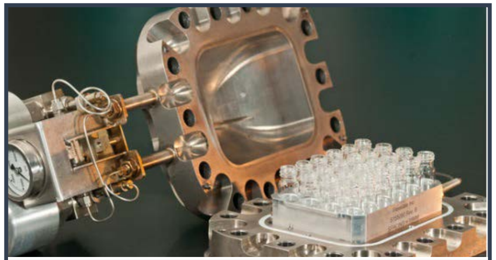


Particle Size Analyzer

25-electrode Fuel Cell

Treatment/Evaluation

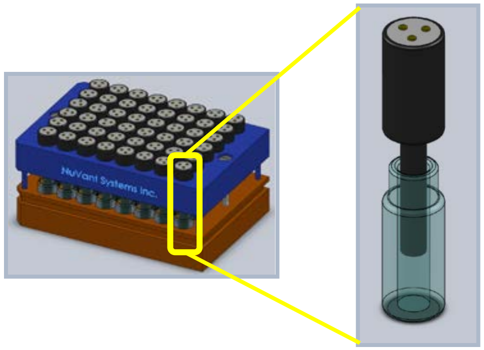
Parallel Plug-Flow Reactor



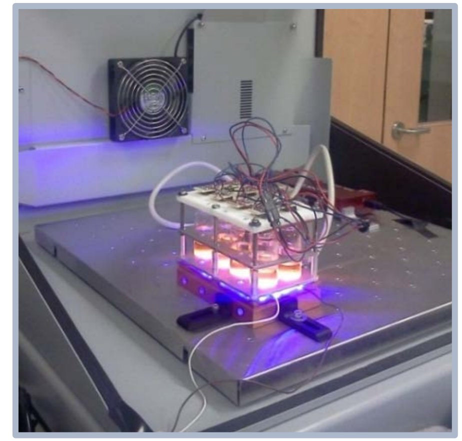
Screening Pressure Reactor

- Two robotic systems for exploring a wide range of compositional phase space
- X-ray diffractometer designed to integrate seamlessly with HT equipment
- Nuvant 25-electrode array fuel cell hardware for electrocatalytic activity and electrode performance evaluation
- Reactors with variety of analytic capabilities (e.g., GC-MS, liquid chromatography)

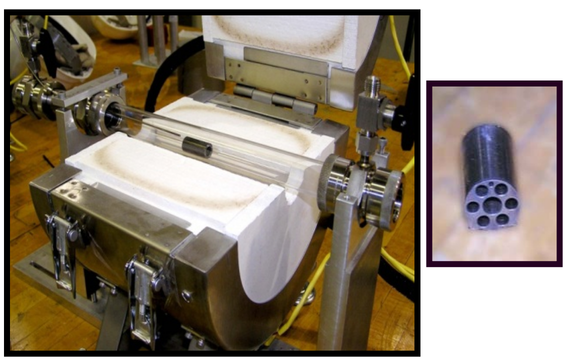
Tools Developed at Argonne for High-Throughput Research



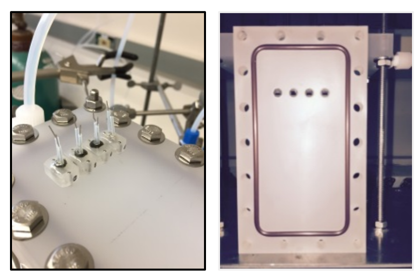
Combinatorial cyclic voltammetry apparatus
Forty-eight parallel CV's in liquid electrolyte; developed in conjunction with NuVant



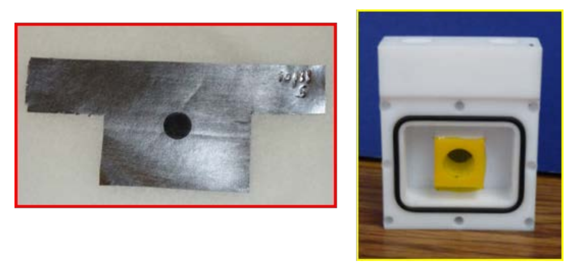
Photochemical reactor system
Simultaneous performance evaluation of eight photocatalysts



Multi-sample (six) X-ray absorption apparatus
EXAFS under controlled gas atmosphere and temperature



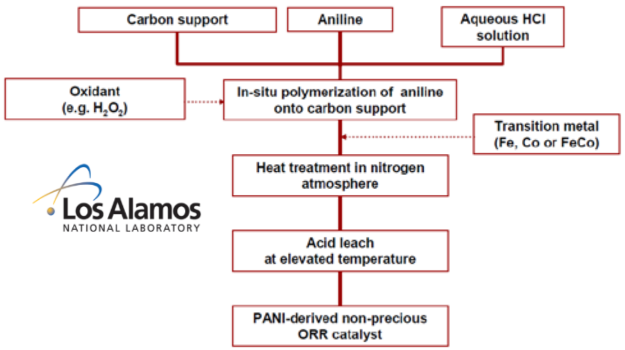
Multi-channel flow double electrode cell
Simultaneous kinetic activity and stability evaluation of four catalysts



Multi-sample aqueous electrolyte X-ray cell
High-throughput X-ray characterization of multiple electrocatalysts under potential control

High-throughput synthesis and characterization of PGM-free electrocatalyst

PANI-Fe_xCo_y/C Catalyst Synthesis



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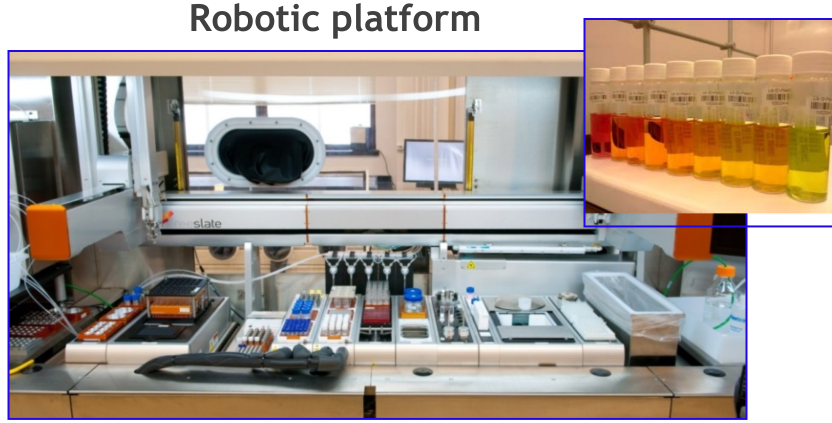
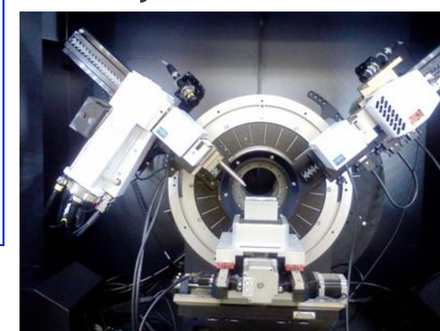
Robotic platform



HT Pyrolysis

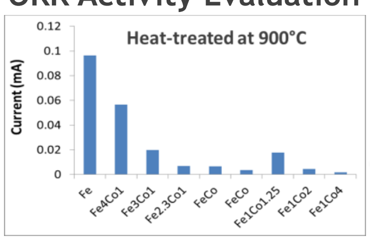
45 variations

HT X-ray Powder Diffraction



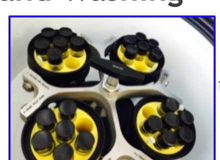
- Robotic platform used to synthesize powder PANI-Fe-Co catalyst precursors with varying Fe to Co ratios (9 compositions)
- Precursors pyrolyzed at five different temperatures to form 45 catalyst variations
- High-throughput methods developed for pyrolysis, acid treatment, washing, and ORR activity evaluation
- High-throughput XRD utilized for determining phase composition
- Will further develop and adapt HT procedures for other materials classes within ElectroCat

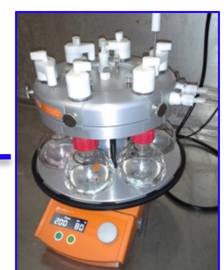
ORR Activity Evaluation

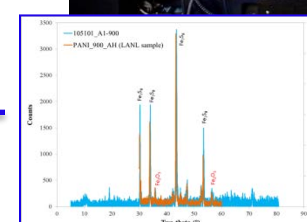


HT Pyrolysis

HT Acid Treatment and Washing







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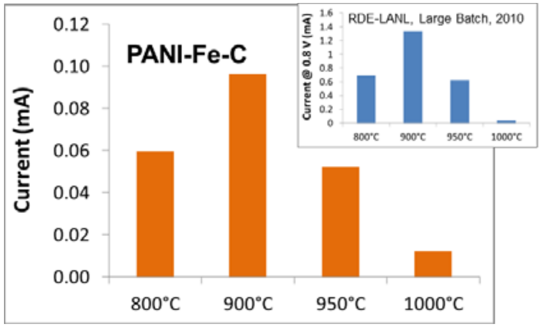
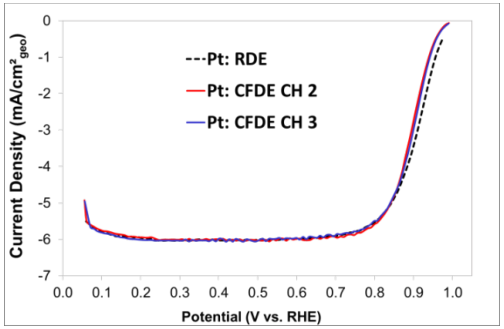
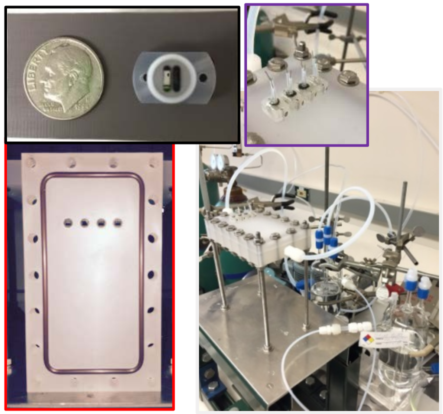
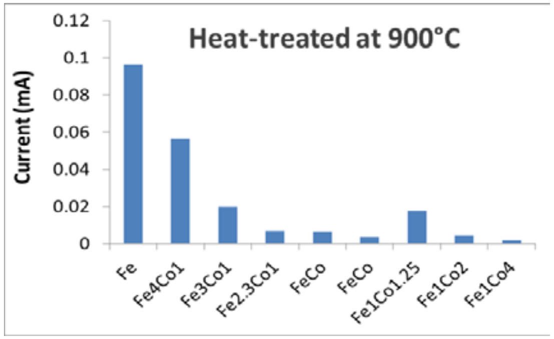
High-throughput screening of electrocatalyst ORR activity and stability

- Argonne multi-channel double electrode (m-CFDE) hydrodynamic cell allows activity and stability screening of four electrocatalyst samples simultaneously
- The Argonne m-CFDE has removal glassy carbon/platinum electrodes to enable high-throughput, robotic deposition of catalyst inks (one of many improvements over Eiwa commercial cell)
- ORR half-wave potential agreement of 9 mV between m-CFDE and RDE results was achieved for commercial Pt/C, verifying validity of cell for catalytic activity screening





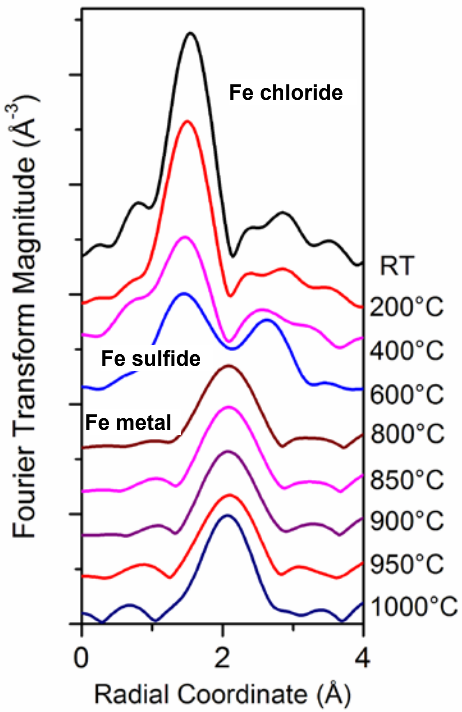


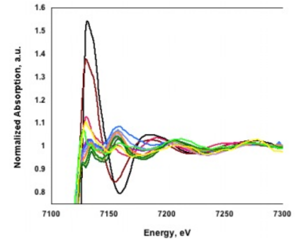


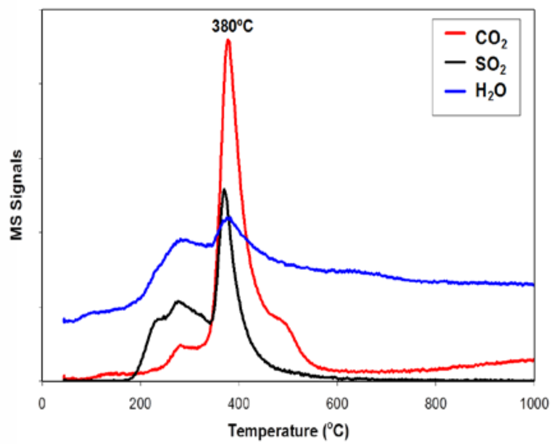
- The m-CFDE was utilized to rapidly screen the ORR activity of high-throughput-synthesized 45 PANI-Fe,Co-C PGM-free catalysts with different Fe to Co contents and pyrolysis temperatures.
  - Same trends of ORR activity with pyrolysis temperature as observed in large batch, LANL-synthesized samples
  - Compositions identified which potentially have higher ORR activity than previous best-in-class

Examples of *in situ* and *operando* EXAFS/XANES of PGM-free catalysts

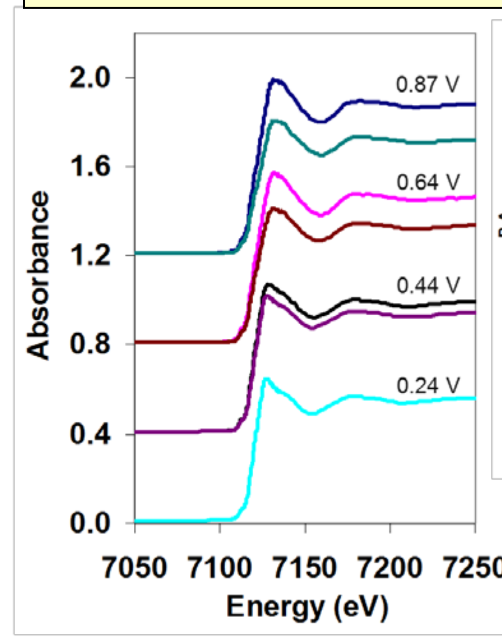
In situ EXAFS/XANES of PANI-Fe/C during pyrolysis with mass spec analysis of effluent

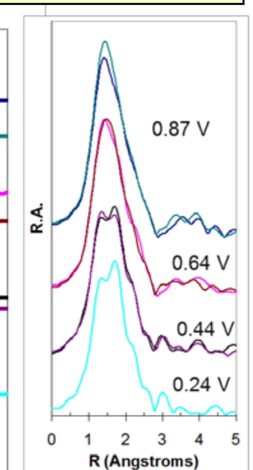


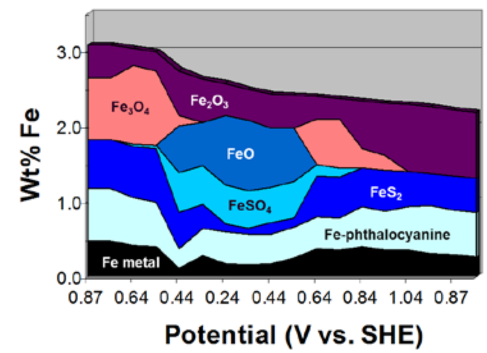




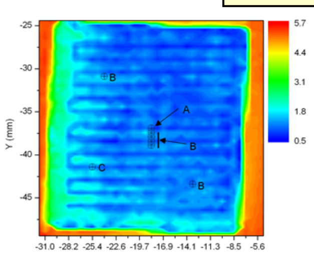
In situ EXAFS/XANES with catalyst under potential control in aqueous cell

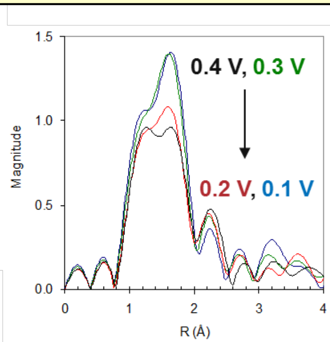


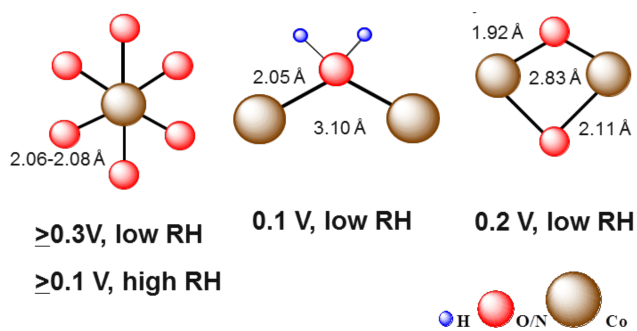




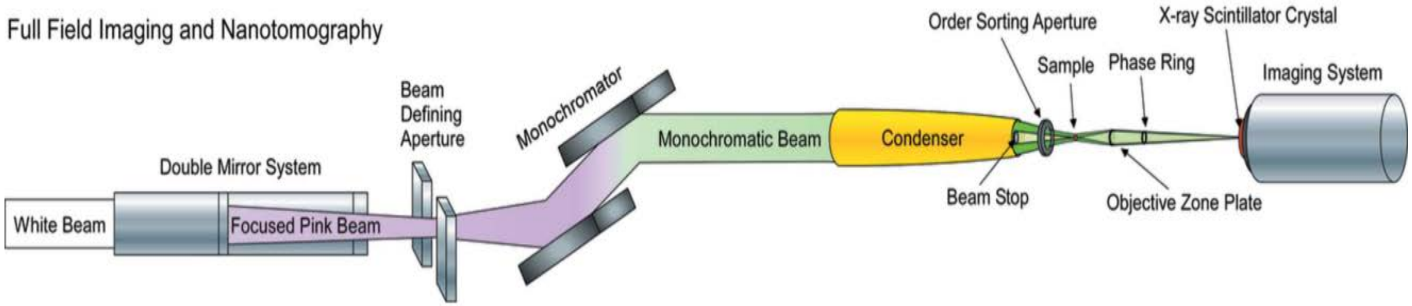
Operando EXAFS of Co/polypyrrole in an MEA

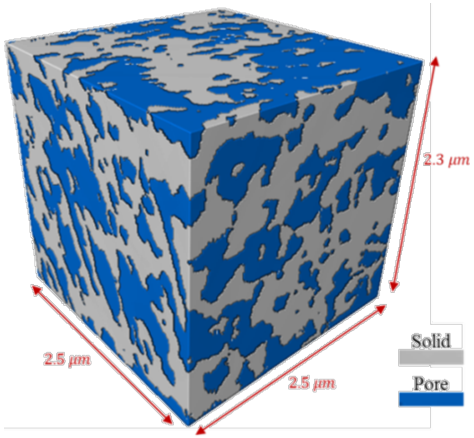






X-ray Tomographic Structural Characterization of Electrodes



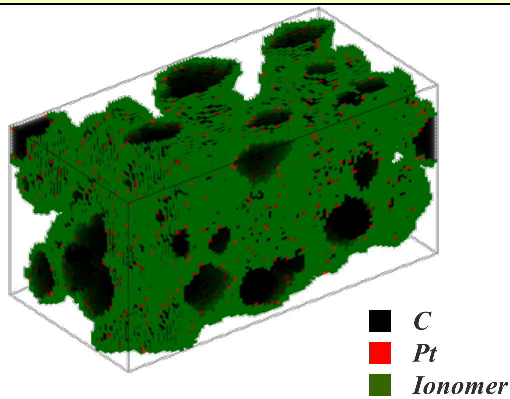


Advanced Photon Source nanoprobe beamlines 26-ID and 32-ID

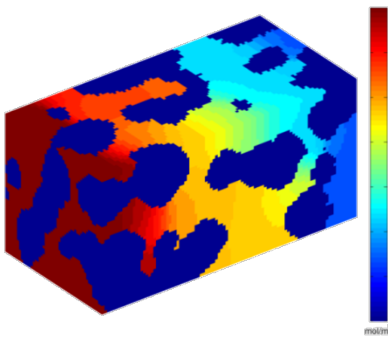
- Hard X-rays can penetrate and image the full thickness of PGM-free electrodes
- The resolution of X-ray instruments is currently limited to ~13 nm with phase contrast and ~22 nm without phase contrast.

Kinetic, Structural, and Transport Modeling

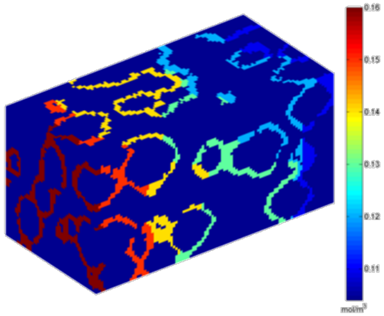
Electrode Structure Simulations and Tomography: 3-D Reconstruction



Electrode Transport Processes

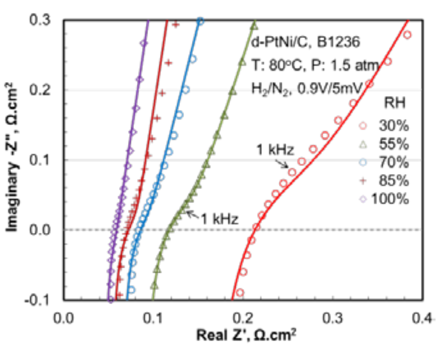


O_2 Concentration in Pores

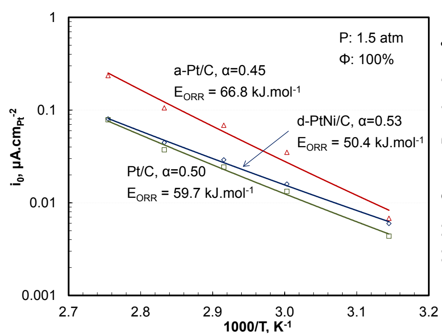


O_2 Concentration in Electrolyte

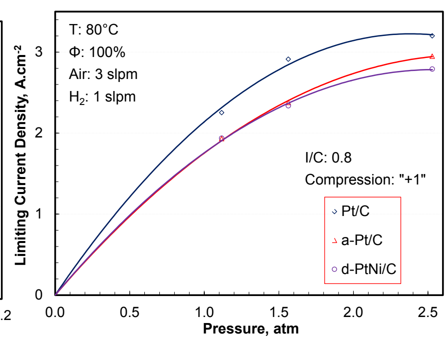
Characterization of In-Cell ORR Kinetics and Transport Losses and Modeling of Stack/System Behavior



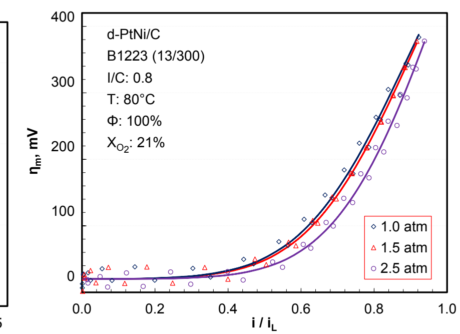
Impedance Analysis



ORR Kinetics



Limiting Currents

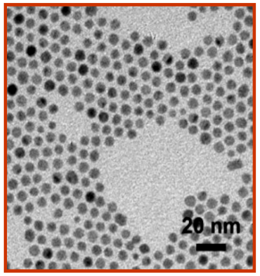


Mass Transfer Overpotentials

R. Ahluwalia

Model System Synthesis and Characterization

Task: Determination of Active and Stable Sites for PGM-free Catalysts

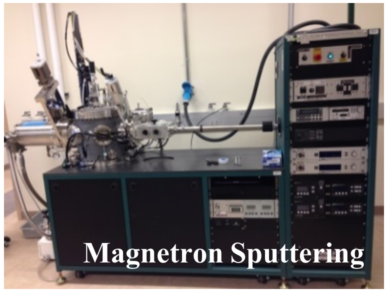


chemical synthesis of materials

defined properties

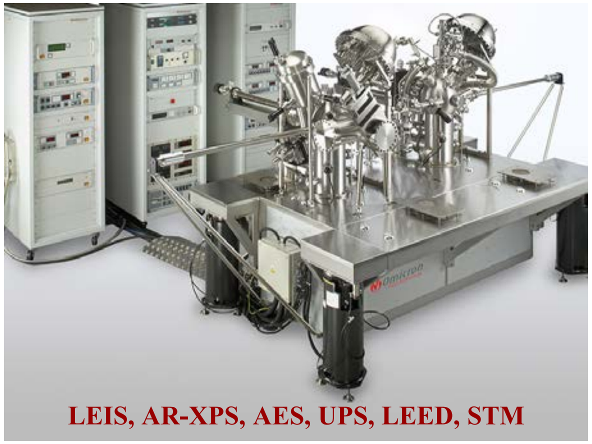
CVD

advanced supports

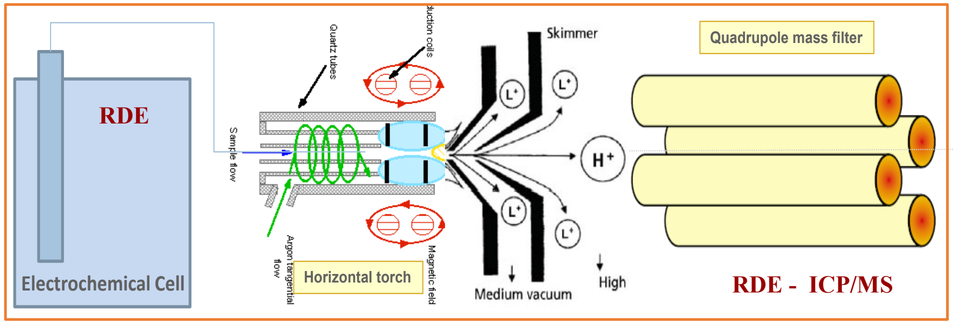


Atomistic insight into structure-function relationship of PGM-free systems will direct the tuning of physical properties responsible for catalyst performance

synthesis of PGM-free model systems with well-defined properties
chemical and physical



surface characterization of PGM-free model systems in ultra-high vacuum



electrochemical characterization of PGM-free model systems by RDE and RDE - ICP/MS

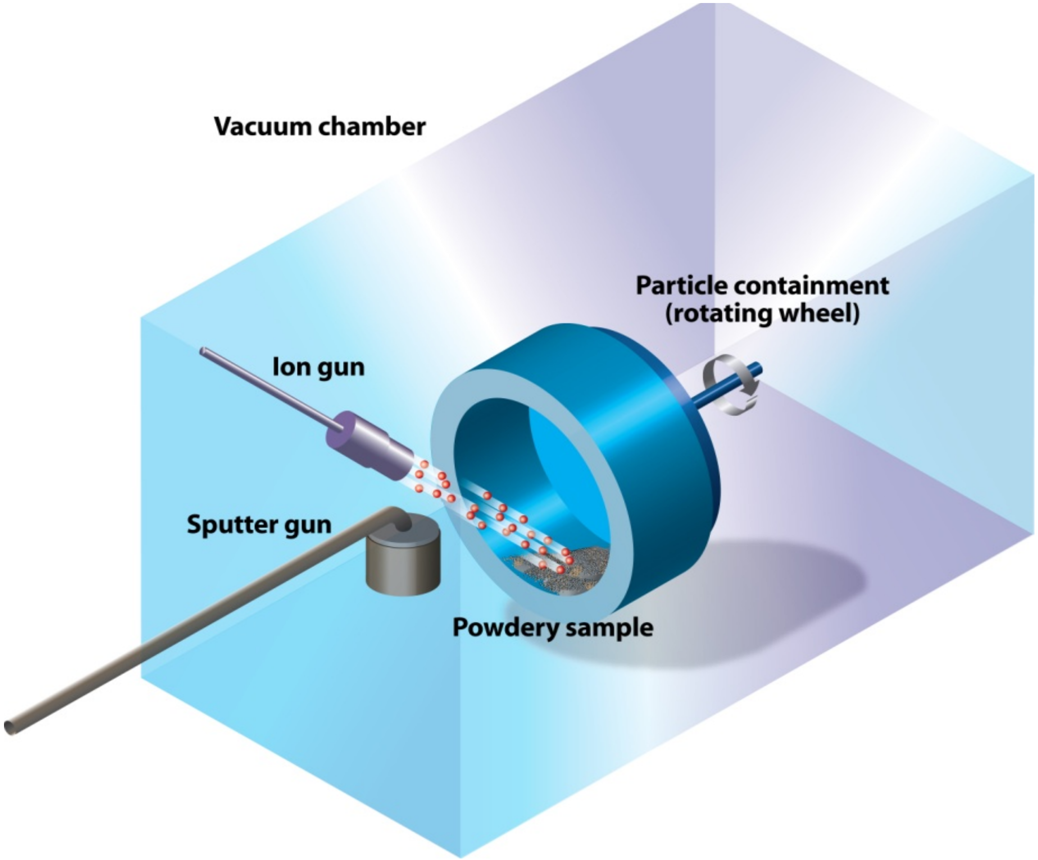
V. Stamenkovic

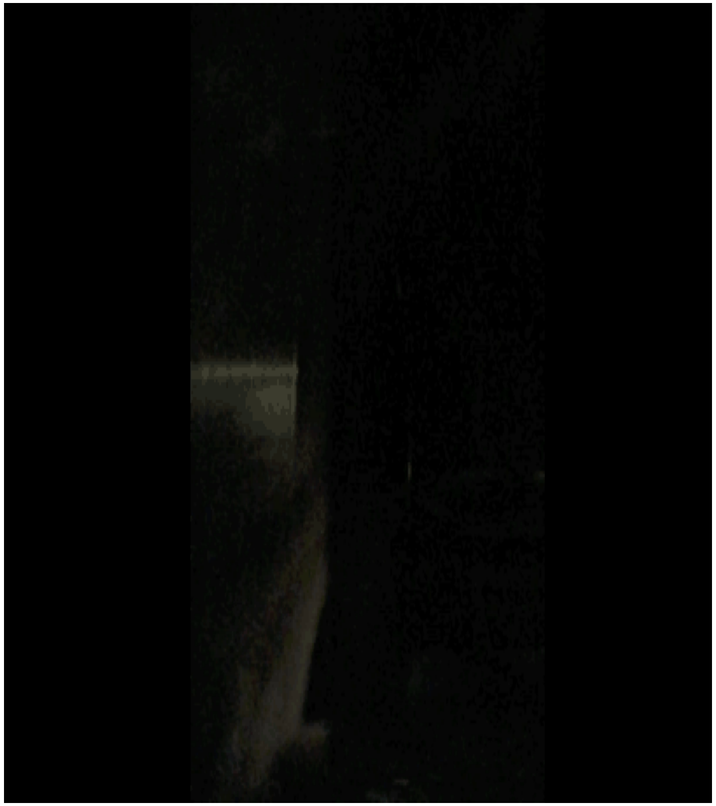
NREL

NATIONAL RENEWABLE ENERGY LABORATORY

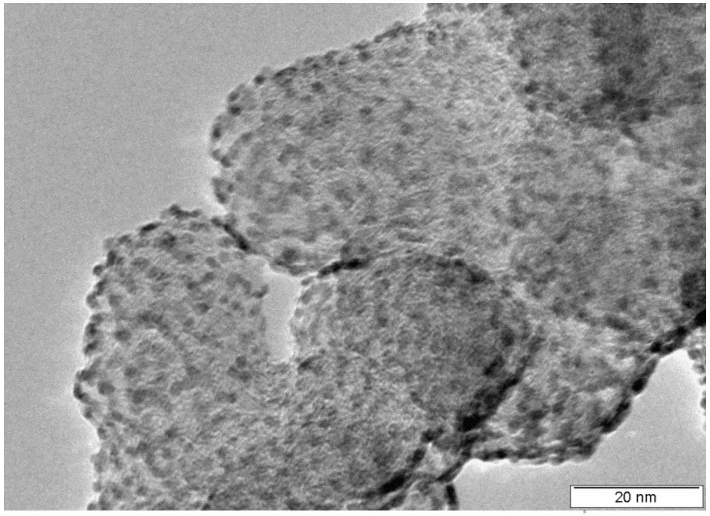
Implant and Sputtering on High Surface Area Substrates

Ion Implantation of powder materials

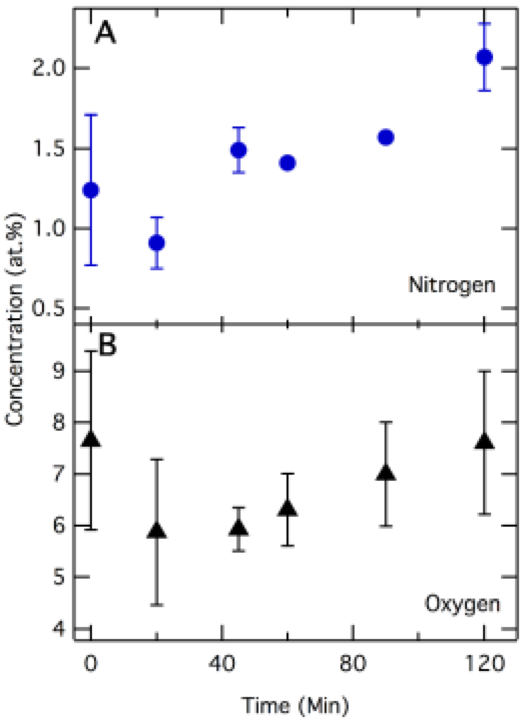




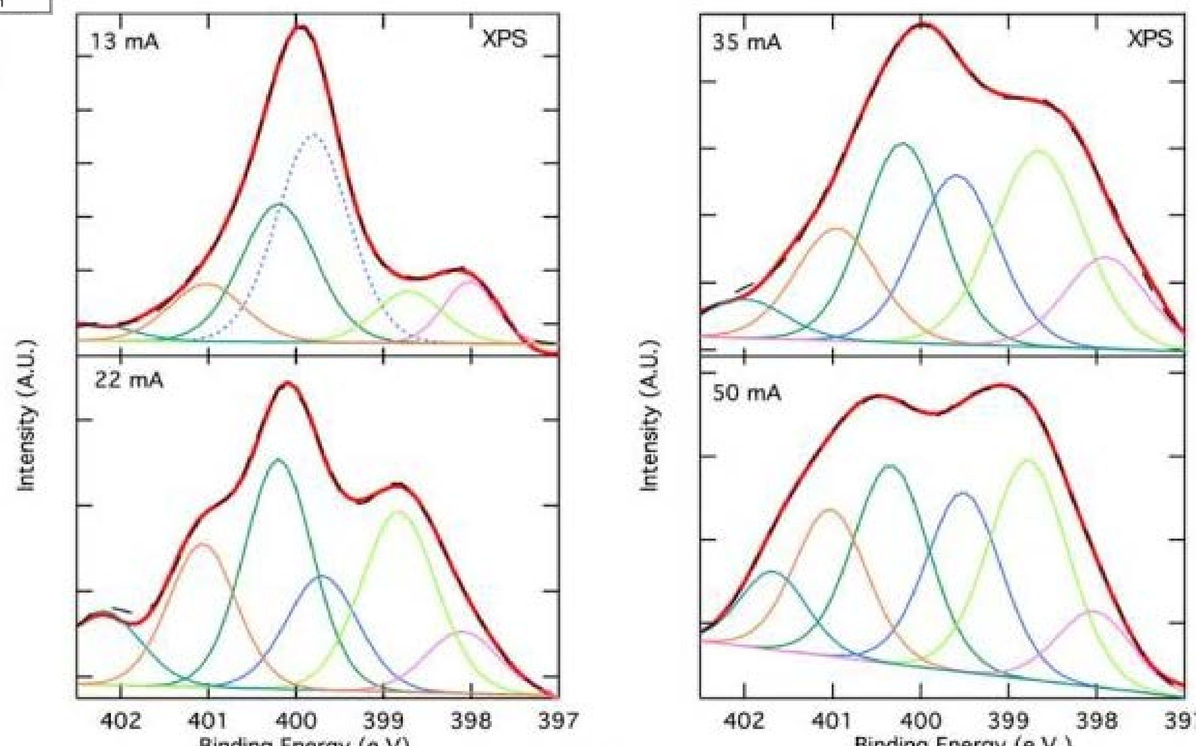
Powder Sputter and Implant System



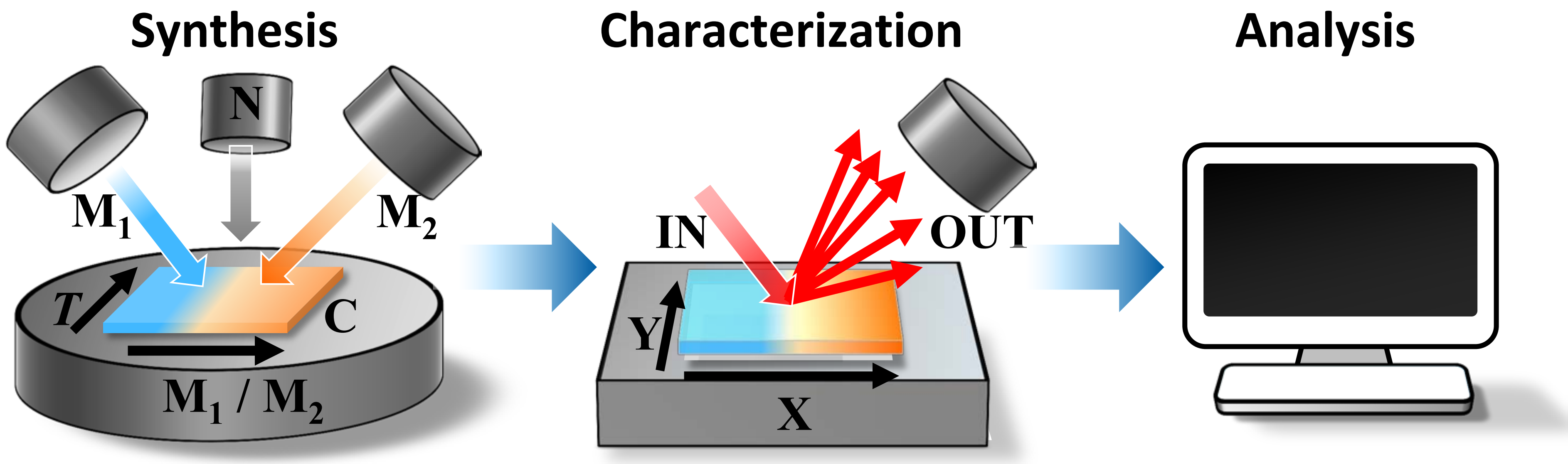
- Produces homogeneous dispersions of discrete nanoparticles on doped carbon supports
- Can tune total and relative dopant concentrations
- Can tune catalyst structure and chemistry (N, Ar, O, F, I, and mixtures)
- Has shown improved catalyst durability



can



Thin Film High-Throughput Experimental (HTE) Capabilities



Combinatorial Synthesis

- multi-element thin films of nanoparticles (metals, oxides, nitrides, sulfides)
- gradients (composition, temperature, film thickness, nanoparticle size etc)
- physical vapor deposition techniques (sputtering, pulsed laser deposition)
- supports (highly oriented pyrolytic graphite, metals, glass etc)

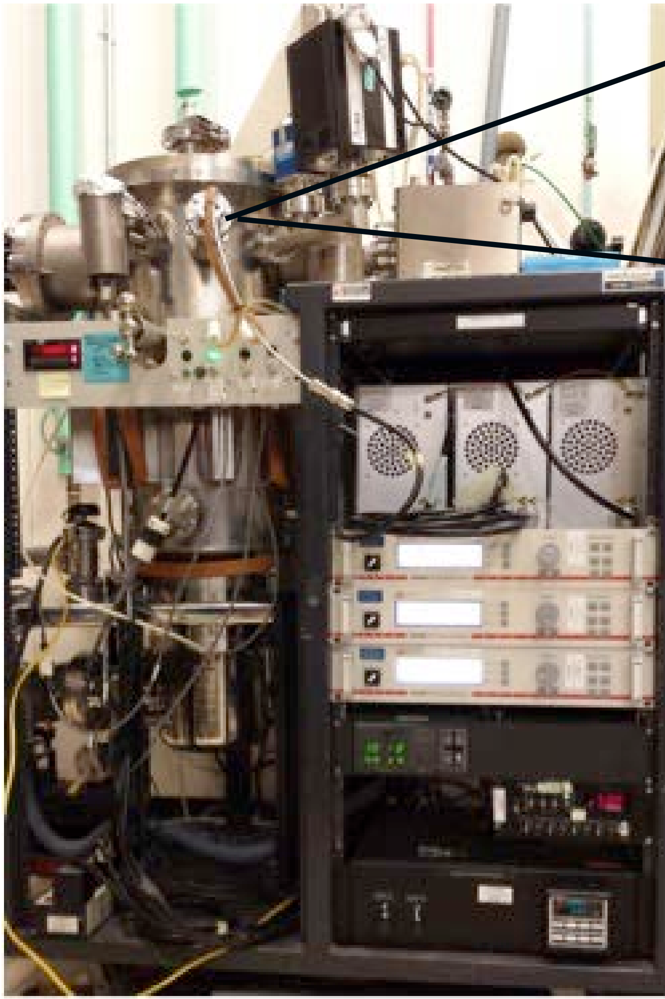
Spatially-resolved characterization

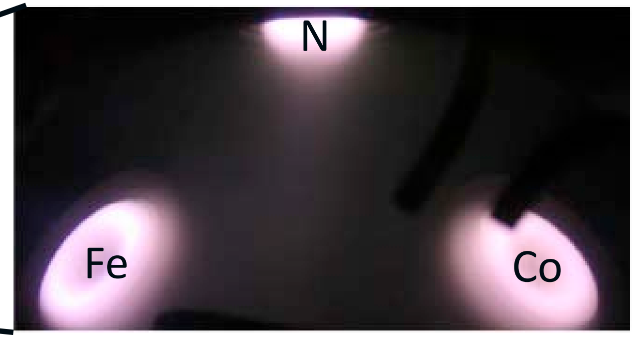
- chemical composition (XRF, RBS)
- crystallographic structure (XRD, Raman)
- microstructure (SEM, AFM)
- surface properties (PES, KP)
- electrical (conductivity, Seebeck)
- electrochemical (cyclic voltammetry, reactivity mapping using SECM)

+ Automated data analysis (Igor PRO)

Thin Film High-Throughput Experimental (HTE) Capabilities

Specifically for ElectroCat demonstration:





Combinatorial Synthesis

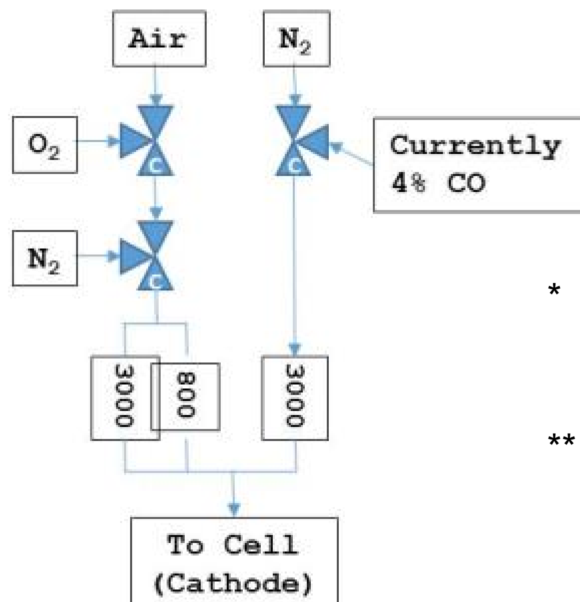
- High vacuum chamber with cryopump
- Three individual RF power supplies (Fe, Co, C)
- Compositional temperature gradient
- Nitrogen plasma source, Ar working gas
- Mass spectrometer for gas monitoring
- Heater for up to 3” samples (typical 2x2”)
- Temperature gradient during synthesis

Spatially-resolved characterization

- XRF for chemical composition
- Raman and XRD for coordination/structure
- XPS for valence state analysis
- AFM for surface morphology
- SECM and RDE for ORR testing

Differential Cell for Electrochemical Kinetics and Transport

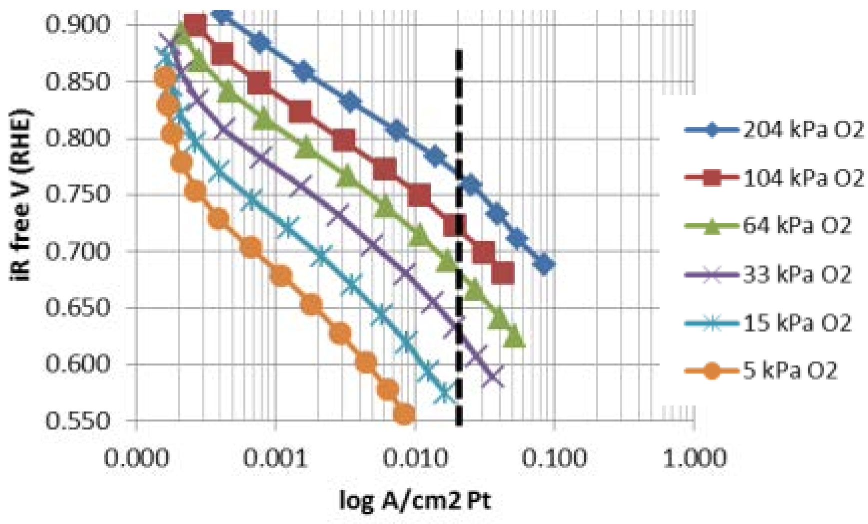
- Fully automated test stands and integrated potentiostats
- Sub ambient to pressurized testing capabilities (~15 kPa_{abs} to 400 kPa_{abs})
  - Automated vacuum system and pressurized DI (100 psi)
- Automatic flow mixing for limiting current studies with multiple gases

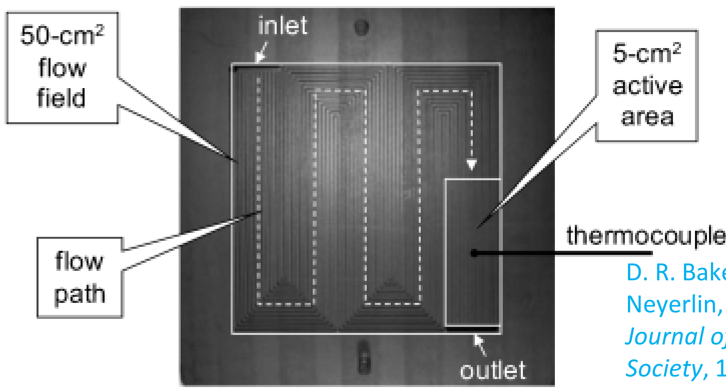


* Can easily be swapped out for another gas

** Not limited by gas toxicity

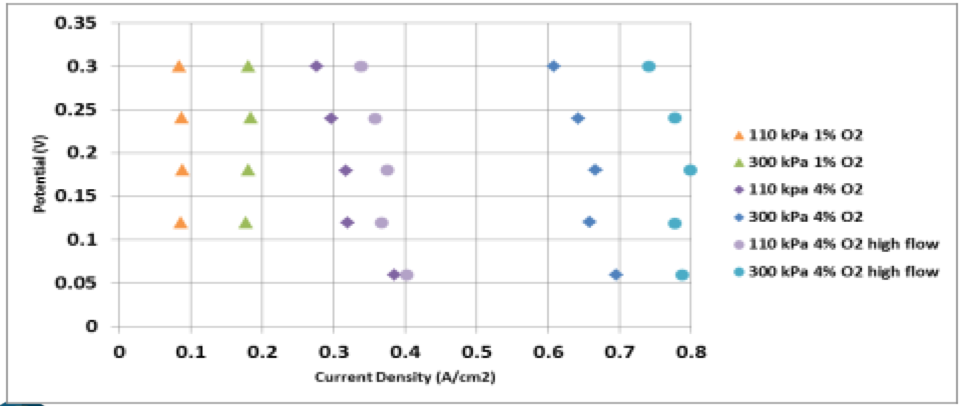
Differential Cell for Electrochemical Kinetics and Transport

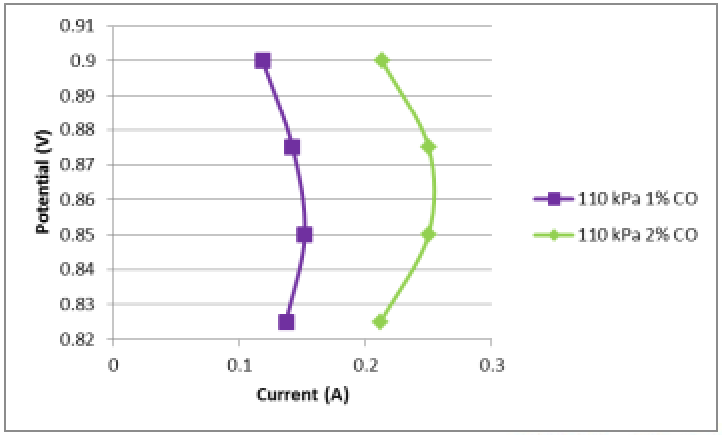




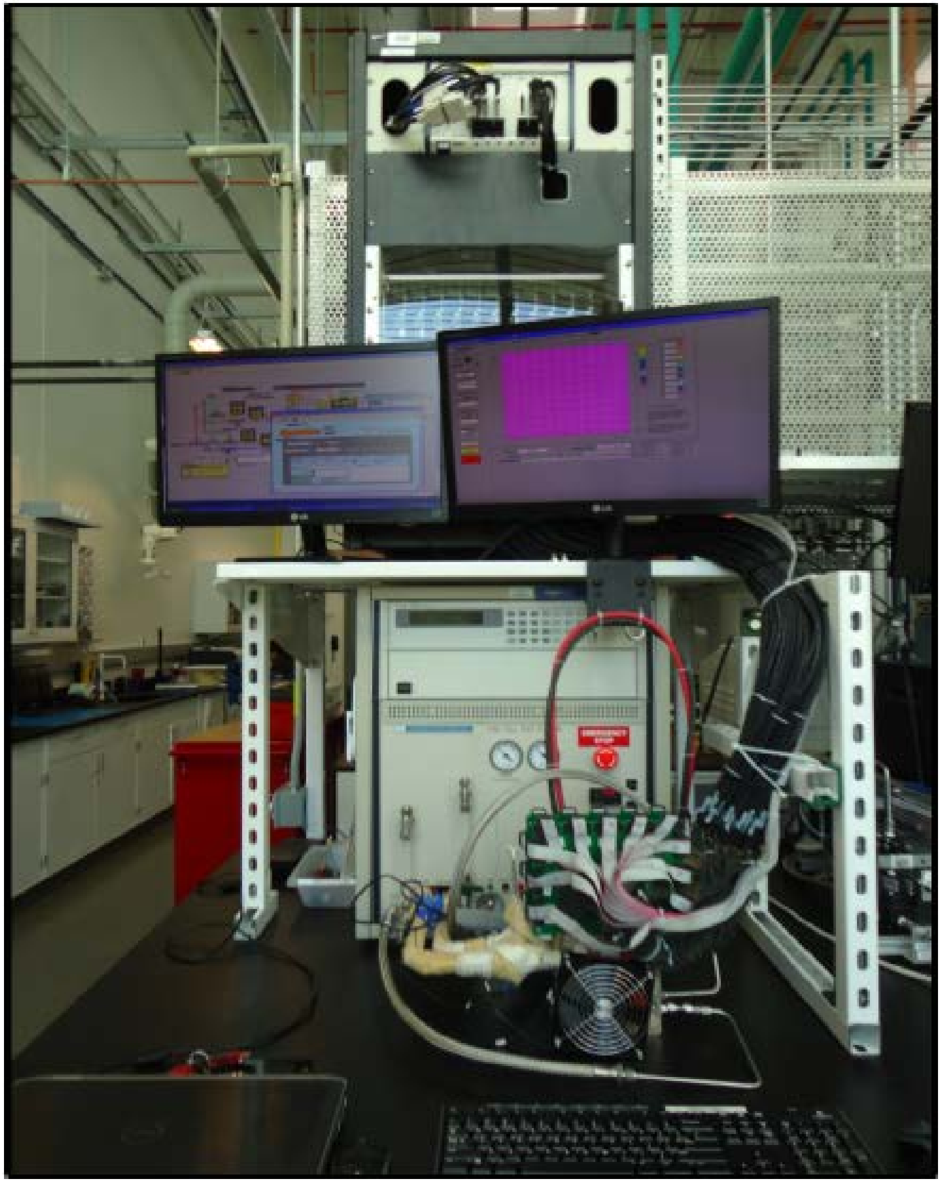
D. R. Baker, D. A. Caulk, K. C. Neyerlin, and M. W. Murphy, *Journal of The Electrochemical Society*, 156, B991 (2009).

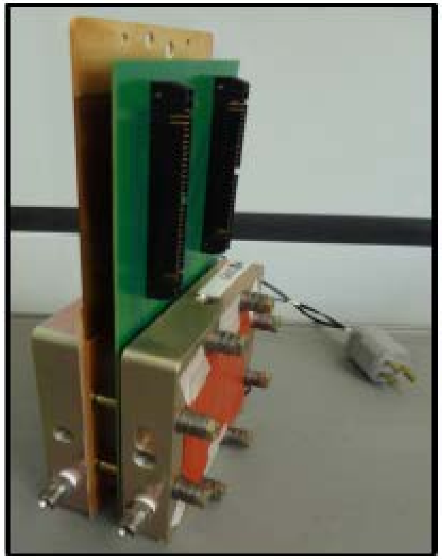
- Examinations of electrocatalyst kinetics for elucidation of reaction mechanisms and separation of kinetic and transport losses
- Limiting current capabilities with various probe molecules to explore transport in a variety of relevant operating conditions and separate pressure dependent and independent resistances

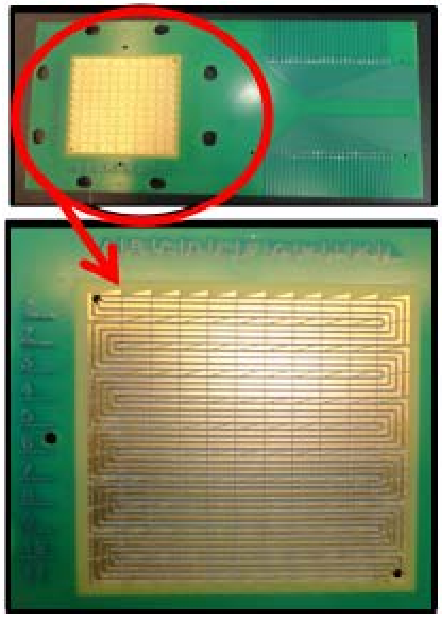




Spatial Diagnostic Capabilities – Segmented Cell





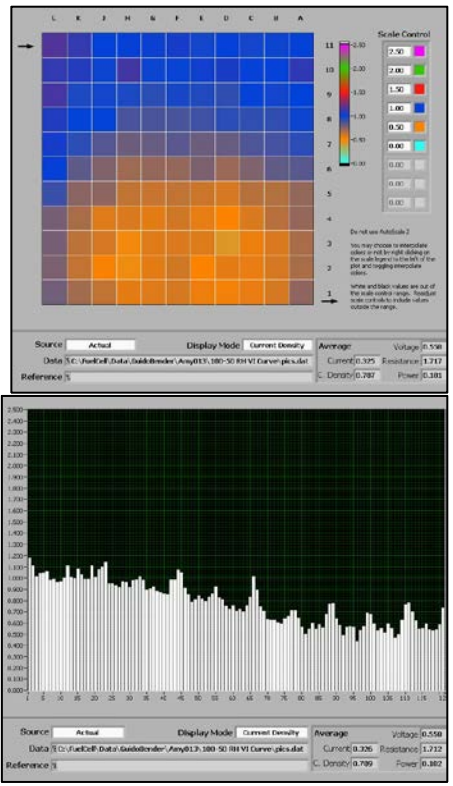


- **121×0.413 cm² segments in 50 cm² area**
- **Individual electronic loads**
- **Optional current or voltage control**
- **2.4 A/cm² max curr. density**
- **Quadruple serpentine flow-field**
- **PC Board style segmented cell hardware**
- **Custom control software with visual and numerical data presentation & analysis features**

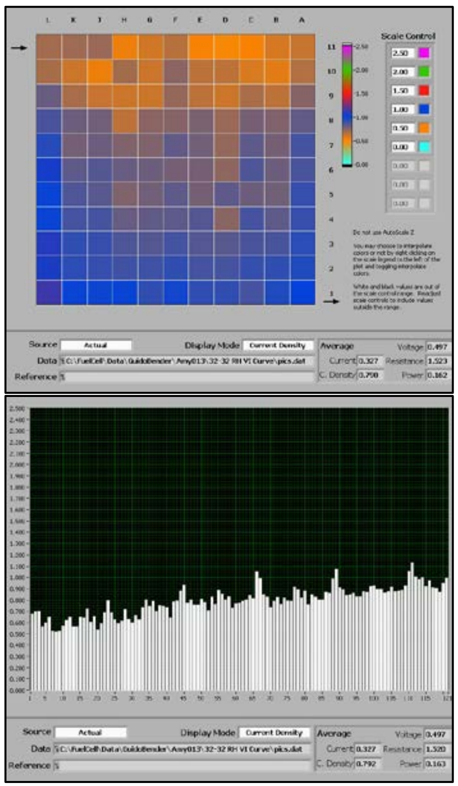
Spatial Diagnostic Capabilities – Segmented Cell

Possible R&D topics include but are not limited to combinatorial catalyst development, effect of: (i) local operating conditions, (ii) discrete inhomogeneities, and (iii) contamination effects.

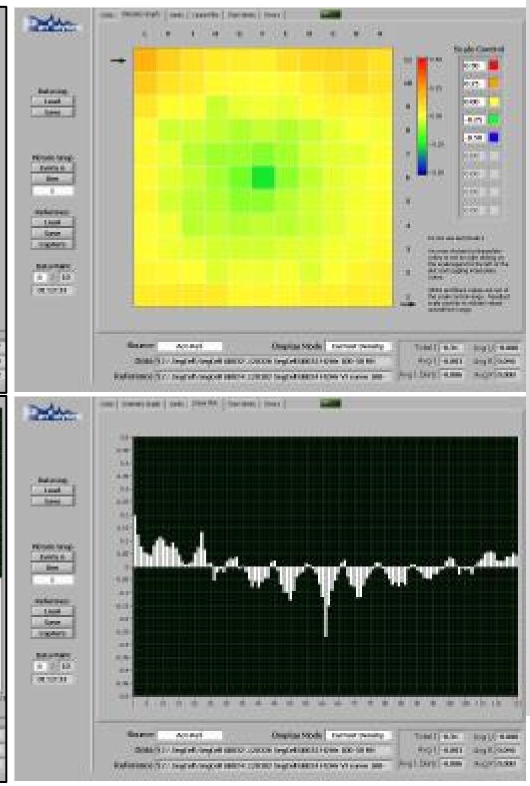
Wet Operation
100/100% RH



Dry Operation
32/32% RH



MEA with planted Defect

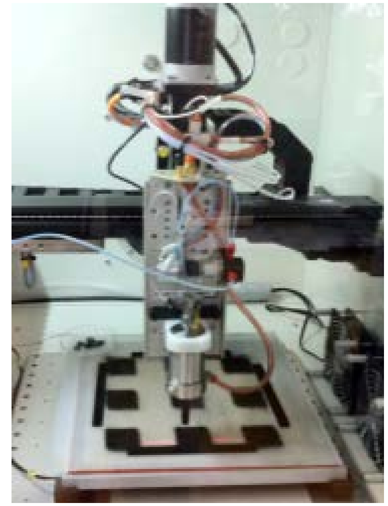


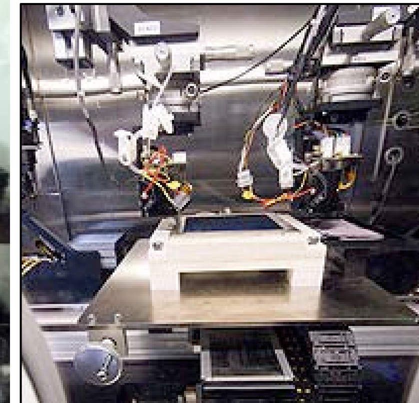
- **Sensitive to track effect of local operating conditions**
- **Total cell performance and spatial performance modes**
- **As measured and differential data representation modes available**
- **Lowest / highest performing area representation available**

High-throughput Scale-up of PGM-free Catalysts to Electrodes

High-throughput (HT) Scaling Concepts

- Important to understand scalability of new PGM-free electrode structures
  - Material-process-performance relationships
- Extend combinatorial aspect of EMNs by enabling gradient/matrixed electrodes via scalable processes
  - Gradients can be in composition or structure
  - Gradients can be fabricated in X-Y or Z (thickness)
- Gradient materials would feed spatially resolved HT in situ and ex situ testing capabilities
  - e.g. segmented cell, scanning XRF





Processing Capabilities

- Small-scale ink processing
  - Formulation, mixing, viscosity, rheometry
- Small-scale coating
  - Spin, knife, rod
- Spray coating
  - Ultrasonic, aerosol jet, ink jet, electro-spin/spray
- R2R coating
  - Slot die, micro-gravure

Enable accelerated evaluation of PGM-free electrode ink composition and properties as well as process parameters for optimal uniformity, performance and durability

OAK RIDGE

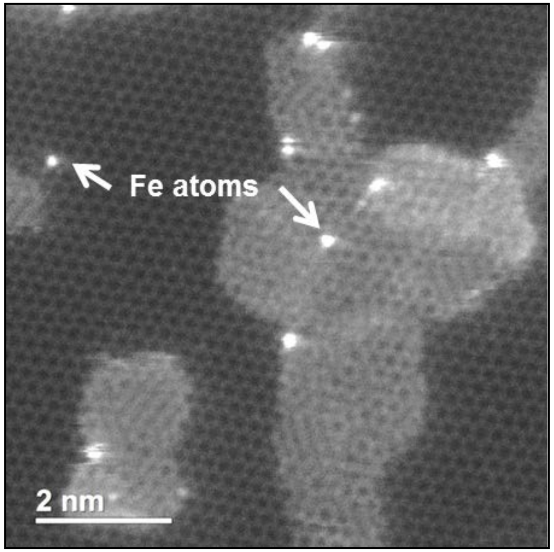
National Laboratory

ORNL ElectroCat Capability: Analytical Electron Microscopy

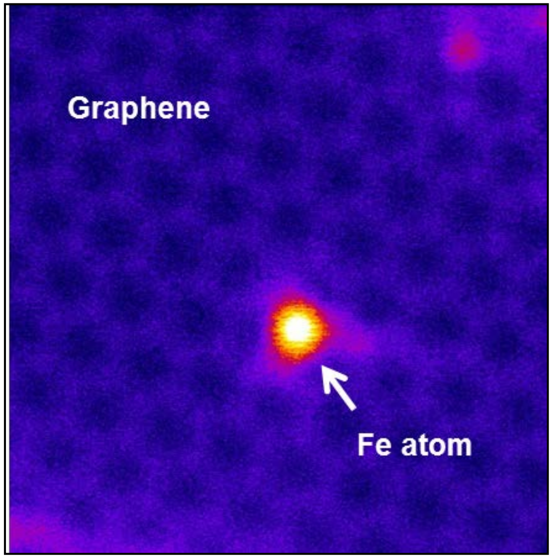
Comprehensive Suite of Analytical TEM/STEMs:

μm-scale → to → atomic-level imaging and spectroscopy of PGM-free catalysts and MEAs

- **Low voltage (60kV) Nion UltraSTEM**
  - Voltage operation below damage threshold for carbon-based structures
  - Single atom EELS
- **Multiple aberration-corrected STEMs (200-300kV operation)**
  - Equipped with both EELS and EDS for simultaneous data acquisition
  - ~0.7Å image resolution
  - Equipped with multiple imaging detectors
- **Sample preparation facilities**

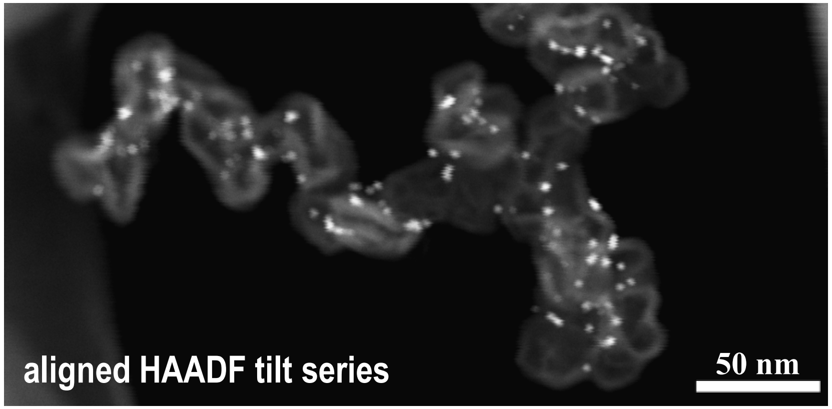


Single Fe atoms in graphene

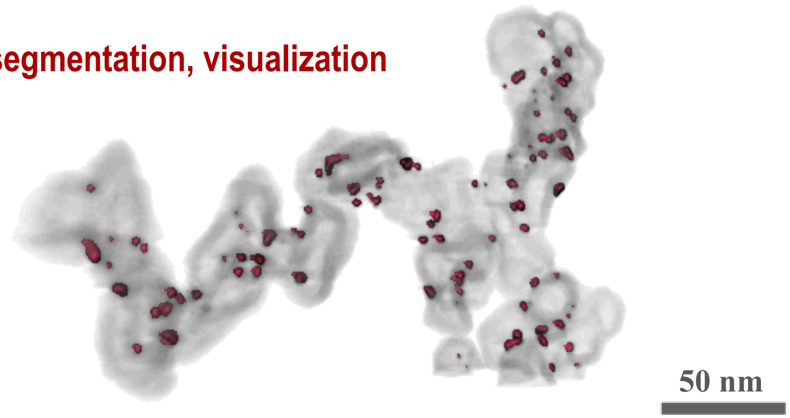


ORNL ElectroCat Capability: 3D Electron Tomography

- Capabilities for 3D tomography via:
  - ±70° high-angle tilting
  - 360° micropillar rotation
  - Microtomy serial sectioning
- Electron tomography can be performed on *ANY* material or MEA constituent – segmentation and visualization of individual components:
  - High-resolution imaging
  - High-resolution spectroscopy
- Quantification of physical characteristics
  - particle size and shape
  - constituent connectivity
  - porosity
  - iionomer dispersions



segmentation, visualization

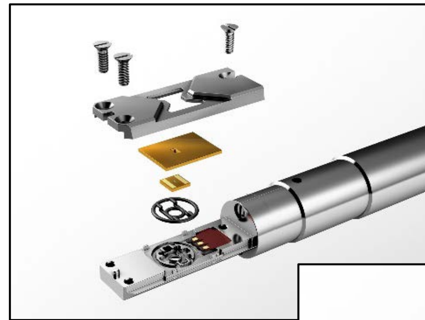


ORNL ElectroCat Capability: *In Situ* Electron Microscopy

Monitor/Track the Dynamic Behavior of Materials:

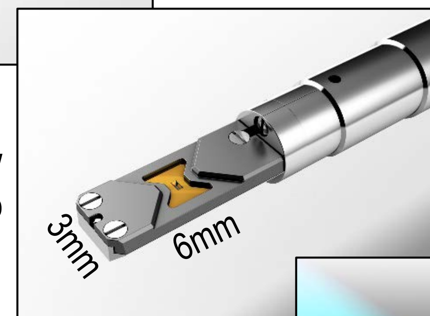
Rapid capture of *in situ* high-resolution imaging and spectroscopy via specialized closed-cell holder systems:

- **Gas-cell reactor holder**
  - Slow-flow mixed gases into cell
  - Gas pressures up to 1atm.
  - Temperatures up to 1000° C
- **MEMS-based heating holder**
  - Temperatures up to 1200° C
- **Liquid electrochemistry cell holder**
  - Slow-flow or static liquid environment
  - Three electrical contacts connected to external potentiostat

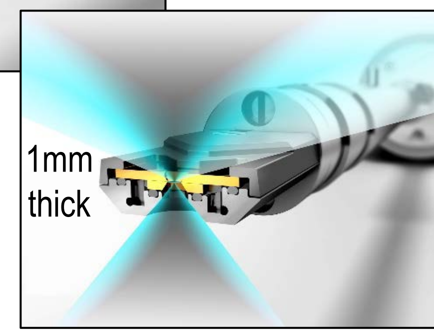


exploded view of holder tip

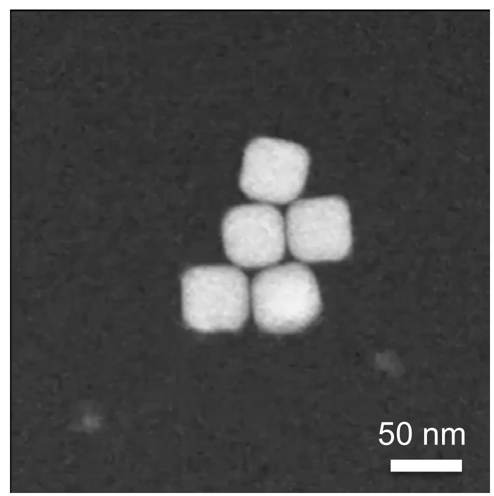
total cell thickness ~150-200nm (gap ~50nm)



assembled view of holder tip



cross-sectional view with e-beam

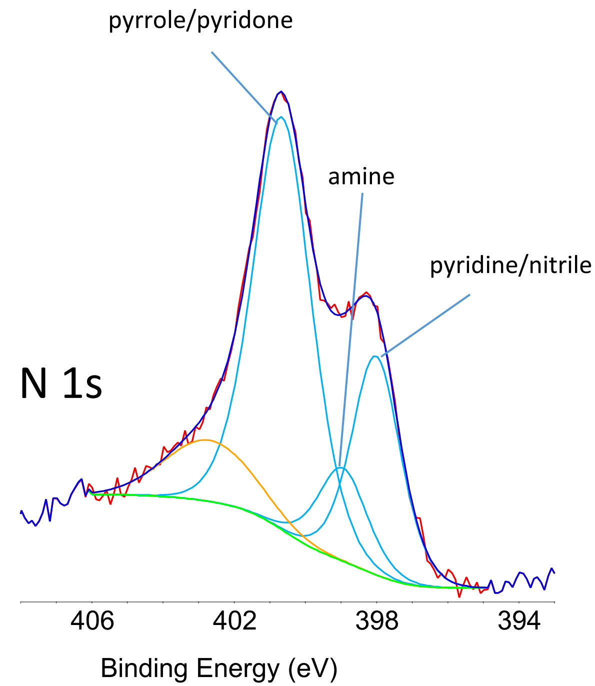


In situ liquid STEM of dendritic Pd growth on Au seed crystals

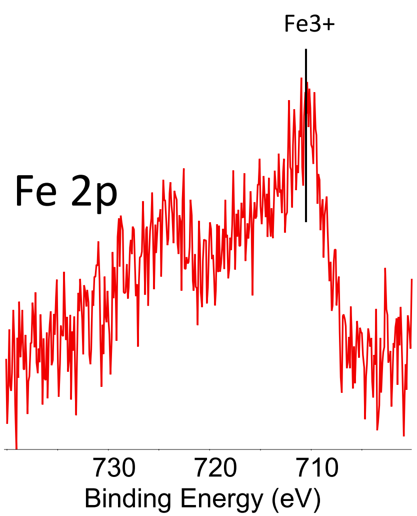
ORNL ElectroCat Capability: Surface Chemistry with XPS

Primary strengths of XPS:

- Detailed chemical bonding by acquiring high-energy-resolution core-level scans
- Overall surface composition can be quickly measured using wide-energy-range survey scans
- XPS is complementary to other ORNL core techniques (TEM, STEM/EELS, XRD, etc.)
- Ease of sample preparation



Chemical bonding of N-doped PGM-free catalyst; N-functionalities are identified in the N 1s core level spectrum

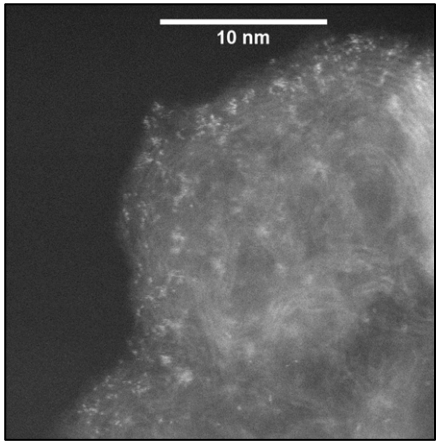


In the Fe 2p core level spectrum, atoms show a 3^{+} oxidation state even at dopant levels well below 1 atomic %

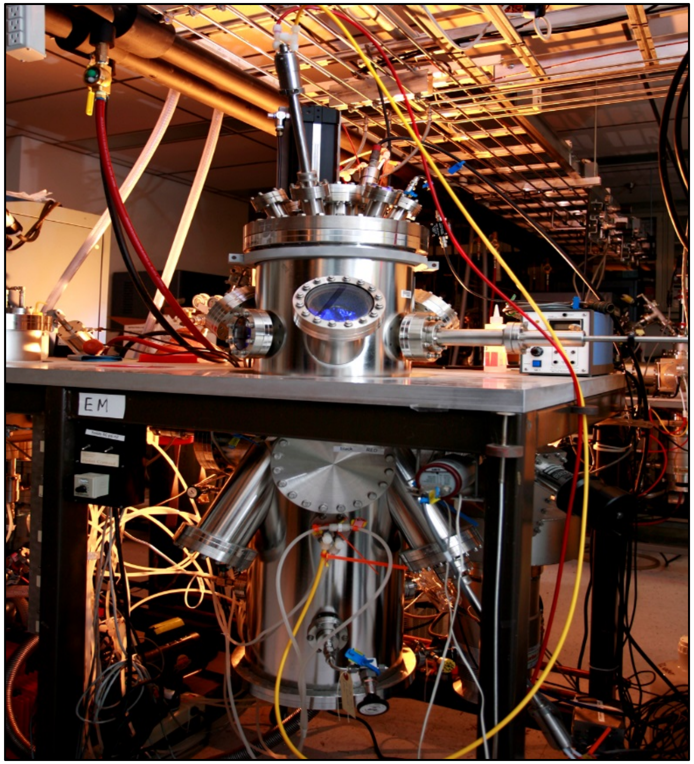
ORNL ElectroCat Capability: Sputter Deposition System

Sputter Deposition of PGM-free Catalysts

- Vapor deposit supported nanoparticle catalysts on any vacuum-stable support material that cannot be easily prepared from solution processes:
  - Metal oxides
  - Carbides
  - Nitrides
- Rapid prototyping and screening
- Reproducible and scalable to large volumes (tens of gallons)



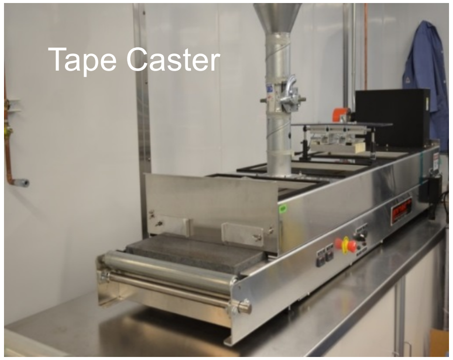
Vapor deposited metal nitride nanoparticles on carbon support

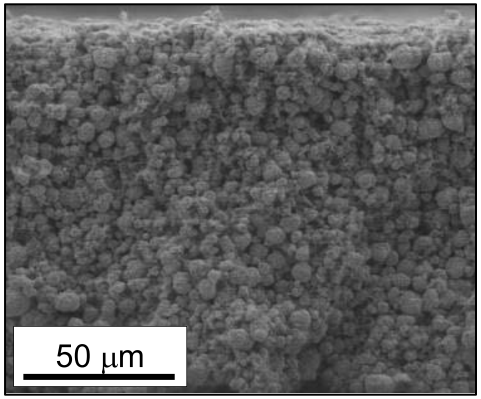


ORNL Sputter Deposition System

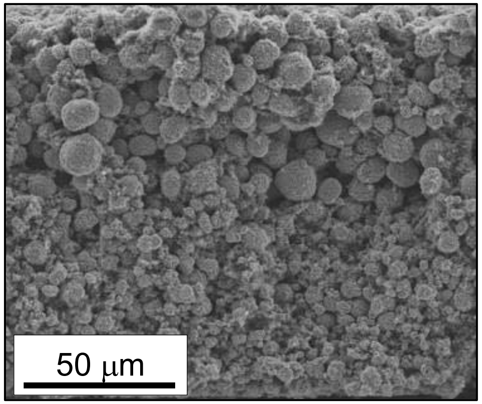
ORNL ElectroCat Capability: Manufacturing Porous Electrodes

- Advanced colloidal processing and formulation science for making highly dispersed catalyst inks
- Ability to make thick coatings with graded structures for alleviation of inherent catalyst-layer mass-transport resistance
- Integration of multilayer MEA structures by dual-slot die coating on membrane, GDL, or both
- Roll-to-roll heated calendaring to make "unitized" MEAs





Single-layer LIB-NMC cathode produced on ORNL slot-die coating line



double-layer LIB-NMC cathode produced on ORNL slot-die coating line

ElectroCat
Electrocatalysis Consortium

contact@electrocat.org

www.electrocat.org

Los Alamos National Laboratory

Argonne National Laboratory

NREL National Renewable Energy Laboratory

Oak Ridge National Laboratory

Backup

LANL Capabilities Relevant to ElectroCat (I)

- **Catalyst and catalyst support synthesis:**
  - ✓ Demonstrated in the past 15 years capabilities in fine-tuning the activity and morphology of PGM-free catalysts by using specific transition-metal, nitrogen, and carbon precursors, *e.g.* dual nitrogen precursors and bimetallic structures;
  - ✓ Multiple-batch and plug-flow reactors with controllable pressure, temperature, atmospheres, and variable residence times;
  - ✓ Ultrasonic-spray synthesis system and screening tools;
  - ✓ Catalyst and support synthesis *via* ultrasonic freeze dried synthesis route;
  - ✓ PGM-free electrocatalyst synthesis *via* electrospinning.
- **Synthesis of "model" catalysts via the controlled introduction of heteroatom and metal dopants using neutral atom beam technology (ENABLE) and other techniques:**
  - ✓ ENABLE is a controlled method for the clean and selective introduction of heteroatom dopants at high kinetic energies, overcoming high thermal barriers;
  - ✓ Tunable parameters including neutral atom beam energy, substrate temperature, exposure times, and co-evaporation of dopants provide extensive control over the selective introduction of dopants and/or defect sites for improved electrocatalysis.
- **Multi-scale modeling techniques that leverage world-class computing facilities for the rational design of catalysts with optimal activity, selectivity, and durability:**
  - ✓ Density functional theory (DFT) models;
  - ✓ *Ab initio* molecular dynamics;
  - ✓ Mass transport properties in electrochemical electrode environments, as a function of mesoscale structure (obtained from Lattice-Boltzmann modeling);

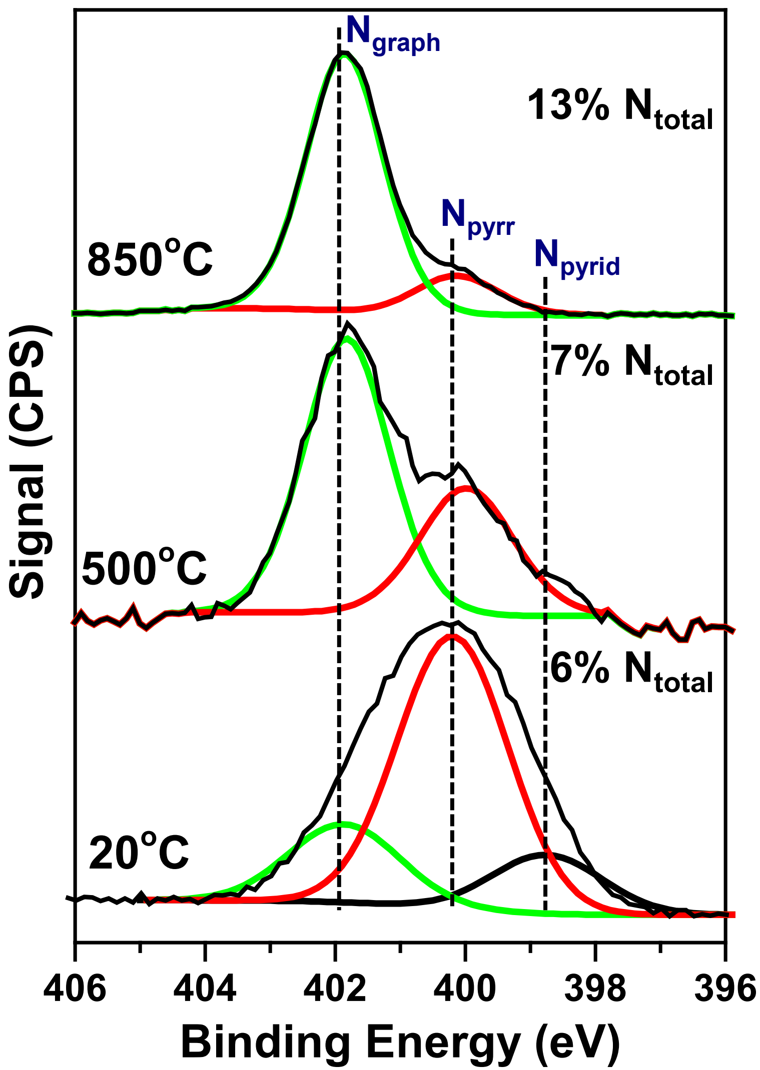
LANL Capabilities Relevant to ElectroCat (II)

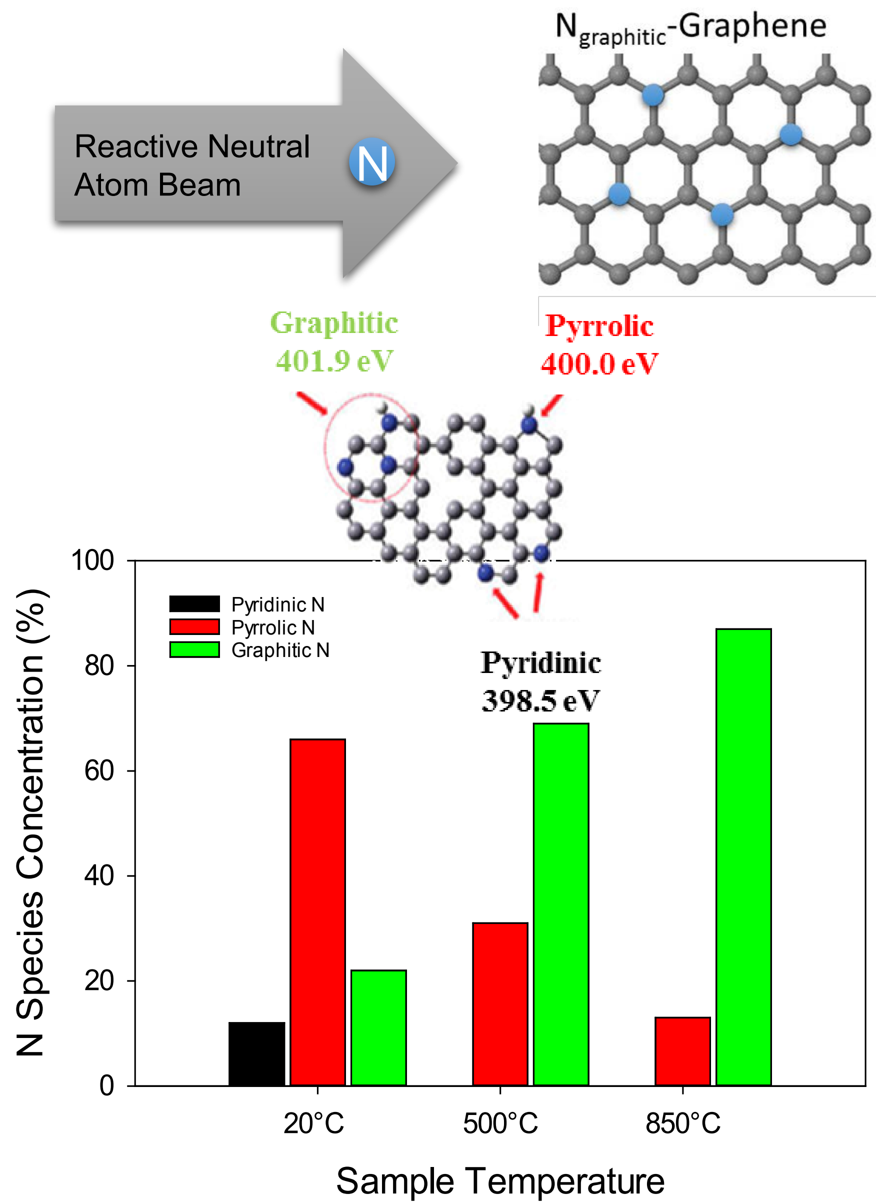
- ✓ Electrochemical reaction rate modeling (activity, selectivity, and corrosion) combined with input from other modeling approaches and experimental studies;
- ✓ Close integration of modeling and experiment.

- **Unique in the field experience in the (i) design, (ii) development, and (iii) integration of fuel cell electrodes and membrane-electrode assemblies (MEAs), established in the Los Alamos Fuel Cell program that has been ongoing for over 35 years, including:**
  - ✓ Development and optimization of PGM-free electrodes and MEAs for acidic polymer systems (for nearly 15 years);
  - ✓ Implementation of PGM-free catalysts and MEAs in alkaline fuel cell systems (applicable to the development of both ORR and HOR catalysts).
- **World-leading high-performance computing (HPC) capabilities:**
  - ✓ Theoretical Division largely devoted to HPC;
  - ✓ Newly-constructed Cielo supercomputer with nearly 9,000 nodes and over 140,000 cores;
  - ✓ Nine additional supercomputers with between 68 and 1,600 nodes and 1,000 and 38,000 cores;
  - ✓ Hundreds of CPUs for large and complex simulations, structural analyses, heat and mass transfer, *etc.*
- **Exclusive in the field characterization capabilities:**
  - ✓ Los Alamos Neutron Science Center (LANSCE), including Surface Profile Analysis Reflect (SPEAR) and other neutron techniques;
  - ✓ Proton radiography technique;
  - ✓ Micro X-ray computed tomography (MicroXCT) instrument for non-destructive characterization of PGM-free catalyst MEAs via cross-sectional imaging.

Controlled Functionalization of Model Catalysts

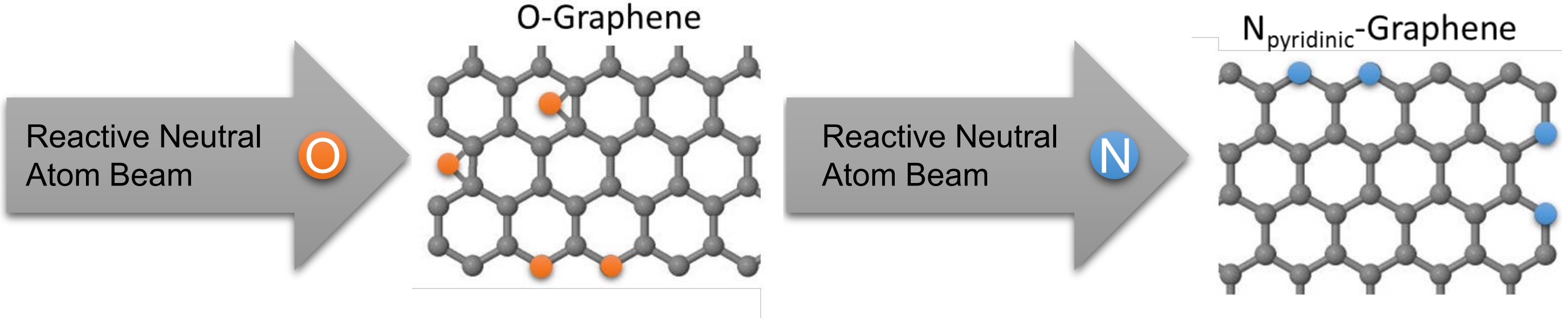
Effect of Substrate Temperature on N Speciation

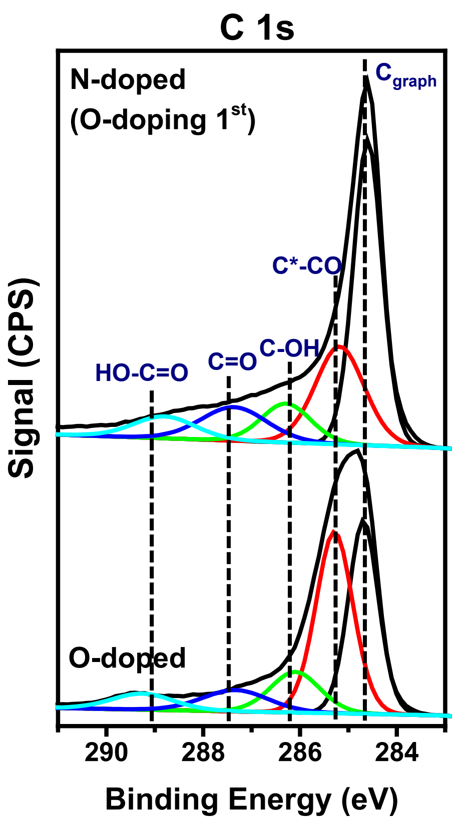


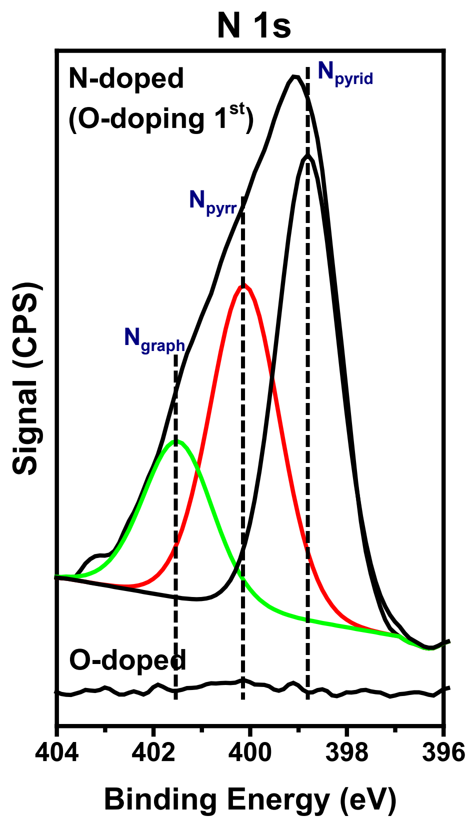


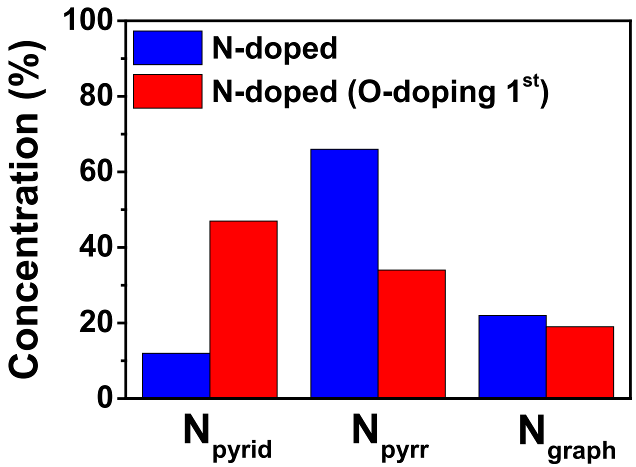
Controlled Functionalization of Model Catalysts

Sequential Reactive Atom Doping









- Highest concentration of pyridinic N obtained from sequential doping
- Constant concentration of graphitic N

NREL ElectroCat Capabilities

Capability	POC
1. Powder Implant and Sputter System	Thomas Gennett, thomas.gennett@nrel.gov Arrelaine Dameron, arrelaine.dameron@nrel.gov
2. Thin Film High-Throughput Experimental Capabilities	Andriy Zakutayev, andriy.zakutayev@nrel.gov
3. In-Operando Differential Cell Measurements of Electrochemical Kinetics and Transport	KC Neyerlin, kenneth.neyerlin@nrel.gov
4. Spatial Performance Evaluation using a Segmented Cell with a 121 Multichannel Electrical Load	Guido Bender, guido.bender@nrel.gov
5. High-Throughput Approaches to Scaling New PGM-free Catalysts to Electrodes using Relevant Production Technologies	Michael Ulsh, michael.ulsh@nrel.gov
6. Experimental and Computational Materials Data Infrastructure	Kristin Munch, kristin.munch@nrel.gov Robert White, robert.white@nrel.gov

Experimental & Computational Materials Data Infrastructure: Overview

The Materials Data Infrastructure at NREL supports both **experimental** and **computational** materials data management and analysis:

- Experimental data system automatically harvests, translates, and extract data from processing and characterization tools into network – accessible databases (38 instruments across 7 laboratories)
- Metadata is automatically extracted from raw data files, and data is expressed into databases -> enabling advanced search, query and the creation of "project-specific" databases for informatics
- Computational results from materials discovery workflows (i.e. HPC) is processed and expressed in databases for search and query.
- Web interfaces enables easy access to search for data, find related data by metadata (i.e. project, sample, collection time, etc.), and visualize resulting plots, (i.e. Comparing results across samples by plot overlay)
- Materials-specific web interfaces enable chemistry-focused search and visualization
- Public-facing subsets of cleaned data is made available at materials.nrel.gov.

Experimental & Computational Materials Data Infrastructure: Concept