2014 Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting
Washington, DC – June 16-20, 2014

Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

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Project ID: FC107

Overview

Timeline

- **Project start date:** April 1, 2013
- **Project end date:** March 31, 2016

Budget

- **FY13 DOE funding:** $745K
- **Planned FY14 funding:** $1,275K
- **Total DOE project value:** $3,999K
- **Cost share:** 20.1%

Barriers

- **A. Activity** (catalyst; MEA)
- **B. Durability** (catalyst; MEA)
- **C. Power density** (MEA)

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Note: *New project, not reviewed in 2013*

Partners – Principal Investigators

Carnegie Mellon University

– Shawn Litster

University of Rochester

– Michael Neidig

University of Waterloo

– Zhongwei Chen

Oak Ridge National Laboratory

– Karren More

IRD Fuel Cells

– Madeleine Odgaard

General Motors

– Joseph Ziegelbauer

Relevance: Objective and Targets

Objective

Advance non-PGM cathode technology through the development and implementation of novel materials and concepts for cathode catalysts and electrodes with (i) oxygen reduction reaction (ORR) activity viable for practical fuel cell systems; (ii) improved durability; (iii) high ionic/electronic conductivity within the catalyst layer; (iv) adequate oxygen mass transport; and (v) effective removal of the product water.

Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Unit	2011 Status	Targets	
			2017	2020
Non-Pt catalyst activity per volume of supported catalyst	A / cm^3 @ 800 $mV_{IR\text{-}free}$	60 (measured at 0.8 V) 165 (extrapolated from >0.85 V)	300	300

Technical Targets (Subject to Modification as Required)

Volumetric catalyst activity in MEA at 0.80 V (*iR*-free), 80°C:	$\geq$ 300 A cm^{-3}
Four-electron selectivity (RRDE):	$\geq$ 99% (H_2O_2 yield $\leq$ 1%)
MEA maximum power density at 80°C:	$\geq$ 1.0 W cm^{-2}
Performance loss at 0.80 A cm^{-2} after 30,000 cycles in N_2:	$\leq$ 40%

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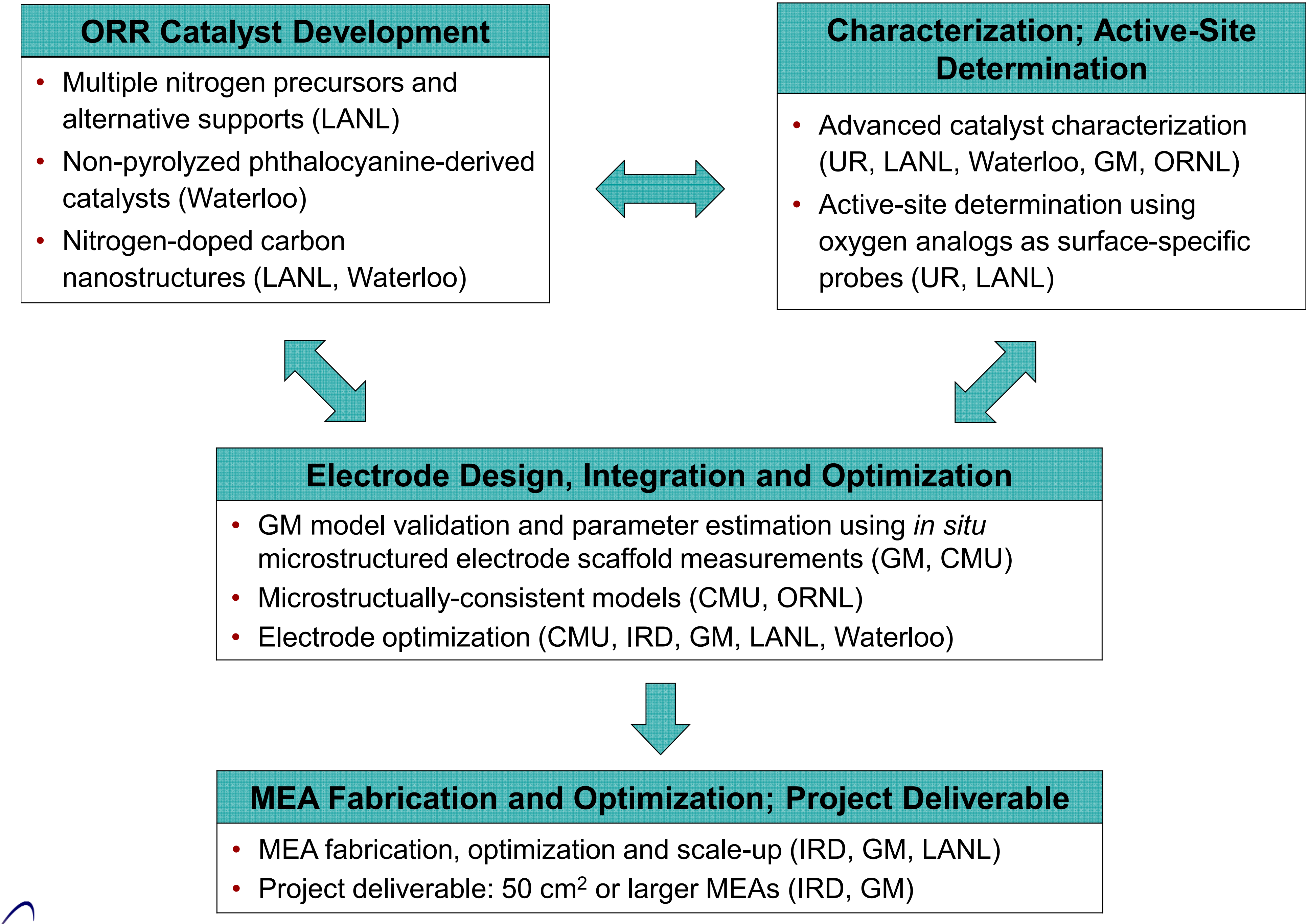
Approach: Project Overview



ORR Catalyst Development

- Multiple nitrogen precursors and alternative supports (LANL)
- Non-pyrolyzed phthalocyanine-derived catalysts (Waterloo)
- Nitrogen-doped carbon nanostructures (LANL, Waterloo)

Characterization; Active-Site Determination

- Advanced catalyst characterization (UR, LANL, Waterloo, GM, ORNL)
- Active-site determination using oxygen analogs as surface-specific probes (UR, LANL)

Electrode Design, Integration and Optimization

- GM model validation and parameter estimation using *in situ* microstructured electrode scaffold measurements (GM, CMU)
- Microstructually-consistent models (CMU, ORNL)
- Electrode optimization (CMU, IRD, GM, LANL, Waterloo)

MEA Fabrication and Optimization; Project Deliverable

- MEA fabrication, optimization and scale-up (IRD, GM, LANL)
- Project deliverable: 50 cm^2 or larger MEAs (IRD, GM)

Approach: Achieving Performance Targets

Catalyst Activity

- Develop novel synthetic approaches to increase active site density and access
- Tune porous structures to improve accessibility of active sites to reactants
- Probe active sites to understand structure-activity relationships
- Introduce alternative metals and/or elements to enhance activity through possible synergistic effects

Durability

- Use advanced carbon or non-carbon supports to mitigate carbon corrosion
- Discover alternative transition metals to overcome intrinsic instability of Fe-catalysts in high potential/voltage ranges
- Optimize electrode structure to relieve water flooding at non-PGM cathodes

MEA Performance

- Image, model (transport properties) and optimize non-PGM cathode structures

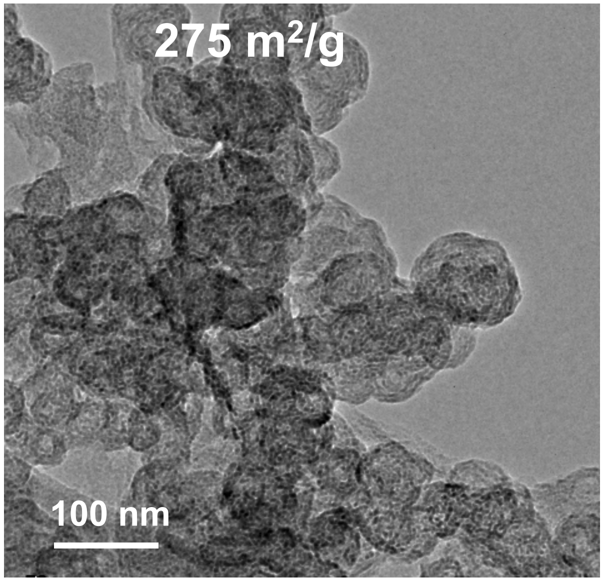
Approach: Project Milestones

Date	Milestones	Status	Comments
Dec 2013	Image 3D structure of a state-of-the-art LANL electrode by Nano-XRT and compute effective transport properties.	**Complete**	3D imaging of electrode with 50 nm resolution and hierarchical structure characterization accomplished; transport-property analysis complete.
Mar 2014	Validate surface-probe approach for a non-PGM catalyst using at least two characterization techniques.	**Complete**	Validity of ^{57}Fe Mössbauer spectroscopy and nuclear resonance vibrational spectroscopy (NRVS) to probe Fe-site perturbation demonstrated.
Jun 2014	Develop non-PGM catalyst that demonstrates volumetric current density of at least 100 A cm^{-3} at 0.80 V in a membrane electrode assembly, over 50% enhancement in activity compared to the 2011 baseline of 60 A cm^{-3}.	**On schedule**	84 A cm^{-3} (iR-corrected) achieved for high surface-area PANI-Fe-C catalyst, approaching volumetric current density milestone.
Sep 2014	Demonstrate $i_{0.8V} \geq 150$ mA cm^{-2}, $\eta > 95\%$, and 30,000-cycle performance loss of no more than 50 mV ($\Delta E_{½}$ and/or ΔV at 0.8 A cm^{-2}).	**Current density target complete** **Durability target pending**	190 mA cm^{-2} at 0.8 V (iR-corrected) achieved with PANI-Fe-C catalyst; 160 mA cm^{-2} at 0.8 V shown with cyanamide (CM)-PANI-Fe-C; durability testing underway.

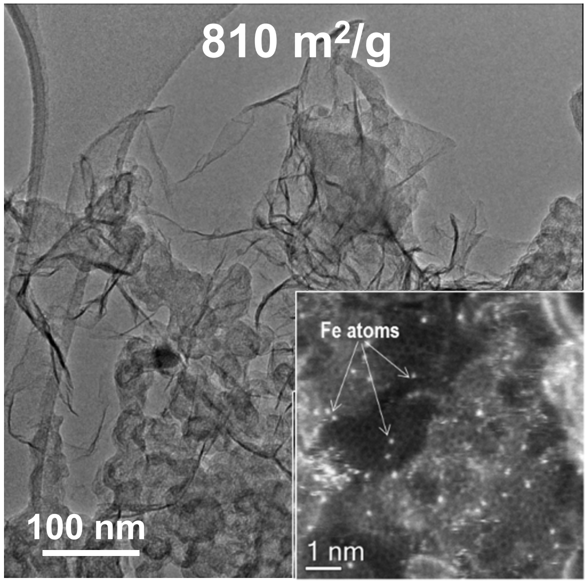
Go/no-go decision for further development of metal-free catalysts based on nitrogen-doped nanostructures:
Demonstrate with $E_{½} \geq$ **0.60 V** vs. RHE (*September 2014*)

New Catalysts: High Surface Area PANI-Fe-C

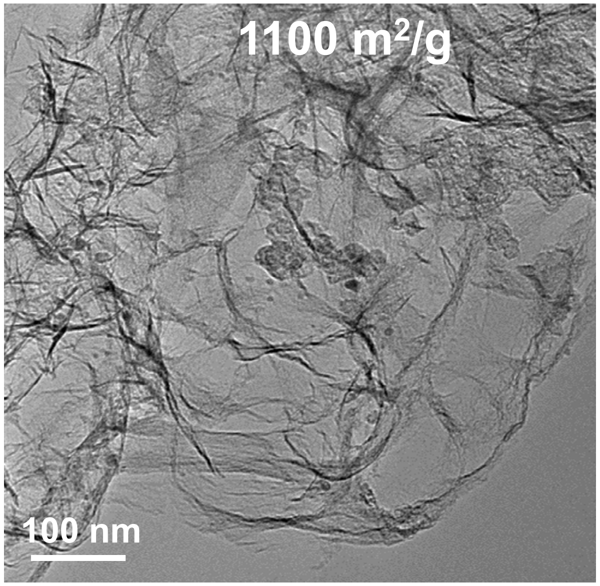
“Standard” PANI-Fe-C, 10 wt% Fe
Two-step heat treatment

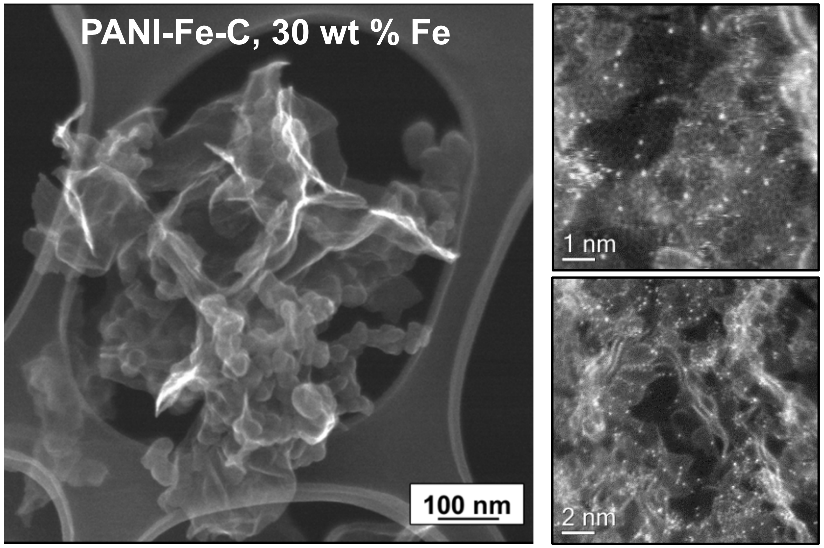


PANI-Fe-C, 30 wt % Fe
Two-step heat treatment



PANI-Fe-C, 30 wt % Fe
Three-step heat treatment

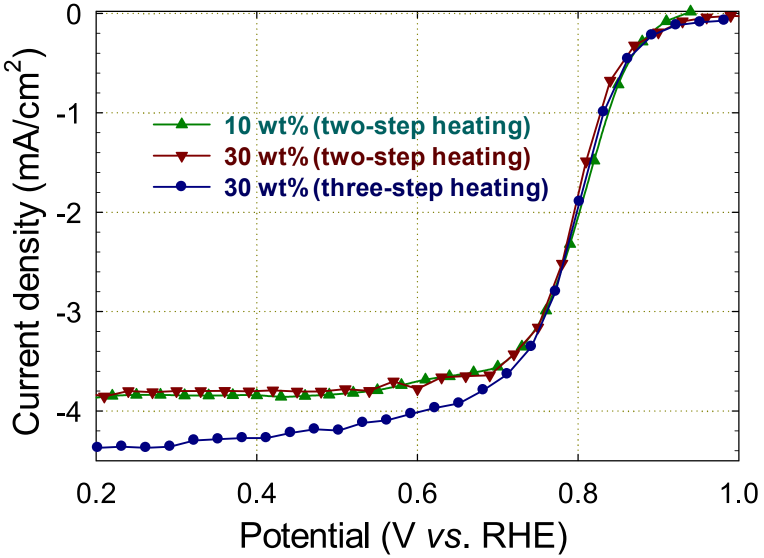


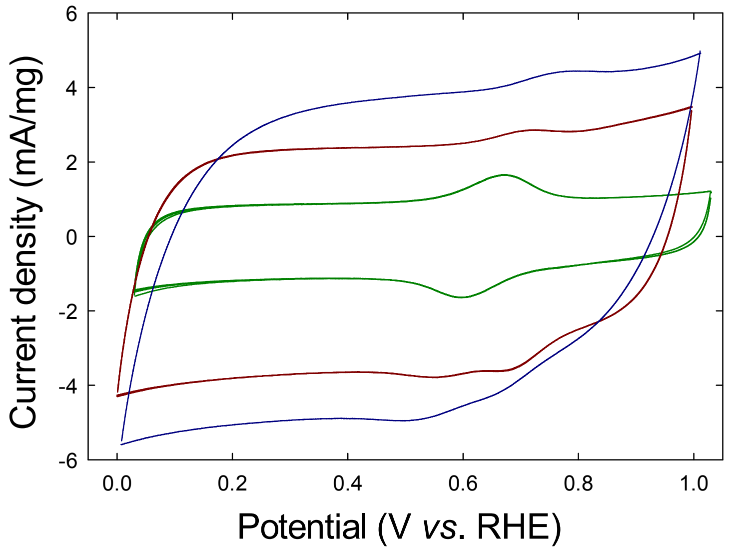


- **Highlight:** Catalysts with surface area values as high as **1100 m^2 g^{-1}** synthesized by new, three-step heat-treatment synthesis strategy
- Rumpled, multi-layered graphene sheet-like morphology with dispersed Fe atoms (bright spots)

New Catalysts: High Surface Area PANI-Fe-C

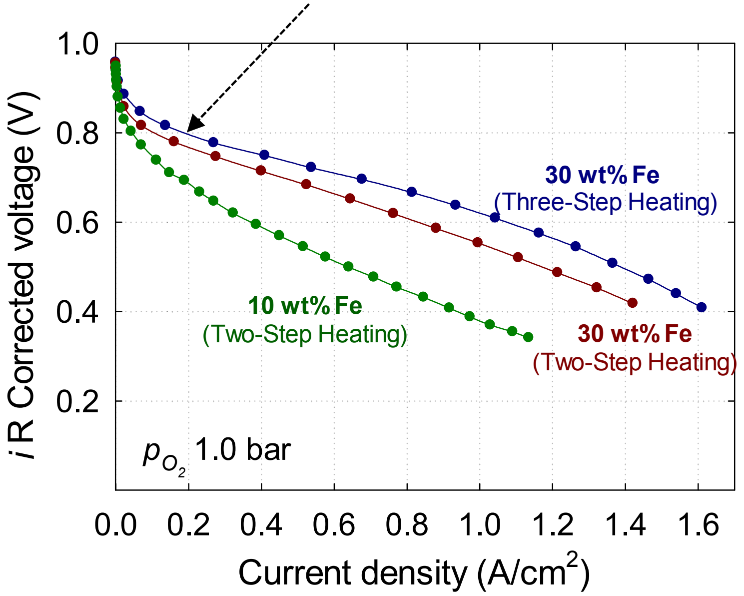
RDE: 0.5 M H_2SO_4; 900 rpm; 25ºC; Hg/$HgSO_4$ (0.5 M H_2SO_4) reference electrode; graphite counter electrode; steady-state potential program: OCP, 300 s, 30 mV steps, 30 s/step; **CV:** 0.5 M H_2SO_4; 900 rpm; 25ºC; 50 mV/s





Anode: 2.0 mg cm^{-2} Pt; **Cathode:** 4.1 mg cm^{-2}; **Cell:** 80°C; 100% RH; **Membrane**: Two Nafion® 212

~190 mA cm^{-2} at 0.80 V (*iR*-corrected)

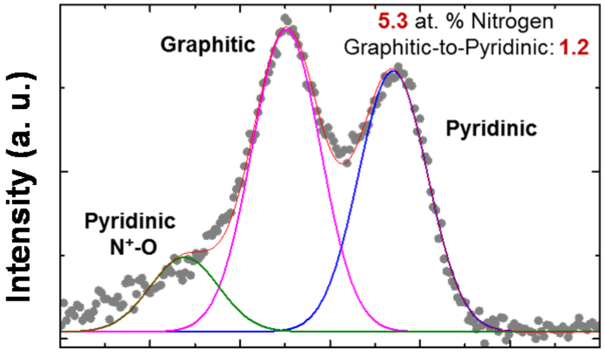


- Fe content and heat-treatment regime have minimal impact on ORR half-wave ($E_{½}$) and onset potential through RDE testing
- Electrochemically accessible surface area increases significantly up to **363 m^2 g^{-1}**
- **Highlight: 190 mA cm^{-2}** current density at 0.80 V (*iR*-corrected) through MEA testing

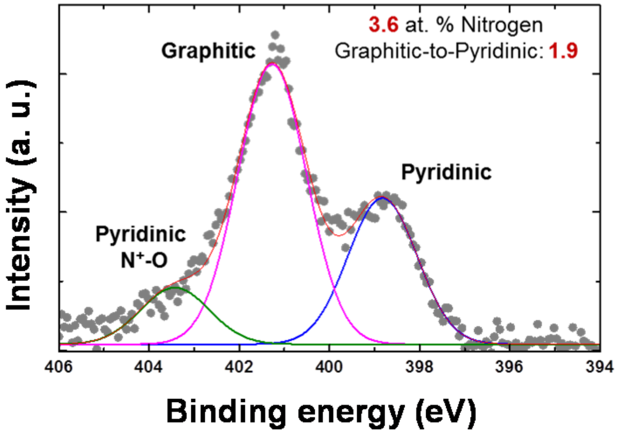
September 2014 current-density milestone of 150 mA cm^{-2} met and exceeded by *ca.* 25%

New Catalysts: High Surface Area PANI-Fe-C

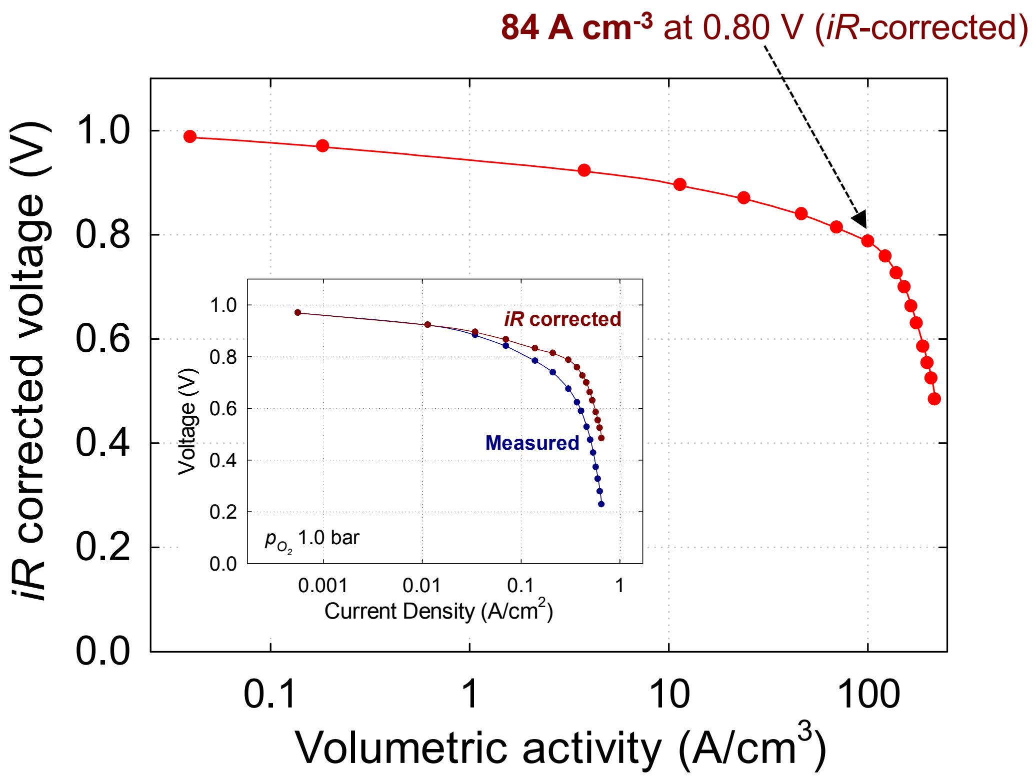
Three-step heat treatment



Two-step heat treatment



Anode: 2.0 mg cm^{-2} Pt; **Cathode**: Three-step heat-treated PANI-Fe-C catalyst, 2.0 mg cm^{-2}, thickness 30 μm; **Cell:** 80°C; 100% RH, **Membrane**: Two Nafion® 1135

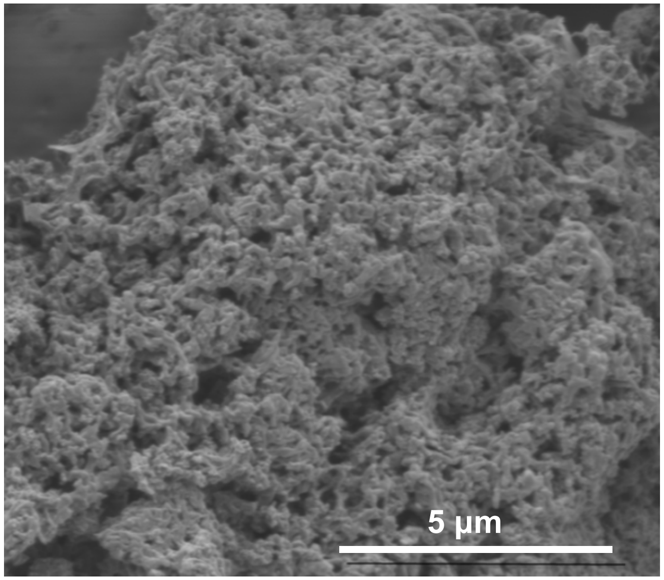

84 A cm^{-3} at 0.80 V (*iR*-corrected)

- Changing heat-treatment regime modulates nitrogen doping, likely enhancing performance
- Significantly increased nitrogen content and relative amount of pyridinic-nitrogen doping with three-step heat treatment
- **Highlight:** **84 A cm^{-3}** volumetric current density at 0.80 V (*iR*-corrected) through MEA testing

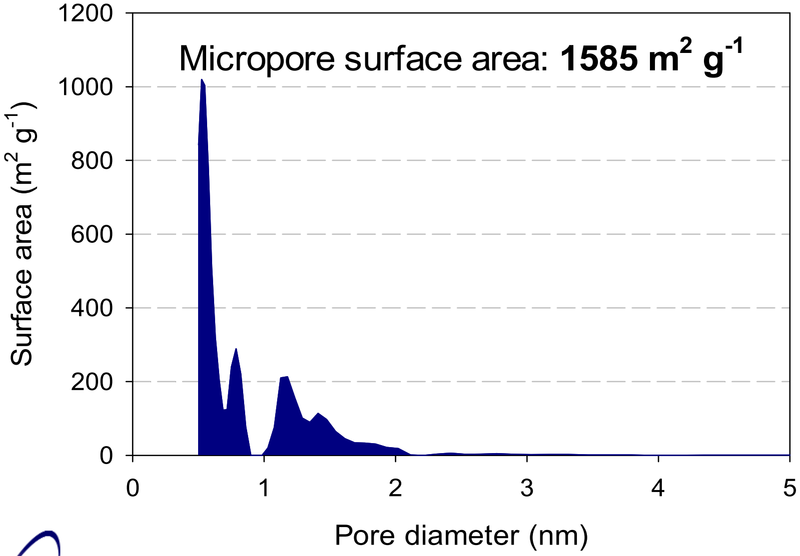
40% enhancement in volumetric current density compared to 2011 baseline (60 A cm^{-3}); approaching June 2014 milestone of 100 A cm^{-3}

New Catalysts: CM-PANI-Fe-C

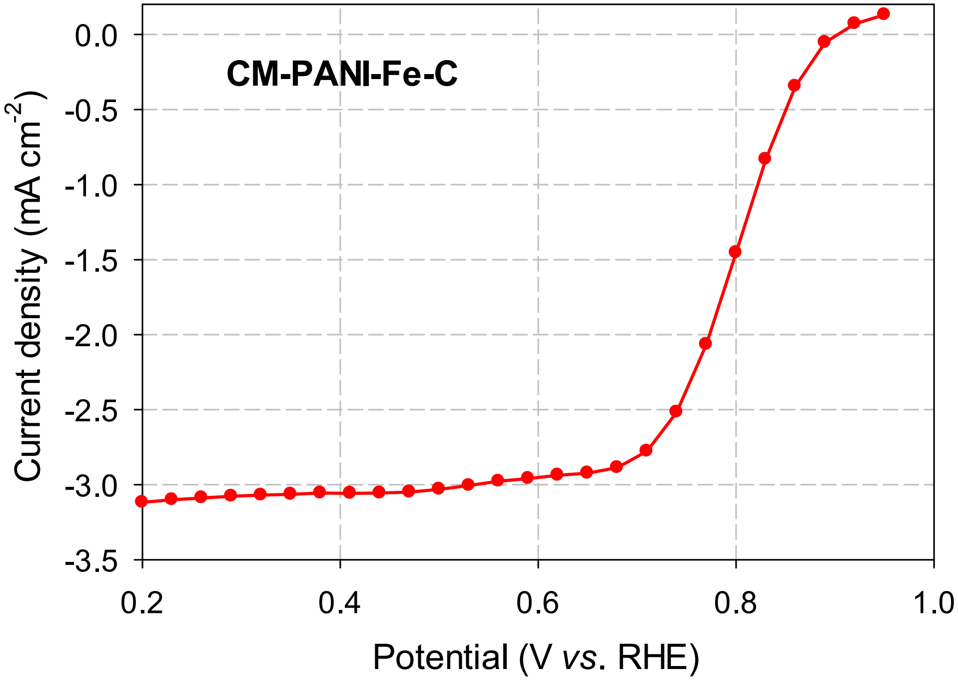
SEM



Pore-size distribution



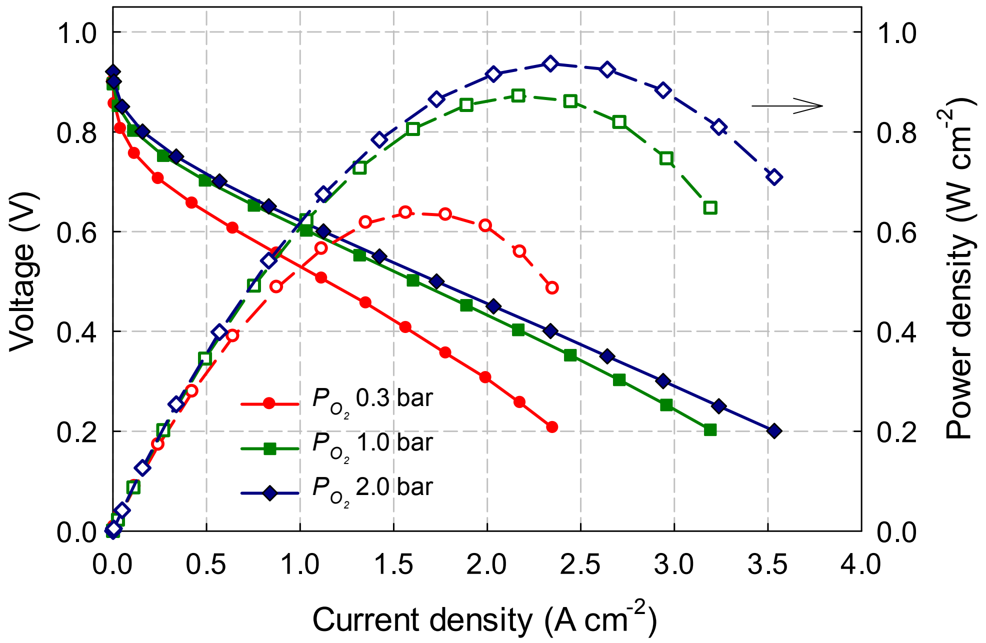
RDE: 0.6 mg cm^{-2}; 0.1 M H_2SO_4; 900 rpm; 25ºC; Hg/$HgSO_4$ (0.5 M H_2SO_4) reference electrode, graphite counter electrode, steady-state potential program: OCP, 300 s, 30 mV steps, 30 s/step



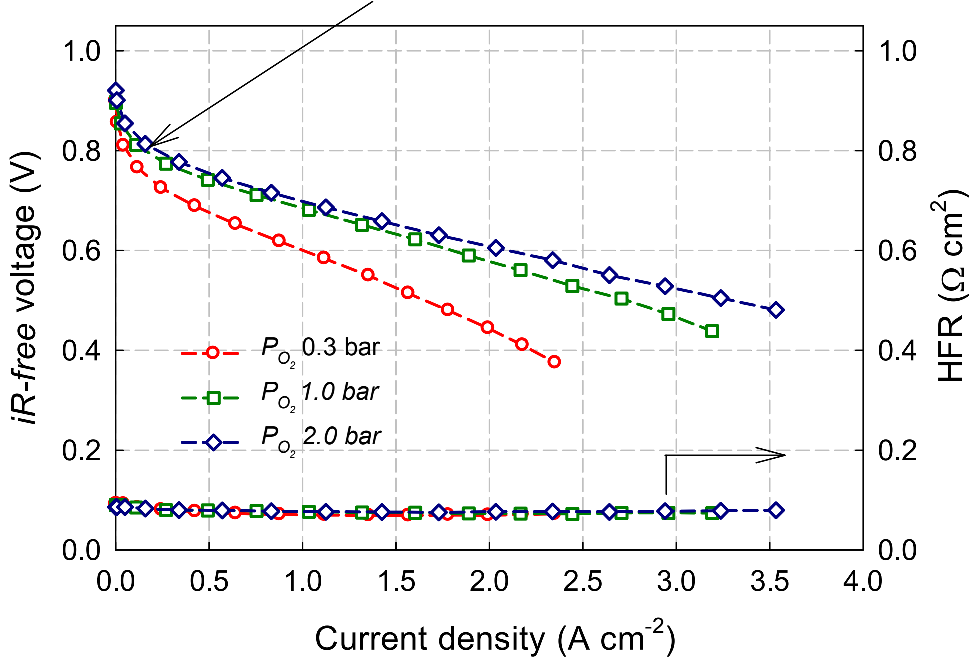
- New catalyst developed combining multiple nitrogen precursors
- **Highlight:** Microporous surface area of 1585 m^2 g^{-1}; $E_{½}$ value of **0.80 V** *vs.* RHE, comparable with best non-PGM catalysts reported to date

New Catalysts: CM-PANI-Fe-C; H_2/O_2 Fuel Cell Performance

Anode: 2.0 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm; **Cathode:** ~ 4.0 mg cm^{-2} O_2 200 sccm; **Membrane:** Nafion®211; **Cell:** 80°C



160 A cm



- MEA performance less dependent on back pressure – improved mass transport evident
- Power density of **0.87 W cm^{-2}** reached at 0.40 V and p_{O2} of 1.0 bar thanks to high catalyst activity and facile mass transport
- **Highlight:** Current density of **160 mA cm^{-2}** at 0.80 V (*iR*-corrected)

Second catalyst formulation that meets and exceeds September 2014 current density milestone of 150 mA cm^{-2}

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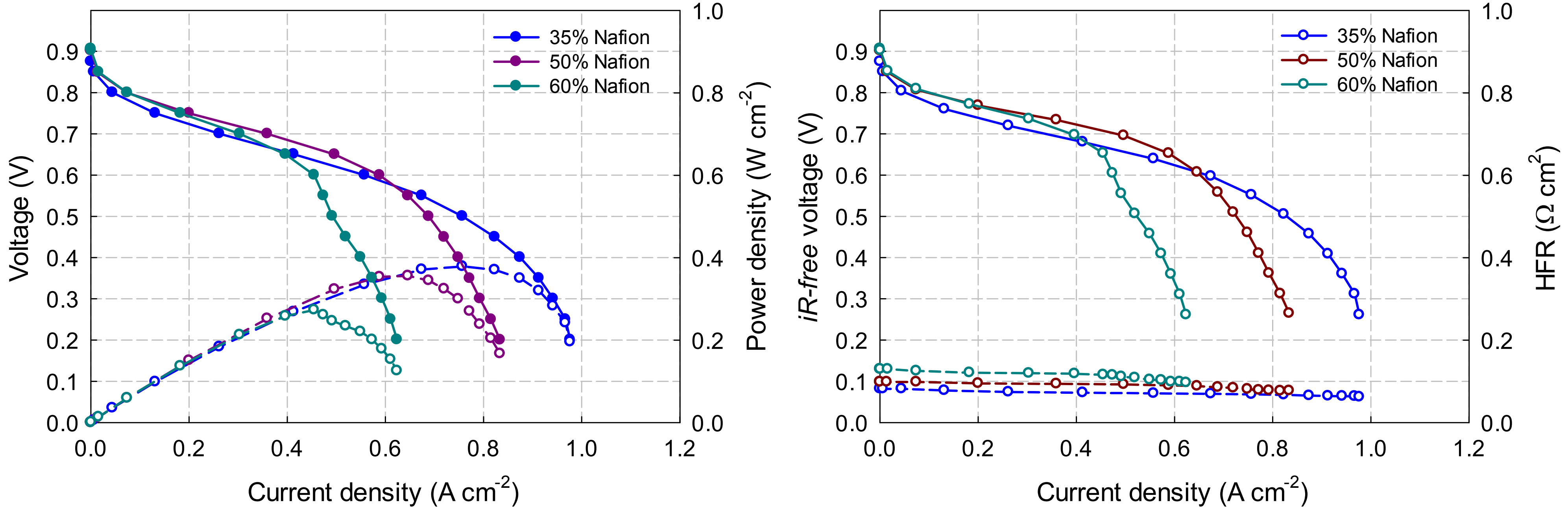
New Catalysts: CM-PANI-Fe-C; H_2/Air Fuel Cell Performance

Anode: 2.0 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.0 mg cm^{-2} air, 200 sccm (2.5 stoichiometry at 1.0 A cm^{-2}), 1.0 bar air partial pressure; **Membrane:** Nafion®, 211; **Cell:** 80°C



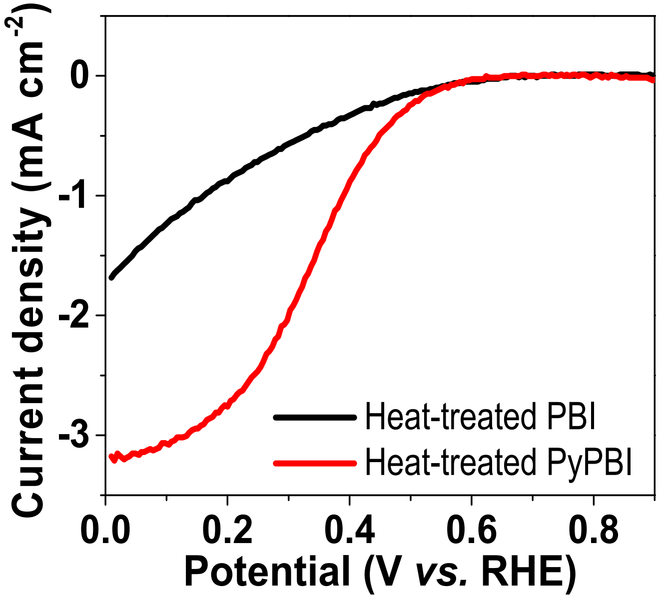
- Higher Nafion® content enhancing current density in kinetic region with performance sacrifice in mass transport region
- **Highlight:** Current density of **74 mA cm^{-2}** measured at 0.80 V on air (**90 mA cm^{-2}**, *iR*-corrected)
- **Highlight:** Power density of **0.35 W cm^{-2}** reached at 0.60 V

Record fuel cell performance achieved with an air-operated non-PGM cathode

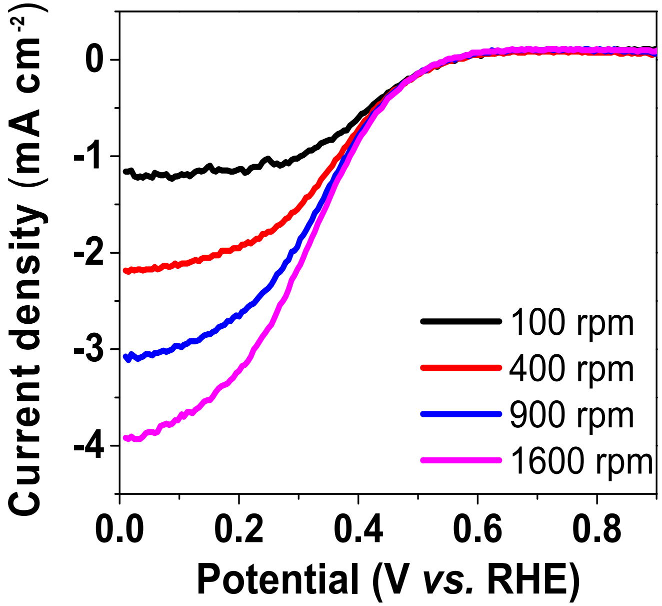
New Catalysts: Metal-Free Non-PGM Formulations

RDE: 0.6 mg cm^{-2}, 0.1 M $HClO_4$, 900 rpm, 25ºC, RHE reference electrode, graphite counter electrode, linear sweep voltammetry at 10 mV s^{-1}, not resistance corrected

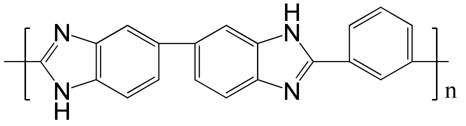
RDE Evaluation: PBI and PyPBI



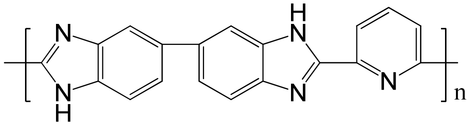
RDE Evaluation: Heat-treated PyPBI



Polybenzimidazole (PBI)



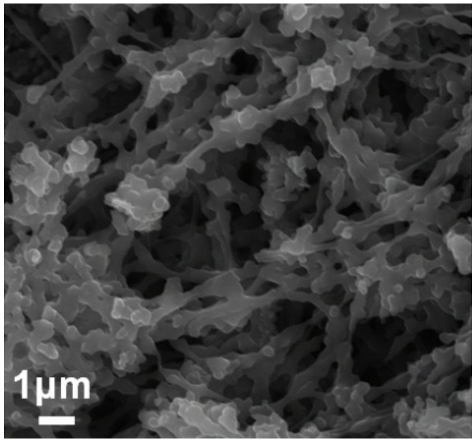
or



PyPBI developed “in house”

Mixing with pore forming agent

Heat treatment

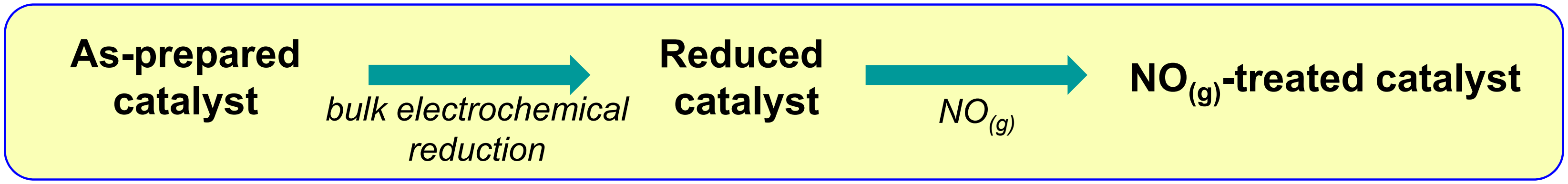


$E_{1/2}$ of 0.32 V *vs.* RHE for **metal-free** non-PGM catalyst

Catalyst Characterization: $NO_{(g)}$ as a Molecular Probe

- **Nitric oxide, $NO_{(g)}$, an O_2-analog forming stable, non-reactive complexes with Fe used to study O_2 binding to Fe sites in metalloenzymes**
- **When combined with Fe-specific spectroscopic methods the O_2-analog approach**
  - ✓ Probes the presence of surface/near-surface Fe accessible to $O_{2(g)}$
  - ✓ Provides insight into the electronic/geometric structure of O_2-binding Fe site
  - ✓ Promises to help clarify mechanism of O_2 activation/reduction (in combination with DFT methods)

General O_2-Analog Methodology

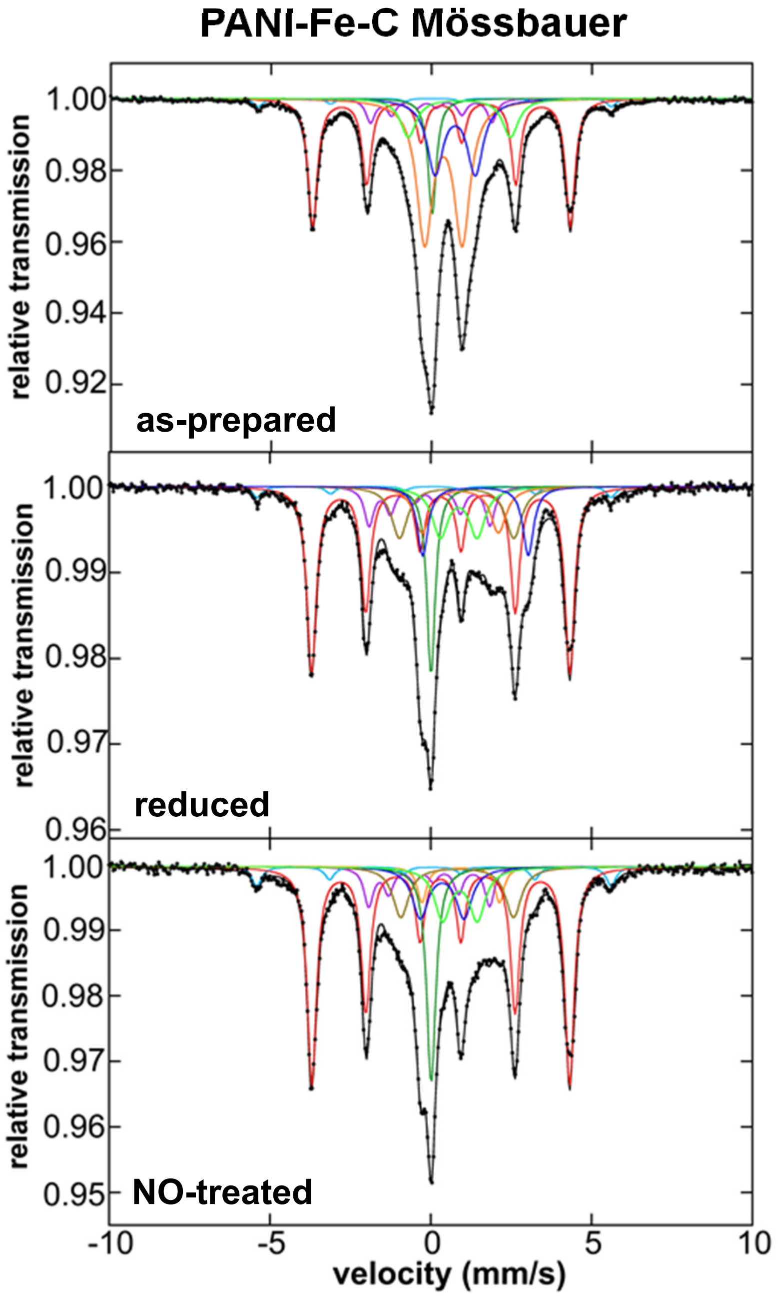


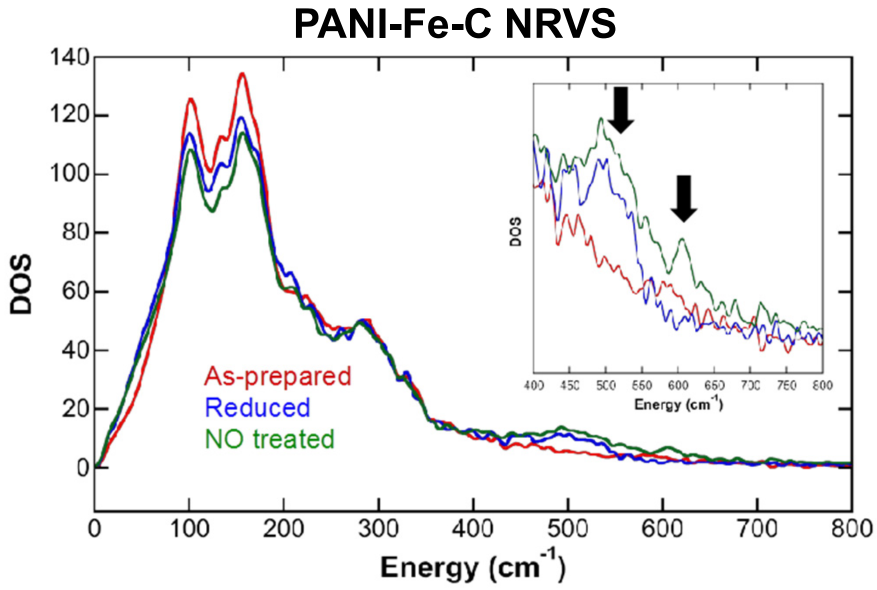
As-prepared catalyst → *bulk electrochemical reduction* → **Reduced catalyst** → *$NO_{(g)}$* → **$NO_{(g)}$-treated catalyst**

Key Challenge: **How to characterize Fe in each of the three forms in order to determine the effects of reduction and $NO_{(g)}$ treatment?**

- **Inorganic spectroscopic methods focusing on Fe are ideal for studying changes in molecular-level structures upon reduction/($NO_{(g)}$ addition)**
  - ✓ Nuclear resonance vibrational spectroscopy (NRVS) – complete set of bands corresponding to the motion of Mössbauer-active nuclei, *i.e.,* ^{57}Fe
  - ✓ ^{57}Fe Mössbauer spectroscopy – ^{57}Fe nuclear transitions; sensitivity to oxidation state; bulk *vs.* single-site Fe species, ligation environment changes; quantification of individual Fe components

Catalyst Characterization: Mössbauer Spectroscopy and NRVS


PANI-Fe-C Mössbauer

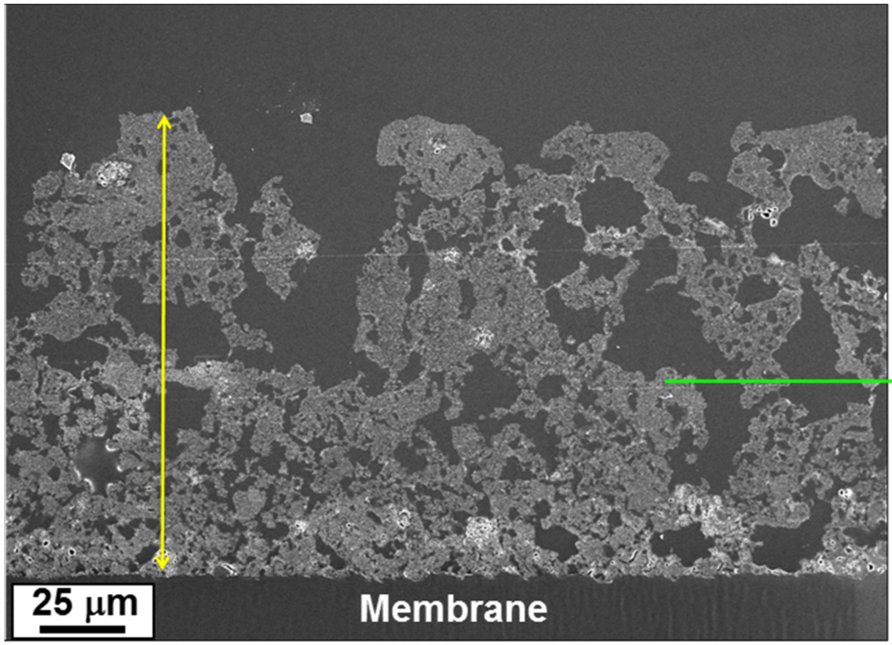

PANI-Fe-C NRVS

- **Mössbauer**: Demonstrates surface or near-surface iron species which can be reduced via bulk electrolysis
- **Mössbauer**: NO$_{(g)}$ treatment consumes some original doublets while generating new doublet Fe species, consistent with NO coordination
- **NRVS**: Spectral changes at low energy upon reduction at 450-550 cm^{-1}, and distinct new NRVS feature upon NO(g) treatment at ~ 606 cm^{-1} observed upon NO$_{(g)}$ treatment
- **Highlight:** Viability of the surface probe approach in combination with Mössbauer and NRVS demonstrated

March 2014 catalyst surface-probe characterization milestone achieved

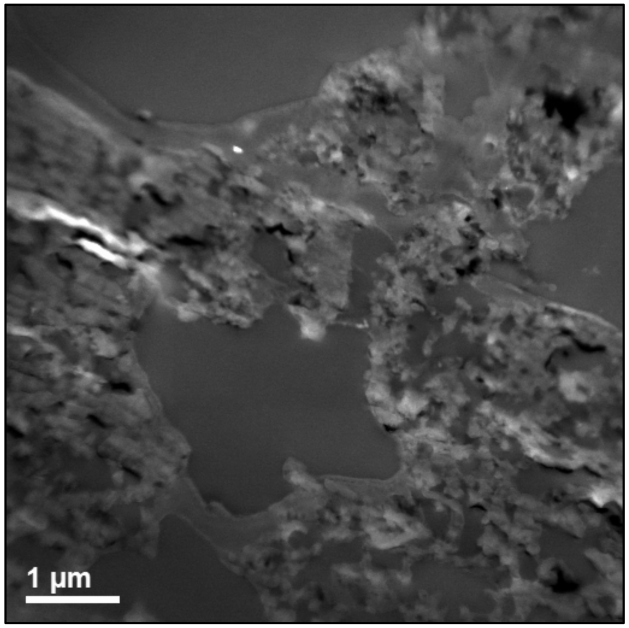
Electrode Studies: Electrode Microstructure (CM-PANI-Fe-C)

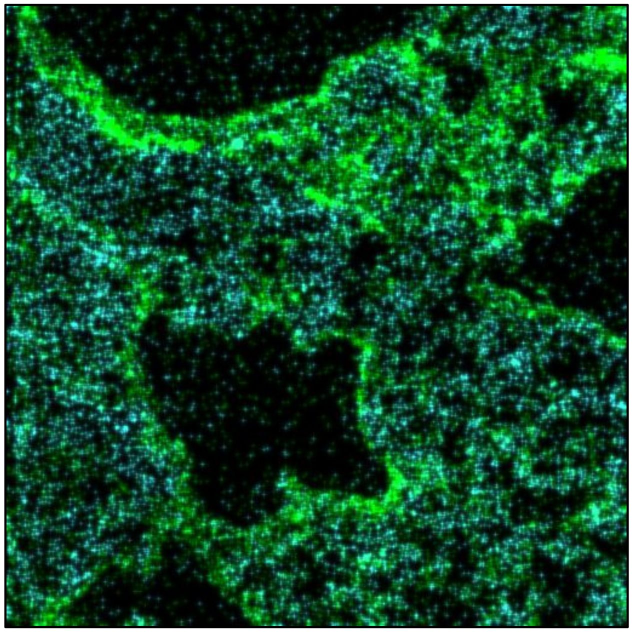
CM-PANI-C catalyst with 35% Nafion®



Upper “half” of electrode: ca. 52% porosity, open to surface

Lower “half” of electrode: ca. 41% porosity

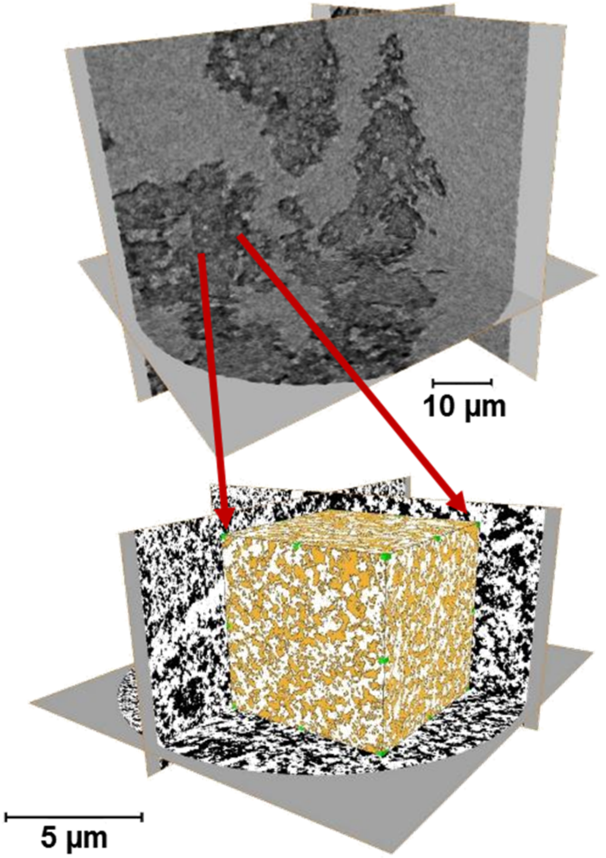




- Lower “half” of electrode (adjacent to membrane) denser than upper “half”, due to particle packing and smaller pore size
- Relatively thick (0.1-0.5 µm) ionomer film surrounds CM-PANI-C agglomerates; very little ionomer penetration into agglomerates
- Elemental map: fluorine from ionomer (**green**) and sulfur from PANI synthesis (associated with carbon phase; **blue**)

Electrode Studies: Nano-XRT Imaging (CM-PANI-Fe-C)

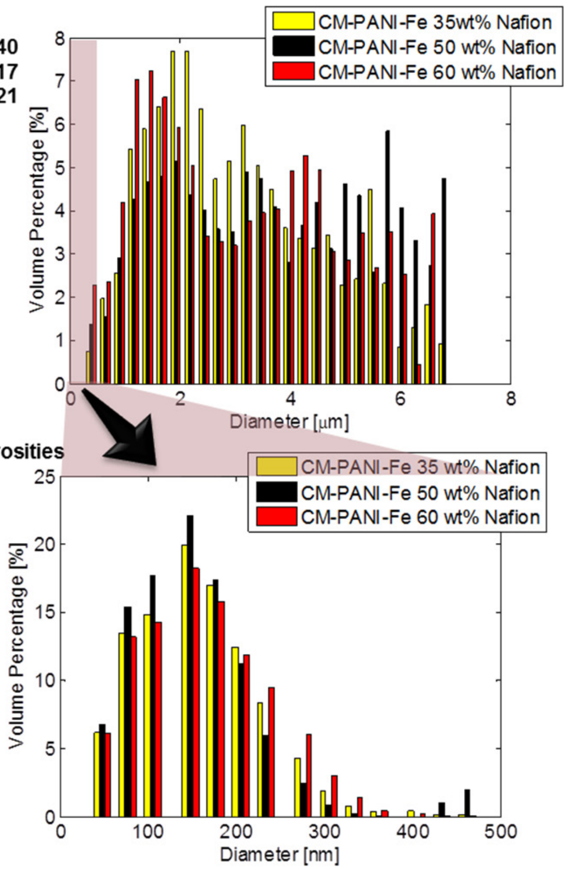
Large Field-of-View Scan



High-Resolution Scan

Pore Diameter

Pore diameter based on maximum inscribed sphere

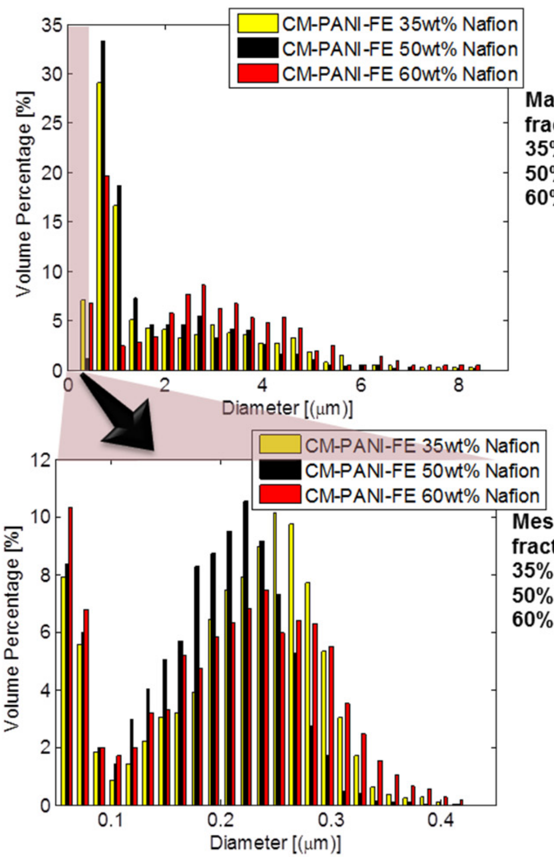


Macro-pore porosities
35% wt. = 0.40
50% wt. = 0.17
60% wt. = 0.21

Meso-pore porosities
35% wt. = 0.47
50% wt. = 0.49
60% wt. = 0.46

Solid Diameter

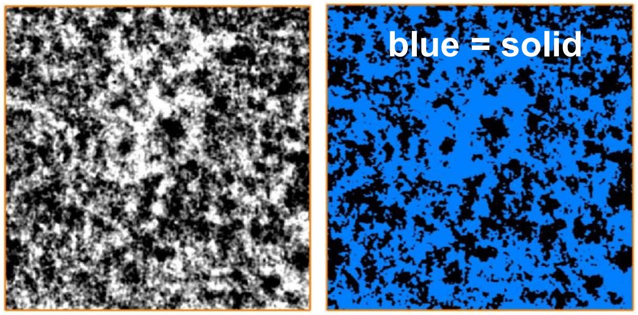
Solid dia. based on volume to surface area ratio



Macro-solid vol. fractions
35% wt. = 0.60
50% wt. = 0.83
60% wt. = 0.79

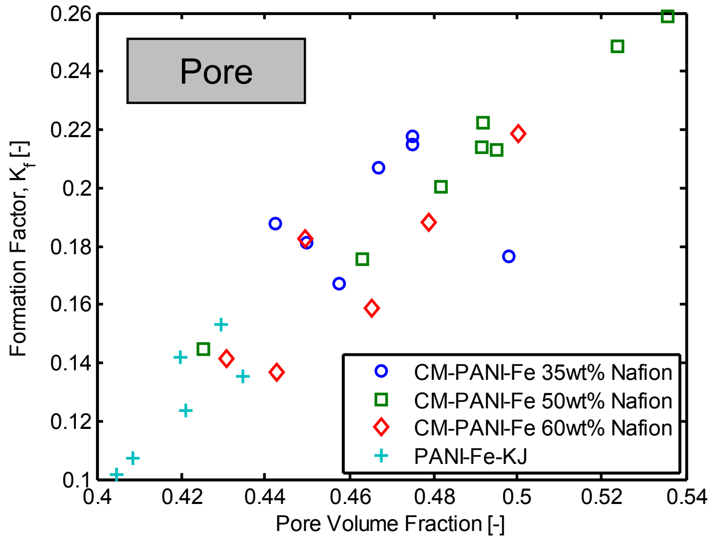
Meso-solid vol. fractions
35% wt. = 0.53
50% wt. = 0.51
60% wt. = 0.54

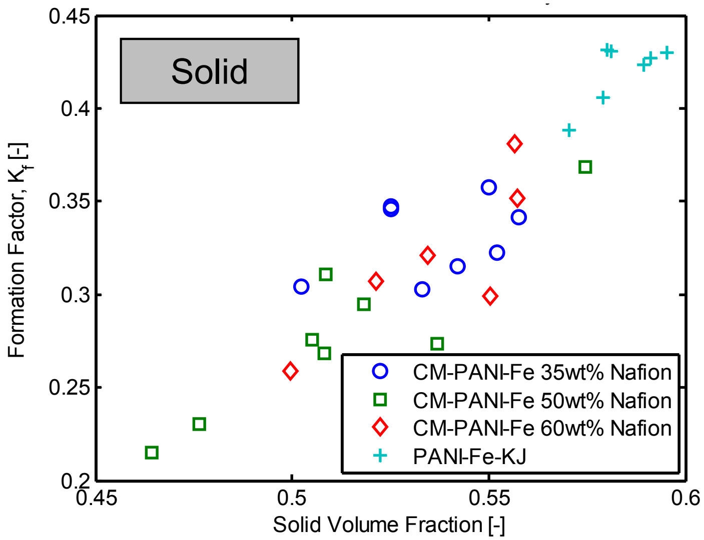
Segmented Slice (16 nm thickness)



- Macro- and mesopores observed throughout the electrode layer
- **Highlight:** Effective length scales and effective diameters of pore/solid domains in non-PGM electrode characterized

Electrode Studies: Transport Property Computation (CM-PANI-Fe-C)





Effective diffusivity:

$$D_{eff} = K_f \bar{D}_{pore}$$

Formation factor:

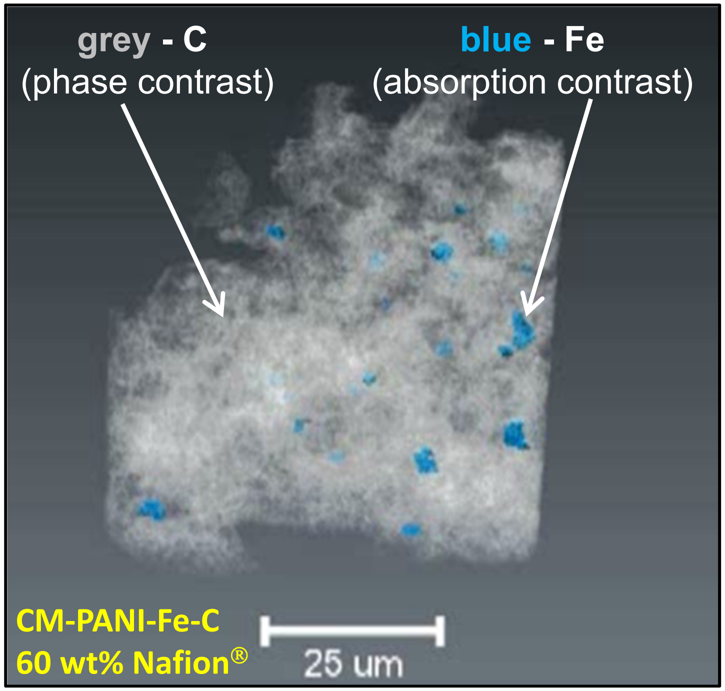
$$K_f = \frac{\varepsilon}{\tau}$$

ε - volume fraction

τ - tortuosity factor

Bruggeman correction factor (α): $D_{eff} = \varepsilon^{\alpha} \bar{D}_{pore}$

Pore		Solid	
CM-PANI-Fe 35 wt% Nafion $\varepsilon = 0.47 \pm 0.03$ $K_f = 0.19 \pm 0.03$	$\alpha = 2.2 \pm 0.32$	**CM-PANI-Fe 35 wt% Nafion** $\varepsilon = 0.54 \pm 0.03$ $K_f = 0.33 \pm 0.03$	$\alpha = 1.8 \pm 0.14$
CM-PANI-Fe 50 wt% Nafion $\varepsilon = 0.49 \pm 0.06$ $K_f = 0.21 \pm 0.06$	$\alpha = 2.2 \pm 0.07$	**CM-PANI-Fe 50 wt% Nafion** $\varepsilon = 0.52 \pm 0.06$ $K_f = 0.28 \pm 0.09$	$\alpha = 1.9 \pm 0.18$
CM-PANI-Fe 60 wt% Nafion $\varepsilon = 0.46 \pm 0.04$ $K_f = 0.17 \pm 0.05$	$\alpha = 2.3 \pm 0.16$	**CM-PANI-Fe 60 wt% Nafion** $\varepsilon = 0.54 \pm 0.04$ $K_f = 0.32 \pm 0.06$	$\alpha = 1.8 \pm 0.19$



grey - C
(phase contrast)

blue - Fe
(absorption contrast)

CM-PANI-Fe-C
60 wt% Nafion®

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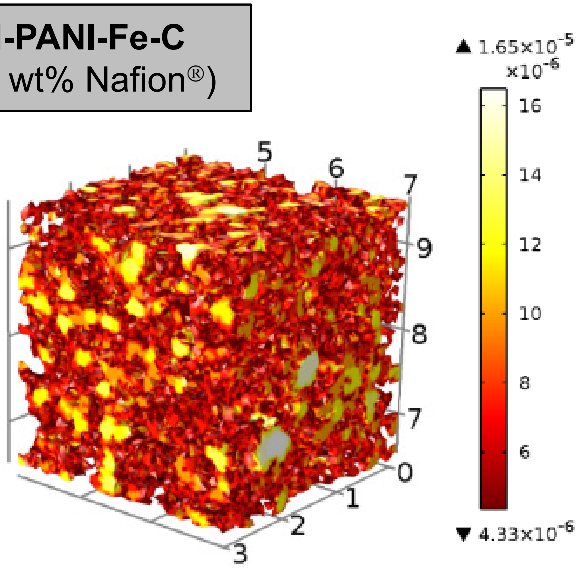
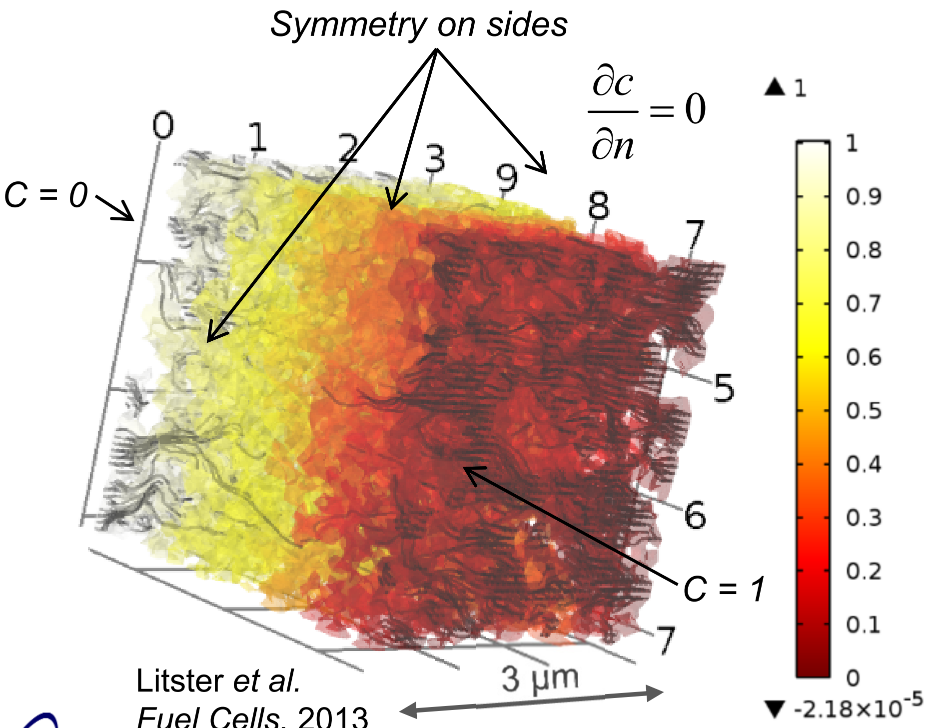
Carnegie Mellon University

Electrode Studies: Transport Property Computation (CM-PANI-Fe-C)

CM-PANI-Fe-C
(35 wt% Nafion®)





Litster *et al.*
Fuel Cells, 2013

Bosanquet formulation for diffusivity in pore:

$$\frac{1}{D_{DG}(d_{pore})} = \frac{1}{D_{Kn}(d_{pore})} + \frac{1}{D_m}$$

Knudsen diffusivity:

$$D_{Kn}(d_{pore}) = \frac{d_{pore}}{3}\sqrt{\frac{8RT}{\pi M}}$$

Pore-size dependent local diffusivity (*D*):

$$-\nabla\cdot\left(D_{DG}\nabla c\right) = 0$$ – *does not assume uniform D*

- Morphology parameters of porous electrode obtained from nano-XRT images
- Effective transport properties extracted from model
- **Highlight:** Computational simulation of transport process in nano-XRT imaged electrode completed

December 2013 electrode imaging milestone achieved

Collaborative Electrode Performance Evaluation and Characterization

Los Alamos
NATIONAL LABORATORY

→

OAK RIDGE
National Laboratory

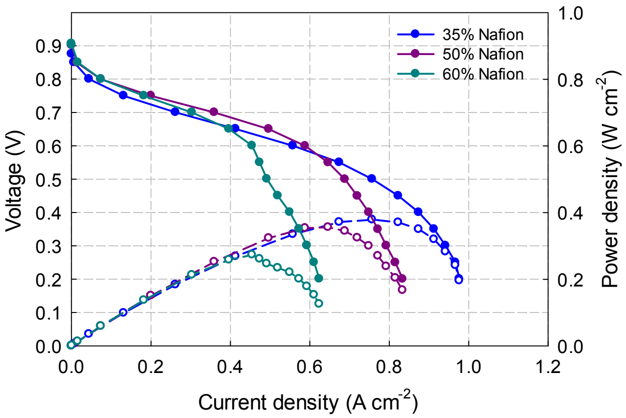
→

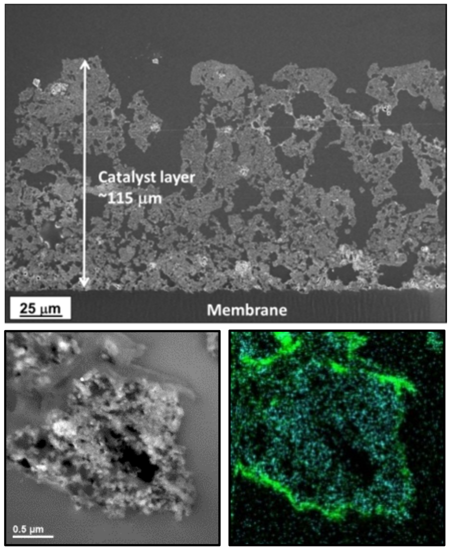
Carnegie Mellon University

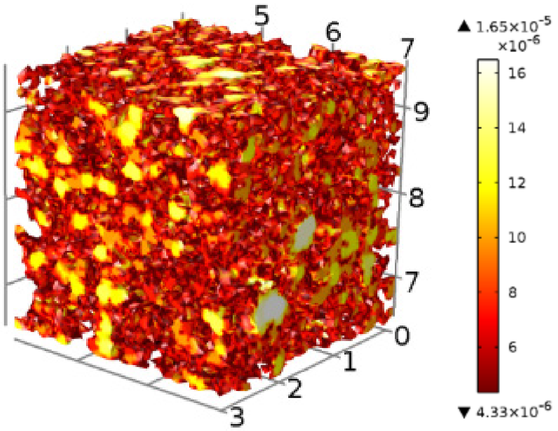
Electrode fabrication and performance evaluation

Microstructure and ionomer distribution imaging

Nano-XRT imaging and transport property modelling





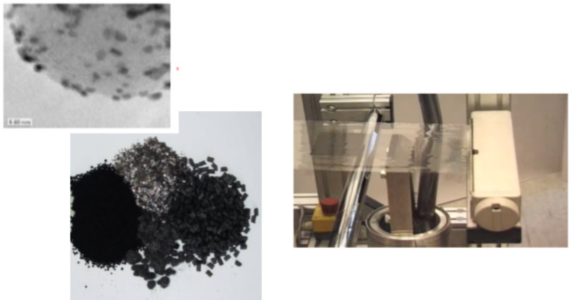


Synergism between partners ensured by sequential execution of project tasks

MEA Fabrication: CM-PANI-Fe-C Catalyst

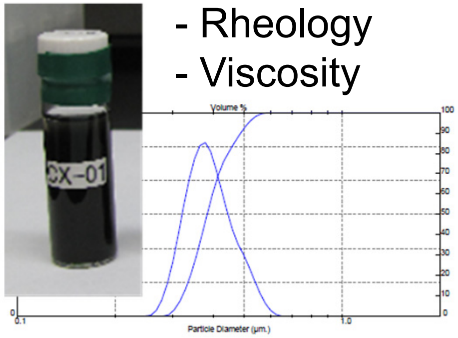
MEA Fabrication Process

Raw Materials



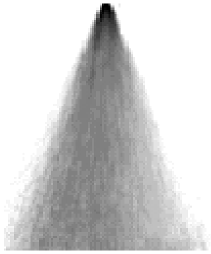
- Catalyst
- Membrane
- GDL

Ink



- Stability
- Rheology
- Viscosity

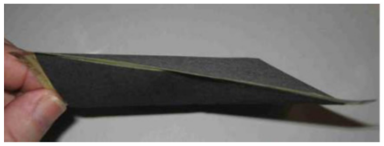
Coating



Substrate

- Electrode deposition

Final MEA

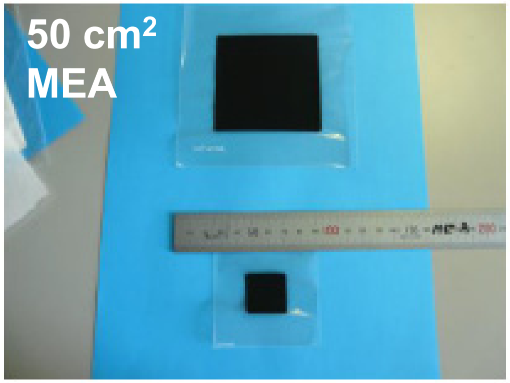


- CCM's
- 5 & 7-layer MEAs

Anode: 0.2 $mg_{Pt}\ cm^{-2}$ Pt/C
Cathode: 0.5 $mg_{catalyst}\ cm^{-2}$
Membrane: 25 µm PFSA

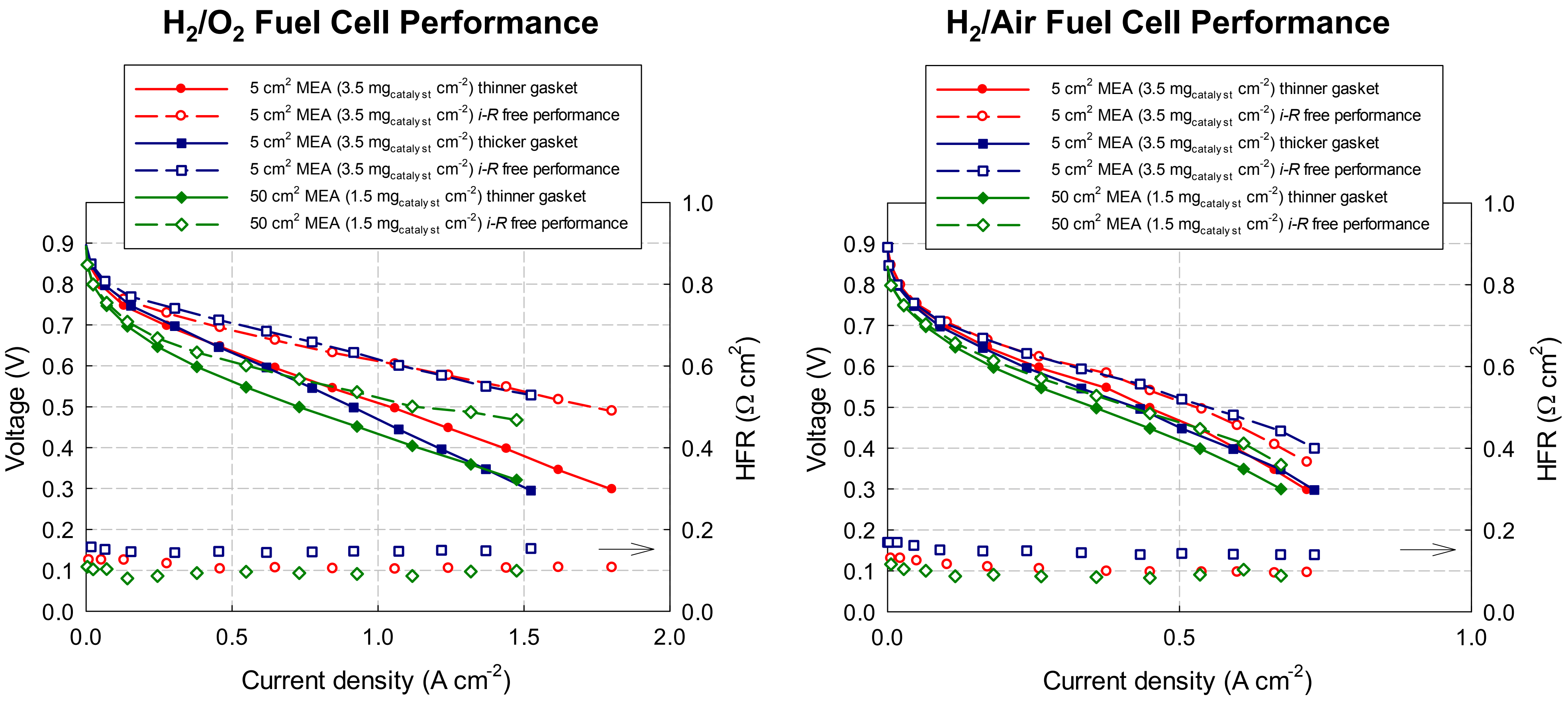
Anode: 0.2 $mg_{Pt}\ cm^{-2}$ Pt/C
Cathode: 3.5 $mg_{catalyst}\ cm^{-2}$
Membrane: 25 µm PFSA

Anode: 0.2 $mg_{Pt}\ cm^{-2}$ Pt/C
Cathode: 1.5 $mg_{catalyst}\ cm^{-2}$
Membrane: 25 µm PFSA



Fuel Cell Performance with CM-PANI-Fe-C Catalyst

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C, H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** 3.5/1.5 mg cm^{-2} O_2/air, 200 sccm, 1.0 bar O_2/air partial pressure; **Membrane:** 25 µm PFSA; **Cell:** 80°C



- Two 5 cm^2 and one 50 cm^2 non-PGM MEAs prepared and tested at IRD
- **Highlight:** First-generation spray-coated MEAs with CM-PANI-Fe-C catalyst demonstrated and tested in H_2/O_2 and H_2/air fuel cells

Collaborations

- **Seven organizations with highly complementary skills and capabilities in catalyst development, electrode structure design, materials characterization, MEA fabrication, fuel cell system development and commercialization:**
  - ✓ Los Alamos National Laboratory – *direct DOE-EERE contract*
  - ✓ Oak Ridge National Laboratory – *direct DOE-EERE contract*
  - ✓ Carnegie Mellon University – *subcontract to Los Alamos National Laboratory*
  - ✓ University of Rochester – *subcontract to Los Alamos National Laboratory*
  - ✓ University of Waterloo – *subcontract to Los Alamos National Laboratory*
  - ✓ IRD Fuel Cells – *subcontract to Los Alamos National Laboratory*
  - ✓ General Motors – *collaborative research and development agreement (CRADA) with Los Alamos National Laboratory (nearing completion)*
- **Collaborations outside Fuel Cell Technologies Office:**
  - ✓ Ballard Power Systems, Burnaby, British Columbia, Canada
  - ✓ Automotive Fuel Cell Corporation, Burnaby, British Columbia, Canada
  - ✓ CellEra, Caesarea, Israel
  - ✓ Pajarito Powder, Albuquerque, New Mexico
  - ✓ Chevron Energy Technology Company, Richmond, California

Remaining Challenges and Barriers

- Oxygen reduction reaction activity of non-PGM catalysts
- Long-term stability and performance durability of non-PGM catalysts
- Identification of the active-site and reaction mechanism
- Electrode integration: (i) sufficient ionic and electronic conductivity in thick catalytic layer and (ii) efficient mass transport to/from the active reaction sites
- Scale-up of non-PGM catalyst synthesis
- MEA design, optimization, fabrication and scale-up
- Integration with existing automotive fuel cell stack and system technology

Proposed Future Work: Remainder of FY14 and FY15

Non-PGM Catalyst Development:

- Achieve remaining activity/durability FY14 catalyst performance targets
- Go/no-go decision for metal-free catalysts – complete research needed; make decision
- Identify and follow two-three most promising catalyst synthesis paths in FY15 (*e.g.*, two-nitrogen precursor path); focus on both activity and durability

Catalyst Structure and ORR Mechanism Studies:

- Validate suitability of additional techniques in structural and mechanistic studies by surface-probe and other approaches (*e.g.,* MCD, EPR, low-voltage aberration-corrected STEM, high-resolution SEM/STEM, various X-ray absorption techniques, *etc.*)
- Propose preliminary ORR mechanism for one PANI-based catalyst

Electrode Design and Modeling:

- Initiate predictive model for non-PGM catalyst layers (ORR activity, conductivity, and O_2 transport); perform preliminary model validation; refine original GM model in conjunction with CMU's MES studies; adopt CMU's agglomerate model to non-PGM cathodes
- Complete implementation of the pore-scale model
- Integrate alternative catalyst formulations into electrode studies

MEA Fabrication and Optimization:

- Optimize first-generation spray-coated MEAs; initiate complete electrode optimization work

Summary

- Fuel cell specific activities of **190 mA cm^{-2}** and **160 mA cm^{-2}** at 0.80 V, much in excess of the project milestone (150 mA cm^{-2}), were achieved independently with two new catalysts:
  (a) high surface-area PANI-Fe-C
  (b) dual nitrogen-precursor CM-PANI-Fe-C
- Volumetric activity of **84 A cm^{-3}** at 0.8 V was demonstrated with the PANI-Fe-C catalyst; the activity represents **40%** enhancement over the DOE baseline (60 A cm^{-3})
- Record on-air performance for a non-PGM catalyst was accomplished with CM-PANI-Fe-C:
  (a) current density of **74 mA cm^{-2}** at 0.80 V (90 mA cm^{-2}, *iR*-corrected)
  (b) power density of **0.35 W cm^{-2}** at 0.60 V
- A promising $E_{½}$ of **0.32 V *vs.* RHE** was achieved in RDE testing of a metal-free catalyst prepared by pyrolysis of a polymer/pore-forming agent
- Validity of the **surface probe** ($NO_{(g)}$) approach to active-site characterization was confirmed for PANI-Fe-C catalyst using Mössbauer spectroscopy and NRVS
- Considerable progress was achieved in non-PGM electrode-structure studies using nano-XRT, TEM, and STEM equipped with EDX mapping; **electrode morphology parameters** were obtained from nano-XRT and computational simulation of transport processes
- State-of-the-art ink and electrode preparation techniques were applied to non-PGM catalysts; well-performing **5 cm^2** and **50 cm^2** MEAs were demonstrated using these techniques
- **All project milestones** have either been met (some exceeded) or remain on schedule

Co-Authors

Los Alamos
NATIONAL LABORATORY

- **Catalyst research and characterization; project management**

  Piotr Zelenay (Project Lead), Hoon Chung, Ulises Martinez, Gerie Purdy, Gang Wu

OAK RIDGE
National Laboratory

- **Catalyst and electrode characterization**

  Karren More (PI), David Cullen

Carnegie Mellon University

- **Electrode characterization, modeling and design**

  Shawn Litster (PI), Siddharth Komini Babu

1850 MELIORA
UNIVERSITY of ROCHESTER

- **Catalyst characterization**

  Michael Neidig (PI), Jeff Kehl, Jared Kneebone

University of Waterloo

- **Catalyst development and characterization**

  Zhongwei Chen (PI), Drew Higgins, Gaopeng Jiang, Min-Ho Seo

IRD
POWERING PEOPLE ANYWHERE

- **MEA design, integration, testing and scale-up**

  Madeleine Odgaard (PI), Debbie Schlueter

GM

- **Electrode and MEA research; MEA validation**

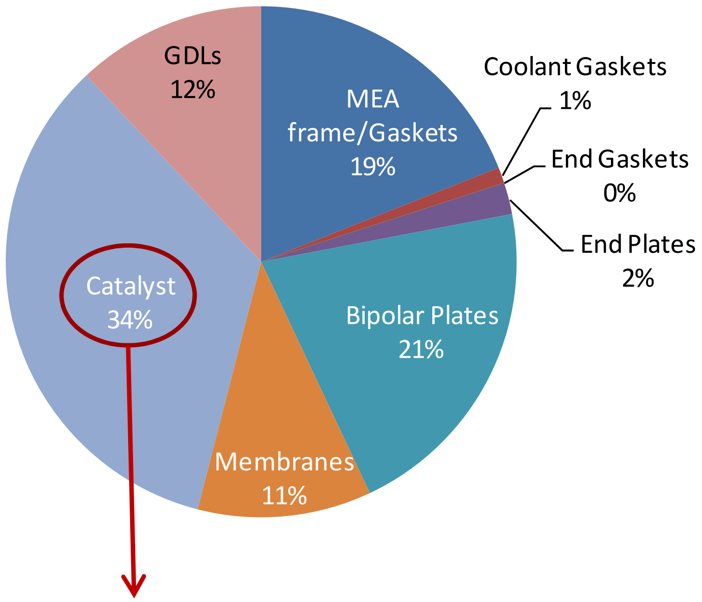
  Joseph Ziegelbauer (PI)

Back-Up Slides

Relevance: Motivation

Fuel Cell Cost Breakdown

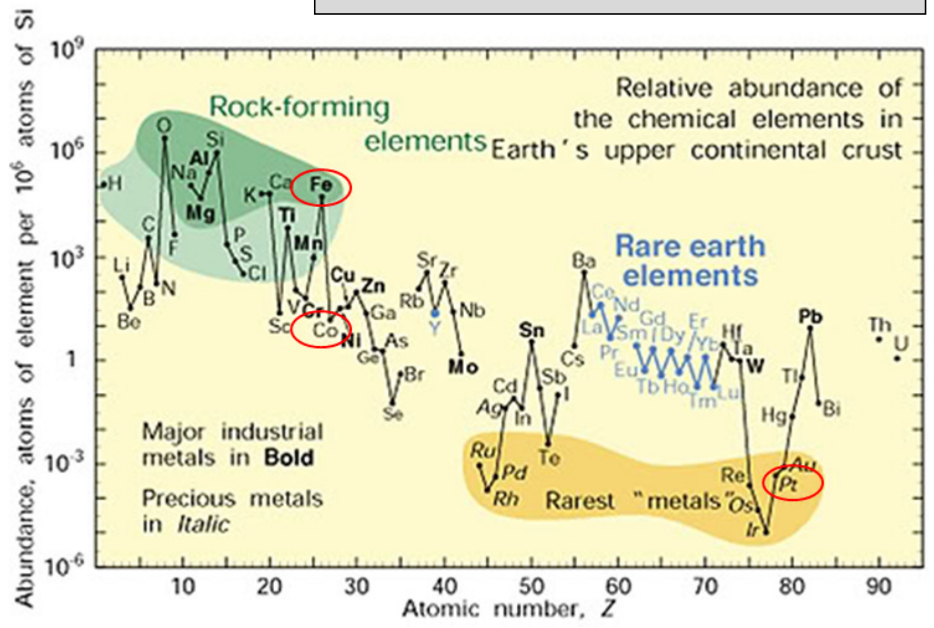
(at Pt price of $1,100/oz)



ca. **44%** at ~$1,435/oz today

James *et al.,* DTI, Inc., 2010 DOE Hydrogen Program Review, Washington, DC, June 9, 2010

Frédéric Jaouen, LANL Presentation, April 2012

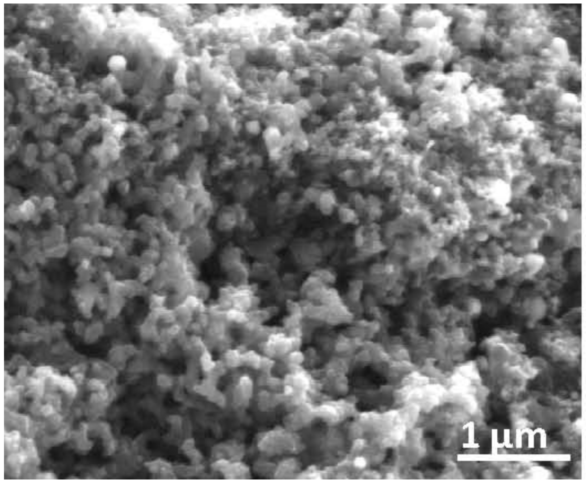


May 9, 2014: **$1435/oz Pt**

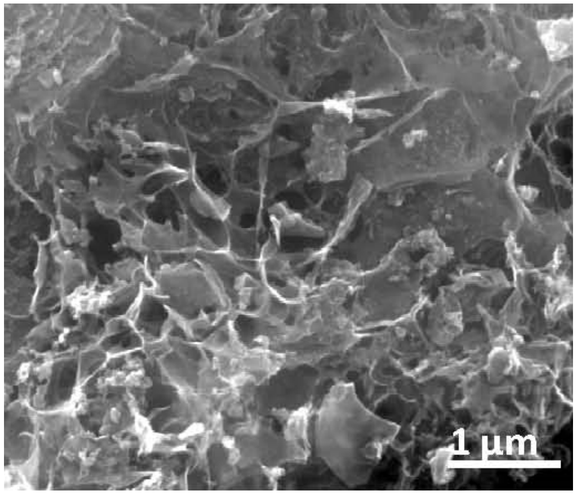
http://www.platinum.matthey.com/prices/price-charts

New Catalysts: High Surface Area PANI-Fe-C

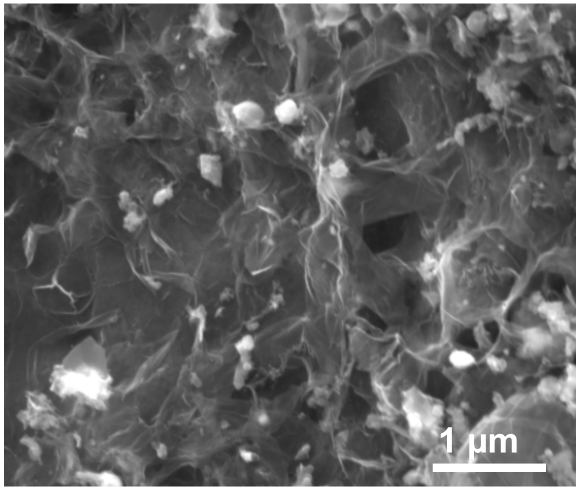
“Standard” PANI-Fe-C, 10wt% Fe
Two-step heat treatment

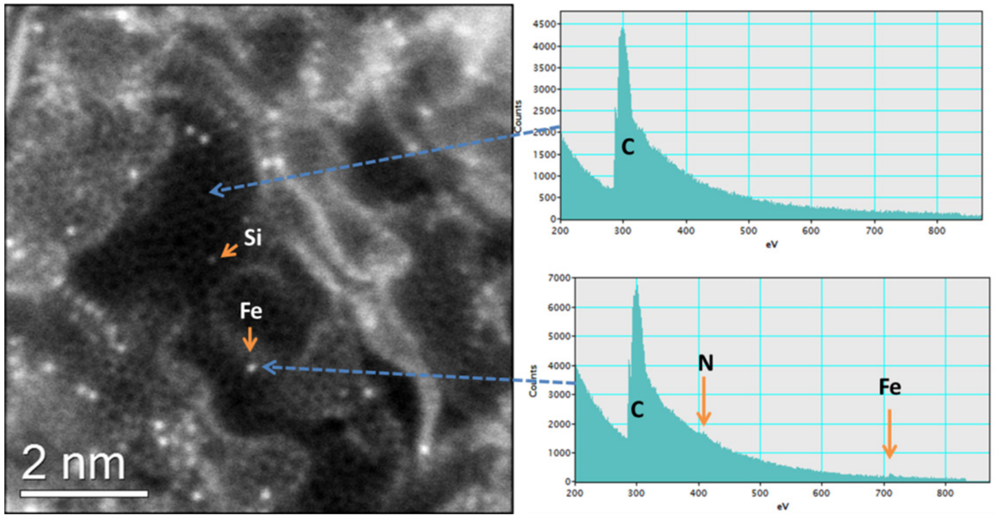


PANI-Fe-C, 30 wt % Fe
Two-step heat treatment



PANI-Fe-C, 30 wt % Fe
Three-step heat treatment





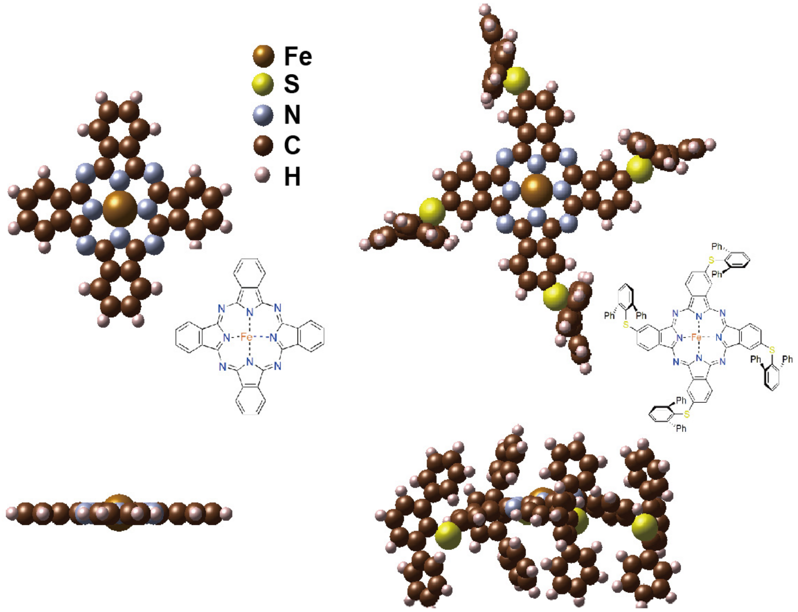
- Overall catalyst morphology depends on synthesis conditions (Fe content, heat-treatment regime)
- Electron energy loss spectroscopy of single atoms on graphene sheet surface
- Fe ions highly mobile under electron beam, indicating that Fe is not incorporated within carbon lattice
- Nitrogen found in thicker areas of layered graphene

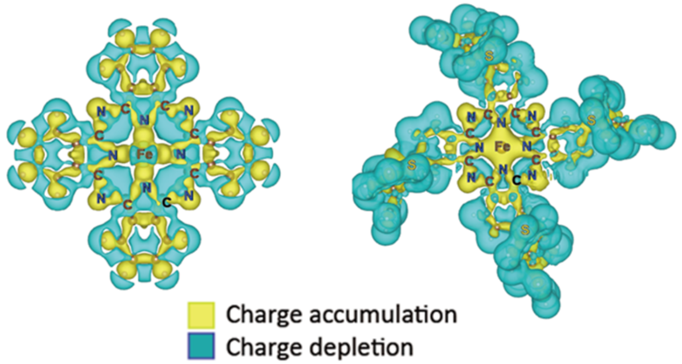
New Catalysts: Low Temperature Fe-Pc & Fe-SPc (DFT and Experimental)

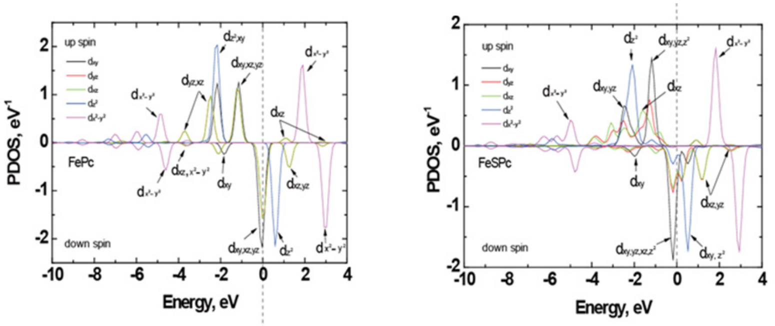
Fe-Pc **Fe-SPc**

Top view

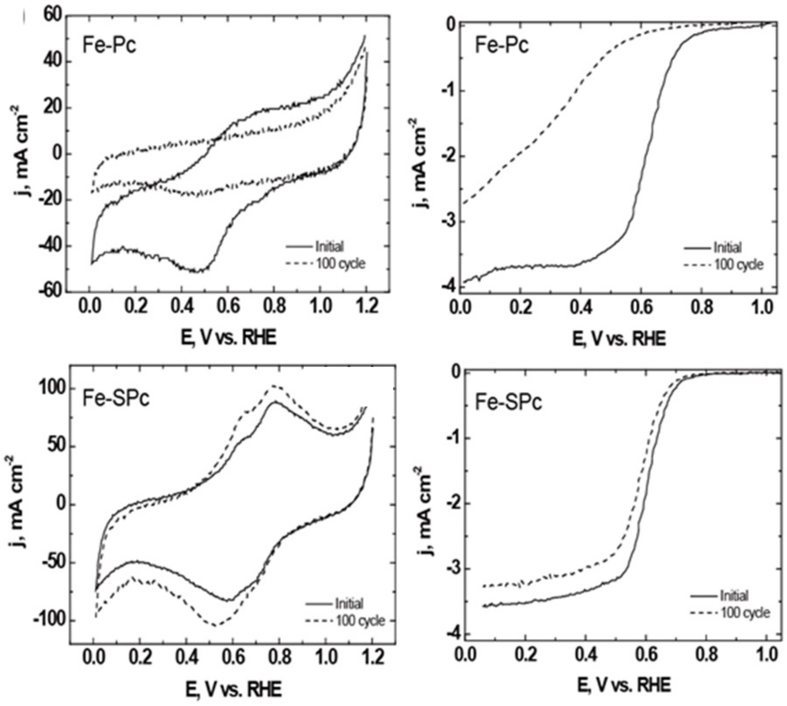
Side view







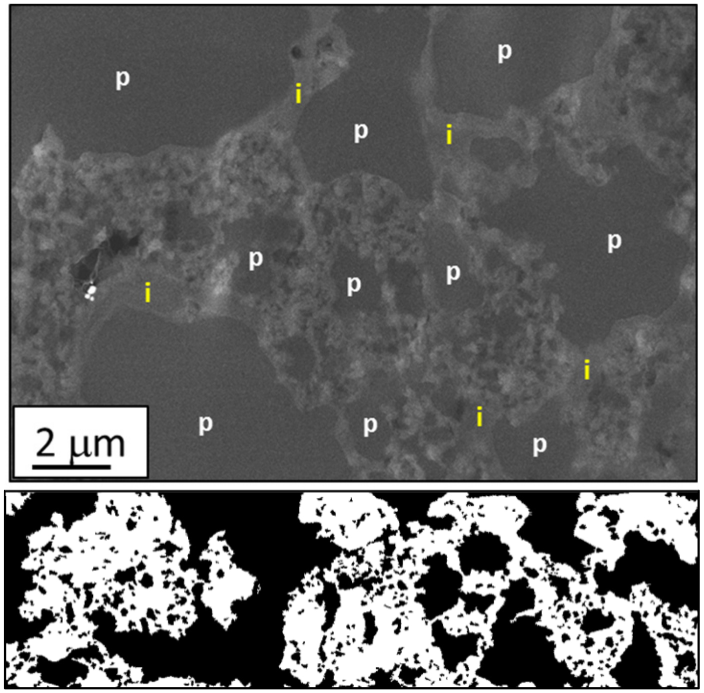
RDE: 0.6 mg cm^{-2}; 0.1 M $HClO_4$; 400 rpm; 25ºC; Ag/AgCl reference electrode; graphite counter electrode; 10 mV/s; Non-resistance corrected.
Cycling: 50 mV/s; O_2 saturation



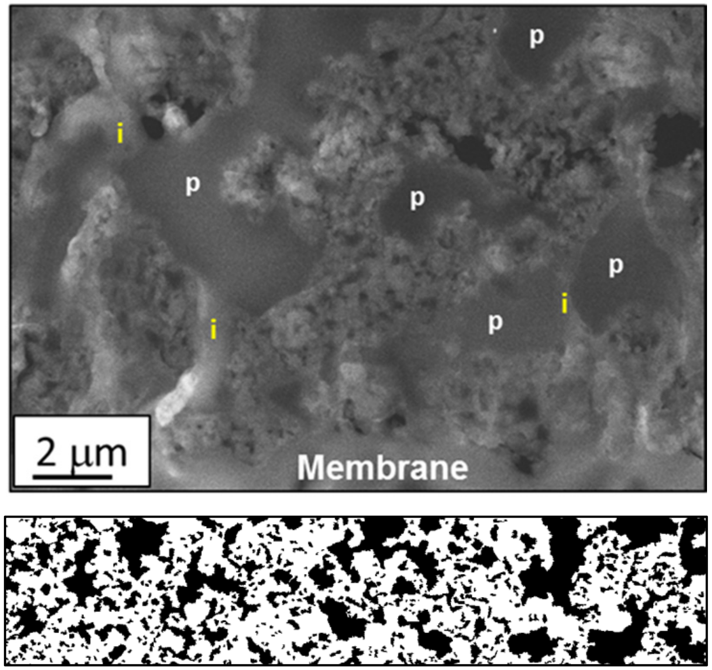
- Addition of diphenylphenthioether substituent group to Fe-Pc (Fe-SPc) modulates electronic properties
- Negative Fe-center charge accumulation in Fe-SPc increases Fe-O cohesive energy, enhancing stability
- Unoccupied O 2p orbital shift in Fe-SPc hinders initial electron transfer to oxygen, reducing ORR activity

Electrode Studies: CM-PANI-CM-Fe 35% Nafion® Electrode Microstructure

Upper "half" of electrode



Lower "half" of electrode



Binary imaging:

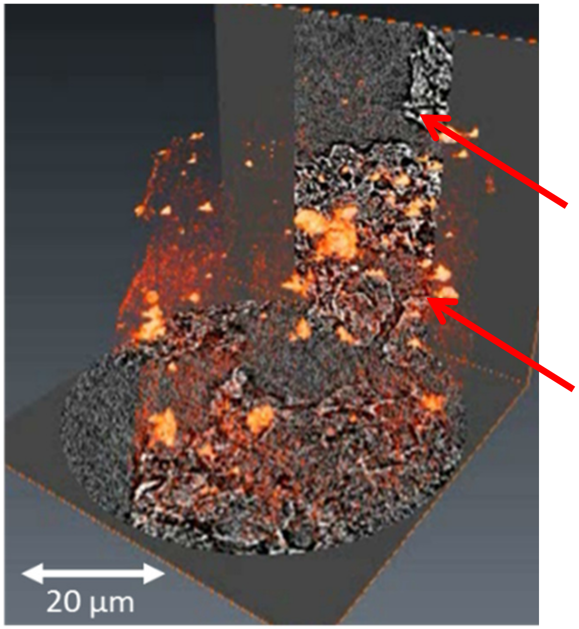
Black = pore

White = solid

- Upper "half" of electrode has *ca.* 52% porosity (p) open to surface
- Particle agglomerates are held together by ionomer strings/films (i), which also surround agglomerates
- Lower "half" of electrode (adjacent to membrane) denser due to particle packing/settling denser with fewer pores
- Lower "half" porosity of *ca.* 41%; not clear whether pores are closed or percolating

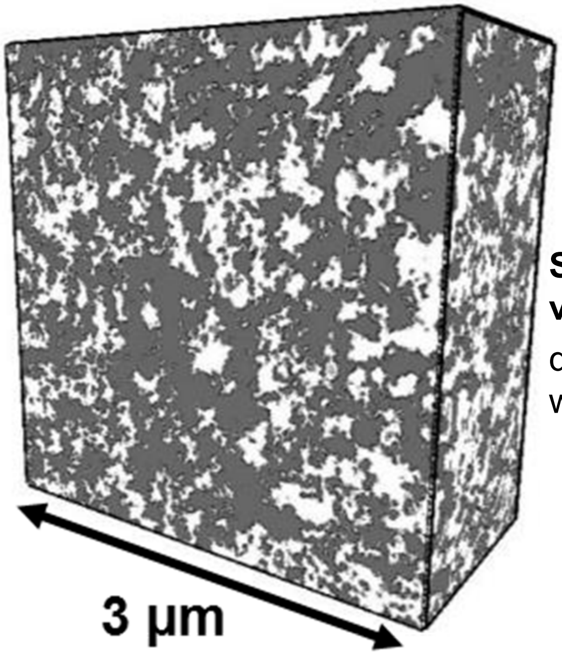
Electrode Studies: Nano-XRT

Large Field of View: Phase and Absorption Contrast



white/black = carbon/pore from phase contrast

orange = iron concentration from absorption contrast scan

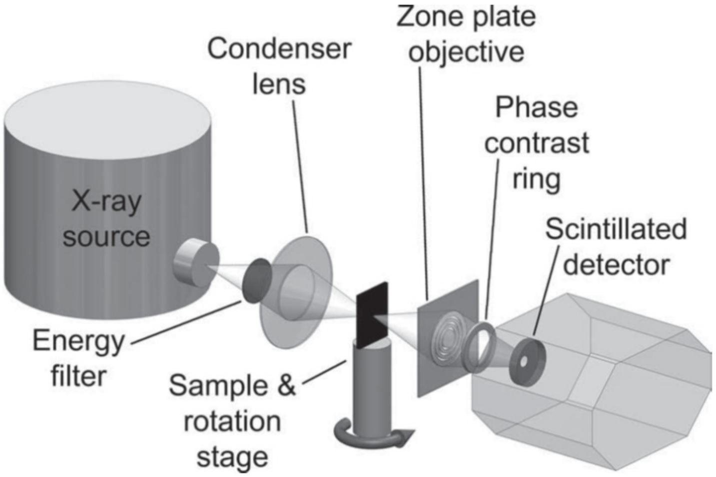


Segmented volumes:

dark = solid

white = pore

3D imaging of Electrodes with 50-nm Resolution for Material Morphology and Transport Properties



- Highest level resolution outside of a synchotron using proprietary optics
- Laboratory 8 keV Cu rotating anode x-ray source
- Phase contrast for low Z materials
- Non-destructive imaging under ambient and controlled environments