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Advanced Cathode Catalysts

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Project ID: FC005

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Overview

Timeline

- **Start date:** March 2007
- **End date:** Four-year duration

Budget

- **Total funding estimate:**
  - DOE share: $10,000K
  - Contractor share: $445K
- **FY09 funding received:** $2,565K
- **FY10 funding estimate:** $2,545K

Barriers

- **A. Durability** (catalyst; electrode)
- **B. Cost** (catalyst; MEA)
- **C. Electrode Performance** (ORR kinetics; O_2 mass transport)

Partners – Principal Investigators

Brookhaven National Laboratory

– Radoslav Adzic

Argonne National Laboratory

– Debbie Myers

University of Illinois, Urbana

– Andrzej Wieckowski

University of New Mexico

– Plamen Atanassov

University of California, Riverside

– Yushan Yan

Cabot Fuel Cells

– Paolina Atanassova

Oak Ridge National Laboratory

– Karren More

Relevance: Objective & Targets

Objective: Develop oxygen reduction reaction (ORR) catalysts alternative to pure Pt and electrode structures suitable for new catalysts that are together capable of fulfilling cost, performance, and durability requirements established by DOE for the polymer electrolyte fuel cell cathode; assure path to large-scale fabrication of successful compositions

Technical targets:

- **Platinum group metal loading:** 0.3 mg_{PGM}/cm^2 (both electrodes)
- **Activity** (PGM catalysts)**:** 0.44 A/mg_{PGM} at 0.90 $V_{iR\text{-}free}$ 720 $\mu A/cm^2$ at 0.90 $V_{iR\text{-}free}$
- **Activity** (non-PGM catalysts)**:** > 130 A/cm^3 at 0.80 $V_{iR\text{-}free}$
- **Durability with cycling:** 5,000 hours at T ≤ 80ºC, 2,000 hours at T > 80ºC

Project impact in past year:

- **Significantly advanced the knowledge of factors affecting ORR activity of the Pt monolayer (facet, shape, particle size); achieved specific activity and mass activity targets for catalysts with ultra-low Pt content**
- **Developed non-PGM catalyst with combined activity and durability better than shown in any prior reports; met DOE 2010 activity target (after mass-transport correction)**
- **Demonstrated active non-PGM catalyst with high durability to voltage cycling (DOE protocol, 30,000 cycles, 0.60-1.0 V)**
- **Scaled-up the synthesis of selected core-shell catalyst to 20 g per batch**

Approach: Focus Areas

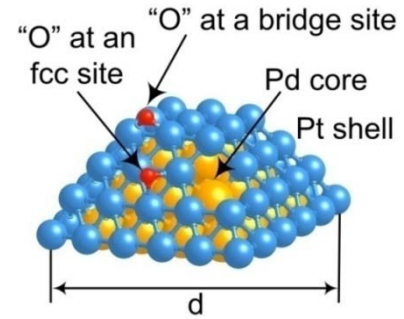
- **Two classes of ORR catalysts:**
  - catalysts with ultra-low platinum content (stable metals or alloys as cores; non-precious-metal core catalysts; mixed-metal shells for higher ORR activity)
  - non-precious metal catalysts obtained by high-temperature treatment of various precursors of carbon, nitrogen, and transition metals
- **Understanding of the key factors impacting activity and performance durability of ORR catalysts**
- **Electrode-structure development:**
  - synthetic-carbon electrodes with hierarchical structure by emulsion/reverse-emulsion method
  - carbon- and non-carbon-based nanostructures for efficient mass transport, improved durability, and maximum catalyst utilization
- **Comprehensive catalyst characterization using electrochemical and non-electrochemical techniques; non-PGM catalyst active-site and ORR mechanism determination**
- **Development of industrial scale-up methods for viable catalysts**

Approach: Milestones

DATE	MILESTONE	STATUS	COMMENTS
Jan 10	Synthesize and test Co/Ni and Co and/or Ni ORR catalysts in porphyrin and dendrimer matrices	**Re-scoped**	Dendrimer catalyst synthesized; no activity detected; effort re-scoped to anthraquinones – ORR activity found
Apr 10	Develop methodology for increasing the number of high-coordination surface atoms of core-shell nanoparticles to enhance their ORR activity and stability	**Complete**	Particle-size distribution improved and low-coordination atoms removed by Br^--adsorption method; activity of Pd and Pt_{ML}/Pd/C catalysts enhanced
May 10	Demonstrate PANI-derived catalyst that performs well with mass transport resistance in fuel cell operation reduced by 50%	**Pending**	To date, mass transport resistance reduced by ~20% at 0.40 V using graded Nafion® content in electrode
May 10	Complete process/composition optimization of Pt/Pd/C catalyst in the scaled-up process	**Complete**	Successful scale-up achieved; performance validated at LANL
May 10	Demonstrate hierarchically structured non-precious-metal ORR catalyst with $E_{½} \geq 0.77$ V in RDE testing	**Pending**	Synthesis proved more challenging than expected; delay possible
Jun 10	Improve high-voltage activity of non-precious-metal ORR catalysts to OCV > 1.0 V and MEA current density > 15 mA/cm^2	**Complete**	Fe-CM-C catalyst: OCV 1.04 V; current density 25 mA/cm^2 at 0.90 V and 180 mA/cm^2 at 0.80 V (80°C)
Jul 10	Demonstrate high-activity Pt_{ML}/Pd_{alloy}/C electrocatalyst with Pt mass activity of 2.5 A/mg and specific activity of 1.2 mA/cm^2 (both at 0.9 V)	**Complete**	2.4 A/mg$_{Pt}$ and 1.2 mA/cm^2 at 0.9 V achieved by Au-displacement of low-coordination Co-atoms in Pt/Au/Pd_xCo
Sep 10	Complete study of the effect of Fe on the stability of non-precious-metal catalysts; propose and test methods for minimizing possible detrimental role of Fe	**Pending**	After 7,000 cycles in the 0.4-1.0 V range 30% Fe loss observed; no significant ORR performance loss
Sep 10	Determine the oxidation state, chemical composition, and stability of three advanced cathode catalyst classes as a function of potential and time using in situ and ex situ x-ray absorption spectroscopy and electrochemical measurements	**Complete**	Analysis completed for PANI-Fe-KJ, PANI-Fe-KJ (S-free), and PANI-Fe-MWNT; electrochemical stability determined for PANI-Fe-KJ

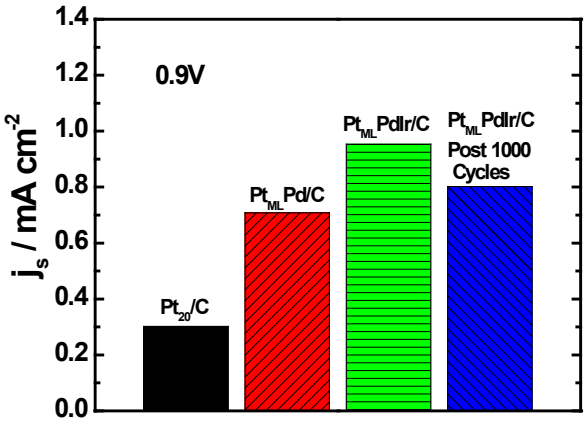
Ultra-Low Pt Content Catalysts: Overview & Sub-Surface Core Modification

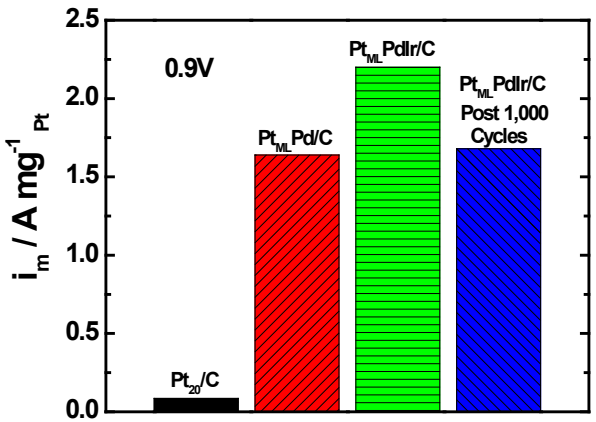
- **Understanding of factors affecting ORR activity of Pt monolayer:**
  (**i**) facet; (**ii**) shape; (**iii**) particle size
- **Enhancement in catalytic activity and stability:**
  (**i**) surface and sub-surface modification of cores to tune interaction with Pt monolayer; (**ii**) reduction in number of low-coordination surface atoms; (**iii**) Pt-Pt bond contraction in hollow particles (moderately compressed (111) facet most conducive to ORR on nanoparticles); (**v**) intermetallic compounds as supports; (**iv**) Prussian-blue analogues for efficient synthesis
- **Scale-up synthesis and MEA testing at LANL** (Pd-core for increased Pt-shell stability and higher Pt oxidation potential; galvanic protection of Pt by Pd)



Coordination-dependent surface atomic contraction (out-of-plane at edges, in-plane at (111) facets)

Sub-Surface Core Modification for Fine-Tuning of Interaction with Pt Monolayer





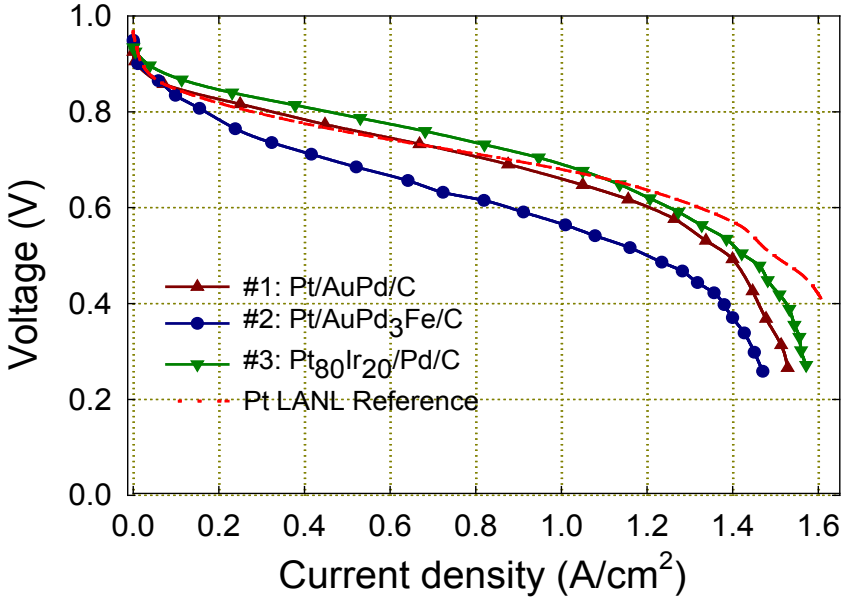
Approach: *Ir layer placed on Pd/C, annealed at 300-400°C to cause segregation of Pd to the surface; subsurface Ir inducing contraction of top Pd layers; Pt_{ML} on PdIr/C compressed more than on Pd/C → weakened Pt-O interaction*

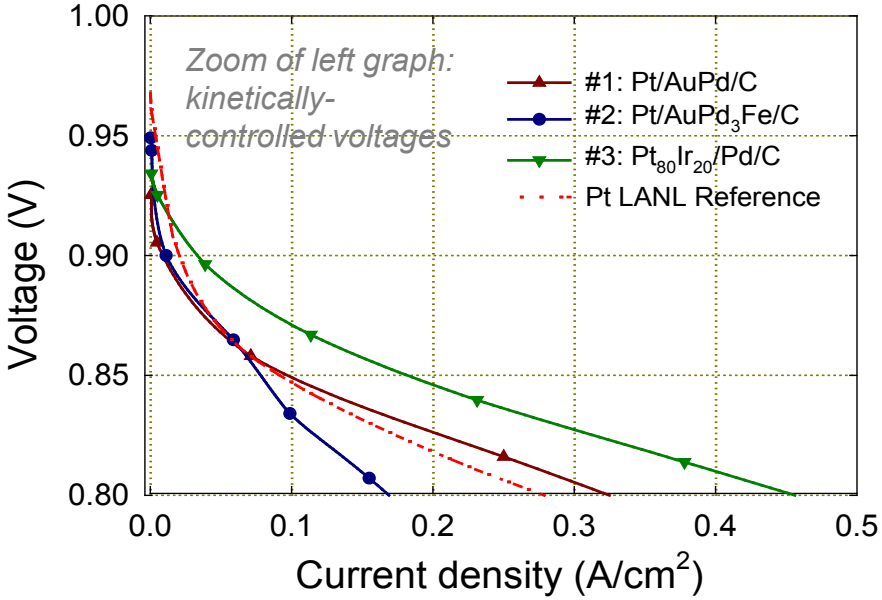
Cycling: *0.75-1.05 V, 30-second pause at potential limits*

- **Specific ORR activity of Pt_{ML}PdIr/C: 940 μA/cm^2 (3× that of Pt/C)**
- **Mass activity of Pt in Pt_{ML}PdIr/C: 2.2 A/mg$_{Pt}$ (more than 20× that of Pt/C)**

Ultra-Low Pt Content Catalysts: Fuel Cell Performance

Anode: *E-TEK Pt-catalyzed cloth GDE, 0.25 mg cm^{-2} Pt; 30 psig H_2;* ***Cathode:*** *BNL catalysts, 0.2 mg$_{PGM}$ cm^{-2}; 30 psig air, carbon cloth ELAT LT 1400W GDL;* ***Membrane:*** *Nafion® 212;* ***Cell:*** *80ºC*

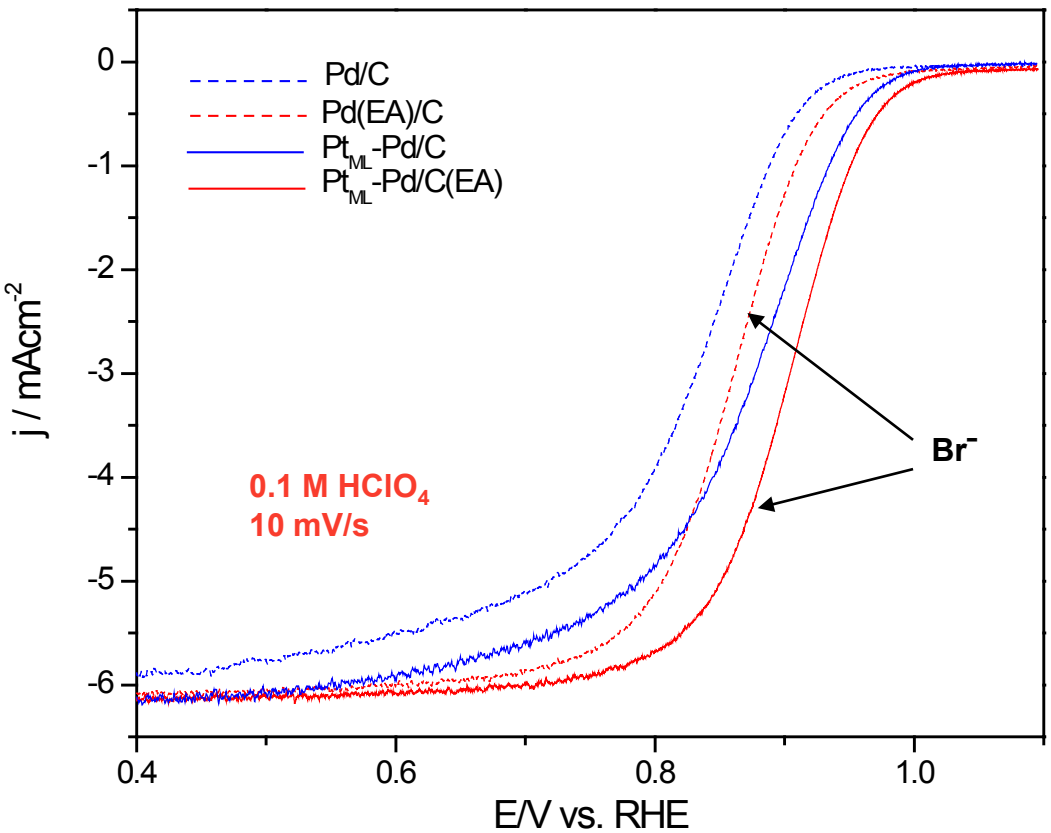




- **$Pt_{80}Ir_{20}$/Pd/C catalyst exhibiting the best ORR performance in MEA fuel cell test**
- **Superior performance at kinetically-controlled voltages demonstrated**
- **Mass activity of $Pt_{80}Ir_{20}$/Pd/C at 0.90 V:** **0.53 A/mg$_{Pt}$**
  0.19 A/mg$_{PGM}$

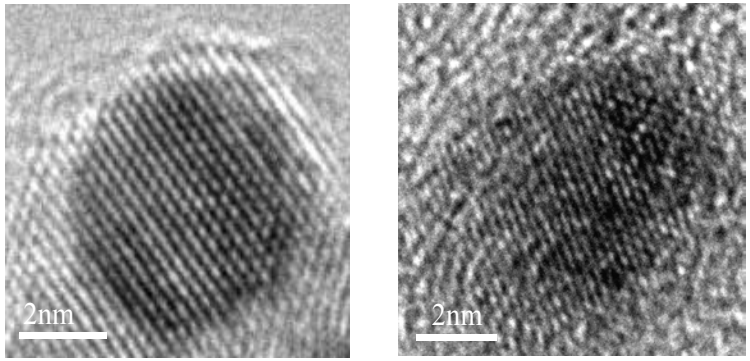
  (RDE data: 0.66 A/mg$_{Pt}$ at 0.90 V)

Ultra-Low Pt Content Catalysts: Br^- Adsorption/Desorption



Pd nanoparticles

before Br^- | after Br^-

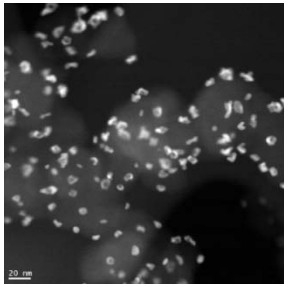


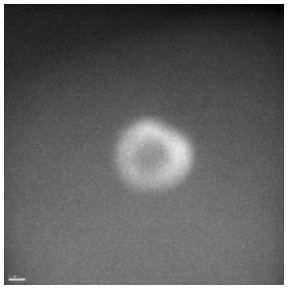
Catalyst	$E_{½}$ (V) *vs.* RHE	
	No treatment	Br^--treated
Pd/C	0.831	0.859
Pt_{ML}/Pd/C	0.876	0.903

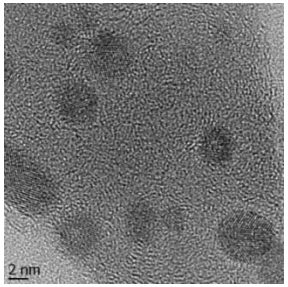
- **Low-coordination Pt (Pd) atoms susceptible to OH formation, ORR inhibition, and ultimately to dissolution**
- **Highlight: Adsorption/desorption of Br^- on Pd nanoparticles resulting in: (i) removal of low-coordination atoms, (ii) formation of nearly mono-dispersed particles, (iii) contraction of Pd lattice (XRD data) and ensuing increase in ORR activity of Pd and Pt_{ML}/Pd/C catalysts**

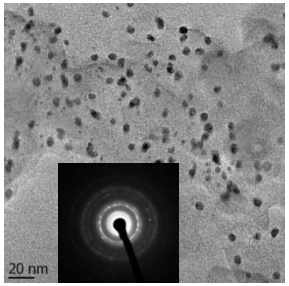
Milestone for increasing site-coordination number achieved!

Ultra-Low Pt Content Catalysts: Pt Contraction in Hollow Nanoparticles

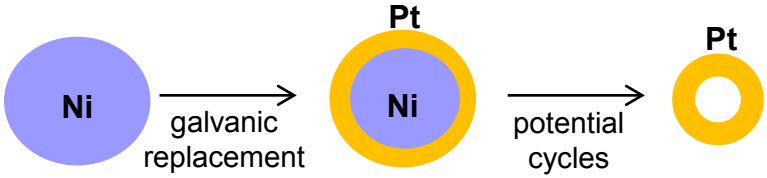








Pt hollow spheres produced by galvanic replacement of electrodeposited Ni nanoparticles on Vulcan XC-72, followed by anodic dissolution of Ni



STEM image of Pt hollow spheres:

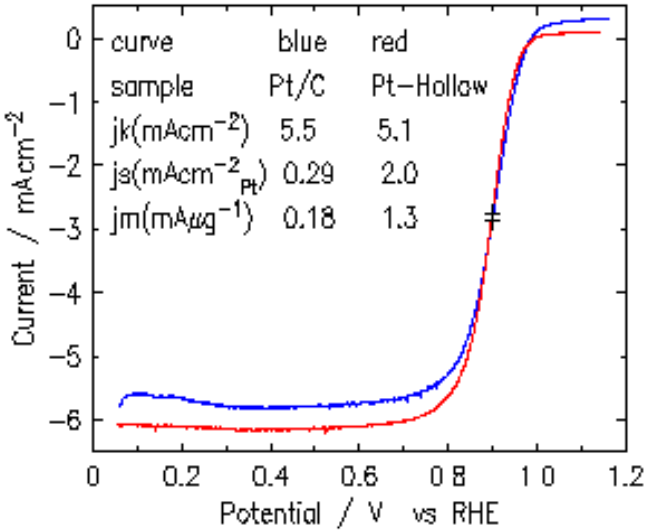
- No Ni detected by EELS, ICP
- 4-nm hollow, 2-to-3-nm thick Pt shell

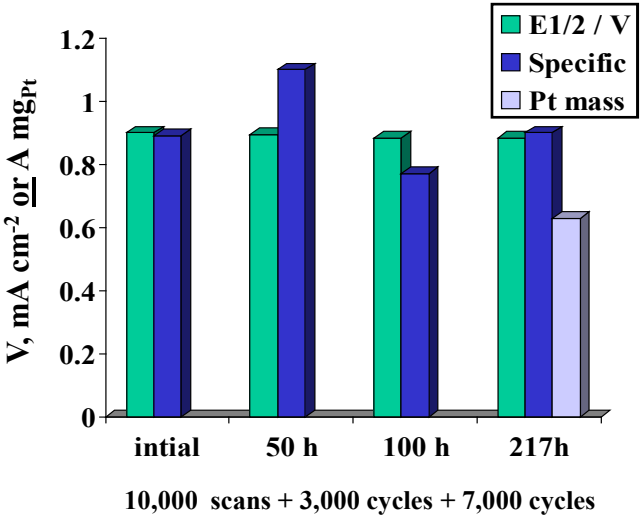
TEM images of Pt hollow sphere after 227-hour stability test:

- 1.2% average lattice contraction (from 3.923 Å to 3.876 Å)

- **0.60-1.05 V scan at 50 mV/s, followed by a 30-second pause at potential limits**
- **17 mV loss in $E_{1/2}$ after 3,000 cycles**
- **Highlight: No further loss in 7,000 cycles**

Hollow Pt Nanoparticles: ORR Activity & Stability



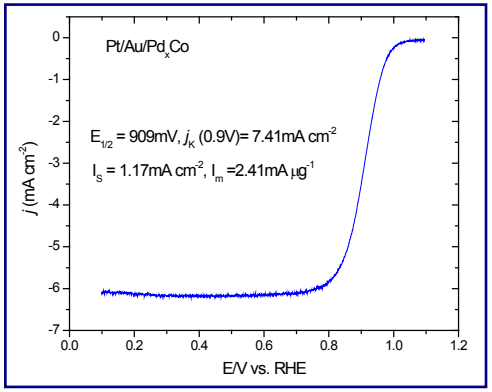


Ultra-Low Pt Content Catalysts: Displacement Method & Prussian-Blue Analogues

Au-Displacement Method: Pt/Au/Pd_xCo Catalyst

- Surface-reactive low-coordination atoms displaced by more noble atoms (more effective approach than "acid wash")
- Pt/Au/Pd_xCo catalyst – Pt_{ML} on Au-submonolayer-modified Pd_xCo catalyst (reactive Co atoms displaced by Au); scale-up to 2 g batch
- Highlight: 1170 μA/cm^2 and 1.10 A/mg_{PGM} (2.41 A/mg_{Pt}) at 0.90 V

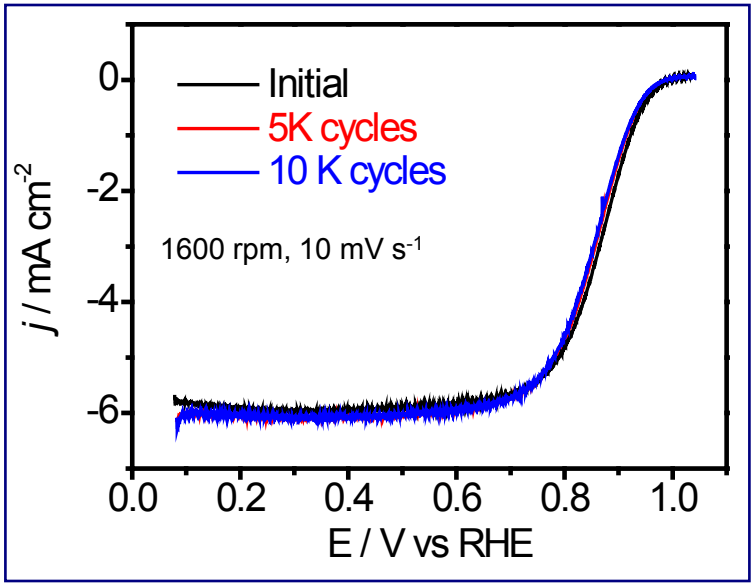
Specific activity and mass activity milestones achieved!



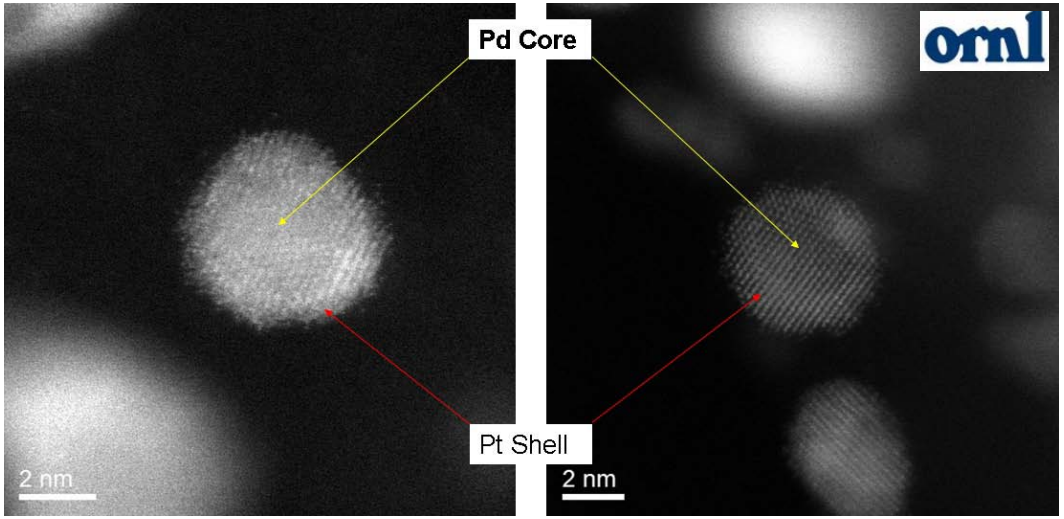
Catalyst Synthesis Using Prussian-Blue Analogues: $Pt_{ML}/Pd_2Au_1Ni_1$ Catalyst

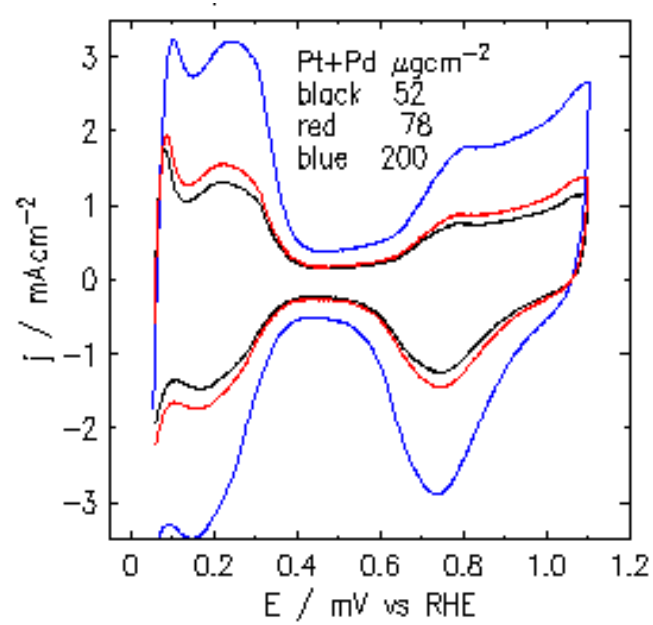
- Prussian blue analogues of the type $Me_x[Me'(CN)_6]_y$ facilitating surfactant-free synthesis of multi-metallic aggregates; convenient for further engineering
- $Pt_{ML}/Pd_2Au_1Ni_1$ catalyst – Pt_{ML} on $Pd_2Au_1Ni_1$ core, obtained by replacement reaction of $PdCl_2$ with Au_1Ni_3 (result of decomposition of $AuNi_{2.5}[Ni(CN)_6]_2$)

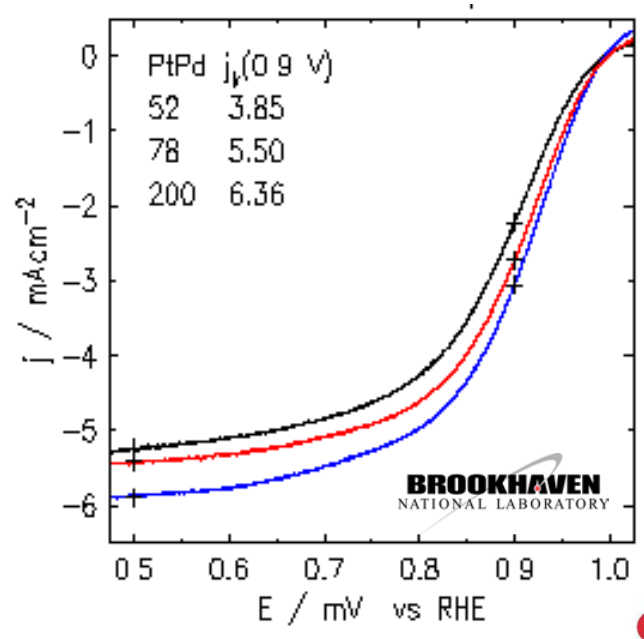
$E_{½}$ (V)	Activity (A/mg_{Pt})	Activity (μA/cm^2)	ESA (cm^2)	$E_{½}$ loss (mV)
0.865	0.728	524	0.718	6



Ultra-Low Pt Content Catalysts: Pt_{ML}/Pd/C Catalyst Scale-Up by Cabot



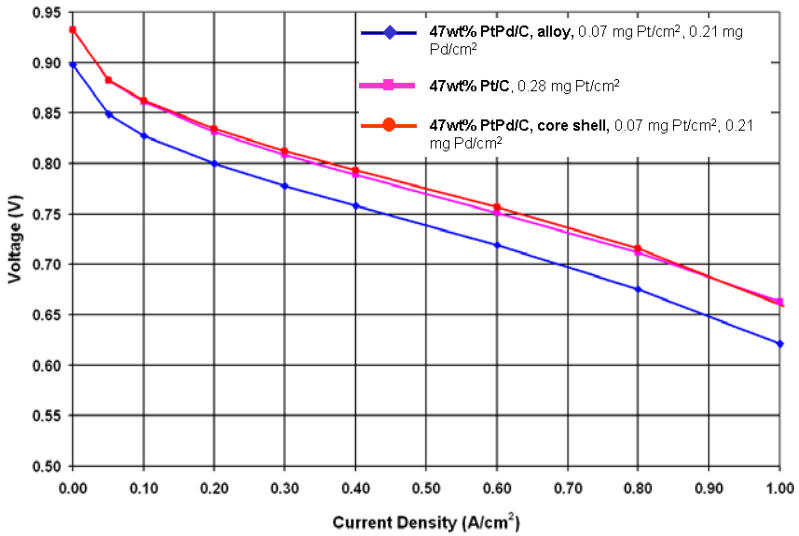




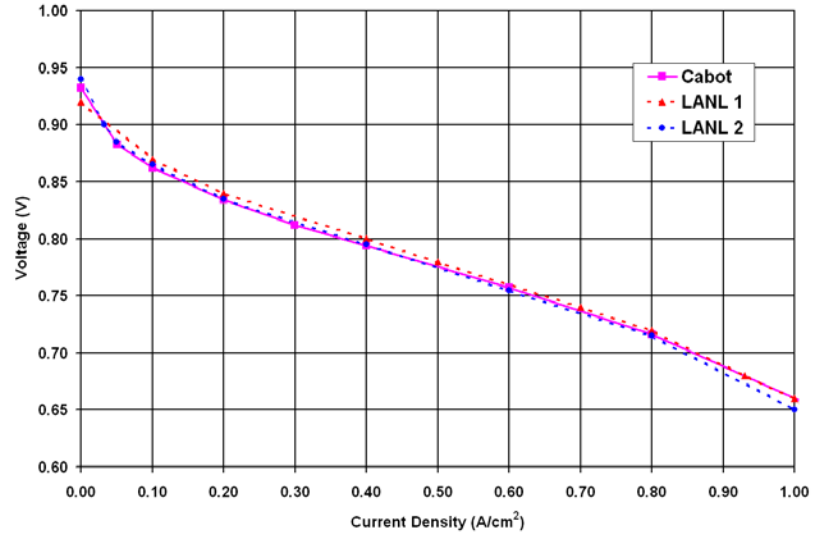
- **Highlight: Successfully developed scalable (1-20 g/batch) synthesis approach for Pt shell on Pd/C, the catalyst developed and demonstrated on a laboratory scale at Brookhaven**
- **Core-shell structure of the Pt_{ML}/Pd/C catalyst confirmed by HAADF-STEM at ORNL; identified areas for improvement (Pt-layer uniformity and coverage)**
- **RDE testing at Brookhaven of an early Pt/Pd/C catalyst yielding 0.35 A/mg_{Pt} at 0.90 V (total metal loading of 52 μg cm^{-2}); higher value expected following optimization of the loading and catalyst distribution on disk**

Ultra-Low Pt Content Catalysts: Pt_{ML}/Pd/C Catalyst Scale-Up by Cabot

Anode: *0.05 mg cm^{-2} Pt, 30 psig H_2 (1.5× at 1.0 A/cm^2), 100% RH;* ***Cathode:*** *30 psig air, (2.5× at 1.0 A/cm^2), RH 100% ;* ***Membrane:*** *NRE-212;* ***Cell:*** *80ºC*



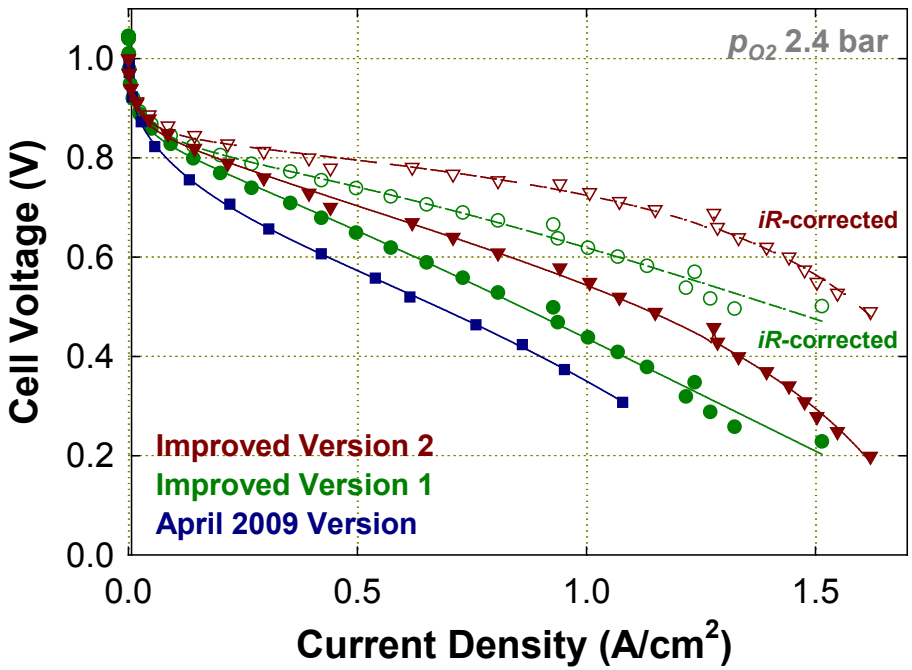
Anode: *0.05 mg cm^{-2} Pt, 30 psig H_2 (1.5× at 1.0 A/cm^2), 100% RH;* ***Cathode:*** *0.07 mg_{Pt} cm^{-2} + 0.21 mg_{Pd} cm^{-2}, 30 psig air (2.5× at 1.0 A/cm^2), 100% RH;* ***Membrane:*** *NRE-212;* ***Cell:*** *80ºC*

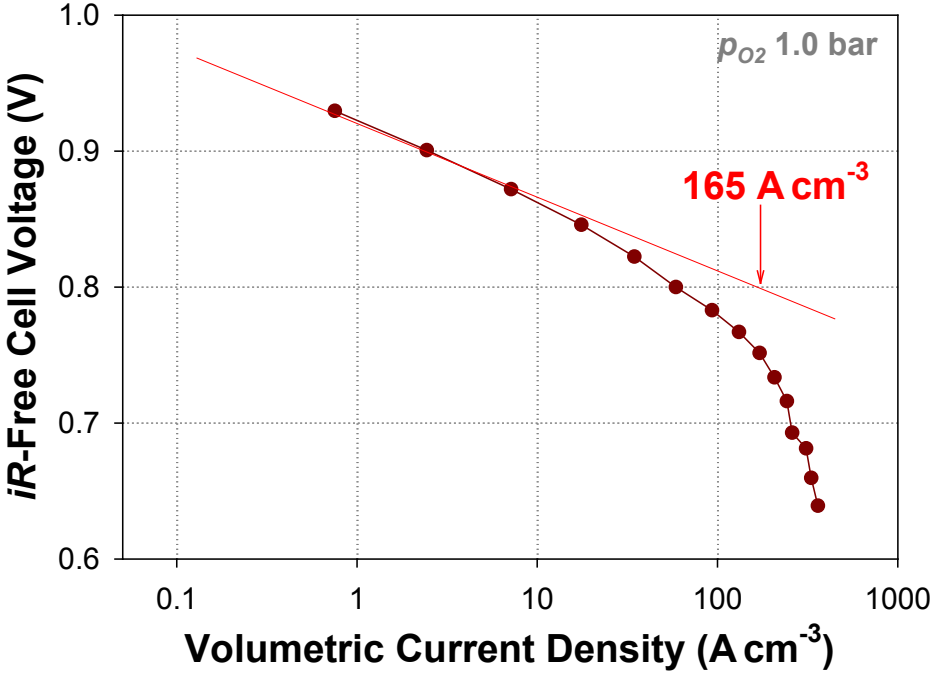


- **Highlight: Pt_{ML}/Pd/C core-shell catalyst delivering significantly better ORR performance than PtPd/C alloy with same composition; identical performance as Pt/C but with four times less Pt**
- **LANL fuel cell test data with catalyst from a 5 g batch agreeing with Cabot's testing within 5 mV throughout the entire polarization plot**
- **Further optimization of catalyst composition ongoing**

Cyanamide-Fe-C Catalyst: Improvement since April 2009

Anode: *0.25 mg cm^{-2} Pt (E-TEK);* ***Cathode:*** *~3.5 mg cm^{-2} CM-Fe-C;* ***Membrane:*** *Nafion® 117* ***Cell:*** *80ºC*

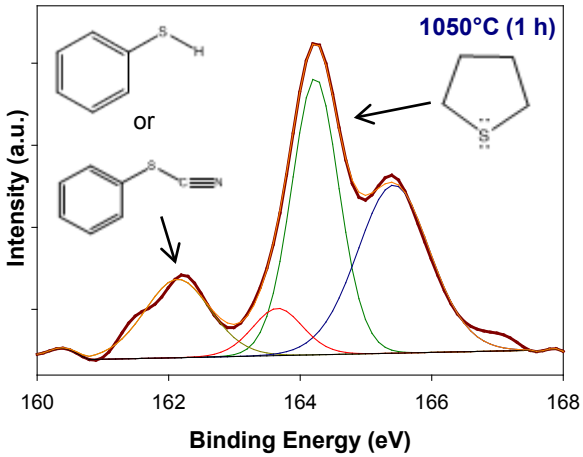


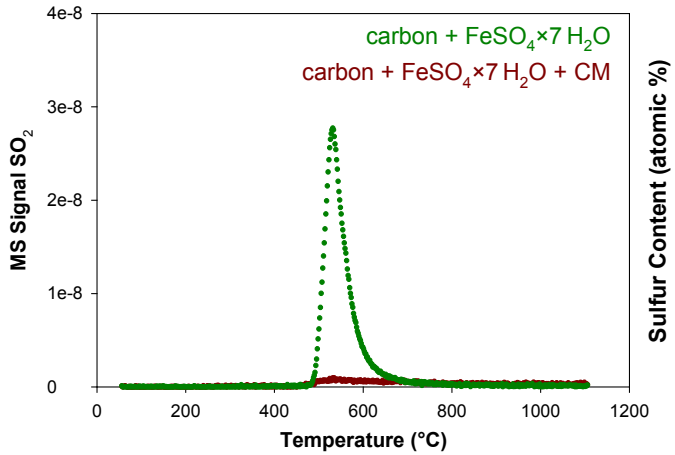


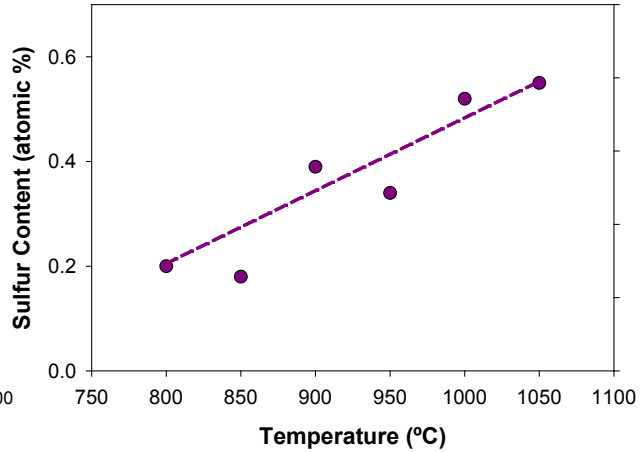
- **Version 1 achieved with change in the carbon support and adjustment of precursor ratios**
- **Version 2 generated by including additional sulfur-containing precursor**

Highlight: **0.39 A cm^{-2} – measured per MEA surface area at 0.80 V (*iR*-corrected)**
60 A cm^{-3} – measured per electrode volume at 0.80 V (*iR*-corrected)
165 A cm^{-3} – extrapolated per electrode volume at 0.80 V (*iR*-corrected)

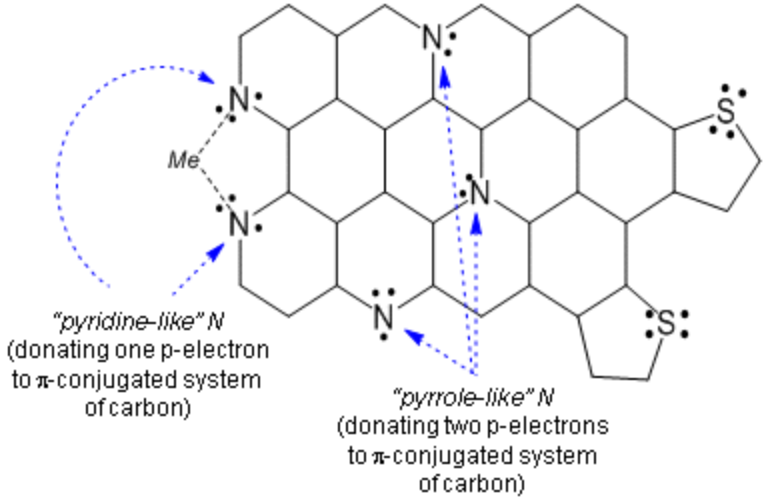
Cyanamide-Fe-C Catalyst: Sulfur Content and Performance







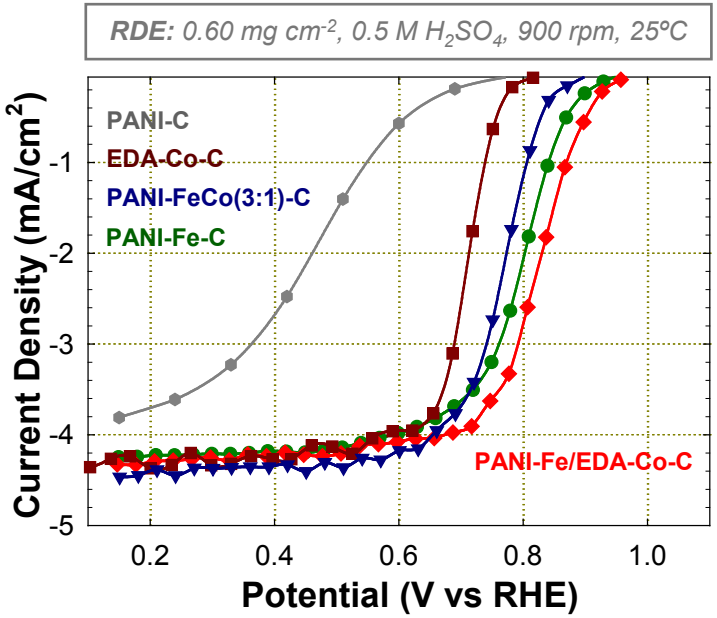
Visualization of Possible Sulfur Sites

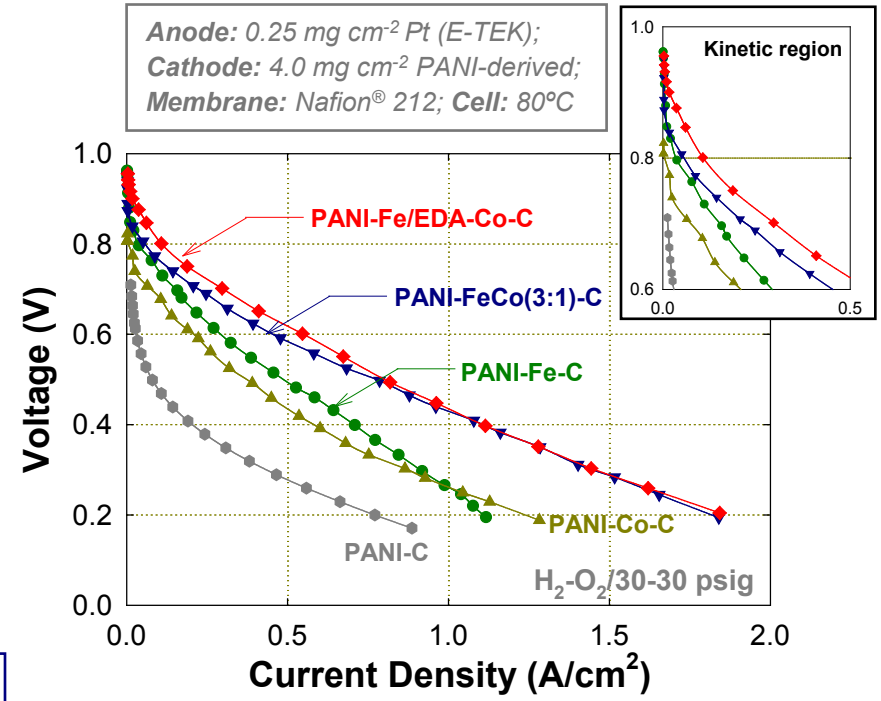


- **Sulfur found mostly in thiophene-like form (XPS); sulfur loss suppressed by cyanamide (SO_2 MS signal)**
- **Sulfur content increased as heat-treatment temperature increased (XPS); overall, tendency for activity increase with temperature**
- **Role of sulfur either electronic via ORR active sites or indirect (aiding Fe removal or modifying carbon structure*)**
- **Additional electrochemical, spectroscopic, and microscopic analysis needed**

* *Herrmann et al., J. Electrochem Soc, **156**, B1283, 2009*

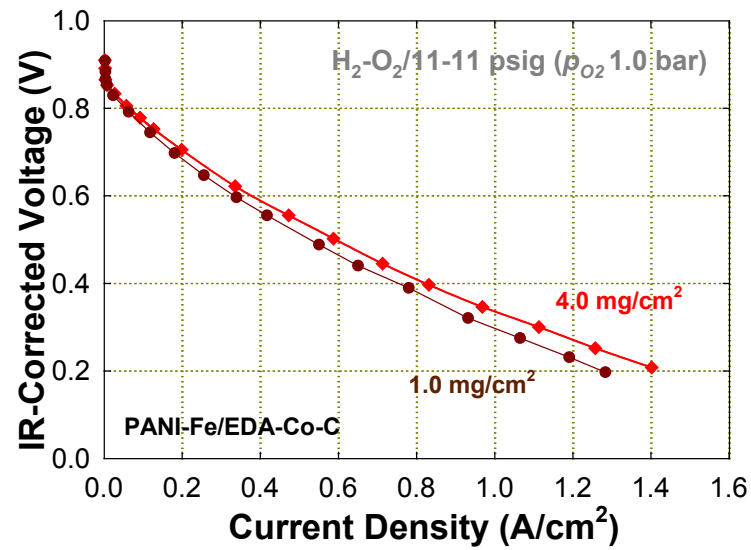
PANI-Fe/EDA-Co-C: RDE Activity and Fuel Cell Performance





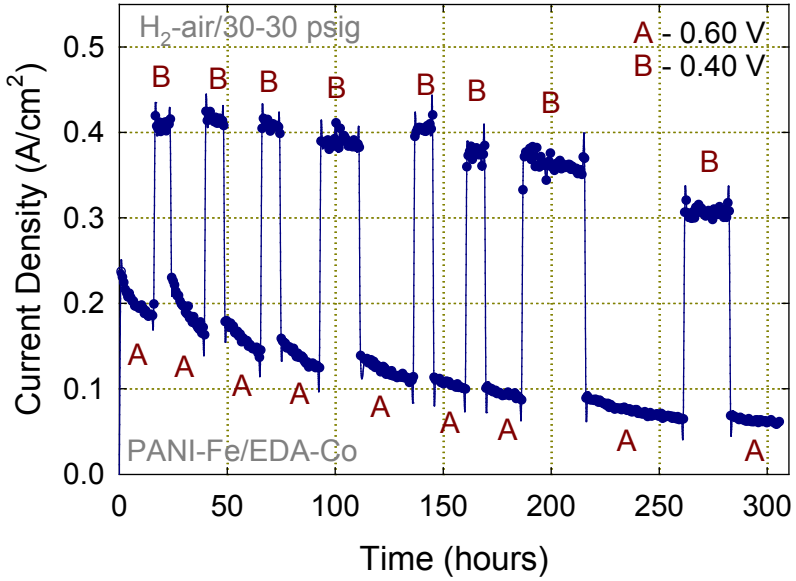
- **Highlight: Two-step process resulting in:**
  - ✓ **20 mV positive shift in $E_{½}$ relative to PANI-Fe-C** (most active PANI catalyst in FY2009)
  - ✓ **40 mV versus PANI-FeCo(3:1)-C** (best overall PANI catalyst in FY2009)
  - ✓ **Better fuel cell performance in kinetic region**
- **Volumetric activity significantly enhanced when using low catalyst loading in MEA:**

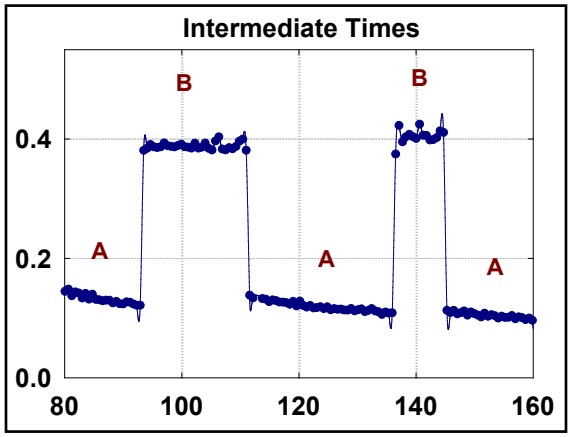
  100 A/cm$^3_{catalyst}$ (31 A/cm$^3_{electrode}$) at 0.80 V



PANI-Fe/EDA-Co-C: Performance Stability at 0.40 V and 0.60 V

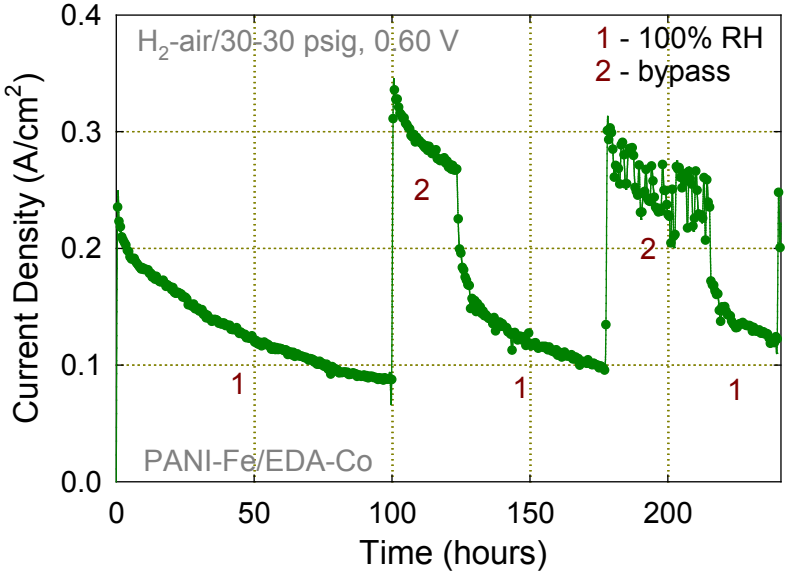
Anode: *0.25 mg cm^{-2} Pt (E-TEK);* ***Cathode:*** *4.0 mg cm^{-2} PANI-derived;* ***Membrane:*** *Nafion® 1135;* ***Cell:*** *80ºC*





- **PANI-Fe/EDA-Co showing high durability at 0.40 V**
- **Performance degradation significantly accelerated at 0.60 V relative to 0.40 V**
- **Most of the activity loss at 0.60 V found to be reversible with lowered humidity; flooding of active sites, rather than active site degradation, likely responsible for much of the loss**
- **Advanced electrode structure design needed**

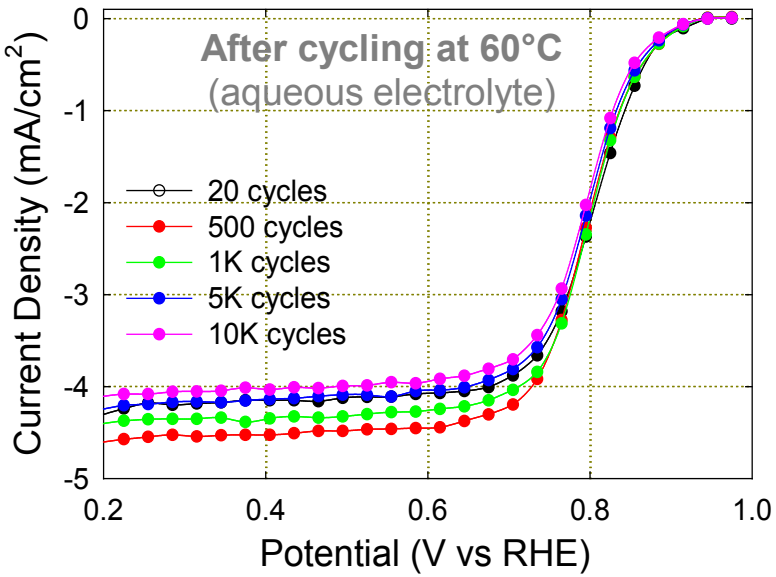
Effect of Humidification

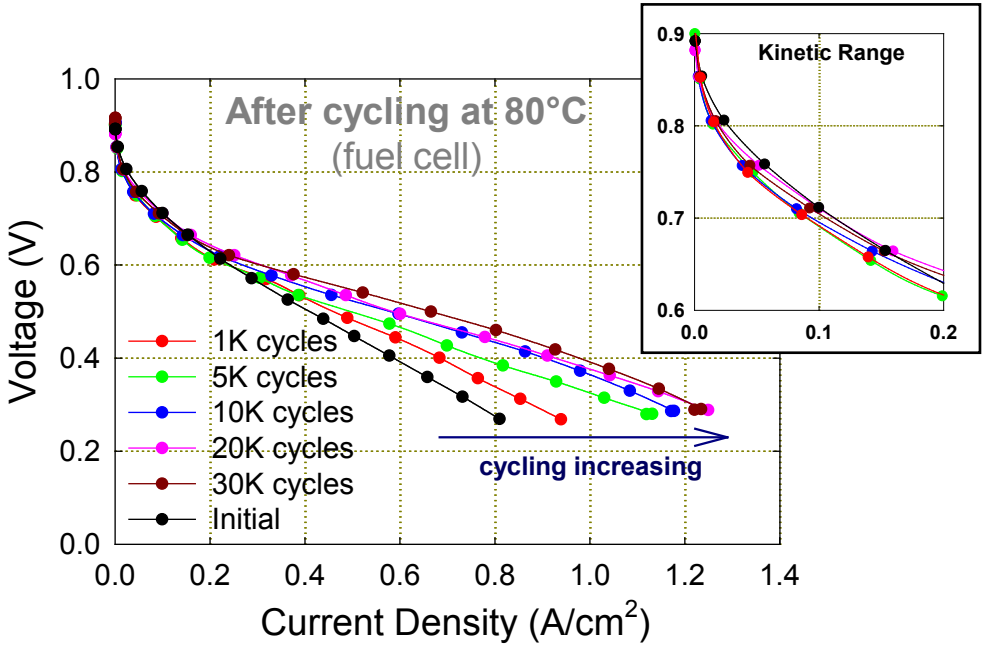


PANI-Fe-C: Effect of Potential Cycling on Activity

RDE: *0.6 mg cm^{-2}; 0.5 M H_2SO_4; 900 rpm;* ***Cycling:*** *50 mV/s, 0.0-1.0 V in 0.5 M N_2-saturated H_2SO_4*

Anode: *0.25 mg cm^{-2} Pt;* ***Cathode:*** *2.0 mg cm^{-2} PANI-Fe-C ;* ***Membrane:*** *NRE-212;* ***Cell:*** *80ºC; H_2-O_2/1.0-1.0 bar;* ***Cycling****: 0.6-1.0 V, 50 mV/s, N_2 at 100% RH*

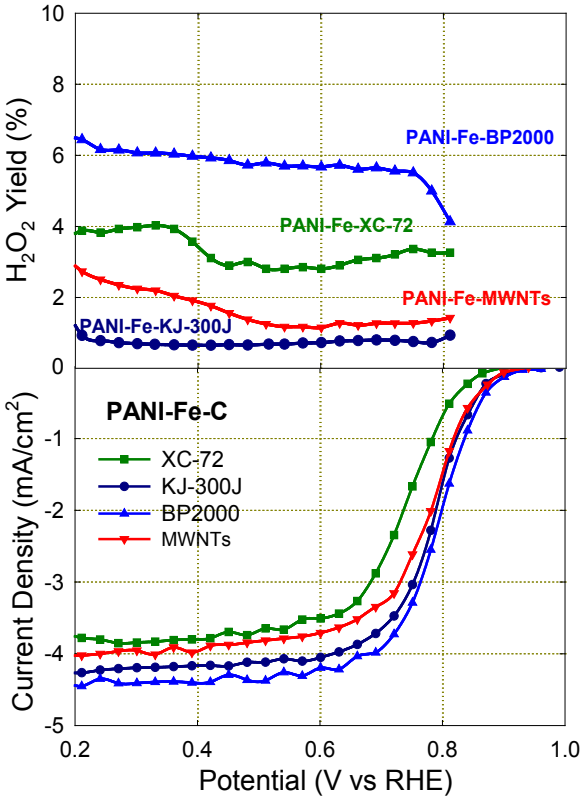


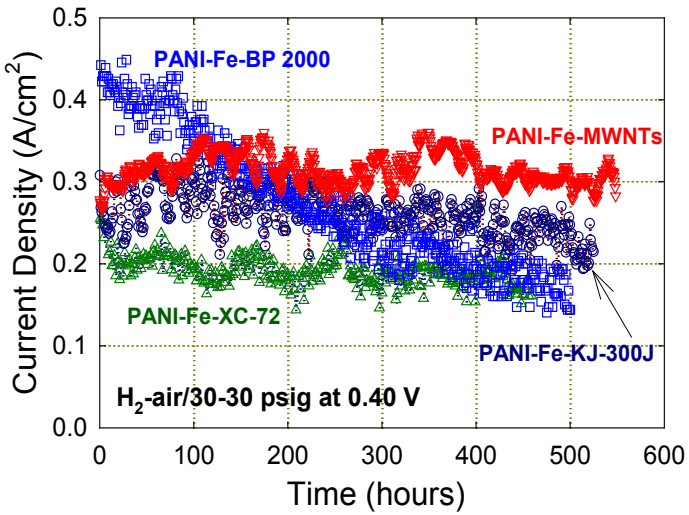


- **Highlight: Only ~10 mV loss in $E_{½}$ at RDE testing after 10,000 potential cycles at 60ºC**
- **Highlight: After 30,000 cycles in the fuel cell, performance increase observed with PANI-Fe-C cathode in a H_2-O_2 cell at lower voltages than 0.65 V; *ca.* 25% loss in current density observed at 0.80 V (kinetic range)**
- **Increase in mass-transport controlled performance in fuel cell experiments highlighting the need to understand changes in catalyst and/or ionomer structure, including porosity**
- **ICP results showing 30-35% Fe lost after 7,000 cycles (0.40-1.0 V); by XAS, mostly FeS removed, whereas most of the Fe in Fe-N_4 coordination retained**

PANI-Fe-C Durability Study: Role of Carbon Support

Anode: *0.25 mg cm^{-2} Pt (E-TEK);* ***Cathode:*** *4.0 mg cm^{-2} PANI-derived;* ***Membrane:*** *Nafion®1135;* ***Cell:*** *80ºC*





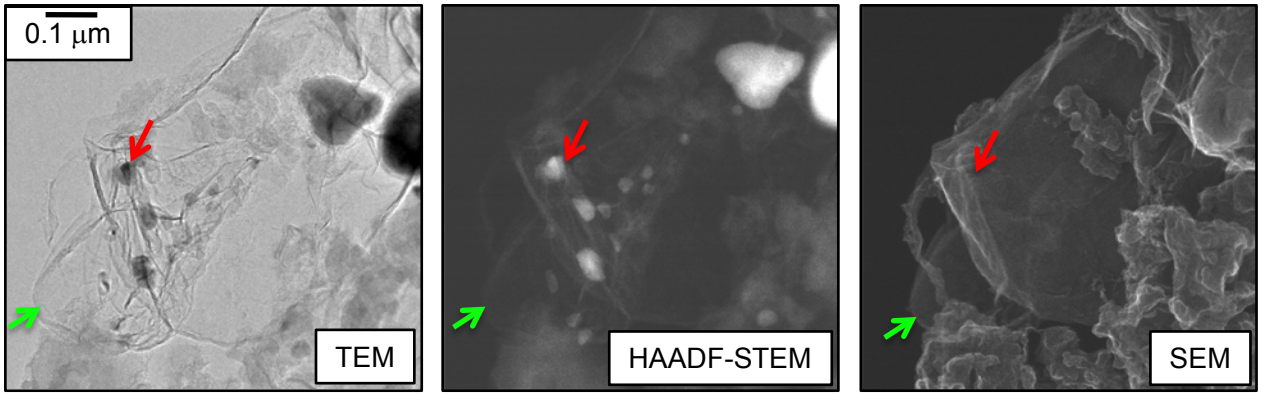
BP 2000 – Black Pearls 2000
KJ-300J – Ketjenblack EC-300J
XC-72 – Vulcan XC-72
MWNTs – multi-walled nanotubes

Catalyst	Corrosion Resistance of Support Carbon	% H_2O_2 Detected 0.40 V *vs.* RHE	% Performance Loss over 500 h
PANI-Fe-BP2000	Poor	5.9	55
PANI-Fe-KJ	Good	0.7	13
PANI-Fe-XC72	Fair	3.1	12
PANI-FeCo(3:1)-KJ	Good	1.4	7.9
PANI-Fe-MWNT	Excellent	1.8	1.3

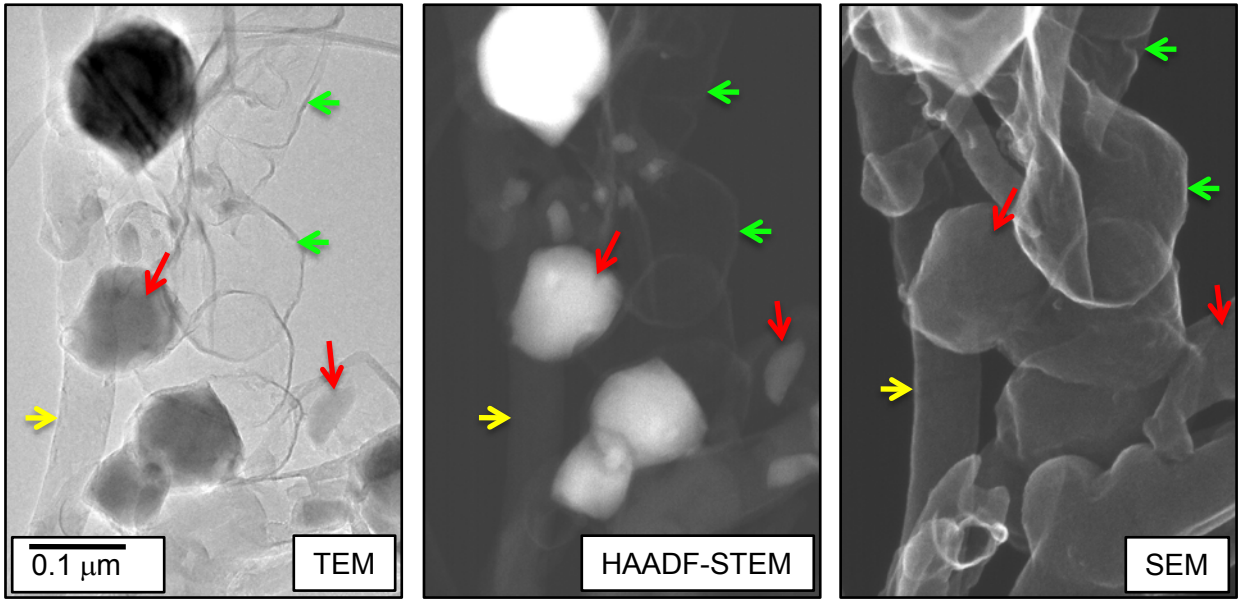
- **Highlight: PANI-Fe-MWNT nearly matching activity of PANI-FeCo(3:1)-C and exceeding its stability**
- **Durability of catalysts not simply a function of support corrosion resistance or H_2O_2 generation (although these two factors still having impact)**
- **Effect of other factors on durability likely; graphene sheet structures formed during synthesis of the two most durable catalysts (TEM)**

PANI-FeCo(3:1)-KJ and PANI-Fe-MWNT: Final Catalysts

PANI-FeCo(3:1)-KJ: Three images, same spot

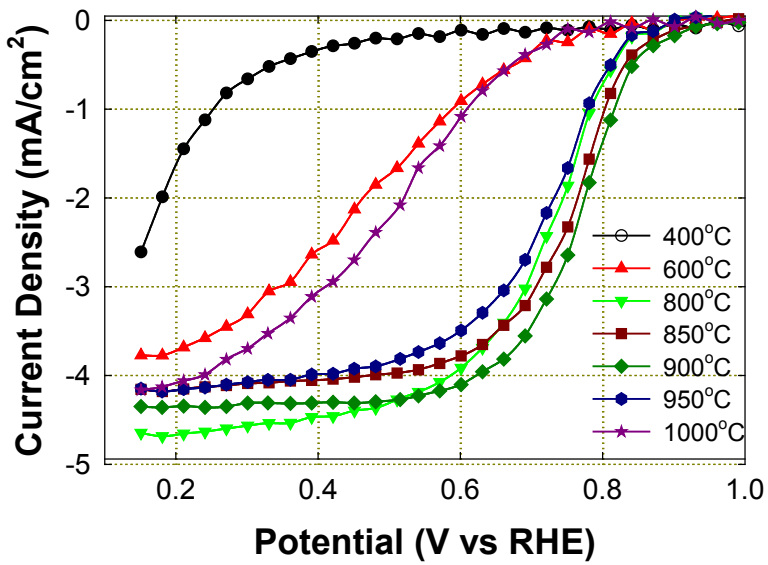


PANI-Fe-MWNT: Three images, same spot



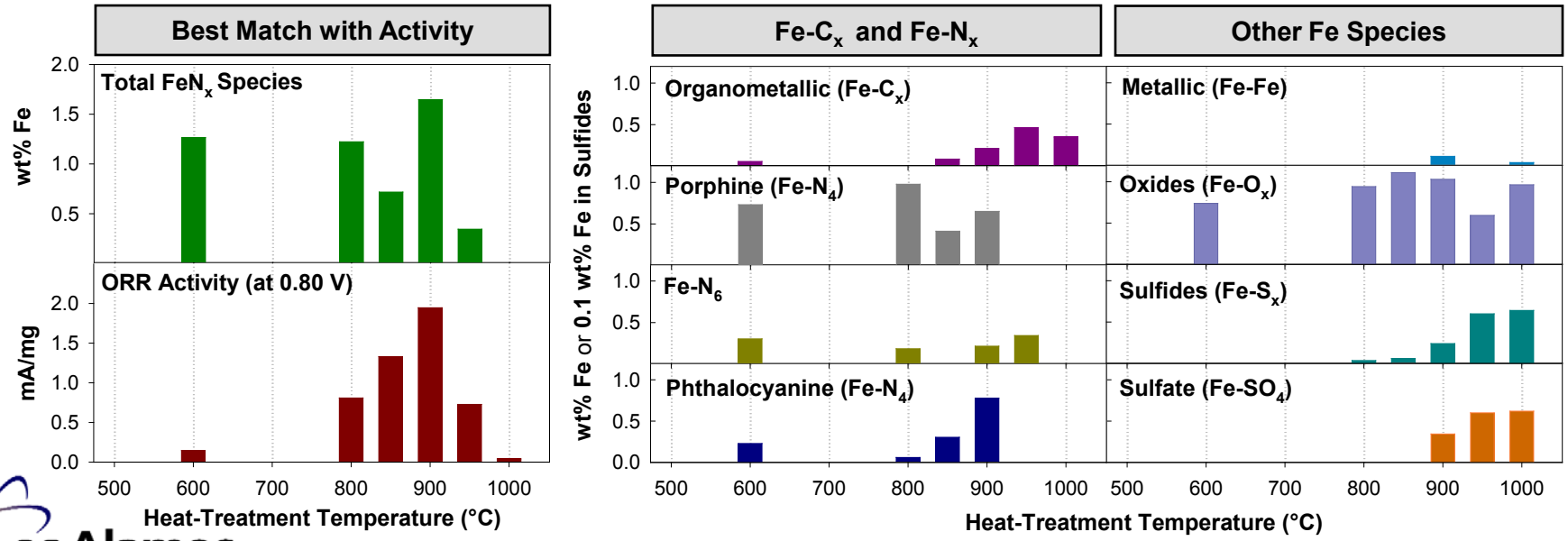
- **The two most durable catalysts showing notable similarities in morphology**
- **Significant number layered graphene "bubbles" formed in PANI-FeCo(3:1) and PANI-Fe-MWNT (→), co-located with the Fe(Co)S_x regions/particles (→); MWNT still present (→)**
- **BF-STEM images of PANI-Fe-MWNT showing graphitic carbon particles that surround/encapsulate FeS_x**
- **Relationship of graphene sheets (e.g. their increased hydrophobicity) to durability requiring further exploration**

PANI-Fe-C: Effect of Heat-Treatment on Activity and Fe Speciation



- Catalysts synthesized at 900ºC consistently showing the highest ORR activity; samples prepared at 850ºC, 800ºC, and 950ºC also ORR active
- 900ºC sample containing the highest amount of Fe-phthalocyanine-type coordination
- Highlight: Correlation between activity and presence of Fe-N_x-type coordination observed; Fe-C_x-type and Fe oxides correlating to a lesser degree
- FeN_x species created at higher temperatures (> 800ºC), not at lower ones, appear to correlate with ORR activity

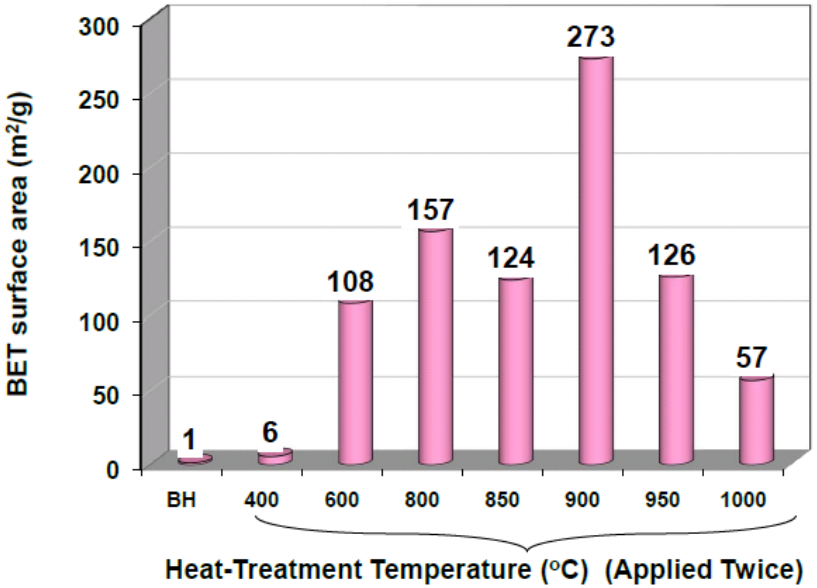
Fe X-Ray Absorption Spectroscopy Results

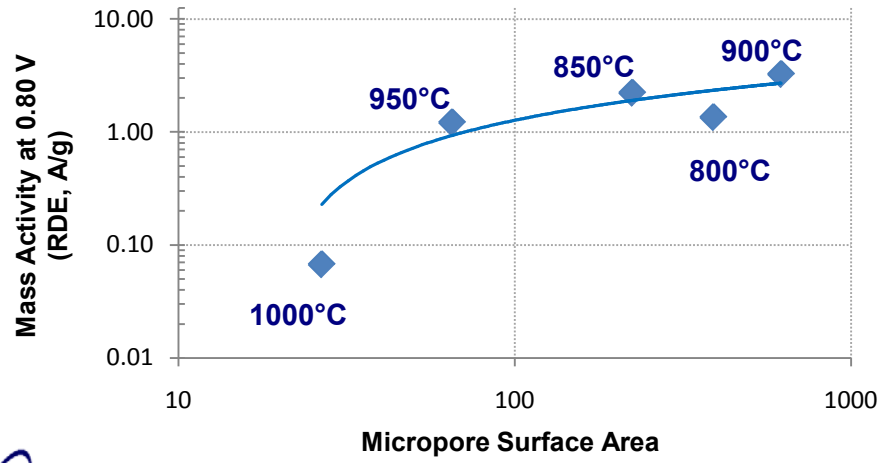


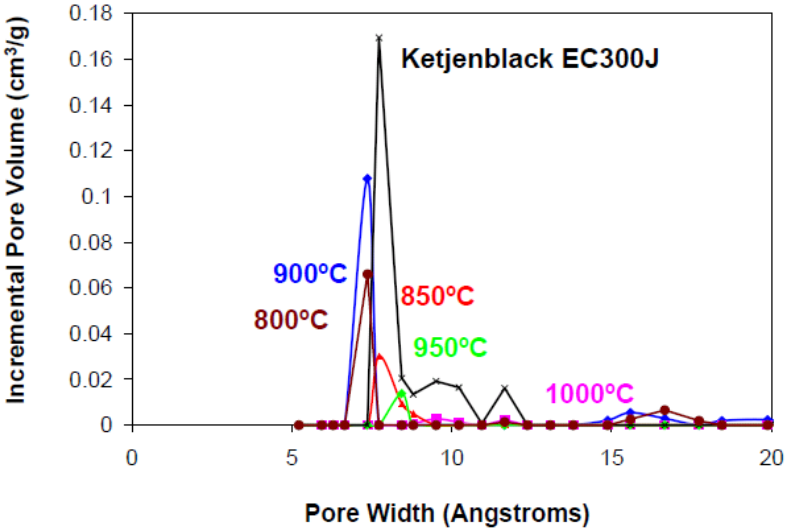
PANI-Fe-C: Effect of Heat-Treatment Temperature on Surface Area and Pores

- All samples heat-treated twice, as specified in synthesis procedure
- Sample heat-treated at 900ºC exhibiting the highest BET surface area and micropore volume/surface area
- BET surface area and micropore volume lower than in initial carbon support, but in-situ generated microporosity likely to be important*
- Highlight: Correlation observed between mass activity and micropore surface area

* M. Lefèvre *et al.*, *Science*, **324**, 71-74, 2009







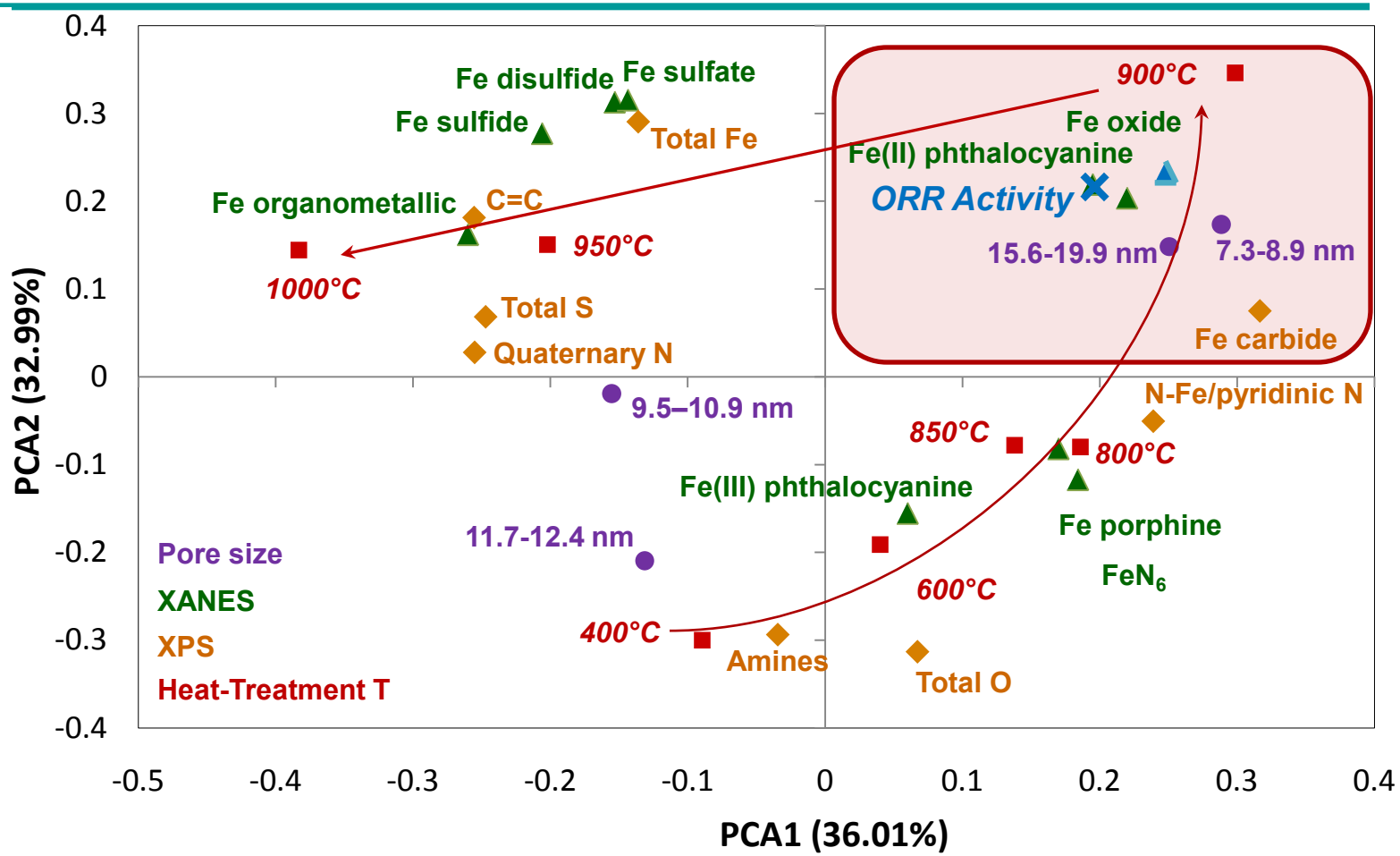
PCA: Correlation of Combined Characterization Data and Activity

Notes on Principle Component Ananlysis (PCA)

Samples and variables with mean composition, activity, BET or pore size would lie on the intersection of axes on this biplot.

The further the variables or samples from the intersection in any direction (vertical, horizontal or diagonal), the more different they are from the average values.

(As-synthesized powders examined.)



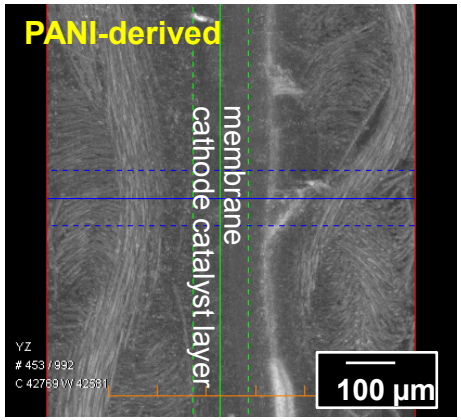
- **Fe-N-type coordination, correlated with ORR activity and ORR-active samples (900°C, 850°C, 800°C), remaining a primary candidate for active site**
- **Highlight: The most active, 900°C catalyst having the highest BET surface area, a bimodal pore distribution, high initial content of Fe carbide, Fe in oxide-like coordination environment, and Fe in phthalocyanine-like coordination**

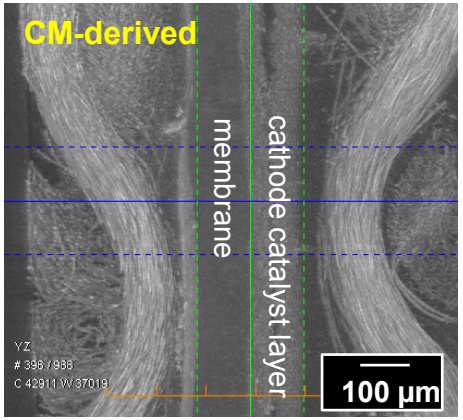
Progress in ORR Activity of Non-precious Catalysts: 2008 → 2009 → 2010

Experiment	Test Conditions	Measured Volumetric Activity per Electrode Volume at 0.8 V (A cm^{-3})			Improvement Factor (2008→2010)
		2008	2009	2010	
RDE at 25°C	900 rpm 0.5 M H_2SO_4 (mass-transport corrected)	0.44 EDA-FeCo-C	2.0 PANI-FeCo(3:1)-C	11 PANI-Fe/EDA-Co-C	25
H_2-O_2 fuel cell at 80°C	30 psig (11 psig) 100% RH	2.0 EDA-FeCo-C	14 PANI-FeCo(3:1)-C	72 (31) PANI-Fe/EDA-Co-C	36
			14 CM-Fe-C	127 (60) CM-Fe-C (v2)	127

Electrode density calculated from X-ray tomography images (and confirmed by SEM):

- *CM-derived catalysts: 0.4 g/cm^3*
- *PANI-derived catalysts: 0.8 g/cm^3*





Collaborations

- **Eight organizations with highly complementary skills and capabilities in catalyst development, electrode-structure design, materials characterization, and catalyst/MEA fabrication:**
  - ✓ Argonne National Laboratory; Brookhaven National Laboratory; Los Alamos National Laboratory; Oak Ridge National Laboratory – *direct DOE contracts*
  - ✓ University of California, Riverside; University of Illinois Urbana-Champaign; University of New Mexico – *subcontracts to Los Alamos National Laboratory*
  - ✓ Cabot Fuel Cells – *subcontract to Los Alamos National Laboratory*
- **Collaborations outside Fuel Cell Technologies Program:**
  - ✓ UTC Power/United Technologies (Lesia Protsailo) – *Cooperative Research and Development Agreement (CRADA) between UTC Power and LANL focusing on non-precious metal catalysts for fuel cell cathode applications*
  - ✓ Institut National de la Recherche Scientifique, Montreal, Canada (Frédéric Jaouen, Jean-Pol Dodelet) – *non-precious metal ORR catalysis*
  - ✓ Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany (Ulrike Kramm, Peter Bogdanoff) – *characterization of Fe-based non-precious metal catalysts by Mößbauer spectroscopy*
  - ✓ Daihatsu Motor Co, Osaka, Japan (Hirohisa Tanaka) – *R&D agreement with UNM on non-precious metal catalysts for cathodes of alkaline-membrane direct hydrazine fuel cells*

Proposed Future Work: Remainder of FY10 and FY11 (Partial)

Ultra-low Pt content catalysts:

- **Utilize sub-surface core modification for fine-tuning of interaction with Pt monolayer in ultra-low Pt-content catalysts to further increase catalyst ORR activity and stability**
- **Complete process/composition optimization of the Pt/Pd/C catalyst in the scaled-up process focusing on the effect of morphology and agglomerate size**

Non-precious metal catalysts:

- **Differentiate between recoverable and non-recoverable performance losses in non-PGM catalysts; evaluate whether long-term operation at high voltage causes irreversible damage to catalyst sites, or if site flooding can explain losses**
- **Reduce mass-transport resistance in non-PGM cathode**

Characterization:

- **Complete analysis of chemical composition and oxidation state of PANI-*Me*-C catalysts in the MEA environment to validate or refute hypotheses concerning activity and durability**
- **Continue characterization of atomic structure of catalysts in both classes**

Catalyst scale-up:

- **Develop scalable synthesis approaches towards additional monolayer catalyst compositions and structures**

Summary

- Specific and mass activity of ultra-low Pt-content core-shell catalysts significantly improved, up to 1200 μA/cm^2 and 1.1 A/mg$_{PGM}$ (2.4 A/mg$_{Pt}$) at 0.90 V, respectively (RDE testing); DOE performance targets met and exceeded
- Excellent stability demonstrated with several PGM catalysts, including hollow-Pt nanoparticle catalyst (less than 17 mV performance loss at $E_{½}$ after 20,000 scans) and Pt$_{ML}$/Pd$_2$AuNi/C nanoparticles ($\Delta E_{½}$ limited to 6 mV after 10,000 potential cycles)
- 2010 DOE activity target for non-PGM catalysts reached; OCV of 1.04 V and volumetric ORR activity of 165 A/cm$^3_{electrode}$ (after mass-transport correction) achieved with CM-Fe-C catalyst in fuel cell testing; rapid improvement in fuel cell performance of several other non-precious metal catalysts shown
- High durability accomplished with PANI-based catalysts to potential holding at OCV as well as to potential (RDE) and voltage (fuel cell) cycling, up to 30,000 cycles (DOE protocols followed)
- ORR activity of PANI-derived catalysts correlated to microporosity and Fe-N coordination; improved durability linked to graphene sheet formation (results of advanced spectroscopic and microscopic characterization)
- Synthesis of BNL's Pt$_{ML}$/Pd/C core-shell catalyst scaled-up to 20 g per batch
- Majority of project milestones accomplished, some exceeded; most other milestones on schedule

Co-Authors

– catalysts with ultra-low Pt content

R. R. Adzic (PI), Y. Cai, K. Gong, K. Sasaki, M. Vukmirovic, J. Wang

– chalcogenide-based catalysts

A. Wieckowski (PI), C. Corcoran, S. Goubert-Renaudin

– non-precious metal catalysts; characterization

P. Zelenay (Project Lead), H. Chung, C. Johnston, N. Mack, M. Nelson, P. Turner, G. Wu

– open-frame catalyst structures

P. Atanassov (PI), K. Artyushkova, W. Patterson, M. Robson

– nanostructure catalyst structures

Y. Yan (PI), K. Jensen, L. Xie, T. Zhang

– characterization & durability

D. Myers (PI), M. Ferrandon, A. J. Kropf, X. Wang

– characterization

K. More (PI)

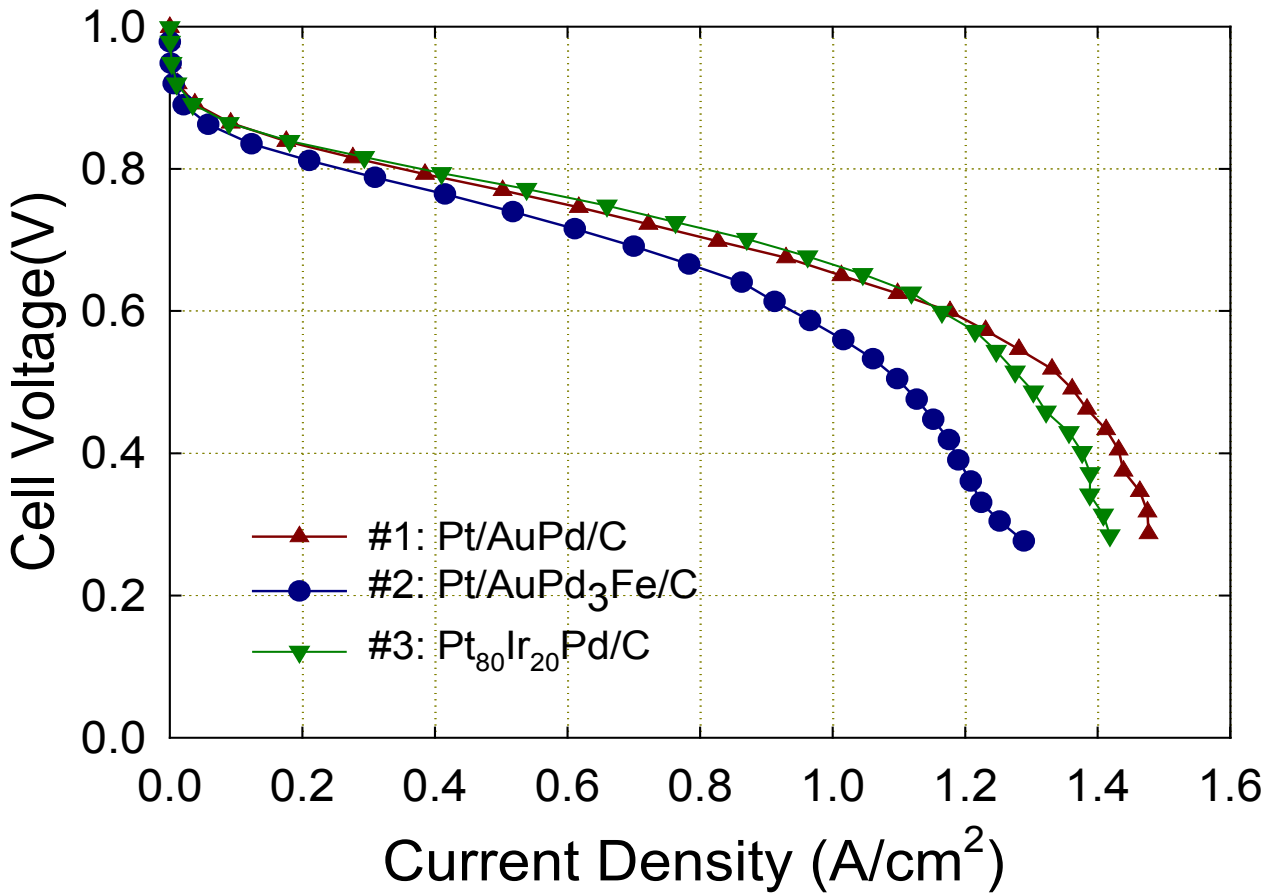
– fabrication & scale-up

P. Atanassova (PI), Y. Sun

Supplemental Slides

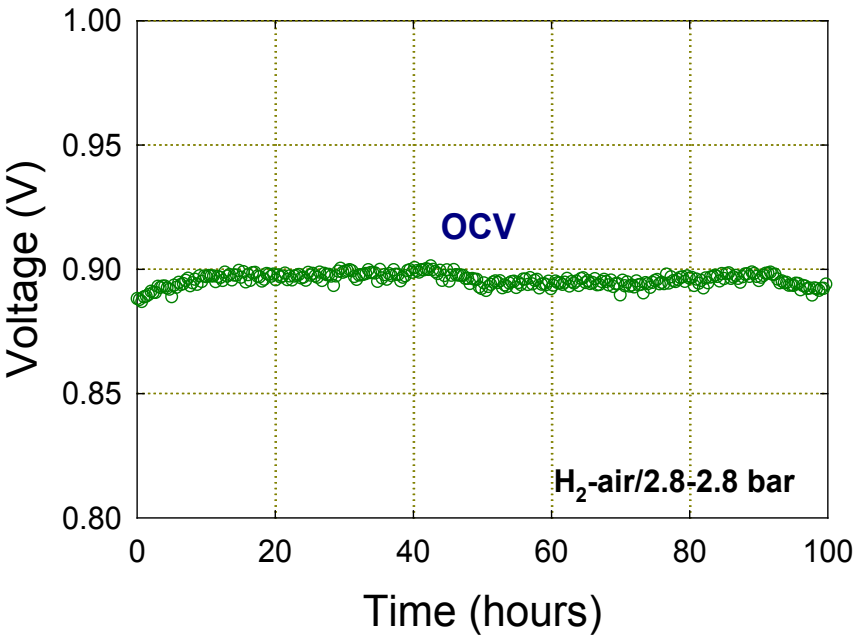
Ultra-Low Pt Content Catalysts: Fuel Cell Performance

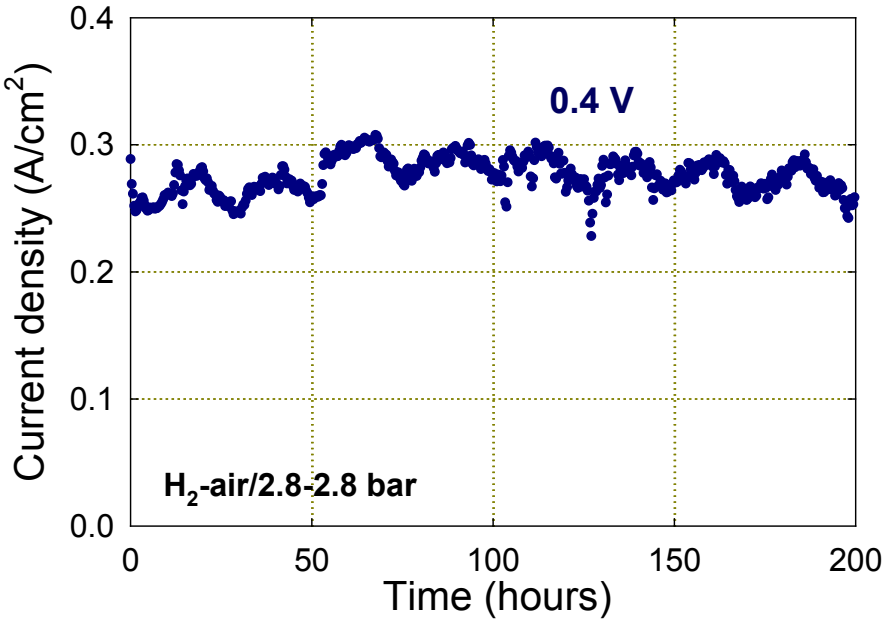
Anode: *E-TEK Pt-catalyzed cloth GDE, 0.25 mg cm^{-2} Pt; 30 psig H_2;* ***Cathode:*** *BNL catalysts, 0.2 mg$_{PGM}$ cm^{-2}; 30 psig air, carbon paper (SGL 24BC) GDL;* ***Membrane:*** *Nafion® 212;* ***Cell:*** *80ºC*



PANI-FeCo(3:1)-C: Stability Testing at Different Voltages

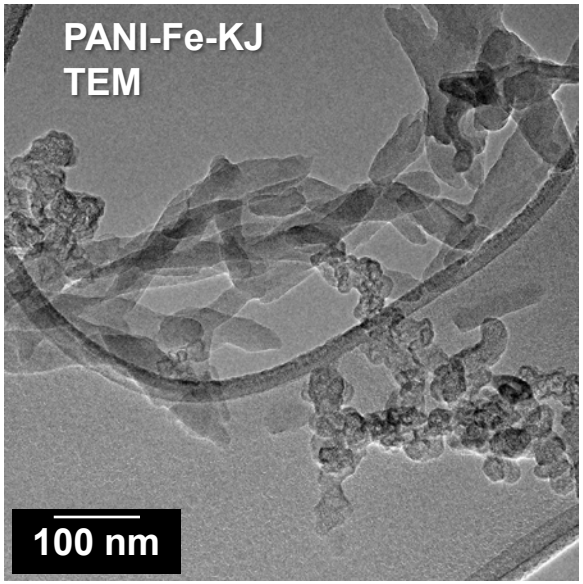
Anode: *0.25 mg cm^{-2} Pt (E-TEK), 2.8 bar;* ***Cathode:*** *4.0 mg cm^{-2} PANI-derived, 2.8 bar;* ***Membrane:*** *Nafion® 1135; Cell: 80°C*

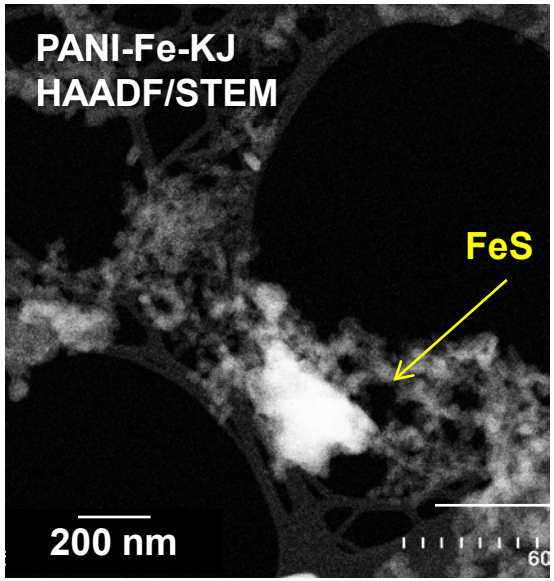


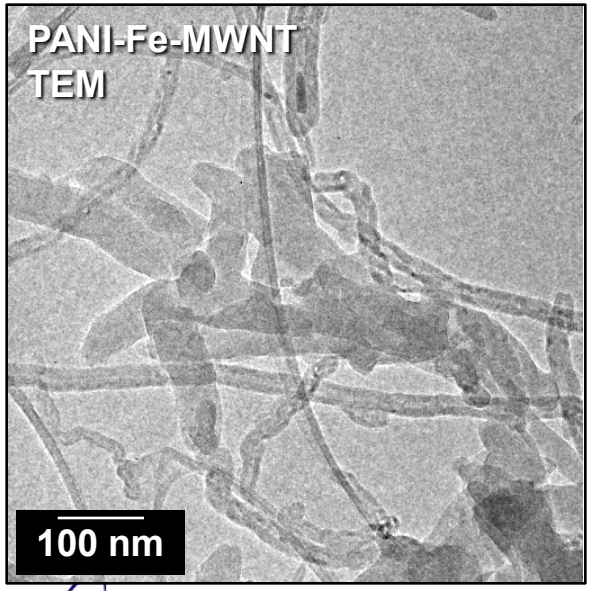


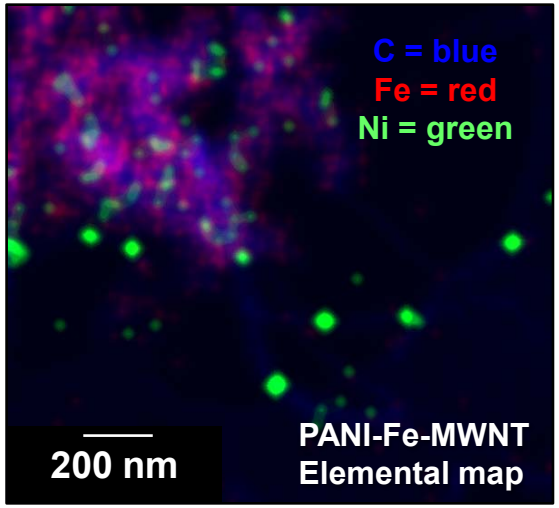
Open-cell voltage of an H_2-air cell maintained at *ca.* 0.90 V for more than 100 hours

PANI-Fe-KJ and PANI-Fe-MWNT: Before Heat-Treatment



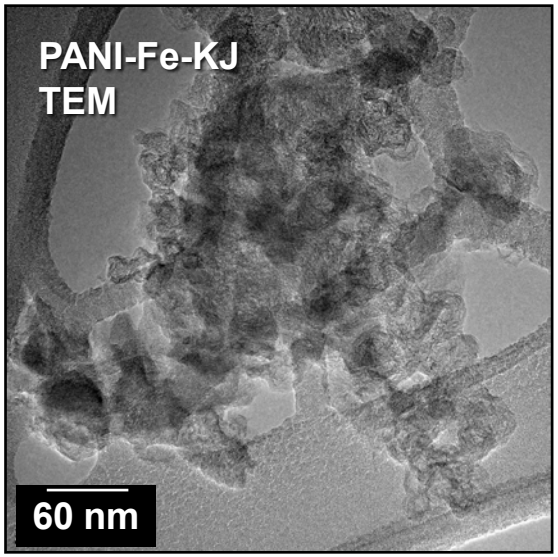


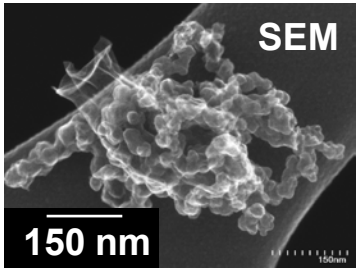


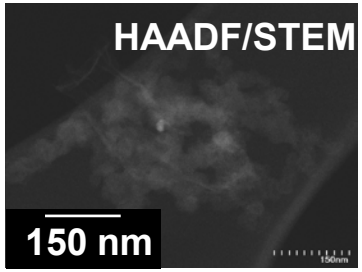


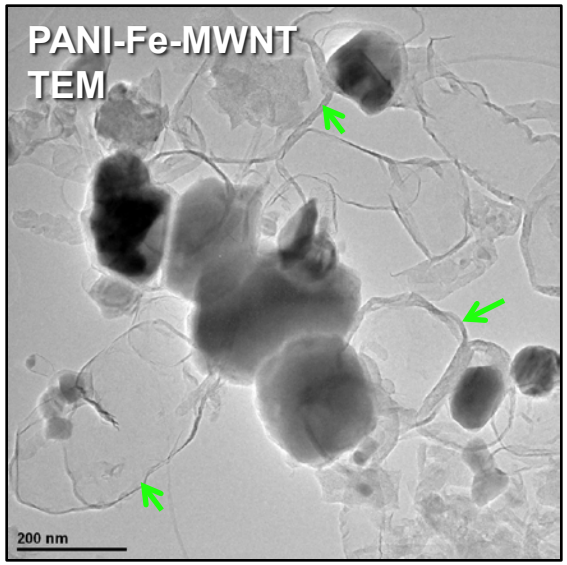
- Separate PANI fibers and support particles (KJ, MWNTs) observed in both sample types
- "Polymer coating" not readily seen on support particles, but major drop in BET surface area indicating covered pores
- KJ imaging brightly by STEM – Fe and S present on <u>all</u> particles
- Ni particles inside MWNTs (growth nucleation)
- Elemental mapping showing that Fe and S are associated with the PANI regions but not MWNTs (in contrast to KJ case)
- Large, isolated FeS particles observed in both samples

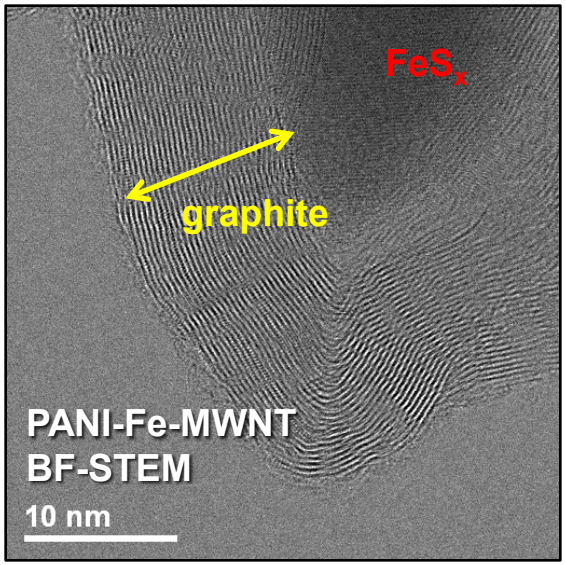
PANI-Fe-KJ and PANI-Fe-MWNT: Final Catalysts











- Final catalysts obtained after heat-treatment, acid-treatment, and 2nd heat-treatment
- "PANI-derived" and "support-derived" particles still observed in both sample types
- Fe and S remaining dispersed across KJ-derived particles
- Very small amount of "graphene sheet" structure observed in PANI-Fe-KJ – much less than when Co present (earlier slide)
- Significant number of layered graphene "bubbles" formed in PANI-Fe-MWNT (green arrows), co-located with the FeS_x regions/particles
- BF-STEM images of PANI-Fe-MWNT showing graphitic carbon particles surround/encapsulate FeS_x

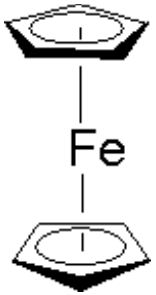
PANI-Fe-C XAS: XANES Iron Standards

Fe^0
Fe metal

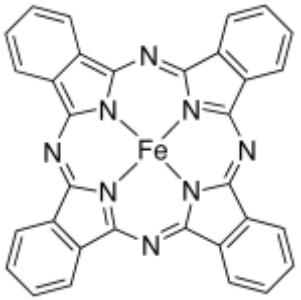
Fe^{2+} compounds
Fe0
Fe^{2+} phthalocyanine (at right)
Fe_2N
Fe_4N
$FeSO_4$ anhydrous
$FeSO_4$ $7H_2O$
Fe II acetylacetonate
Ferrocene (at right)
FeS
FeS_2
tris(2,2'-bipyridine) Iron(II) hexafluoro-phosphate (at right)
1,10-phenanthroline Iron(II) sulfate complex (at right)

$Fe^{3+/2+}$ compounds
Fe_3O_4

Activity of non-precious catalysts attributed by many groups to FeN_4–type or FeN_{2+2}–type sites

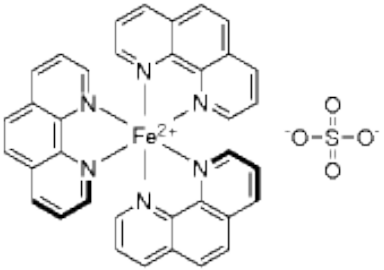


di(cyclopentadienyl) iron (ferrocene) (organometallic)

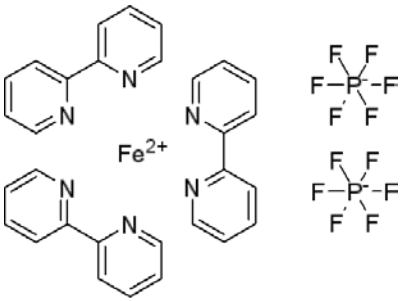


iron(II) phthalocyanine

High degree of symmetry of Fe^{2+} square planar environment (e.g., Fe-pc) causing unique spectral feature near 7115 eV; inclusion of this standard required to fit data well



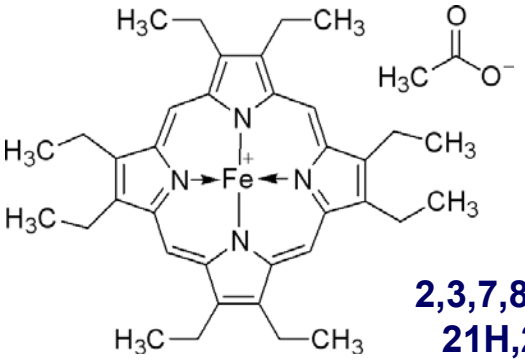
1,10-phenanthroline iron(II) sulfate complex (FeN_6)



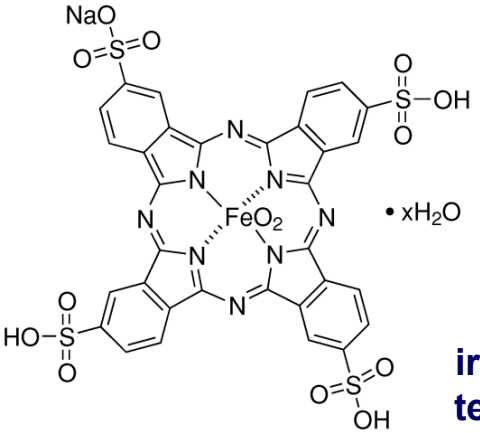
tris(2,2'-bipyridine) iron(II) hexafluoro-phosphate (FeN_6)

PANI-Fe-C XAS: XANES Iron Standards

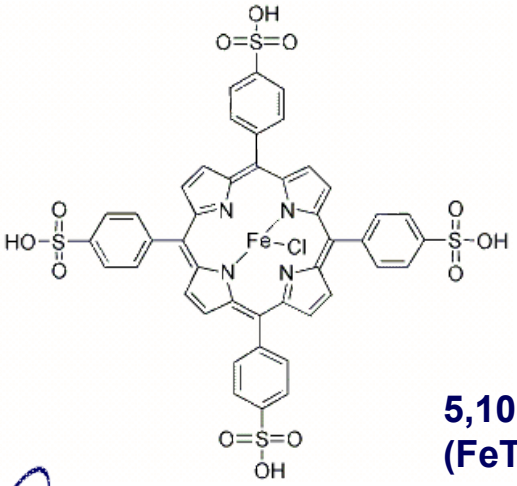
Fe^{3+} compounds
- $FeCl_3$ $6H_2O$
- Fe III acetylacetonate
- $Fe(NO_3)_3$ $9H_2O$
- Fe_2O_3
- Fe porphine (at right)
- Fe^{3+} phthalocyanine (at right)
- modified Fe^{+} porphine (FeTPPS, below)



2,3,7,8,12,13,17,18-octaethyl-21H,23H porphine iron(III) acetate (porphine)



iron(III) phthalocyanine-4,4′,4″,4‴-tetrasulfonic acid, compound with oxygen monosodium salt

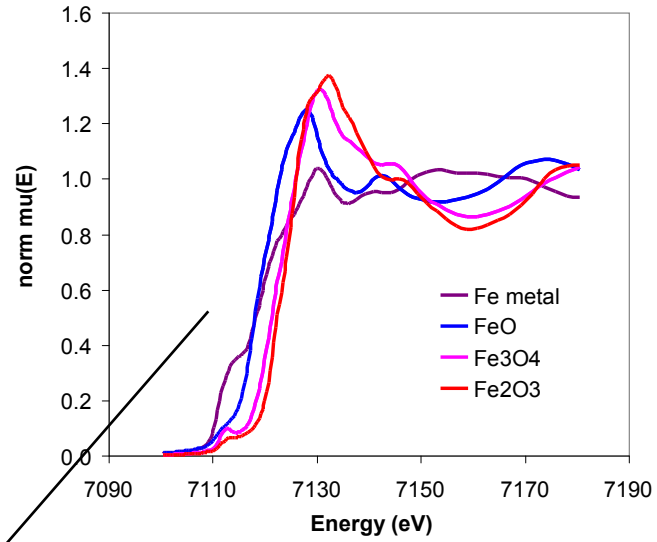


5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphine iron(III) chloride (FeTPPS)

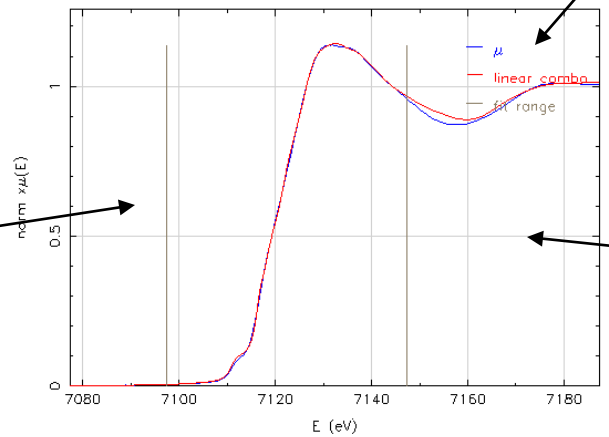
PANI-Fe-C XAS: Comments on Interpretation of Spectra

- **Multi-component nature of samples rendering analysis of EXAFS region of Fe K-edge spectra virtually impossible – only XANES region proving useful**
- **Linear combination of XANES spectra of standards providing mole fraction of Fe species in coordination environments similar to those of the given standards**
- **XAFS edge step and/or destructive ICP-OES analyses yielding total loading of Fe in materials**

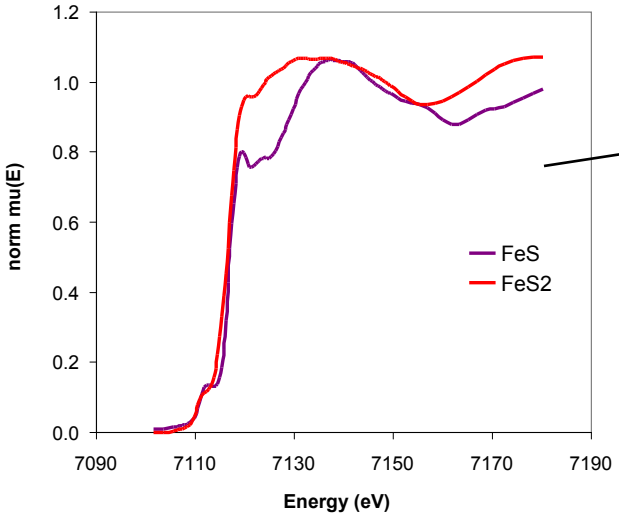
Fe Metal/Fe Oxides Standards



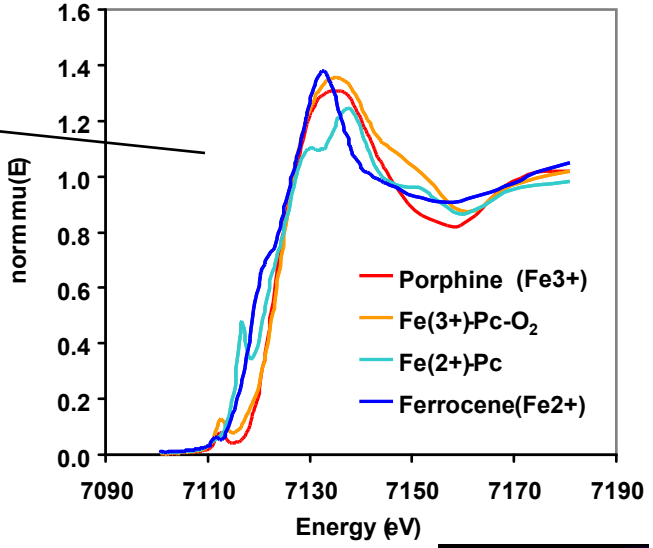
Fit of Spectrum by Linear Combination of Standards



Fe Sulfides Standards

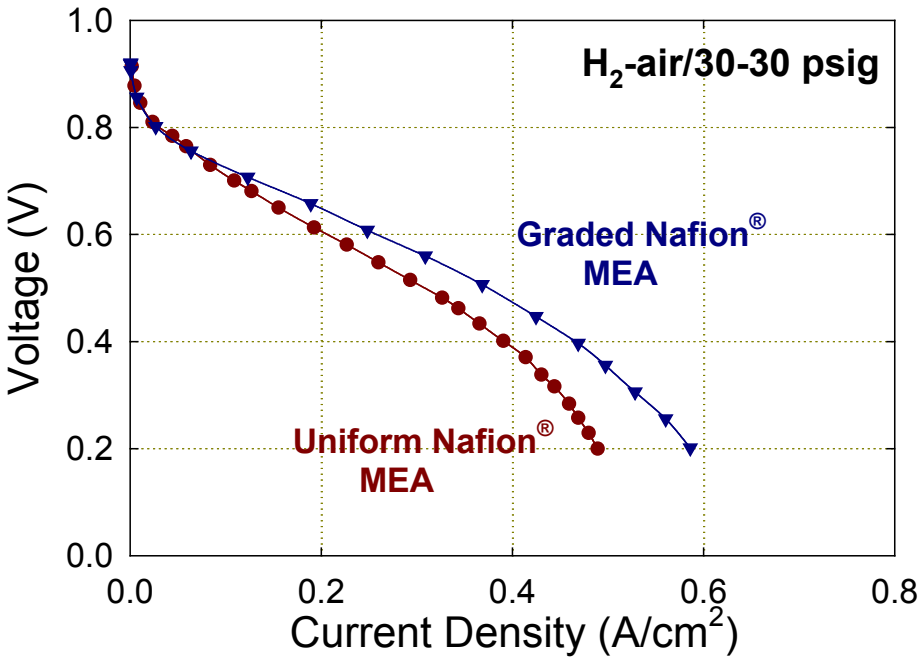


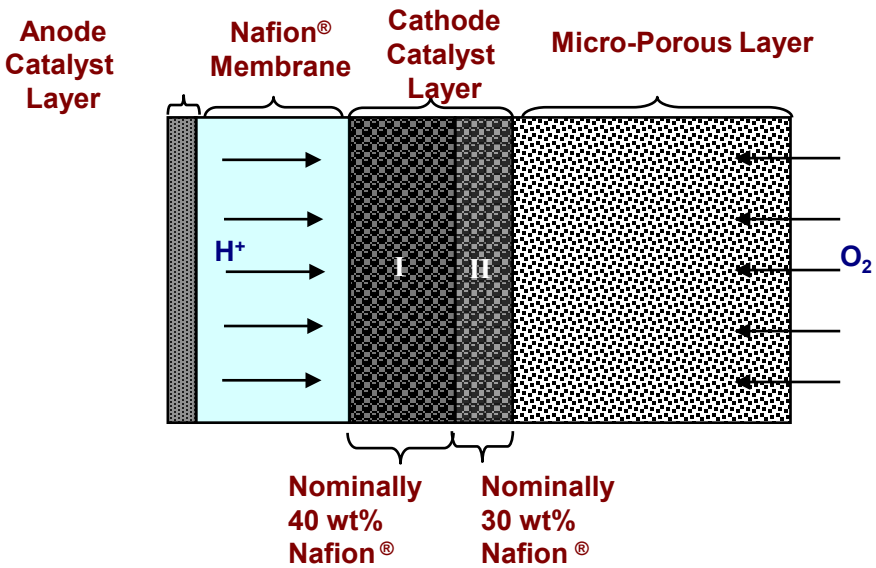
Examples of Fe-Complexes Standards



Graded Nafion® Content: Impact on Performance of PANI-Fe-C

Anode: *0.25 mg cm^{-2} Pt (E-TEK), 30 psig;* ***Cathode:*** *4.0 mg cm^{-2} PANI-derived, 30 psig;* ***Membrane:*** *Nafion® 1135; Cell: 80ºC*

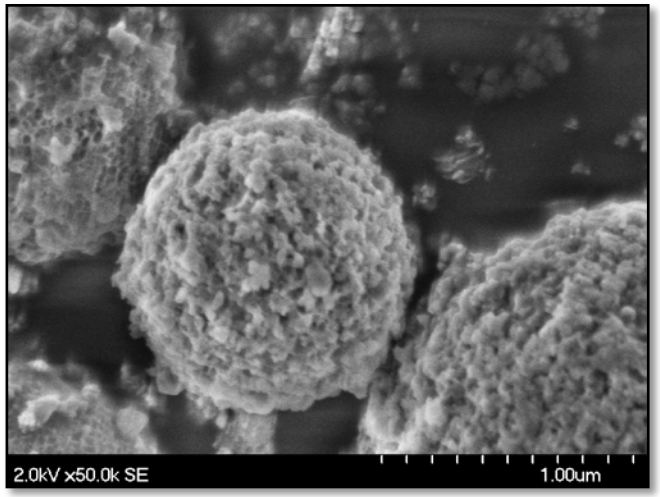




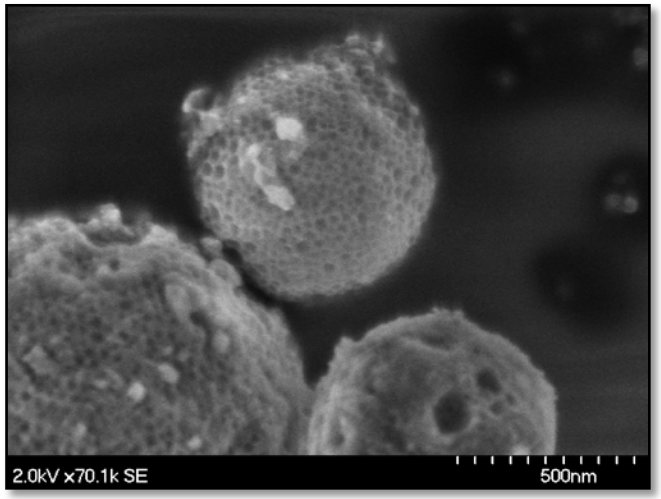
Graded Nafion® content in the cathode catalyst layer leading to improved performance by 20% at mass-transport controlled voltages

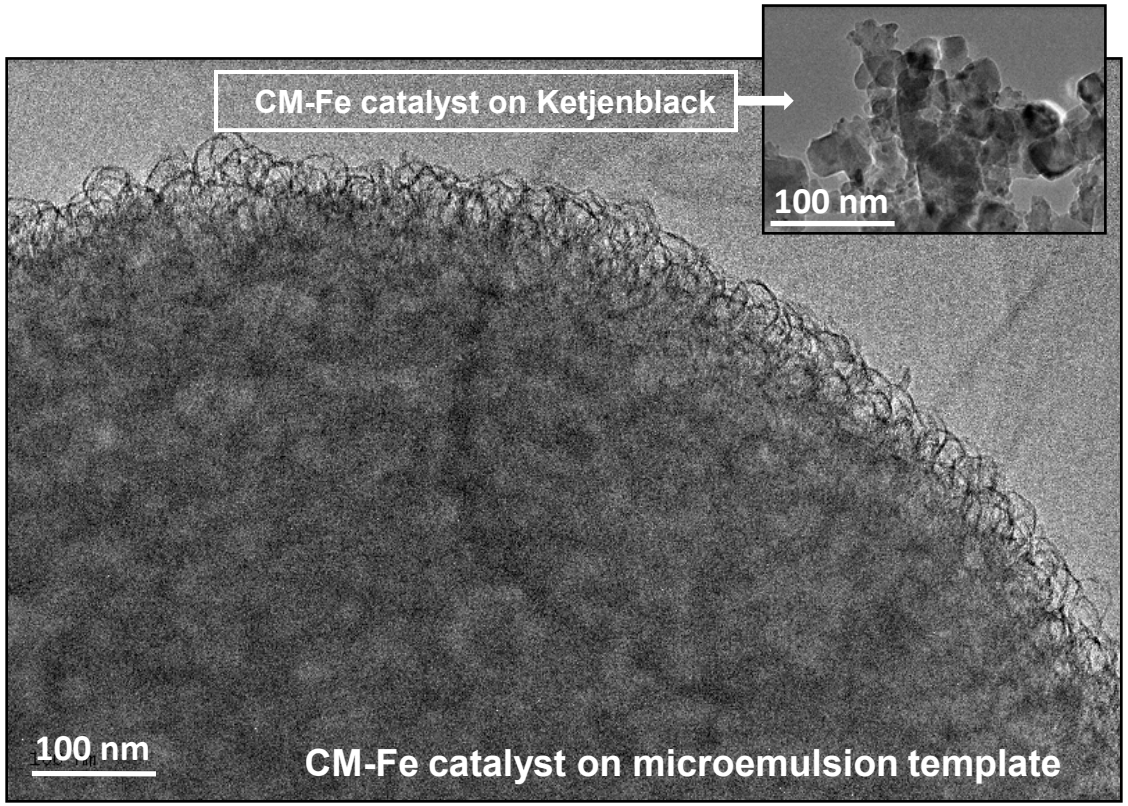
Open Frame Structure for Non-PGM Catalysts: Templated CM-Fe-C

Templated CM-Fe-C after pyrolysis, no etch



Templated CM-Fe-C after 7.0 M KOH etch





- Explored several precursors for pyrolytic formation of N-containing carbon-backbone structures in combination with transition metals (Co, Fe)
- At present, research focusing on the CM-Fe-C catalyst using LANL-formulated synthesis, a silica template, and sucrose as a carbon backbone precursor

Acknowledgments

- **DOE-EERE Fuel Cell Technologies Program**
- **Technology Development Manager: Dr. Nancy Garland**