# Advanced Cathode Catalysts

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**Project ID: FC005**

# 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**

BROOKHAVEN NATIONAL LABORATORY – Radoslav Adzic

**Argonne National Laboratory**

Argonne NATIONAL LABORATORY – Debbie Myers

**University of Illinois, Urbana**

ILLINOIS UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN – Andrzej Wieckowski

**University of New Mexico**

The University of New Mexico – Plamen Atanassov

**University of California, Riverside**

UC RIVERSIDE UNIVERSITY OF CALIFORNIA – Yushan Yan

**Cabot Fuel Cells**

CABOT – Paolina Atanassova

**Oak Ridge National Laboratory**

ornl – Karren More

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# 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 $V_{iR-free}$ 720 $\mu A/cm^2$ at 0.90 $V_{iR-free}$
- **Activity** (non-PGM catalysts)**:** $> 130$ $A/cm^3$ at 0.80 $V_{iR-free}$
- **Durability with cycling:** 5,000 hours at $T \leq 80°C$, 2,000 hours at $T > 80°C$

**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**

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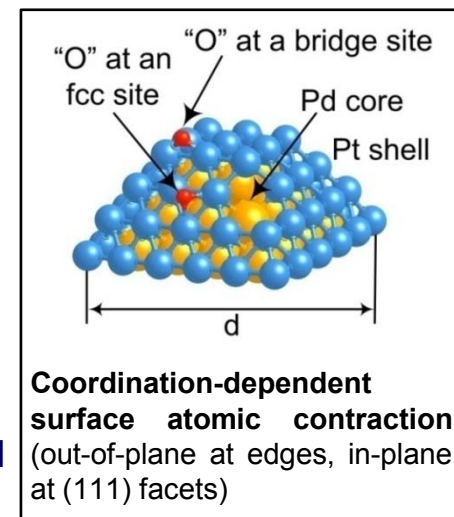NATIONAL LABORATORY

# 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**

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# 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$_x$Co |
| 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 |

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# 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)



"O" at an fcc site  "O" at a bridge site  Pd core  Pt shell  d

**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
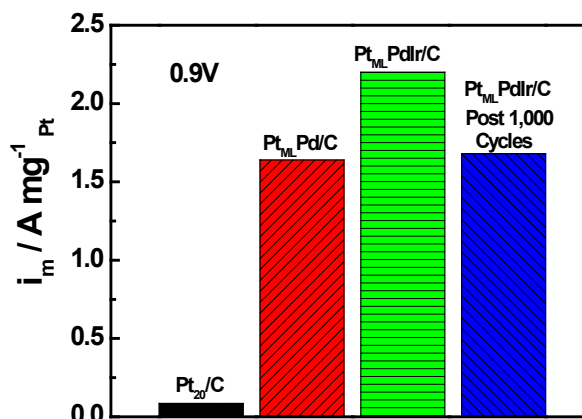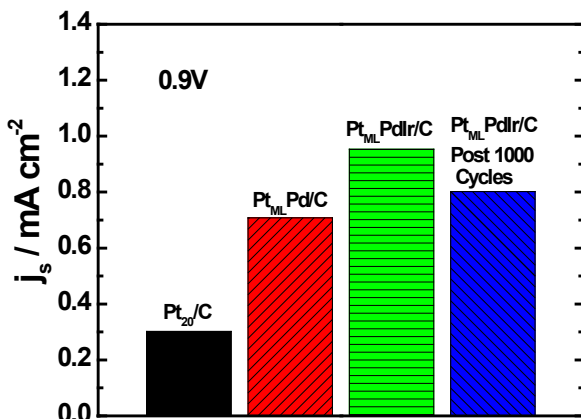


*Approach: Ir layer placed on Pd/C, annealed at 300-400°C to cause segregation of Pd to the surface; subsurface Ir inducing contraction of top Pd layers; $Pt_{ML}$ on PdIr/C compressed more than on Pd/C → weakened Pt-O interaction*

*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)**
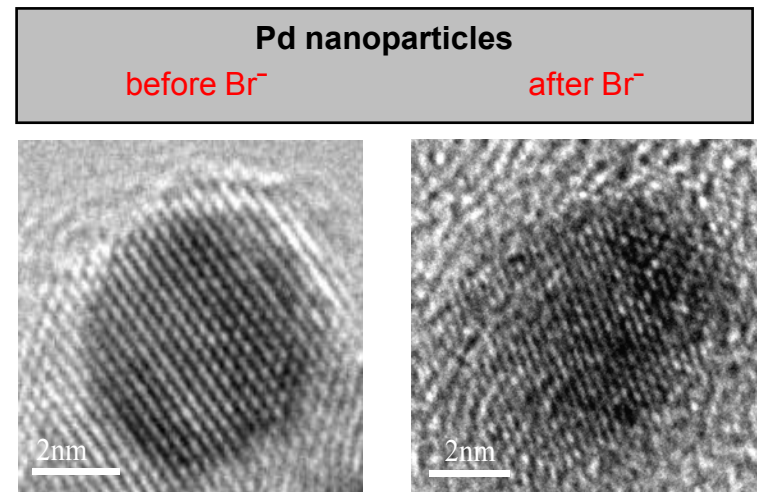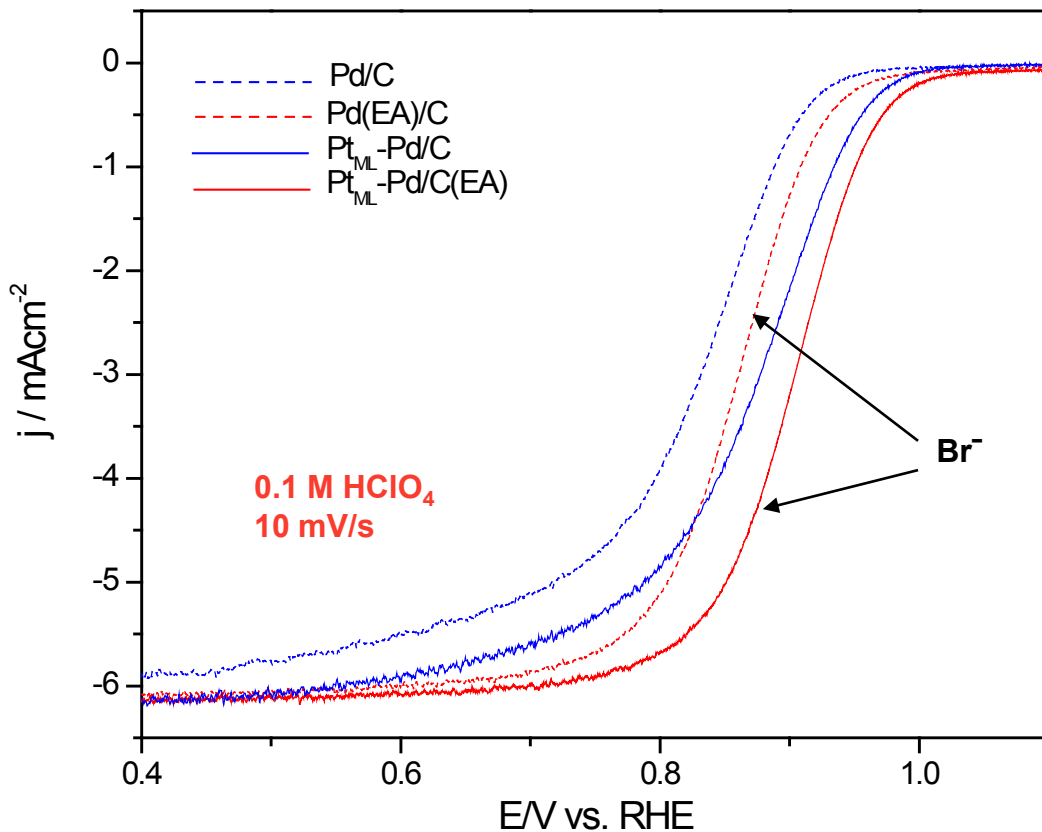
# Ultra-Low Pt Content Catalysts: Fuel Cell Performance

*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:* *80°C*
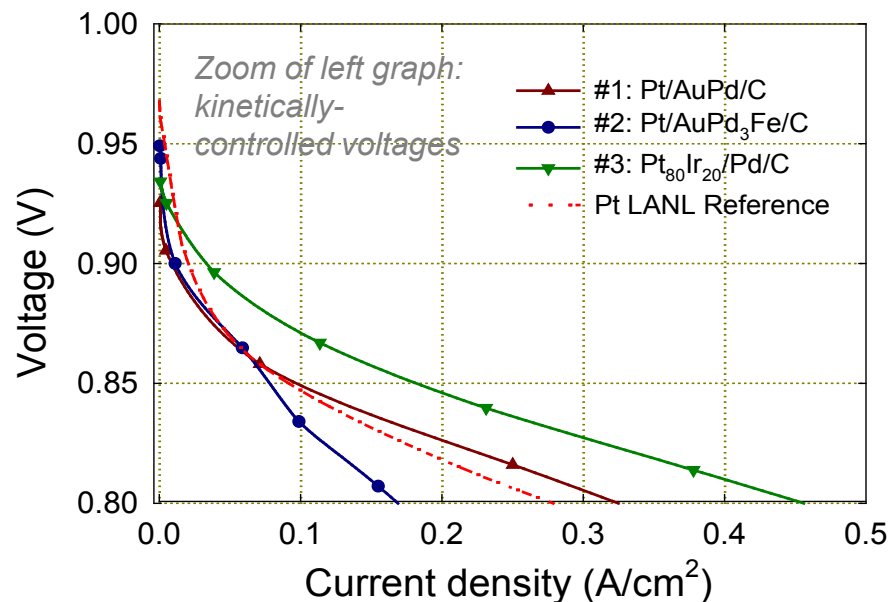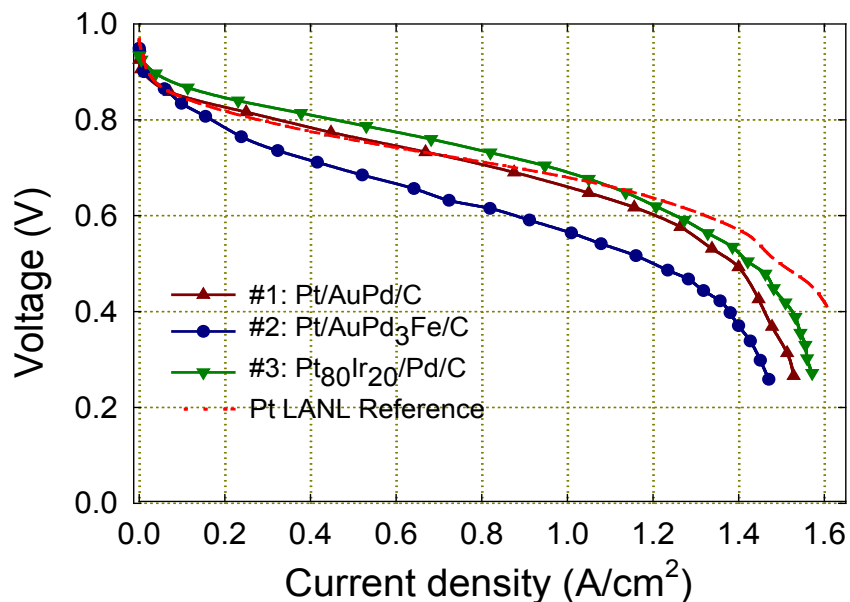


- **Pt$_{80}$Ir$_{20}$/Pd/C catalyst exhibiting the best ORR performance in MEA fuel cell test**
- **Superior performance at kinetically-controlled voltages demonstrated**
- **Mass activity of Pt$_{80}$Ir$_{20}$/Pd/C at 0.90 V:**     **0.53 A/mg$_{Pt}$**
   **0.19 A/mg$_{PGM}$**

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

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# Ultra-Low Pt Content Catalysts: Br⁻ Adsorption/Desorption



Legend:
- Pd/C
- Pd(EA)/C
- $Pt_{ML}$-Pd/C
- $Pt_{ML}^t$-Pd/C(EA)

0.1 M $HClO_4$
10 mV/s

Br⁻

y-axis: $j$ / mAcm$^{-2}$
x-axis: E/V vs. RHE

### Pd nanoparticles

before Br⁻          after Br⁻



2nm          2nm

| Catalyst | $E_{1/2}$ (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!*

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# Ultra-Low Pt Content Catalysts: Pt Contraction in Hollow Nanoparticles
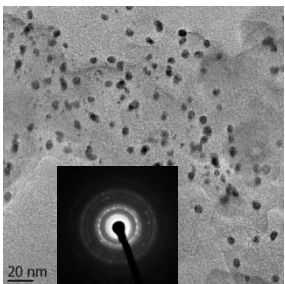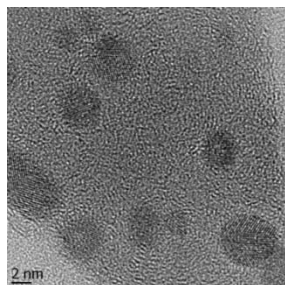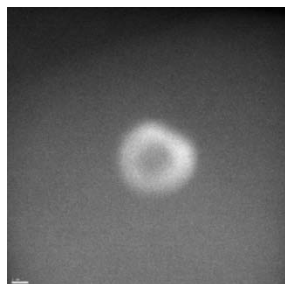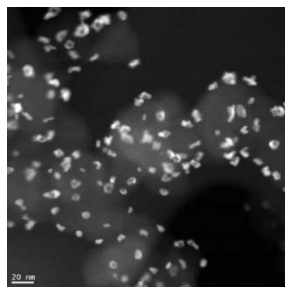
Pt hollow spheres produced by galvanic replacement of electrodeposited Ni nanoparticles on Vulcan XC-72, followed by anodic dissolution of Ni
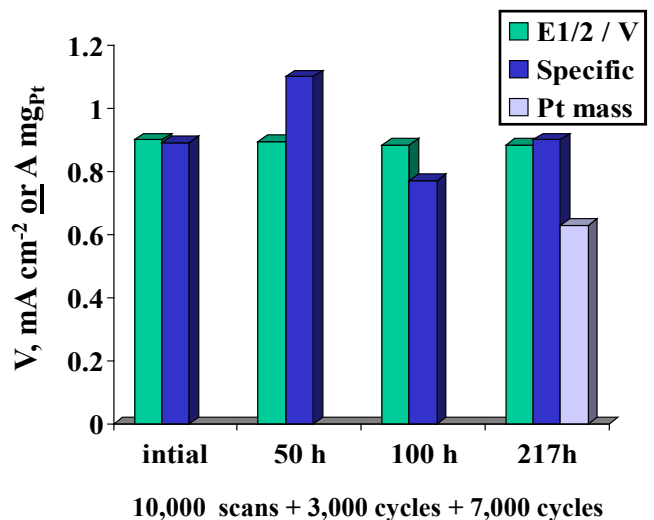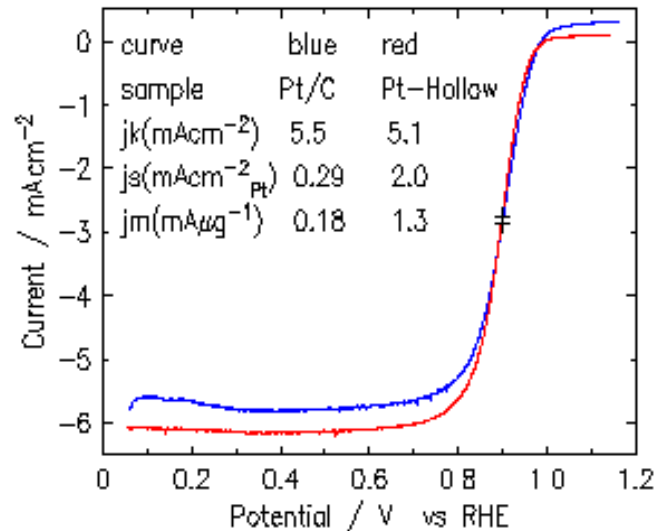
**Pt**

**Ni** → galvanic replacement → **Pt** / **Ni** → potential cycles → **Pt**

**Hollow Pt Nanoparticles: ORR Activity & Stability**

| curve | blue | red |
|-------|------|-----|
| sample | Pt/C | Pt–Hollow |
| $jk(mAcm^{-2})$ | 5.5 | 5.1 |
| $js(mAcm^{-2}_{Pt})$ | 0.29 | 2.0 |
| $jm(mA\mu g^{-1})$ | 0.18 | 1.3 |

**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**

Legend: E1/2 / V, Specific, Pt mass

x-axis: intial, 50 h, 100 h, 217h

**10,000 scans + 3,000 cycles + 7,000 cycles**

y-axis: V, mA cm$^{-2}$ or A mg$_{Pt}$

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

## Au-Displacement Method: Pt/Au/Pd$_x$Co Catalyst

- **Surface-reactive low-coordination atoms displaced by more noble atoms (more effective approach than "acid wash")**

- **Pt/Au/Pd$_x$Co catalyst – Pt$_{ML}$ on Au-submonolayer-modified Pd$_x$Co catalyst (reactive Co atoms displaced by Au); scale-up to 2 g batch**

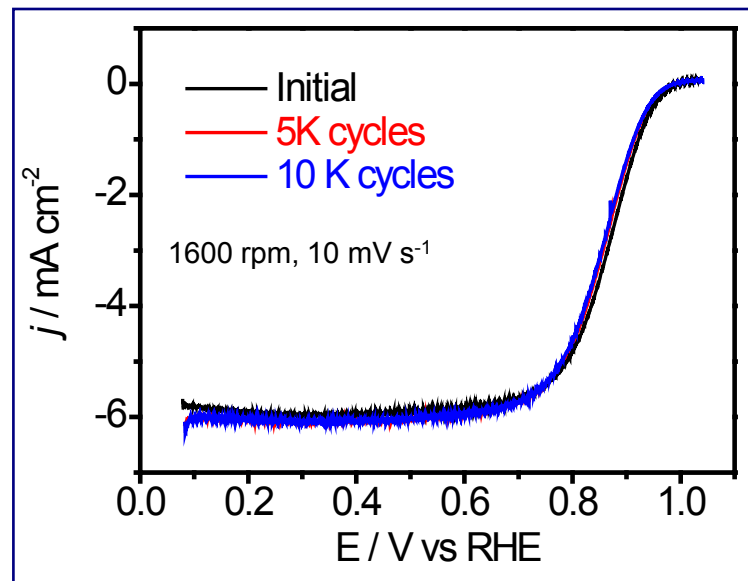- **Highlight: 1170 μA/cm$^2$ and 1.10 A/mg$_{PGM}$ (2.41 A/mg$_{Pt}$) at 0.90 V**

  *Specific activity and mass activity milestones achieved!*



Pt/Au/Pd$_x$Co

$E_{1/2}$ = 909mV, $j_K$ (0.9V)= 7.41mA cm$^{-2}$

$I_S$ = 1.17mA cm$^{-2}$, $I_m$ =2.41mA μg$^{-1}$
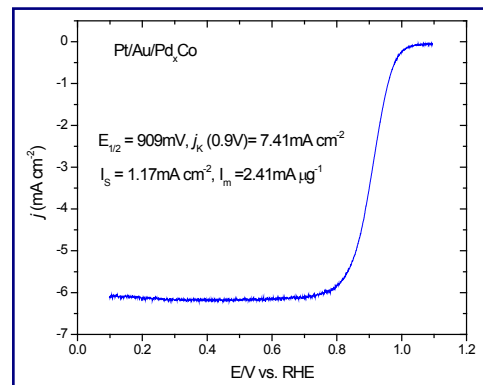
## Catalyst Synthesis Using Prussian-Blue Analogues: Pt$_{ML}$/Pd$_2$Au$_1$Ni$_1$ Catalyst

- **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$_2$Au$_1$Ni$_1$ catalyst – Pt$_{ML}$ on Pd$_2$Au$_1$Ni$_1$ core, obtained by replacement reaction of PdCl$_2$ with Au$_1$Ni$_3$ (result of decomposition of AuNi$_{2.5}$[Ni(CN)$_6$]$_2$)**

| $E_{1/2}$ (V) | Activity (A/mg$_{Pt}$) | Activity (μA/cm$^2$) | ESA (cm$^2$) | $E_{1/2}$ loss (mV) |
|---|---|---|---|---|
| 0.865 | 0.728 | 524 | 0.718 | 6 |



Initial
5K cycles
10 K cycles

1600 rpm, 10 mV s$^{-1}$

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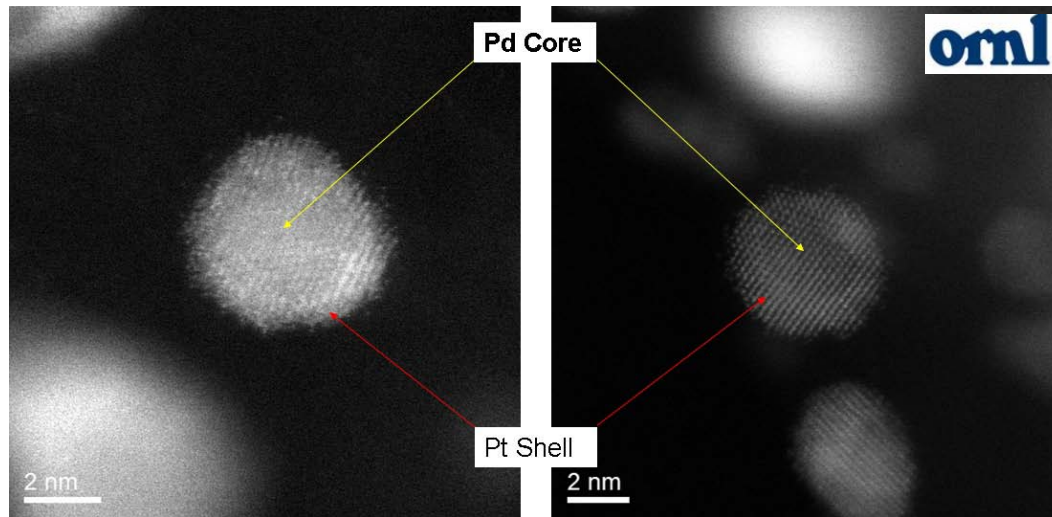


- **Highlight: Successfully developed scalable (1-20 g/batch) synthesis approach for Pt shell on Pd/C, the catalyst developed and demonstrated on a laboratory scale at Brookhaven**

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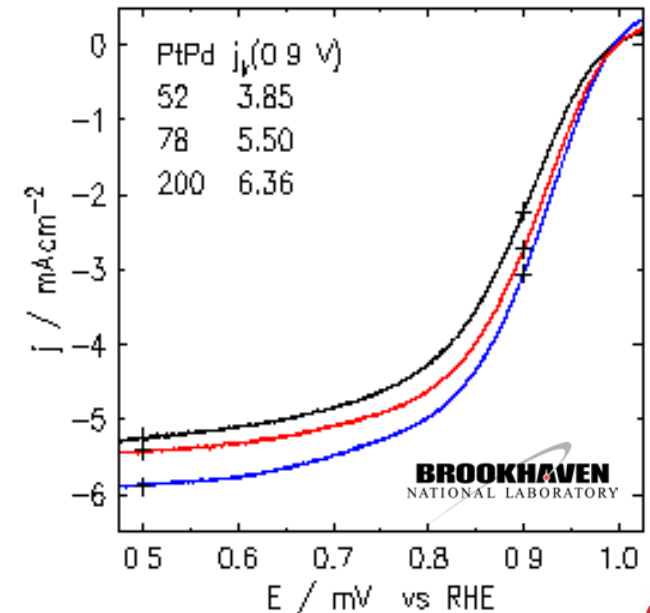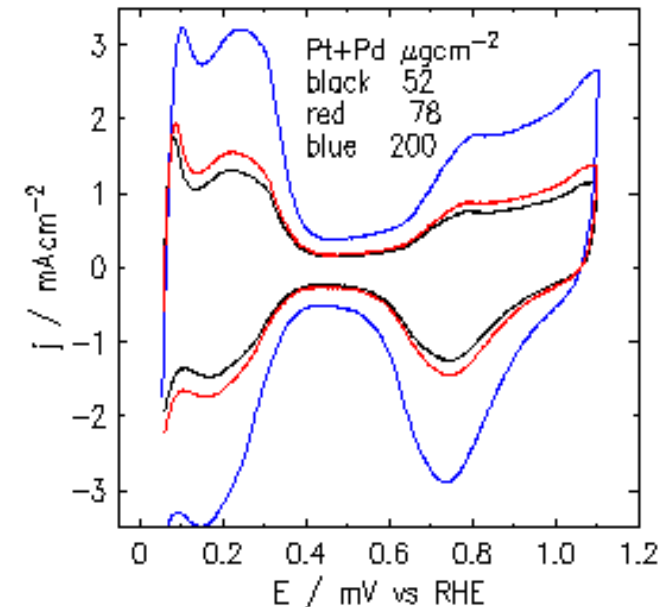
# Ultra-Low Pt Content Catalysts: Pt$_{ML}$/Pd/C Catalyst Scale-Up by Cabot

*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
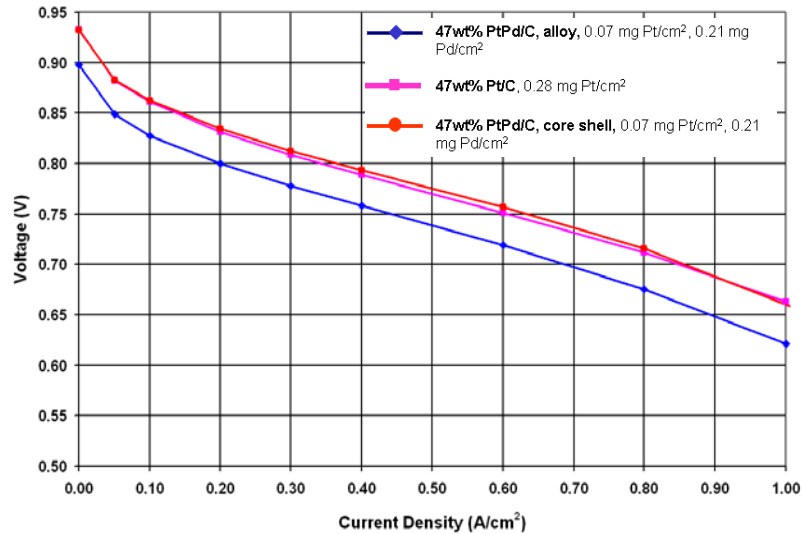
*Anode:* 0.05 mg cm$^{-2}$ Pt, 30 psig H$_2$ (1.5✕ at 1.0 A/cm$^2$), 100% RH; *Cathode:* 0.07 mg$_{Pt}$ cm$^{-2}$ + 0.21 mg$_{Pd}$ cm$^{-2}$, 30 psig air (2.5✕ at 1.0 A/cm$^2$), 100% RH; *Membrane:* NRE-212; *Cell:* 80ºC
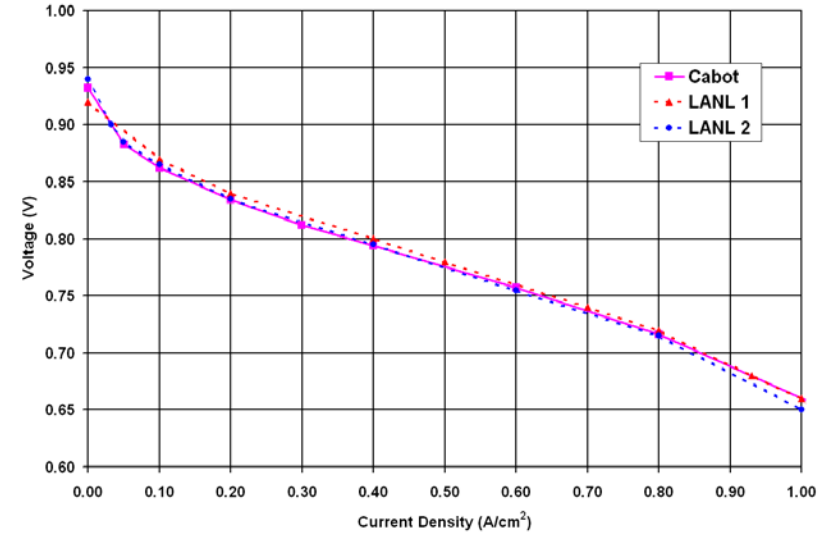


- **Highlight: Pt$_{ML}$/Pd/C core-shell catalyst delivering significantly better ORR performance than PtPd/C alloy with same composition; identical performance as Pt/C but with four times less Pt**
- **LANL fuel cell test data with catalyst from a 5 g batch agreeing with Cabot's testing within 5 mV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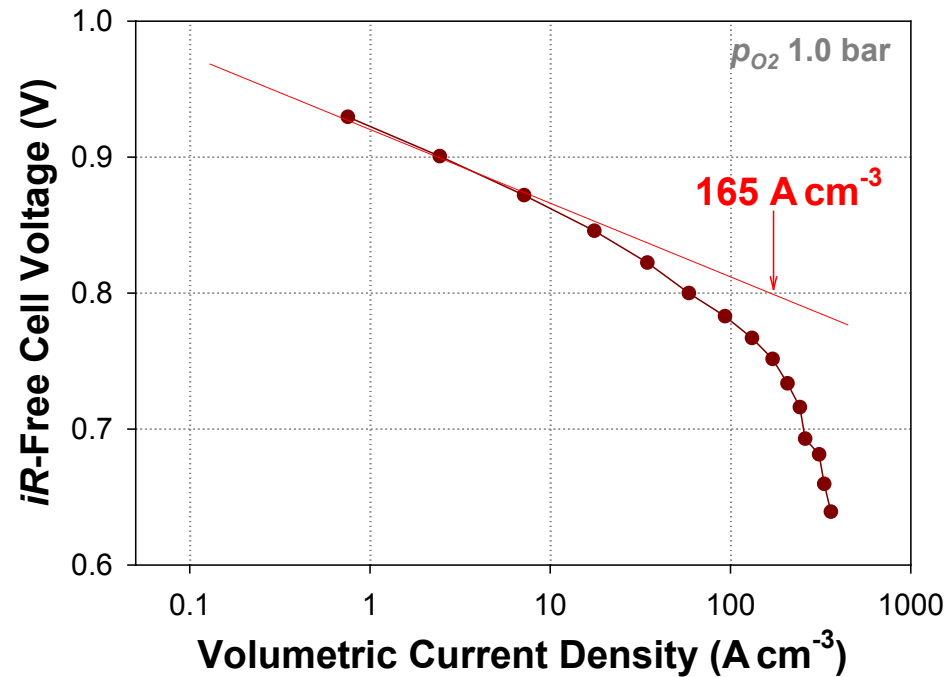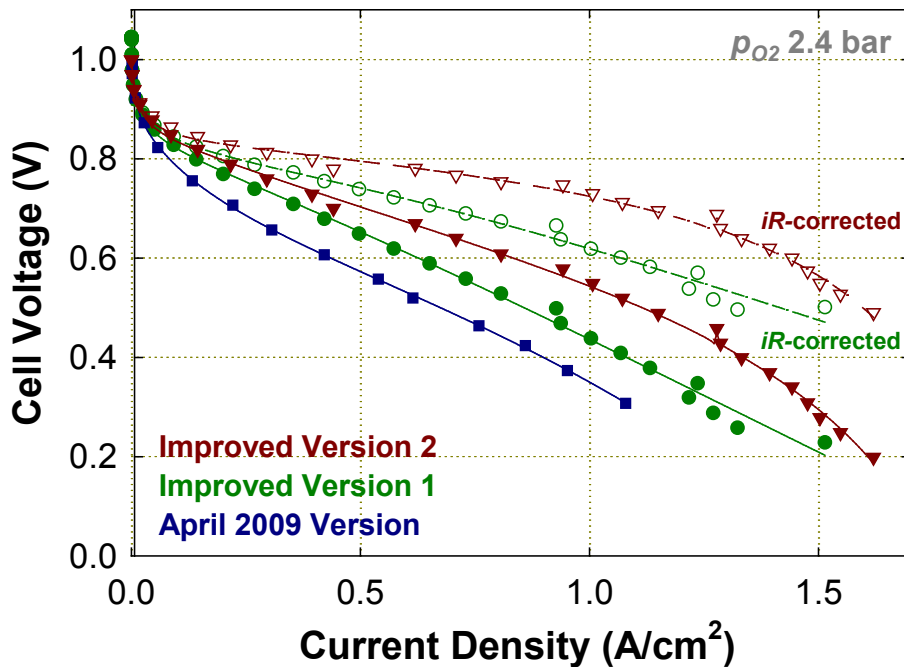


- • **Version 1** achieved with change in the carbon support and adjustment of precursor ratios
- • **Version 2** generated by including additional sulfur-containing precursor

  **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)

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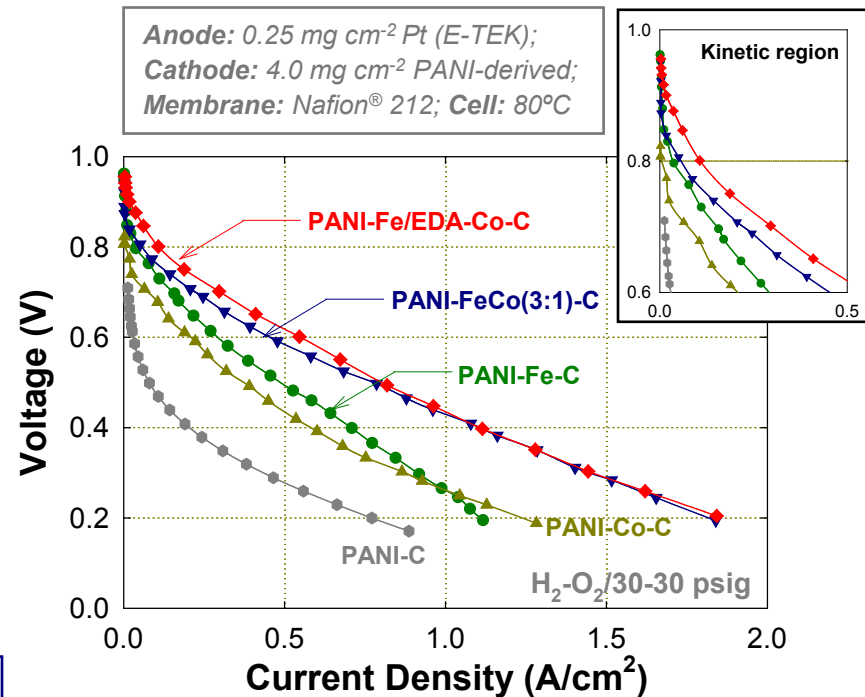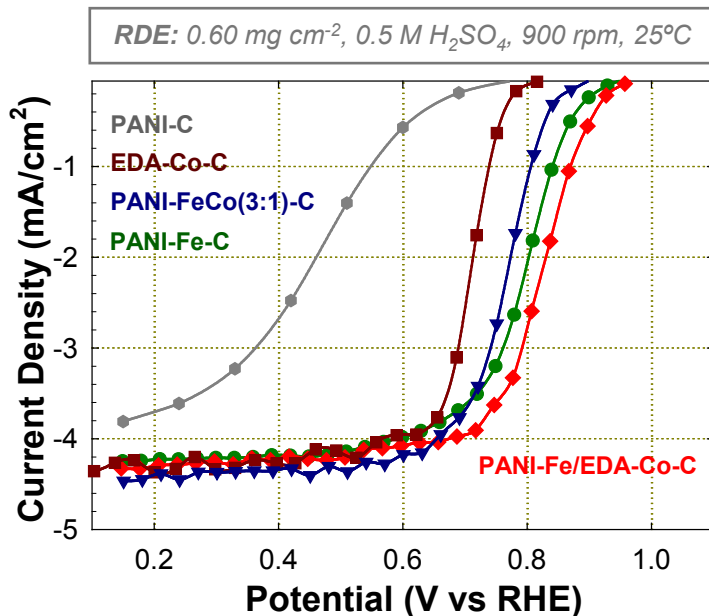# Cyanamide-Fe-C Catalyst: Sulfur Content and Performance
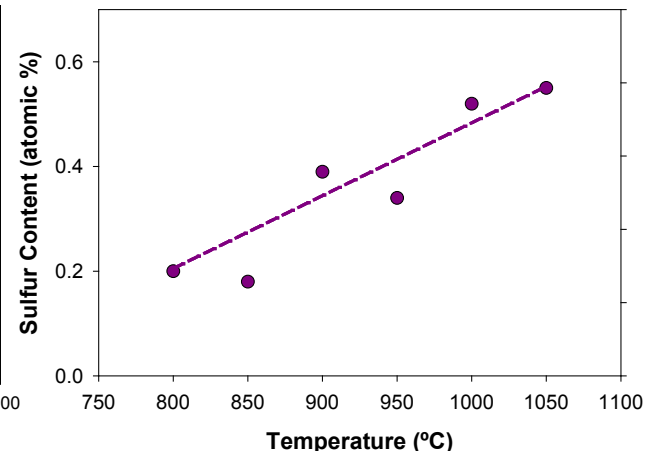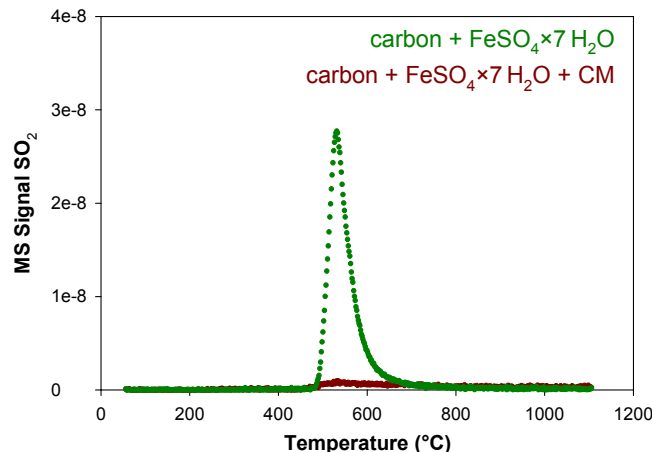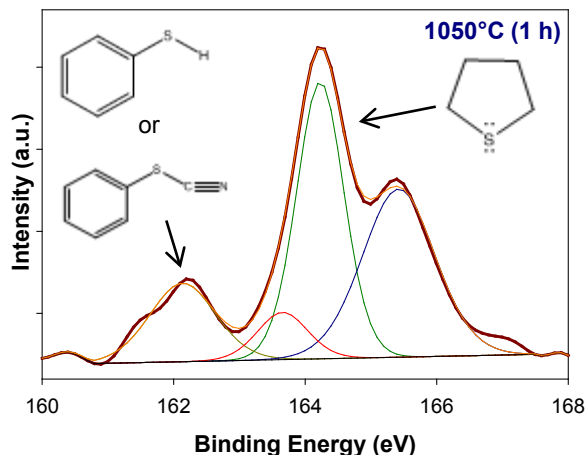


## Visualization of Possible Sulfur Sites
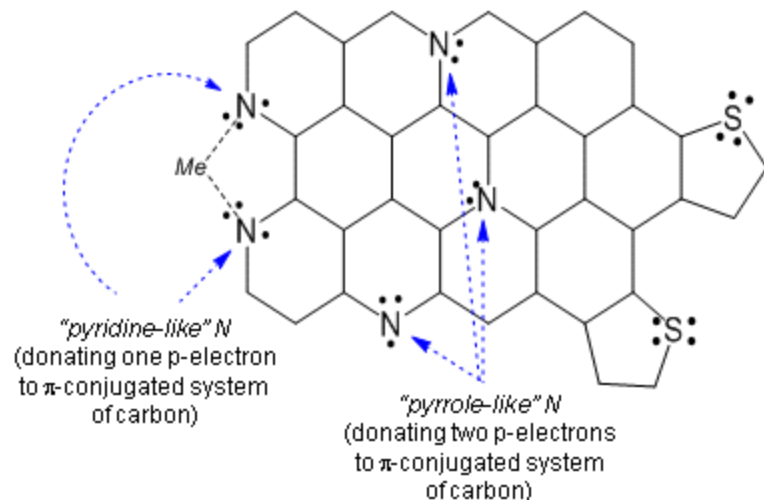


- **Sulfur found mostly in thiophene-like form (XPS); sulfur loss suppressed by cyanamide ($SO_2$ MS signal)**
- **Sulfur content increased as heat-treatment temperature increased (XPS); overall, tendency for activity increase with temperature**
- **Role of sulfur either electronic via ORR active sites 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*

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



*RDE: 0.60 mg cm$^{-2}$, 0.5 M H$_2$SO$_4$, 900 rpm, 25ºC*

PANI-C
EDA-Co-C
PANI-FeCo(3:1)-C
PANI-Fe-C

PANI-Fe/EDA-Co-C

*Anode: 0.25 mg cm$^{-2}$ Pt (E-TEK);*
*Cathode: 4.0 mg cm$^{-2}$ PANI-derived;*
*Membrane: Nafion® 212; Cell: 80ºC*

Kinetic region

PANI-Fe/EDA-Co-C
PANI-FeCo(3:1)-C
PANI-Fe-C
PANI-Co-C
PANI-C

H$_2$-O$_2$/30-30 psig

H$_2$-O$_2$/11-11 psig ($p_{O2}$ 1.0 bar)

4.0 mg/cm$^2$
1.0 mg/cm$^2$
PANI-Fe/EDA-Co-C

- **Highlight:** Two-step process resulting in:

  ✓ **20 mV positive shift in $E_{1/2}$ 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**
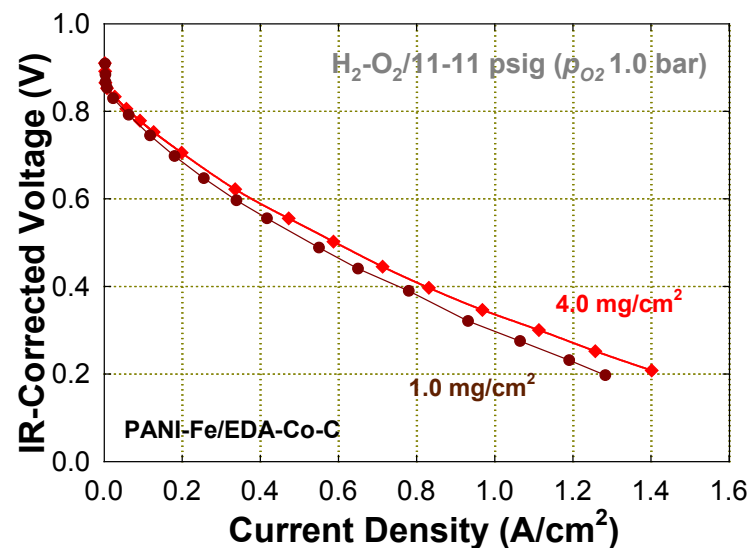
# PANI-Fe/EDA-Co-C: Performance Stability at 0.40 V and 0.60 V

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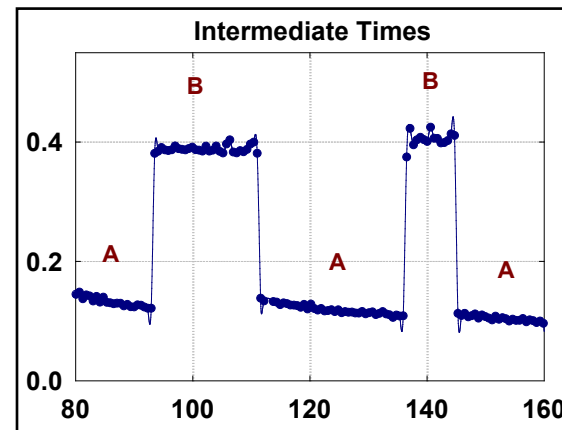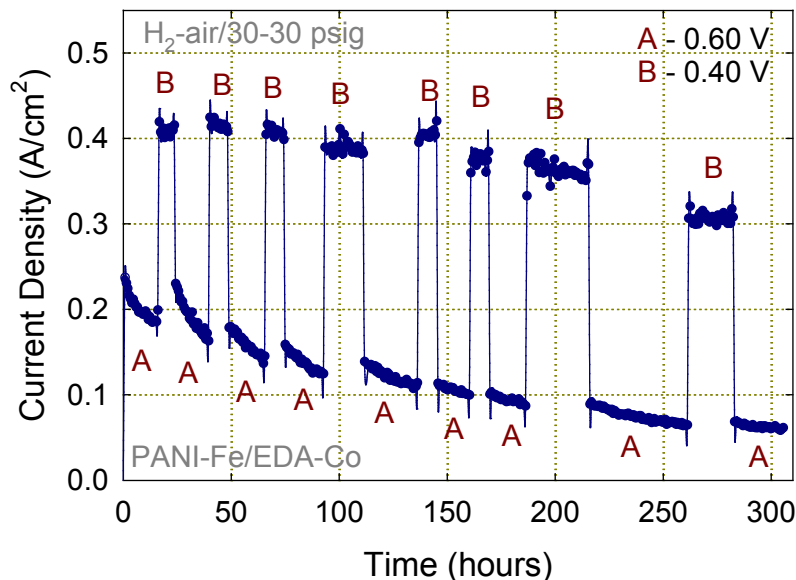


- **PANI-Fe/EDA-Co showing high durability at 0.40 V**

- **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**
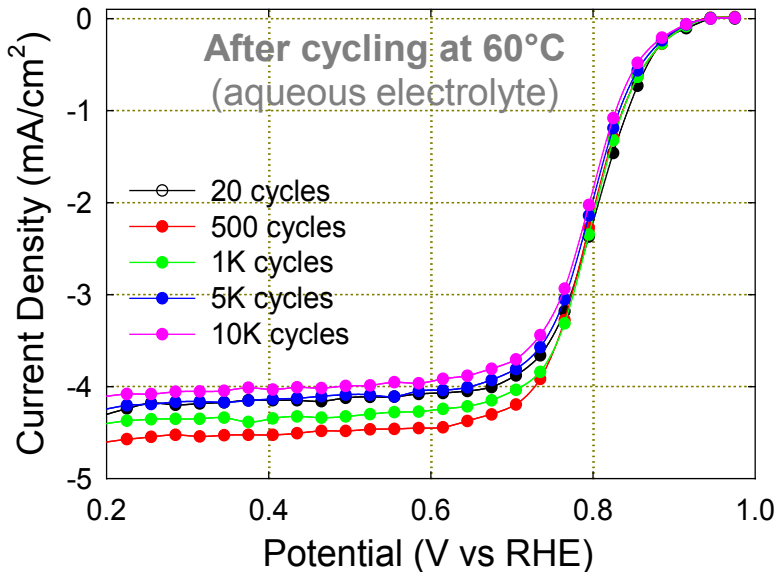
- **Advanced electrode structure design needed**
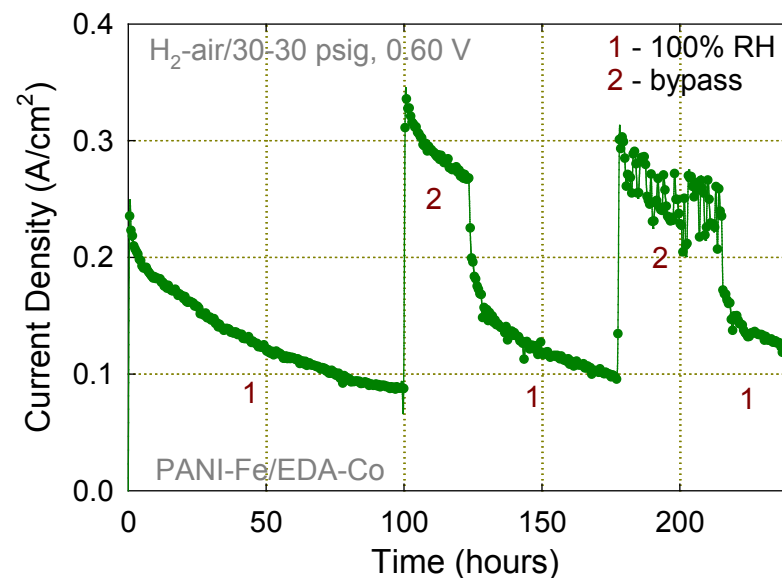
# PANI-Fe-C: Effect of Potential Cycling on Activity

*RDE: 0.6 mg cm$^{-2}$; 0.5 M H$_2$SO$_4$; 900 rpm; **Cycling**: 50 mV/s, 0.0-1.0 V in 0.5 M N$_2$-saturated H$_2$SO$_4$*

*Anode: 0.25 mg cm$^{-2}$ Pt; **Cathode**: 2.0 mg cm$^{-2}$ PANI-Fe-C ; **Membrane**: NRE-212; **Cell**: 80°C; H$_2$-O$_2$/1.0-1.0 bar; **Cycling**: 0.6-1.0 V, 50 mV/s, N$_2$ at 100% RH*
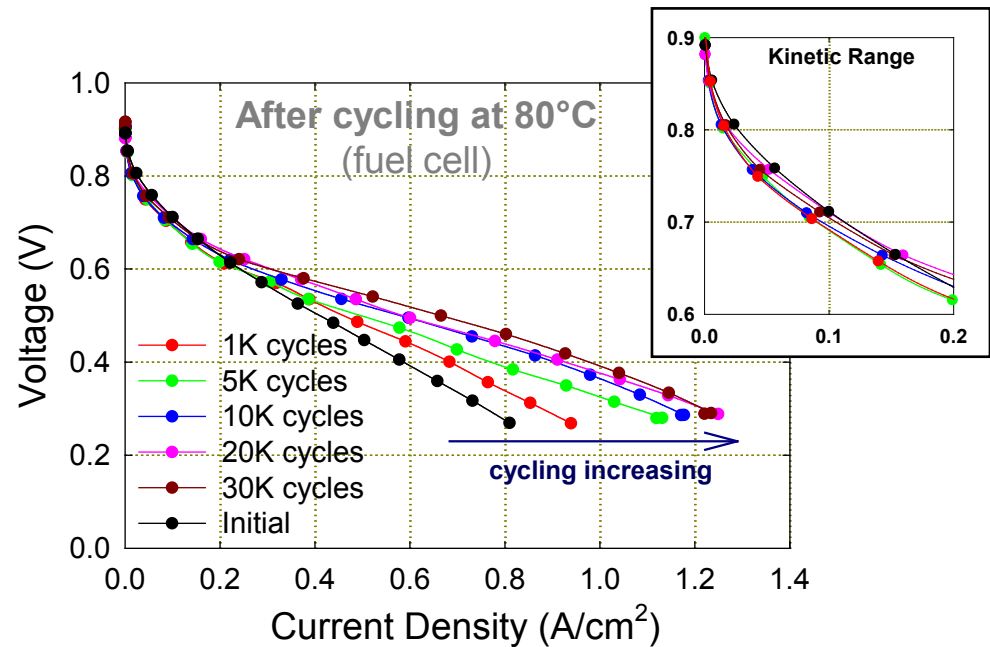


- **Highlight**: **Only ~10 mV loss in $E_{1/2}$ at RDE testing after 10,000 potential cycles at 60°C**

- **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**

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# 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:* 80°C
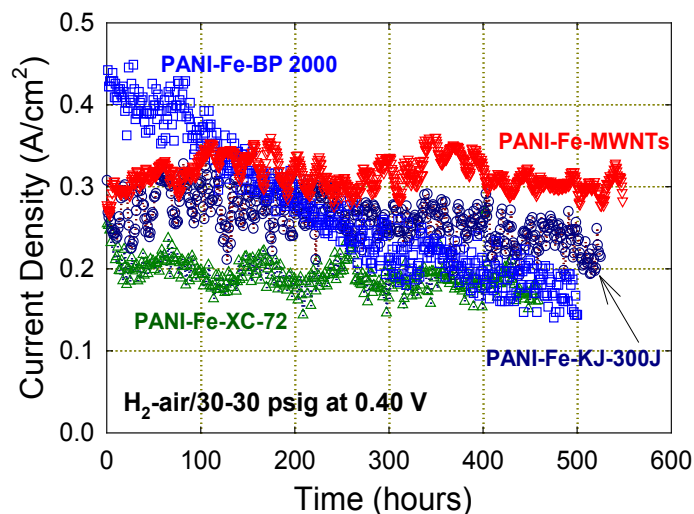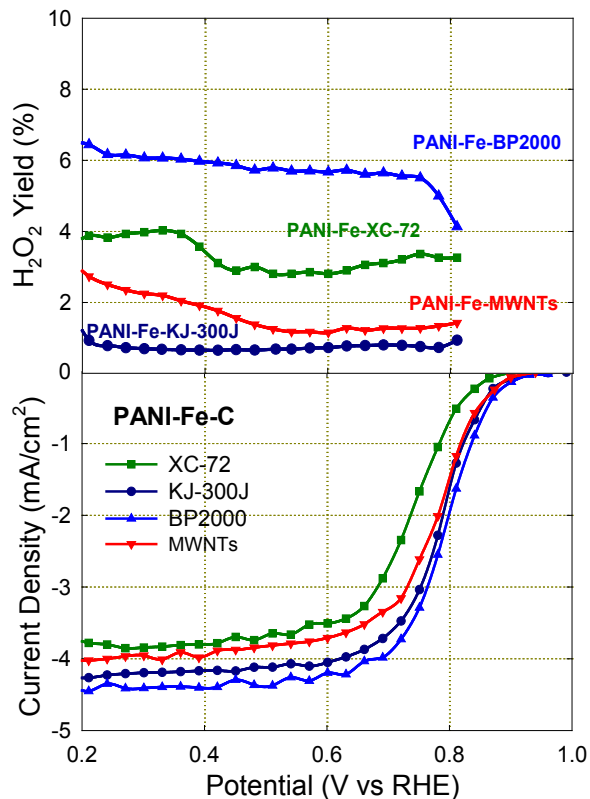


BP 2000 – Black Pearls 2000
KJ-300J – Ketjenblack EC-300J
XC-72 – Vulcan XC-72
MWNTs – multi-walled nanotubes

| Catalyst | Corrosion Resistance of Support Carbon | % H$_2$O$_2$ 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$_2$O$_2$ 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)**

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

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



TEM | HAADF-STEM | SEM
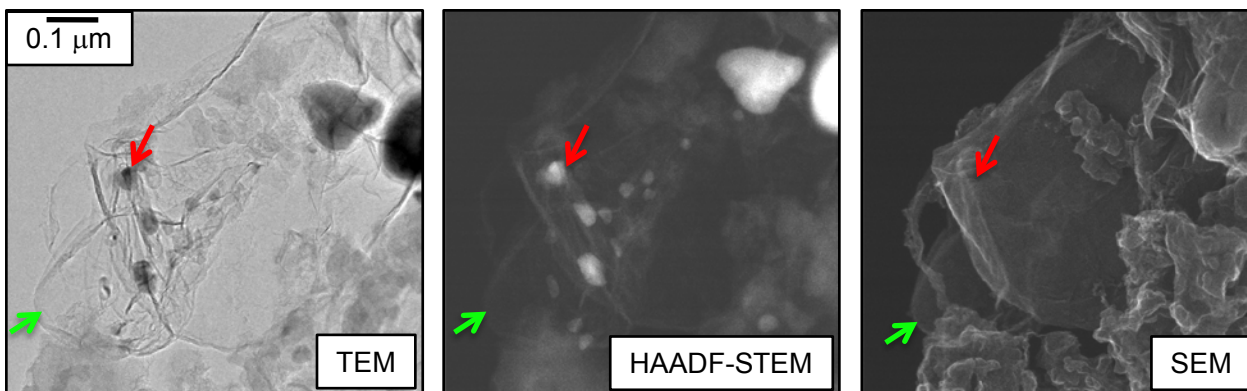
## PANI-Fe-MWNT: Three images, same spot



TEM | HAADF-STEM | SEM
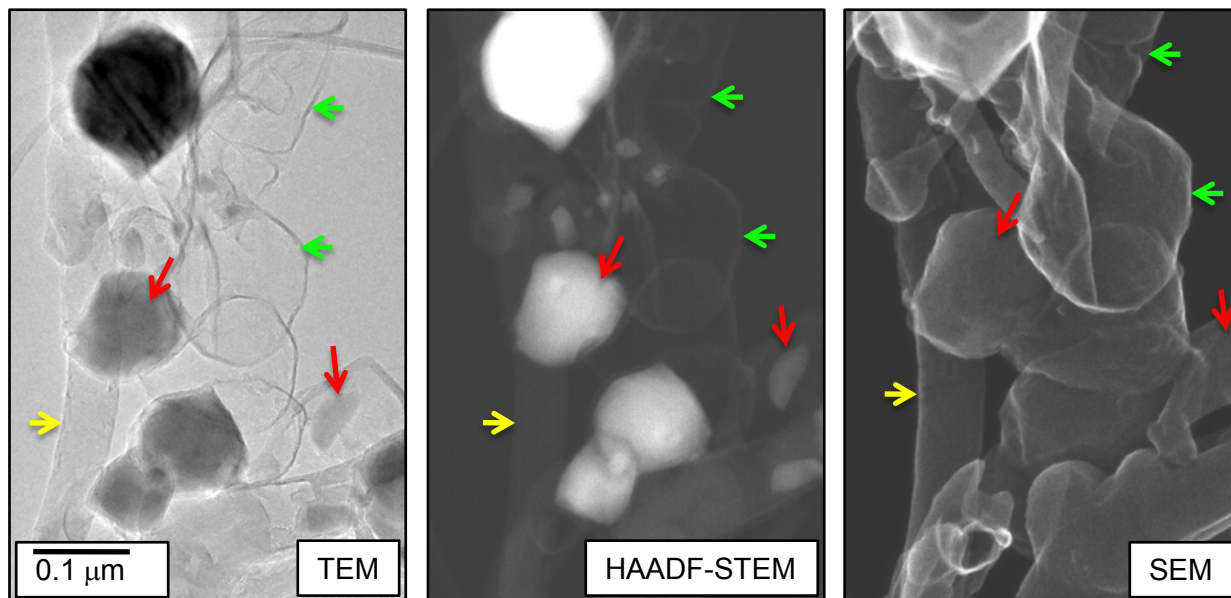
- **The two most durable catalysts showing notable similarities in morphology**
- **Significant number layered graphene "bubbles" formed in PANI-FeCo(3:1) and PANI-Fe-MWNT (→), co-located with the Fe(Co)$S_x$ regions/particles (→); MWNT still present (→)**
- **BF-STEM images of PANI-Fe-MWNT showing graphitic 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
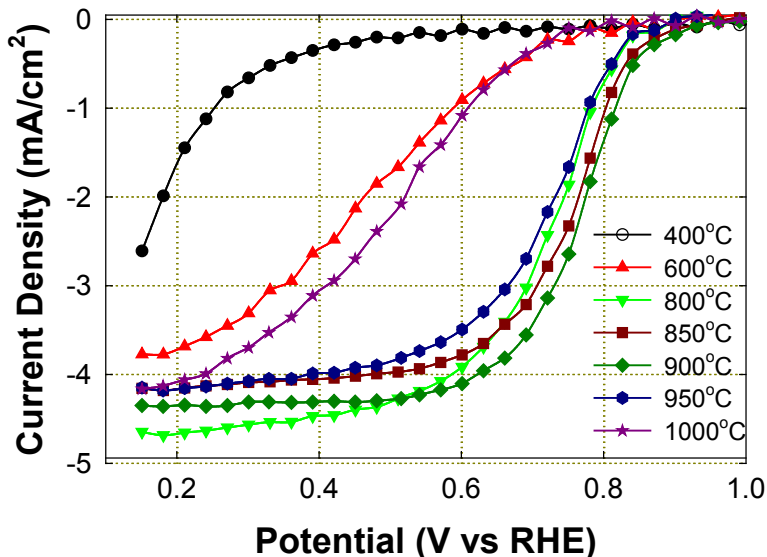


- **Catalysts synthesized at 900ºC consistently showing the highest ORR activity; samples prepared at 850ºC, 800ºC, and 950ºC also ORR active**

- **900ºC sample containing <u>the highest amount </u>of Fe-phthalocyanine-type coordination**

- **<u>Highlight</u>: 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
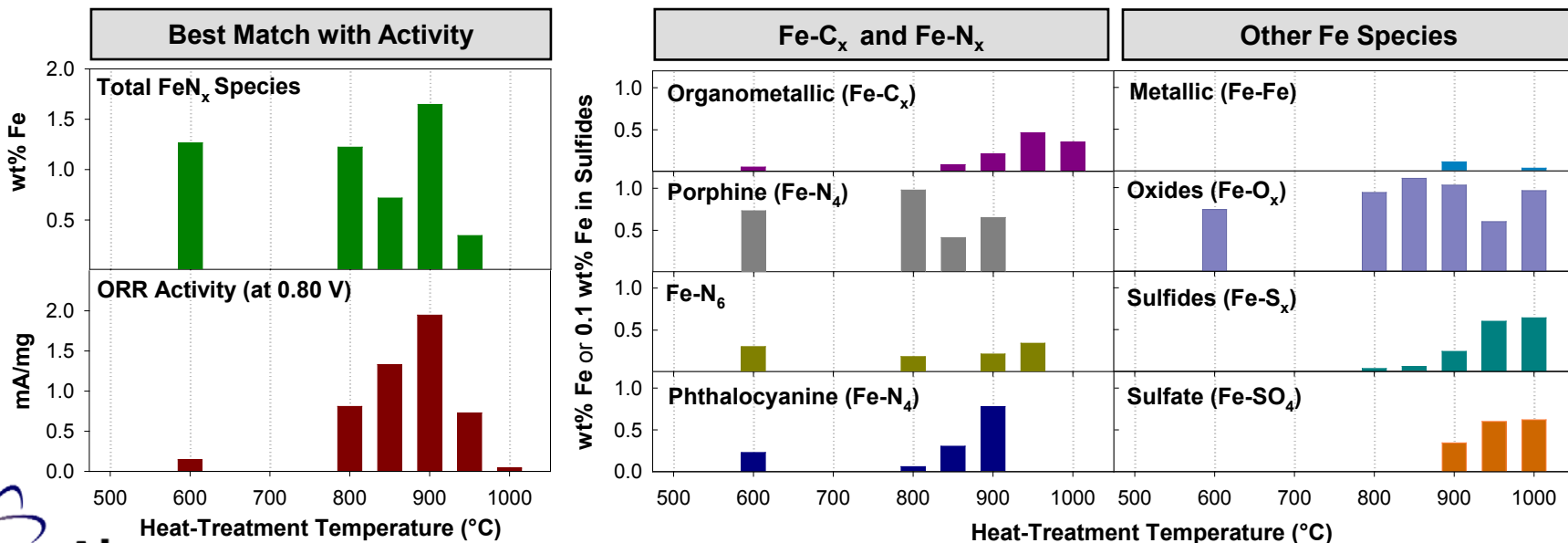
# PANI-Fe-C: Effect of Heat-Treatment Temperature on Surface Area and Pores

- **All samples heat-treated twice, as specified in synthesis procedure**

- **Sample heat-treated at 900°C 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**

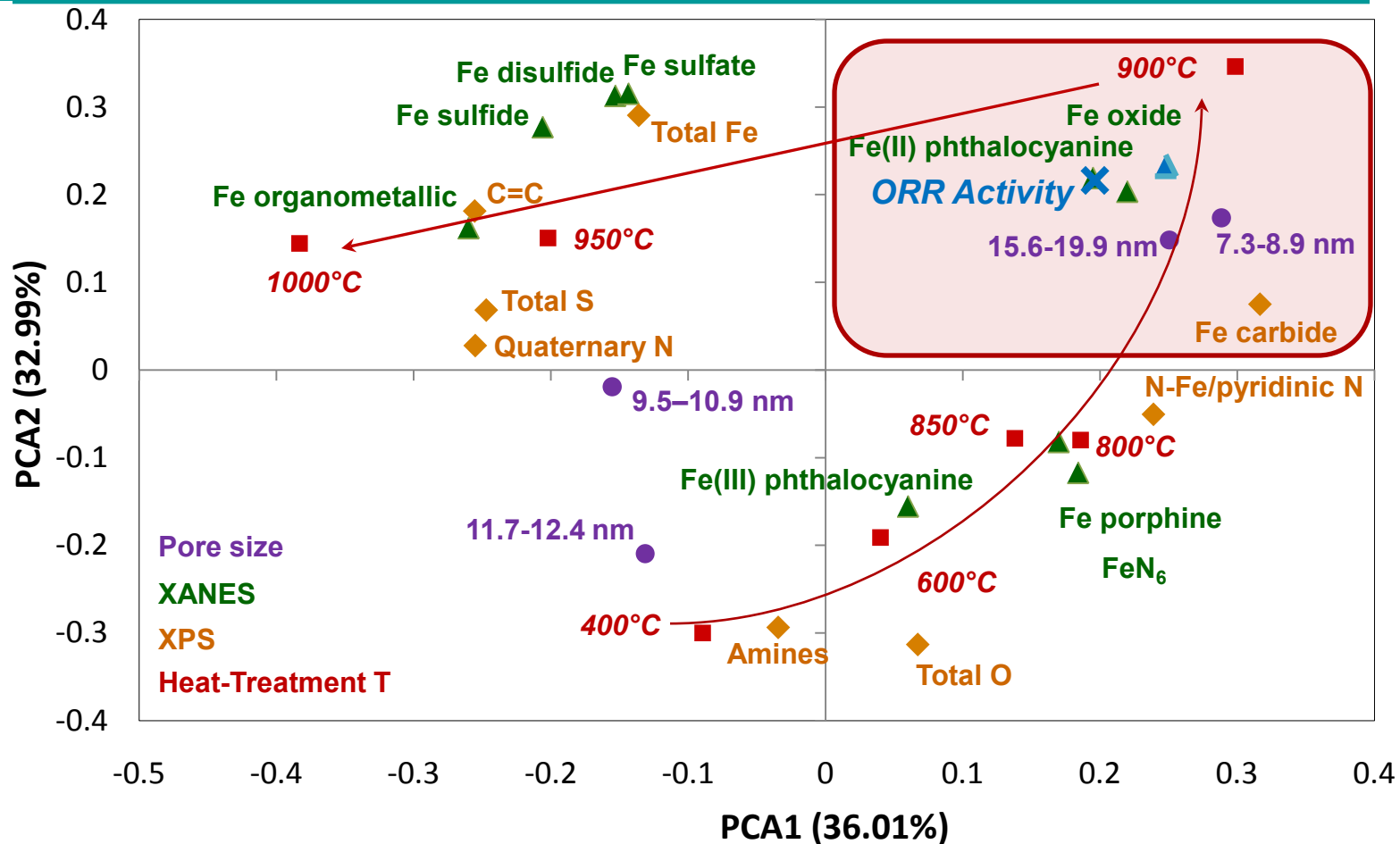  * M. Lefèvre *et al.*, *Science,* **324**, 71-74, 2009
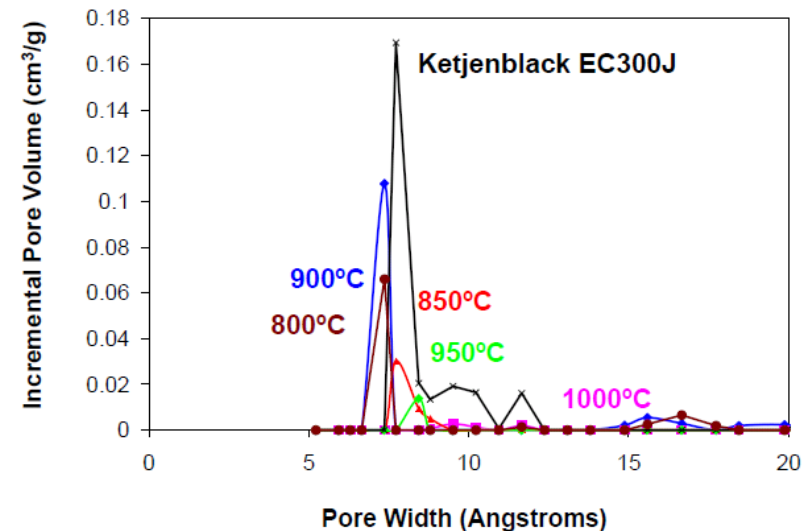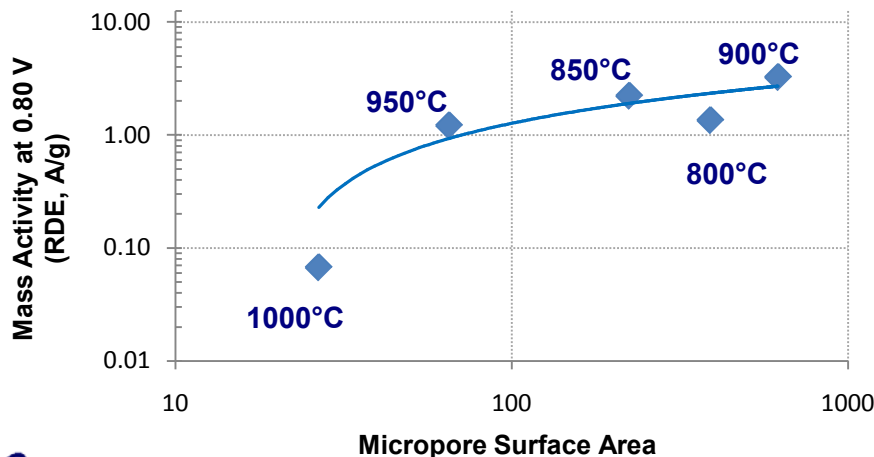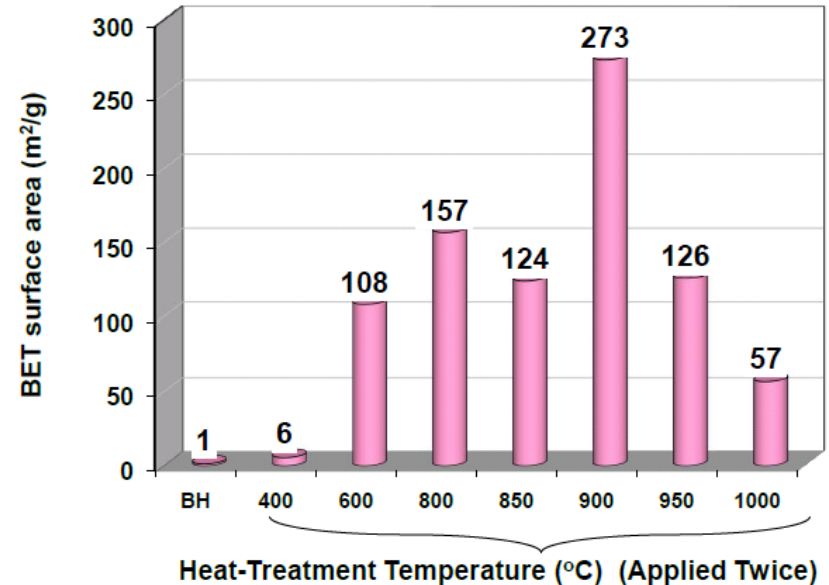
# PCA: Correlation of Combined Characterization Data and Activity



*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.)*

Plot axes: PCA2 (32.99%) vs PCA1 (36.01%)

Legend:
- Pore size
- XANES
- XPS
- Heat-Treatment T

Labeled points: Fe disulfide, Fe sulfate, Fe sulfide, Total Fe, Fe organometallic, C=C, Fe(II) phthalocyanine, ORR Activity, Fe oxide, 900°C, 15.6-19.9 nm, 7.3-8.9 nm, 1000°C, 950°C, Total S, Quaternary N, Fe carbide, N-Fe/pyridinic N, 9.5–10.9 nm, 850°C, 800°C, Fe(III) phthalocyanine, Fe porphine, FeN$_6$, 11.7-12.4 nm, 600°C, 400°C, Amines, Total O
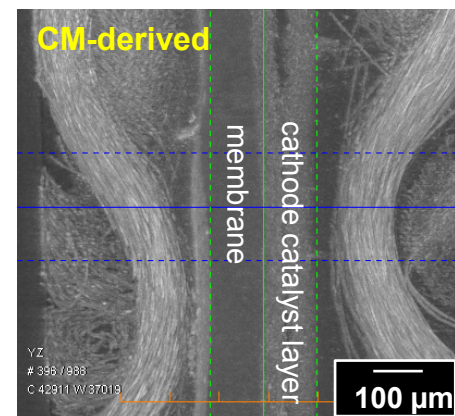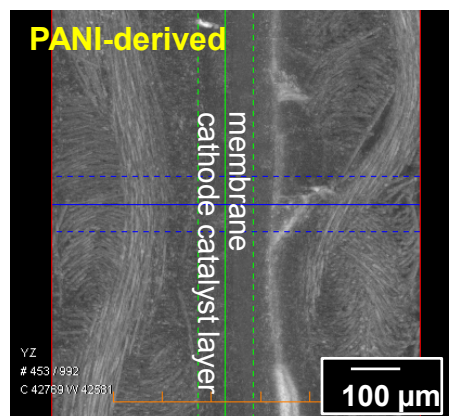
- Fe-N-type coordination, correlated with ORR activity and ORR-active samples (900°C, 850°C, 800°C), remaining a primary candidate for active site
- **Highlight**: The most active, 900°C catalyst having the highest BET surface area, a bimodal pore distribution, high initial content of Fe carbide, Fe in oxide-like coordination environment, and Fe in phthalocyanine-like coordination

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# 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$_2$SO$_4$** (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$^3$*



PANI-derived

membrane | cathode catalyst layer

100 µm

CM-derived

membrane | cathode catalyst layer

100 µm

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# 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 $E_{1/2}$ after 20,000 scans) and Pt$_{ML}$/Pd$_2$AuNi/C nanoparticles ($\Delta E_{1/2}$ 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**

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# Co-Authors

**BROOKHAVEN** NATIONAL LABORATORY – **catalysts with ultra-low Pt content**

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

**ILLINOIS** UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN – **chalcogenide-based catalysts**

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

**Los Alamos** NATIONAL LABORATORY – **non-precious metal catalysts; characterization**

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

The University of New Mexico – **open-frame catalyst structures**

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

**UCRIVERSIDE** UNIVERSITY OF CALIFORNIA – **nanostructure catalyst structures**

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

**Argonne** NATIONAL LABORATORY – **characterization & durability**

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

**ornl** – **characterization**

K. More (PI)

**CABOT** – **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:* 80°C



#1: Pt/AuPd/C
#2: Pt/AuPd$_3$Fe/C
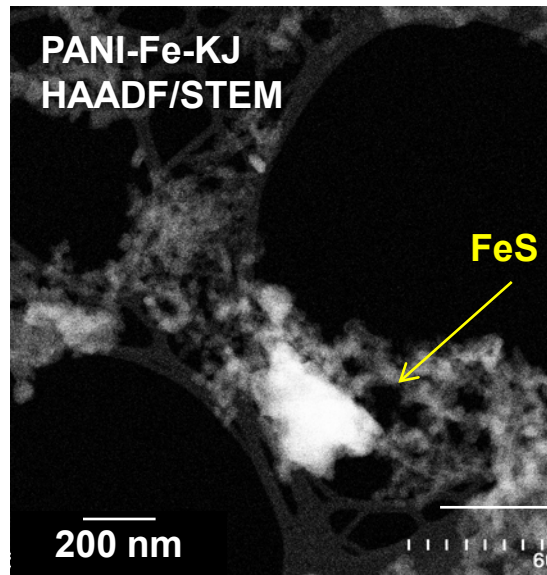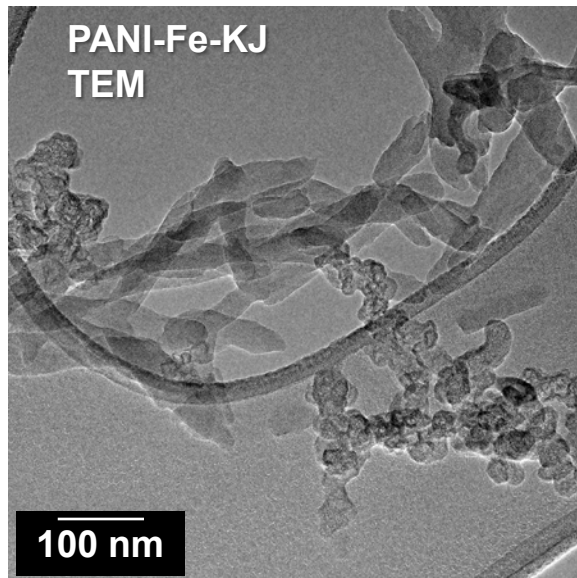#3: Pt$_{80}$Ir$_{20}$Pd/C

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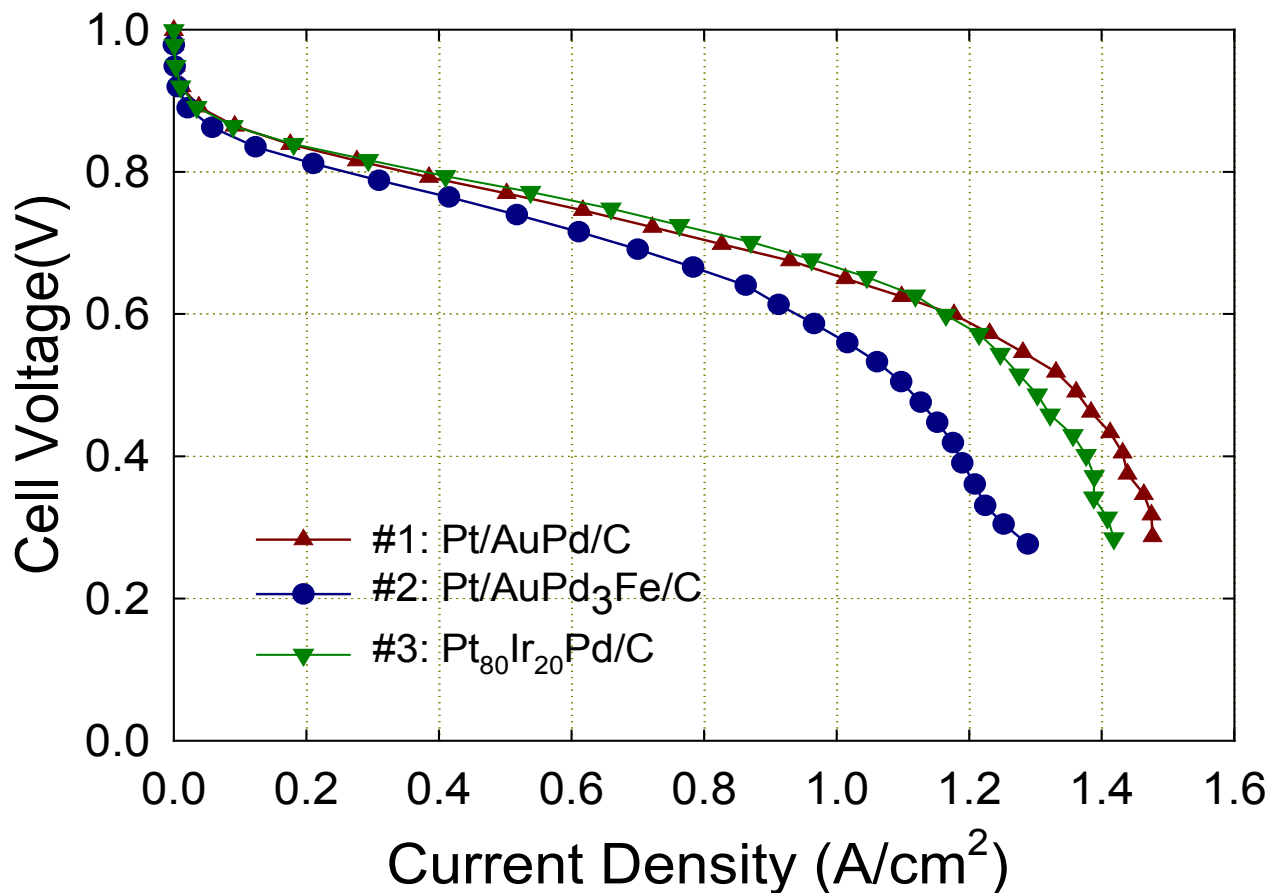
# PANI-FeCo(3:1)-C: Stability Testing at Different Voltages

*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
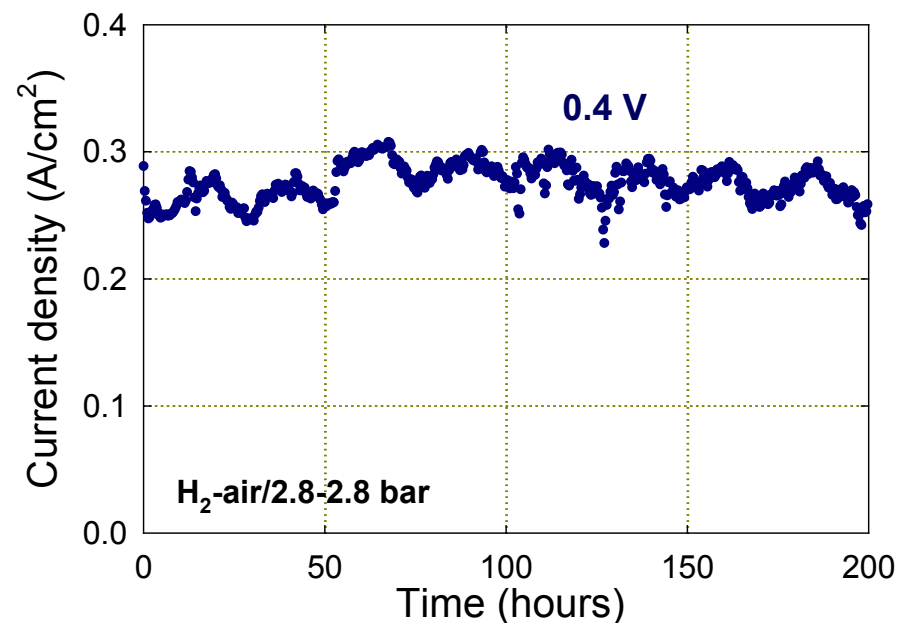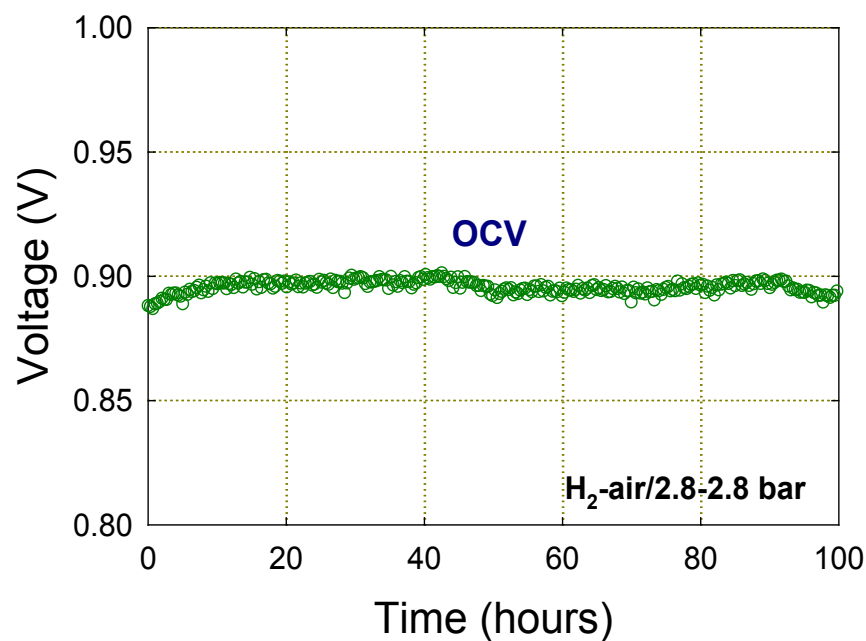


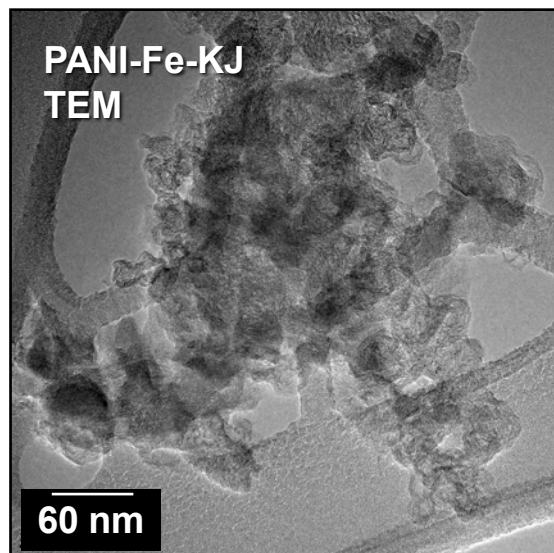**Open-cell voltage of an H₂-air cell maintained at *ca*. 0.90 V for more than 100 hours**

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



PANI-Fe-KJ
TEM

100 nm



PANI-Fe-KJ
HAADF/STEM

FeS

200 nm



PANI-Fe-MWNT
TEM

100 nm



C = blue
Fe = red
Ni = green

200 nm

PANI-Fe-MWNT
Elemental map
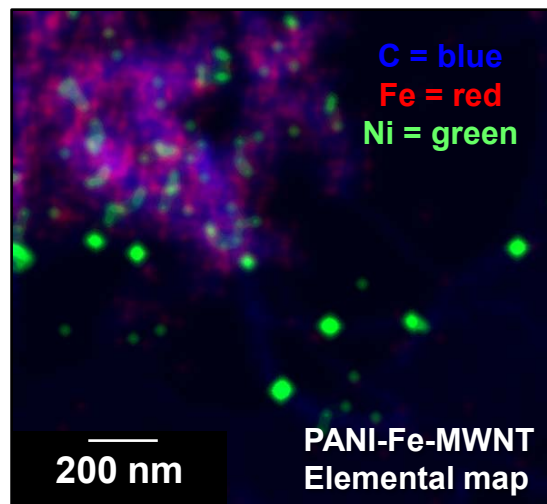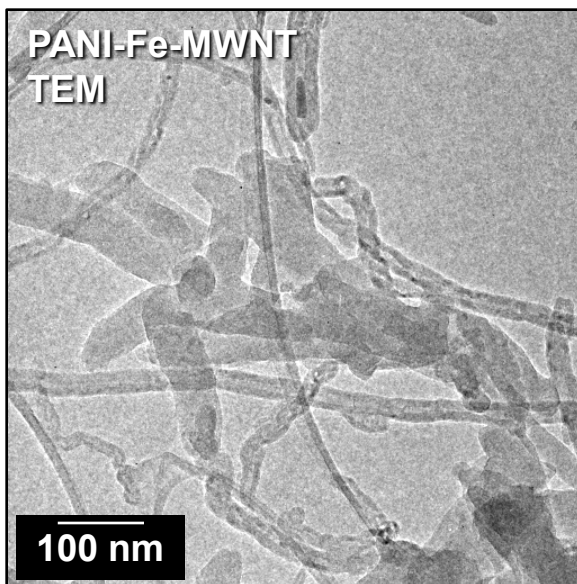
- Separate PANI fibers and support particles (KJ, MWNTs) observed in both sample types

- "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

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



PANI-Fe-KJ TEM — 60 nm



SEM — 150 nm



HAADF/STEM — 150 nm



PANI-Fe-MWNT TEM — 200 nm



PANI-Fe-MWNT BF-STEM — FeS$_x$ — graphite — 10 nm
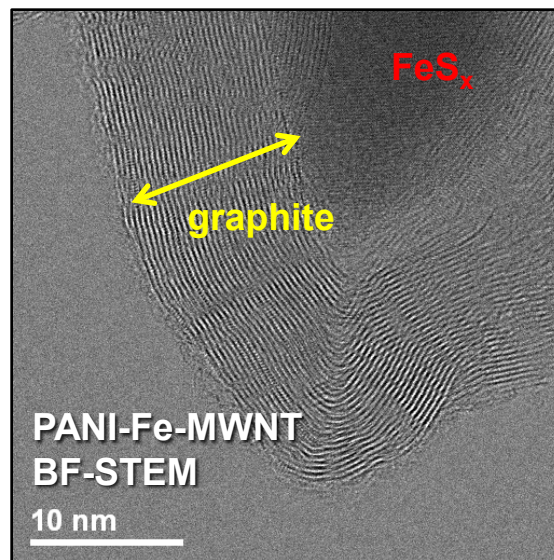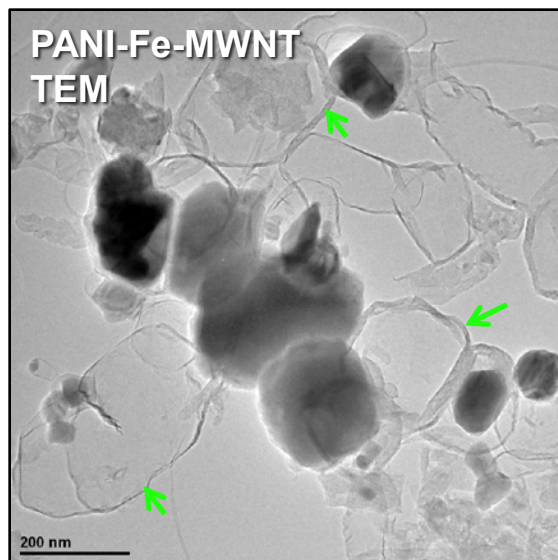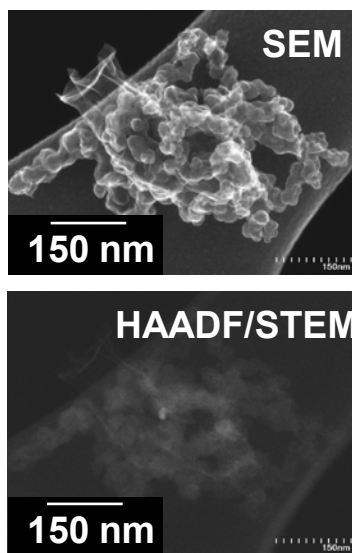
- Final catalysts obtained after heat-treatment, acid-treatment, and 2nd heat-treatment
- "PANI-derived" and "support-derived" particles still observed in both sample types
- Fe and S remaining dispersed across KJ-derived particles
- Very small amount of "graphene sheet" structure observed in PANI-Fe-KJ – 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

**Fe⁰**
**Fe metal**

**Fe²⁺ compounds**
**Fe0**
**Fe²⁺ phthalocyanine (at right)**
**Fe₂N**
**Fe₄N**
**FeSO₄ anhydrous**
**FeSO₄ 7H₂O**
**Fe II acetylacetonate**
**Ferrocene (at right)**
**FeS**
**FeS₂**
**tris(2,2'-bipyridine) Iron(II)**
**    hexafluoro-phosphate (at right)**
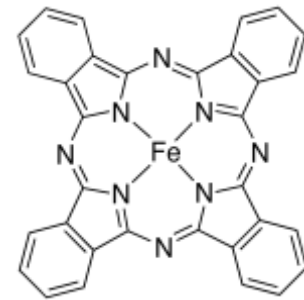**1,10-phenanthroline Iron(II) sulfate**
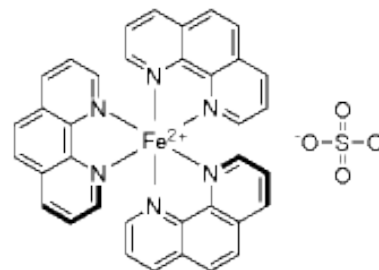**    complex (at right)**

**Fe³⁺/²⁺ compounds**
**Fe₃O₄**

*Activity of non-precious catalysts attributed by many groups to FeN₄– type or FeN₂₊₂–type sites*
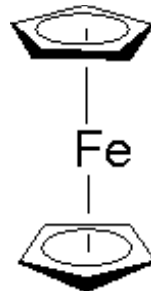


**di(cyclopentadienyl) iron (ferrocene) (organometallic)**



**iron(II) phthalocyanine**

*High degree of symmetry of Fe²⁺ 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 (FeN₆)**
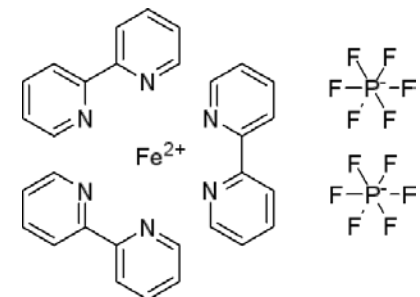


**tris(2,2'-bipyridine) iron(II) hexafluoro-phosphate (FeN₆)**

# PANI-Fe-C XAS: XANES Iron Standards

**Fe$^{3+}$ compounds**
**FeCl$_3$ 6H$_2$O**
**Fe III acetylacetonate**
**Fe(NO$_3$)$_3$ 9H$_2$O**
**Fe$_2$O$_3$**
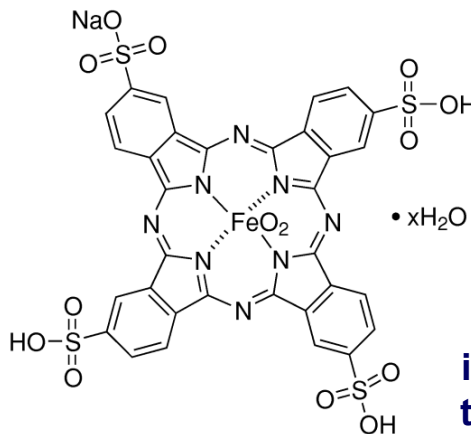**Fe porphine (at right)**
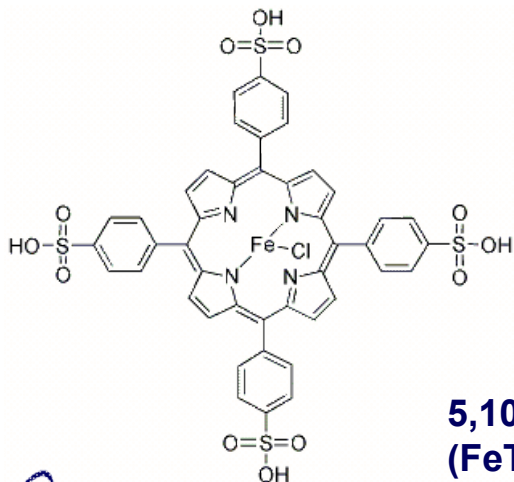**Fe$^{3+}$ phthalocyanine (at right)**
**modified Fe$^+$ porphine**
**(FeTPPS, below)**
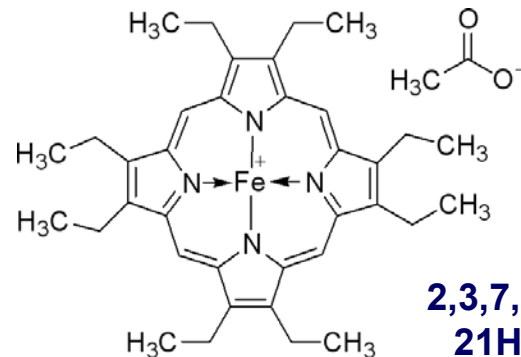
**2,3,7,8,12,13,17,18-octaethyl-21H,23H porphine iron(III) acetate (porphine)**

**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)**

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# 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**

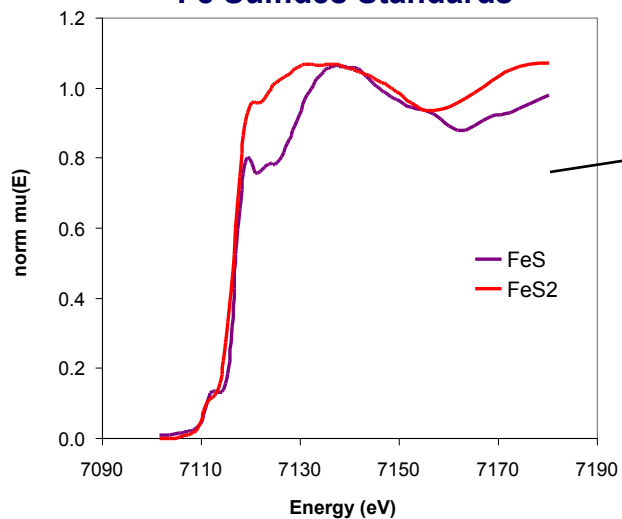- **XAFS edge step and/or destructive ICP-OES analyses yielding total loading of Fe in materials**
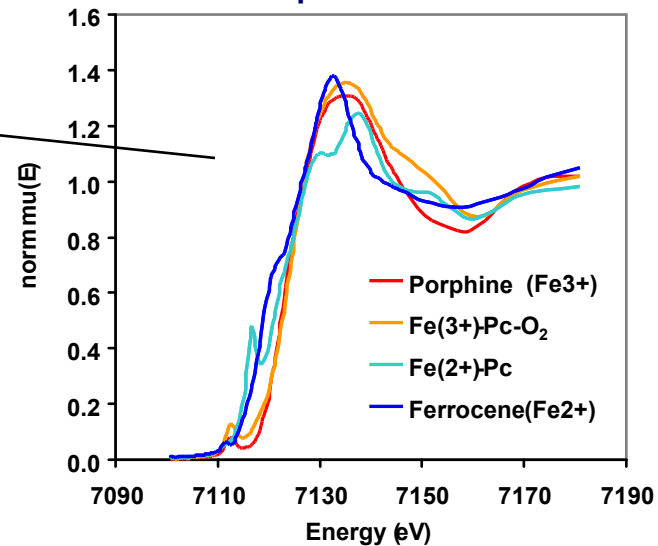
**Fe Metal/Fe Oxides Standards**
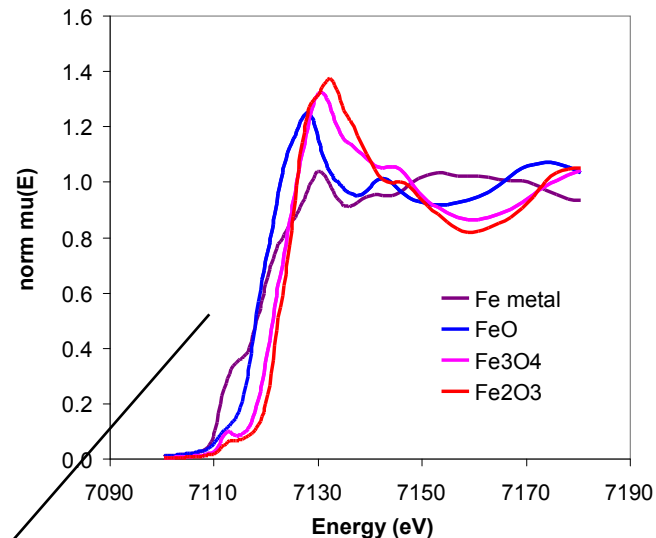


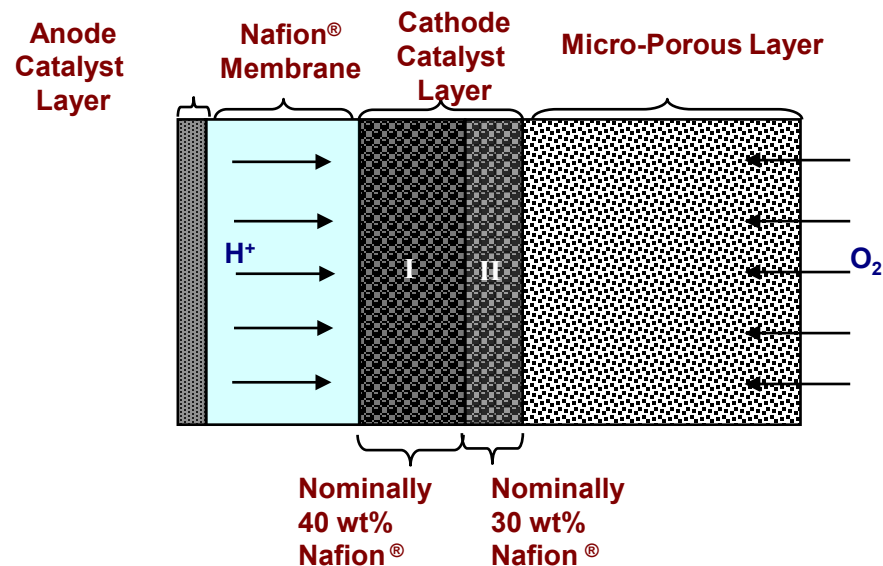**Fit of Spectrum by Linear Combination of Standards**
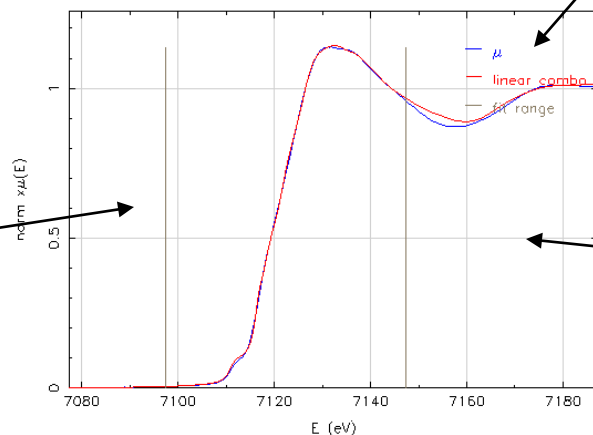


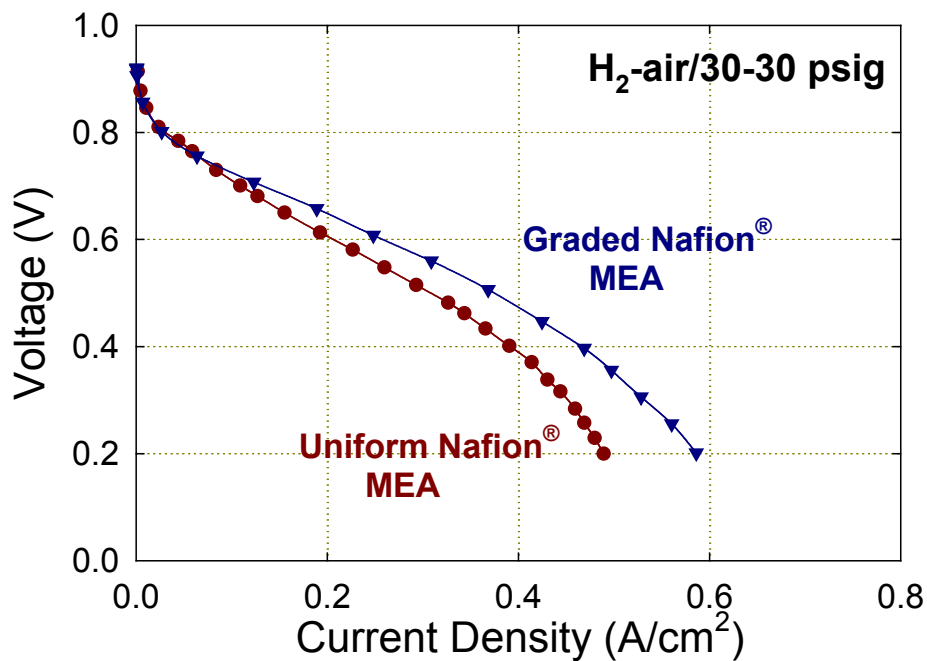**Fe Sulfides Standards**



**Examples of Fe-Complexes Standards**
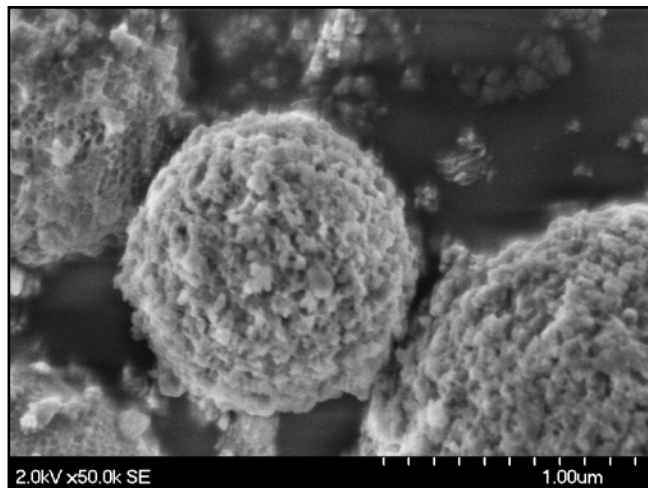
# Graded Nafion® Content: Impact on Performance of PANI-Fe-C

*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: 80°C*



H$_2$-air/30-30 psig

Graded Nafion® MEA

Uniform Nafion® MEA

Voltage (V)

Current Density (A/cm$^2$)

Anode Catalyst Layer

Nafion® Membrane

Cathode Catalyst Layer

Micro-Porous Layer
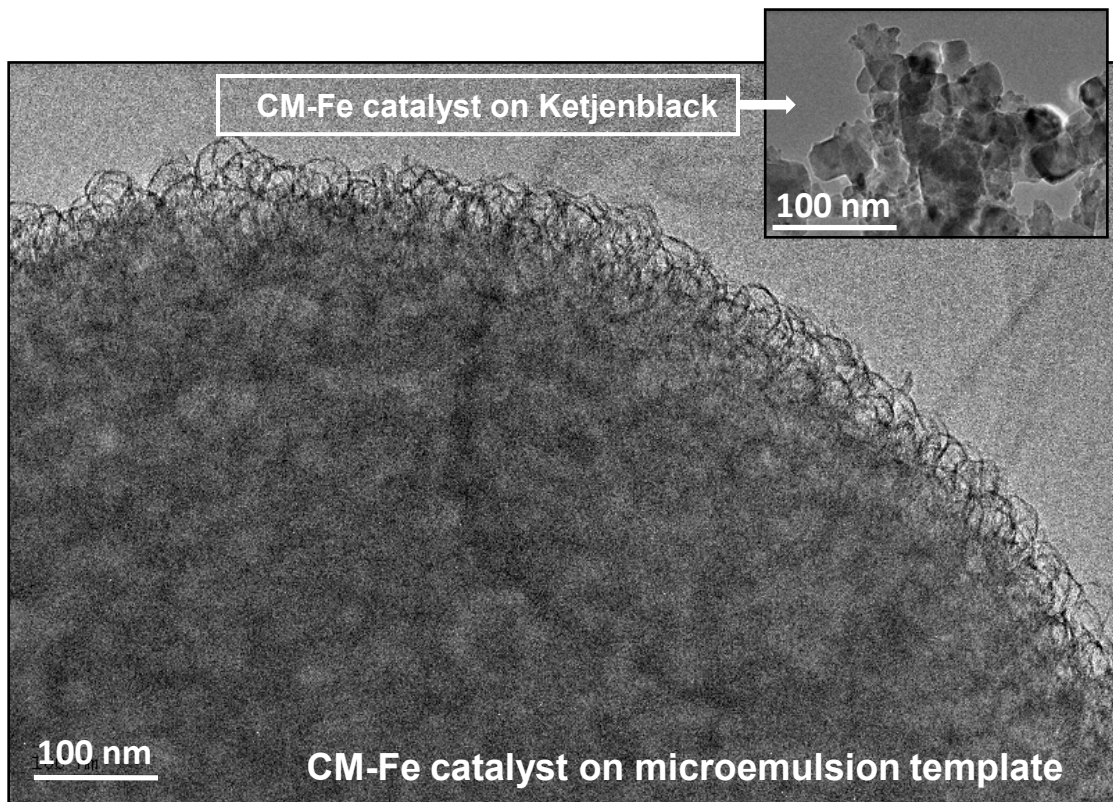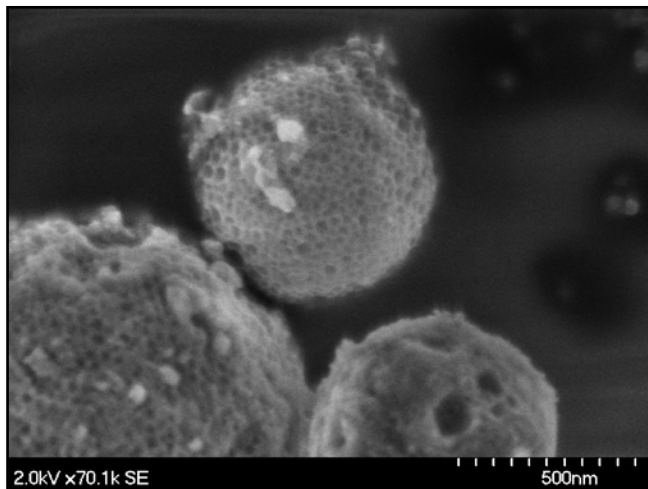
H$^+$

O$_2$

Nominally 40 wt% Nafion®

Nominally 30 wt% Nafion®

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

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

**Templated CM-Fe-C after pyrolysis, no etch**



2.0kV x50.0k SE          1.00um

**Templated CM-Fe-C after 7.0 M KOH etch**



2.0kV x70.1k SE          500nm



CM-Fe catalyst on Ketjenblack

100 nm

100 nm

CM-Fe catalyst on microemulsion template

- **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**

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- **Technology Development Manager:  Dr. Nancy Garland**

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