Science Magazine Highlight: Moving Towards Near Zero Platinum Fuel Cells

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DOE Fuel Cell Technologies Webinar – April 25, 2011

Outline

- **Introduction:**
  - rationale
  - recent developments in non-precious metal oxygen reduction reaction (ORR) catalysis
- **Low-temperature Oxygen Reduction Reaction (ORR) catalysts (PPy-Co-C)**
- **Catalysts obtained by heat treatment of organic and transition-metal precursors:**
  - polyaniline-derived catalysts as a best combination of activity and stability
  - cyanamide-based catalysts
  - ORR activity *vs.* catalyst structure and composition
- **Summary**
- **Acknowledgements**

The Catalyst Cost Challenge

Analysis:

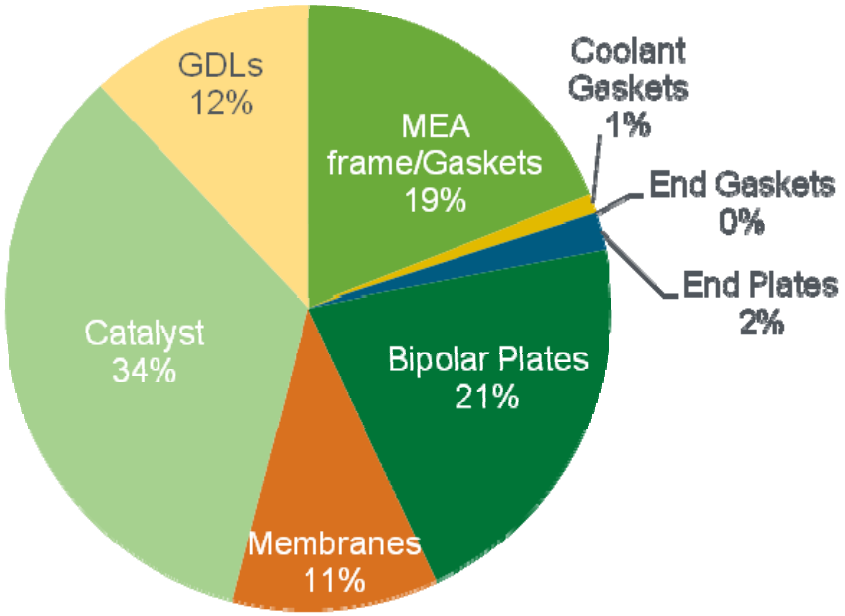
- Scaled to high-volume production of 500,000 units/year
- Assumed Pt cost of $1100/oz

Challenges:

- Platinum cost representing ~34% of total stack cost
- Catalyst durability in need of improvement

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

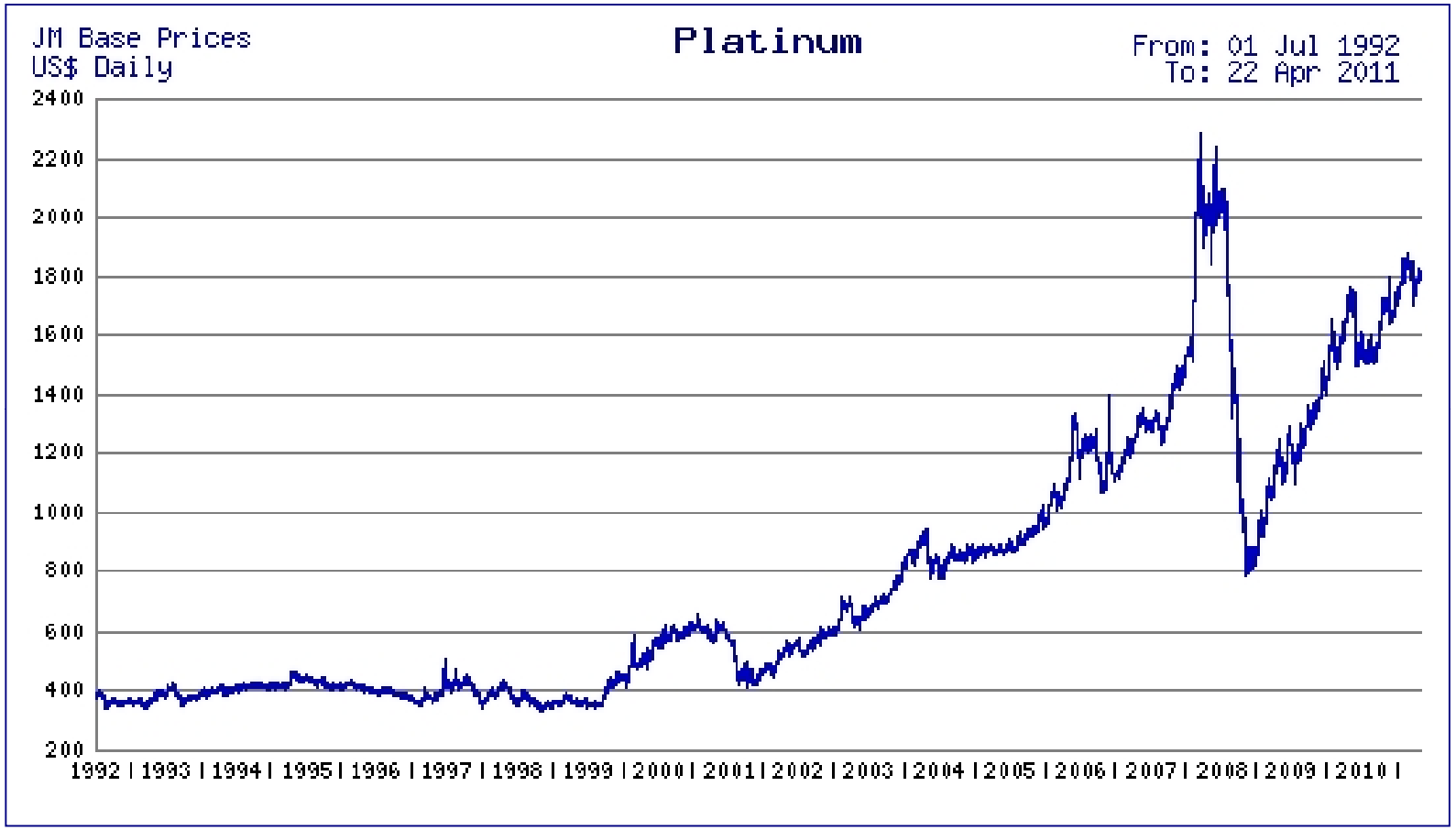
Stack Cost - $26/kW



Main strategies to address catalyst cost challenge:

- Reduction in the platinum group metal (PGM) content
- Improvements to Pt catalyst utilization and durability
- Pt alloy catalysts with comparable performance to Pt but costing less
- Non-precious metal catalysts with improved performance and durability

Platinum Challenge



Grand challenge: High platinum cost, price volatility, and resource concentration in virtually one location in the world (South Africa)

Non-Precious Metal ORR Catalysts

- Catalysts derived from **macrocycle precursors**, e.g. metal porphyrins, phthalocyanine, etc.

  Jasinski, 1968; CWRU (Yeager, Savinell; 1980s-1990s); 3M, 2000s; UNM, 2000s; Tokyo Tech, 2000s;

- Materials synthesized from **non-aromatic precursors by** heat treatment, e.g. ammonia, cyanamide, ethylenediamine

  INRS, 1990s-2000s; University of Calgary, 2000s; University of South Carolina *et al.* 2000s; Michigan State University, 2000s; LANL, 2000s

- Catalysts obtained via pyrolysis of **aromatic precursors**, including polymers (phenantroline, polypyrrole, polyaniline, etc.)

  INRS, 1990s-2000s; 3M, 2000s; LANL, 2000s

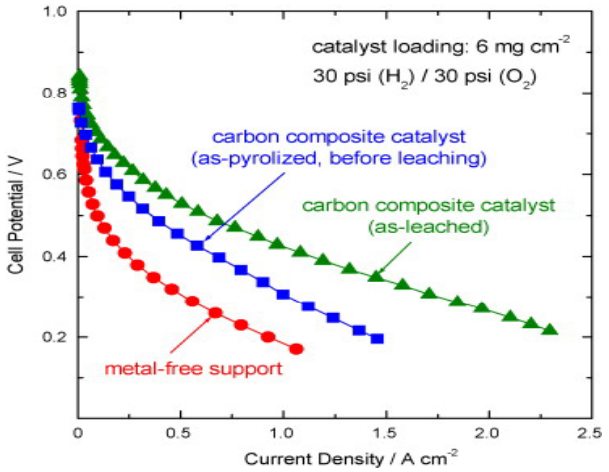
- **Inorganic ORR catalysts** obtained by high-temperature treatment, e.g. oxides, oxynitrides

  Yokohama National University *et* al., 2000s; Dalhousie University, 2000s

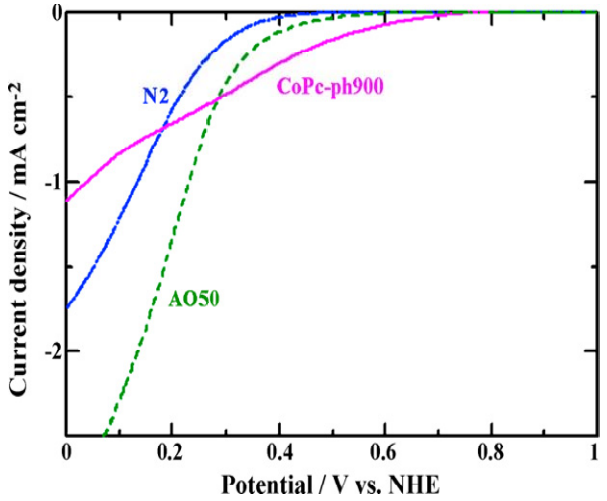
- **Catalysts produced without heat treatment**

  MIT, 2000s; LANL, 2000s; Daihatsu, 2000s; Indian Institute of Technology, 2000s

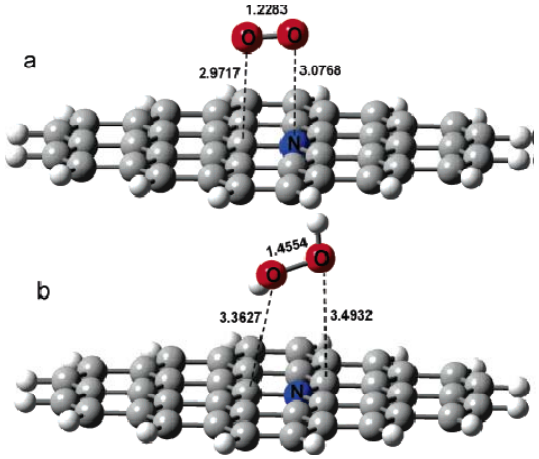
Non-Precious ORR Catalysis – Concept 1: Metal Not Participating in ORR

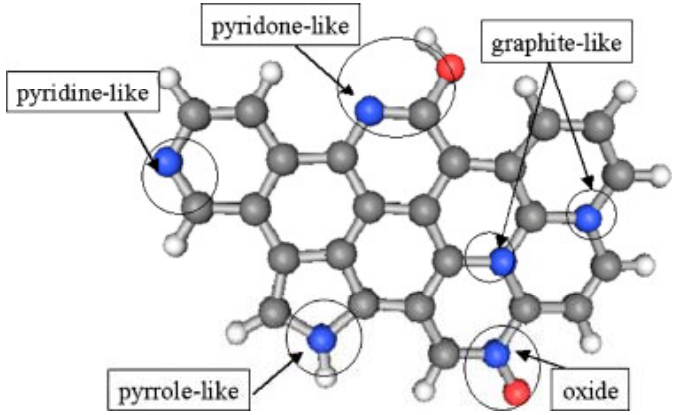


Nallathambi *et al*, *J. Power Sources* 183, 34, 2008
Sidik *et. al*, *J. Phys. Chem. B* 110, 1787, 2006



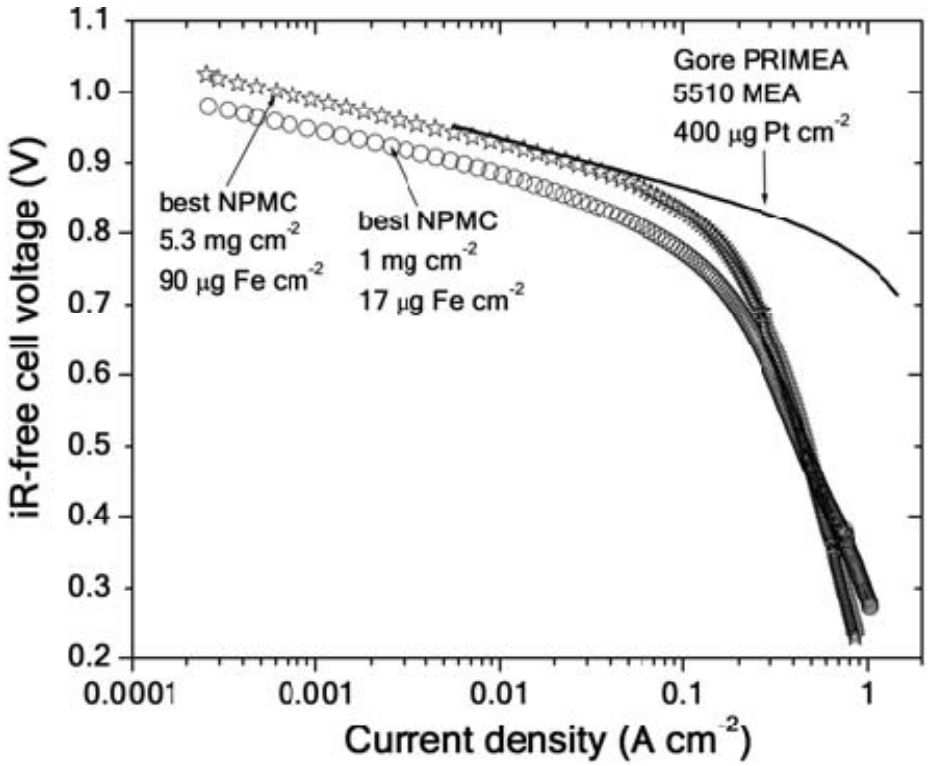
Niwa *et al*, *J. Power Sources*, 187, 93, 2009

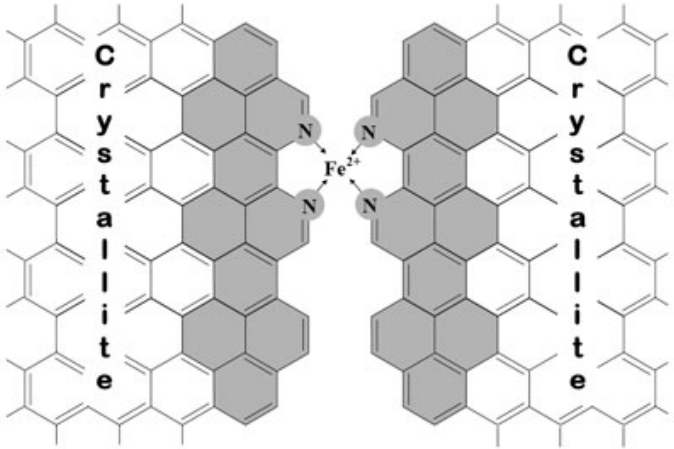




Nanostructured carbon doped with nitrogen (CNx) often viewed as ORR active site

Non-Precious ORR Catalysis – Concept 2: Metal Participating in ORR





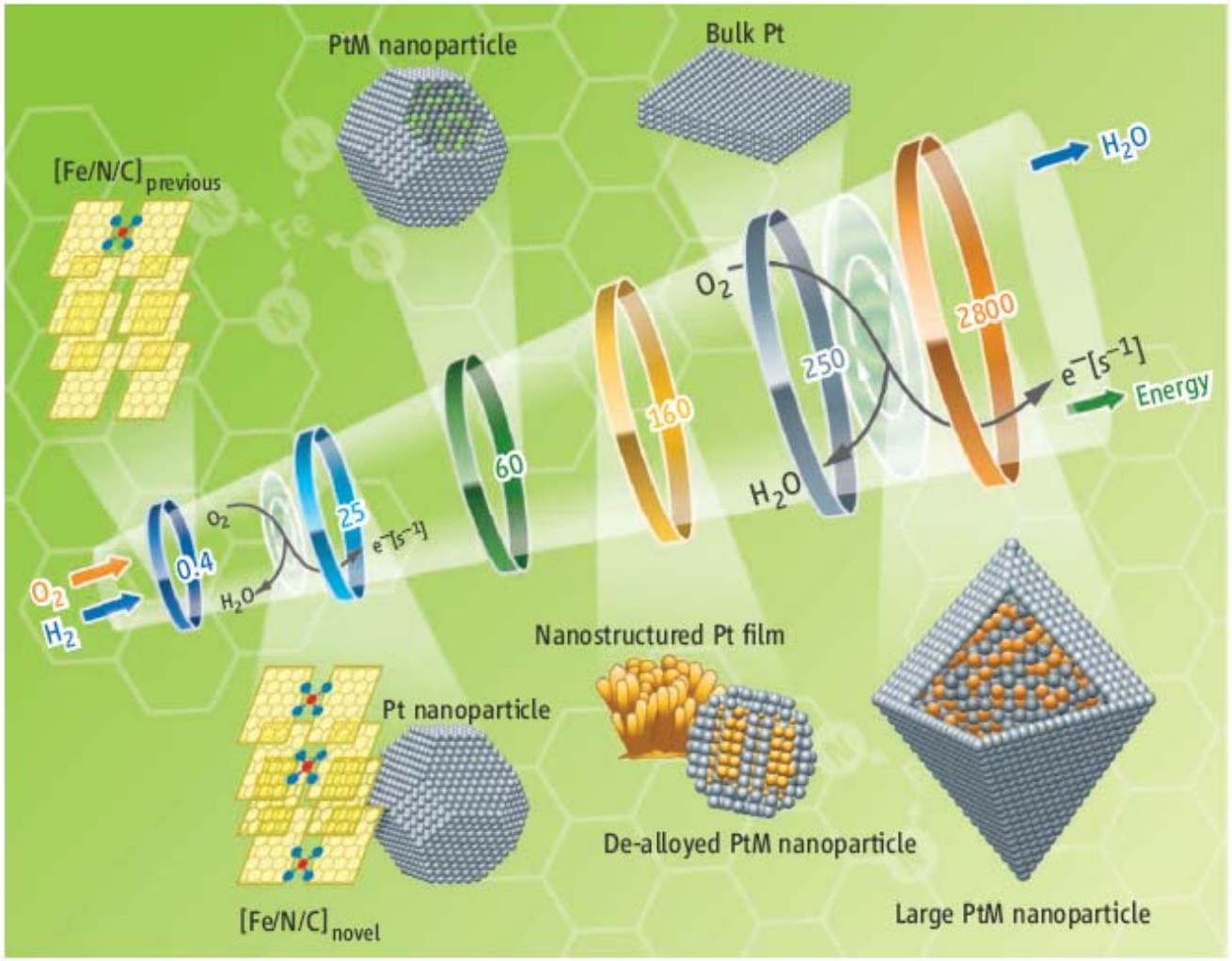
Lefèvre *et al*, *Science*, 324, 71, 2009

MeN_4/C (Me: Co or Fe) species embedded in carbon micropores – an alternative ORR active site concept

Turnover Frequency of Various ORR Catalysts

ORR turnover frequency: $f\ (s^{-1}) = i / (e\,N)$

i – current density ($A\,cm^{-2}$), e – electron charge ($1.6\ 10^{-19}$ C), N – active site density (cm^{-2})



Gasteiger and Markovic, *Science* 324, 48 2009

DOE-EERE-Funded *Advanced Cathode Catalysts* Project (2006-2010)

- **Catalysts with ultra-low Pt content, e.g. non-precious-metal core catalysts; mixed-metal shells for higher ORR activity (Brookhaven National Laboratory, Radoslav Adzic, PI)**
- **Non-precious metal catalysts obtained by high-temperature treatment of various precursors of carbon, nitrogen, and transition metals (Los Alamos National Laboratory)**

DOE Cathode Catalyst Performance Targets

- Platinum group metal loading: 0.2 mg_{PGM}/cm^2 (both electrodes)
- Activity of PGM catalysts:

  mass activity 0.44 A/mg_{Pt} at 0.90 $V_{iR\text{-}free}$

  area specific activity 720 $\mu A/cm^2$ at 0.90 $V_{iR\text{-}free}$
- Activity of non-PGM catalysts (per catalyst volume):

  > 130 A/cm^3 at 0.80 $V_{iR\text{-}free}$ (2010); 300 A/cm^3 at 0.80 $V_{iR\text{-}free}$ (2015)
- Durability with cycling: 5,000 hours at $T \leq 80^oC$, 2,000 hours at $T > 80^oC$
- Electrochemical surface area (ESA) loss: < 40%; Cost: < 5 $/kW

Low-Temperature Non-Precious Metal Composites: Co-PPy-XC72

- Hypothesis: CoN_2 (CoN_4) sites claimed to act as ORR active sites (e.g. in pyrolyzed Co porphyrins)
- Objective: Generate ORR active sites without destroying the ordered structure of the polymer catalyst
- Approach: Heteroatomic polymer as a matrix for entrapping and stabilizing non-precious metal
- Choice: Cobalt-polypyrrole-carbon composite (Co-PPy-XC72)

Pyrrole + XC72

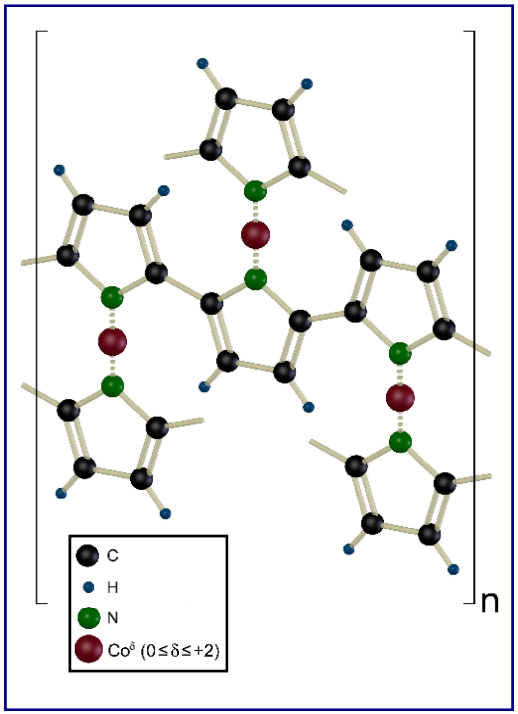
↓

PPy-XC72

↓ *(i) Co precursor*
(ii) reduction

Co-PPy-XC72

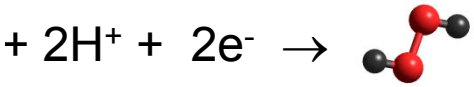
Bashyam and Zelenay, *Nature* **443**, 63, 2006



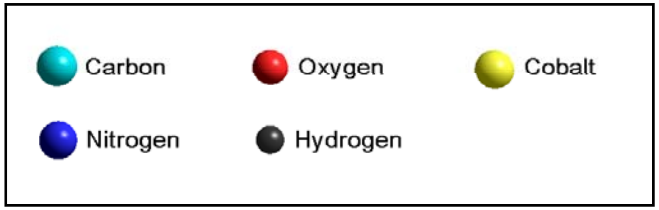
Co-PPy-XC72 Catalyst: Molecular Modeling

D_{O-O} = 1.21 Å

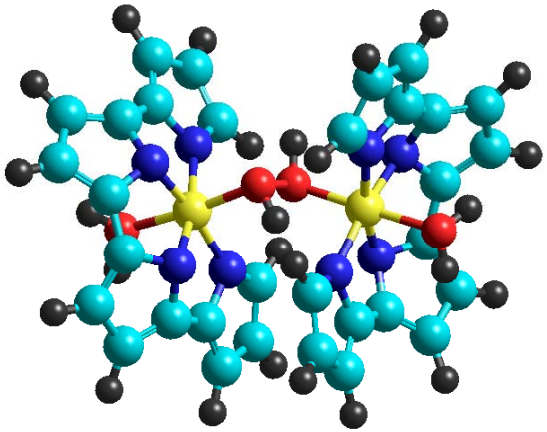
dioxygen



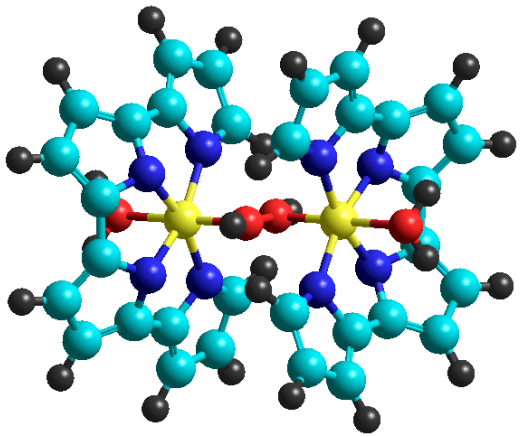
D_{O-O} = 1.47 Å



D_{O-O} = 1.56 Å



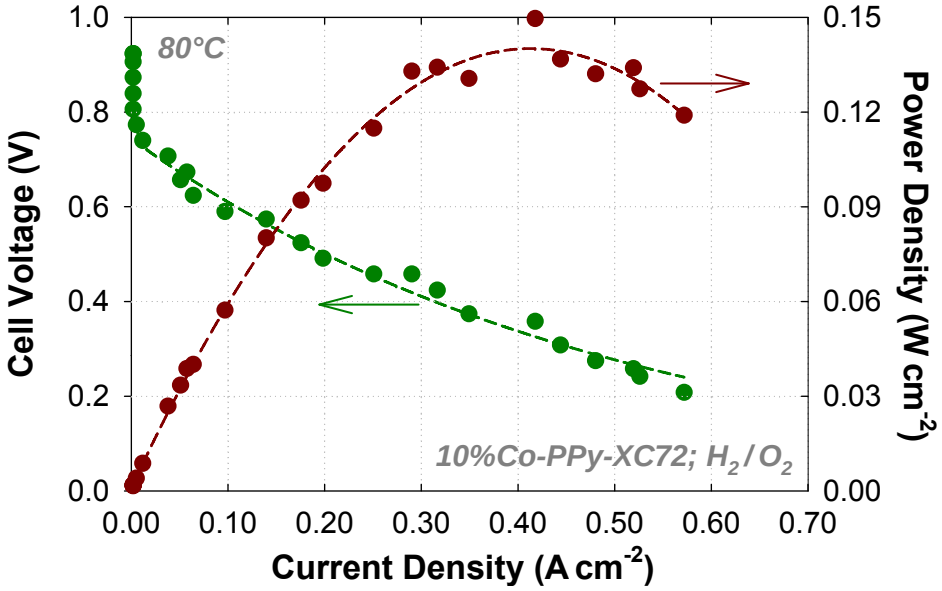
D_{O-O} = 1.99 Å

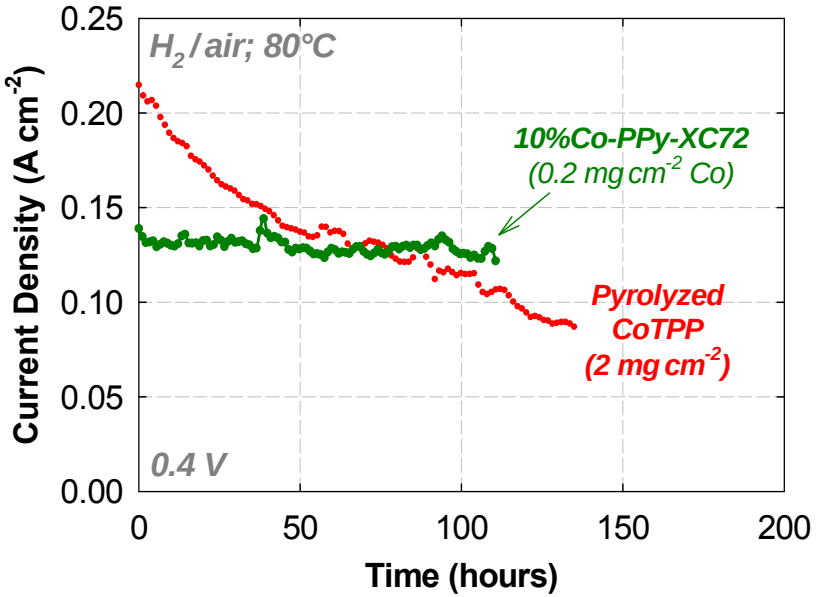


[(tetrapyrrole) H_2O Co-OH-HO-Co H_2O (tetrapyrrole)]$^{2-}$

Dioxygen interaction with two Co centers significantly weakening O-O bond relative to the O_2/H_2O_2 reference system

Low-Temperature Non-precious Metal Composites: Co-PPy-XC72



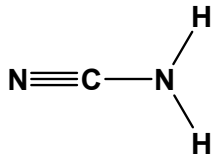


Bashyam and Zelenay, *Nature* **443**, 63, 2006

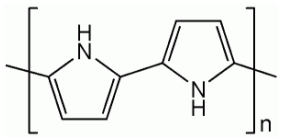
- **Significant improvement in the stability over the state of the art**
- **ORR activity in dire need of improvement**

High-Temperature Synthesis

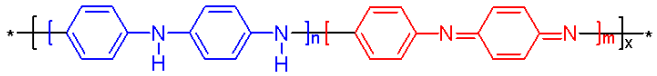
Cyanamide



Polypyrrole



Polyaniline



Carbon support

Transition metal

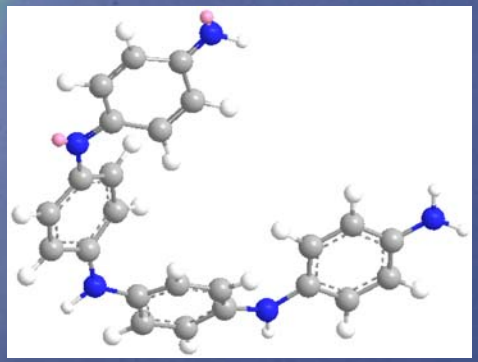
First heat treatment at up to 1100°C in inert atmosphere

0.5 M H_2SO_4 leach at 80-90°C

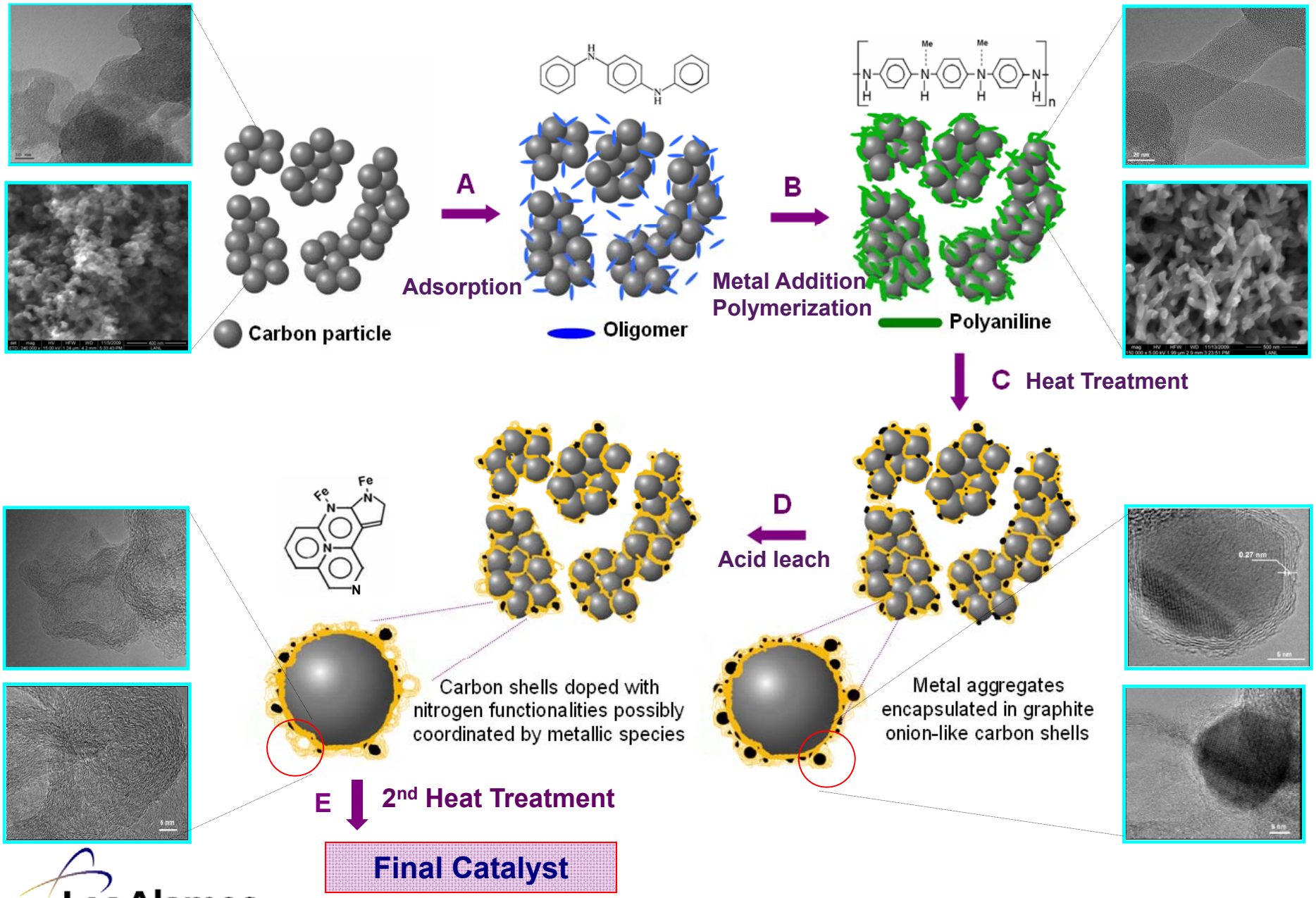
Second heat treatment at 900°C in inert atmosphere

ORR performance evaluation; characterization

Polyaniline-Derived Catalysts

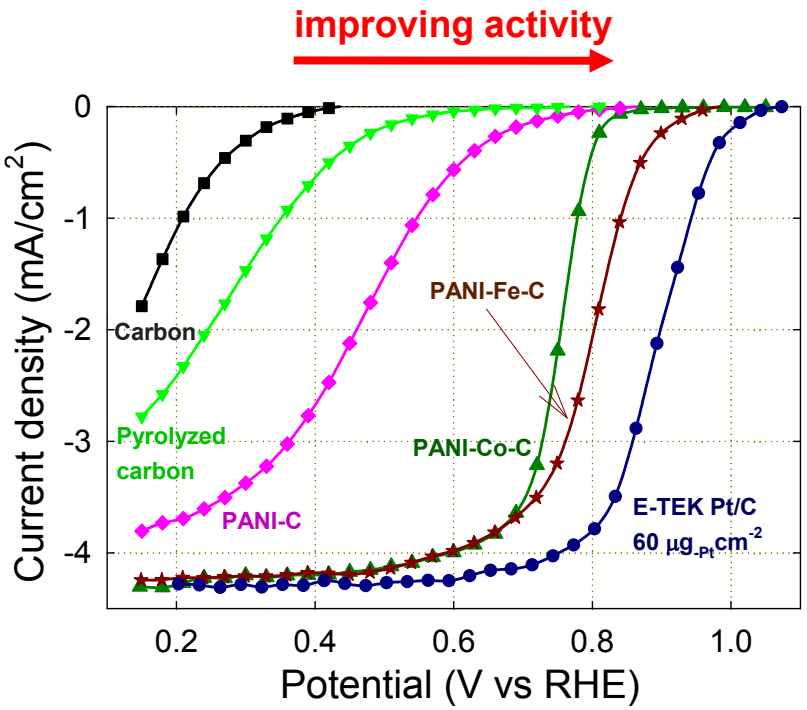


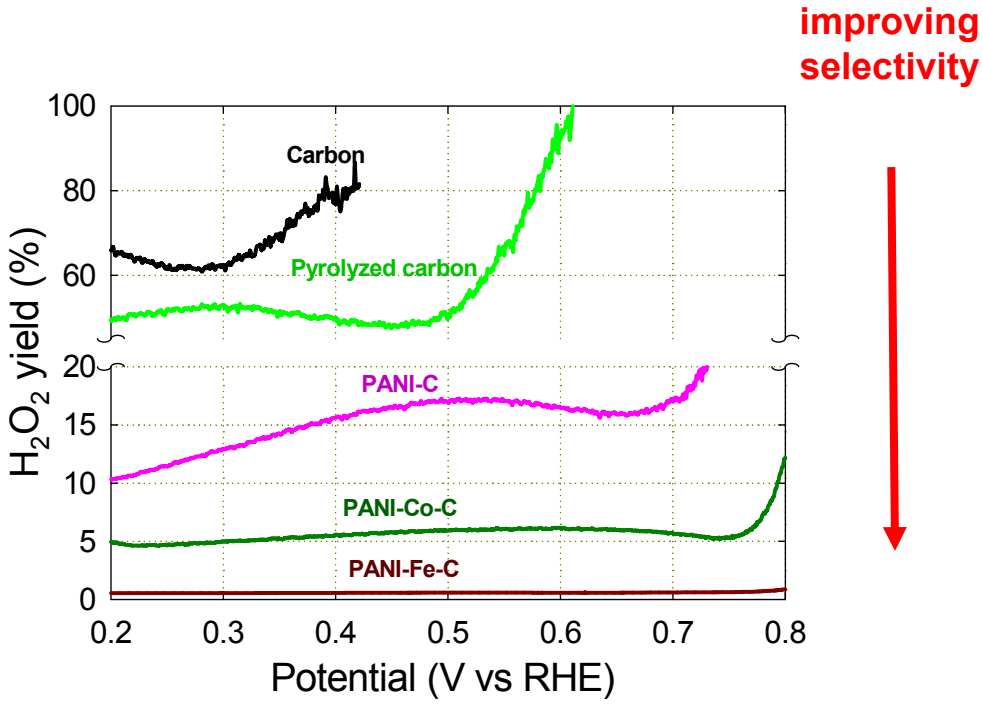
Schematic Representation of Polyaniline-Derived Catalyst Synthesis



PANI Catalysts: Evolution of ORR Activity and 4e⁻ Selectivity (RRDE)

Rotating Ring Disk Electrode (RRDE) Data

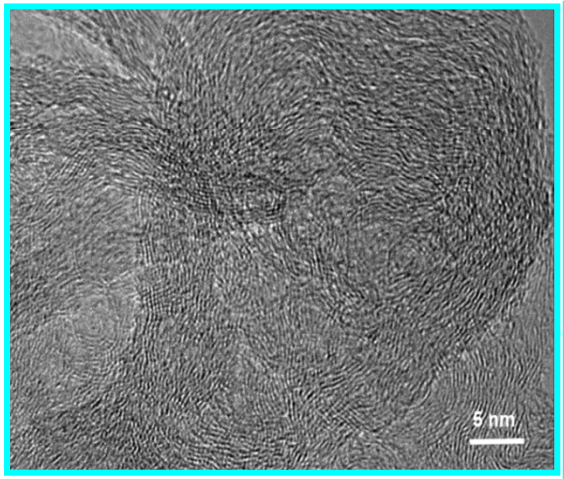


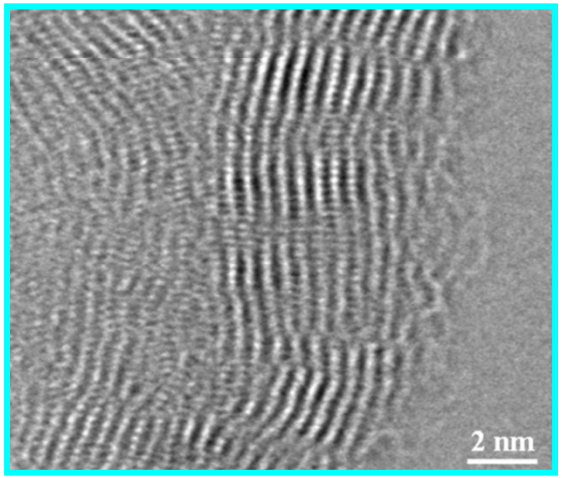


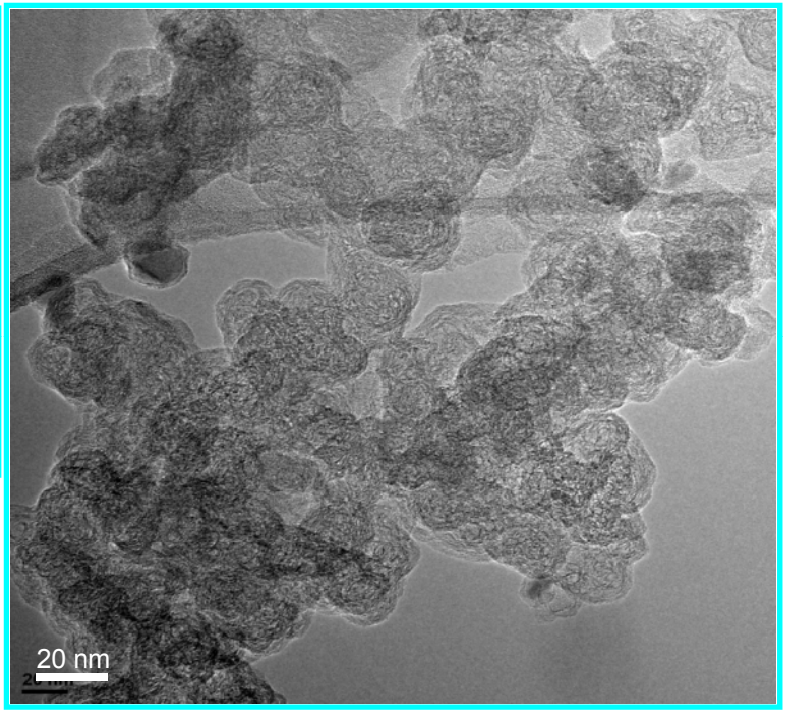
- **Best-performing PANI-derived catalyst trailing Pt/C reference catalyst by no more than 80 mV at $E_{½}$**
- **H_2O_2 generation reduced to ~ 0.5%**

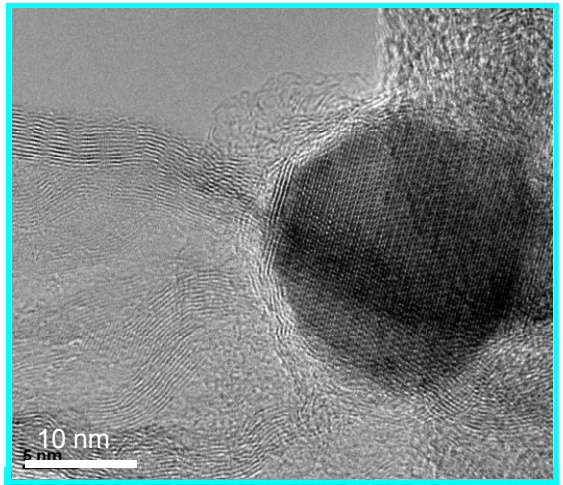
Nanostructure of PANI-Derived Catalysts: HR-TEM Images

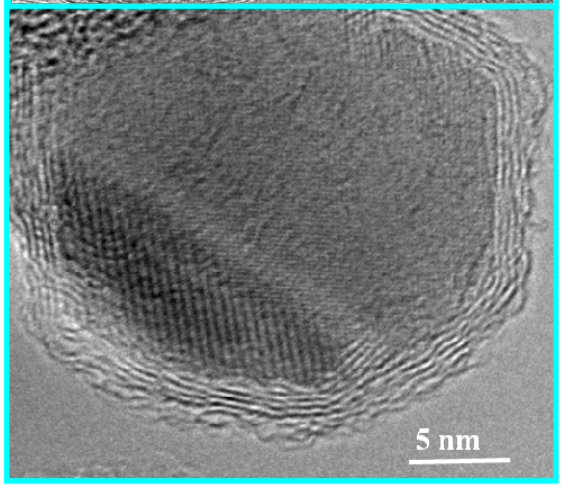
Composite catalysts derived from heteroatomic organic precursors (e.g. polyaniline - PANI, transition metals, and carbon; heat-treated at 600ºC - 1100ºC; and subjected to post-synthesis purification and activation steps





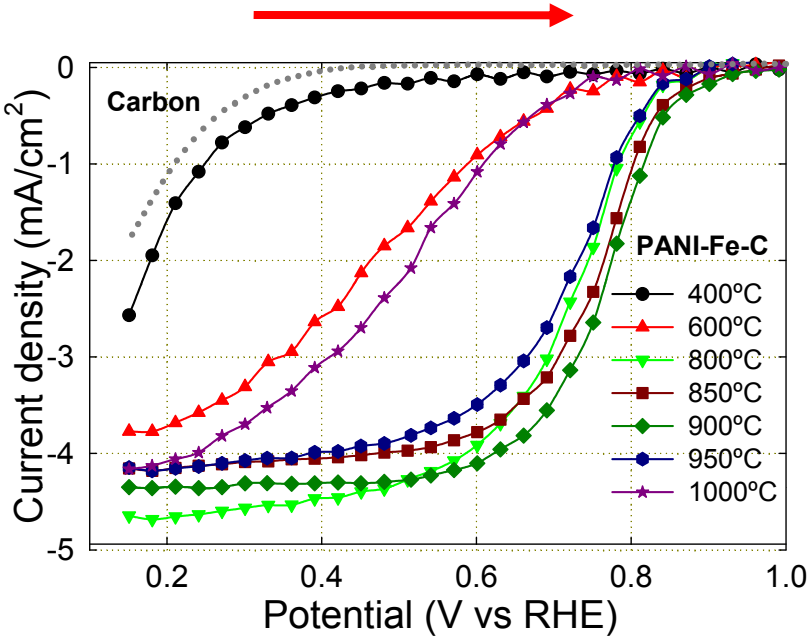


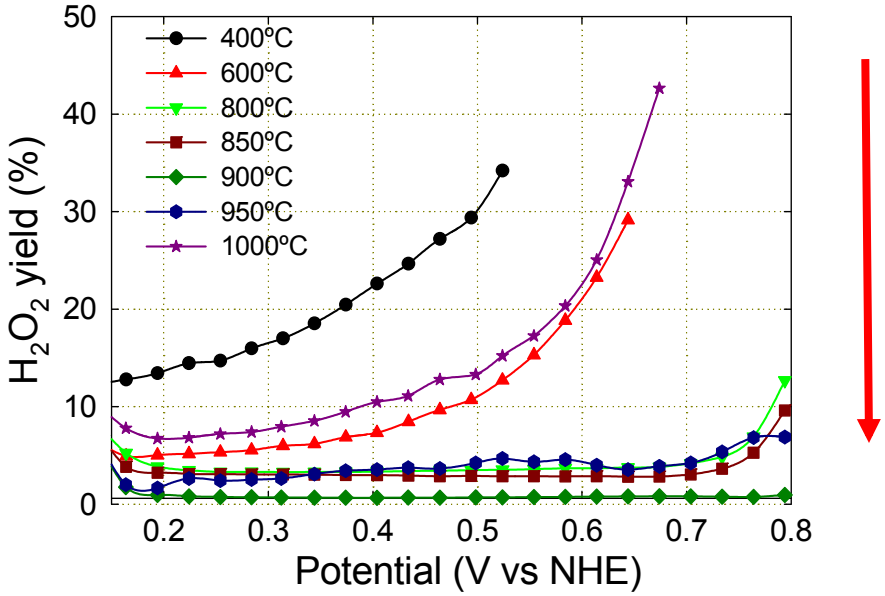




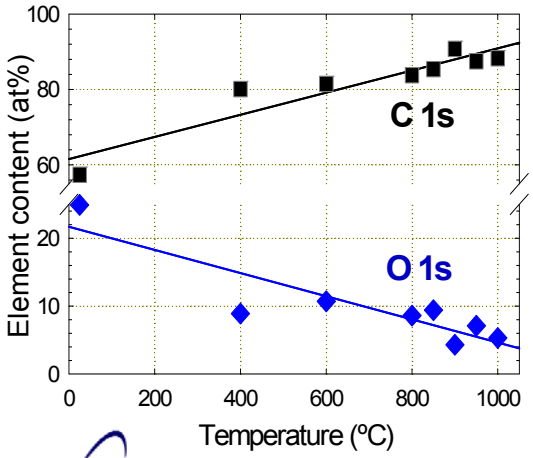
Onion-like filled and hollow turbostratic carbon layers, disordered nanofiber and metal-containing nanoparticles visible after pyrolysis in PANI-derived catalyst

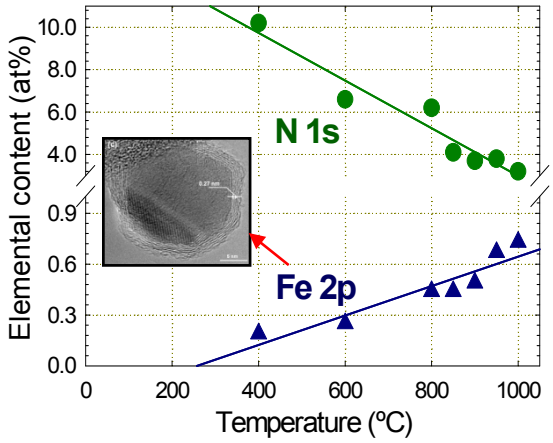
PANI-Fe-C: Effect of Heat-Treatment Temperature on Activity and Speciation





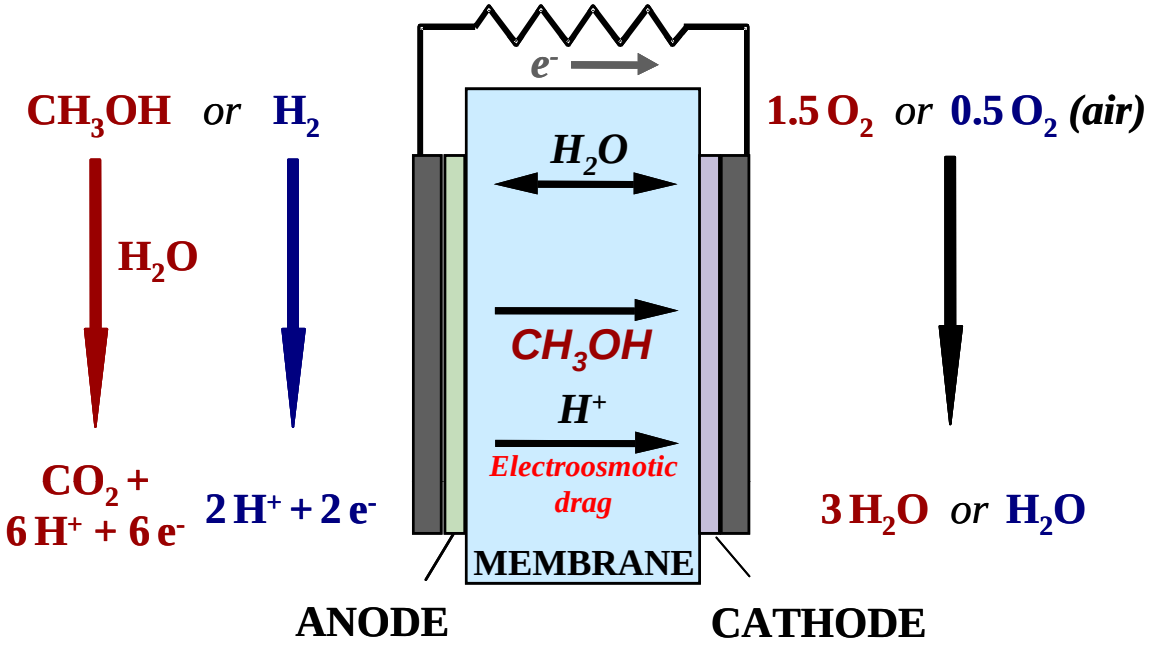
Elemental quantification by XPS

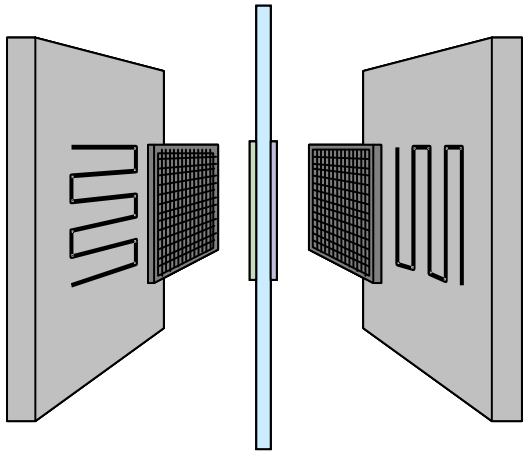




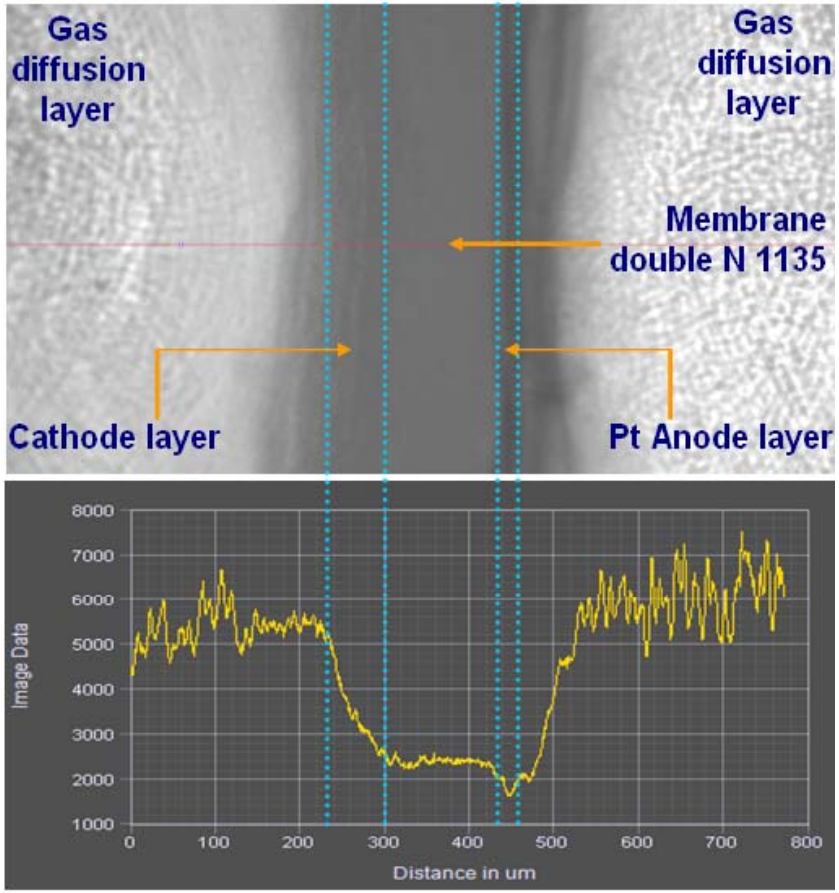
- **Catalysts synthesized at 900°C showing the highest ORR activity and the lowest H_2O_2 yield (~1.0%)**
- **Gradual loss in the total nitrogen content with heat-treatment temperature representing the most notable result from XPS analysis of the PANI-Fe-C catalyst**

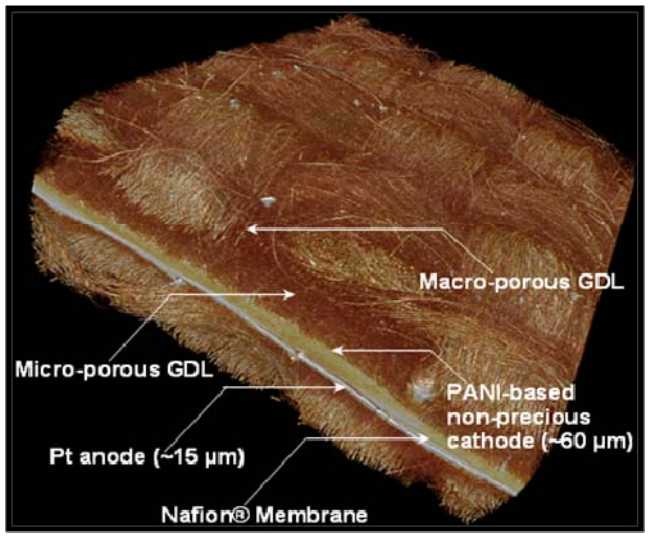
Polymer Electrolyte Fuel Cell (PEFC)



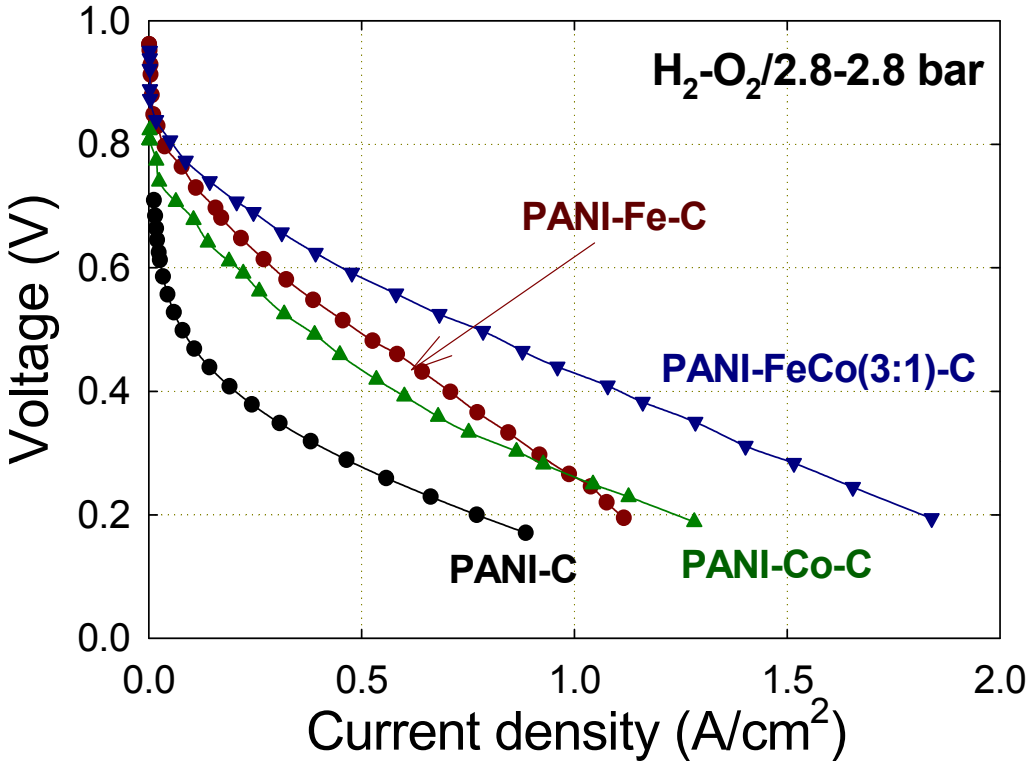


X-Ray Tomography: MEA Image



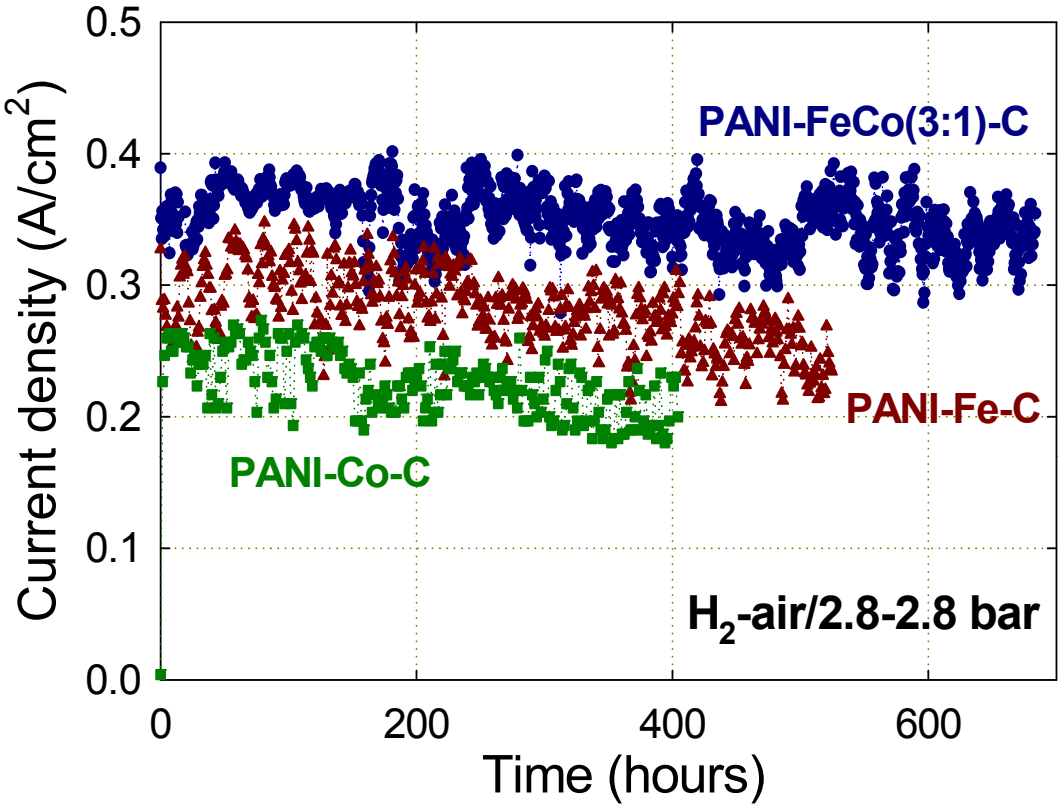


Fuel Cell Testing of PANI-derived ORR Catalysts: Performance

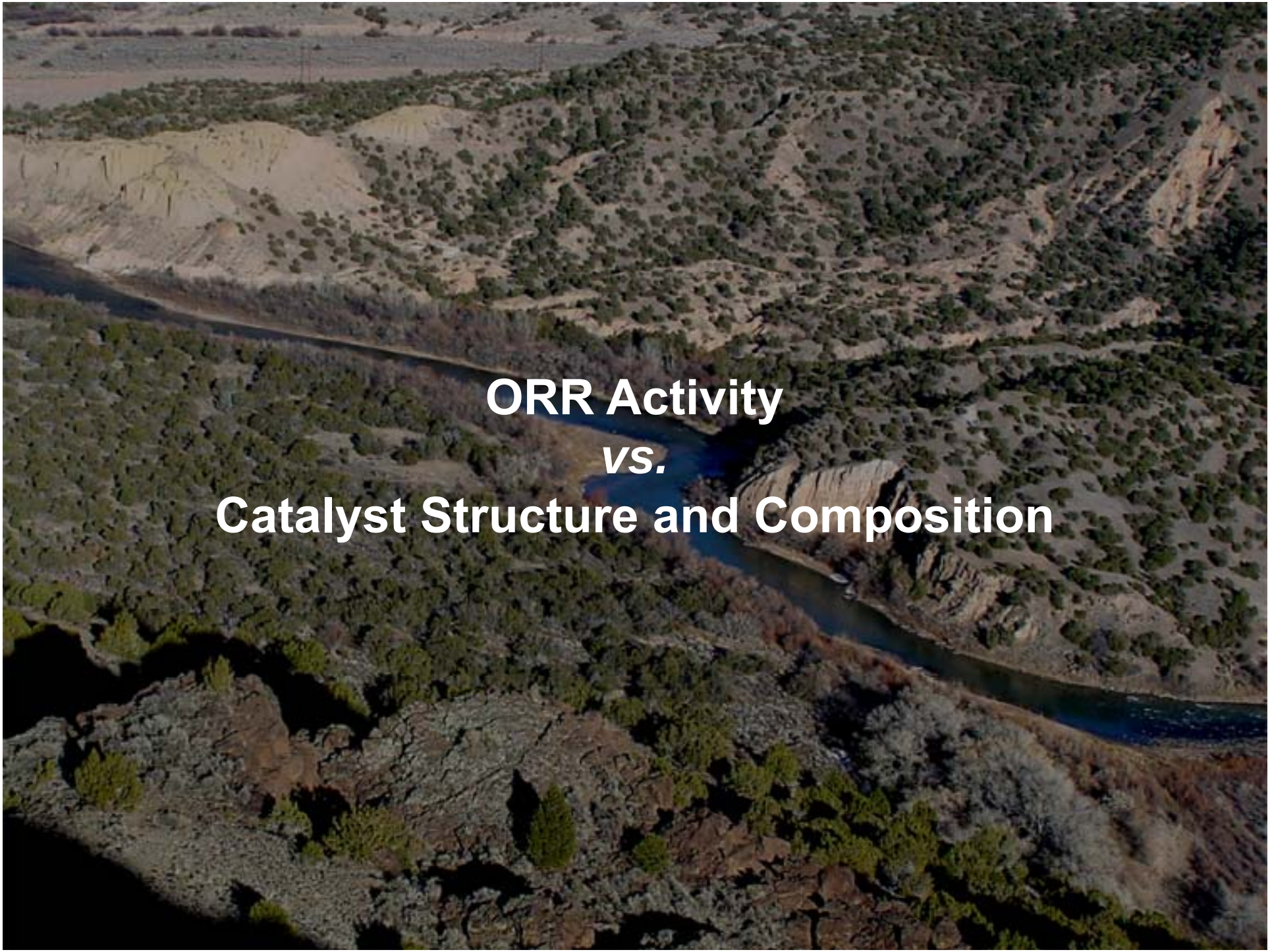


- **Relative performance observed in RDE experiments reproduced in fuel cell testing (except for relatively lower PANI-Fe-C performance, possibly due to limited stability)**
- **PANI-FeCo(3:1)-C showing the best activity**

Fuel Cell Testing of PANI-derived ORR Catalysts: Performance Stability

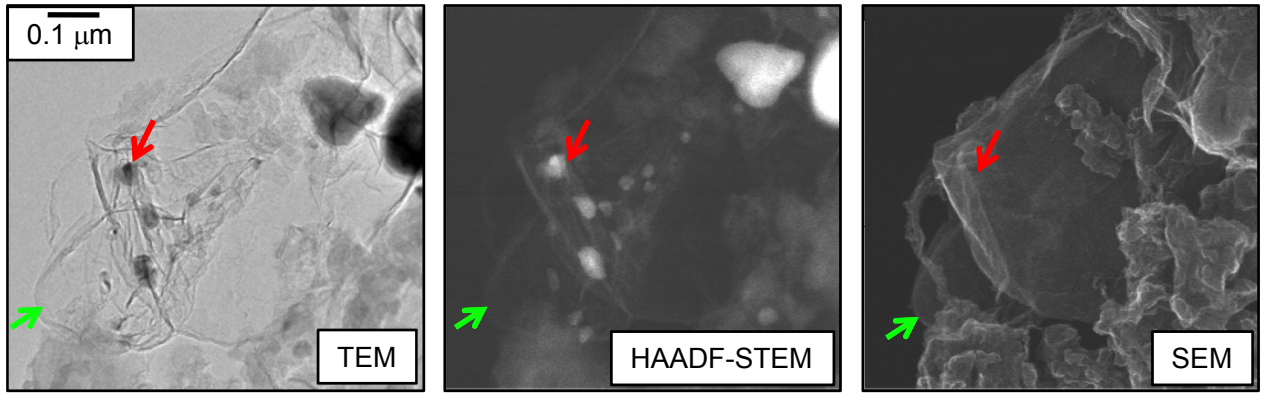


- **PANI-FeCo(3:1)-C showing the best combined activity/durability, never before observed with non-precious metal catalysts in fuel cell testing**
- **Co likely to responsible for improved activity, Fe for stability**

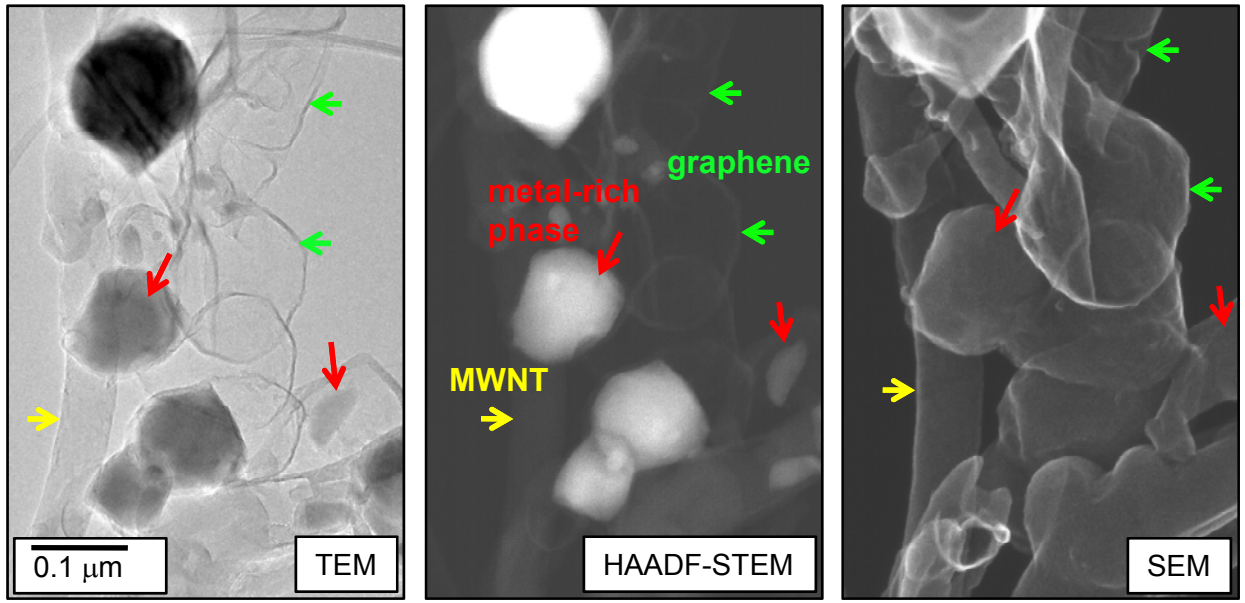

ORR Activity
vs.
Catalyst Structure and Composition

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

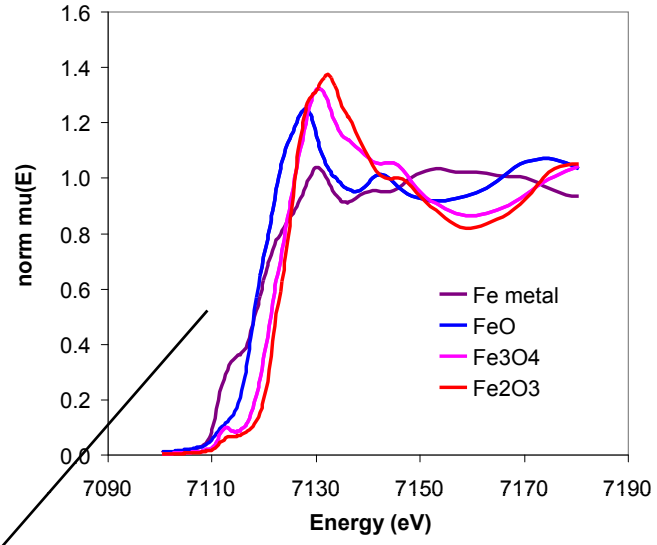


- **The two most durable catalysts showing notable similarities in morphology**
- **Significant number layered graphene "bubbles" formed in PANI-FeCo(3:1) and PANI-Fe-MWNT (→), co-located with the Fe(Co)S_x regions/particles (→); MWNT still present (→)**
- **BF-STEM images of PANI-Fe-MWNT showing graphitic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

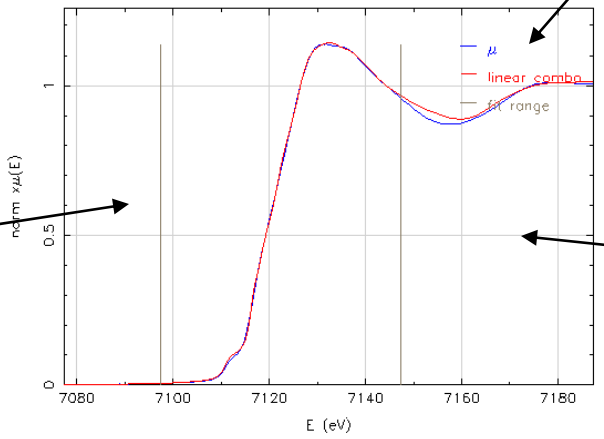
PANI-Fe-C XAS: Comments on Interpretation of Spectra

- **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**

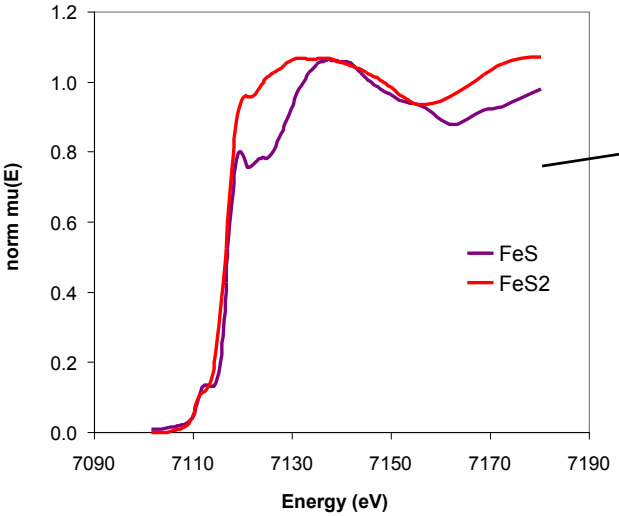
Fe Metal/Fe Oxides Standards



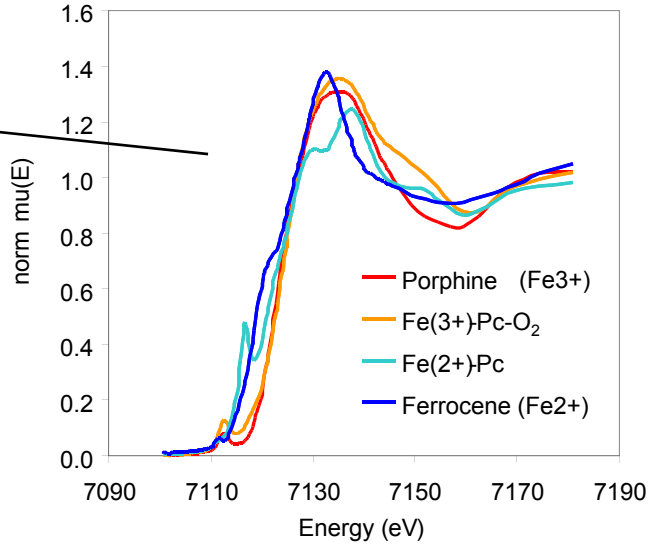
Fit of Spectrum by Linear Combination of Standards



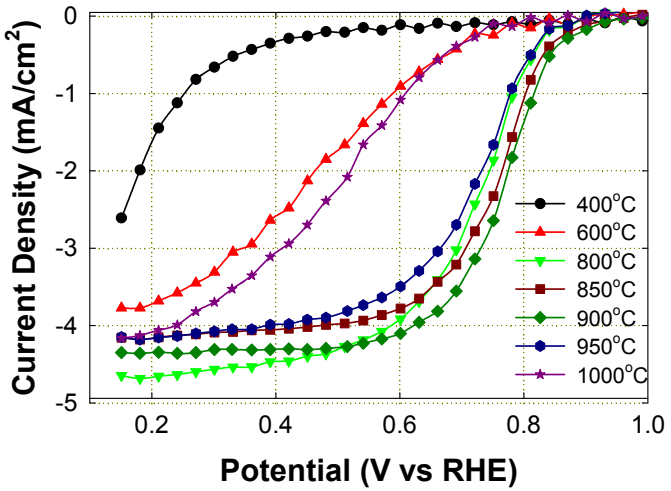
Fe **Sulfides** Standards



Examples of Fe-Complexes Standards

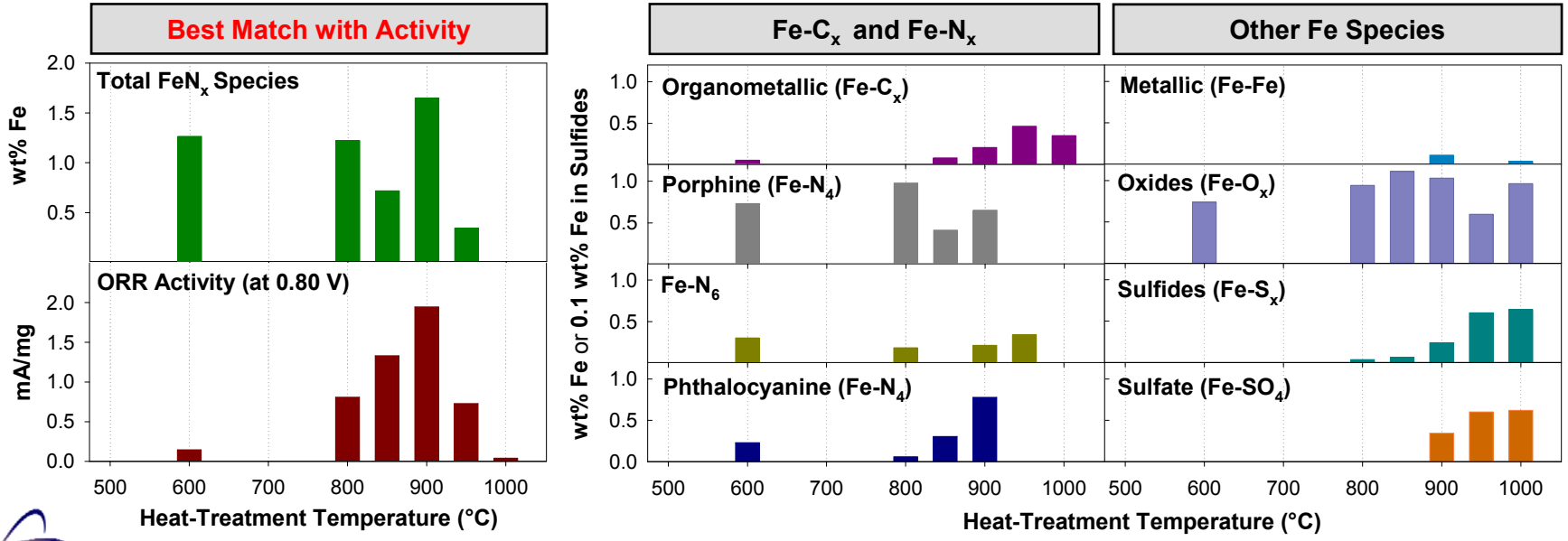


PANI-Fe-C: Effect of Heat-Treatment on Activity and Fe Speciation



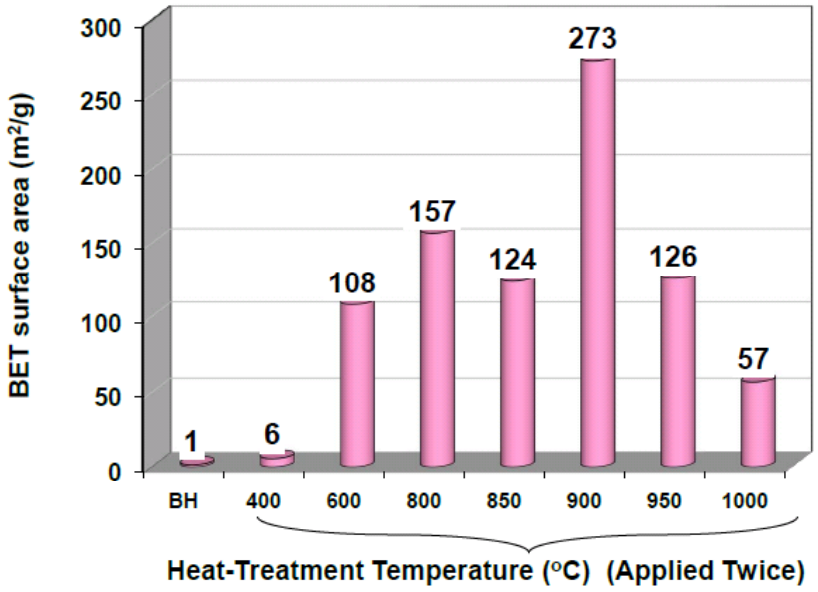
Correlation between activity and presence of Fe-N_x-type coordination observed; Fe-C_x-type and Fe oxides correlating to a lesser degree

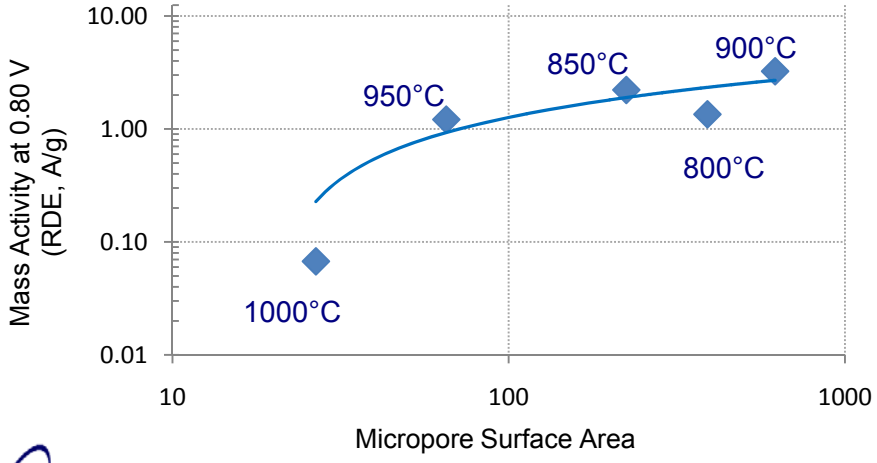
Fe X-Ray Absorption Spectroscopy Results

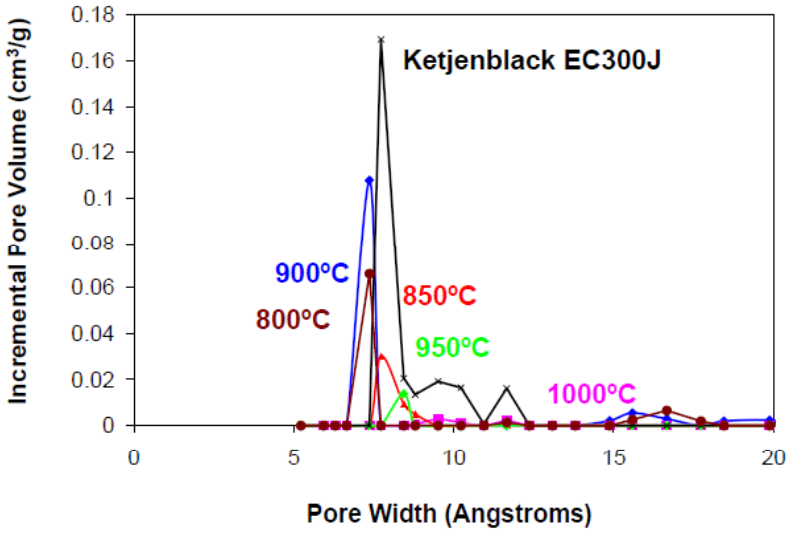


PANI-Fe-C: Effect of Heat-Treatment Temperature on Surface Area and Pores

- Sample heat-treated at 900ºC exhibiting the highest BET surface area and micropore volume/surface area
- Clear correlation observed between mass activity and micropore surface area







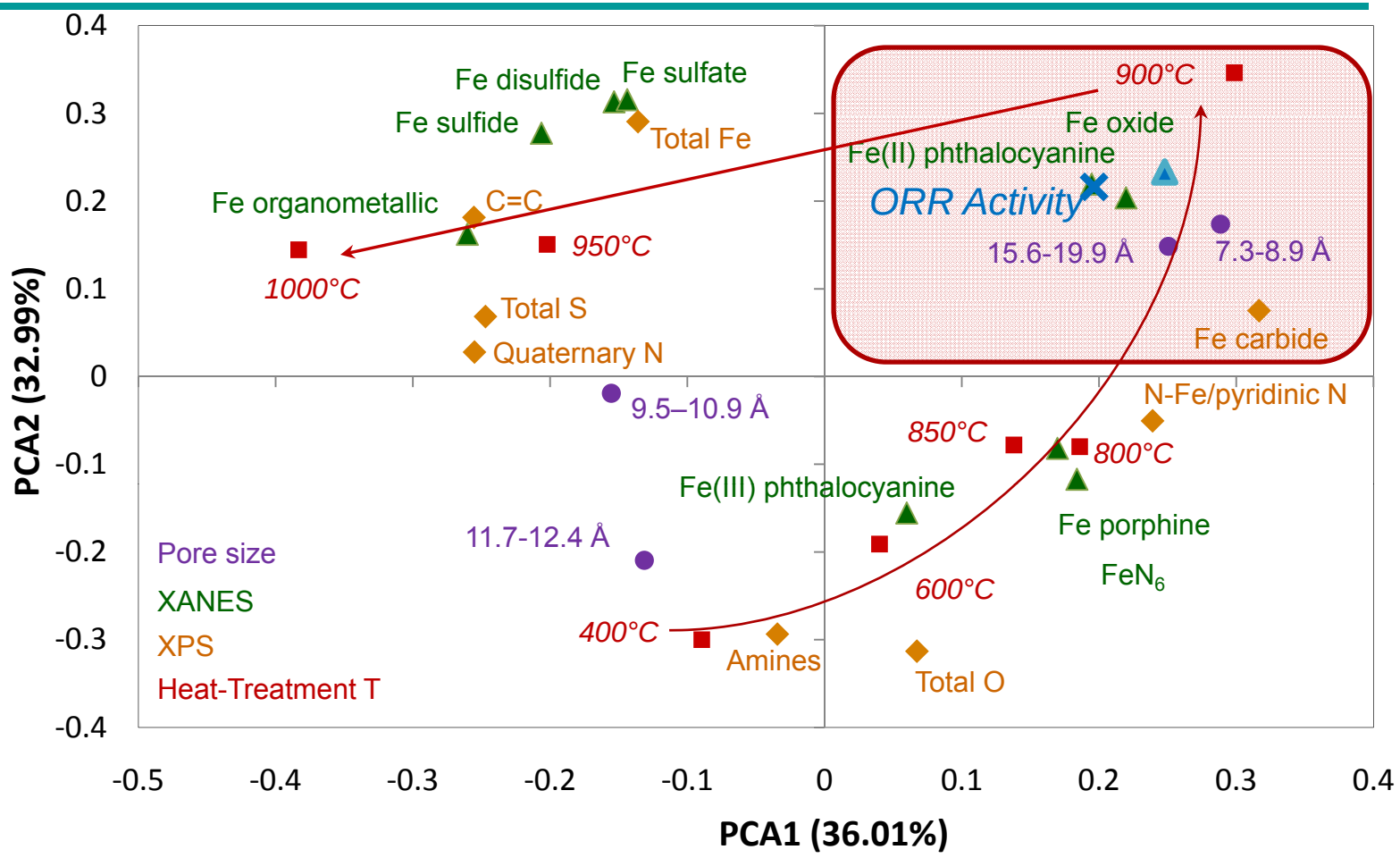
PCA: Correlation of Combined Characterization Data and Activity

Notes on Principle Component Analysis (PCA)

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

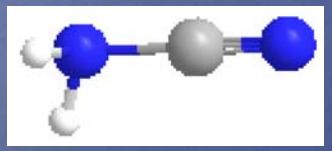
The further the variables or samples from the intersection in any direction (vertical, horizontal or diagonal), the more different they are from the average values.

(As-synthesized powders examined.)

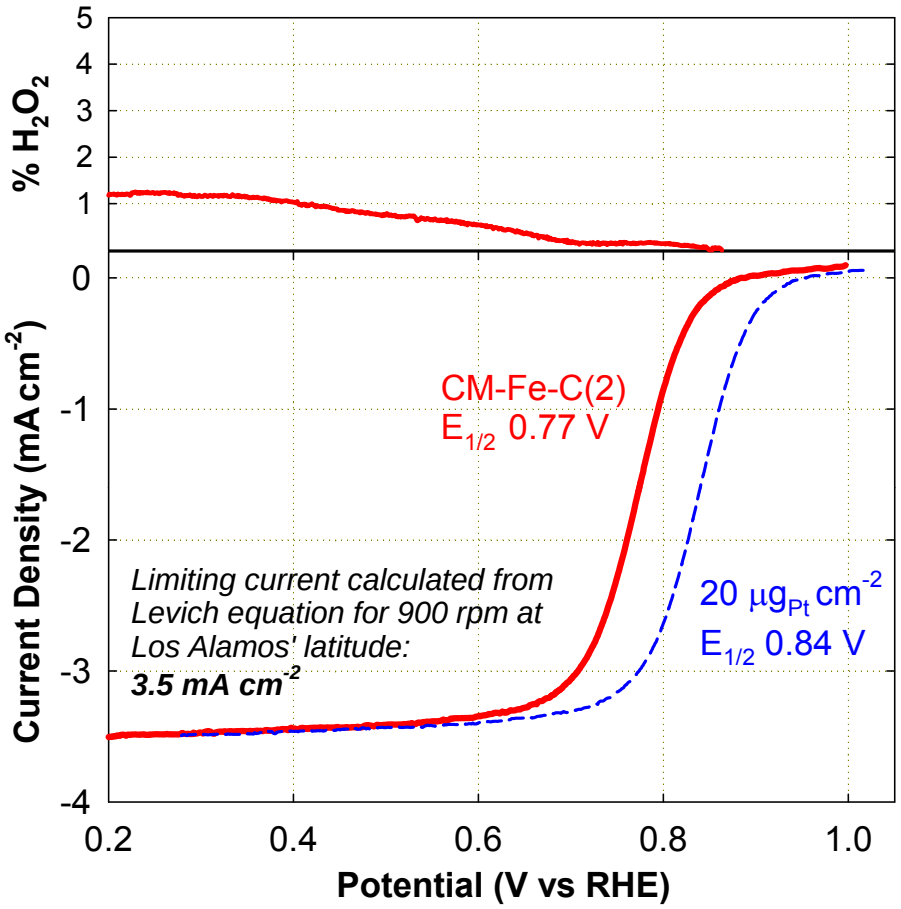


- **Fe-N-type coordination, correlated with ORR activity and ORR-active samples (900°C, 850°C, 800°C), remaining a primary candidate for active site**
- **The most active, 900°C catalyst having the highest BET surface area, a bimodal pore distribution, high initial content of Fe carbide, Fe in oxide-like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

Cyanamide-Fe-C Catalyst

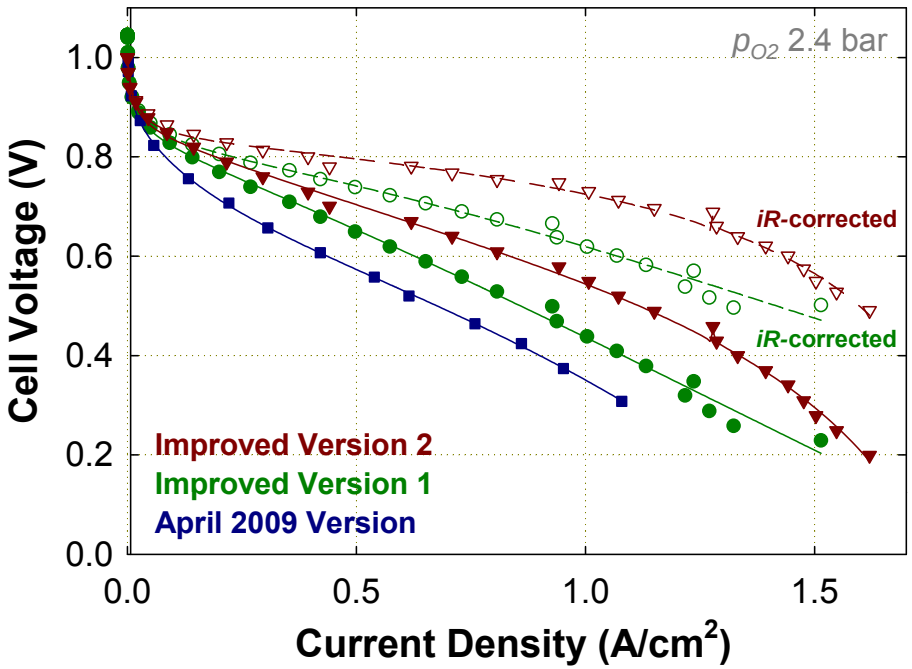


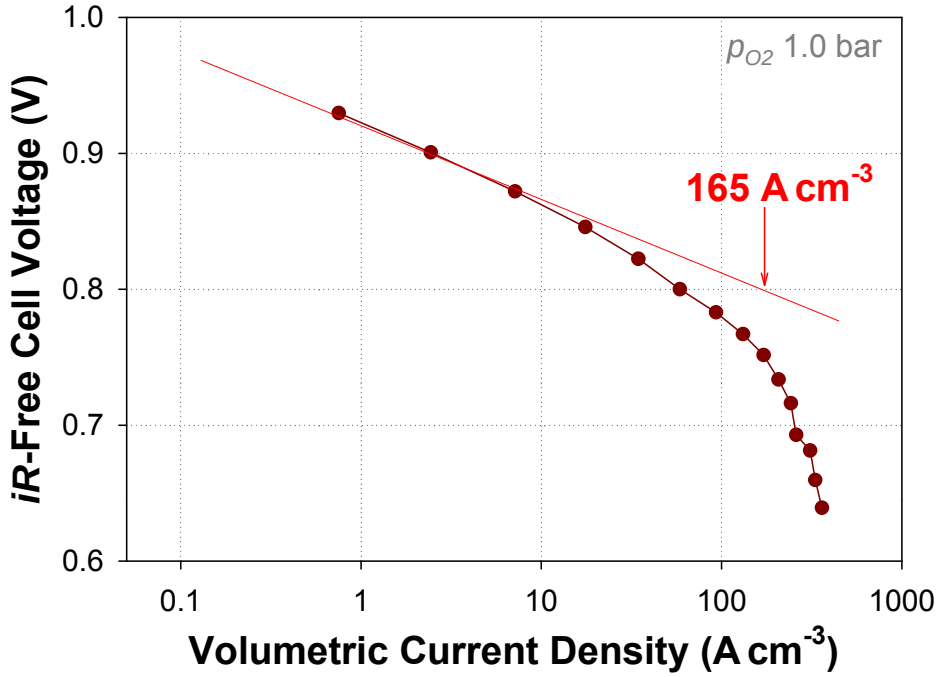
Cyanamide-Fe-C Catalyst: RRDE Performance



- **~70 mV difference in $E_{1/2}$ between CM-Fe-C catalyst and Pt reference catalyst (20 µg$_{Pt}$ cm^{-2})**
- **H_2O_2 generation: ~1%**

Cyanamide-Fe-C Catalyst: Performance



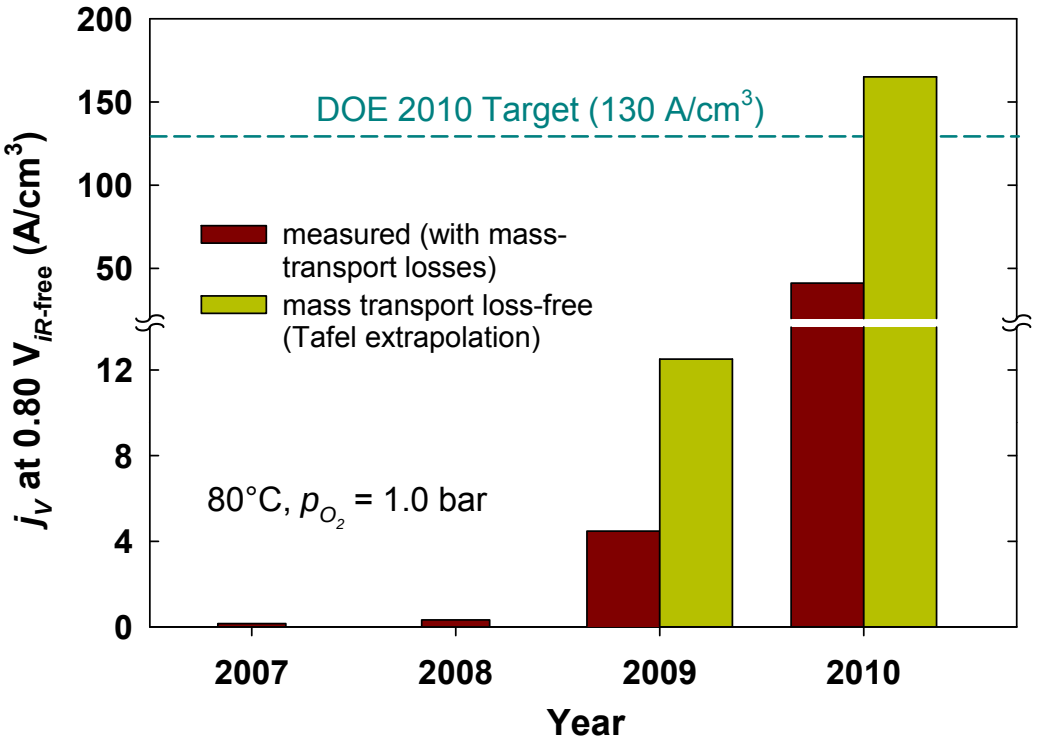


- **Version 1** achieved with change in carbon support and adjustment of precursor ratios
- **Version 2** generated by including additional sulfur-containing precursor

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)**

- **CM-Fe-C to Pt performance ratio at 0.60 V** (standard Pt loading of 0.2 mg/cm^2): **~ 0.65**

Performance Summary: Non-PGM Catalysis Research at Los Alamos



- **Fuel cell performance improved by more than 100× since 2008**
- **DOE 2010 activity target of 130 A/cm^3 at 0.80 V achieved**

Summary

- **PANI-FeCo-C catalyst** (possibly the most promising non-PGM catalysts to date):

  (i) high activity
  (ii) respectable performance durability
  (iii) excellent selectivity for four electron reduction process

  Gang Wu, Karren L. More, Christina M. Johnston, Piotr Zelenay
  Science, 443-447, **332**, 2011

- **Open cell voltage** (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
- **High durability** demonstrated with PANI-based catalysts to potential holding at OCV and 0.4 V in fuel cell testing; much of the performance loss at 0.60 V recoverable with reduced humidity
- **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)
- **Immediate future research:**

  (i) active ORR site determination
  (ii) improvements to stability and activity

Non-Precious Metal Oxygen Reduction Catalysts *vs.* Platinum

Catalyst	Potential at 0.10 mA/cm^2 (V *vs.* RHE)
EDA-Co-C	0.81
PANI-Fe-C	0.94
PANI-Fe/ EDA-Co-C	0.96
20 wt% Pt/C (60 µg cm^{-2})	1.00

- ORR activity: At least 40 mV needed, especially at low overpotential (η); low Tafel slope of help at higher η values
- Stability: In spite of a major progress, still not there yet (factor of ~10)
- Selectivity: Sufficient with the best performing catalysts
- Novel electrode structures required to accommodate high non-precious catalyst volume and prevent O_2 mass-transfer loss

Acknowledgements

U.S. Department of Energy for funding of "Advanced Cathode Catalysts" project through **Office of Fuel Cell Technologies (EERE)**

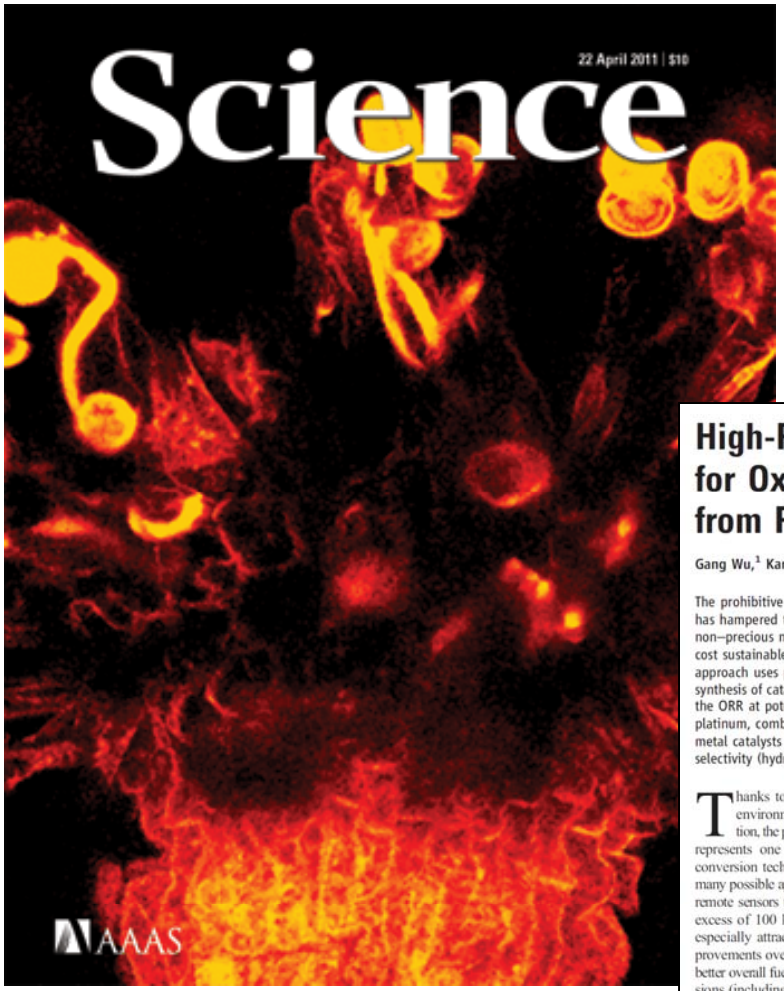
Los Alamos National Laboratory for initial funding of non-precious metal catalysis research through **Laboratory Directed Research and Development (LDRD) Program**

Deborah Myers, Magali Ferrandon, Jeremy Kropf for X-ray absorption spectroscopy characterization

Karren More for characterization by electron microscopy

Kateryna Artyushkova for principal component analysis

Science Paper Reference



Gang Wu, Karren L. More, Christina M. Johnston, Piotr Zelenay
Science, 443-447, **332**, 2011

High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt

Gang Wu,[1] Karren L. More,[2] Christina M. Johnston,[1] Piotr Zelenay[1]*

The prohibitive cost of platinum for catalyzing the cathodic oxygen reduction reaction (ORR) has hampered the widespread use of polymer electrolyte fuel cells. We describe a family of non–precious metal catalysts that approach the performance of platinum-based systems at a cost sustainable for high-power fuel cell applications, possibly including automotive power. The approach uses polyaniline as a precursor to a carbon-nitrogen template for high-temperature synthesis of catalysts incorporating iron and cobalt. The most active materials in the group catalyze the ORR at potentials within ~60 millivolts of that delivered by state-of-the-art carbon-supported platinum, combining their high activity with remarkable performance stability for non–precious metal catalysts (700 hours at a fuel cell voltage of 0.4 volts) as well as excellent four-electron selectivity (hydrogen peroxide yield <1.0%).

Thanks to the high energy yield and low environmental impact of hydrogen oxidation, the polymer electrolyte fuel cell (PEFC) represents one of the most promising energy conversion technologies available today. Of the many possible applications, ranging from sub-watt remote sensors to residential power generators in excess of 100 kW, automotive transportation is especially attractive. PEFCs promise major improvements over gasoline combustion, including better overall fuel efficiency and reduction in emissions (including CO_2). The spectacular progress in fuel cell technology notwithstanding, a large-scale market introduction of fuel cell–powered vehicles continues to face various challenges, such as the lack of hydrogen infrastructure and the technical issues associated with PEFC performance and durability under the operating conditions of an automotive power plant. The high cost of producing PEFCs represents the most formidable challenge and has driven much of the applied and fundamental fuel cell research in recent years.

According to the latest cost analysis, the fuel cell—more precisely, the fuel cell stack—is responsible for more than 50% of the PEFC power system cost (*1*, *2*). Although a state-of-the-art PEFC stack uses several high-priced components, the catalysts are by far the most expensive constituent, accounting for more than half of the stack cost. Because catalysts at both the fuel cell anode and cathode are based on platinum (Pt) or platinum alloys, their cost is directly linked to the price of Pt in the volatile and highly monopolized precious metal market. The precious metal catalyst is the only fuel cell stack component that will not benefit from economies of scale, and an increase in the demand for fuel cell power systems is bound to drive up the already high price of Pt, about $1830 per troy ounce at present ($2280 per troy ounce at its maximum in March 2008) (*3*). Thus, PEFCs are in need of efficient, durable, and inexpensive alternatives to Pt and Pt-based catalysts.

Ideally, Pt should be replaced at both fuel cell electrodes; however, its substitution at the cathode with a non–precious metal catalyst would have comparatively greater impact, because the slow oxygen reduction reaction (ORR) at this electrode requires much more Pt than the faster hydrogen oxidation at the anode. As a consequence, the development of non–precious metal catalysts with high ORR activity has recently become a major focus of PEFC research (*4*–*8*). The Pt replacement candidates that have attracted the most attention have been synthesized by heating precursors comprising nitrogen, carbon, and geologically abundant transition metals, iron and cobalt (M = Co and/or Fe) in particular (*9*–*14*). Although the nature of the active ORR catalytic sites in such N-M-C catalysts continues to be at the center of an ongoing debate (*6*, *7*, *10*, *15*), there is no doubt that the ORR performance of N-M-C catalysts strongly depends on the type of nitrogen and transition-metal precursors used, heat treatment temperature, carbon support morphology, and synthesis conditions.

We recently initiated a research effort to develop non–precious metal catalysts that combine high ORR activity with good performance stability, originally concentrating on materials obtained without heat treatment. The polypyrrole (PPy)-Co-C system prepared this way showed respectable performance durability for a non–precious metal

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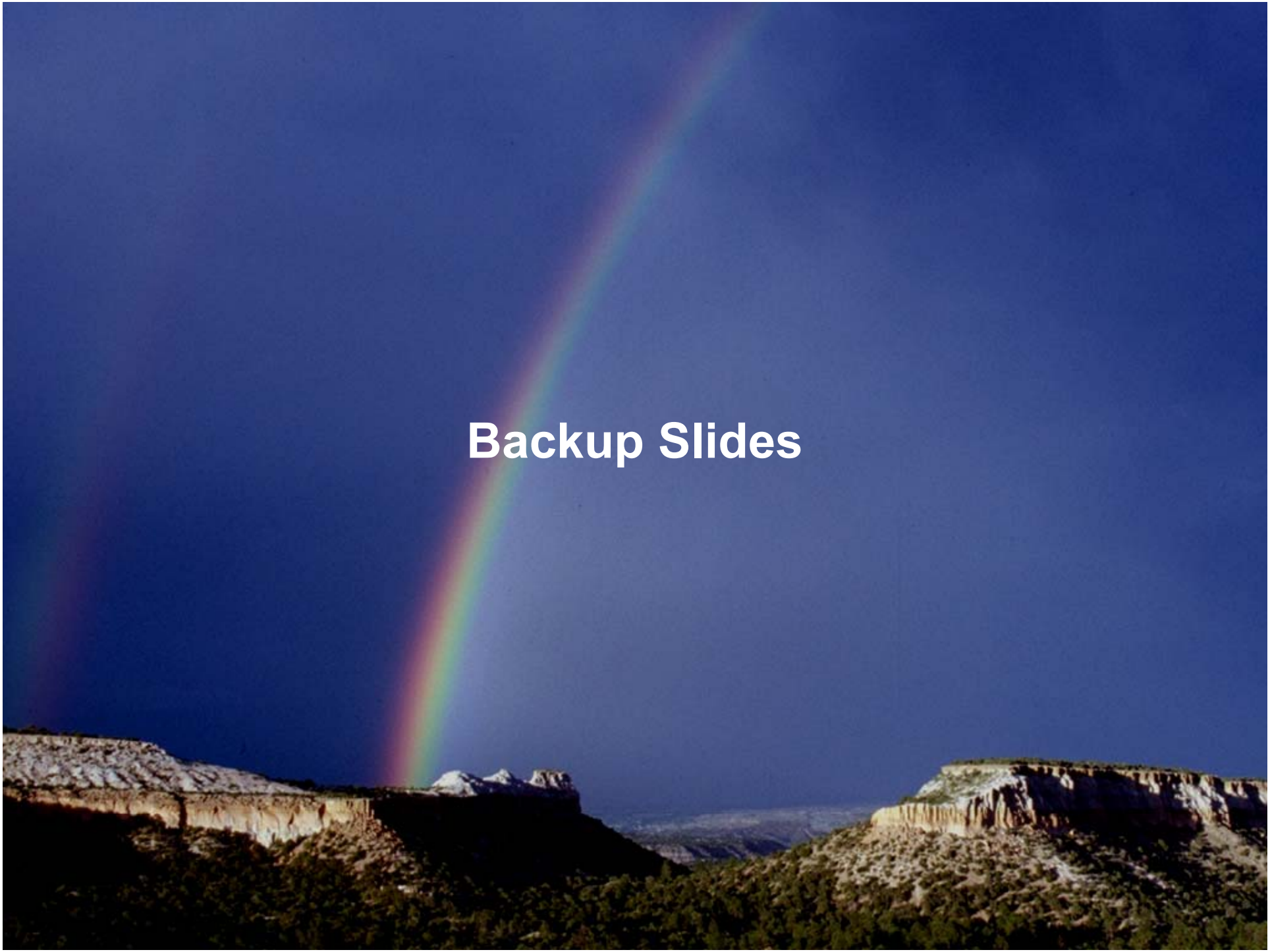
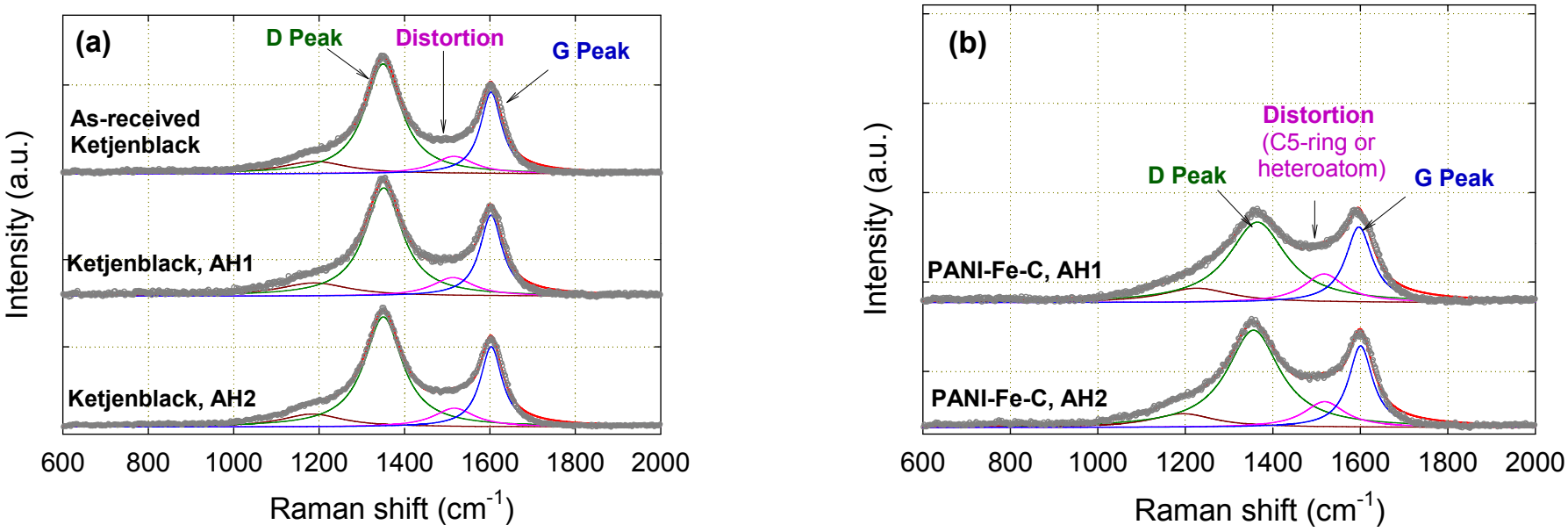

Backup Slides

Raman Spectra: Carbon Black *vs.* PANI-derived Catalyst

Raman spectra of (a) Ketjenblack support and (b) PANI-Fe-C catalysts subject to the single and double heat-treatment at 900ºC

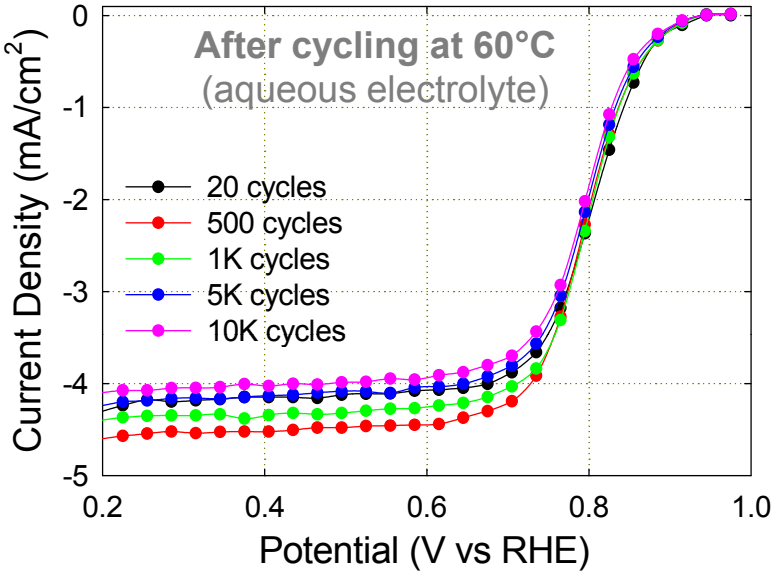


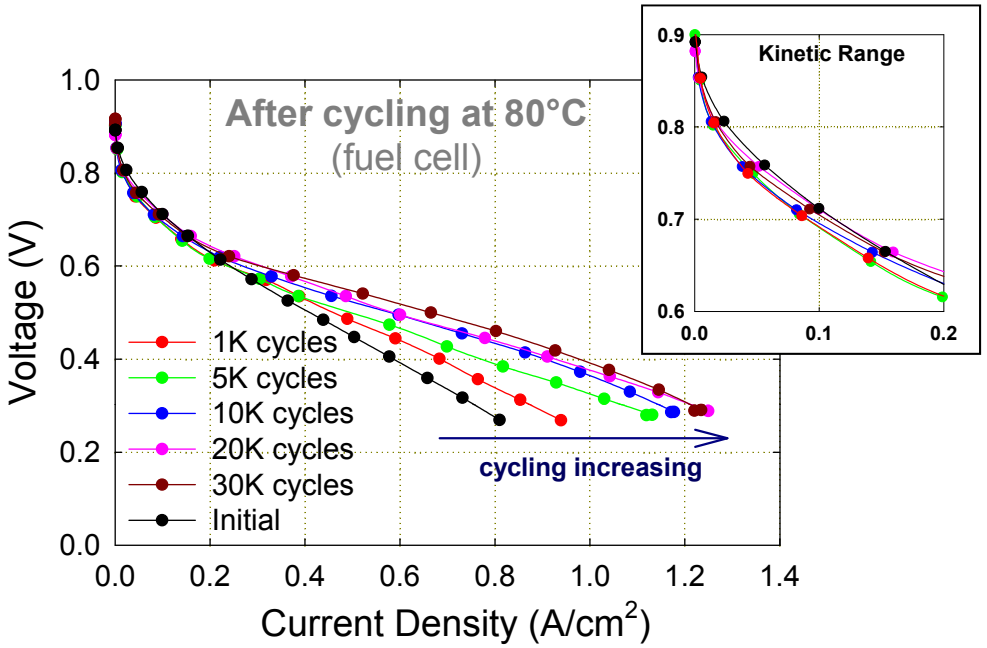
Both the support and polymer-derived carbon contributing to the catalyst morphology

PANI-Fe-C: More on Durability (Cycling)

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*

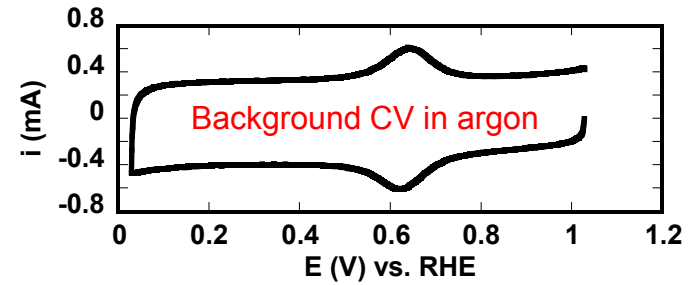
Anode: *0.25 mg cm^{-2} Pt; Cathode: 2.0 mg cm^{-2} PANI-Fe-C;* ***Membrane:*** *NRE-212;* ***Cell:*** *80 ℃; H_2-O_2/1.0-1.0 bar;* ***Cycling:*** *0.6-1.0 V, 50 mV/s, N_2 at 100% RH*

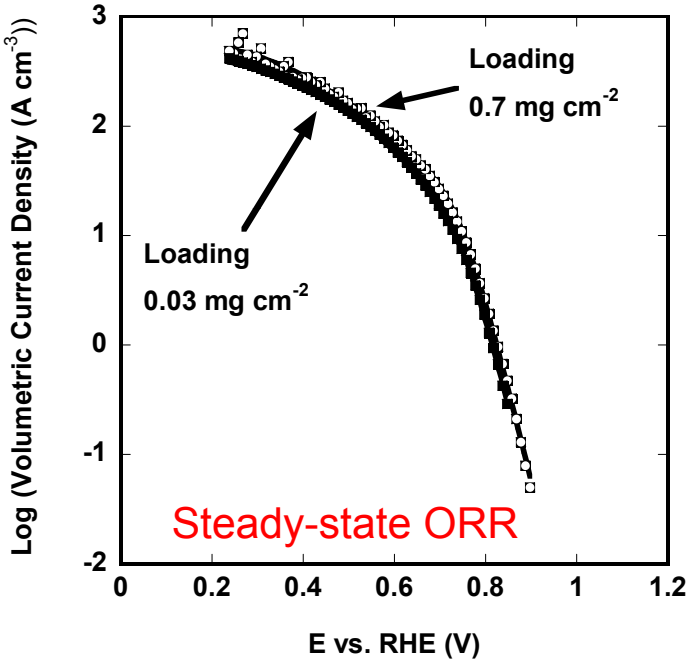




- **Only ~10 mV loss in $E_{½}$ at RDE testing after 10,000 potential cycles at 60ºC**
- **After 30,000 cycles in the fuel cell, performance increase observed with PANI-Fe-C cathode in a H_2-O_2 cell at lower voltages than 0.65 V; *ca.* 25% loss in current density observed at 0.80 V (kinetic range)**
- **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**

Mechanistic Analysis of ORR Kinetic Data for PANI-Fe-C Catalyst





$Ox + e^- \Leftrightarrow Red$	$k_{fwd} = k_s \exp[-\alpha F(E-E^o)/RT]$ $k_{bw} = k_s \exp[(1-\alpha)F(E-E^o)/RT]$
$Red + O_2 + H^+ \rightarrow Ox + (HO_2)^*$	rds (k_{chem} - rate constant)
$(HO_2^-)^* + 3e^- + 3H^+ \rightarrow 2H_2O$	fast reaction

Fitting equation:

$$\log (i) = \log(nFA\Gamma k) + \log\{\{\exp[-\alpha F(E-E^o)/RT]/\{\exp[-\alpha F(E-E^o)/RT] + (k/k_s) + \exp[(1-\alpha)F(E-E^o)/RT]\}\}$$

Γ - surface concentration of mediator sites ($\Gamma = \Gamma_{red} + \Gamma_{ox}$)
$k = k_{chem} C_{H+} C_{O2}$; A - real catalyst surface area;
n - number of electrons exchanged in ORR

Average parameter values obtained:

$\alpha = 0.25$; $k/k_s = 12.6$; $E^o = 0.662$ V
(E^o measured for the reversible surface system - 0.646 V)

- **Variable Tafel slopes in RDE experiments unrelated to catalyst-layer porosity; ORR Tafel 80-90 mV/decade at low overpotential**
- **Intrinsic catalytic properties of the PANI catalyst responsible for the Tafel plot curvature**
- **ORR likely mediated by a fast red-ox system on the catalyst surface**

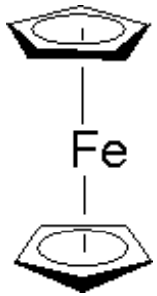
PANI-Fe-C XAS: XANES Iron Standards

Fe^0
Fe metal

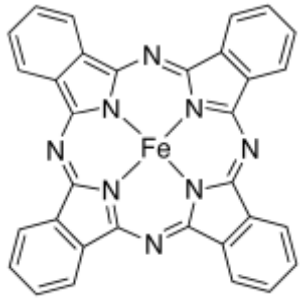
Fe^{2+} compounds
Fe0
Fe^{2+} phthalocyanine (at right)
Fe_2N
Fe_4N
$FeSO_4$ anhydrous
$FeSO_4$ $7H_2O$
Fe II acetylacetonate
Ferrocene (at right)
FeS
FeS_2
tris(2,2'-bipyridine) Iron(II) hexafluoro-phosphate (at right)
1,10-phenanthroline Iron(II) sulfate complex (at right)

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

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

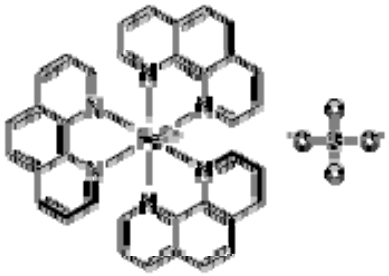


di(cyclopentadienyl) iron (ferrocene) (organometallic)

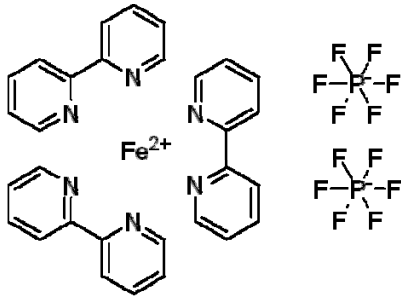


iron(II) phthalocyanine

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



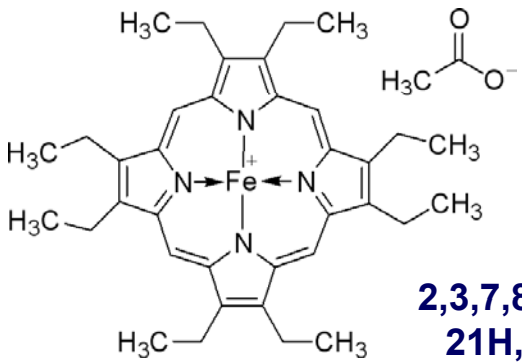
1,10-phenanthroline iron(II) sulfate complex (FeN_6)



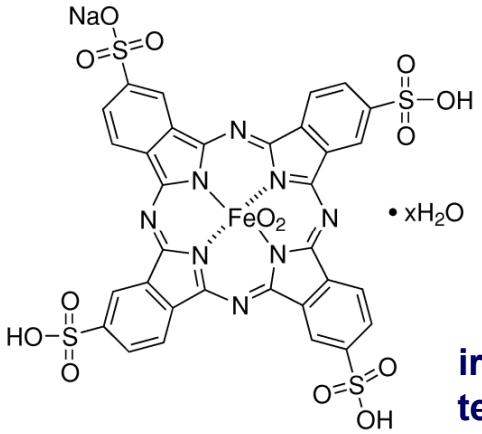
tris(2,2'-bipyridine) iron(II) hexafluoro-phosphate (FeN_6)

PANI-Fe-C XAS: XANES Iron Standards

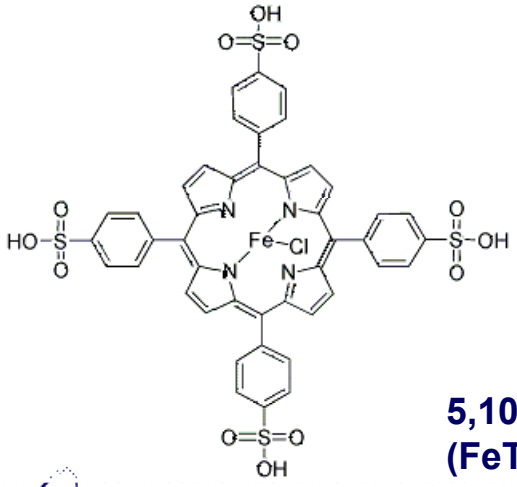
Fe^{3+} compounds
$FeCl_3$ $6H_2O$
Fe III acetylacetonate
$Fe(NO_3)_3$ $9H_2O$
Fe_2O_3
Fe porphine (at right)
Fe^{3+} phthalocyanine (at right)
modified Fe^{+} porphine (FeTPPS, below)



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)