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

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

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

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

MeN₄/C (Me: Co or Fe) species embedded in carbon micropores – an alternative ORR active site concept

Lefèvre et al, Science, 324, 71, 2009
Turnover Frequency of Various ORR Catalysts

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

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

Gasteiger and Markovic, *Science* 324, 48 2009
• 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-free}
  - area specific activity 720 μA/cm² at 0.90 V_{iR-free}

- Activity of non-PGM catalysts (per catalyst volume):
  - > 130 A/cm³ at 0.80 V_{iR-free} (2010); 300 A/cm³ at 0.80 V_{iR-free} (2015)

- Durability with cycling: 5,000 hours at T ≤ 80°C, 2,000 hours at T > 80°C

- 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)

Pyrrrole + XC72

↓

PPy-XC72

(i) **Co precursor**  
(ii) **reduction**

Co-PPy-XC72

Co-PPy-XC72 Catalyst: Molecular Modeling

\[ D_{O-O} = 1.21 \text{ Å} \quad \text{DO-O} = 1.47 \text{ Å} \]

\[
\text{dioxygen} + 2H^+ + 2e^- \rightarrow \text{dioxygen}
\]

\[ D_{O-O} = 1.56 \text{ Å} \quad \text{DO-O} = 1.99 \text{ Å} \]

\[
\text{[(tetrapyrrole) H}_2\text{O Co-OH-HO-Co H}_2\text{O (tetrapyrrole)]}^2^-
\]

Dioxygen interaction with two Co centers significantly weakening O-O bond relative to the O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} reference system
Low-Temperature Non-precious Metal Composites: Co-PPy-XC72

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


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High-Temperature Synthesis

Cyanamide

\[
\text{N} = \text{C} - \text{N} - \text{H}
\]

Polypyrrole

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\]

Polyaniline

Transition metal

Carbon support

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

0.5 M H₂SO₄ 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

A. Adsorption
B. Metal Addition
C. Heat Treatment
D. Acid leach
E. 2nd Heat Treatment

Final Catalyst

Carbon particle
Oligomer
Polyaniline
Metal aggregates encapsulated in graphite onion-like carbon shells
Carbon shells doped with nitrogen functionalities possibly coordinated by metallic species
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 E½
- H₂O₂ 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

- Catalysts synthesized at 900°C showing the highest ORR activity and the lowest \( \text{H}_2\text{O}_2 \) 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.

Elemental quantification by XPS

- **C 1s**, **O 1s**, and **Fe 2p** content variation with heat-treatment temperature.
Polymer Electrolyte Fuel Cell (PEFC)

- Anode: \(CH_3OH \text{ or } H_2\)
  - Reaction: \(CO_2 + 6H^+ + 6e^- \rightarrow 2H^+ + 2e^-\)
- Cathode: \(1.5O_2 \text{ or } 0.5O_2 \text{(air)}\)
  - Reaction: \(H_2O \rightarrow 3H_2O \text{ or } H_2O\)
- Electrosomotic Drag

Diagram:
- \(CH_3OH\) or \(H_2\) enter from the left.
- \(1.5O_2\) or \(0.5O_2\) (air) enter from the right.
- \(H_2O\) exits on the right.
- \(CO_2\) or \(H_2O\) exits on the left.
- \(H_2O\) is distributed through the membrane.

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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
• 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
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)Sx regions/particles (→); MWNT still present (→)

- BF-STEM images of PANI-Fe-MWNT showing graphitic carbon particles that surround/encapsulate FeSx

- 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

Fe Metal/Fe Oxides Standards

Fe Sulfides Standards

Examples of Fe-Complexes Standards

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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

- **Best Match with Activity**: Total FeN$_x$ Species and ORR Activity (at 0.80 V)

- **Fe-C$_x$ and Fe-N$_x$**: Organometallic (Fe-C$_x$) and Porphine (Fe-N$_4$)

- **Other Fe Species**: Metallic (Fe-Fe), Oxides (Fe-O$_x$), Sulfides (Fe-S$_x$), Phthalocyanine (Fe-N$_4$), Sulfate (Fe-SO$_4$)
PANI-Fe-C: Effect of Heat-Treatment Temperature on Surface Area and Pores

- Sample heat-treated at 900°C 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

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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 $\mu$g Pt cm$^{-2}$)
- $H_2O_2$ generation: ~1%

Graph showing:
- % $H_2O_2$ vs Potential (V vs RHE)
- Current Density (mA cm$^{-2}$) vs Potential (V vs RHE)
- CM-Fe-C(2) $E_{1/2}$ 0.77 V
- 20 $\mu$g Pt cm$^{-2}$ $E_{1/2}$ 0.84 V

Limiting current calculated from Levich equation for 900 rpm at Los Alamos' latitude: 3.5 mA cm$^{-2}$
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/cm²): ~ 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/cm³ 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

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*Science, 443-447, 332, 2011*

• **Open cell voltage** (OCV) of 1.04 V and volumetric ORR activity of 165 A/cm$^3_{\text{electrode}}$ (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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential at 0.10 mA/cm² (V vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA-Co-C</td>
<td>0.81</td>
</tr>
<tr>
<td>PANI-Fe-C</td>
<td>0.94</td>
</tr>
<tr>
<td>PANI-Fe/EDA-Co-C</td>
<td>0.96</td>
</tr>
<tr>
<td>20 wt% Pt/C (60 µg cm⁻²)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

- ORR activity: At least 40 mV needed, especially at low overpotential (\(\eta\)); low Tafel slope of help at higher \(\eta\) 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

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

Gang Wu, Karren L. More, Christina M. Johnston, Piotr Zelenay

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 40 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 (960 hours at a fuel cell voltage of 0.4 volt) as well as excellent four-electron selectivity (hydrogen peroxide yield <2%).

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 to multi-kilowatts, marine to vehicular 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 CO₂). The volumetric 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 automobile powerplant. 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 monopolar 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 $1300 per troy ounce at present ($2820 per troy ounce at its maximum in March 2001) (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 fast 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 (4–6). The Pt replacement candidate that has 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 (9–15).

Although the nature of the active ORR catalysts is still under debate (6, 7, 15, 16), 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 polyaniline (PPy)-based system prepared this way showed respectable performance durability for a non-precious metal 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\(_2\)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.

**After cycling at 60°C (aqueous electrolyte):**

- Only ~10 mV loss in \(E_{1/2}\) at RDE testing after 10,000 potential cycles at 60°C.
- 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.

**After cycling at 80°C (fuel cell):**

- Kinetic Range

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

\[ \text{Ox} + e^- \Leftrightarrow \text{Red} \]

\[ k_{\text{fwd}} = k_s \exp\left[-\alpha F (E - E^0)/RT\right] \]

\[ k_{\text{bw}} = k_s \exp\left[(1-\alpha)F (E - E^0)/RT\right] \]

\[ \text{Red} + \text{O}_2 + \text{H}^+ \rightarrow \text{Ox} + (\text{HO}_2)^* \quad \text{rds (} k_{\text{chem}} \text{ - rate constant)} \]

\[ (\text{HO}_2)^* + 3e^- + 3\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad \text{fast reaction} \]

Fitting equation:

\[ \log(i) = \log(nF A \Gamma k) + \log\left\{ \exp\left[-\alpha F (E - E^0)/RT\right] \right\} / \left\{ \exp\left[-\alpha F (E - E^0)/RT\right] + (k/k_s) + \exp\left[(1-\alpha)F (E - E^0)/RT\right] \right\} \]

\( \Gamma \) - surface concentration of mediator sites \( \Gamma = \Gamma_{\text{red}} + \Gamma_{\text{ox}} \)

\( k = k_{\text{chem}} C_{\text{H}+\text{C}_2\text{O}_2}; A \) - real catalyst surface area;

\( n \) - number of electrons exchanged in ORR

Average parameter values obtained:

\( \alpha = 0.25; \ k/k_s = 12.6; \ E^0 = 0.662 \text{ V} \)

\( E^0 \) 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

<table>
<thead>
<tr>
<th>Fe$^0$</th>
<th>Fe metal</th>
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**Fe$^{2+}$ compounds**
- Fe0
- Fe$^{2+}$ phthalocyanine (at right)
- Fe$_2$N
- Fe$_4$N
- FeSO$_4$ anhydrous
- FeSO$_4$ 7H$_2$O
- 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$_3$O$_4$

*Activity of non-precious catalysts attributed by many groups to FeN$_4$–type or FeN$_{2+2}$–type sites*

**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**

- di(cyclopentadienyl) iron (ferrocene) *(organometallic)*
- 1,10-phenanthroline iron(II) sulfate complex *(FeN$_6$)*
- tris(2,2'-bipyridine) iron(II) hexafluoro-phosphate *(FeN$_6$)*
**Fe³⁺ compounds**

FeCl₃ 6H₂O  
Fe III acetylacetonate  
Fe(NO₃)₃ 9H₂O  
Fe₂O₃  
Fe porphine (at right)  
Fe³⁺ phthalocyanine (at right)  
modified Fe⁺ porphine  
(FeTPPS, below)

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

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

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