In-situ X-ray Spectroscopy and Scattering Diagnostic Studies of PEFC Cathode Catalysts

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DIAGNOSTIC TOOLS FOR FUEL CELL TECHNOLOGIES

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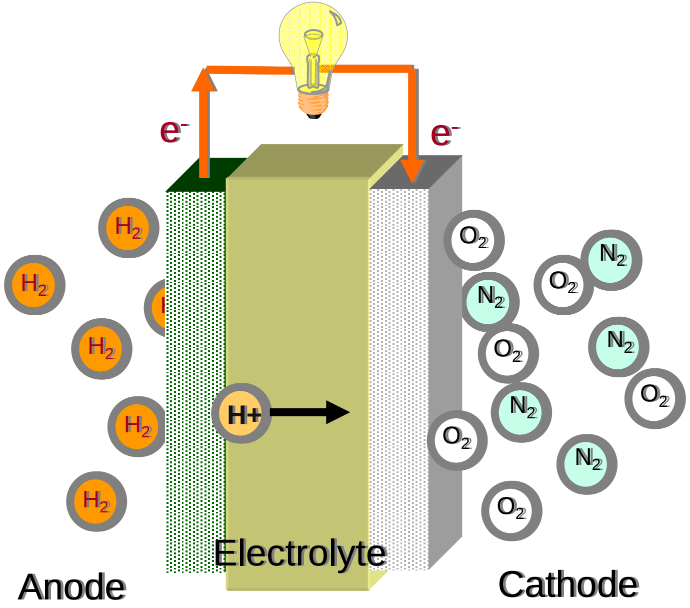
Why don't we have "two fuel cell cars in every garage"?

- Major hurdles to overcome
  - Cost
    - *50% of cost of PEFC stack is due to Pt catalyst**
  - Durability
    - *Pt and Pt alloy cathode electrocatalysts lose electrochemically-active surface area with time*
  - Fuel storage, availability, and delivery

- How can we get there?
  - Materials and engineering advances
    - *better utilization/performance*
    - *lower cost (e.g., PGM alternatives)*
  - Fundamental studies of materials
    - *how they work*
    - *what limits their performance*

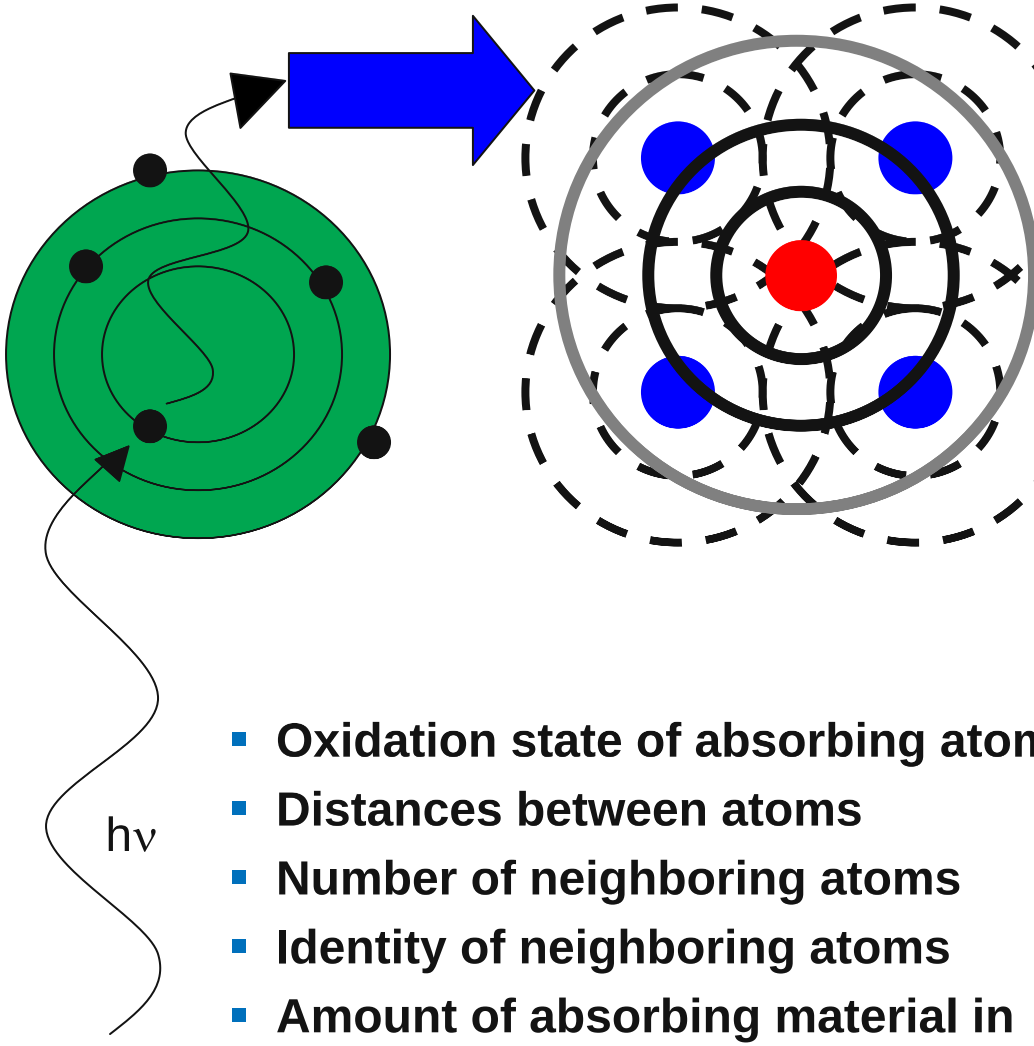


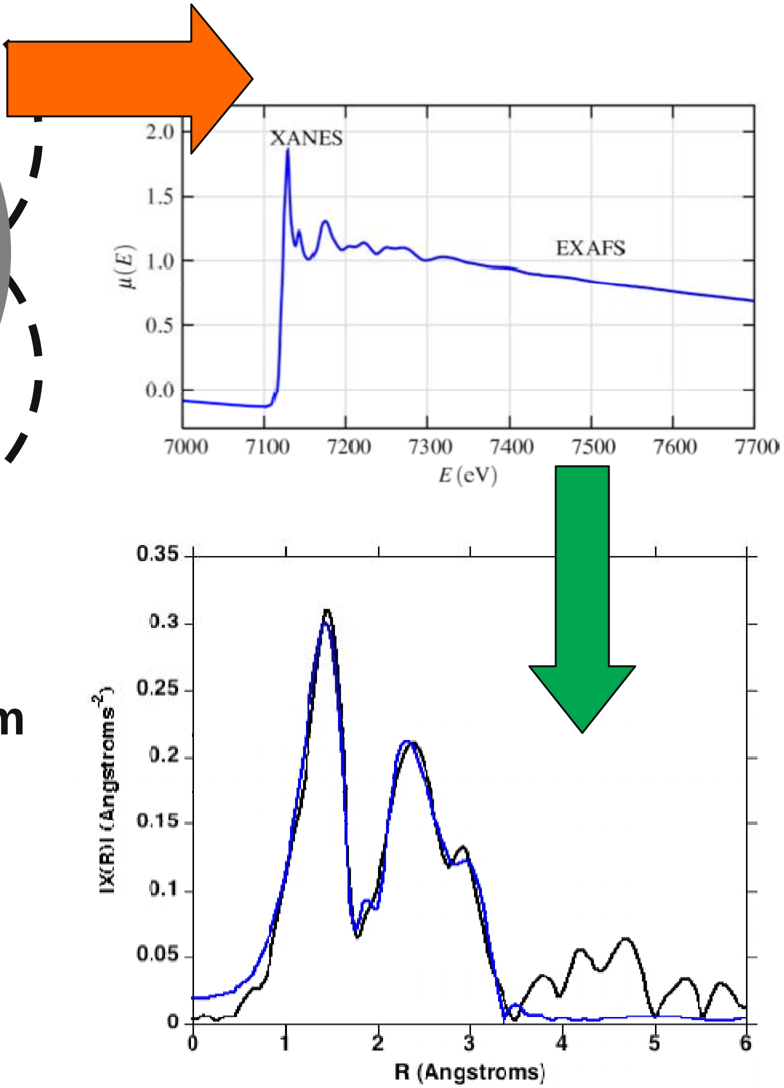
**2007 Status, Directed Technologies Incorporated Study, Feb. 2008*

How can we get the necessary information?

- What's needed for rational design of catalysts: identity of active site; relationship between structure and degradation
- Must "see" inside the fuel cell while it's running with 0.1-10 nm "vision"
- Probe must penetrate through flow field, gas diffusion layer, and ionomer to characterize catalyst on the atomic level
- X-rays can penetrate through low atomic number materials and have wavelengths on the order of atomic dimensions
- Synchrotron X-ray sources (high intensity, tunable wavelength), such as Argonne's Advanced Photon Source, give us "X-ray vision"

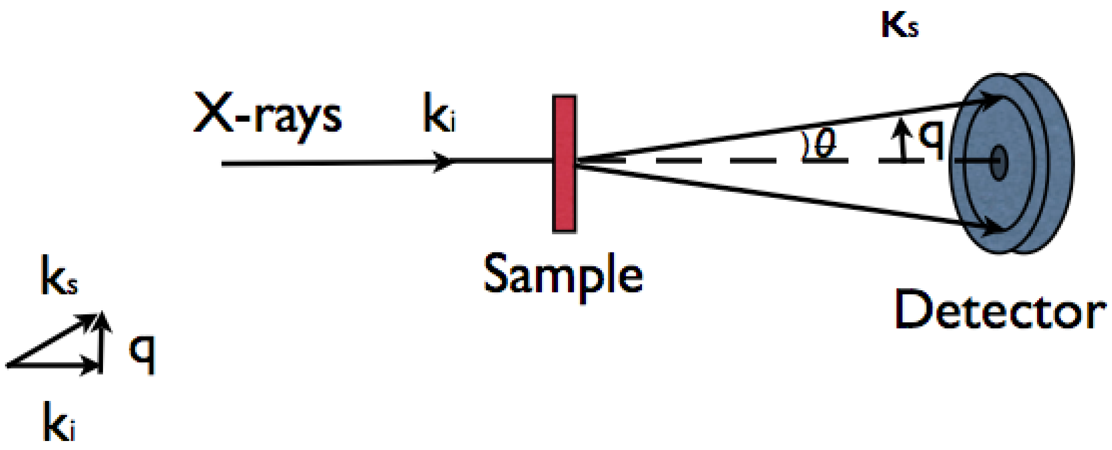
X-ray Absorption Fine Structure (XAFS)

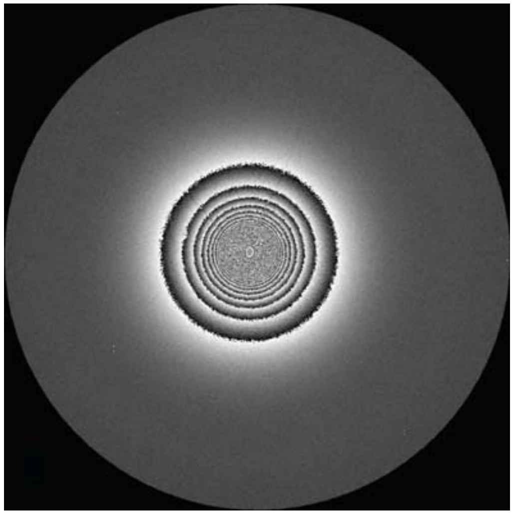




- **Oxidation state of absorbing atom**
- **Distances between atoms**
- **Number of neighboring atoms**
- **Identity of neighboring atoms**
- **Amount of absorbing material in beam**

Small-Angle X-ray Scattering (SAXS)





$$q = |\mathbf{q}| = \frac{4\pi}{\lambda}\sin(\theta/2)$$

Gives information on particles 1 - 100 nm in size

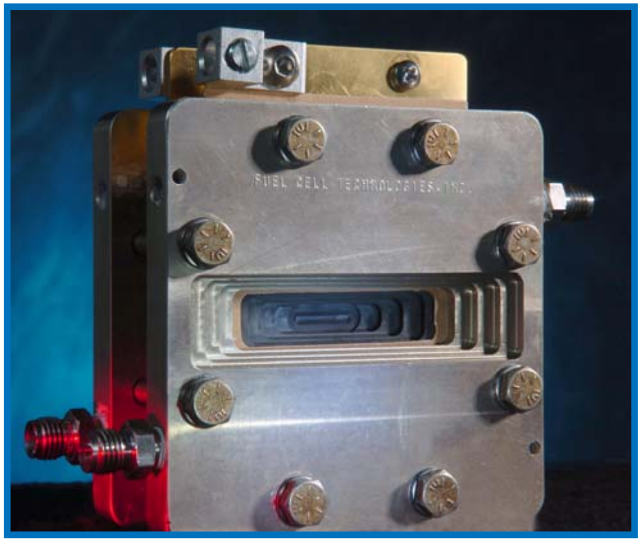
- Shape
- Mean Size
- Size Distribution

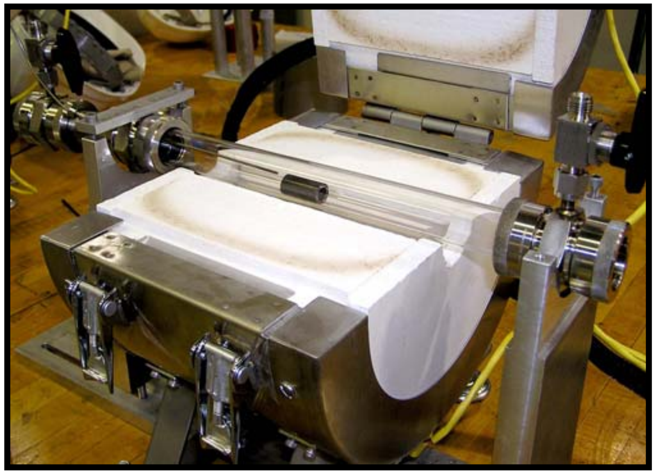
Examples of systems studied with in-situ and ex-situ X-ray techniques

- Pt-based electrocatalyst degradation
  - Oxidation state and correlation of loss of Pt with voltage
    - *X-ray absorption in an aqueous environment*
  - Oxide formation and Pt particle growth as a function of potential cycling
    - *Small angle X-ray scattering and anomalous small angle X-ray scattering*
    - *Aqueous environment and MEA*

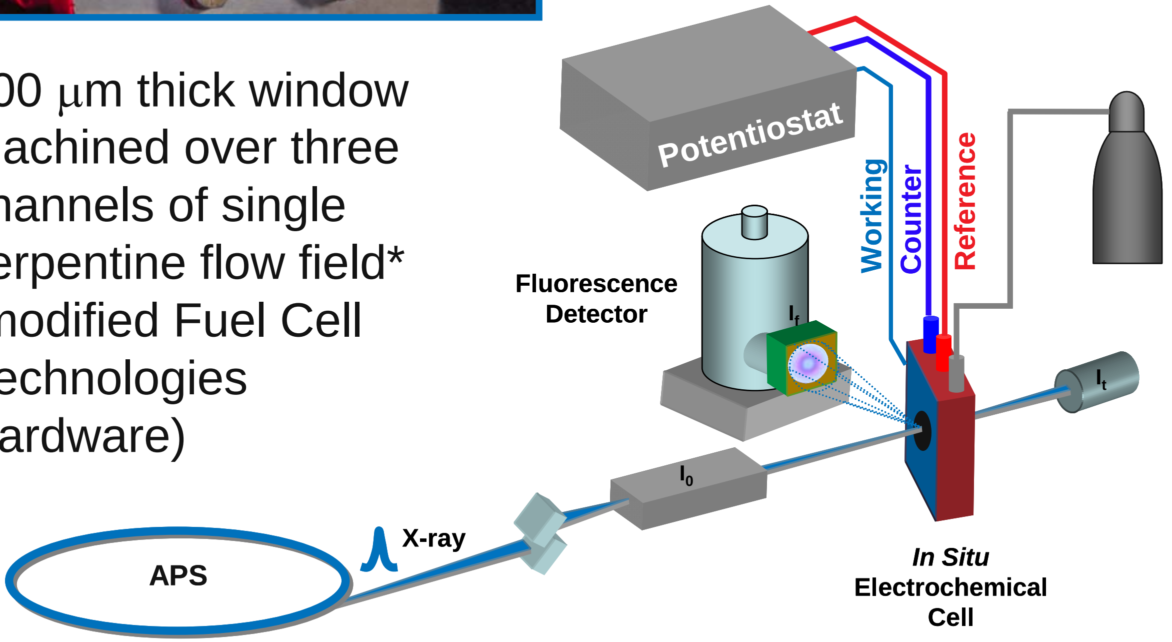
- Non-platinum group metal catalyst composition, structure, oxidation state, and amount of absorbing metal using X-ray absorption
  - During pyrolysis
  - Effect of post-pyrolysis acid treatment
  - As a function of potential in aqueous environment
  - In MEA during polarization

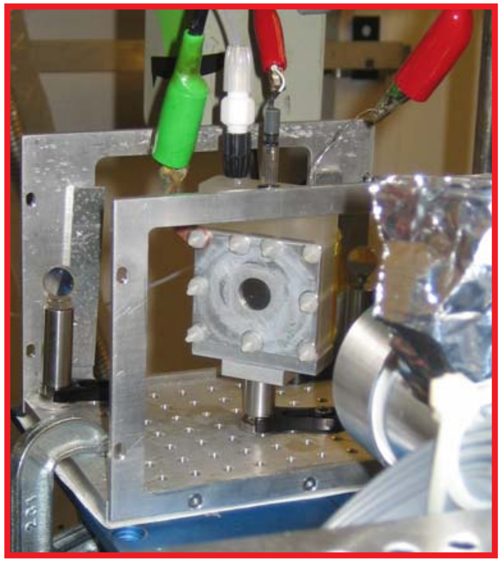
Cells for in situ X-ray studies of cathode catalysts





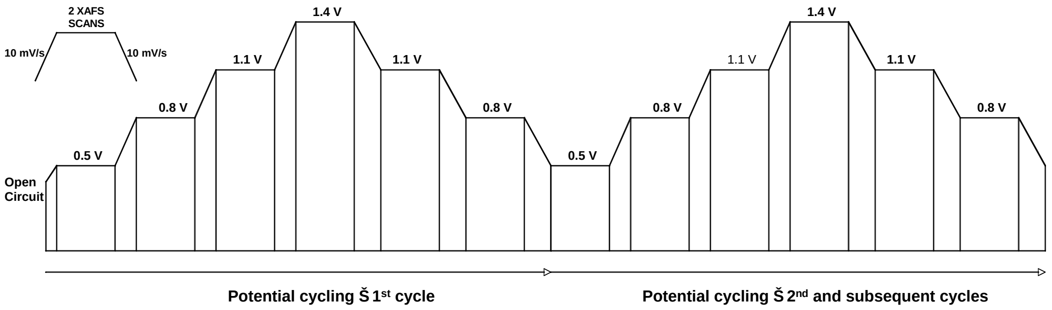
- 300 μm thick window machined over three channels of single serpentine flow field* (modified Fuel Cell Technologies Hardware)

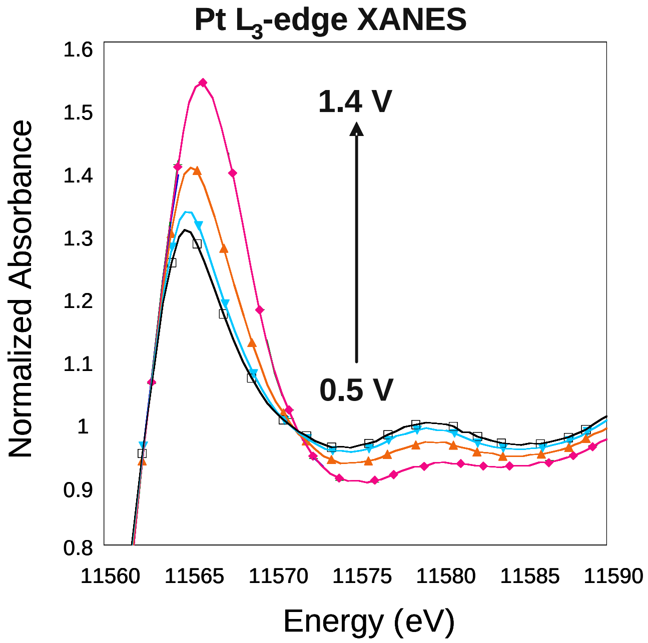


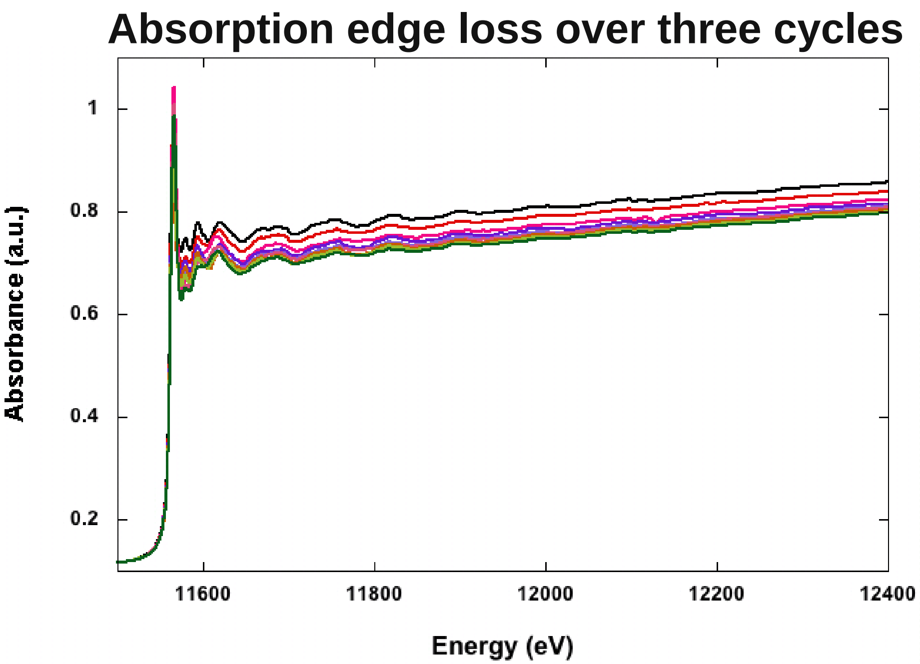


*Based on published design: Principi, E.; Di Cicco, A.; Witkowski, A.; Marassi R. J. Synchrotron Rad., 2007, 14, 276.

Aqueous in-situ XAFS shows potential dependence of Pt loss and Pt oxidation state



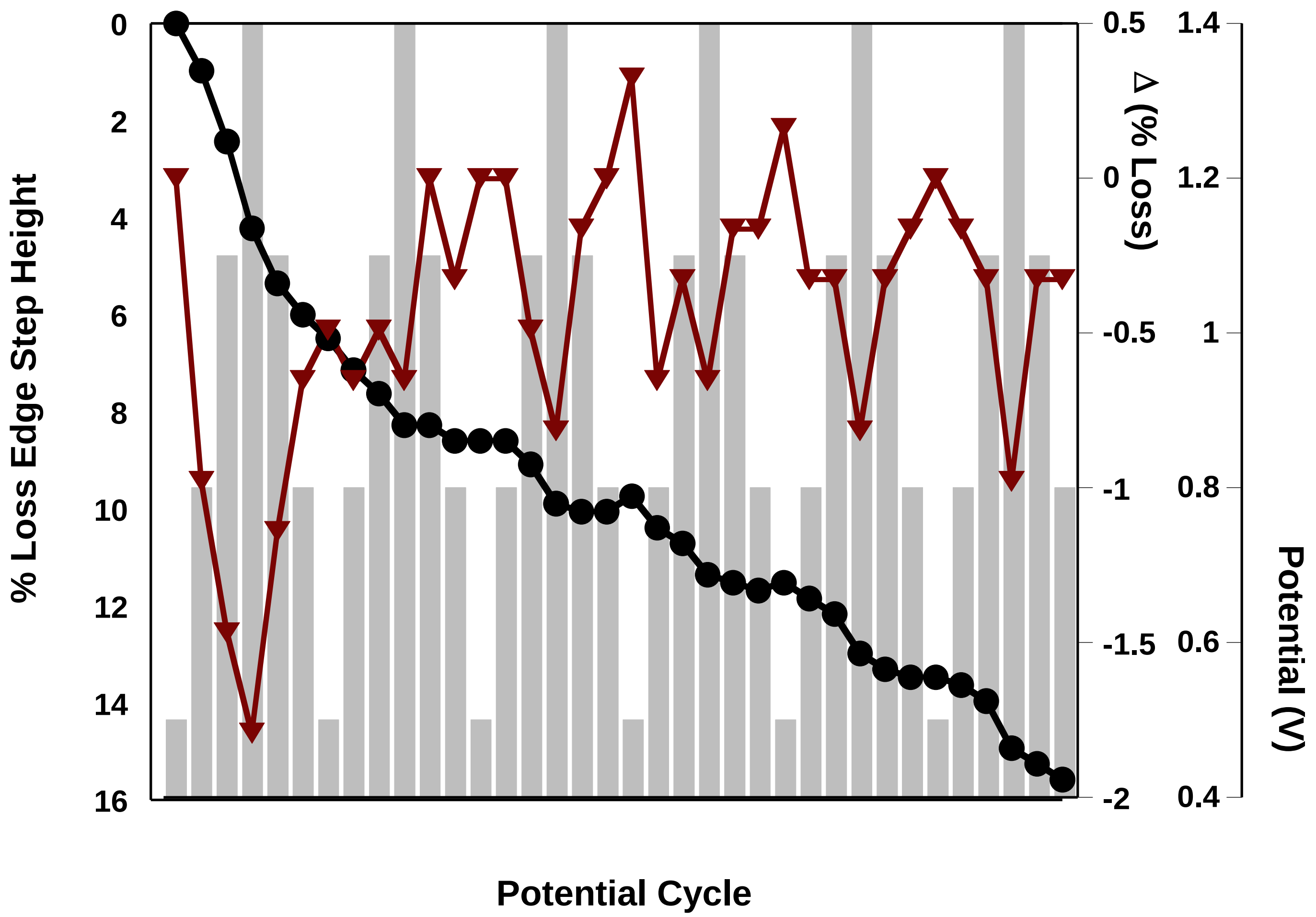

Pt L_3-edge XANES


Absorption edge loss over three cycles

- Height of “white line” α extent of oxidation of Pt
- Height of Pt L_3 absorption edge α amount of Pt in electrode

Platinum loss occurs during anodic and cathodic potential scans

- Greatest Pt loss observed in anodic step from 1.1 to 1.4 V



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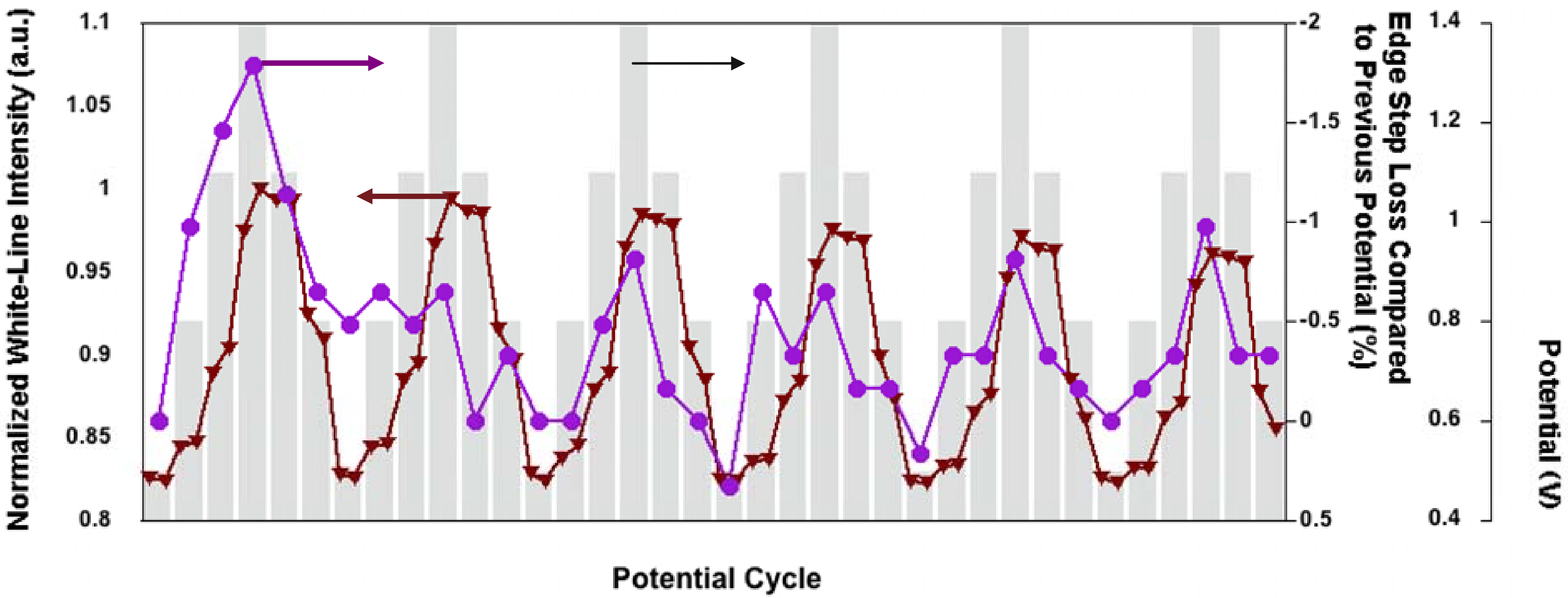
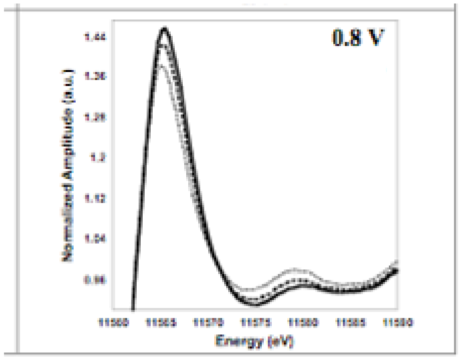
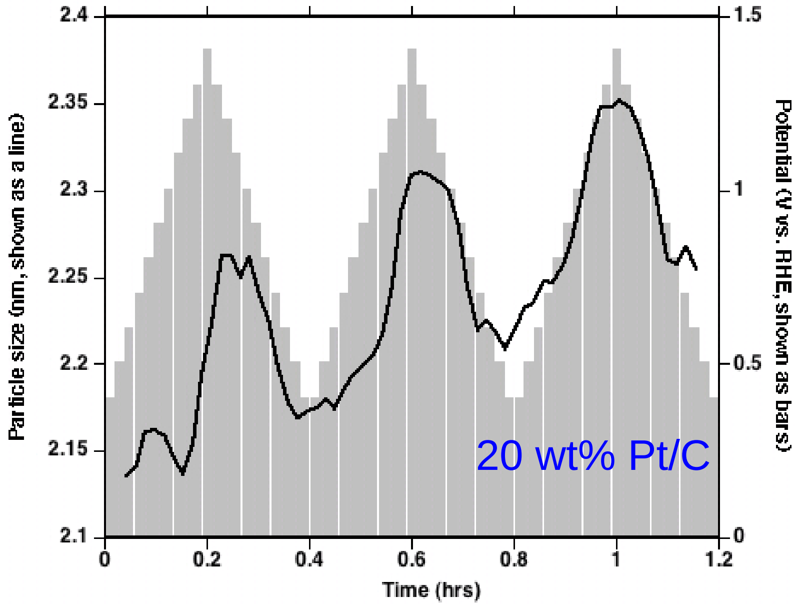
XAFS shows platinum loss and oxide formation are linked

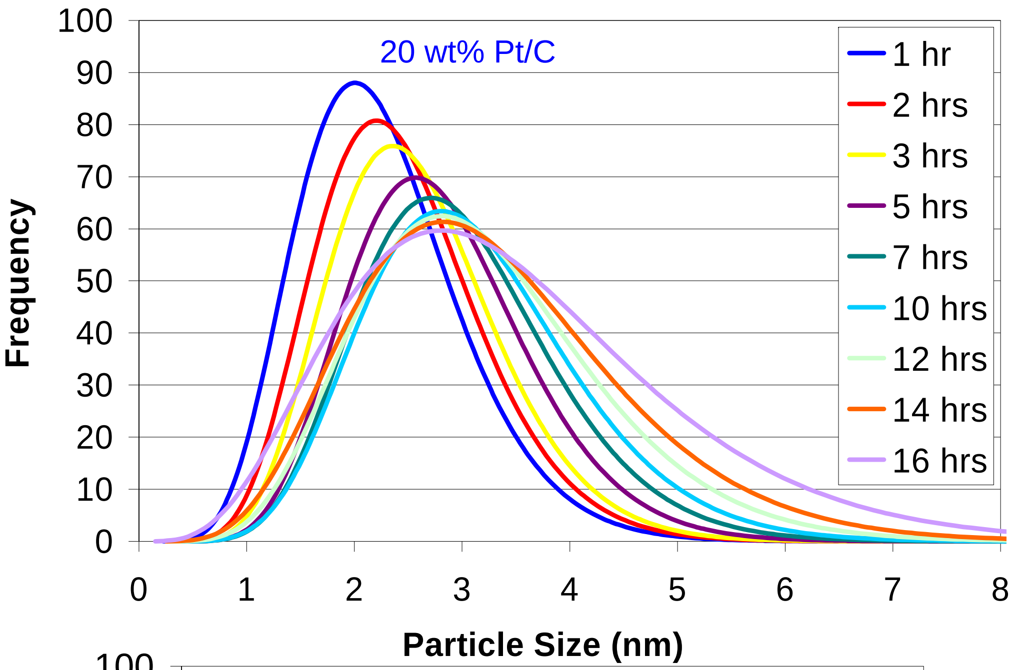


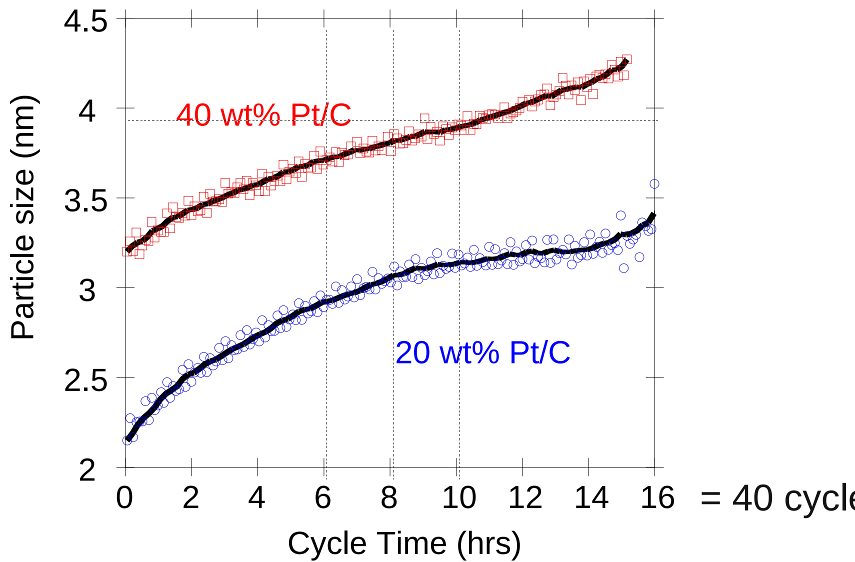
- Pt loss is highest during oxide formation
- Approximately same extent of oxidation show different Pt loss rates
  - Evidence against major role of oxide dissolution
  - Evidence for dissolution of metal
  - "Time-resolved" experiments are underway
- Extent of Pt oxidation decreases with potential cycling - may be indicative of particle growth

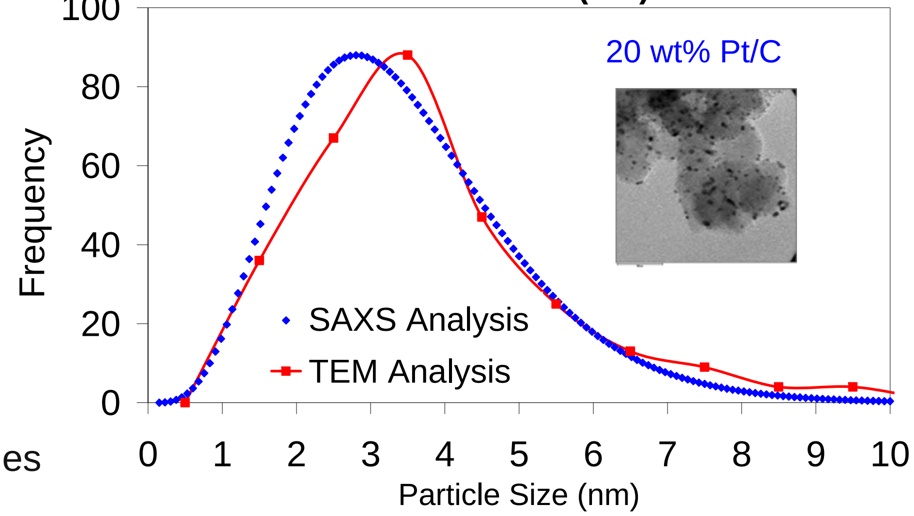


SAXS studies shows Pt particle growth with cycling





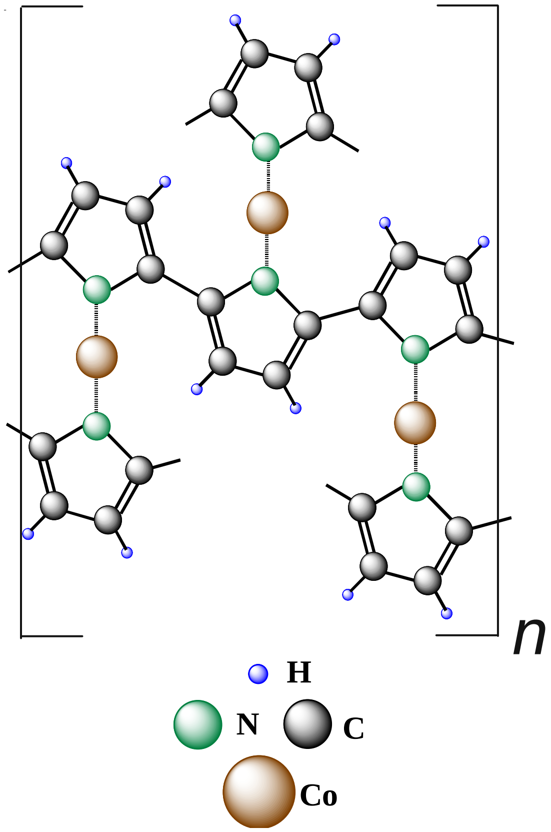




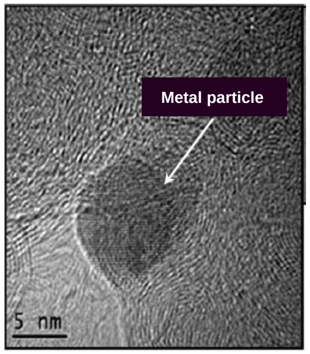
M.C. Smith et al., J. Am. Chem. Soc., 2008.

Non-platinum group metal electrocatalysts

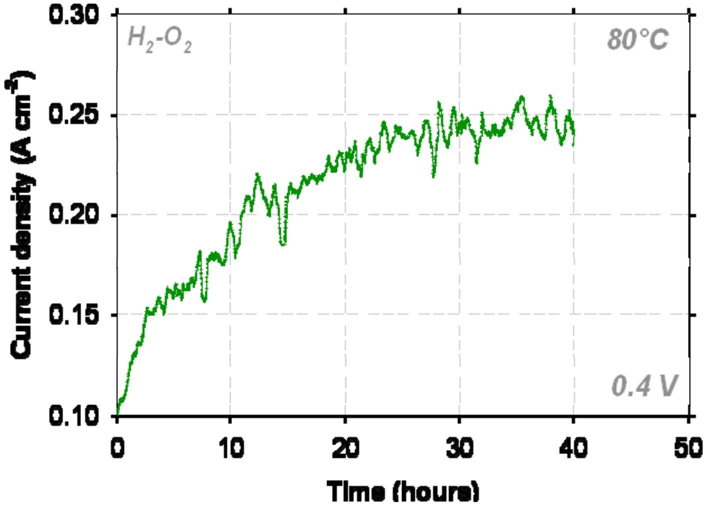
- Cobalt or iron either complexed with C-N polymer/molecule or pyrolyzed (J.P. Dodelet, Los Alamos NL, U. South Carolina, 3M, et al.)
  - Low cost
    - *(Co ~US$ 3 /oz, abundance 20,000-30,000 ppb in Earth's crust vs 3-37 ppb for Pt)*
  - Promising oxygen reduction activity, but lower than platinum group metals
  - Good durability, but longer testing and cycling tests are needed (>1000 hrs)
- Issues:
  - Identity of the active site is unknown
    - *Metal center coordinated to pyridinic nitrogen*
    - *Encapsulated metal catalyzes formation of active site*
  - Metal leaches from catalyst during operation



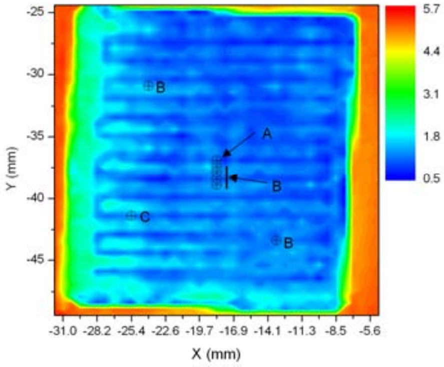
R. Bashyam and P. Zelenay, Nature, 2006.

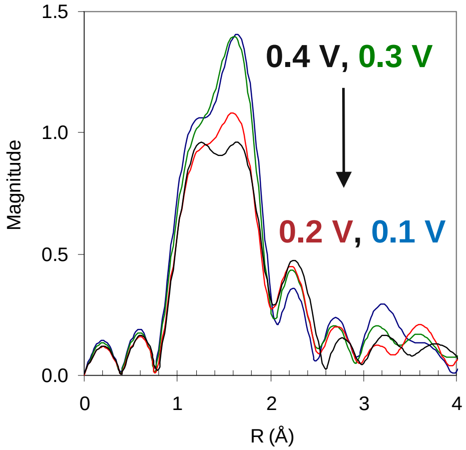


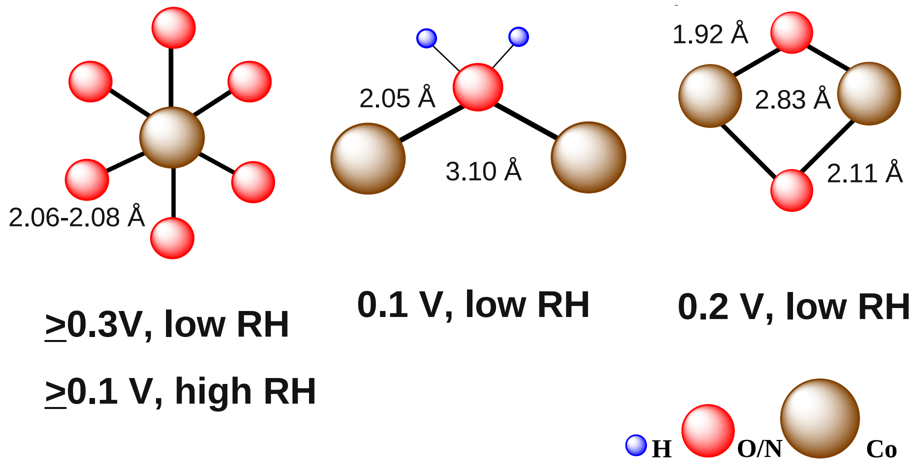
XAFS analysis shows Co-polypyrrole (not pyrolyzed) catalyst changes with time/potential



- Slow break in: possible formation of ORR sites during operation or removal of site-blocking species
- *Ex-situ* XAFS data: as-prepared MEA contained a mixture of cobalt metal and a small oxide fraction
- *In-situ* XAFS data: cobalt metal fraction is removed and/or converted to higher oxidation state
- Three cobalt species observed *in-situ*:







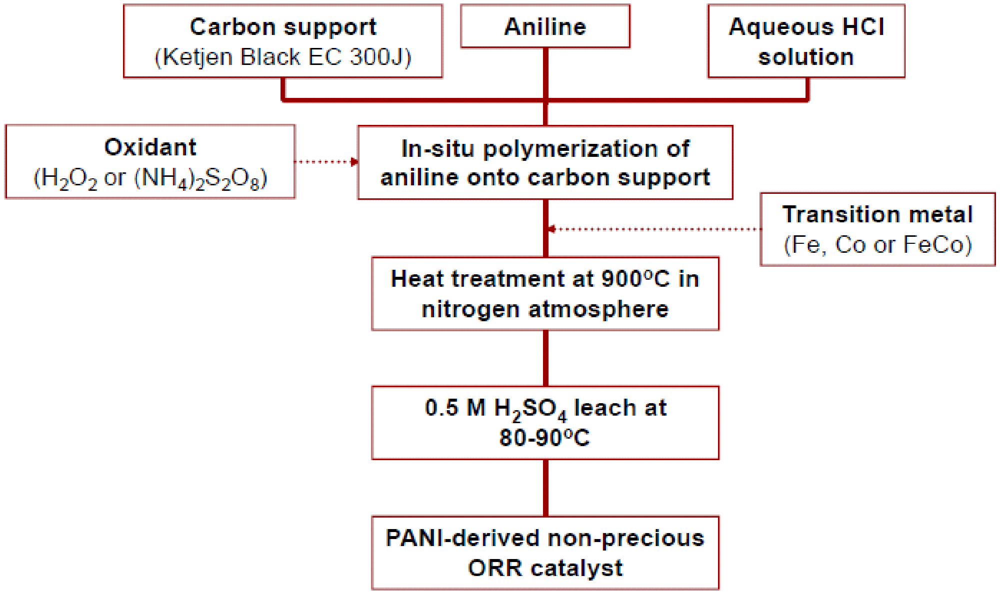
≥0.3V, low RH

≥0.1 V, high RH

0.1 V, low RH

0.2 V, low RH

Los Alamos NL's pyrolyzed polyaniline-Fe(Co)-C ORR catalysts



Carbon support (Ketjen Black EC 300J)

Aniline

Aqueous HCl solution

Oxidant (H_2O_2 or $(NH_4)_2S_2O_8$)

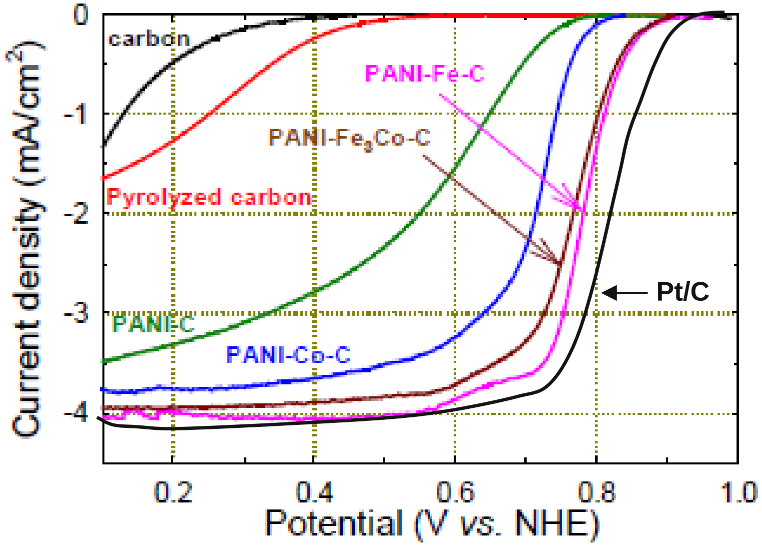
In-situ polymerization of aniline onto carbon support

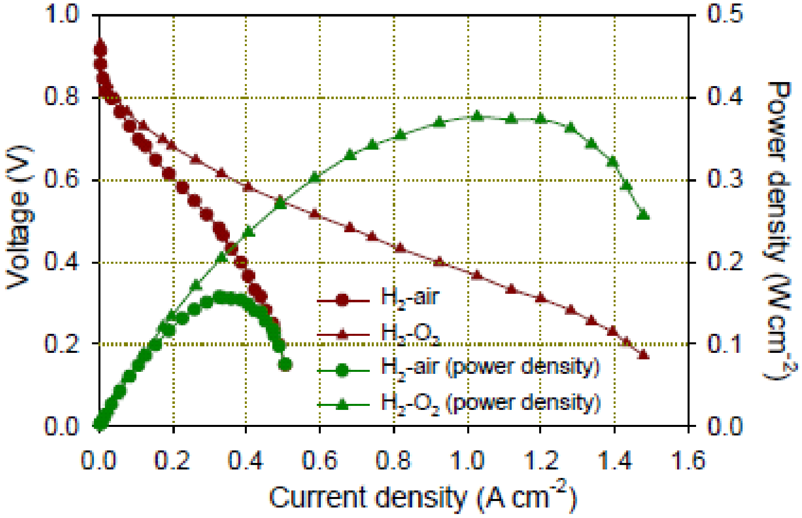
Transition metal (Fe, Co or FeCo)

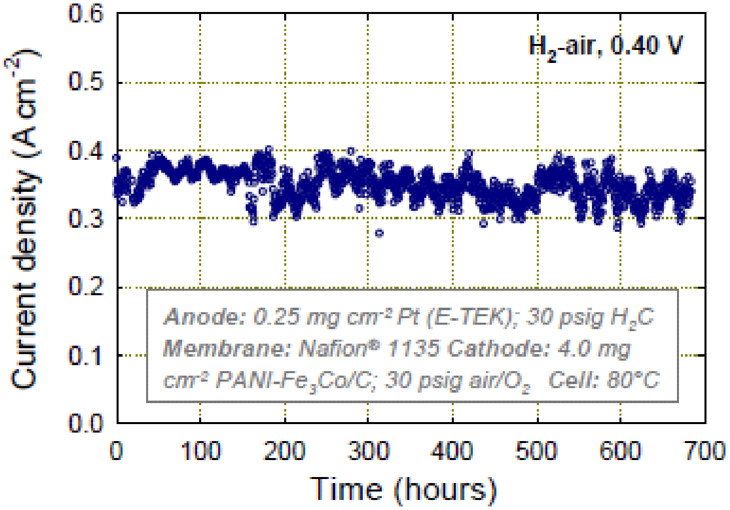
Heat treatment at 900°C in nitrogen atmosphere

0.5 M H_2SO_4 leach at 80-90°C

PANI-derived non-precious ORR catalyst

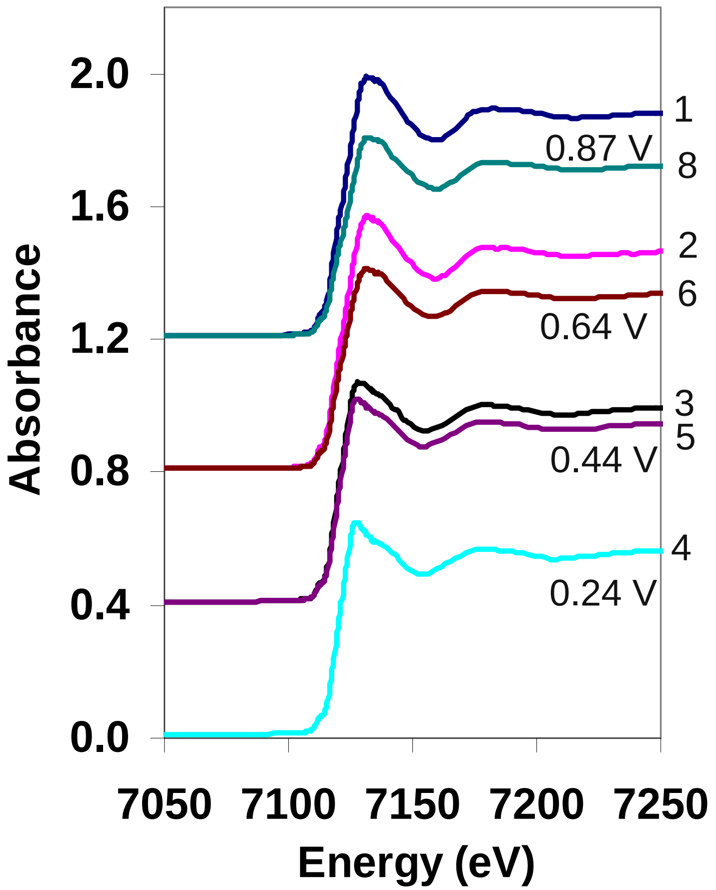


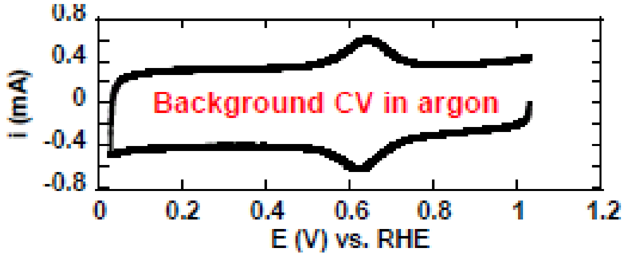




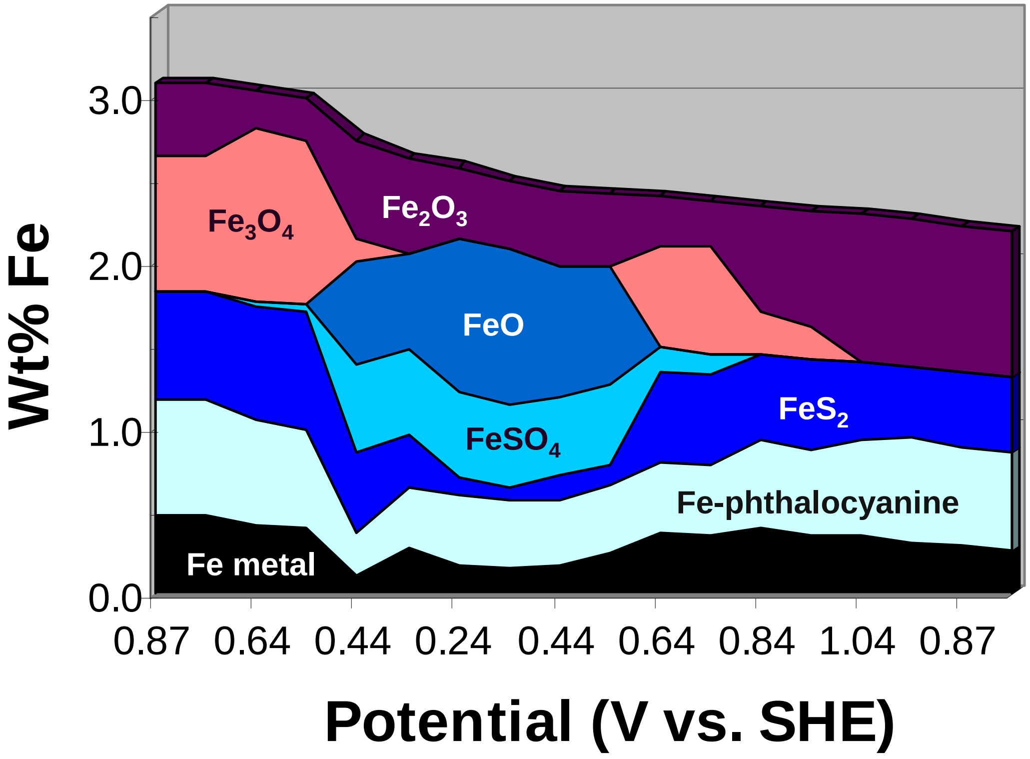
Anode: 0.25 mg cm^{-2} Pt (E-TEK); 30 psig H_2C Membrane: Nafion® 1135 Cathode: 4.0 mg cm^{-2} PANI-Fe_3Co/C; 30 psig air/O_2 Cell: 80°C

Aqueous cell in-situ data for pyrolyzed polyaniline-Fe-C system

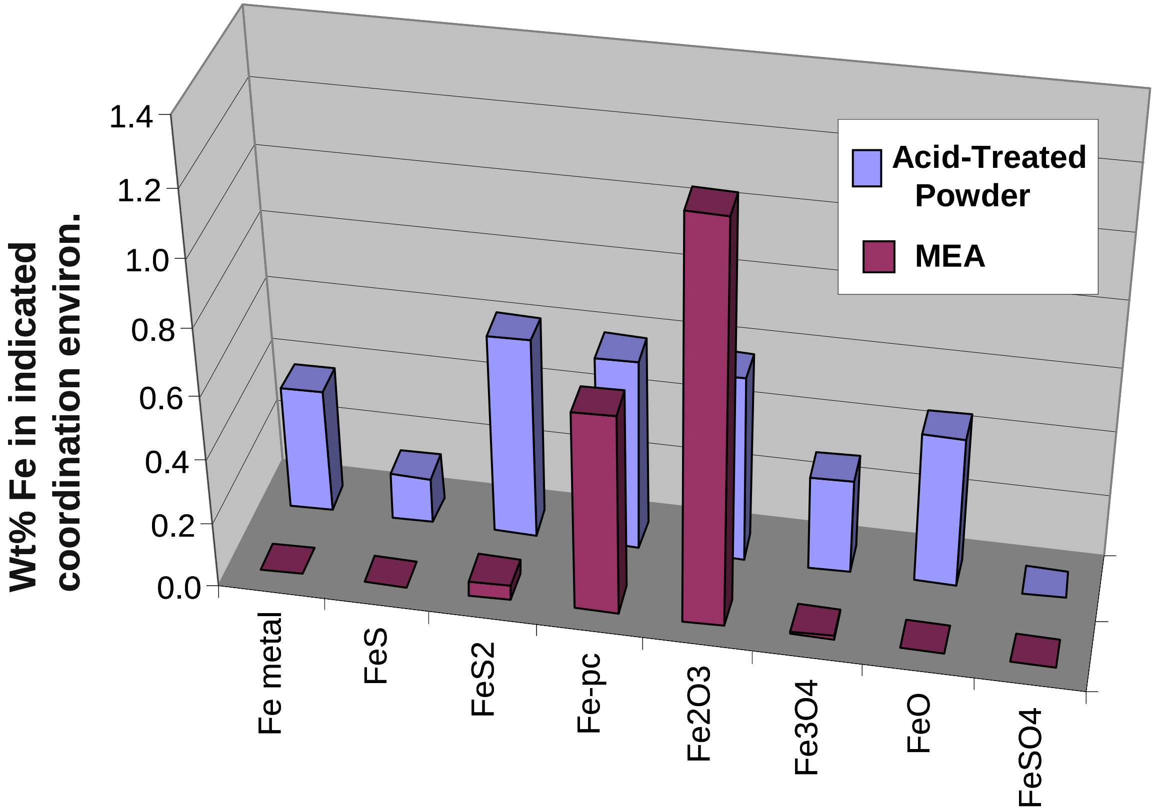




- XAFS shows reversible reduction of Fe^{3+} catalyst component between 0.64 and 0.44 V
- Fe is lost from the electrode with greatest loss observed during this reduction step

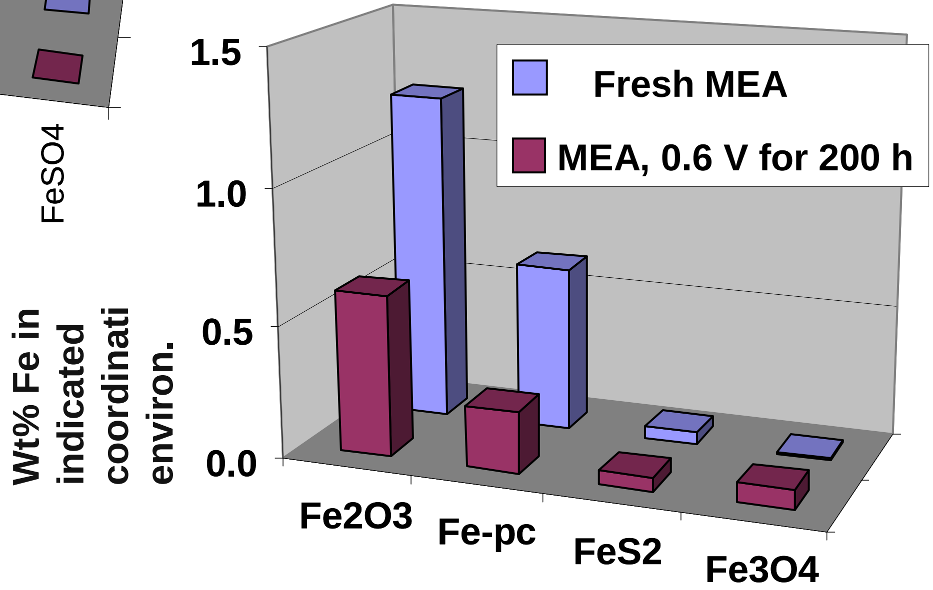


Pyrolyzed polyaniline-Fe-C catalyst composition



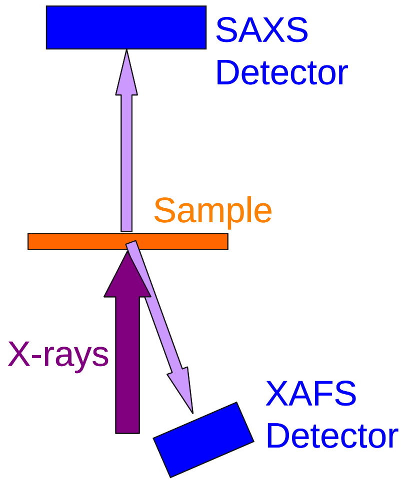
- MEA preparation:
  - Removes metal
  - Removes sulfides
  - Oxidizes Fe^{2+} to Fe^{3+}

- Fe is lost from MEA during long-term polarization at 0.6 V (approx. 50% loss)
- Ratio of Fe_2O_3 to Fe-pc coordination is approx. unchanged



Summary

- *In-situ* X-ray absorption and scattering techniques are powerful for diagnosing the state of PEFC catalysts during operation
- New *in-situ* X-ray fuel cell block design allows XAFS studies in fluorescence mode
  - Enables study of very low loadings of low Z metals (e.g., Fe and Co)
  - Eliminates the need to modify flow field design
  - Allows the study of one electrode of a cell when the opposing electrode contains the same metal (e.g., can study Pt in a Pt cathode with a Pt anode)
- Future needs/experiments
  - Combination of scattering and absorption experiments with microsecond time resolution
  - **Simultaneous** spatio-temporal resolved (micrometer and microsecond) atomic, electronic, and particle size characterization for a wide range of metals (e.g., Pt and Co in Pt_3Co catalyst)



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- DOE, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cells & Infrastructure Technologies