X-ray Absorption Spectroscopy and applications to fuel cell catalysts

Carlo Segre

Physics Department & CSRRI, Illinois Institute of Technology
and
Materials Research Collaborative Access Team

Sponsors: Department of Energy & Army Research Office
Outline

• Synchrotron Radiation
  – How it is produced (bending magnets & undulators)
  – Interaction of x-rays with matter (scattering & absorption)
  – X-ray absorption spectroscopy basics

• Fuel Cell Catalysts
  – Polymer electrolyte membrane fuel cell & ORR
  – Operando fuel cell & measurements

• XAS experiments on Pt/C and PtNi/C cathodes
  – Delta XANES experiment and calculation
  – Structural model of metal nanoparticle
  – Simple model of subsurface Ni
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What is a synchrotron?

figure courtesy of the Australian Synchrotron

Wichita State University - April 6, 2011
“Headlight” effect

electron rest frame

emission is symmetric about the axis of the acceleration vector

laboratory frame

emission is pushed into the direction of motion of the electron and Doppler shifted up
Bending magnet radiation

- Broad spectrum – visible to x-ray
- Large horizontal divergence
- Small vertical divergence
- Universal spectral curve
Undulator radiation

- Highly peaked, tunable, spectrum
- Small horizontal and vertical divergence
- Some coherence (like a laser!)

![Undulator diagram](image)

![Graph showing Brilliance vs Photon Energy](image)
Elastic x-ray scattering

- Elastic process – energy of x-ray does not change
- Change in direction of photon momentum corresponds to scattering vector
- Interference effects from all electrons in sample give structural information
The x-ray scattering experiment

\[ I_0 = \text{Incident Flux} \]

2D — CCD or Image Plate Detector

diffraction

small angle scattering
Inelastic x-ray processes

Synchrotron radiation makes practical a number of inelastic processes

- XAS
- XRR
- RIXS
- XMCD
X-ray absorption spectroscopy

- Photon is absorbed and promotes an electron from a core level
- Core hole is filled by an upper level electron, emitting a fluorescence photon
- Self-interference effects provide local structural and electronic information
The x-ray absorption experiment

\[ I = I_o e^{-\mu(E)x} \]

\[ \mu(E)x = \ln \left( \frac{I_o}{I_t} \right) \]

\[ \mu(E) \propto \frac{I_f}{I_o} \]
The x-ray absorption event (simplified)

\[ \chi(k) = \sum_j \frac{N_j f_j(k)}{kR_j^2} \cdot e^{-2\sigma_j^2 k^2} \cdot e^{-2R_j/\lambda(k)} \cdot \sin[2R_j + \delta_j(k)] \]

- \( N_j \): Nearest neighbors of type \( j \)
- \( R_j \): Nearest neighbor distance between central atom and backscatters in \( j^{th} \) shell
- \( \sigma_j \): “Debye-Waller” factor accounting for thermal and static disorder
- \( \lambda \): Inelastic electron mean free path
- \( \delta_j \): Phase shift due to potentials of the central atom and backscattering atoms \( j \).
Example of XAFS analysis

Remove background

EXAFS region

XANES region

Extract structural parameters for first shell and more distant atoms as well

Fourier transform and fit with simple structural model

k-weight = 3
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What is a catalyst?

cat·a·lyst  \'ka-tə-ləst\ 
1 : a substance that enables a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible
2 : an agent that provokes or speeds significant change or action
Catalysts are big business!

- Over $12 billion in worldwide sales in 2008
- Commercial uses include
  - Automotive applications (catalytic converter)
  - Chemical production (e.g. production of ammonia)
  - Petroleum industry (hydrocarbon cracking)
  - Power industry (removal of sulfur)
  - Food processing (hydrogenation)
  - Fuel cells
Fuel cell catalysts are news!

New Fuel Cell Catalyst Uses Two Metals: Up To Five Times More Effective

ScienceDaily, May 19, 2009 — Materials scientists at Washington University in St. Louis have developed a technique for a new, more fuel-efficient catalyst that is efficient, robust and two to five times more effective than commercial catalysts. This novel technique eventually will enable a cost-effective fuel cell technology, which has been waiting in the wings for decades, and will give a boost for cleaner use of fuel worldwide.

New Scientist

Nanotubes outshine costly platinum as fuel-cell catalyst

Abstract: Nanoparticles with a completely new shape may lead to cheaper catalysts that could make many experimental-energy technologies more practical.

Improved Fuel Cell Oxidation Catalysis in Pt3+–Taf1

Methanol Oxidation

Orthorhombic

Wichita State University - April 6, 2011
Anode: \(2H_2 \rightarrow 4H^+ + 4e^- (0V\text{ SHE})\)

Cathode: \(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O (1.229V\text{ SHE})\)

(a) \(O_2 + Pt \rightarrow Pt\text{—}O_2\)

(b) \(Pt\text{—}O_2 + H^+ + e^- \rightarrow Pt\text{—}O_2H\)

(c) \(Pt\text{—}O_2H + Pt \rightarrow Pt\text{—}OH + Pt\text{—}O\)

(d) \(Pt\text{—}OH + Pt\text{—}O + 3H^+ + 3e^- \rightarrow 2Pt + 2H_2O\)

U.S. Department of Defense (DoD) Fuel Cell Test and Evaluation Center (FCTec)

Open questions (among many...)

• **Pt**: How do reactants adsorb on platinum surface?
  – Do all faces of Pt adsorb equally well?
  – Is there a change in location with coverage?

• **PtNi**: Why is ORR improved with bimetallic catalyst?
  – Pt electronic structure modified
  – Pt catalyst geometric structure is modified
  – Static oxygen adsorbates inhibited
  – Overpotential reduced

• How do real catalysts differ from model systems?
Catalyst nanoparticle

- Study under *operando* conditions
- Use a surface or local structural probe
- Combine with computational modeling
Probing the steady state

- Version 2 operando cell
- Air-breathing cathode
- Pd on anode
- 1.2 mg/cm$^2$ loading
- 50°C operating temperature
- Pt L$_3$ and Ni K edges
- Continuous scan (1-2 min) mode @ MRCAT
Fuel cell performance

- **PtNi/Pd** shows higher open circuit voltage
- **Pt/Pd** and **PtNi/Pd** have similar performance
Data quality: Pt edge in Pt/C

- Merge of 10-20 scans
- Data good to \( k = 13 \)
- Oxygen peak just below 2 Å
Data quality: Ni edge in PtNi/C

- Merge of 10-20 scans
- Data good to $k=11$
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Pt/C and PtNi/C comparison
XANES modeling of Pt-O adsorption

• Modeling of oxygen at Pt surface using FEFF8
  – Self-consistent calculations including multiple scattering
  – Models XANES region accurately (getting better and better...)

• Position of oxygen results in distinctive signatures in $\Delta \mu$

• Experimental data on model surfaces

Extension to more realistic system

Structural model

Attempt to get global information about oxygen

• Fit all potentials with same metal core parameters for each catalyst
• Simultaneous fit of Pt and Ni edges in PtNi/C with constraint on Pt-Ni path
• Fit in $k$, $k^2$, and $k^3$ weighting simultaneously
• M-O path constraints
  – length common across potentials
  – $\sigma^2$ fixed to 0.01
  – Pt-O in PtNi/C are refined with a single occupation #
Example fits

\[ |\chi(R)| \text{[Å}^{-3}] \]

\[ \chi(q) \text{[Å}^{-2}] \]

Pt in Pt/C

Pt-O

Pt in PtNi/C

Pt-O

Ni in PtNi/C

Ni-O

R [Å]

q [Å\(^{-1}\)]
## Fit results

<table>
<thead>
<tr>
<th></th>
<th>Pt/C</th>
<th>PtNi/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_{Pt}$</td>
<td>$N_{Pt}$</td>
</tr>
<tr>
<td></td>
<td>$6.1 \pm 0.3$</td>
<td>$6.1 \pm 0.3$</td>
</tr>
<tr>
<td></td>
<td>$N_{Ni}$</td>
<td>$N_{Ni}$</td>
</tr>
<tr>
<td></td>
<td>$3.7 \pm 0.2$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
<tr>
<td>$\sigma_{Pt-Pt}^2 \times 10^3$</td>
<td>$6.1 \pm 0.1$</td>
<td>$6.1 \pm 0.7$</td>
</tr>
<tr>
<td>$r_{Pt-Pt}$ (Å)</td>
<td>$2.749 \pm 0.001$</td>
<td>$2.692 \pm 0.003$</td>
</tr>
<tr>
<td></td>
<td>$r_{Pt-Ni}$ (Å)</td>
<td>$2.572 \pm 0.006$</td>
</tr>
<tr>
<td></td>
<td>$N_{Ni}$</td>
<td>$N_{Pt}$</td>
</tr>
<tr>
<td></td>
<td>$3.4 \pm 0.1$</td>
<td>$8.9 \pm 0.5$</td>
</tr>
<tr>
<td>$\sigma_{Pt-Ni}^2 \times 10^3$</td>
<td>$9 \pm 1$</td>
<td>$9 \pm 1$</td>
</tr>
<tr>
<td>$r_{Pt-Ni}$ (Å)</td>
<td>$2.635 \pm 0.004$</td>
<td></td>
</tr>
<tr>
<td>$N$</td>
<td>$9.5 \pm 0.4$</td>
<td>$N$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$12.6 \pm 0.7$</td>
</tr>
<tr>
<td>$r_{Pt-O}$ (Å)</td>
<td>$2.02 \pm 0.01$</td>
<td>$r_{Pt-O}$ (Å)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.09 \pm 0.03$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r_{Ni-O}$ (Å)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.90 \pm 0.01$</td>
</tr>
</tbody>
</table>

Note Pt-Pt, Pt-O bond lengths
Fit results: oxygen coordination

![Graph showing oxygen coordination vs applied potential (mV)].
What does Ni really do?

- Resides predominantly in metal core of nanoparticle
- Eliminates static Pt-O bonds at all potentials
- Number of O near neighbors “increases” with potential
- Lengthens Pt-O and shortens Pt-Pt bond
- Reduces Pt white line in most reduced state (0 mV)
- Open circuit voltage is increased (reduction in overpotential)

- Can we use modeling to establish specific mechanism?
  - Pt-Pt bond reduction (weakening of Pt-O bond)?
  - Electron donation to Pt d-band (weakening of Pt-O bond)?
  - Stronger affinity for oxygen?
Pt cluster modeling

- Separate the effects of
  a) Shorter Pt-Pt distance
  b) Charge transfer from subsurface Ni
- Use experimentally determined distances
- Calculate local density of states
- Calculate XANES spectrum
Cluster calculation results

- Strain effect
  - Shorter Pt-Pt bond → broader and lower Pt d-band
    - Serves to weaken the Pt-O bond
    - White line at absorption edge is reduced
    - In agreement with DFT calculations (Nørskov et al.)

- Ligand effect
  - Subsurface Ni → sharpens and raises Pt d-band
    - Raises chemisorption energy
    - Increases white line

- Net effect of Ni dominated by strain effect

- Predictive ability
  - Moving down periodic table (Ru, Ag)
  - Moving left across periodic table (towards Mn)
Conclusions: where do we go from here?

• Operando cell
  – Produces usable spectra in ~1 min (limited by electronics?)
  – Analyzable data in just 1 scan (can look at time evolution)
Thank you!

• Collaborators
  – Qingying Jia – IIT (Ph.D. student)
  – Eugene Smotkin – Northeastern University
  – Emily Lewis – Northeastern University (M.S. Student)
  – Corey Grice – NuVant Systems, Inc.
  – Harry Riviera – University of Puerto Rico (Ph.D. student)
Abstract

New, improved catalysts for the oxygen reduction reaction (ORR) are regularly being reported. These include carbon nanotubes, iron complexes inserted into graphite, specially nanostructured platinum bimetallic materials and ultra-small platinum particles, for example. Each of them claim to have performance superior to that of commercial platinum catalysts. Despite this, platinum nanoparticles remain unmatched as ORR catalysts for their combination of performance and durability. Furthermore, a complete understanding of how the oxygen reduction catalyst functions in a working fuel cell still eludes us. Physicists have made valuable contributions using a combination of experimental and computational methods centered around x-ray absorption spectroscopy. This local structural and electronic probe gives insights into catalyst operation at timescales from hours to less than a minute. An overview of recent experimental and computational results, including our own work, will be presented.
Initial *operando* fuel cell design

Used for anode studies of PtRu catalysts

Probing the short time scales

Mechanism of water dissociation

Pt charging
- $k_d = 0.011 \text{s}^{-1}$
- $k_{Pt-O} = 0.013 \text{s}^{-1}$

Pt-O formation
- $k_e_1 = 2.86 \text{s}^{-1}$
- $k_{e_2} = 0.049 \text{s}^{-1}$

Pt-O dissociation
- $k'_d = 0.039 \text{s}^{-1}$
- $k'_{e_2} = 0.17 \text{s}^{-1}$

Pt discharging
- $k'_d = 0.39 \text{s}^{-1}$