## Today's Outline - April 14, 2015

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- In situ EXAFS studies


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- Bijvoet (Bay-voot) Pairs

Homework Assignment \#7:
Chapter 7: 2, 3, 9, 10, 11 due Tuesday, April 23, 2015

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- MAD Phasing

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- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering
- Friedel's Law
- Bijvoet (Bay-voot) Pairs
- MAD Phasing
- Quantum Origin of Resonant Scattering

Homework Assignment \#7:
Chapter 7: 2, 3, 9, 10, 11
due Tuesday, April 23, 2015

## Mark I operando fuel cell


R. Viswanathan et al., "In-situ XANES study of carbon supported Pt -Ru anode electrocatalysts for reformate-air polymer electrolyte fuel cells", J. Phys. Chem. B 106, 3458 (2002).

- Transmission mode
- $<1 \mathrm{~mm}$ of graphite
- Pt/Ru on anode
- Pd on cathode
- $35^{\circ} \mathrm{C}$ operating temp
- 1-2 min scan time



## Mark II operando fuel cell


E.A. Lewis et al., "Operando x-ray absorption and infrared fuel cell spectroscopy", Electrochim. Acta. 56, 8827 (2011).

- Air-breathing cathode
- Pd on anode
- $1.2 \mathrm{mg} / \mathrm{cm}^{2}$ loading
- $50^{\circ} \mathrm{C}$ operating temp
- Pt $L_{3}$ and Ni K edges
- Continuous scan mode @ mrcat



## Oxygen reduction at a PtNi cathode



Anode: 0 V vs. SHE

$$
2 \mathrm{H}_{2} \longrightarrow 4 \mathrm{H}^{+}+4 \mathrm{e}^{-}
$$

Cathode: 1.23 V s. SHE

$$
\mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}
$$

breaking $\mathrm{O}-\mathrm{O}$ bond is the rate limiting step
U.S. Department of Defense (DoD) Fuel Cell

Test and Evaluation Center (FCTec)


## Fuel cell performance and open questions



PtNi/Pd has higher open circuit voltage, similar performance to $\mathrm{Pt} / \mathrm{Pd}$.

## Fuel cell performance and open questions


$\mathrm{PtNi} / \mathrm{Pd}$ has higher open circuit voltage, similar performance to $\mathrm{Pt} / \mathrm{Pd}$.

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 modified
- Static oxygen adsorbates inhibited
- Overpotential reduced

How do real catalysts differ from model systems?

## $\mathrm{Pt} / \mathrm{C}$ and $\mathrm{PtNi} / \mathrm{C}$ comparison



## PtNi Structural model

Attempt to get global information about the oxygen

Fit all potentials with same metal core parameters for each catalyst

Simultaneous fit of Pt and Ni edges in $\mathrm{PtNi} / \mathrm{C}$ with constraint on Pt-Ni distance

Fit in $k, k^{2}$, and $k^{3}$ weighting simultaneously
M-O path constraints

- length common across potentials
- $\sigma^{2}$ fixed to 0.01
- $\mathrm{Pt}-\mathrm{O}$ in $\mathrm{PtNi} / \mathrm{C}$ are refined with a single occupation \#


## Example fits



## Fit results



Note the Pt-Pt and $\mathrm{Pt}-\mathrm{O}$ bond lengths as well as total metal near neighbors

## 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 $\mathrm{Pt}-\mathrm{O}$ and shortens $\mathrm{Pt}-\mathrm{Pt}$ 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 $\mathrm{Pt}-\mathrm{O}$ bond)?
- Electron donation to Pt d-band (weakening of $\mathrm{Pt}-\mathrm{O}$ bond)?
- Stronger affinity for oxygen?


## Pt cluster modeling

By using FEFF8.4, which performs full multiple-scattering self-consistent calculations, we can explore the implications of the "ligand effect" and the "strain effect" on the electronic state of Pt .


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
Q. Jia, et al., "Structure-property-activity correlations of Pt-bimetallic nanoparticles: a theoretical study" Electrochimica Acta bf 88, 604 (2013).

## Cluster calculation results

Strain effect: shorter Pt-Pt bond $\rightarrow$ 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 $\mathrm{Ni} \rightarrow$ sharpens and raises Pt d-band

- Raises chemisorption energy
- Increases white line

Net effect dominated by strain effect
Predictive ability

- Moving down periodic table ( $\mathrm{Ru}, \mathrm{Ag}$ )
- Moving left across periodic table (towards Mn)


## Methanol oxidation by a PtRu anode


U.S. Department of Defense (DoD) Fuel Cell

Anode: 0.02 V vs. SHE
$\mathrm{CH}_{3} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 6 \mathrm{H}+$ $\mathrm{CO}_{2}+6 \mathrm{e}^{-}$

Cathode: 1.23 V s. SHE
$\frac{3}{2} \mathrm{O}_{2}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow$ $3 \mathrm{H}_{2} \mathrm{O}$

Pt surface poisoned by CO Test and Evaluation Center (FCTec)

The presence of Ru promotes CO oxidation through a "bi-functional mechanism"

$$
\mathrm{Pt}-(\mathrm{CO})_{\mathrm{ads}}+\mathrm{Ru}-\mathrm{OH} \longrightarrow \mathrm{Pt}+\mathrm{RuCO}_{2}+\mathrm{H}^{+}+2 \mathrm{e}^{-}
$$

## Ru EXAFS fitting



- Addition of Ru-O/C neighbors improves the EXAFS fit
- The peak at about $1.3 \AA$ is ascribed to oxygen bound to Ru
- The asymmetric distribution of the Ru-O/C peak is consistent with disorder


## Metal nanoparticle structure

- First shell analysis
- Fit Pt and Ru EXAFS simultaneously at each potential. No potential dependence observed
- Simultaneously fit Pt and Ru data at all potentials. Identical overall average coordination was observed
- Use fractional coordination numbers, $\times(\mathrm{Pt}$ around Ru$)$ and $y(\mathrm{Ru}$ around Pt$)$ and total coordination number about each atom, N
- Bond lengths and Debye-Waller factors are consistent with literature values for C supported Pt-Ru catalyst (Russel 2001, Camara 2002)

| N | $8.2 \pm 0.2$ |
| :--- | :--- | :--- |
| x | $0.54 \pm 0.02$ |
| y | $0.27 \pm 0.02$ |$\quad \frac{[R u]}{[P t]}=\frac{y}{x}=0.50$

## Metal core restucturing

As-received catalyst
Ru oxidation $\sim 58 \%$
$N=5.6$
$\frac{[R u]}{[P t]}=\frac{y}{x}=0.44$
Pt-O bonds present
\# Ru-O bonds $\sim 2.8$

In-situ catalyst
Ru oxidation ~ 15 \%
$\mathrm{N}=8.2$

$$
\frac{[R u]}{[P t]}=\frac{y}{x}=0.50
$$

No Pt-O bonds
\# Ru-O/C bonds
$\sim 0.24$

- Inner core has more Pt than Ru
- Ru on surface and outside of metallic nanoparticle
S. Stoupin, et al., "Pt and Ru X-ray absorption spectroscopy of PtRu anode catalysts in operating direct methanol fuel cells" J. Phys. Chem. 110, 9932 (2006).


## Role of Ru in CO oxidation?

- PtRu bifunctional catalyst improves performance
- In commercial PtRu catalysts there is always a lot of inactive Ru-oxide (?)
- Ru signal dominated by metallic Ru environment
- How does Ru behave in the presence of reactants adsorbed on platinum surface?

Core-shell nanoparticles can resolve these questions

## Ru-decorated Pt nanoparticles



## Electrochemical performance



Without Methanol
Low $V$ peaks are $\mathrm{H}^{+}$stripping
Dip at $\sim 0.5 \mathrm{~V}$ is oxygen stripping
Ru shifts potential on all peaks

## Electrochemical performance


Without Methanol
Low V peaks are $\mathrm{H}^{+}$stripping
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Ru shifts potential on all peaks

With Methanol
Continual current growth is due to methanol oxidation

Ru improves current by removing the CO which blocks active sites

## Ru EXAFS

## No methanol



## Ru EXAFS

No methanol


With methanol


## Ru-M paths



Without methanol

With methanol

## Ru-M paths



Without methanol
Ru-M distances are longer and $\mathrm{RuO}_{2}$ is formed at high potentials

With methanol

## Ru-M paths



Without methanol
Ru- M distances are longer and $\mathrm{RuO}_{2}$ is formed at high potentials

## With methanol

Ru-M distances are shorter and remain the same at all potentials

## Ru-O/C paths



Without methanol

With methanol

## Ru-O/C paths



Without methanol
Above 375 mV Ru-O paths appear and total number of RuO neighbors increases to that of $\mathrm{RuO}_{2}$

With methanol

## Ru-O/C paths



Without methanol
Above 375 mV Ru-O paths appear and total number of RuO neighbors increases to that of $\mathrm{RuO}_{2}$

## With methanol

Ru has one low $Z$ neighbor at all potentials (carbon); a second above 175 mV (oxygen) with constant bond lengths and slightly increasing numbers

## Bi-functional mechanism


C. Pelliccione et al., "In situ Ru K-Edge x-ray absorption spectroscopy study of methanol oxidation mechanisms on model submonolayer Ru on Pt nanoparticle electrocatalyst" J. Phys. Chem. C 117, 18904 (2013).

## Synthesis of Sn-graphite nanocomposites



> | One-pot | synthesis |  |
| :--- | ---: | :---: |
| produces | evenly dis- |  |
| tributed | $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$ |  | nanoparticles on graphite nanoplatelets

XRD shows a small amount of Sn metal in addition to $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$


## In situ XAS studies of lithiation



## In situ battery box



Pouch cell clamped against front window in helium environment

## In situ battery box



Suitable for both transmission and fluorescence measurements

## In situ XAS studies of lithiation



## In situ XAS studies of lithiation



## In situ XAS studies of lithiation



Fresh electrode can be fit with $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$ structure which is dominated by the near neighbor Sn O distances

## In situ XAS studies of lithiation



Fresh electrode can be fit with $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$ structure which is dominated by the near neighbor Sn O distances

Only a small amount of metallic Sn -Sn distances can be seen

## In situ XAS studies of lithiation



Reduction of number of Sn -O near neighbors and 3 Sn-Li paths characteristic of the $\mathrm{Li}_{22} \mathrm{Sn}_{5}$ structure

## In situ XAS studies of lithiation



Metallic Sn-Sn distances appear but Sn -Li paths are still present, further reduction in Sn -O near neighbors.

## In situ XAS studies of lithiation



## In situ XAS studies of lithiation



Number of Li near neighbors oscillates with the charge/discharge cycles but never returns to zero

## In situ XAS studies of lithiation



Number of Li near neighbors oscillates with the charge/discharge cycles but never returns to zero

In situ cell promotes accelerated aging because of Sn swelling and the reduced pressure of the thin PEEK pouch cell assembly

## In situ XAS studies of lithiation

During $1^{\text {st }}$ Charge
Li intercalate in $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$


Crystalline $\mathrm{Sn}_{3} \mathrm{O}_{2}(\mathrm{OH})_{2}$

Sn aggregates in
center of clusters


## The Photoemission Process

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\mathcal{E}_{k i n}, \theta \longrightarrow \mathcal{E}(\vec{q})
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## The Photoemission Process

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$$
\begin{aligned}
& \mathcal{E}_{k i n}, \theta \longrightarrow \mathcal{E}(\vec{q}) \\
& \mathcal{E}_{k i n}=\frac{\hbar^{2} q_{v}^{2}}{2 m}=\hbar \omega-\phi-\mathcal{E}_{B} \\
& \mathcal{E}_{B}=\mathcal{E}_{F}-\mathcal{E}_{i}
\end{aligned}
$$



## Hemispherical Mirror Analyzer

The electric field between the two hemispheres has a $R^{2}$ dependence from the center of the hemispheres


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## Hemispherical Mirror Analyzer

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Electrons with $\mathcal{E}_{0}$, called the "pass energy", will follow a circular path of radius
$R_{0}=\left(R_{1}+R_{2}\right) / 2$
Electrons with lower energy will fall inside this circular path while those with higher enegy will fall
 outside

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Photon energy

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(c)

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## Forced charged oscillator

Consider an electron under the influence of an oscillating electric field $\vec{E}_{i n}=\hat{x} E_{0} e^{-i \omega t}$.

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$$
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$$
\left(-\omega^{2}-i \omega \Gamma+\omega_{s}^{2}\right) x_{0} e^{-i \omega t}=-\left(\frac{e E_{0}}{m}\right) e^{-i \omega t}
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$$
\begin{gathered}
\left(-\omega^{2}-i \omega \Gamma+\omega_{s}^{2}\right) x_{0} e^{-i \omega t}=-\left(\frac{e E_{0}}{m}\right) e^{-i \omega t} \\
x_{0}=-\left(\frac{e E_{0}}{m}\right) \frac{1}{\left(\omega_{s}^{2}-\omega^{2}-i \omega \Gamma\right)}
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\end{gathered}
$$

The amplitude of the response has a resonance and dissipation

## Radiated field

The radiated (scattered) electric field at a distance $R$ from the electron is directly proportional to the electron's acceleration with a retarded time $t^{\prime}=t-R / c$ (allowing for the travel time to the detector).

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& =\frac{\omega^{2}}{\left(\omega_{s}^{2}-\omega^{2}-i \omega \Gamma\right)}\left(\frac{e^{2}}{4 \pi \epsilon_{0} m c^{2}}\right) E_{0} e^{-i \omega t}\left(\frac{e^{i k R}}{R}\right)
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\end{aligned}
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& =\frac{\omega^{2}}{\left(\omega_{s}^{2}-\omega^{2}-i \omega \Gamma\right)}\left(\frac{e^{2}}{4 \pi \epsilon_{0} m c^{2}}\right) E_{0} e^{-i \omega t}\left(\frac{e^{i k R}}{R}\right) \\
\frac{E_{r a d}(R, t)}{E_{i n}} & =-r_{0} \frac{\omega^{2}}{\left(\omega^{2}-\omega_{s}^{2}+i \omega \Gamma\right)}\left(\frac{e^{i k R}}{R}\right)=-r_{0} f_{s}\left(\frac{e^{i k R}}{R}\right)
\end{aligned}
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which is an outgoing spherical wave with scattering amplitude

## Radiated field

The radiated (scattered) electric field at a distance $R$ from the electron is directly proportional to the electron's acceleration with a retarded time $t^{\prime}=t-R / c$ (allowing for the travel time to the detector).

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f_{s}=\frac{\omega^{2}}{\left(\omega^{2}+\omega_{s}^{2}+i \omega \Gamma\right)}
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The scattering factor can be rewritten

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f_{s}^{\prime} & =\frac{\omega_{s}^{2}\left(\omega^{2}+\omega_{s}^{2}\right)}{\left(\omega^{2}+\omega_{s}^{2}\right)^{2}+(\omega \Gamma)^{2}} \quad f_{s}^{\prime \prime}=\frac{\omega_{s}^{2} \omega \Gamma}{\left(\omega^{2}+\omega_{s}^{2}\right)^{2}+(\omega \Gamma)^{2}}
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## Single oscillator dispersion terms

These dispersion terms give resonant corrections to the scattering factor

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