Using synchrotron radiation to study catalysis

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Outline



- Synchrotron radiation
- X-ray absorption spectroscopy
- Operando synchrotron fuel cells
- Oxygen reduction at the NiPt cathode
- Methanol oxidation on a PtRu catalyst
- Ru@Pt core-shell methanol catalysts





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- 4th generation are free electron lasers (LCLS)

What is a synchrotron?





"Headlight" effect



In electron rest frame:



emission is symmetric about the axis of the acceleration vector

"Headlight" effect



In electron rest frame:

In lab frame:





emission is symmetric about the axis of the acceleration vector

emission is pushed into the direction of motion of the electron



Bending magnet





Bending magnet



• Wide horizontal beam



Bending magnet



- Wide horizontal beam
- Broad spectrum to high energies



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Undulator





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Highly collimated beam



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- Peaked spectrum with harmonics



Bending magnet



- Wide horizontal beam
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Undulator



- Highly collimated beam
- Peaked spectrum with harmonics
- Tunable energies



Bending magnet



The EXAFS experiment



- $I_o =$ incident intensity
- I_t = transmitted intensity
 - $f_f =$ fluorescence intensity

x = sample thickness $\mu(E) = absorption coefficient$

0

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

 $\mu(E) \propto \frac{l_f}{l_c}$

V

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Edge shifts give valence state





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Pre-edge peaks indicate geometry





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Linear combination fitting for phase composition





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Linear combination fitting for phase composition

Complete description requires full quantum codes

The EXAFS equation

The EXAFS oscillations can be modelled and interpreted using a conceptually simple equation (the details are more subtle!)

$$\chi(k) = \sum_{j} \frac{N_{j} S_{0}^{2} f_{j}(k)}{k R_{j}^{2}} e^{-2k^{2} \sigma_{j}^{2}} e^{-2R_{j}/\lambda(k)} \sin \left[2R_{j} + \delta_{j}(k)\right]$$

The sum could be over shells of atoms (Pt-Pt, Pt-Ni) or over scattering paths for the photo-electron.

- $f_j(k)$: scattering factor for the path $\lambda(k)$: photoelectron mean free path $\delta_i(k)$: phase shift for the jth path
- N_j : number of paths of type j R_i : half path length
- σ_j : path "disorder"





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EXAFS analysis
































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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 mm of graphite
- Pt/Ru on anode
- Pd on cathode
- 35°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).



- FTIR & x-rays
- Air-breathing cathode
- Pd on anode
- $1.2\,\text{mg}/\text{cm}^2$ loading
- 50°C operating temp
- Pt L₃ and Ni K edges
- Continuous scan mode @





Oxygen reduction at a PtNi cathode





Anode: 0 V vs. SHE $2 H_2 \longrightarrow 4 H^+ + 4 e^-$

Cathode: 1.23 V s. SHE $O_2 + 4 H^+ + 4 e^- \longrightarrow 2 H_2O$

breaking O-O bond is rate limiting

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



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Fuel cell performance and open questions





PtNi/Pd has higher open circuit voltage, similar performance to Pt/Pd.

Fuel cell performance and open questions





PtNi/Pd has higher open circuit voltage, similar performance to Pt/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?

Pt/C and PtNi/C comparison







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 $\ensuremath{\text{PtNi/C}}$ with constraint on Pt-Ni distance

Fit in k, k², and k³ weighting simultaneously

M-O path constraints

- length common across potentials
- σ^2 fixed to 0.01
- Pt-O in PtNi/C are refined with a single occupation #

Example fits





Fit results



	Pt/C	PtNi/C			
		Pt		Ni	
N _{Pt}	8.7 ± 0.2	N _{Pt}	6.1 ± 0.3	N _{Ni}	3.7 ± 0.2
R _{Pt-Pt}	$\textbf{2.749} \pm \textbf{0.001}$	R _{Pt-Pt}	2.692 ± 0.003	R _{Ni-Ni}	2.572 ± 0.006
		N _{Ni}	3.4 ± 0.1	N _{Pt}	8.9 ± 0.5
			R _{Pt-Ni}	2.635 ± 0.004	
		N _{Total}	9.5 ± 0.4	N _{Total}	12.6 ± 0.7
R _{Pt-O}	2.02 ± 0.01	R _{Pt-O}	2.09 ± 0.03	R _{Ni-O}	1.90 ± 0.01

Note the Pt-Pt and Pt-O bond lengths as well as total metal near neighbors

Q. Jia et al, "In Situ XAFS studies of the oxygen reduction reaction on carbon supported Pt and PtNi(1:1) catalysts", J. Phys. Conf. Series 190, 012157 (2009).

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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



By using FEFF8.4, which performs full multiple-scattering selfconsistent 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 $\text{Ni} \rightarrow \text{sharpens}$ and raises Pt d-band

- Raises chemisorption energy
- Increases white line

Net effect dominated by strain effect

Predictive ability

- Moving down periodic table (Ru, Ag)
- Moving left across periodic table (towards Mn)

Methanol oxidation by a PtRu anode





Anode: 0.02 V vs. SHE $CH_3OH + H_2O \longrightarrow 6H + CO_2 + 6e^-$

 $\begin{array}{c} \mbox{Cathode: } 1.23\,\mbox{V s. SHE} \\ $\frac{3}{2}\,\mbox{O}_2 + 6\,\mbox{H}^+ + 6\,\mbox{e}^- \longrightarrow 3\,\mbox{H}_2\mbox{O} \end{array}$

Pt surface poisoned by CO

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

The presence of Ru promotes CO oxidation through a "bifunctional mechanism"

$${\rm Pt-(CO)}_{\rm ads} + {\rm Ru-OH} \longrightarrow {\rm Pt} + {\rm RuCO}_2 + {\rm H}^+ + 2\,{\rm e}^-$$

Ru EXAFS fitting





Addition of Ru-O/C neighbors improves the EXAFS fit

- The peak at about 1.3 Å 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 (Pt around Ru) and y (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 ± 0.2
x 0.54 ± 0.02
y 0.27 ± 0.02
$$\frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.50$$

Metal core restucturing

As-received catalyst Ru oxidation ~ 58 % N = 5.6 $\frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.44$ Pt-O bonds present

Ru-O bonds \sim 2.8

In-situ catalyst Ru oxidation ~ 15 % N = 8.2 $\frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.50$ No Pt-O bonds # Ru-O/C bonds ~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).

S. Stoupin, et al., "Structural analysis of sonochemically prepared PtRu versus Johnson Matthey PtRu in operating direct methanol fuel cells" *Phys. Chem. Chem. Phys.* **10**, 6430 (2008).





- 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





ANL-EMC 10.0kV 11.7mm x9.01k SE(M) 9/14/2011 5.00um









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Electrochemical performance





Without Methanol Low V peaks are H⁺ stripping Dip at ~ 0.5 V is oxygen stripping Ru shifts potential on all peaks

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With Methanol

Continual current growth is due to methanol oxidation

Ru improves current by removing the CO which blocks active sites

Ru EXAFS





Ru EXAFS





Ru-M paths





Without methanol

With methanol

Ru-M paths





Without methanol

Ru-M distances are longer and RuO_2 is formed at high potentials

With methanol

Ru-M paths





Without methanol

Ru-M distances are longer and 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 Ru-O neighbors increases to that of RuO₂

With methanol

Ru-O/C paths





Without methanol

Above 375 mV Ru-O paths appear and total number of Ru-O neighbors increases to that of RuO₂

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).

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Principal collaborators - Thank you!



$Pt/Ru\ core-shell$

- Christopher Pelliccione IIT (Ph.D. student)
- John Katsoudas IIT (MRCAT staff)
- Elena Timofeeva Argonne, Energy Systems
- Pt/Ru anode catalyst
 - Stanislav Stoupin IIT (Ph.D. Student)
 - Soma Chattopadhyay IIT (MRCAT staff)
 - Harry Rodriguez UPR (Ph.D. student)

PtNi cathode catalyst

- Qingying Jia IIT (Ph.D. Student)
- Eugene Smotkin Northeastern Univ.
- Emily Lewis Northeastern Univ. (M.S. Student)

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Abstract



X-ray absorption spectroscopy using synchrotron radiation has become an essential tool for operando studies of catalysts. I will discuss the fundamentals of synchrotron radiation and x-ray absorption spectroscopy along with several examples of how it is applied to the study of polymer electrolyte fuel cell catalysts. Over the past decade, we have studied the anode and cathode of hydrogen/air and direct methanol fuel cells in operando. Most recently, we have conducted in situ experiments of Ru-decorated Pt catalysts (Ru@Pt) to elucidate the details of the bifunctional mechanism of methanol oxidation. The presence of Ru atoms only at the surface of nanoparticles permits correlation of the x-ray absorption fine structure (XAFS) at the Ru K-edge to the role of Ru atoms in the methanol oxidation process. In-situ XAS spectra of the Ru@Pt nanoparticles were collected at various potentials in background electrolyte, and then in 1 M solution of methanol in the same electrolyte. Significant differences in the catalyst state have been revealed between these two environments. In the background electrolyte, Ru gradually oxidizes from mostly metallic to a Ru(III)/Ru(IV) mixture at the highest potentials. In the presence of methanol, the Ru oxidation state remains a mixture of metallic and Ru(III) even at the highest potentials. CO-type species were found adsorbed on Ruatoms at all potentials, and co-adsorbed with OH species at potentials 0.175 V vs Ag/AgCl and higher. These results provide a better understanding of the role of surface Ru atoms in methanol oxidation by bi-metallic catalysts.