X-ray absorption spectroscopy as a structural probe of dynamics in fuel cell and battery systems

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Outline



- Introduction to CSRRI & MRCAT
- X-ray absorption spectroscopy
- Operando synchrotron fuel cells
- Methanol oxidation on a PtRu catalyst
- Ru@Pt core-shell methanol catalysts
- Sn anodes for Li-ion batteries
- Accelerated capacity fading studies
- "Reversible" Sn₄P₃/graphite composite anode

CSRRI People



Tenure-Track Faculty

Carlo Segre	_
Grant Bunker	—
Jeff Terry	-
David Gidalevitz	-
Tom Irving	-
Andy Howard	-
Joseph Orgel	-
Adam Hock	-

-	Physics
—	Physics
—	Physics
—	Physics
_	Biology
_	Biology
_	Biology
-	Chemistry

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- Chemistry
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 Biology
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- Bernhard Adams

- Physics
- Physics
 - Physics
- Physics
- Physics

MRCAT - historical timeline



- 1993 MRCAT started with materials physics focus Notre Dame, Northwestern, Purdue, IIT, Amoco
- 1995 Construction begins on Insertion Device line Univ. of Florida, Argonne/CSE joins
- 1997 First light on Insertion Device line
- 1998 Argonne/ER joins
- 2002 Honeywell, Sandia fund initial Bending Magnet line
- 2005 EPA joins
- 2007 UOP joins Bending Magnet line buildout begins
- 2009 Bending Magnet line operational

MRCAT - present membership

Current active membership University of Notre Dame Illinois Institute of Technology Argonne Chemical Sci. & Eng. Argonne Biosciences Environmental Protection Agency UOP Honeywell BP plc

General users – catalysis UC Davis, Purdue, Penn State Illinois, Princeton, UCSB Rice, LSU, UC Berkeley, Michigan Wisconsin, Ohio State, MIT, ORNL NREL, WPAFB, Chicago, LANL, ...



ID Line XAFS (4 keV - 65 keV) Continuous scan ($< 2 \min$) Very dilute samples Microprobe Microdiffraction HAXPES BM Line XAFS (4 keV - 32 keV) X-ray lithography High energy tomography Instrumentation



The EXAFS experiment



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

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



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

O

$$\mu(E) \propto rac{l_f}{l_o}$$

XAS data





XAS data

































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Methanol oxidation by a PtRu anode





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

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

Cathode: 1.23 V s. SHE $\frac{3}{2}$ O₂ + 6 H⁺ + 6 e⁻ \longrightarrow 3 H₂O

Pt surface poisoned by CO

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

 $Pt-(CO)_{ads} + Ru-OH \longrightarrow Pt + RuCO_2 + H^+ + 2e^-$



- 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

































Fit example: -225 mV without methanol





Fit example: 675 mV without methanol





Fit example: 675 mV 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

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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Anode - negatively charged electrode

- Cathode positively charged electrode
- Separator allows ions to pass without short circuit

Electrolyte - medium through which ions move





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Cathode - positively charged electrode

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Consider a Li-ion battery







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- Cathode positively charged electrode
- Separator allows ions to pass without short circuit
- Electrolyte medium through which ions move
- Consider a Li-ion battery



Charge - Li^+ ions move from cathode to anode and electrons also flow to the anode externally, anode is reduced



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- Charge ${\rm Li}^+$ ions move from cathode to anode and electrons also flow to the anode externally, anode is reduced
- Discharge ${\rm Li^+}$ ions move back to cathode and electrons flow through the external load, anode is oxidized



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Potential, energy density, and power determined by the chemistry

Common solid state battery chemistries



Lead-acid bat	tery:	$E_{oc} = 2.05 V$
Cathode:	$PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$	\leftrightarrow Pb ₂ SO ₄ + 2 H ₂ O
Anode:	$PbSO_4 + 2 e^-$	\leftrightarrow Pb ² + SO ₄ ²⁻
NiMH battery	<i>,</i>	$F_{ac} = 1.28 V$
Cathode [.]	NiOOH + H ₂ O + e^{-}	\leftrightarrow Ni(OH) _a + OH ⁻
Anode:	$M + H_2O + e^-$	\leftrightarrow MH + OH ⁻
	_	
Li-ion battery	:	$E_{oc} = 4.00 V$
Cathode:	$CoO_2 + Li^+ + e^-$	\longleftrightarrow LiCoO ₂
Anode:	$Li^+ + C_6 + e^-$	\longleftrightarrow LiC ₆

Characteristics

- Medium to high energy density
- Limited cycle life (<1000)
- Large packaging overhead

In situ lithiation of Sn



- In situ box for non-aqueous experiments
- Have measured Sn₃O₂(OH)₂, SnO₂, Sn, ZnO, MoO₂ ...
- Pouch cell simplifies experiment



- MRCAT 10-ID beam line scans EXAFS spectrum in 2 minutes
- Focus on Sn nanoparticles which have rapid failure rate
- Successfully modeled Sn-Li paths in $Sn_3O_2(OH)_2$ using 3 composite paths





Li₂₂Sn₅ has 14 Sn-Li paths with distance 3.4Å or less

Thes are modeled using three Sn-Li paths at "center of mass" location

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 $Li_{22}Sn_5$ has 14 Sn-Li paths with distance 3.4Å or less

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The Sn lithiation process





0.60V - Sn metal begins to break down and Li appears

0.45V – number of Li reaches 11 and stabilizes at near full Li₂₂Sn₅

Synthesis of Sn-graphite nanocomposites





One-pot synthesis produces evenly distributed $Sn_3O_2(OH)_2$ nanoparticles on graphite nanoplatelets

XRD shows a small amount of Sn metal in addition to $Sn_3O_2(OH)_2$













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Fresh electrode can be fit with $Sn_3O_2(OH)_2$ structure which is dominated by the near neighbor Sn-O distances





Fresh electrode can be fit with $Sn_3O_2(OH)_2$ structure which is dominated by the near neighbor Sn-O distances

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



Reduction of number of Sn-O near neighbors and 3 Sn-Li paths characteristic of the $Li_{22}Sn_5$ structure





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









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





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





C. Pelliccione et al., "In situ XAS study of the capacity fading mechanism in hybrid $Sn_3O_2(OH)_2/graphite battery anode nanomaterials", Chem. Mater. 27, 574-580 (2015).$

$\mathsf{Sn}_4\mathsf{P}_3/\mathsf{graphite}\ \mathsf{composite}\ \mathsf{anode}$

 ${\rm Sn_4P_3}$ synthesized by high energy ball milling, then ball milled again with graphite to obtain composite

Theoretically could transfer 9 or more electrons upon lithiation





Composite shows stable, reversible capacity of 610 mAh/g for 100 cycles at C/2 compared to rapidly fading pure material.

How does the lithiation process differ from that of Sn metal?

Li et al., ECS Meeting Abstracts, MA2016-01 (2), 372-372 (2016)

In situ EXAFS of Sn_4P_3 /graphite





Cycle number in situ cells

Sn_4P_3 /graphite initial cycling





OCV spectrum fits well to Sn_4P_3 structure with an additional Sn-O path

 $\rm Sn_4P_3$ structure persists through first two cycles with possible enchancement of the Sn-Sn path at 2.6 Å

Sn_4P_3 /graphite reversible cycling





On third lithiation (charge) the Sn-P path is gone and only Sn-Li remains Delithiation (discharge) produces Sn-P and Sn-Sn paths which are not those of Sn_4P_3 but are reversible

Sn_4P_3 /graphite path lengths





Sn_4P_3 /graphite coordination numbers





Sn_4P_3 /graphite lithiation mechanism





It is possible that the particular structure of Sn_4P_3 along with the graphite composite is responsible for the reversible lithiation compared to other Sn materials. This is being tested for Sn, SnO₂, and SnS₂ nanoparticles.

Improvements still need to be made in the in-situ coin cell, potential designs include keeping a spacer inthe cell for Sn EXAFS or using a vacuum sealed pouch cell.

Principal collaborators - Thank you!



- Christopher Pelliccione IIT Physics (Ph.D. student)
- Yujia Ding IIT Physics (Ph.D. student)
- John Katsoudas IIT (MRCAT staff)
- Elena Timofeeva IIT Chemistry

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