

# In-situ XAFS studies of fuel cell catalysts

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*Workshop on XAFS studies of nanoparticles and chemical transformations*  
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# Acknowledgements

## Collaborators

Eugene Smotkin - NEU

Soma Chattopadhyay - IIT

## Graduate students

Stanislav Stoupin - IIT Physics

Eun-Hyuk Chung - IIT ChE

Harry Rodriguez – UPR

Robert Richard Diaz – UPR

Ramesh Viswanathan - Intel

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Army Research Office – long term support of fuel cell program

MRCAT is supported by contributions from MRCAT member institutions.

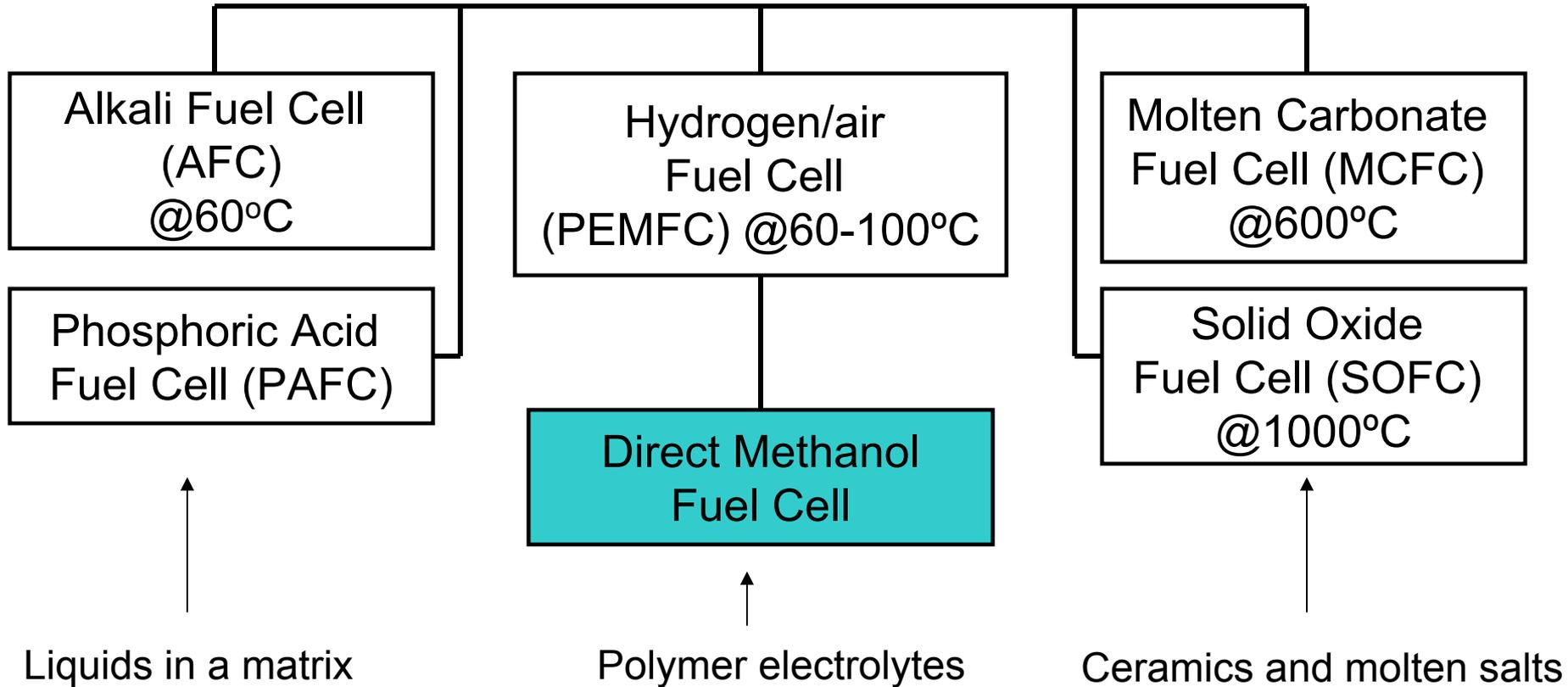
The APS is funded by the U. S. Department of Energy,

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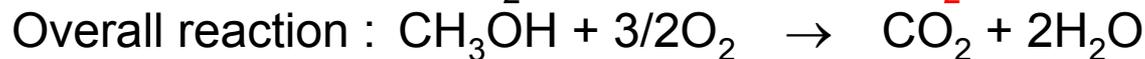
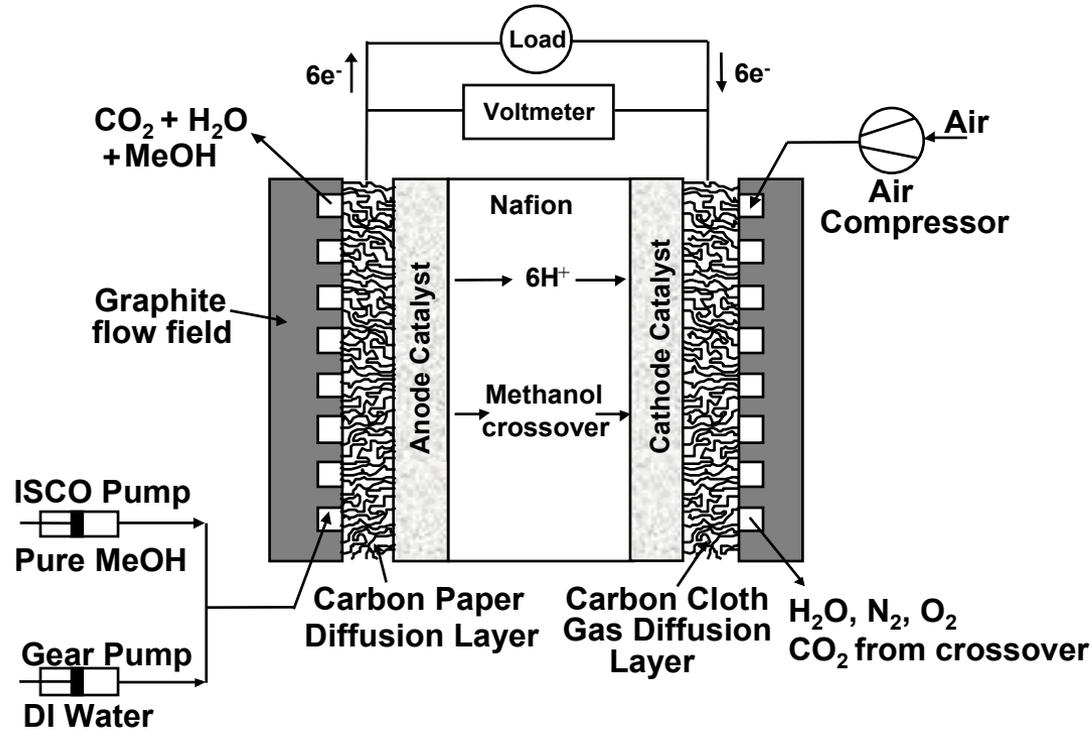
# Outline

- Brief introduction to fuel cells
- Direct Methanol Fuel Cells
  - Anode mechanisms → mixed metal catalysts
- X-ray spectroscopy primer
- EXAFS and XANES of operating liquid feed DMFC
  - Experimental challenges
  - Selection of potential window for experiments
  - Analysis of XANES and EXAFS
  - Lattice parameter analysis of catalysts
- Conclusions

# Types of Fuel Cells



# DMFC Schematics

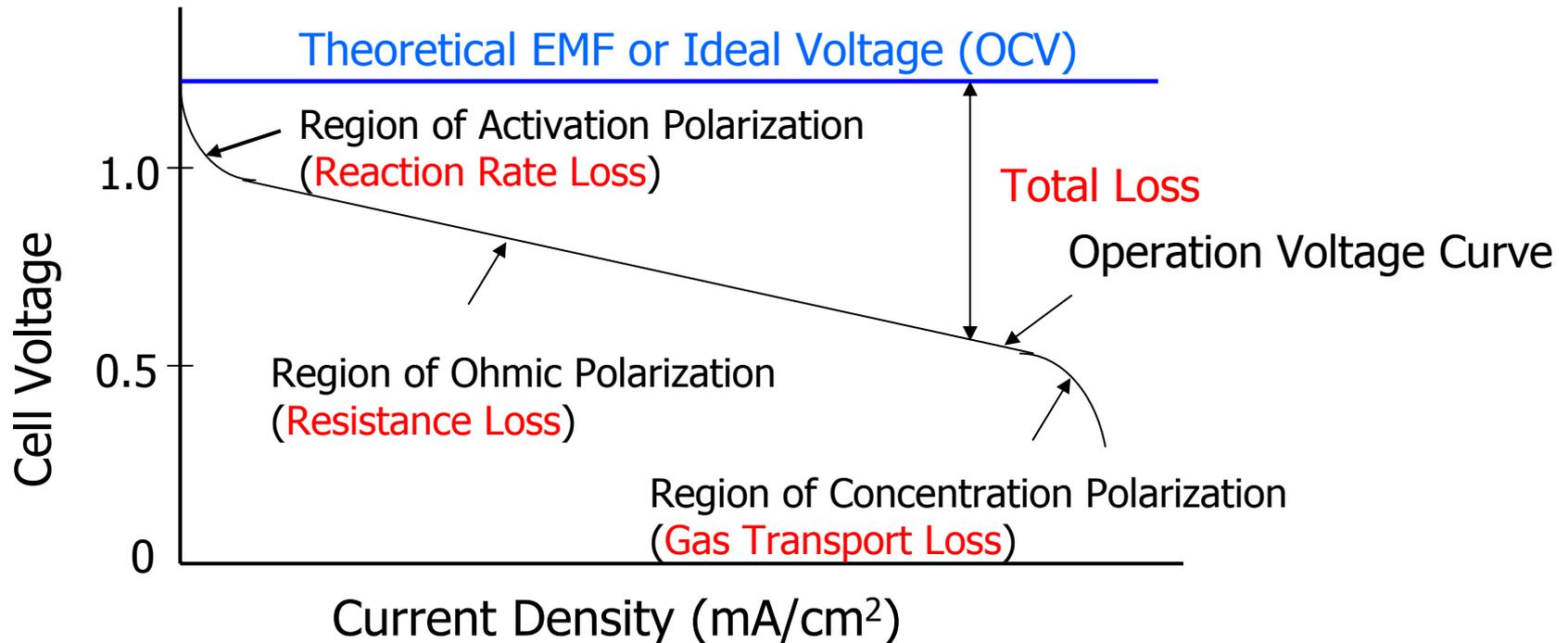


$E^\circ_{\text{anode}} = 0.016\text{V}$

$E^\circ_{\text{cathode}} = 1.23\text{V}$

$E^\circ_{\text{cell}} = 1.214\text{V}$

# Fuel Cell Voltage/Current Characteristics



*Ref. Fuel cell Handbook (6<sup>th</sup> Ed.) by EG&G Technical Services, Inc*

# Major DMFC issues

- Electrocatalyst
  - Anode
    - Methanol oxidation rate using Pt alloys is sluggish
    - CO tolerance of Pt alloys is poor
  - Cathode
    - Oxygen reduction kinetics are sluggish (even with H<sub>2</sub> fuel cells)
    - Cathode performance degraded by methanol crossover
- Membrane electrolyte
  - Methanol is permeable through membrane

# Motivation for synchrotron studies

Develop methods for characterization of catalysts in fully operating fuel cells

- Nanoparticle structure during operation
- Surface chemistry
- Conditioning effects
- Degradation mechanisms

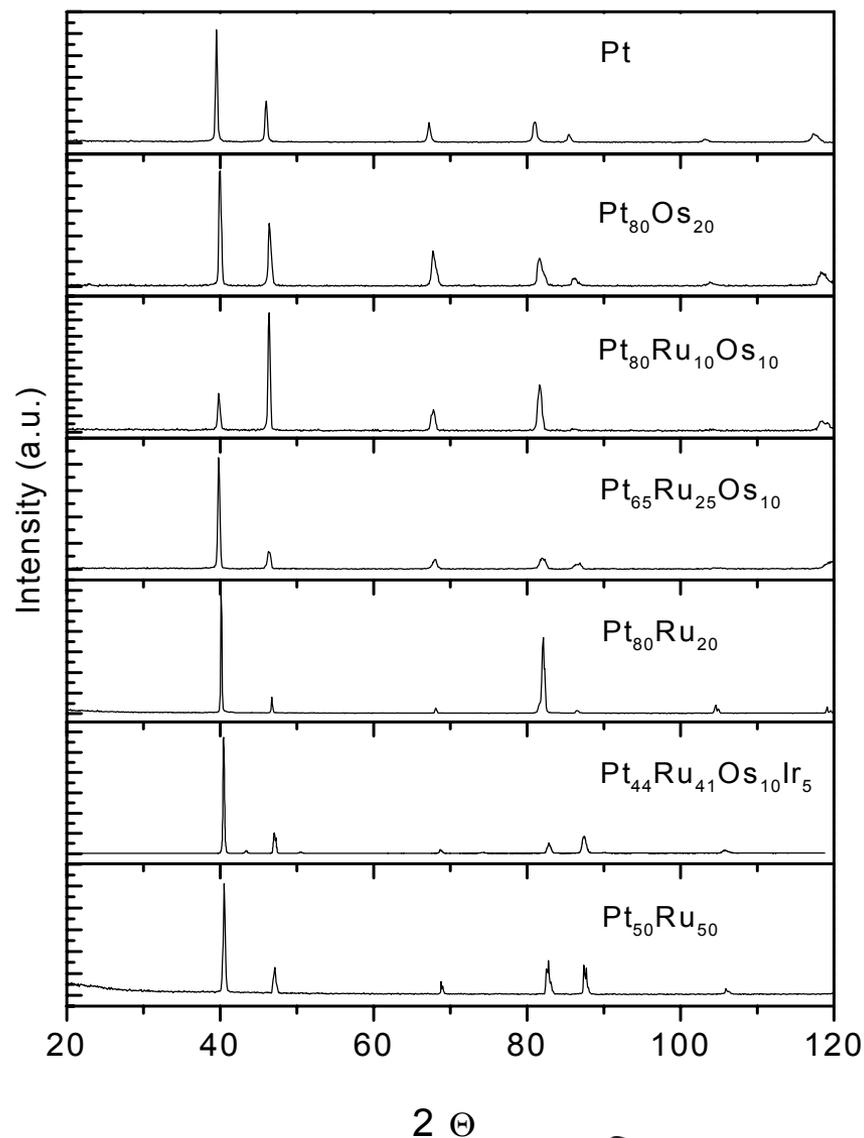
Initial experiments focus on anode

- Supported catalyst in hydrogen/air fuel cell (2001)
- **Unsupported Pt/Ru catalyst in DMFC**

# What do we know about the catalyst?

- Arc-melted alloys
- Nanoparticle catalysts

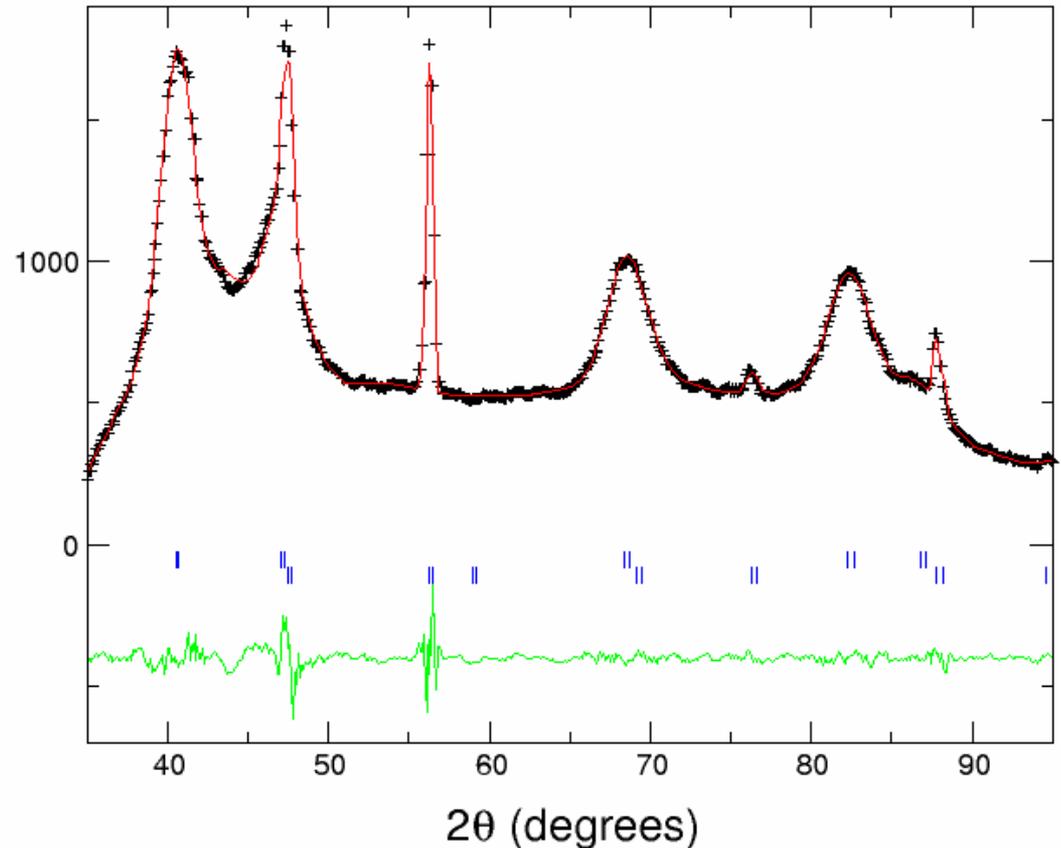
All catalysts are fcc



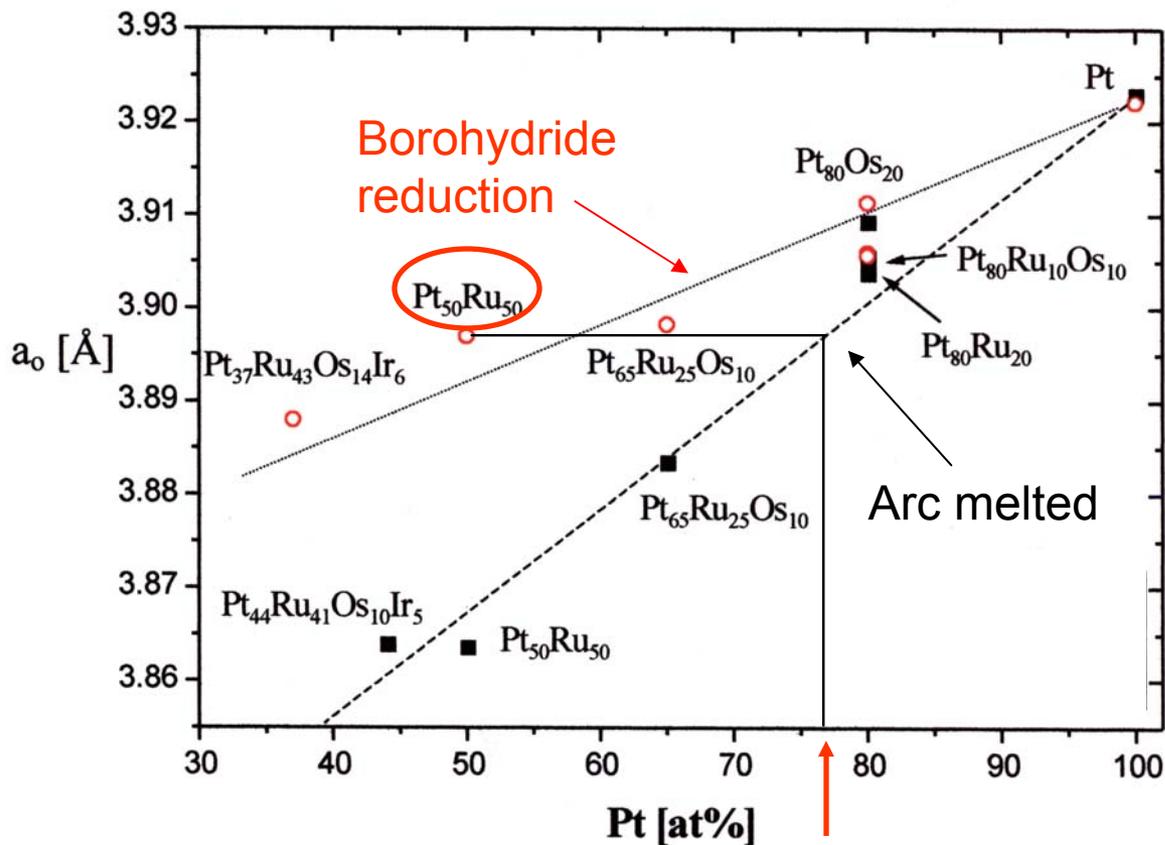
# Lattice parameters of nanoparticle catalysts

- Total pattern fitting
- Internal Si standard
- Accurate lattice parameters
- Particle size broadening

$$a = 3.883 \text{ \AA}$$



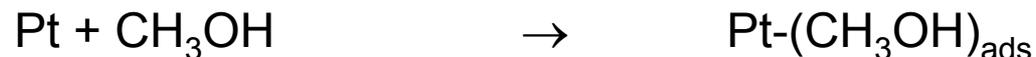
# FCC lattice parameter comparisons



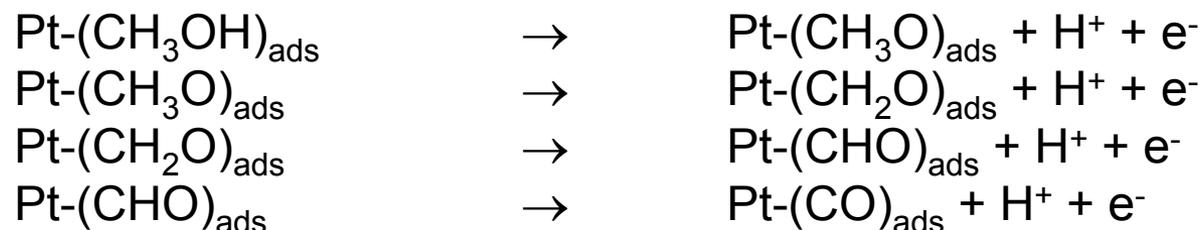
fcc lattice spacings of **catalysts** and arc-melted alloys

# Pt/Ru Catalyst: Bifunctional Mechanism

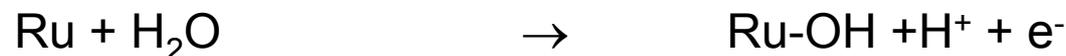
## Methanol Adsorption



## C-H bond Activation



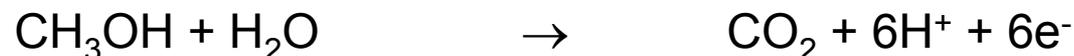
## Water Adsorption



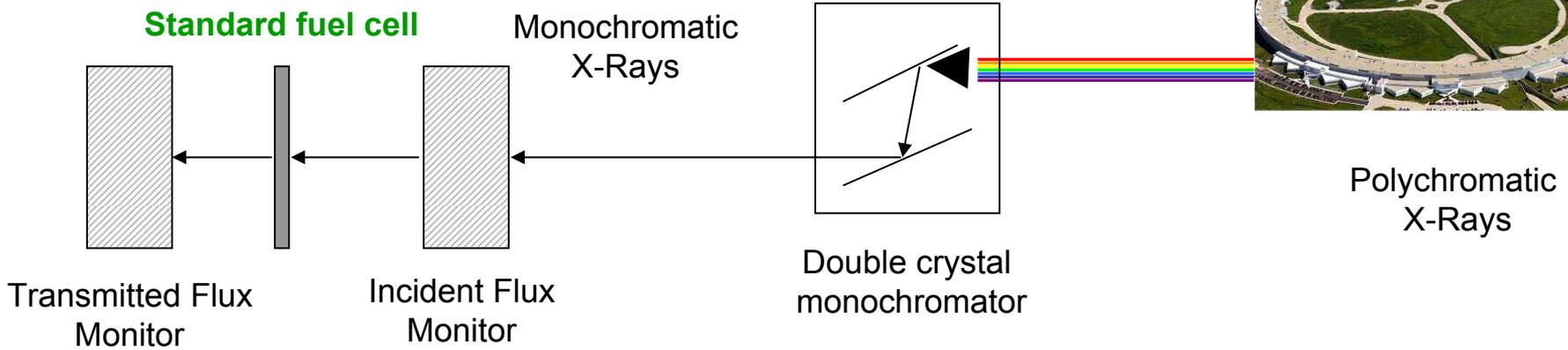
## CO Oxidation



## Overall



# The X-ray absorption experiment



$$\frac{I}{I_0} = e^{-\mu(E)x}$$

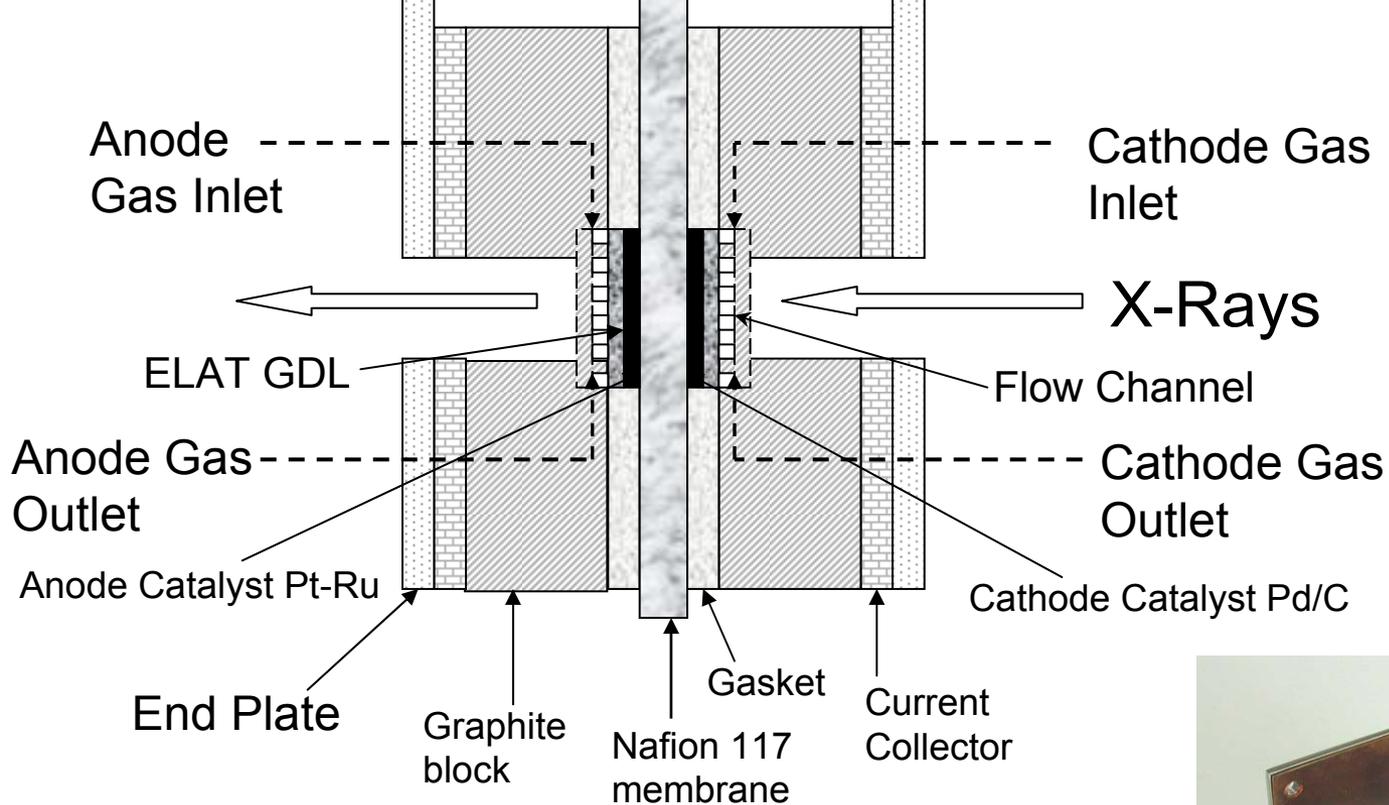
$$\mu(E)x = \ln \left[ \frac{I_0}{I} \right]$$

$I_0$  = Incident Flux

$I$  = Transmitted Flux

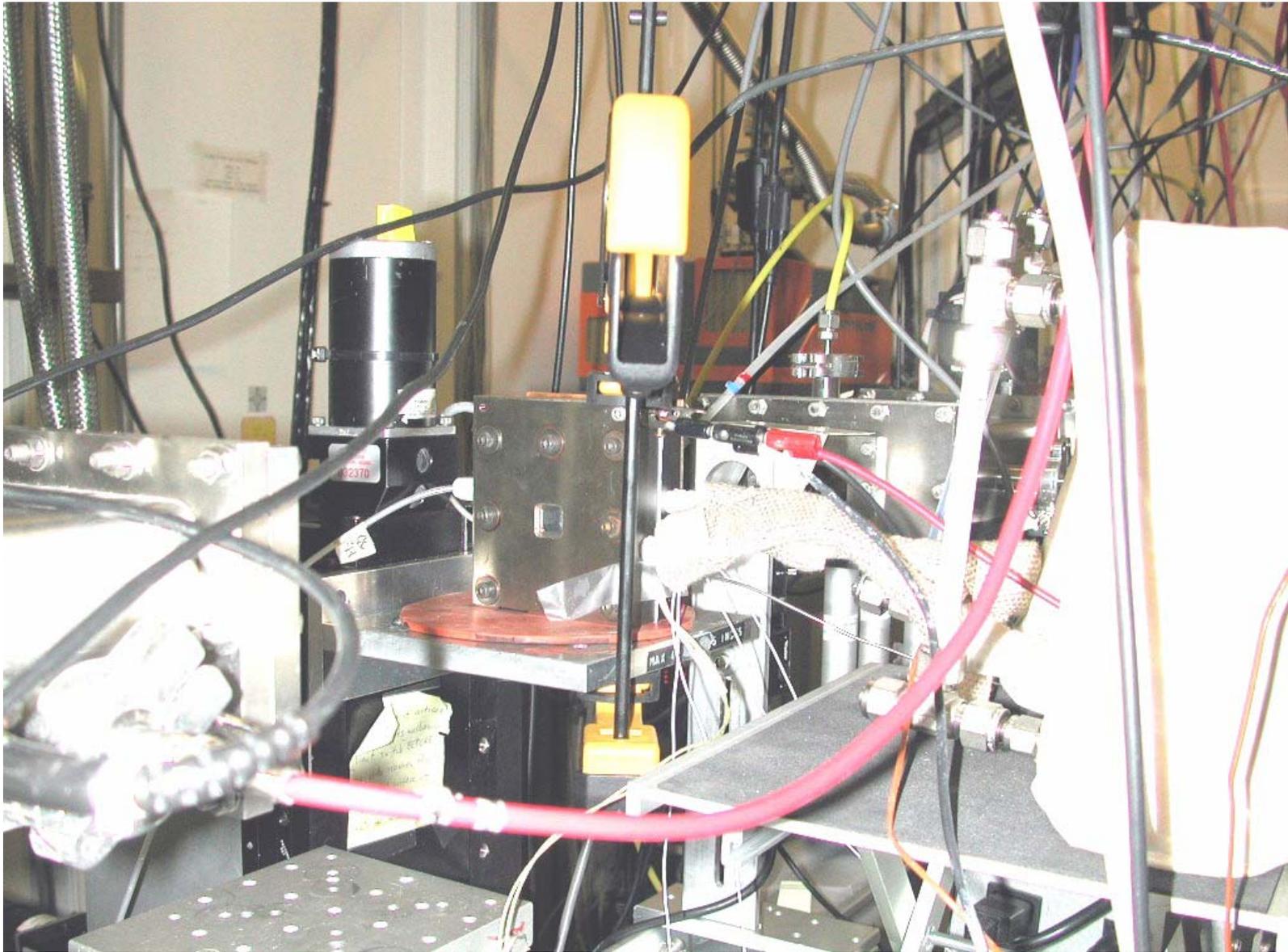
$x$  = Sample Thickness

$\mu(E)$  = Absorption Coefficient at photon energy  $E$



*R. Viswanathan et al., J. Phys. Chem. B 106, 3458 (2002).*

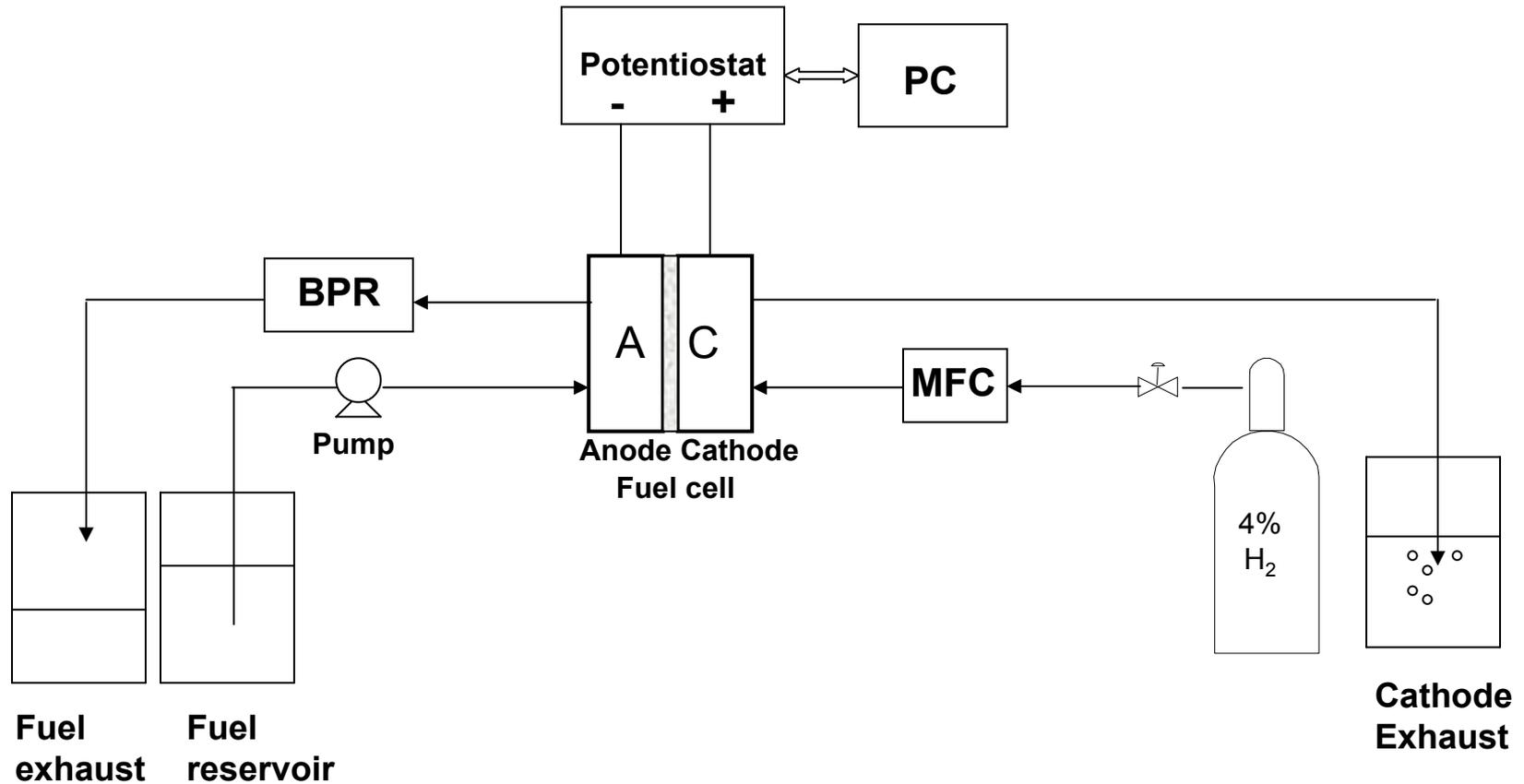




# Planning DMFC synchrotron experiments

- DMFC spectroscopy challenges
  - Density fluctuations
    - CO<sub>2</sub> bubbles at the anode
    - Flooding at the cathode
  - Argonne safety requirements
- Solutions
  - 35°C cell temperature
  - Slight backpressure at the anode
  - 4% H<sub>2</sub> balanced N<sub>2</sub> at the cathode

# DMFC x-ray setup



BPR : Back Pressure Regulator  
MFC : Mass Flow Controller

# Experimental conditions

- DMFC

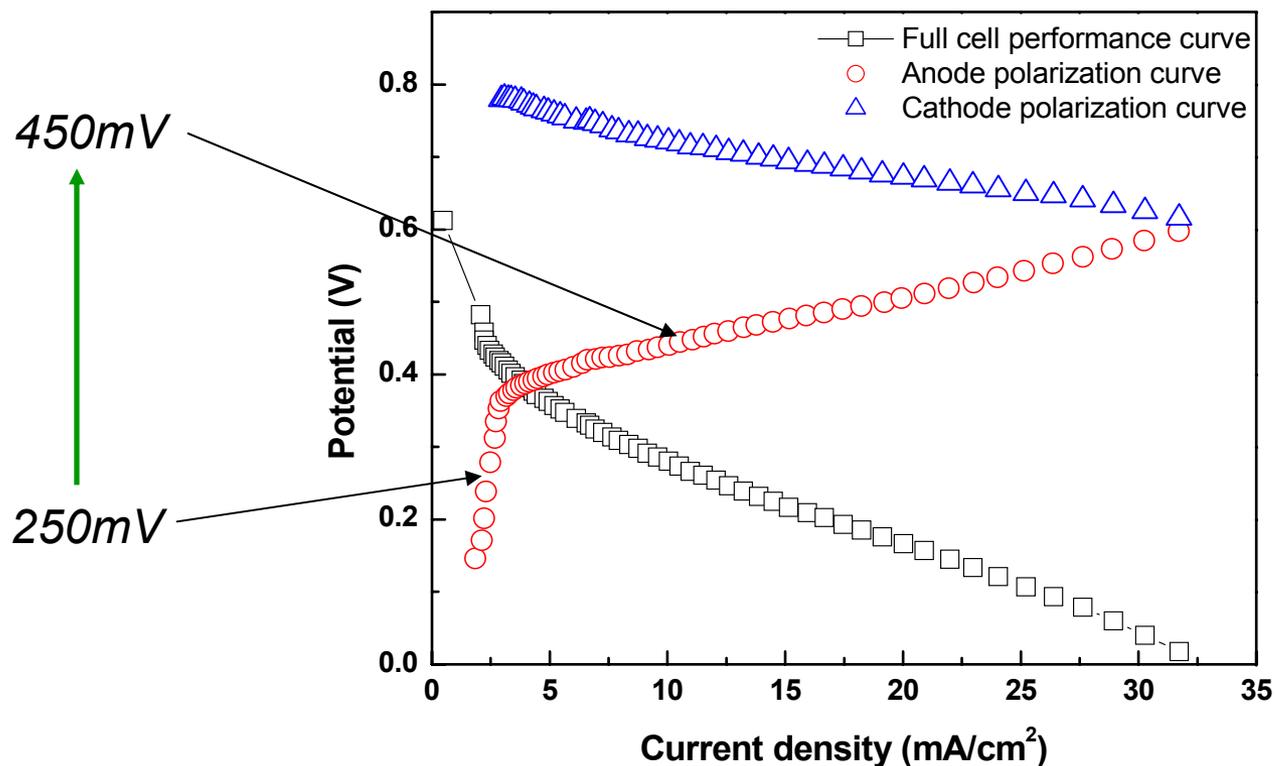
- Anode: PtRu (1:1) —
- Cathode: Pd/C (30wt%)
- Cell temperature: 35°C
- Fuel composition: (1) H<sub>2</sub>O, (2) 0.1M (3) 2M MeOH
- Cathode: 4% H<sub>2</sub> balanced N<sub>2</sub>
- Potential vs DHS: 250mV, 300mV, 350mV, 400mV, 450mV

- In-situ x-ray absorption

- XANES and EXAFS data: Separately taken at Ru K and Pt L<sub>3</sub> edges.
- Absorption edge jumps:  $\Delta\mu x = 0.05$  for Ru and  $\Delta\mu x = 0.17$  for Pt.
- References: Pt foil, Ru metal, RuO<sub>2</sub>, RuO<sub>2</sub>-hydrate, as received PtRu
- Monochromator: Double crystal Si (111)
- Harmonic Rejection Mirror: Pt for Ru edge, Rh for Pt
- Ion chamber detector gases: Incident beam; 80% He- 20% N<sub>2</sub>:  
Transmission; pure N<sub>2</sub>.

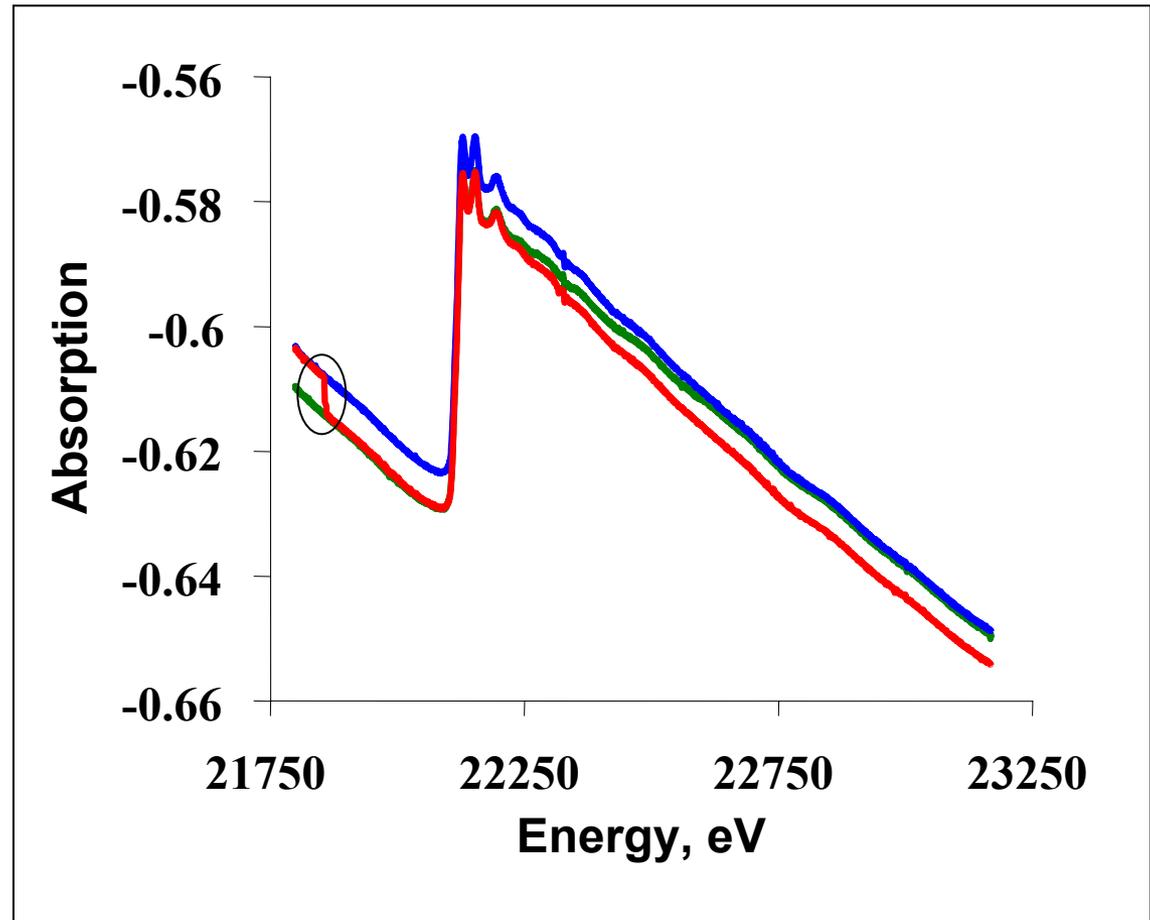
# What is the interesting potential range?

35°C, 0.1M MeOH, 1mL/min



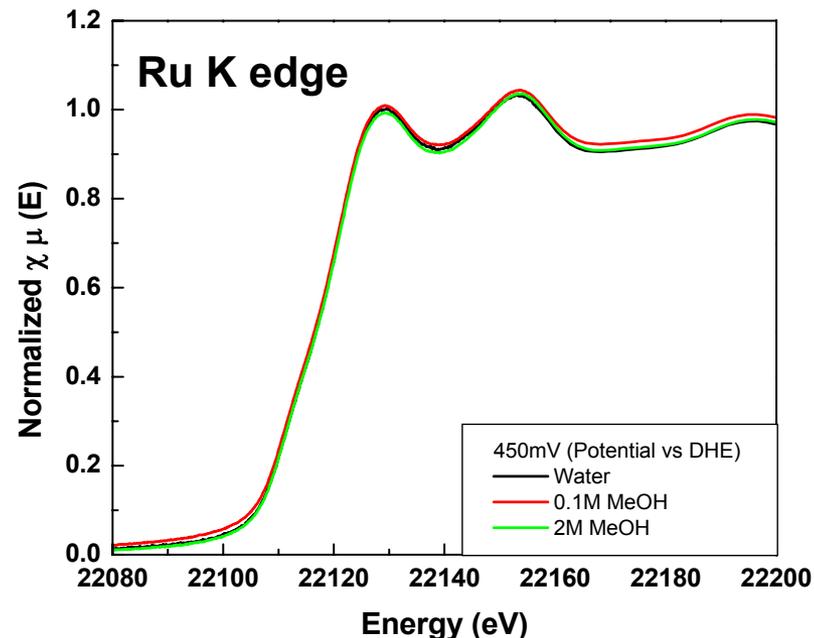
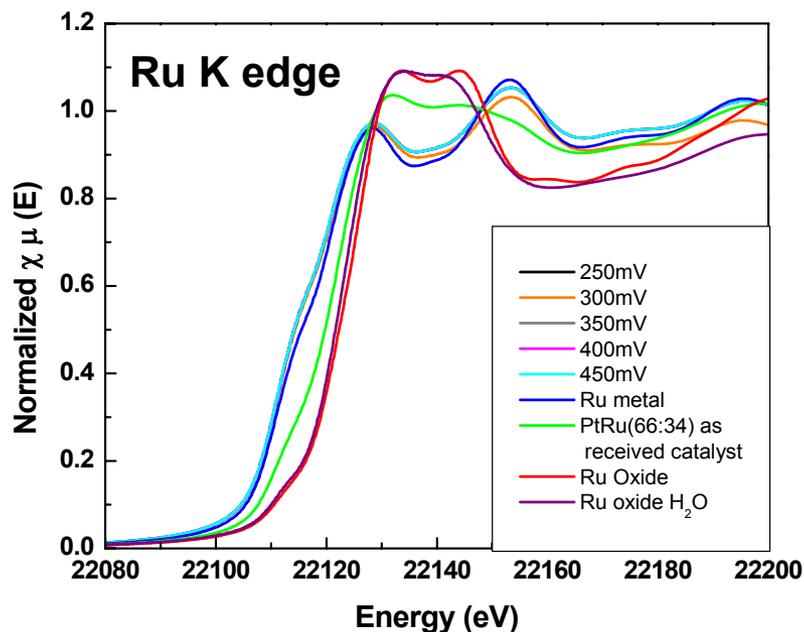
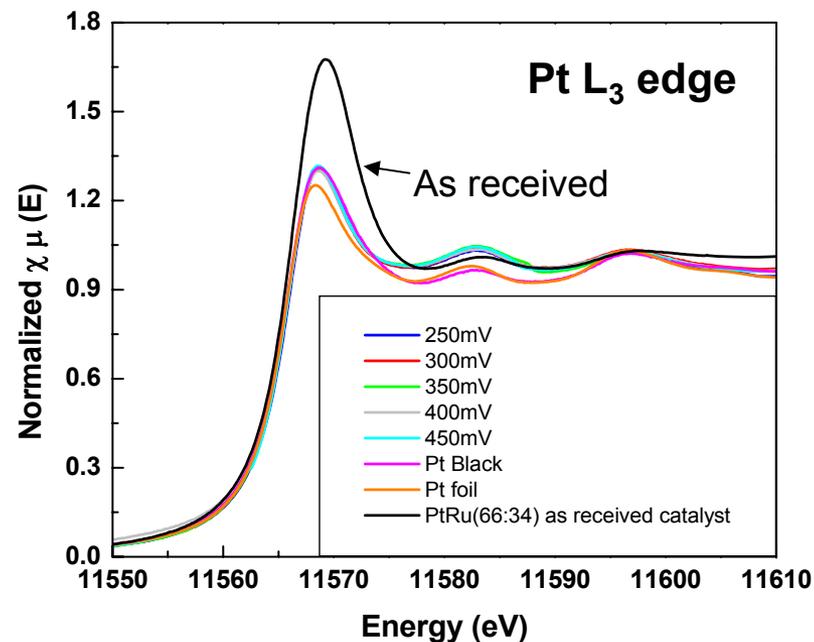
# Experimental approach

- X-ray transmission experiments conducted in continuous scan mode, minimizing absorption transition effects.
- Enables > 85% use of data for averaging.
- Example of transitions in absorption due to density fluctuations (e.g. CO<sub>2</sub>)
- Note magnitude of Ru edge jump!

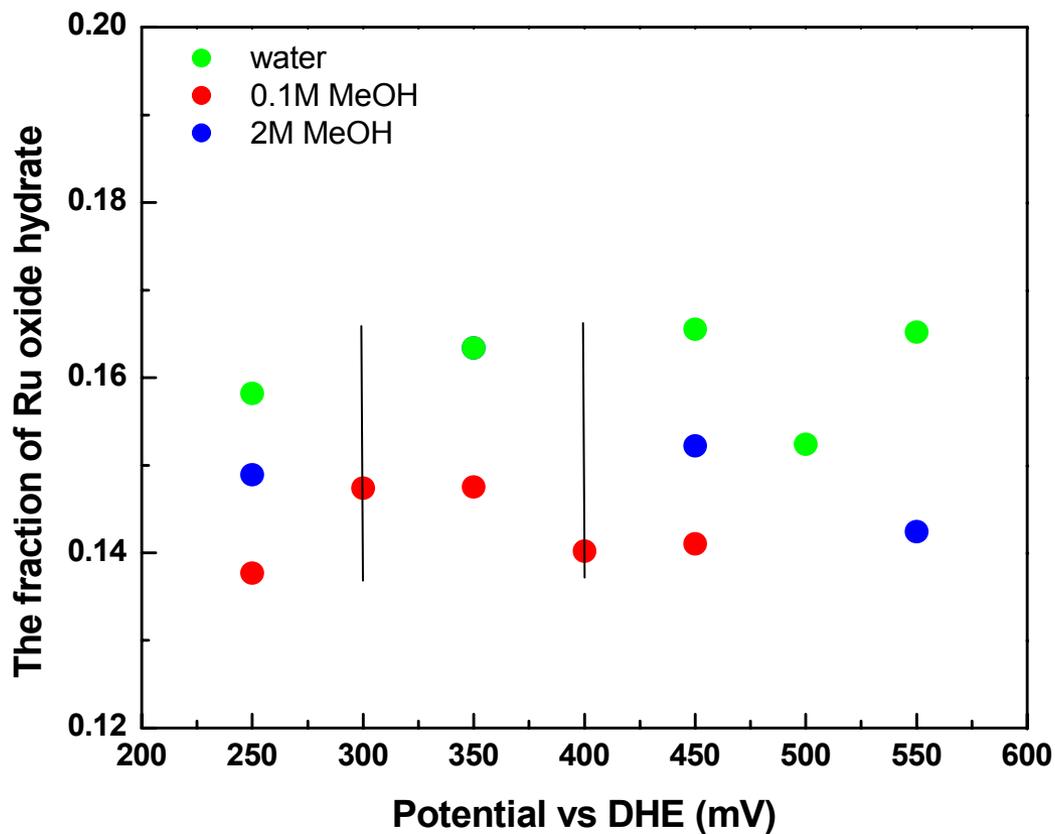


# XANES fitting

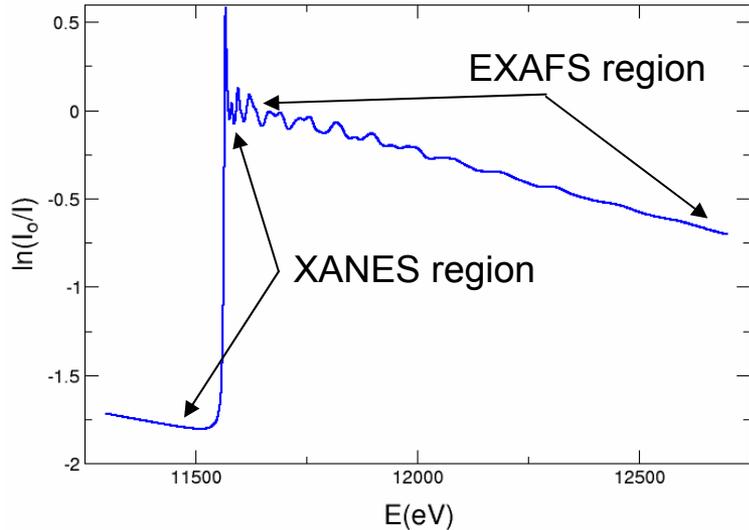
- Data were normalized and aligned using Athena.
- Least squares fitting of Ru edges with Sixpack.
- The standards for the least squares fits were  $\text{RuO}_2$ -hydrate and Ru powder.



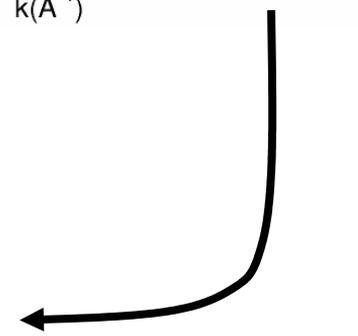
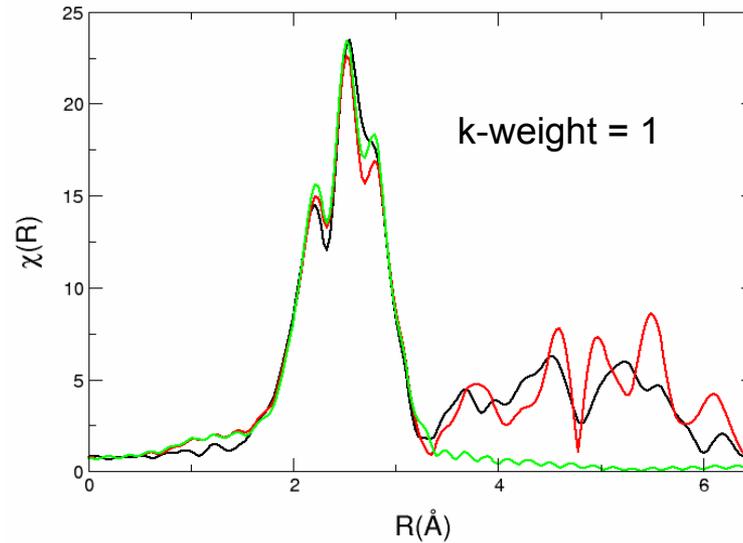
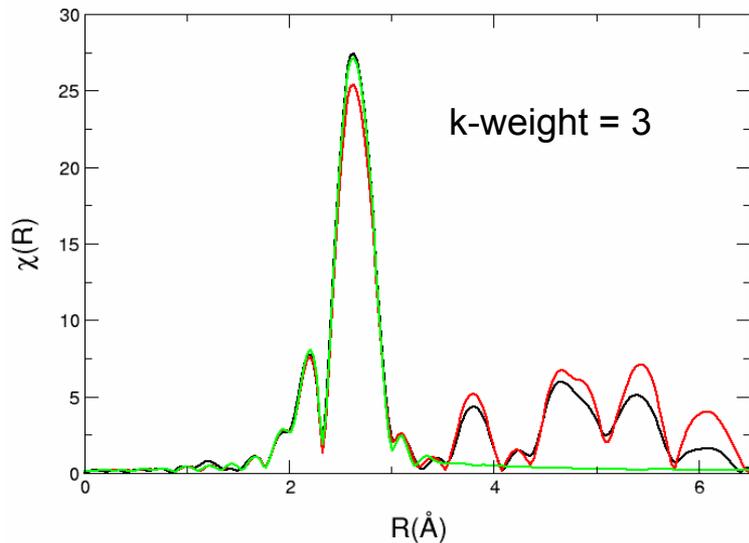
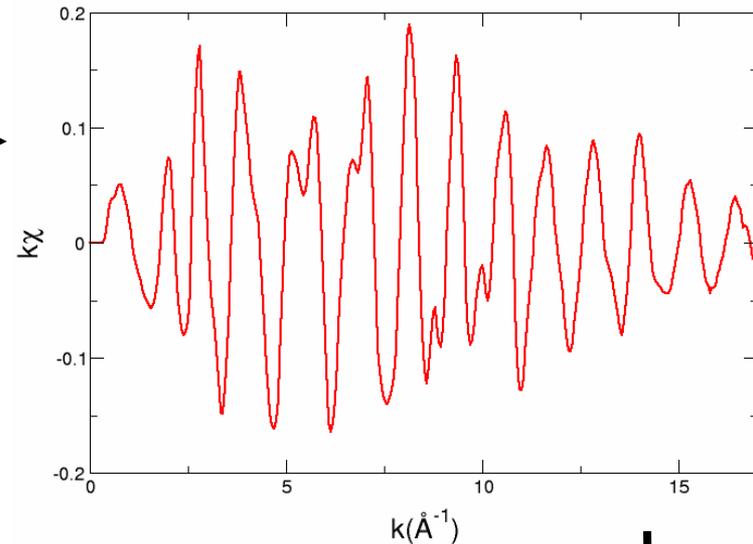
# RuO<sub>2</sub>-hydrate fraction by XANES



# Pt foil XAFS Analysis



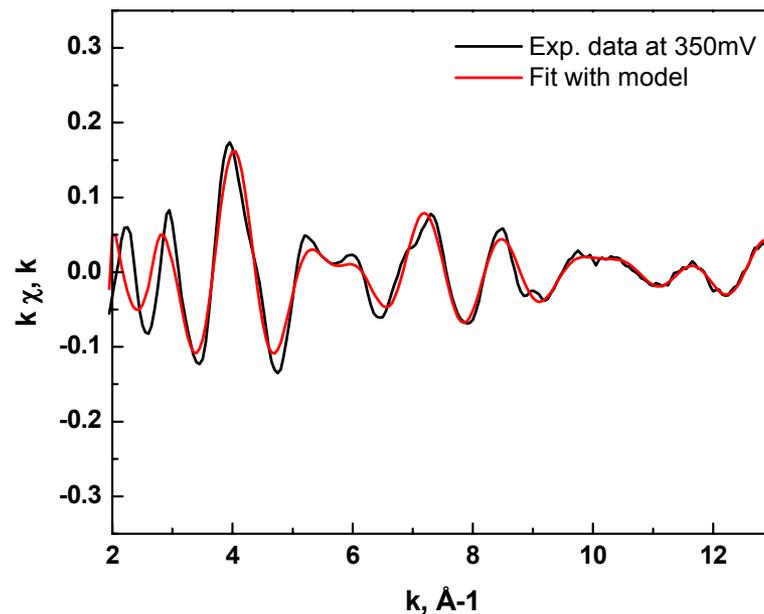
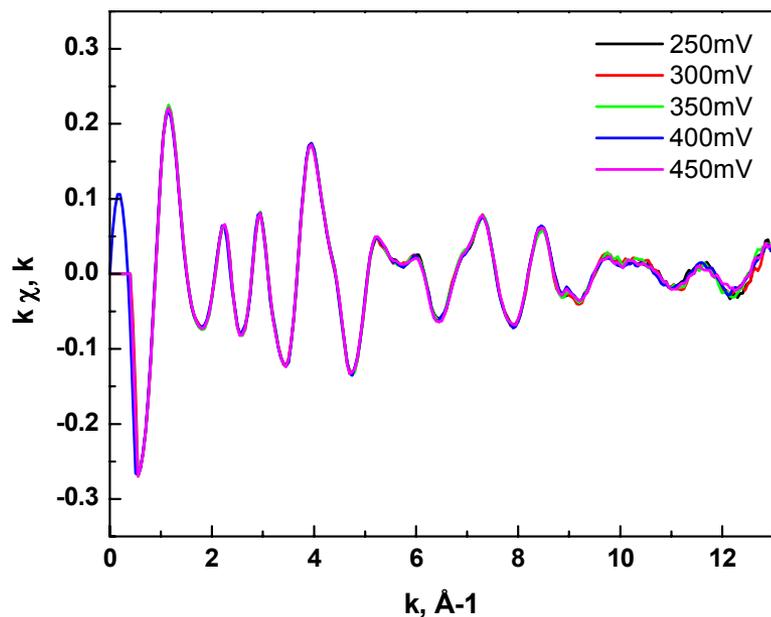
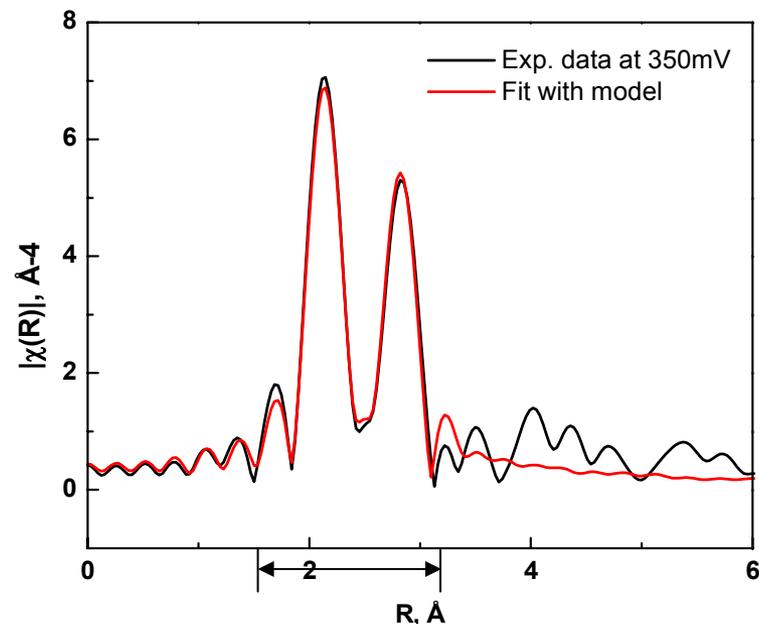
Remove background



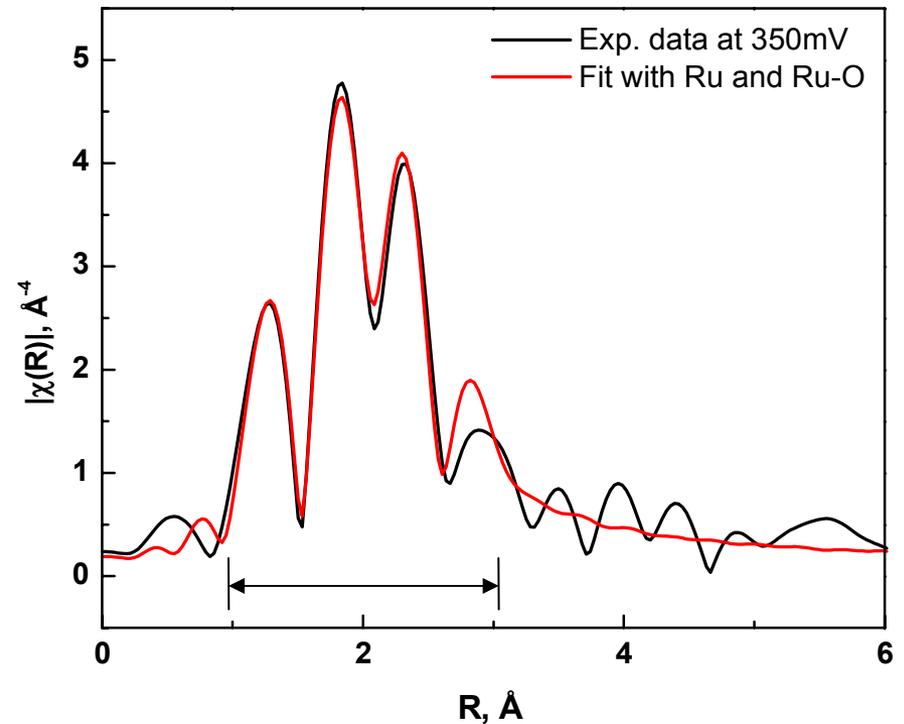
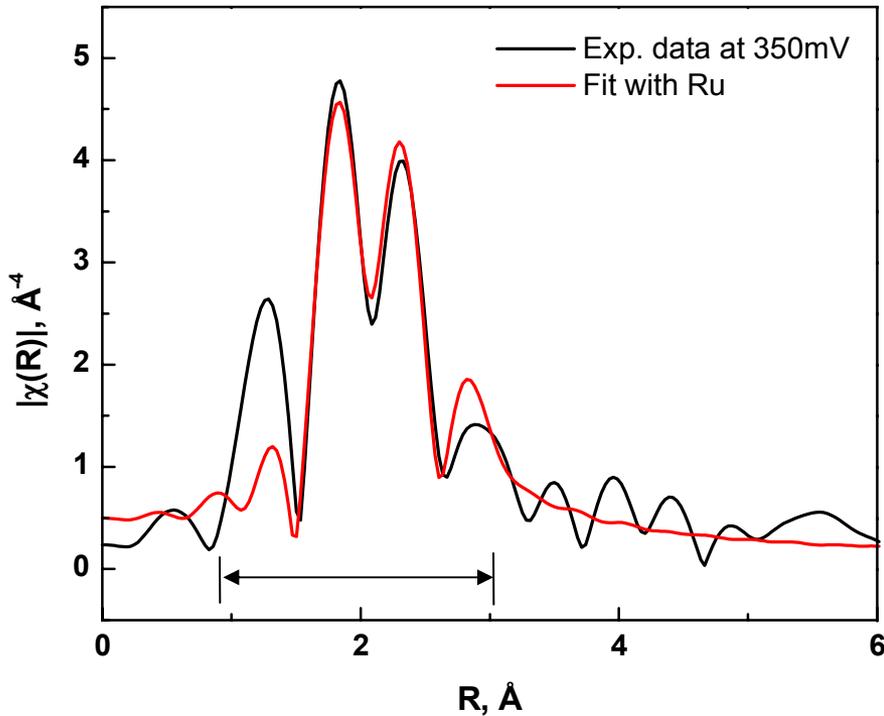
Fit with simple model at multiple  $k$ -weightings

# Pt EXAFS

- Potential dependent EXAFS at 0.1M. Pt EXAFS has excellent fit with a totally metallic environment. All data are nearly identical.
- FT range for k space is 2 Å to 13 Å.
- Fit range for R space is 1.5 Å to 3 Å.



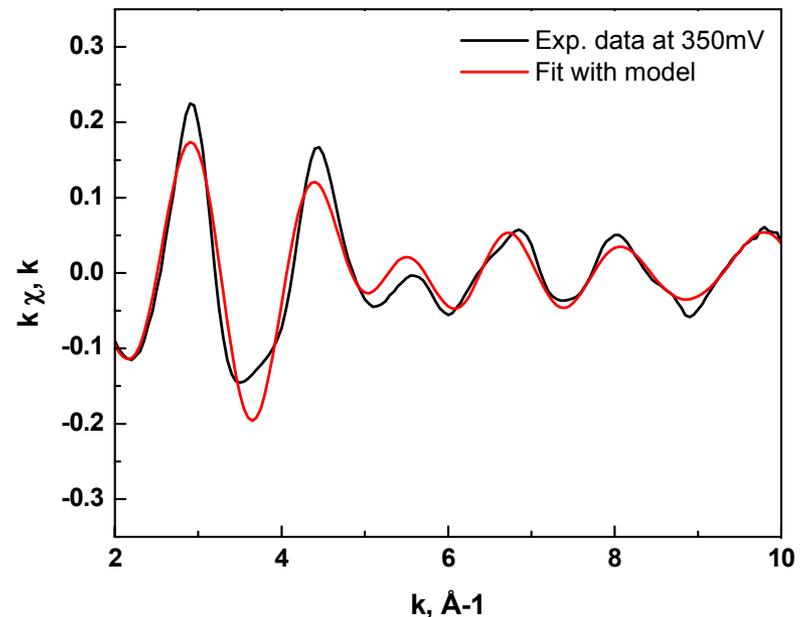
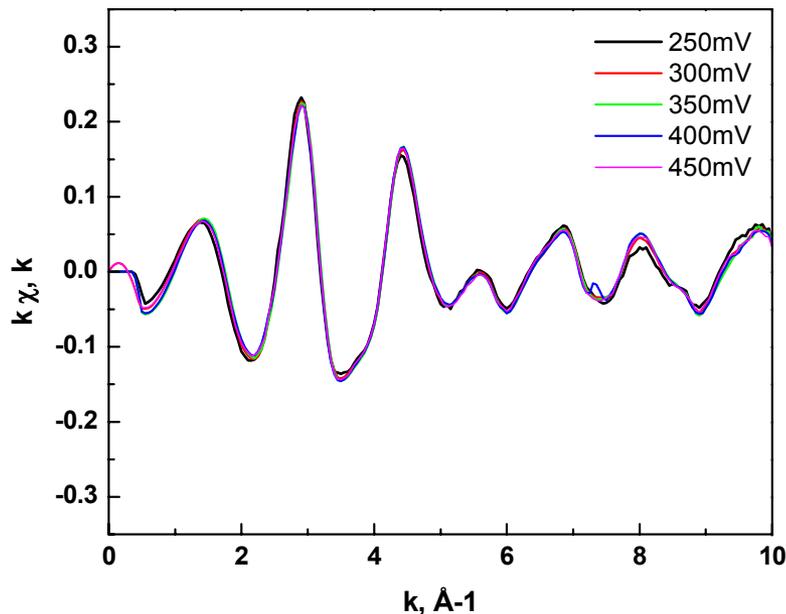
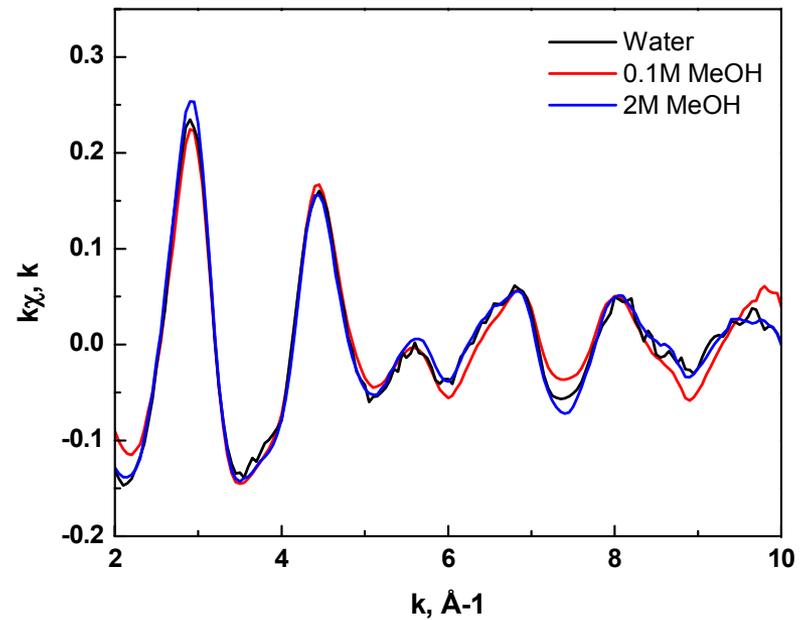
# Ru EXAFS Fitting



- Addition of Ru-O neighbors improves the EXAFS fit.
- The peak at about 1.3Å is ascribed to oxygen bound to Ru.
- The asymmetric distribution of the Ru-O peak is consistent with disorder

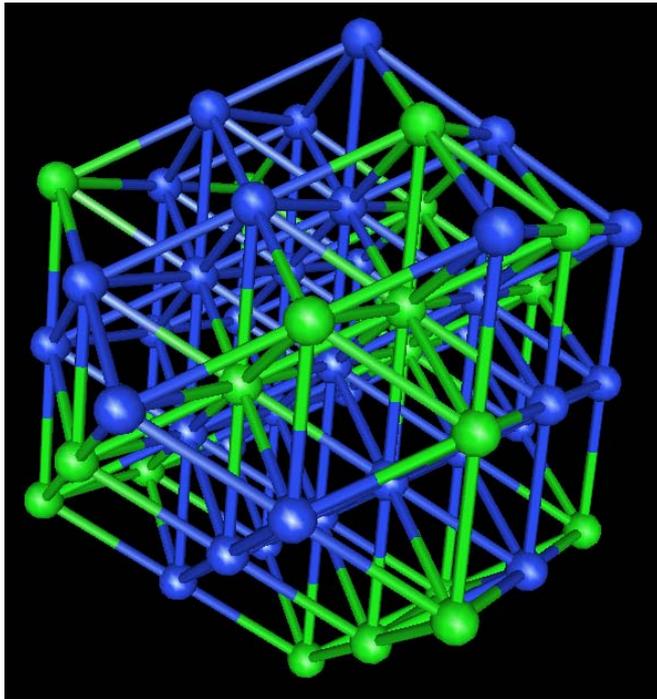
# Ru EXAFS

- Potential dependent EXAFS at 0.1M MeOH
- [MeOH] dependent EXAFS
- Model fit at 350mV



# Metal cluster structural model

FCC structure, count first shell neighbors only from Pt and Ru edges  
This only “sees” atoms in the metallic cluster



Frenkel 1998, Shibata 2003

Average Coordination #'s

$$N_{\text{Ru}}^{\text{Pt}} = \text{Pt around Ru}$$

$$N_{\text{Ru}}^{\text{Ru}} = \text{Ru around Ru}$$

$$N_{\text{Pt}}^{\text{Ru}} = \text{Ru around Pt}$$

$$N_{\text{Pt}}^{\text{Pt}} = \text{Pt around Pt}$$

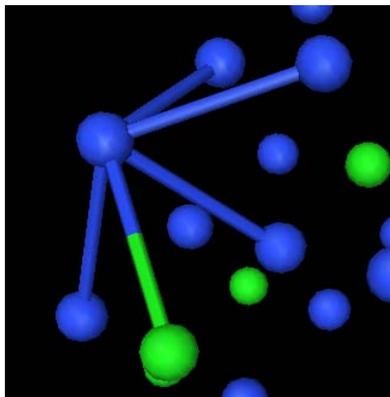
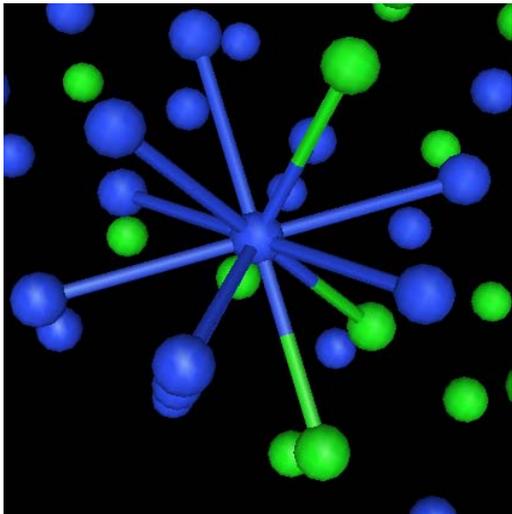
$$n_{\text{Pt}} = \text{Pt coordination}$$

$$n_{\text{Ru}} = \text{Ru coordination}$$

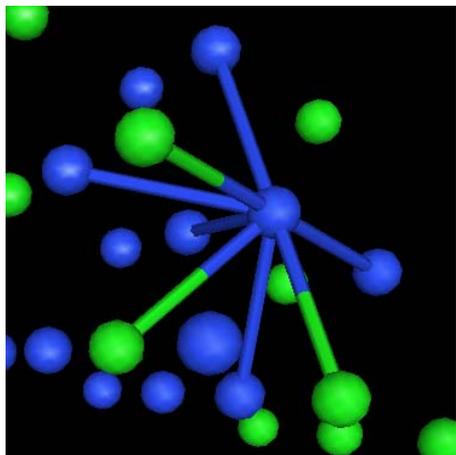
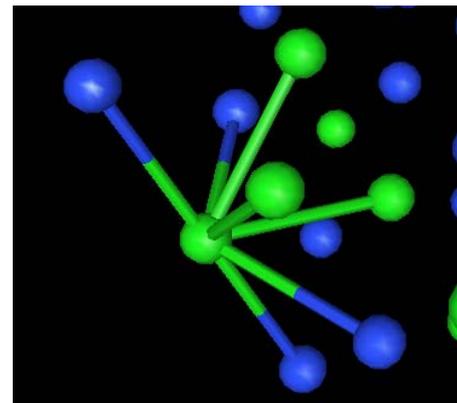
Fractional Coordination #'s

$$Y = \text{Ru around Pt}$$

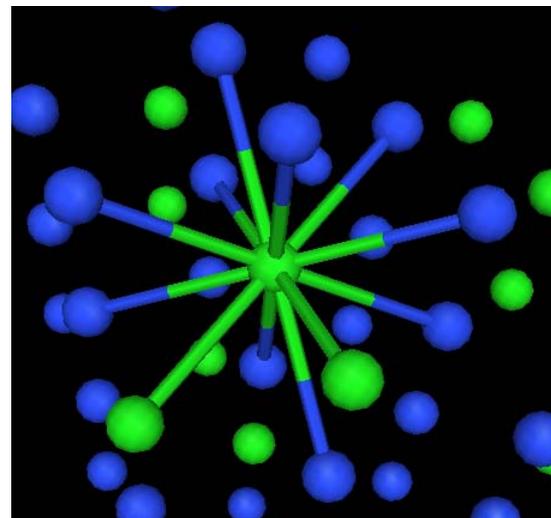
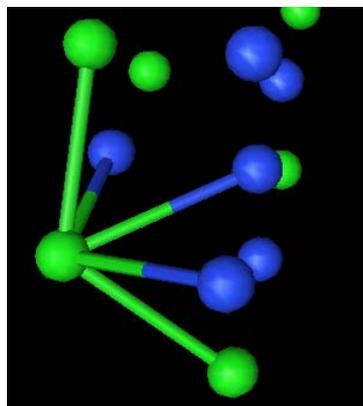
$$X = \text{Pt around Ru}$$



$$X = \frac{B_{\text{Ru-Pt}}}{[\text{Ru}]n_{\text{Ru}}N}$$



$$Y = \frac{B_{\text{Pt-Ru}}}{[\text{Pt}]n_{\text{Pt}}N}$$



$$B_{\text{Pt-Ru}} = B_{\text{Ru-Pt}}$$

# Metallic 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, X (Pt around Ru) and Y (Ru around Pt) and total coordination number about each atom, n (Frenkel 1998, Shibata 2003)
- Bond lengths and Debye-Waller factors are consistent with literature values for C supported Pt-Ru catalyst (Russel 2001, Camara 2002)

$$n \quad 8.2 \pm 0.2$$

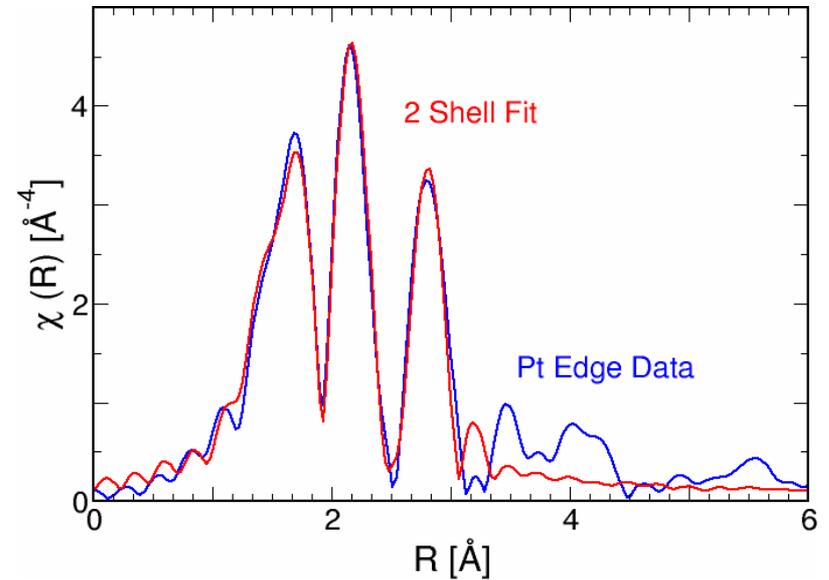
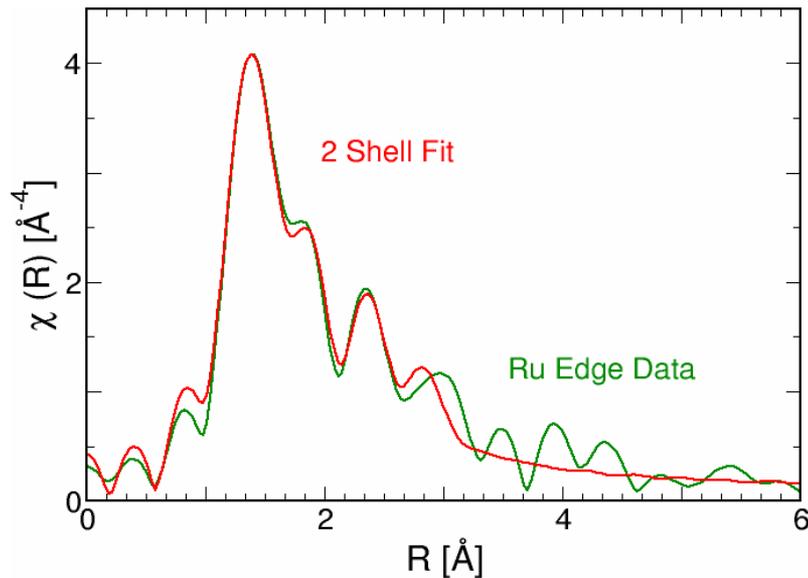
$$X \quad 0.54 \pm 0.02$$

$$Y \quad 0.27 \pm 0.02$$

$$\frac{[\text{Ru}]}{[\text{Pt}]} = \frac{Y}{X} = 0.5$$

# Apply model to as-received catalyst

Pt not simply metallic but has oxygen near neighbors



Ru shows large increase in number of oxygen near neighbors

# Catalyst structural changes

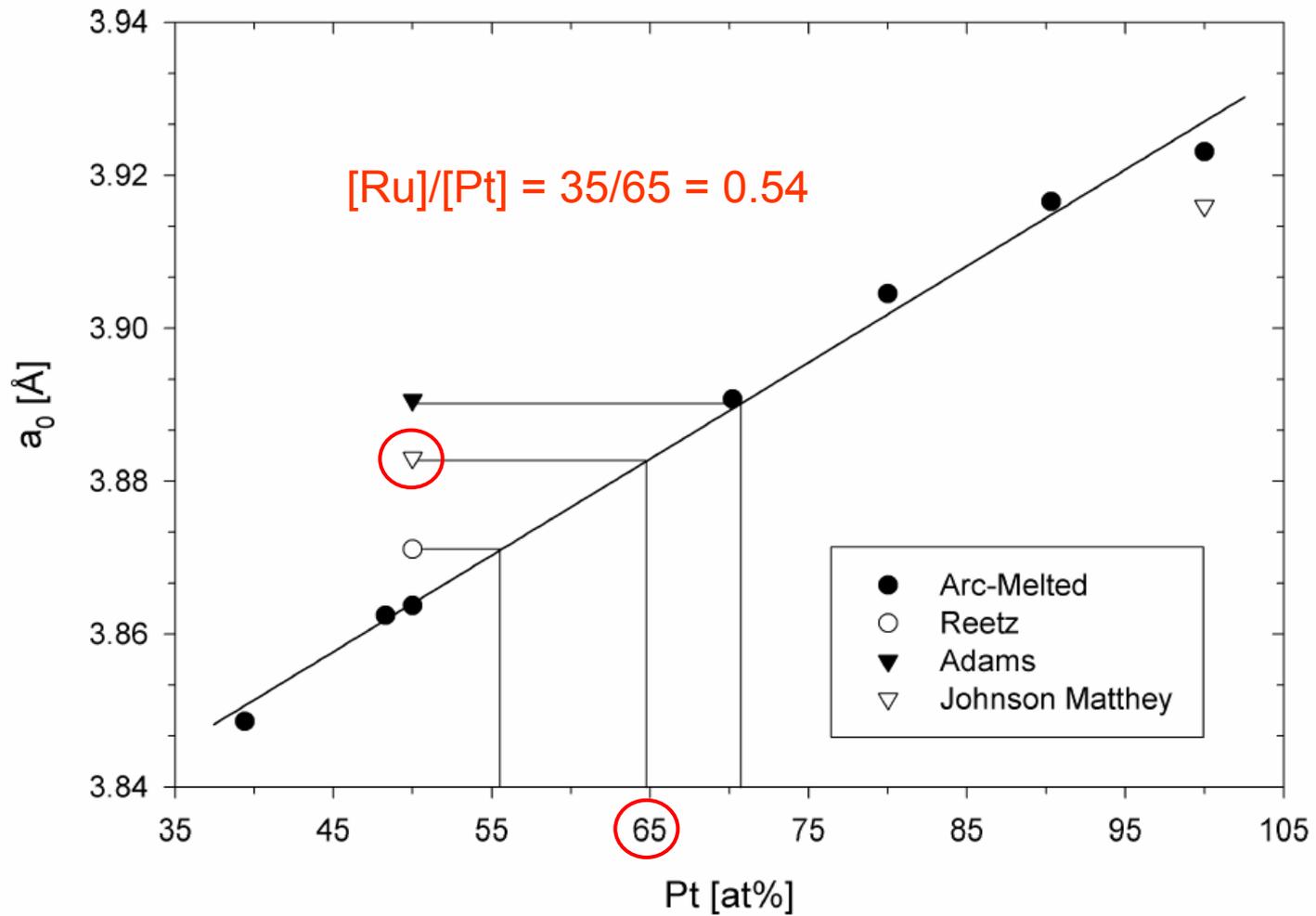
## As received catalyst

- Ru oxidation ~58%
- N = 5.6
- [Ru]/[Pt] = 0.44
- Pt-O bonds present
- Ru-O bonds ~2.8 avg

## In situ catalyst

- Ru oxidation ~15%
- N = 8.2
- [Ru]/[Pt] = 0.50
- No Pt-O bonds
- Ru-O bonds ~0.24 avg

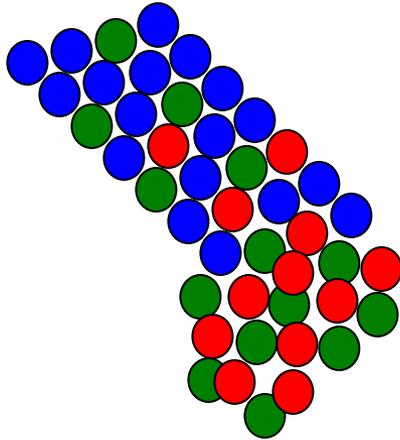
S. Stoupin et al., *J.Phys Chem B*, **110**, 9932 (2006).



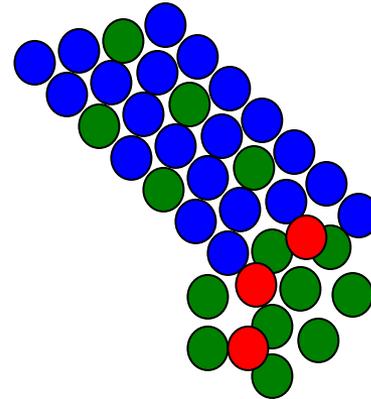
# Possible Structural Model

FCC alloy phase with an amorphous Ru ghost phase

As received catalyst



In situ catalyst



- Higher surface area may be critical in catalyst performance
- Incorporated O eases CO oxidation

# Conclusions

Metallic cluster of the catalyst nanoparticle

Composition is about 2:1 Pt:Ru

Model fit suggests that the alloy is not totally randomized  
(i.e.  $X \neq .65$  &  $Y \neq .35$ )

Pt is metallic within the potential window (250mV and 450mV) in water or aqueous methanol.

Ru–O bonds are not potential or [MeOH] dependent (Rolison)

On the surface?

In a separate phase?

The potential transition point is not accompanied by ensemble changes at the surface.

Lots more to do!

# Extra bonus material

Another example of the kind of experiment which is well-suited to an undulator beamline. Where the sample is damaged rapidly by the x-ray beam!

# Dilute magnetic semiconductors

- Cations replaced by Mn, Co, Fe, etc.
- Typical examples are: ZnO-Mn, CdS-Mn, ZnS-Mn, etc.
- Host s-p band  $\Leftrightarrow$  Mn<sup>2+</sup> d electron exchange interactions
- Unusual magnetotransport and magneto-optical phenomena
  - Carrier induced ferromagnetism in InAs-Mn and GaAs-Mn
- DMS nanocrystals are unique systems
  - semiconductor confinement effects
  - magnetic properties

# Acknowledgements

## Collaborators

Dipankar Das Sarma - IIS  
Soma Chattopadhyay – MRCAT  
Tomohiro Shibata – MRCAT  
Mali Balasubramanian – XOR20  
Shelly Kelly – ANL BioSciences

## Graduate students

Mehdi Ali – IIT Physics  
Ranjani Viswanatha - IIS

## Funding

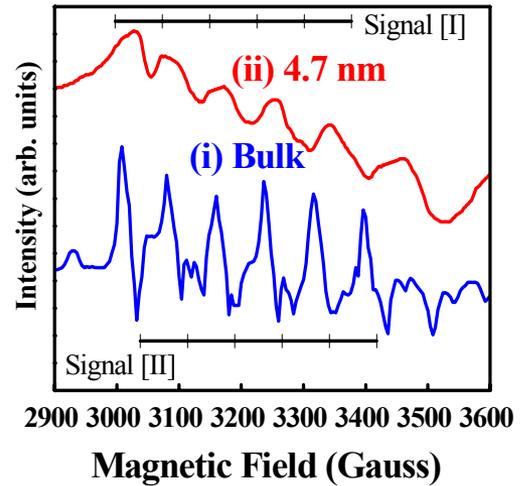
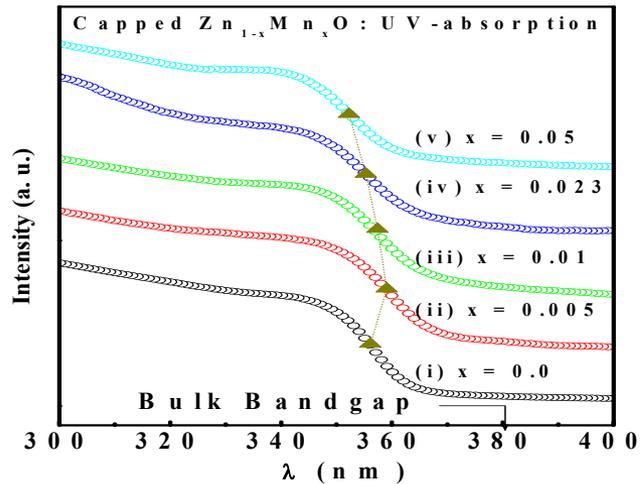
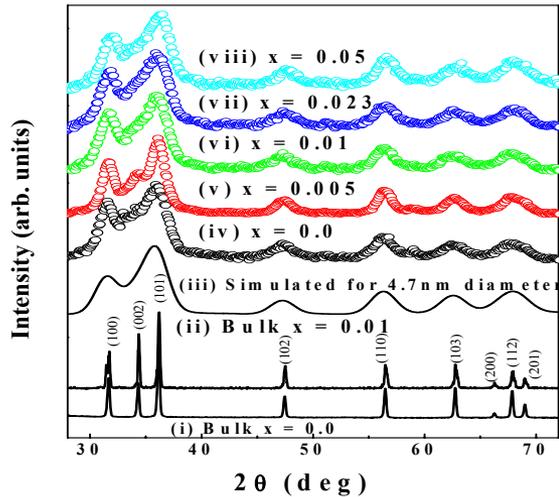
MRCAT is supported by contributions from MRCAT member institutions.

The APS is funded by the U. S. Department of Energy,  
Office of Basic Energy Sciences under Contract number W-31-109-Eng-38.

# Sample preparation and characterization

- Wet chemical synthesis starting with Mn-acetate and Zn-acetate.
- Capping with polyvinylpyrrolidone (PVP) results in smaller sized particles (5 nm or less) with uniform size distribution
- Bulk sample synthesized by annealing the powders at 1200°C for 12 hours in air. The size of the bulk particles is ~1.5 microns.
- Size calculated using Scherrer's equation and verified by TEM.
- The percentage of Mn doping in the samples was estimated by EDAX and ICP-AES.
- Bandgap was measured by UV-VIS Absorption spectroscopy.
- Magnetic properties were measured by Electron Paramagnetic Resonance (EPR).

# XRD , UV-VIS and EPR results

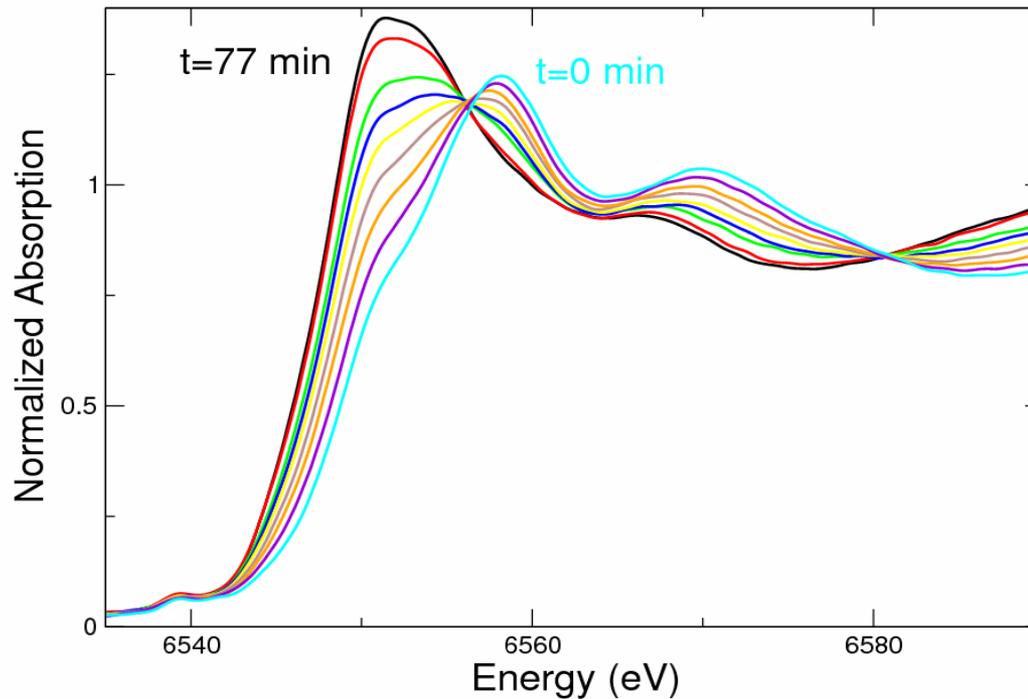


XRD shows formation of wurtzite nanocrystals

Increase in the bandgap compared to the bulk, some variation with Mn concentration

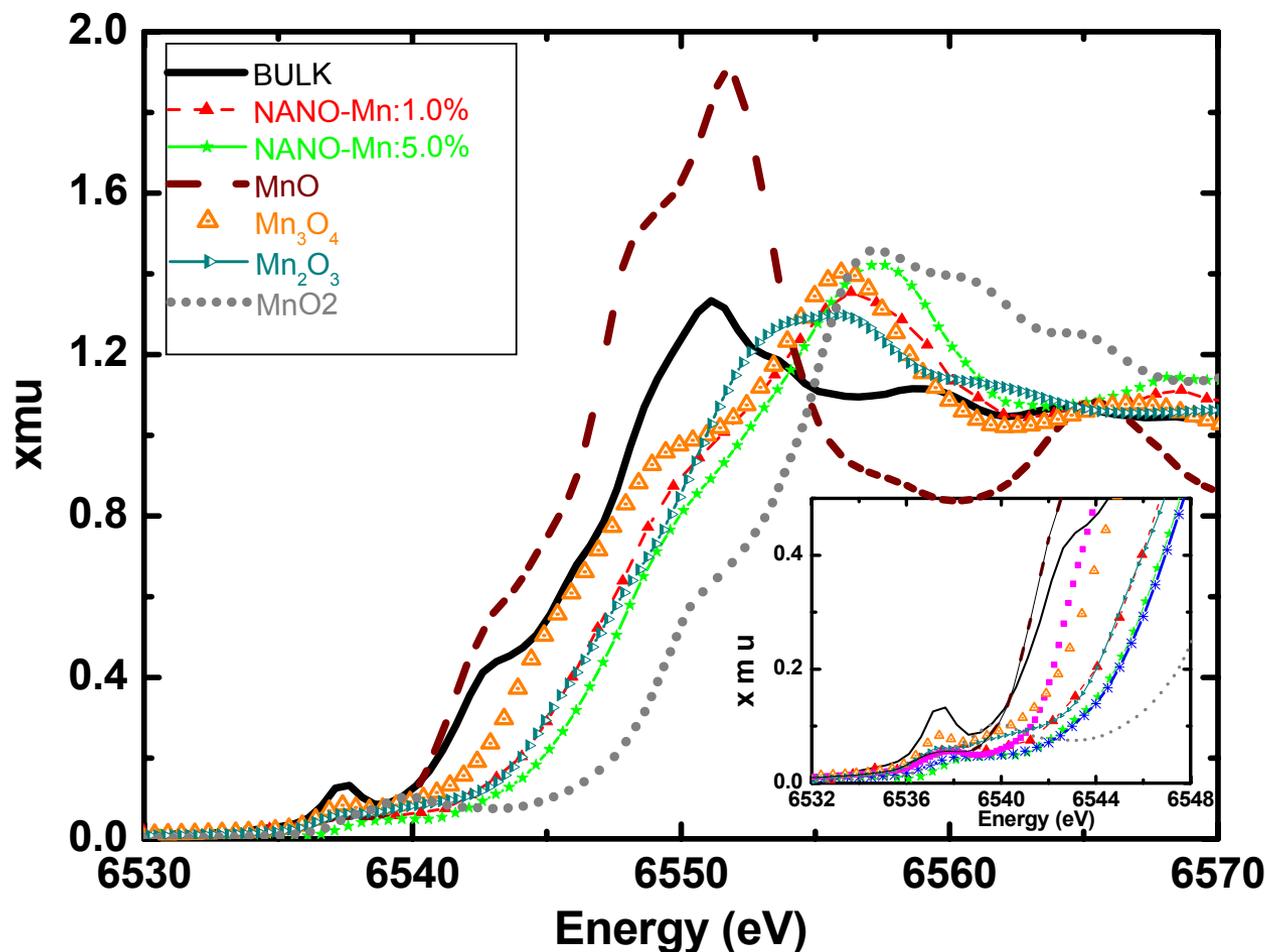
EPR spectra from the doped samples exhibit well resolved hyperfine splitting of isolated  $Mn^{2+}$  ions, suggesting that Mn-Mn interactions are rather weak.

# Sample degradation of ZnO-Mn



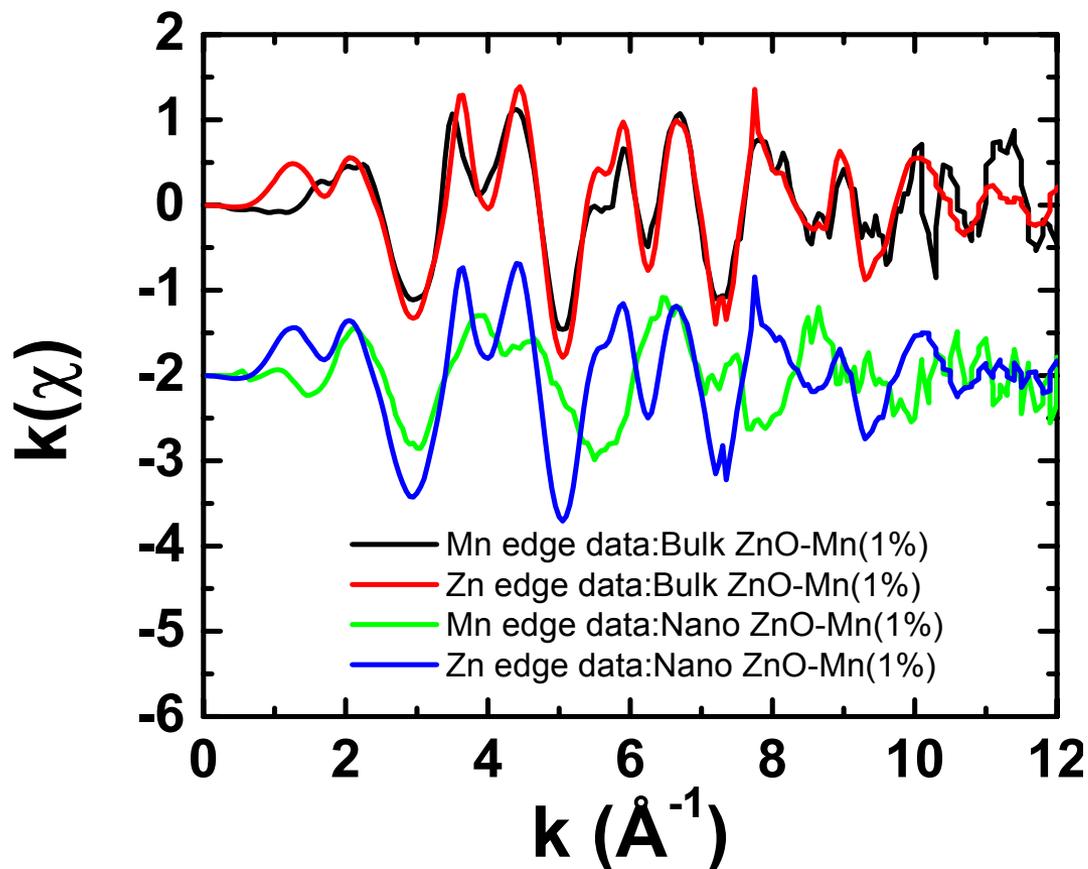
Clear evidence of reduction of Mn with time exposed to x-rays  
Observed with bending magnet beam too  
Undulator quick scans can help!

# ZnO-Mn XANES



- Average valence state changes from bulk to nanoparticle sample
- Mn(II) dominates bulk sample
- Mn(III)-Mn(IV) dominates nanoparticle samples

# EXAFS of bulk and nanoparticle ZnO-Mn(1%)

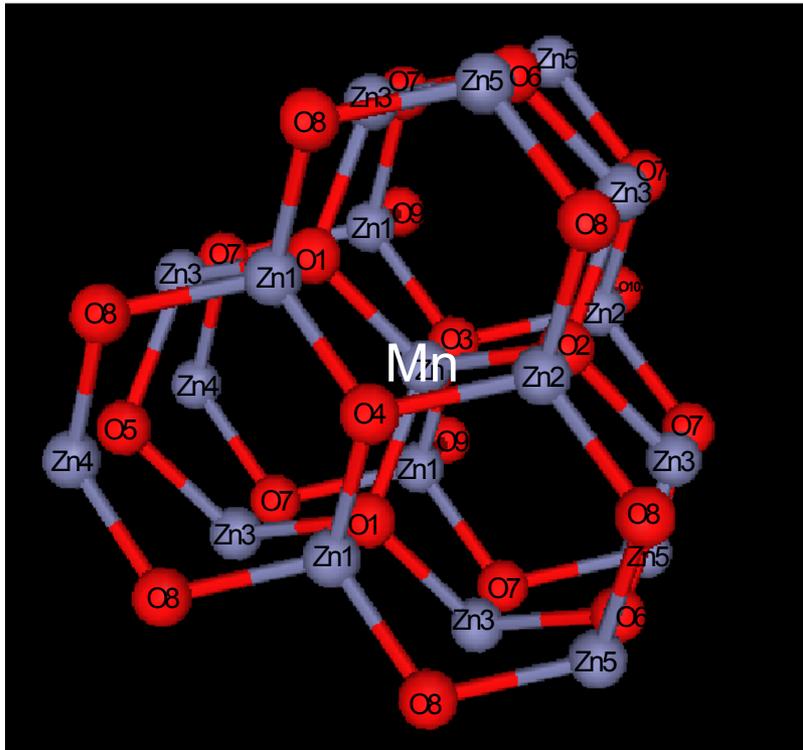


Bulk Zn and Mn spectra are similar

Nanoparticle Zn and Mn spectra are different

Mn replaces Zn in the bulk sample but not in the nanoparticle

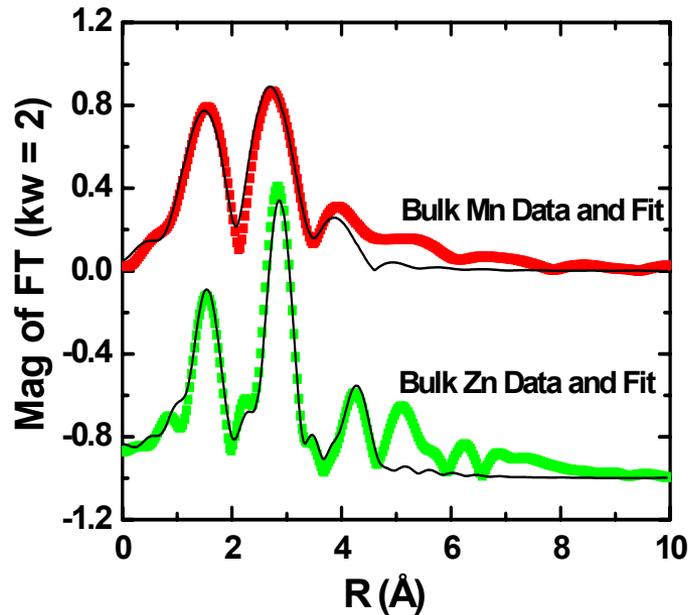
# ZnO structural model



ZnO has wurtzite structure:  
 $a = b = 3.250 \text{ \AA}$ ;  $c = 5.207 \text{ \AA}$   
 $\alpha = \beta = 90^\circ$ .  $\gamma = 120^\circ$ .

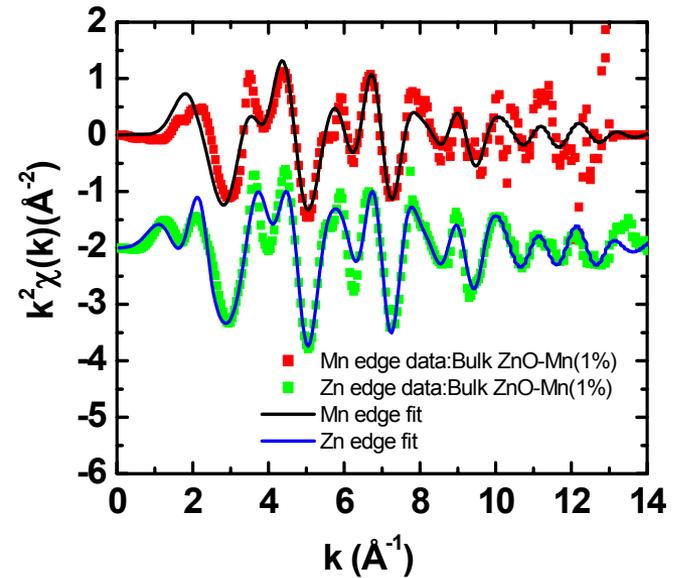
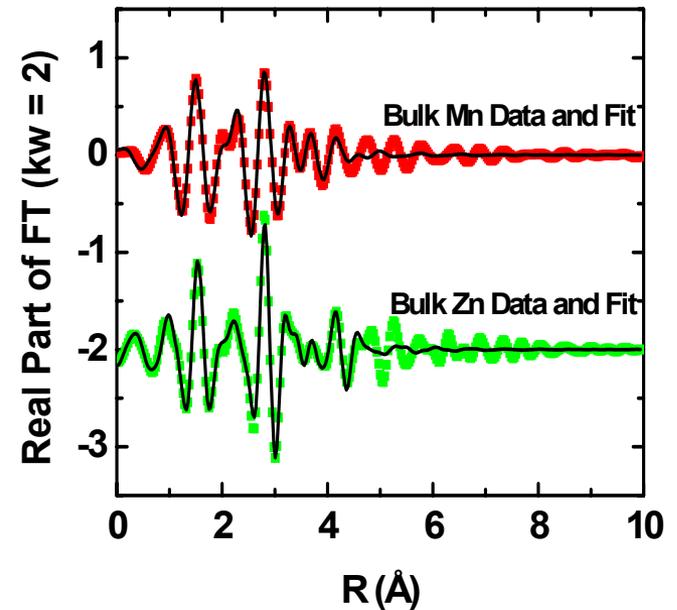
Atoms	Path Degeneracy	Bond Length ( $\text{\AA}$ )
O1	2	1.97
O2	1	1.975
O3	1	1.99
Zn1	4	3.21
Zn2	2	3.21
O4	1	3.22
Zn3	6	3.25
O5	1	3.80
O6	2	3.80
O7	6	3.81
Zn4	2	4.57
Zn5	4	4.57
O8	6	4.57
O9	2	4.96
O10	1	4.96

# Bulk samples fits



Bulk Mn and Zn spectra sets were simultaneously fit in R-space

No question that Mn substitutes for Zn in bulk

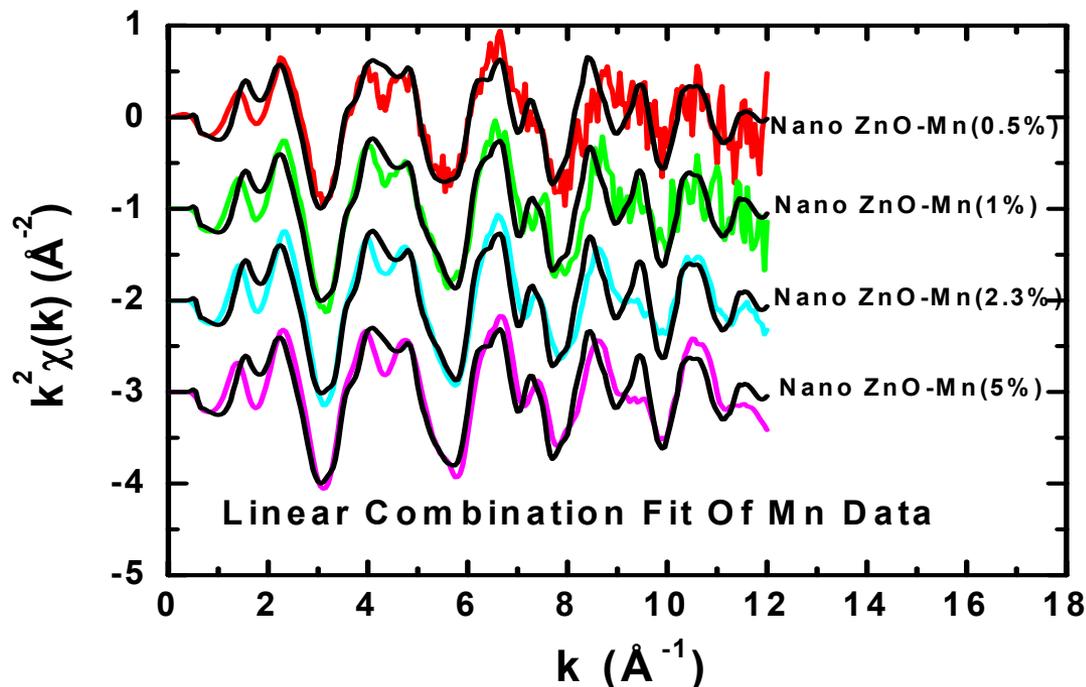


# Fit results for bulk ZnO-Mn

- Model simultaneously optimized to both data sets with common parameters
- The model can describe the features of both data sets simultaneously.
- The  $\sigma^2$  values and distances are the same for the Mn edge and the Zn edge spectra
- The same model was applied to the Zn and Mn spectra from the nano sample, but was not successful in reproducing both spectra.

SAMPLE	a (Å)	c (Å)	$\sigma_{01}^2$ ( $\cdot 10^3 \text{ \AA}^2$ )	$\sigma_{05}^2$ ( $\cdot 10^3 \text{ \AA}^2$ )	$\sigma_{Zn1}^2$ ( $\cdot 10^3 \text{ \AA}^2$ )	$\sigma_{Zn2}^2$ ( $\cdot 10^3 \text{ \AA}^2$ )	$\sigma_{Zn3}^2$ ( $\cdot 10^3 \text{ \AA}^2$ )	$E_0$ (eV)
Bulk: Mn edge ZnO-Mn (1%)	3.19(2)	5.34(2)	6.0(1)	4.0±1	7±1	16±4	10±2	-2.3 ±1.5
Bulk: Zn edge ZnO-Mn (1%)								0.1±1.4

# Nanoparticle XAS



Standards	Sample ZnO-Mn(0.5%)	Sample ZnO-Mn(1.0%)	Sample ZnO-Mn(2.3%)	Sample ZnO-Mn(5.0%)
ZnO-Mn1% BULK	2 ± 2 %	3 ± 2 %	0 %	2 ± 2 %
MnO <sub>2</sub>	14 ± 3 %	29 ± 3 %	19 ± 2 %	19 ± 2 %
Mn <sub>3</sub> O <sub>4</sub>	57 ± 4 %	60 ± 4 %	64 ± 3 %	57 ± 4 %
Mn <sub>2</sub> O <sub>3</sub>	28 ± 6 %	16 ± 5 %	17 ± 4 %	23 ± 5 %

# Summary: DMS nanoparticles

- XANES results suggest that the valence state of the nanoparticle samples is very different than that of the bulk sample
- EXAFS results show that Mn atoms replace Zn atoms in the bulk ZnO-Mn.
- Nanoparticles (4.7 nm) of ZnO-Mn with Mn doping varying from 0.5% to 5%, appear to be in core-shell structure with Mn located on the surface
- The shell consists of various oxides of Mn.
- Preliminary analysis on CdS-Mn indicates same core-shell structure and radiation damage similar to ZnO-Mn