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

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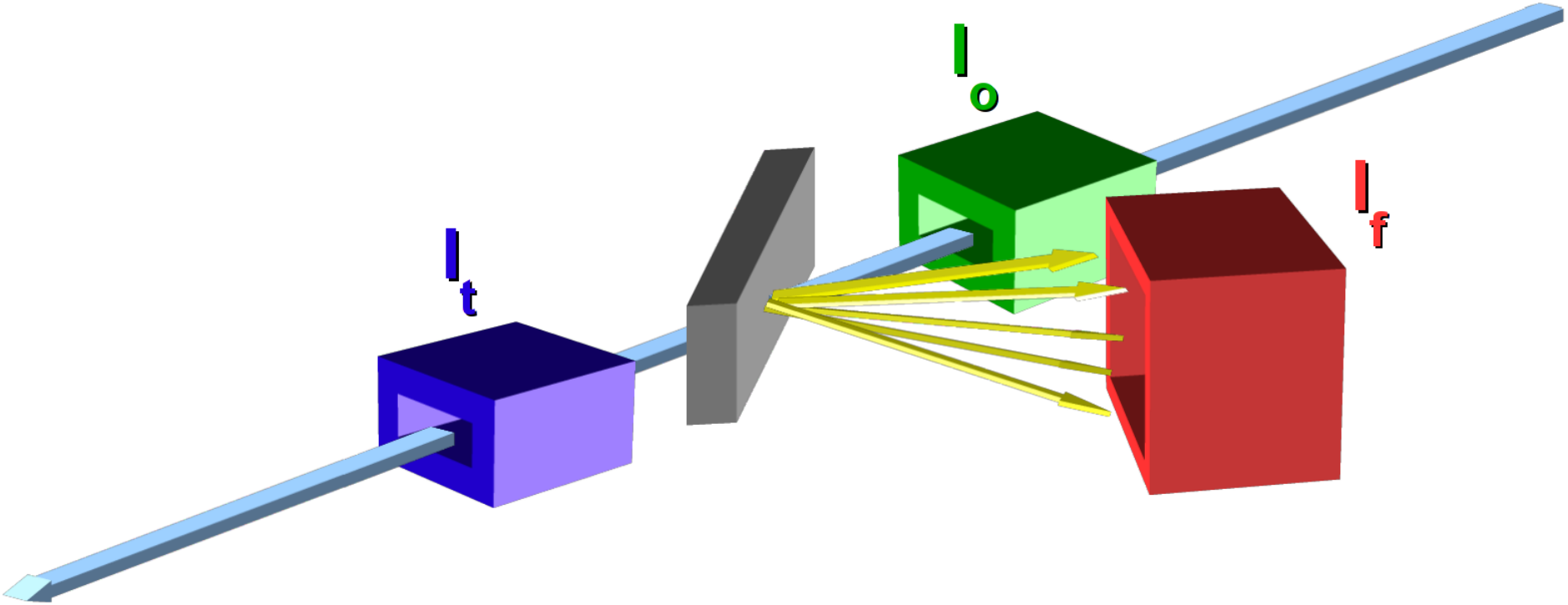
Outline

- 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

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity

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

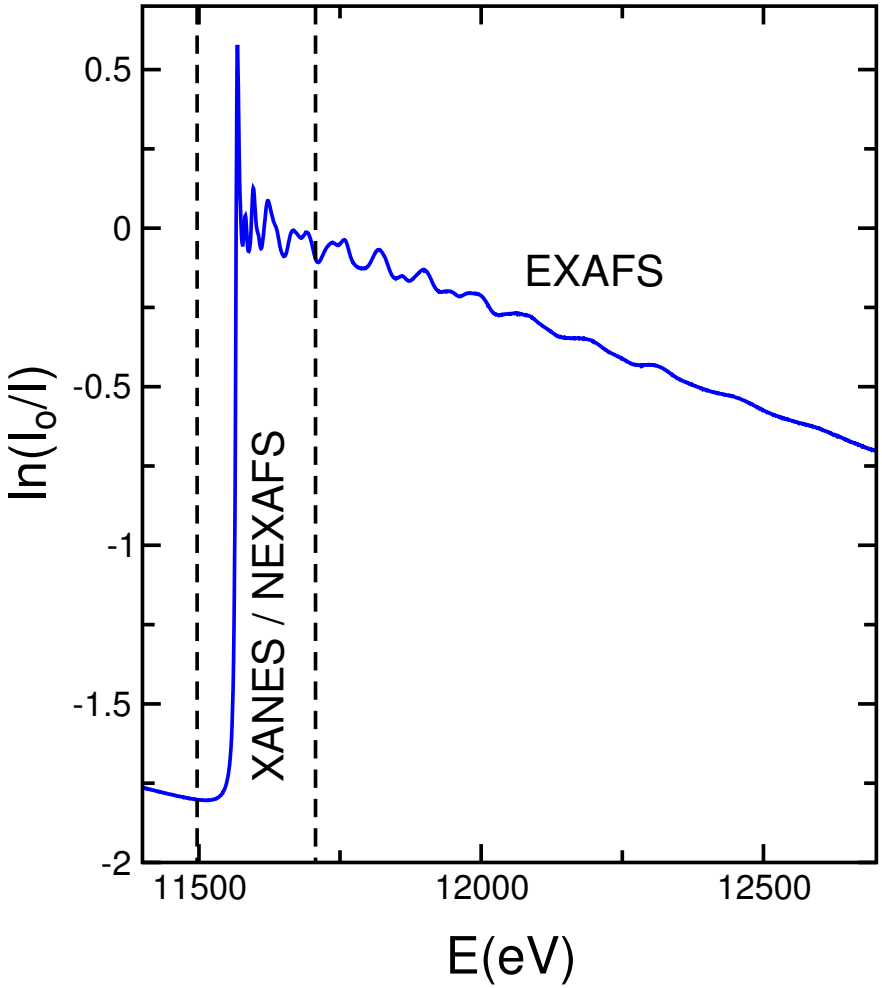


$$I_t = I_o e^{-\mu(E)x}$$

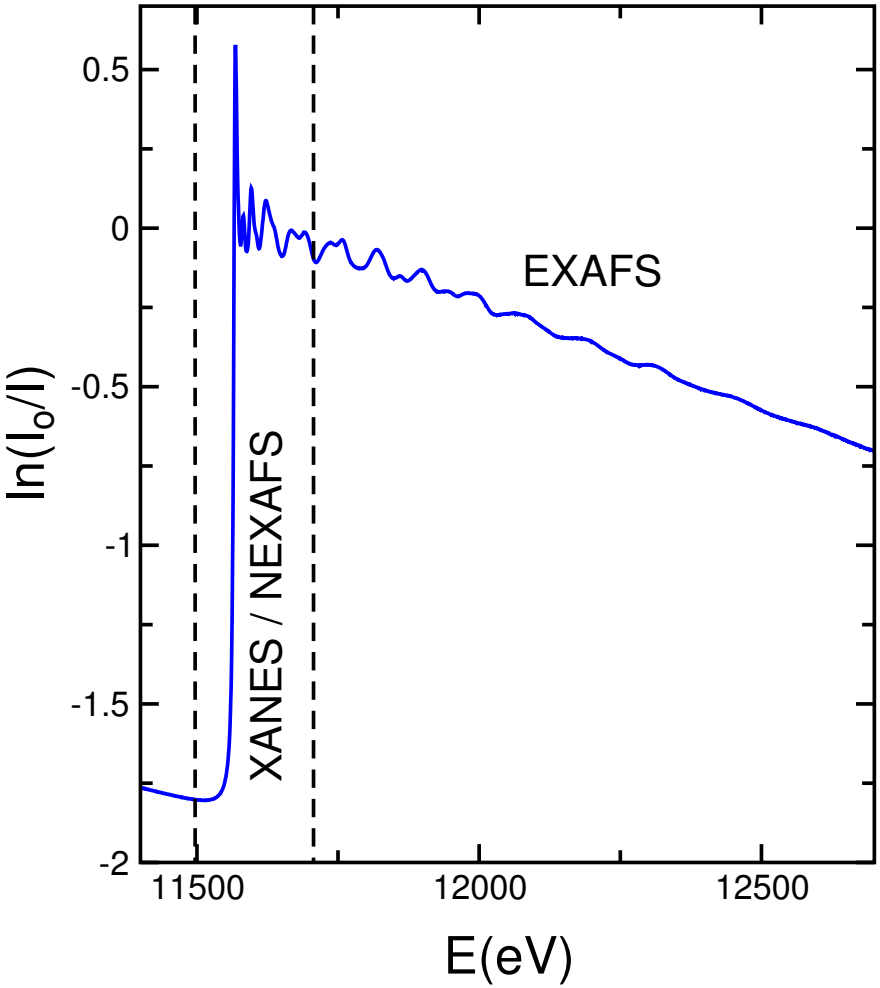
$$\mu(E)x = \ln\left(\frac{I_o}{I_t}\right)$$

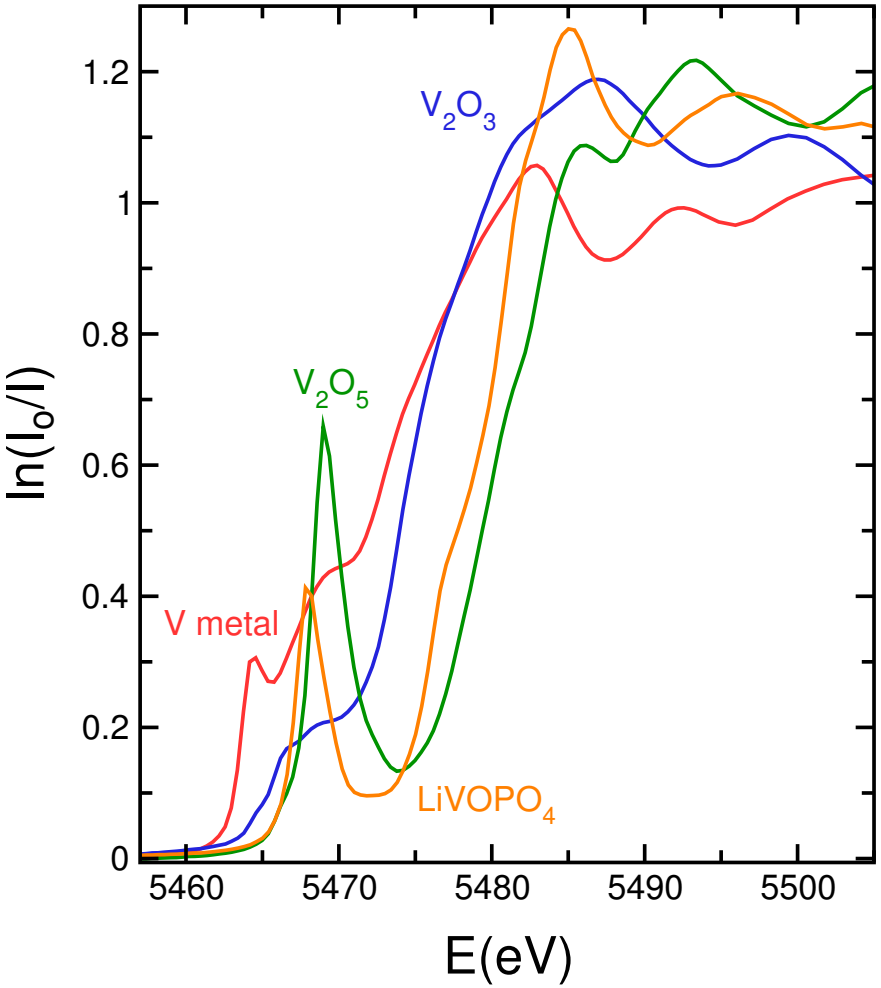
$$\mu(E) \propto \frac{I_f}{I_o}$$

XAS data

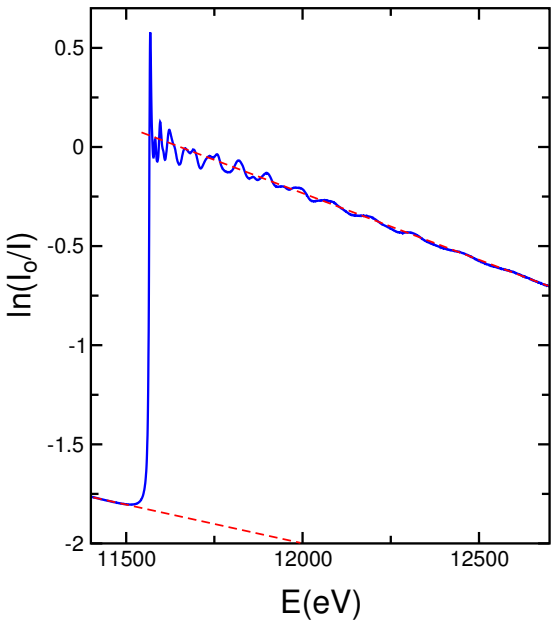


XAS data

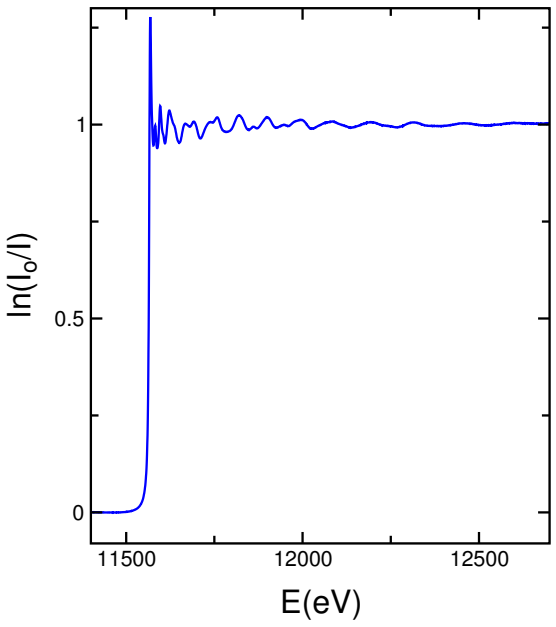

0.5
0
-0.5
-1
-1.5
-2
11500
12000
12500
ln(I_o/I)
E(eV)
XANES / NEXAFS
EXAFS


1.2
1
0.8
0.6
0.4
0.2
0
5460
5470
5480
5490
5500
ln(I_o/I)
E(eV)
V2O3
V2O5
V metal
LiVOPO4

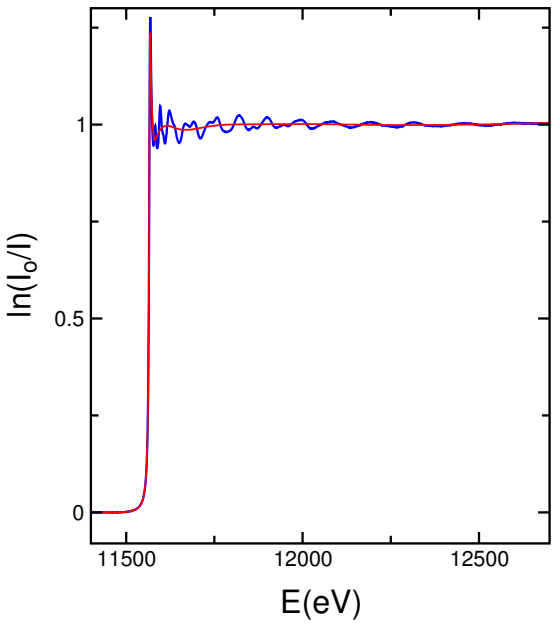
EXAFS analysis



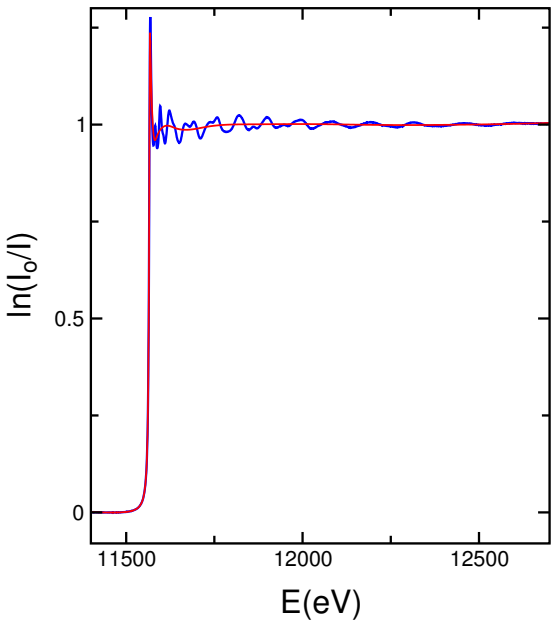
EXAFS analysis



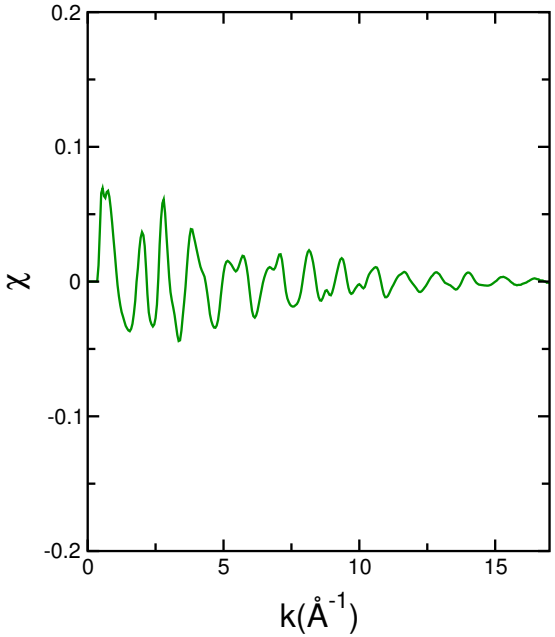
EXAFS analysis



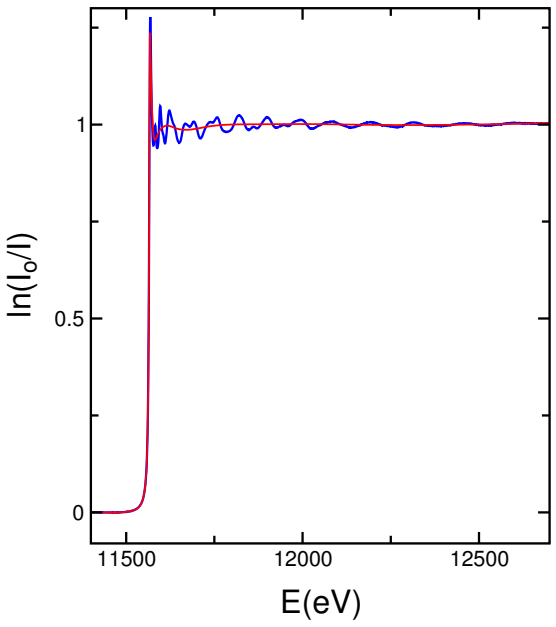
EXAFS analysis



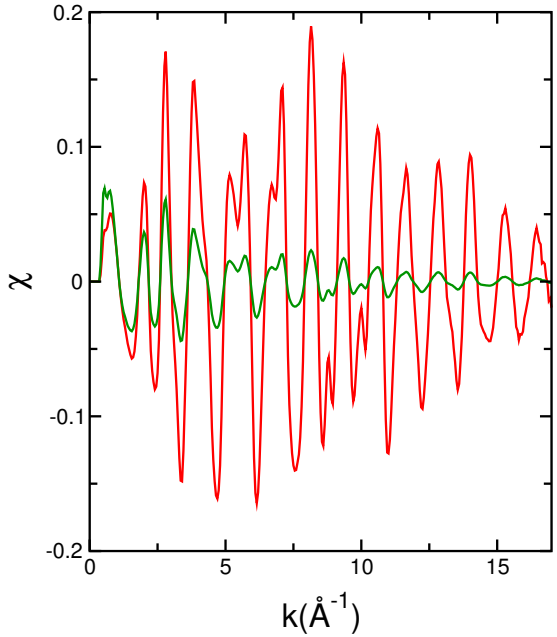
remove background



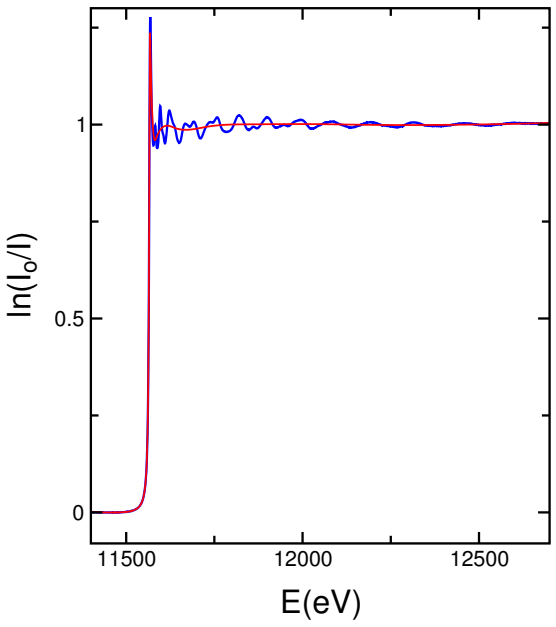
EXAFS analysis



remove background and apply k-weighting



EXAFS analysis



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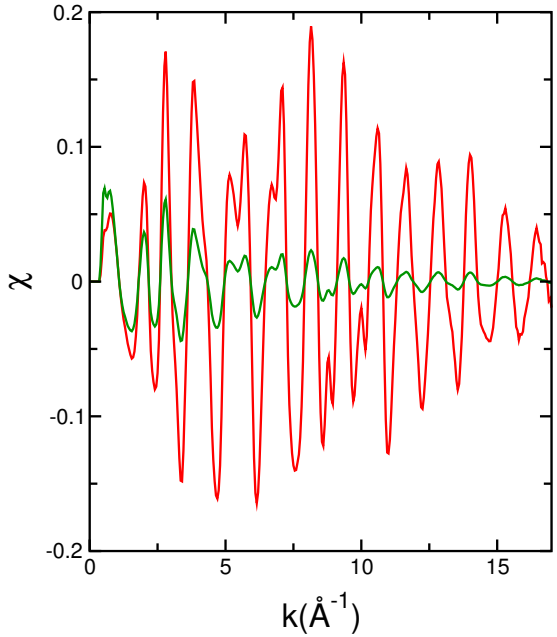
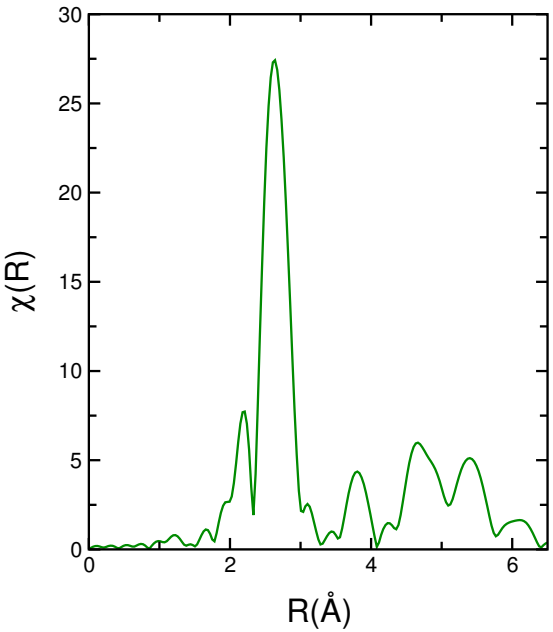
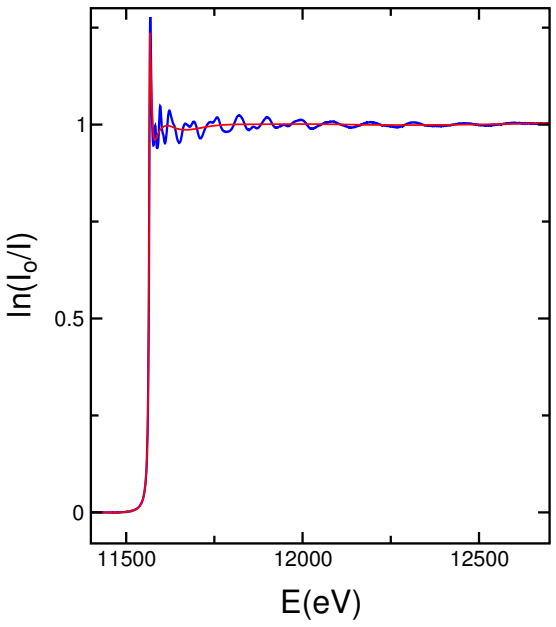


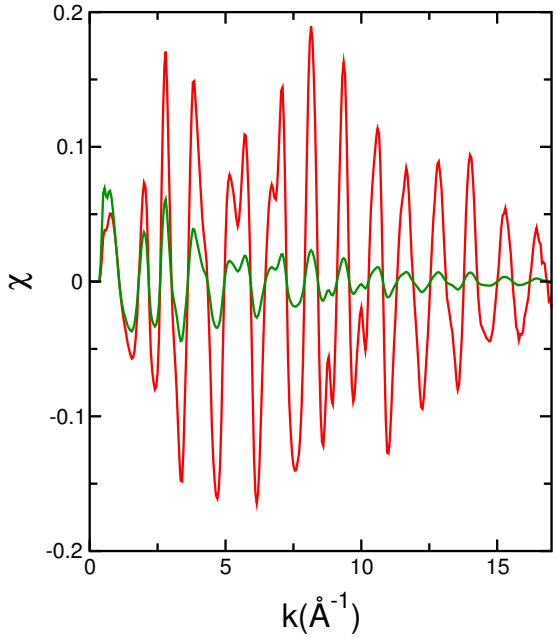
take Fourier Transform



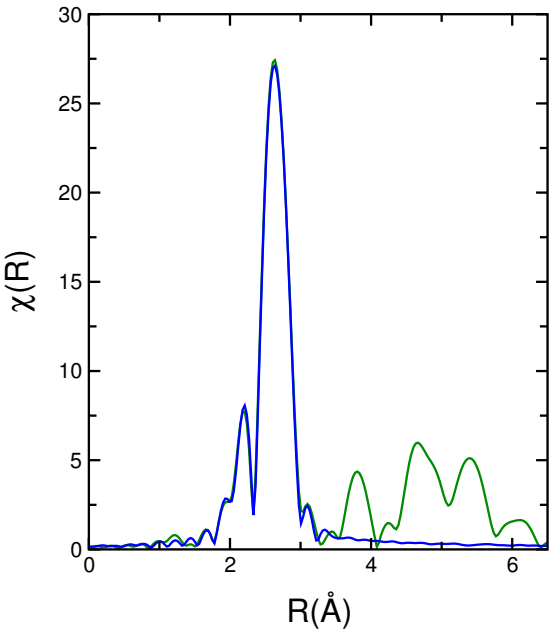
EXAFS analysis



remove background and apply k-weighting

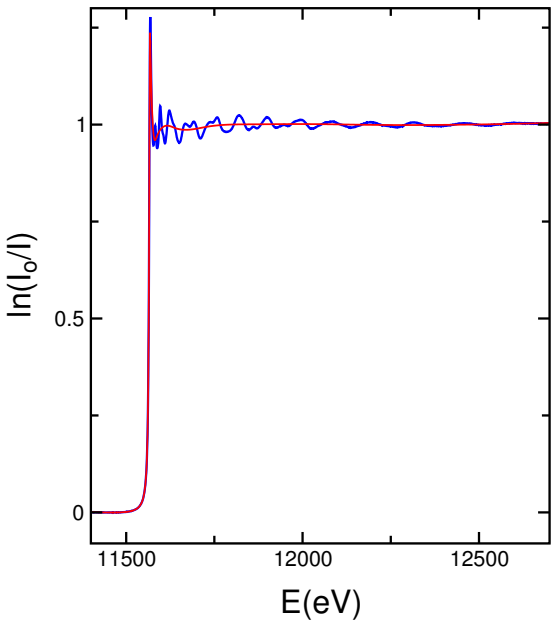


take Fourier Transform and fit with a structural model

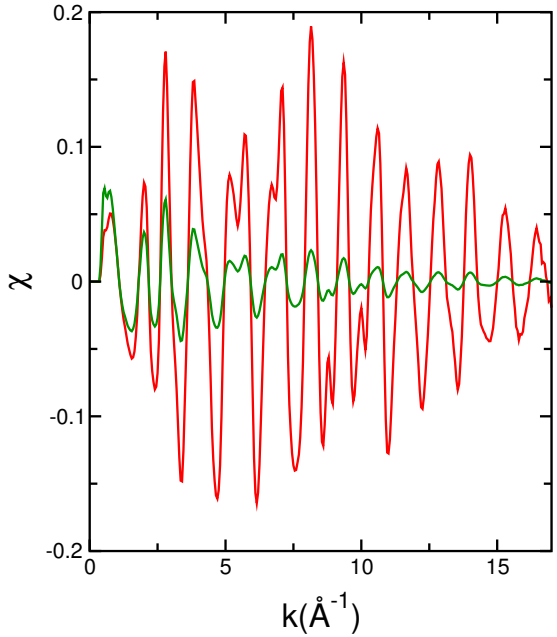


extract structural parameters for first shell

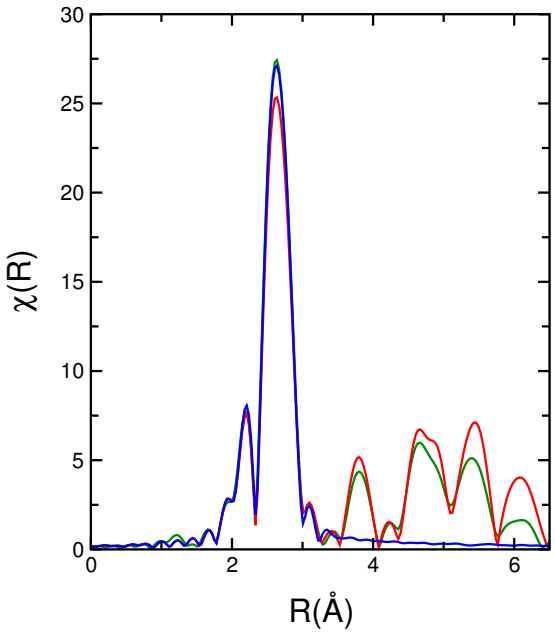
EXAFS analysis



remove background and apply k-weighting

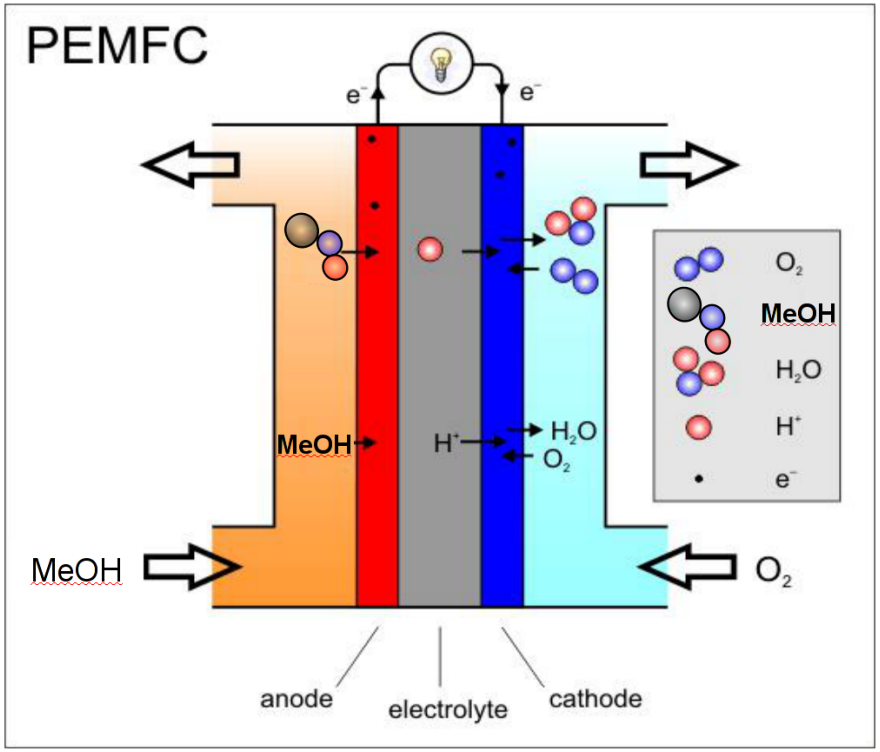


take Fourier Transform and fit with a structural model



extract structural parameters for first shell or more distant atoms as appropriate

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

$$CH_3OH + H_2O \longrightarrow 6\,H + CO_2 + 6\,e^-$$

Cathode: 1.23 V s. SHE

$$\frac{3}{2}\,O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O$$

Pt surface poisoned by CO

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

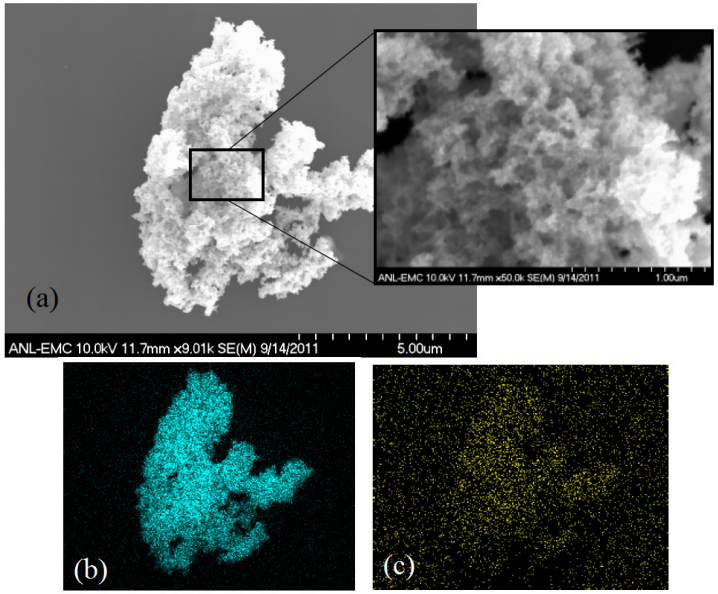
$$Pt{-}(CO)_{ads} + Ru{-}OH \longrightarrow Pt + RuCO_2 + H^+ + 2\,e^-$$

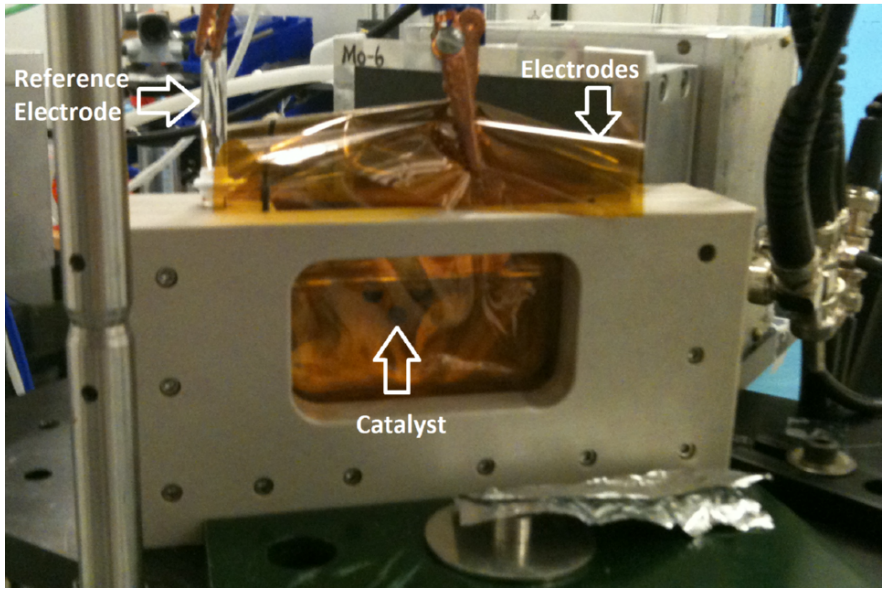
Role of Ru in CO oxidation?

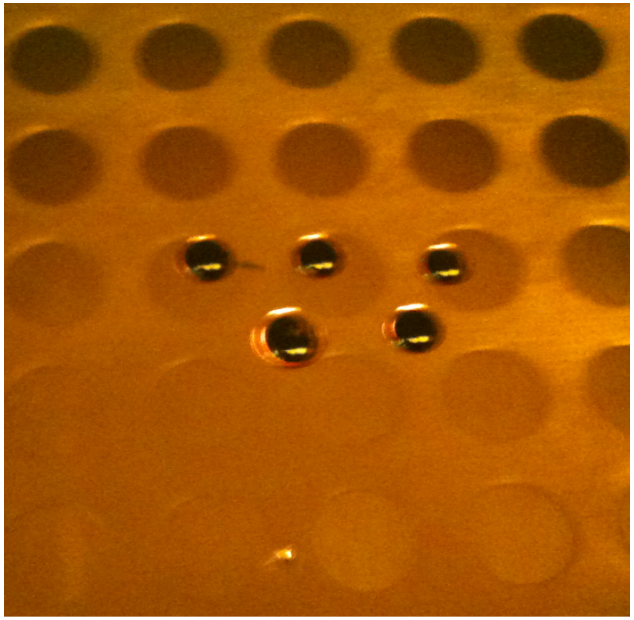
- PtRu bifunctional catalyst improves performance
- In commercial PtRu catalysts there is always a lot of inactive Ru-oxide (?)
- Ru signal dominated by metallic Ru environment
- How does Ru behave in the presence of reactants adsorbed on platinum surface?

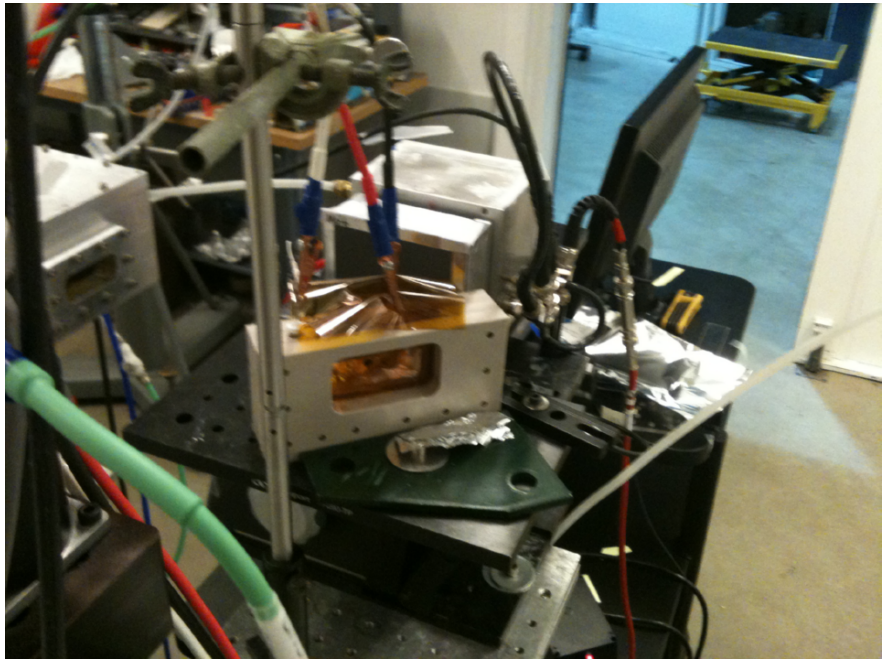
Core-shell nanoparticles can resolve these questions

Ru-decorated Pt nanoparticles

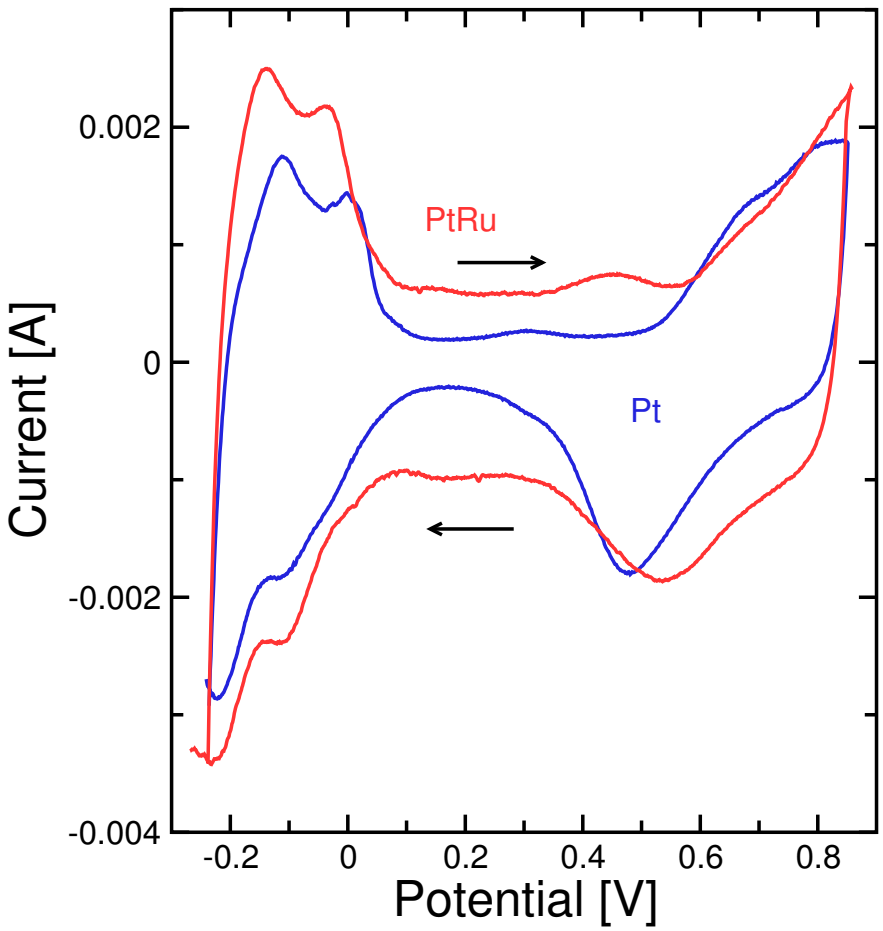








Electrochemical performance



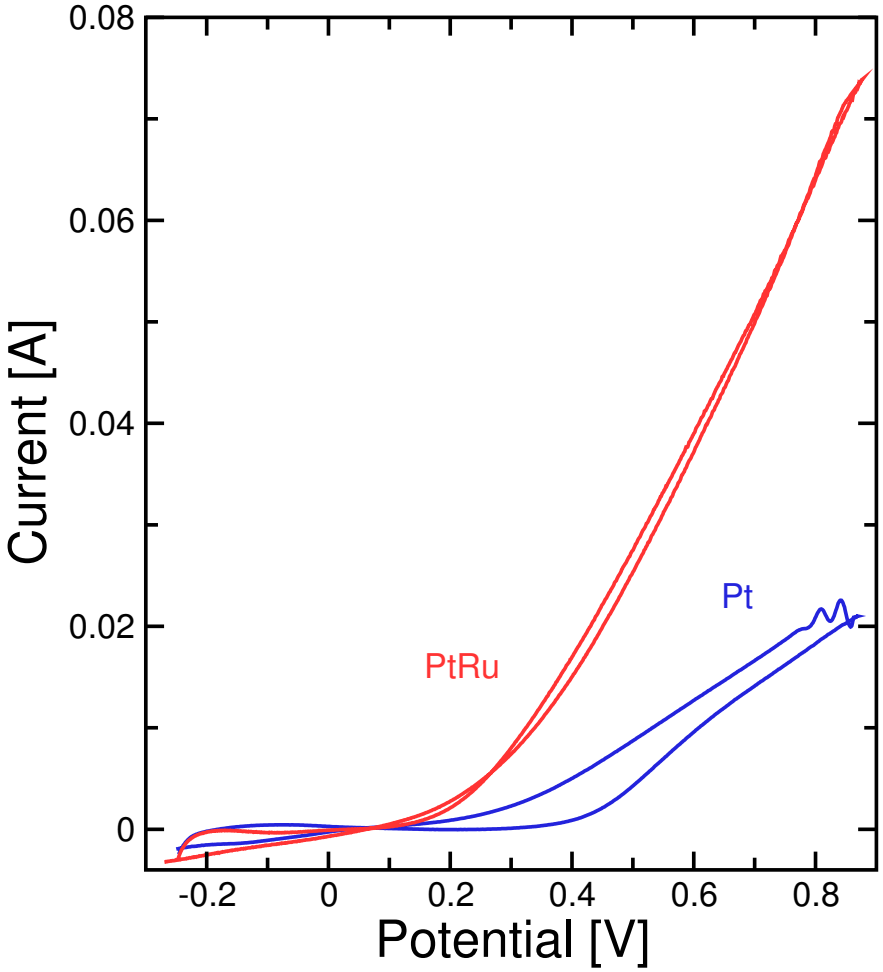
Without Methanol

Low V peaks are H^+ stripping

Dip at $\sim$0.5 V is oxygen stripping

Ru shifts potential on all peaks

Electrochemical performance



Without Methanol

Low V peaks are H^+ stripping

Dip at $\sim$0.5 V is oxygen stripping

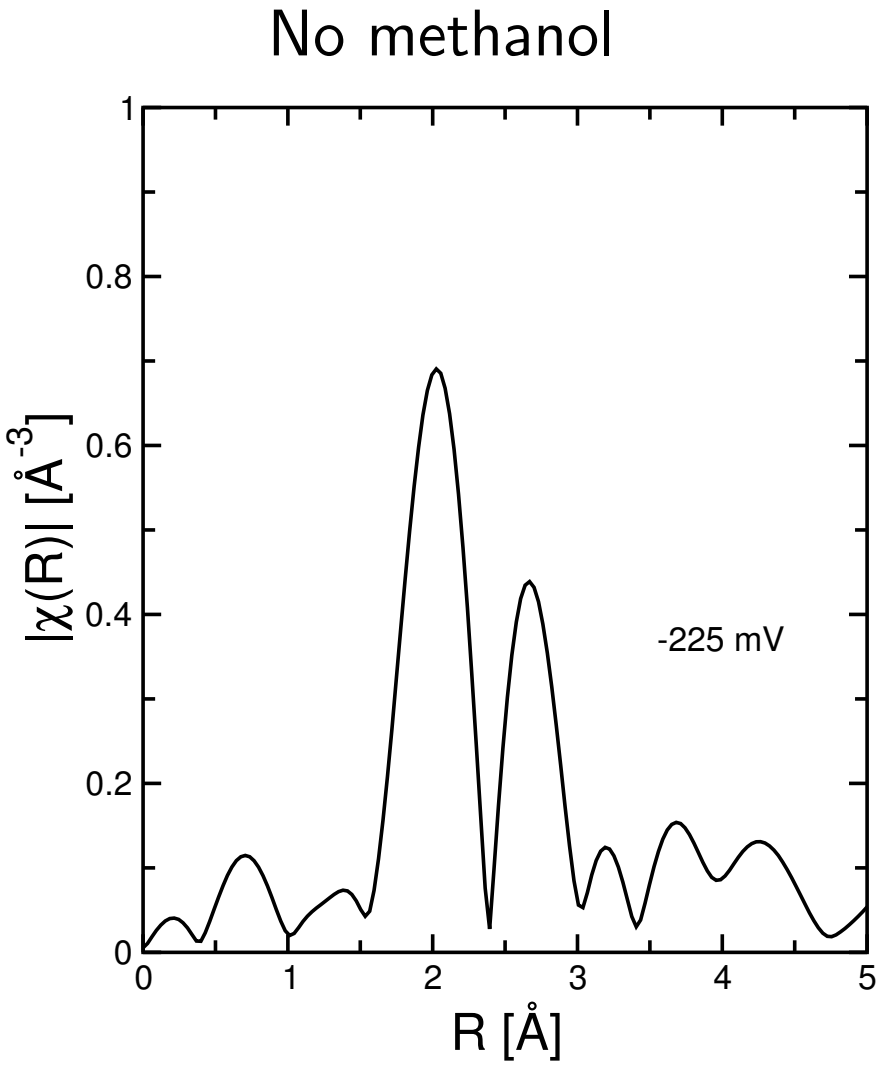
Ru shifts potential on all peaks

With Methanol

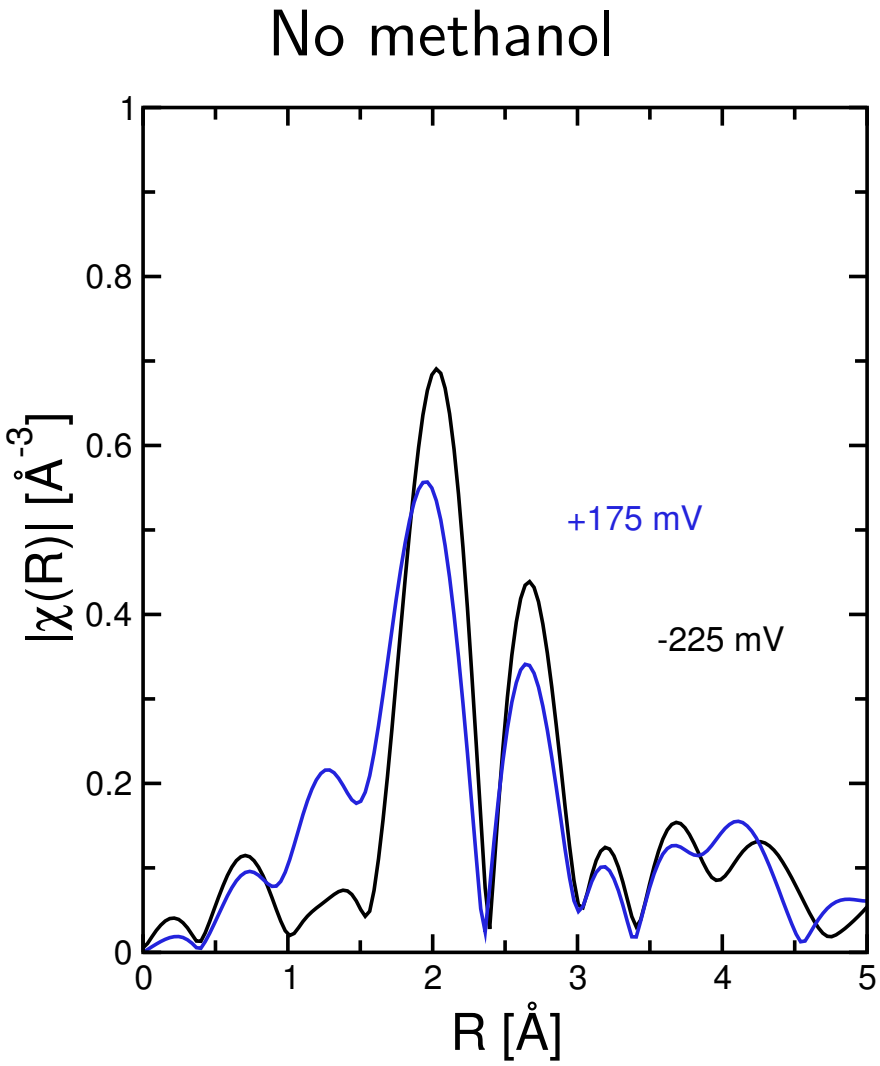
Continual current growth is due to methanol oxidation

Ru improves current by removing the CO which blocks active sites

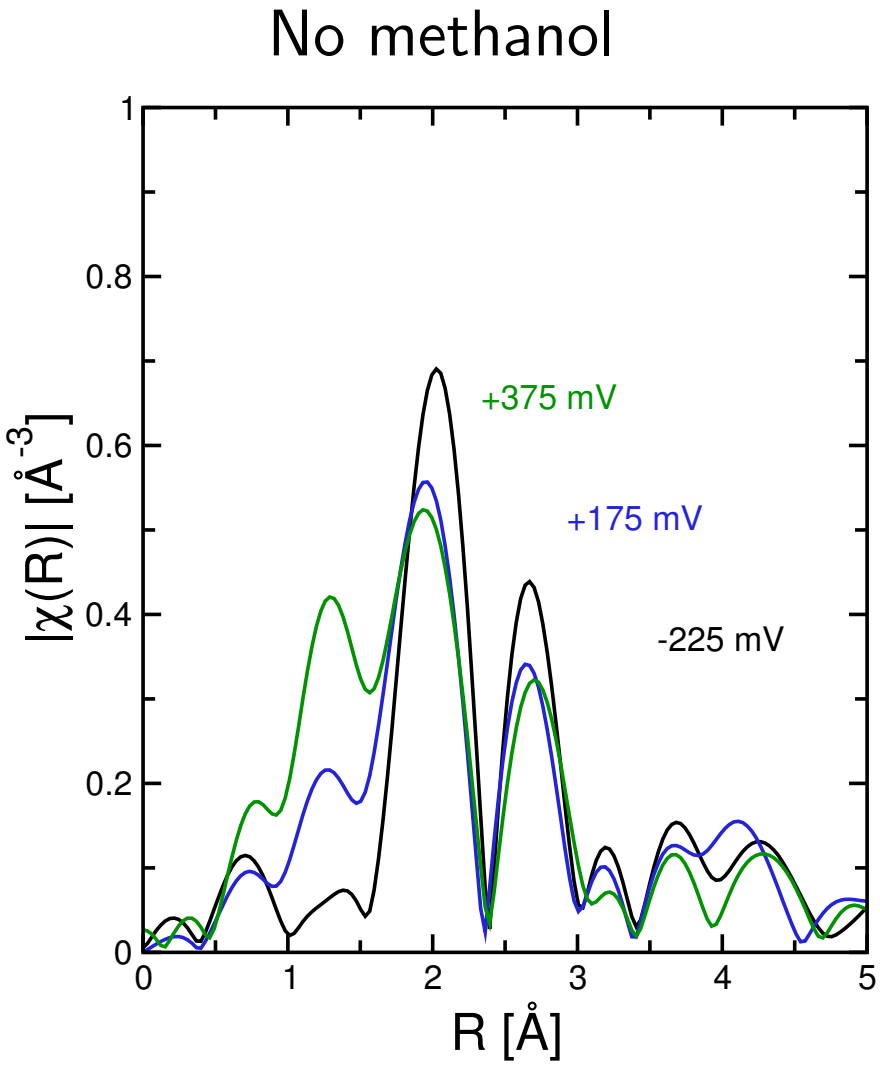
Ru EXAFS



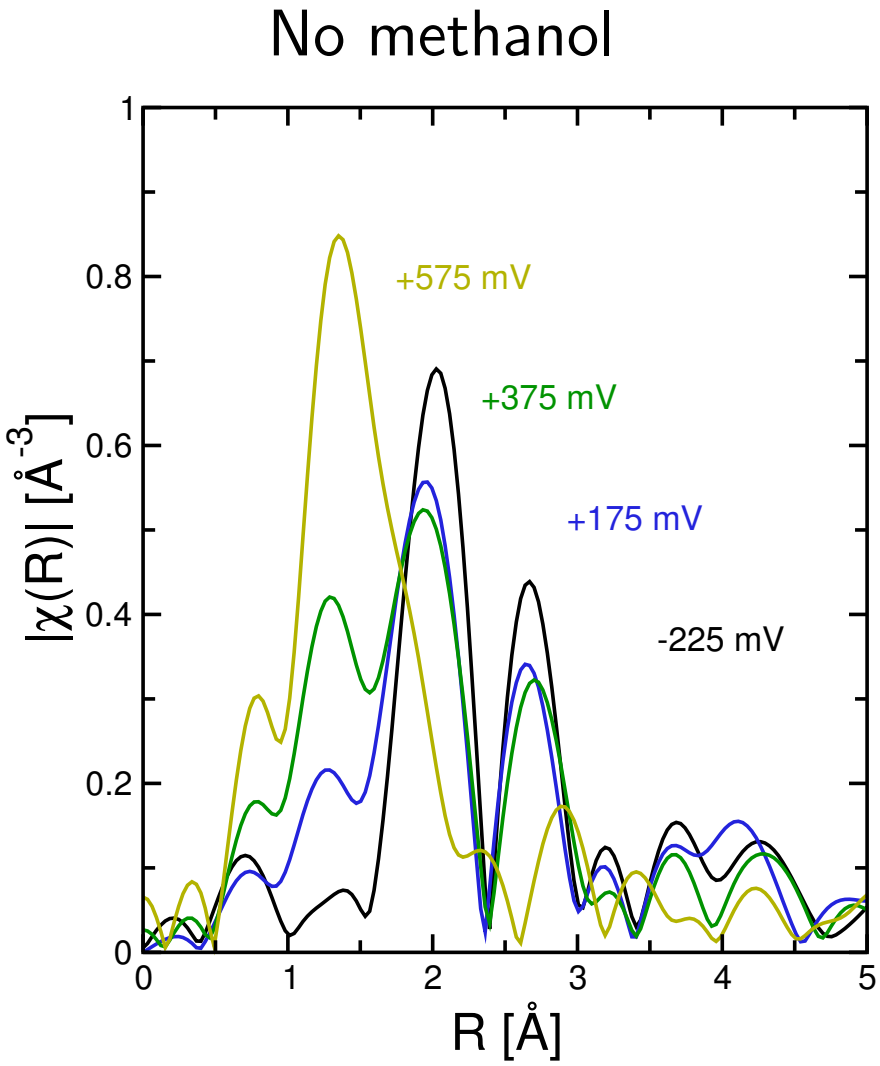
Ru EXAFS



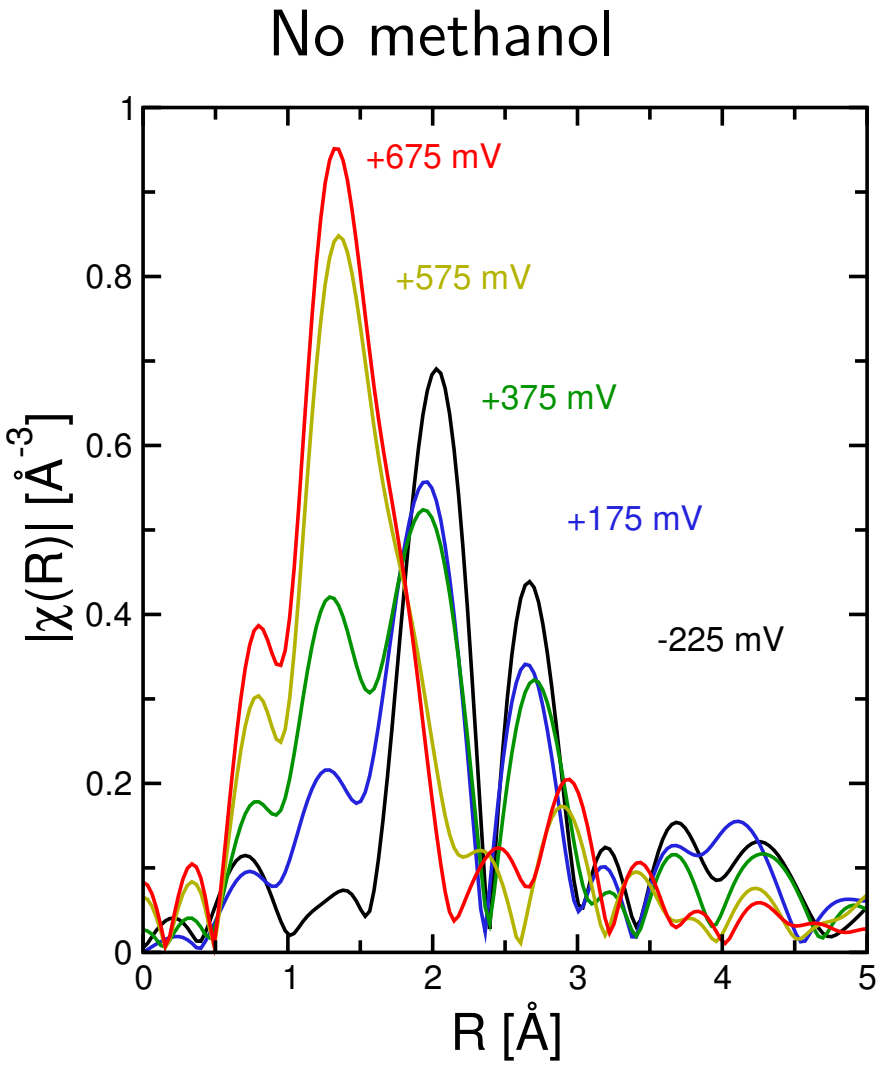
Ru EXAFS



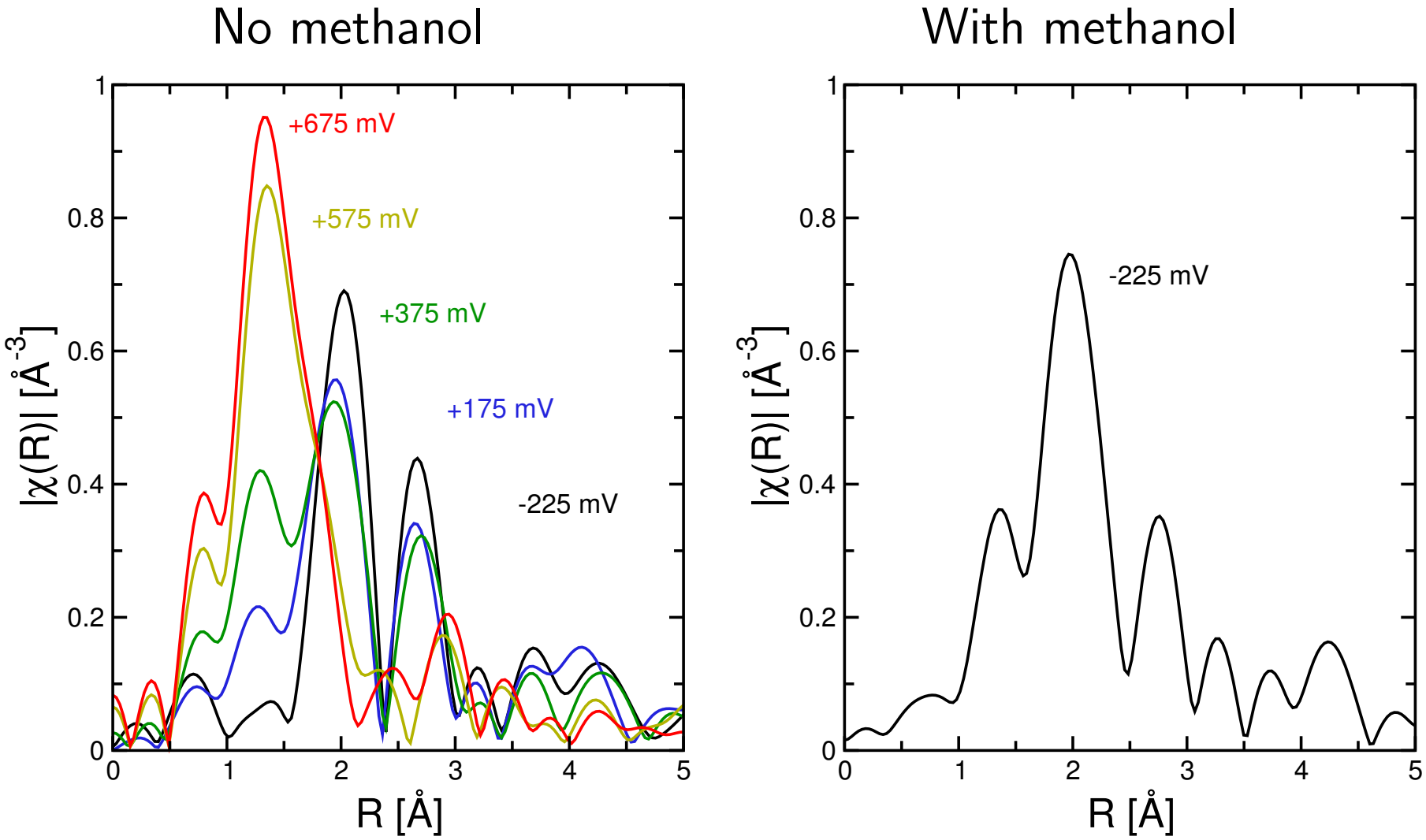
Ru EXAFS


No methanol
+575 mV
+375 mV
+175 mV
-225 mV
|χ(R)| [Å-3]
R [Å]
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5

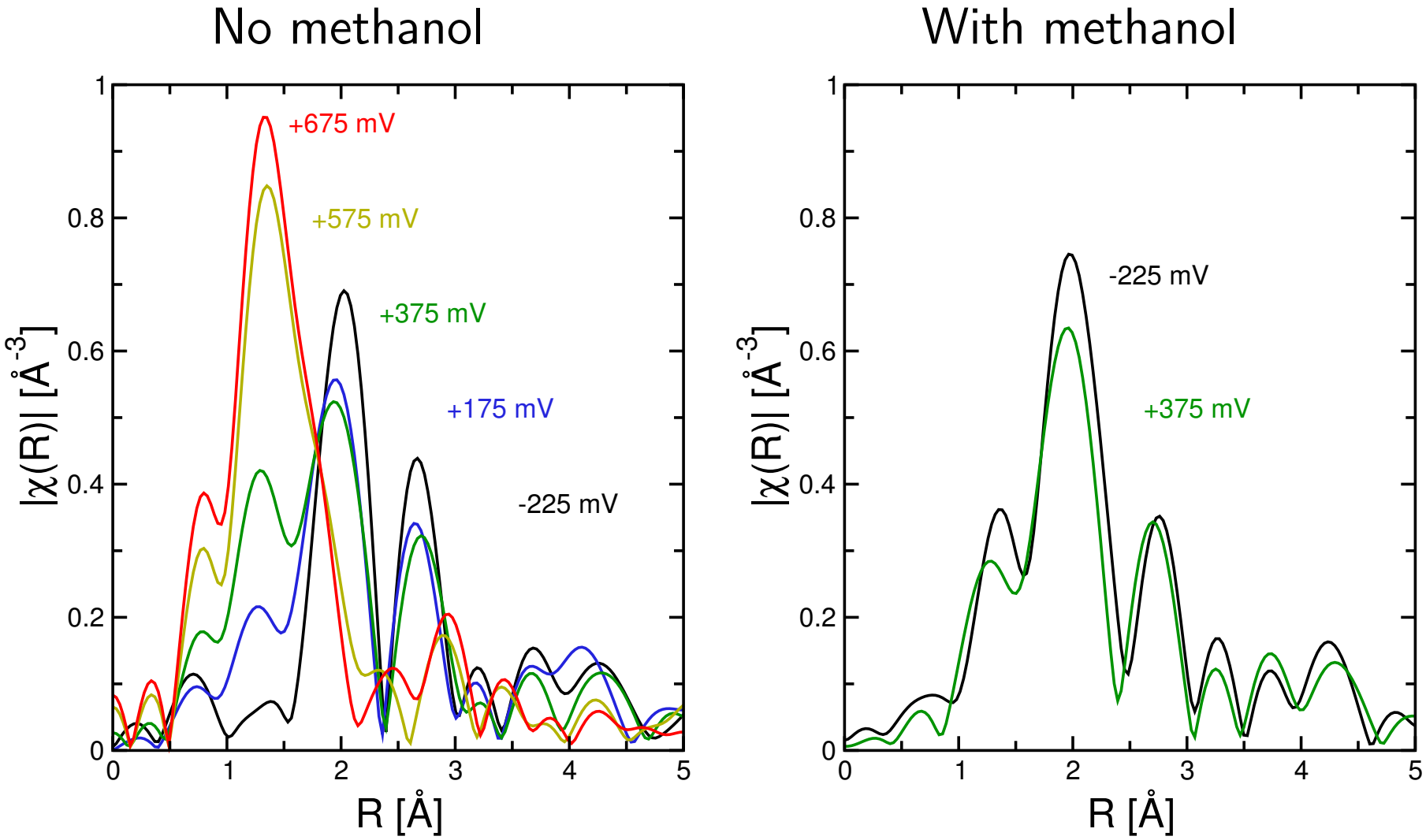
Ru EXAFS


No methanol
+675 mV
+575 mV
+375 mV
+175 mV
-225 mV
|χ(R)| [Å^-3]
R [Å]
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5

Ru EXAFS


No methanol
+675 mV
+575 mV
+375 mV
+175 mV
-225 mV
|χ(R)| [Å^-3]
R [Å]
With methanol
-225 mV
|χ(R)| [Å^-3]
R [Å]

Ru EXAFS


No methanol
+675 mV
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-225 mV
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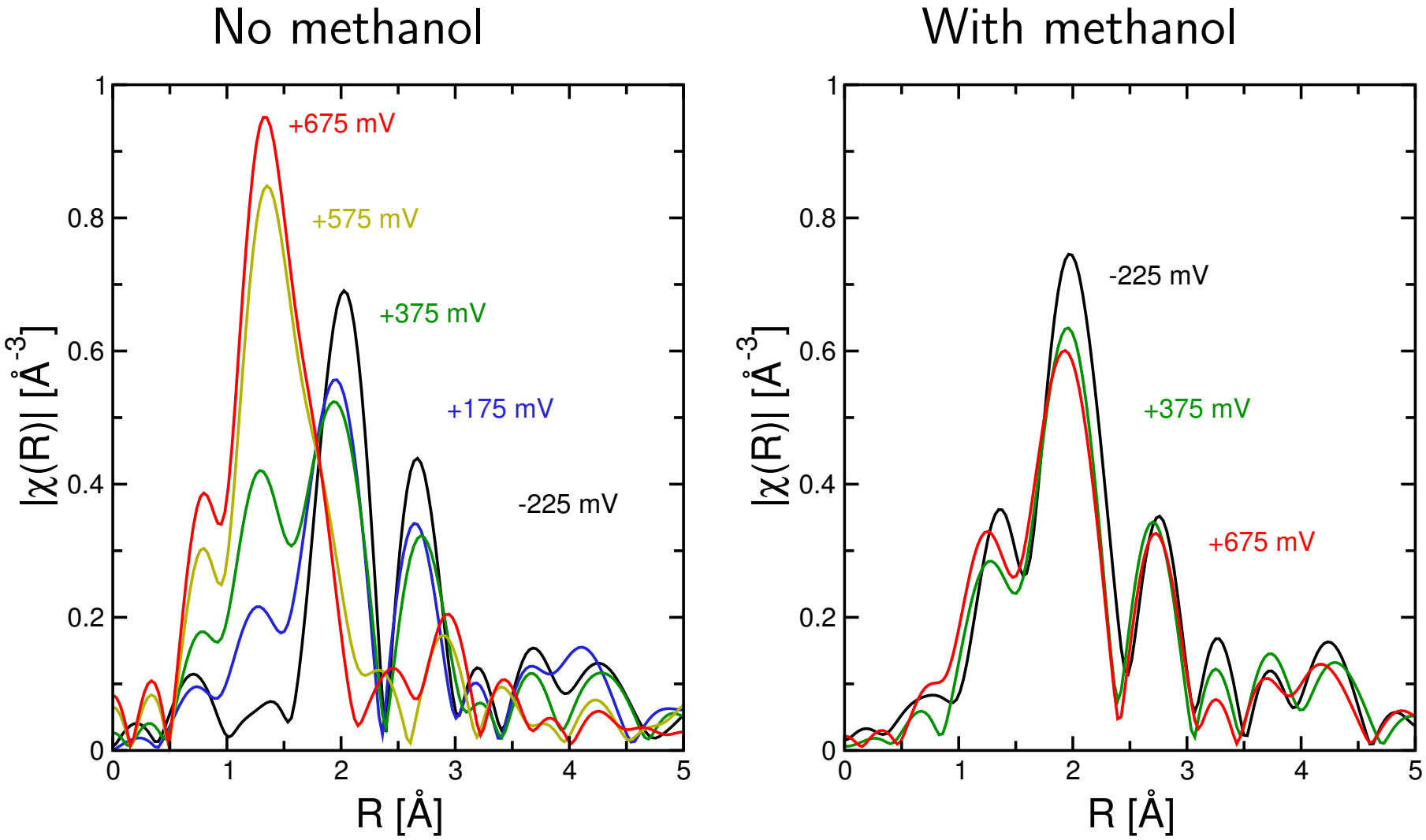
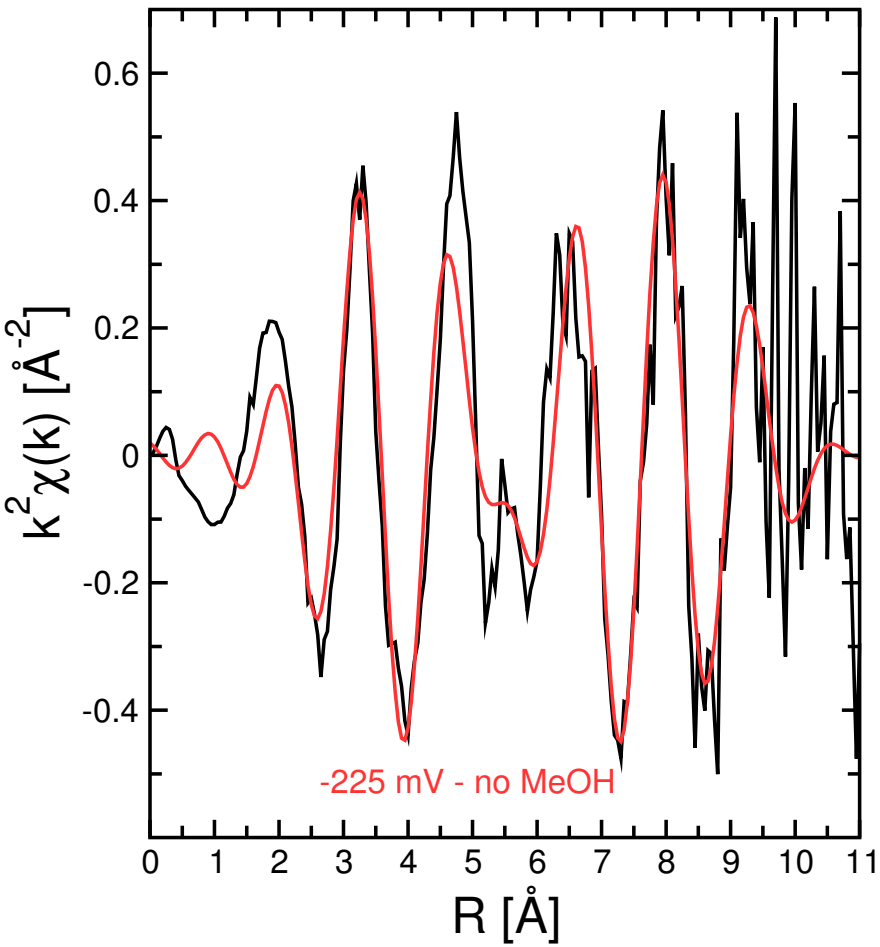
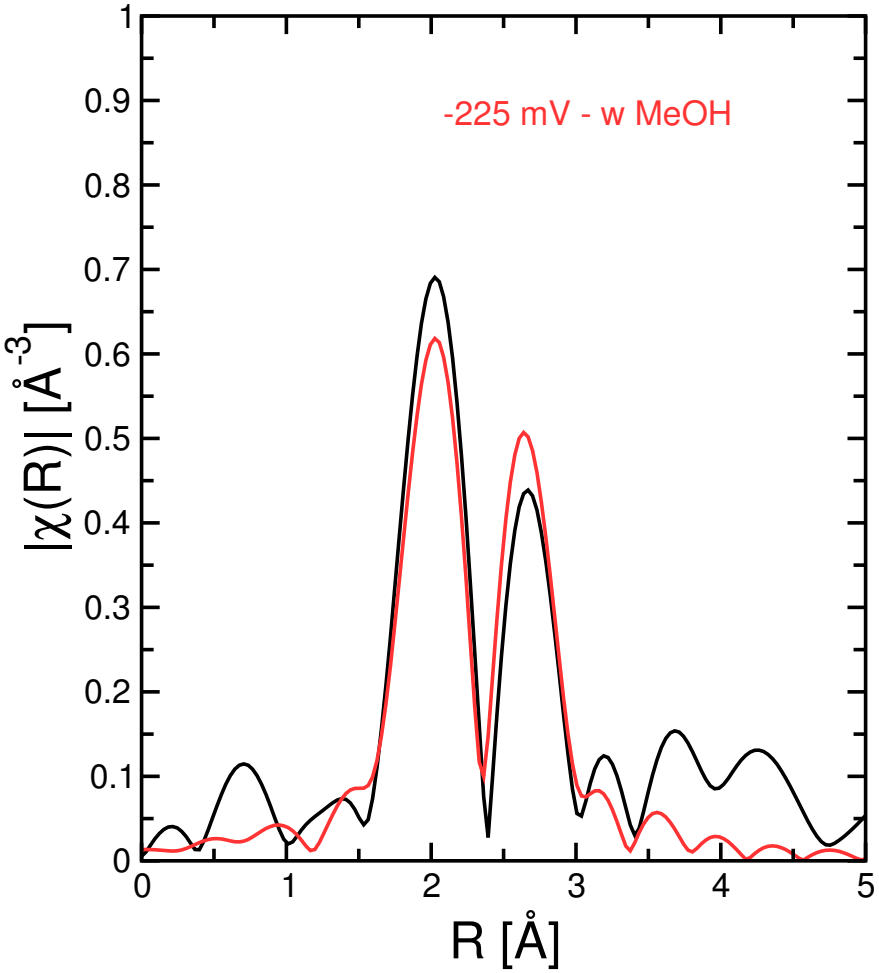
Ru EXAFS

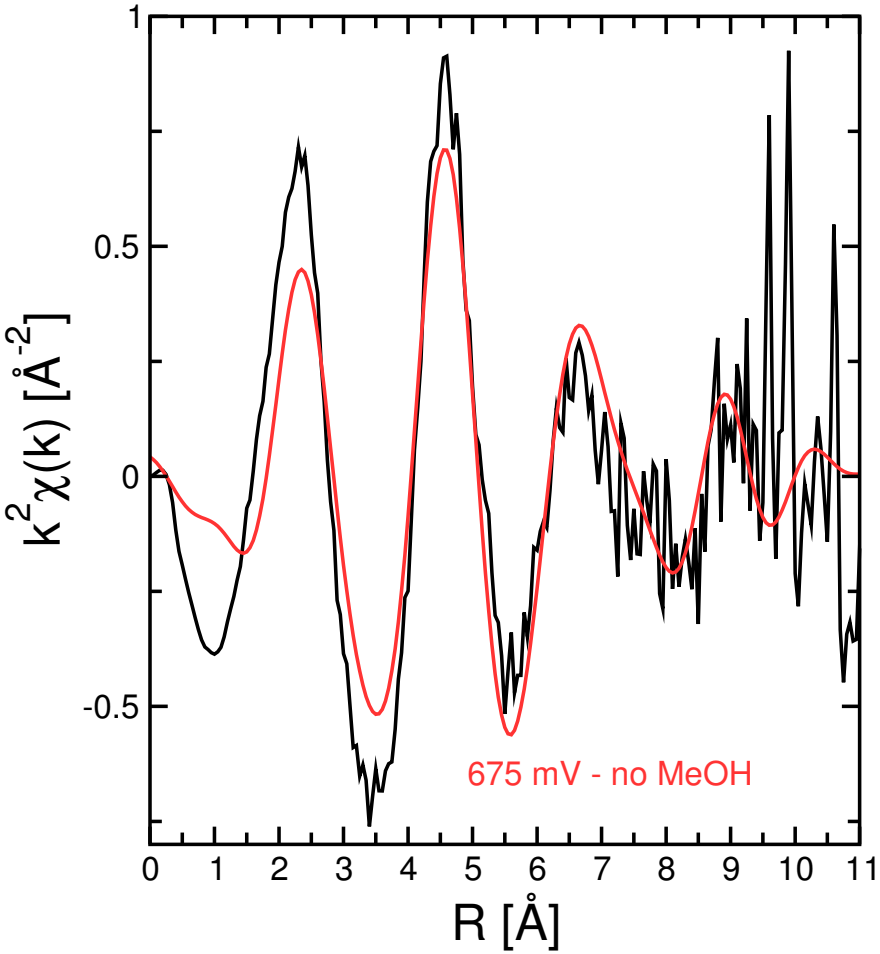

No methanol
+675 mV
+575 mV
+375 mV
+175 mV
-225 mV
|χ(R)| [Å^-3]
R [Å]
With methanol
-225 mV
+375 mV
+675 mV
|χ(R)| [Å^-3]
R [Å]

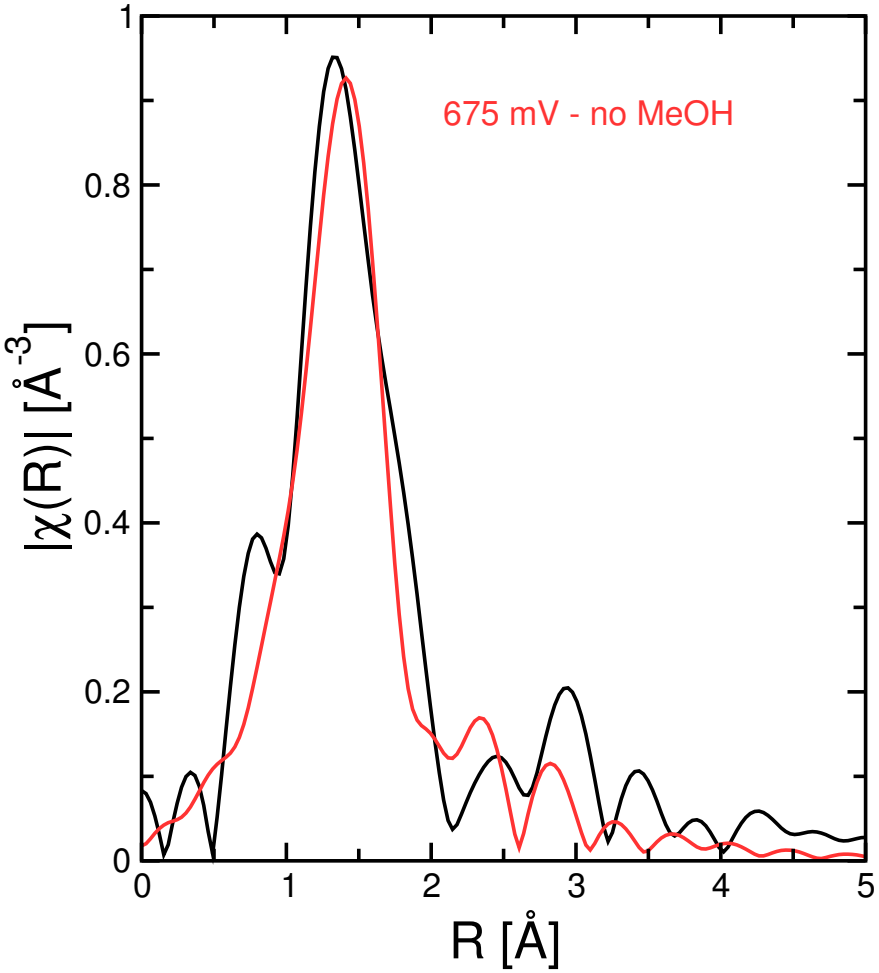
Fit example: -225 mV without methanol



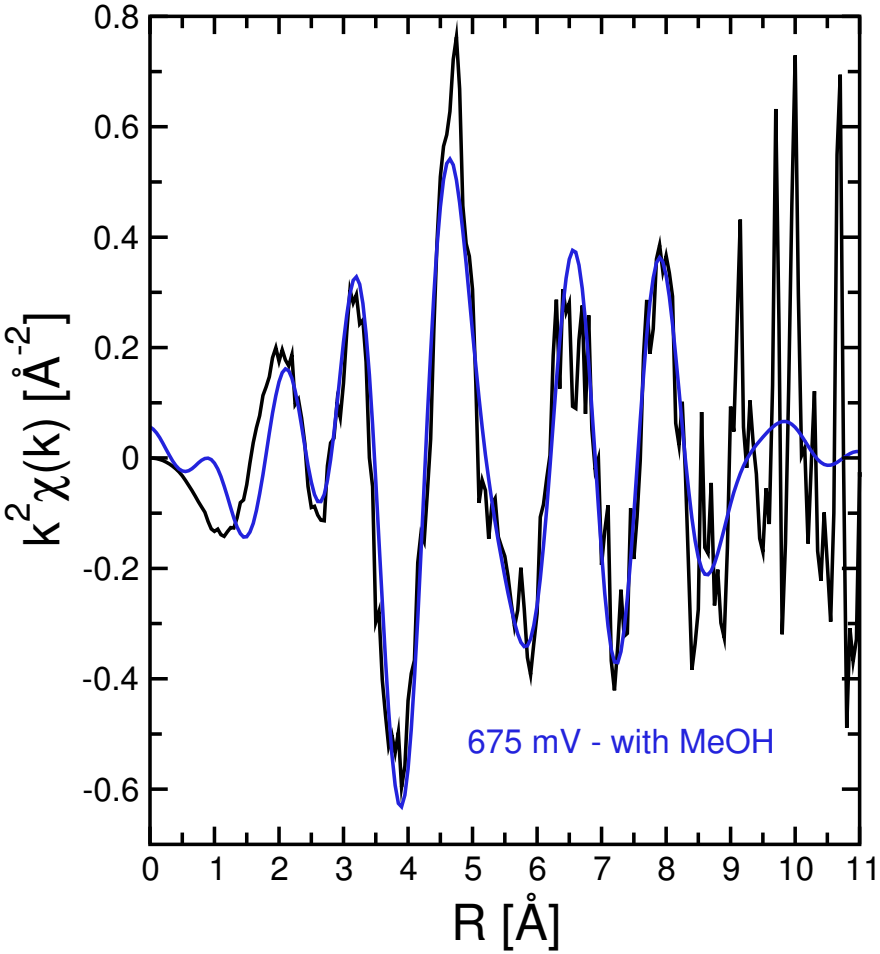


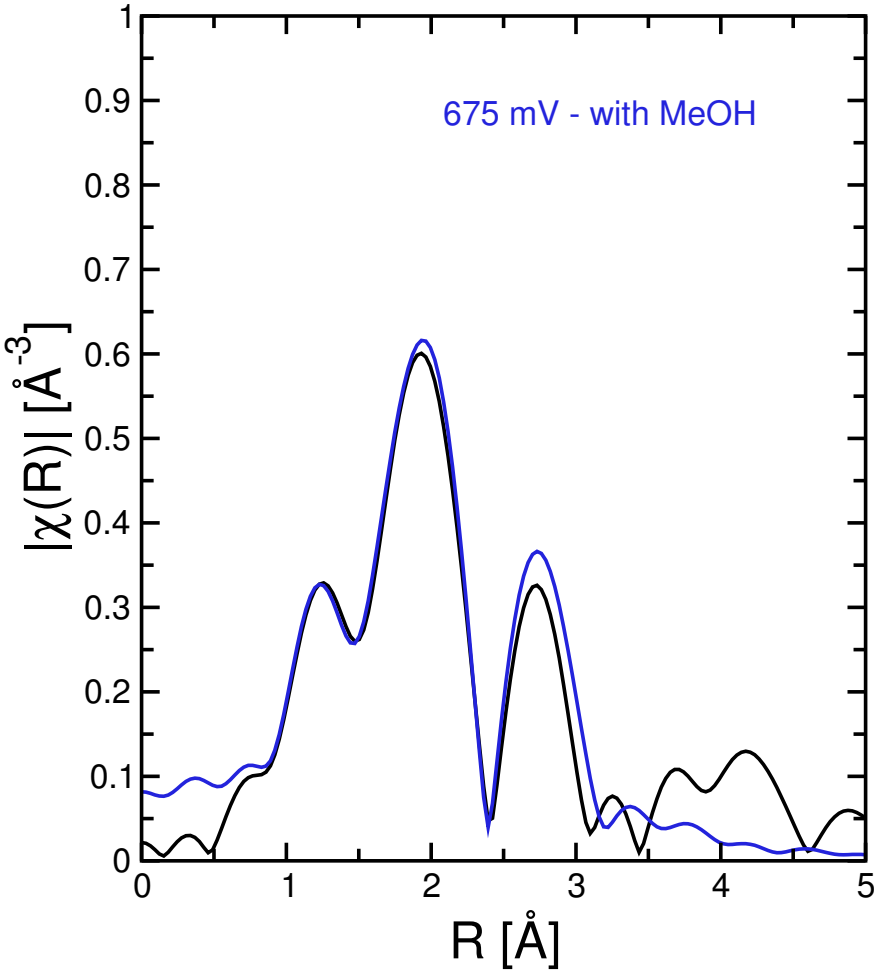
Fit example: 675 mV without methanol



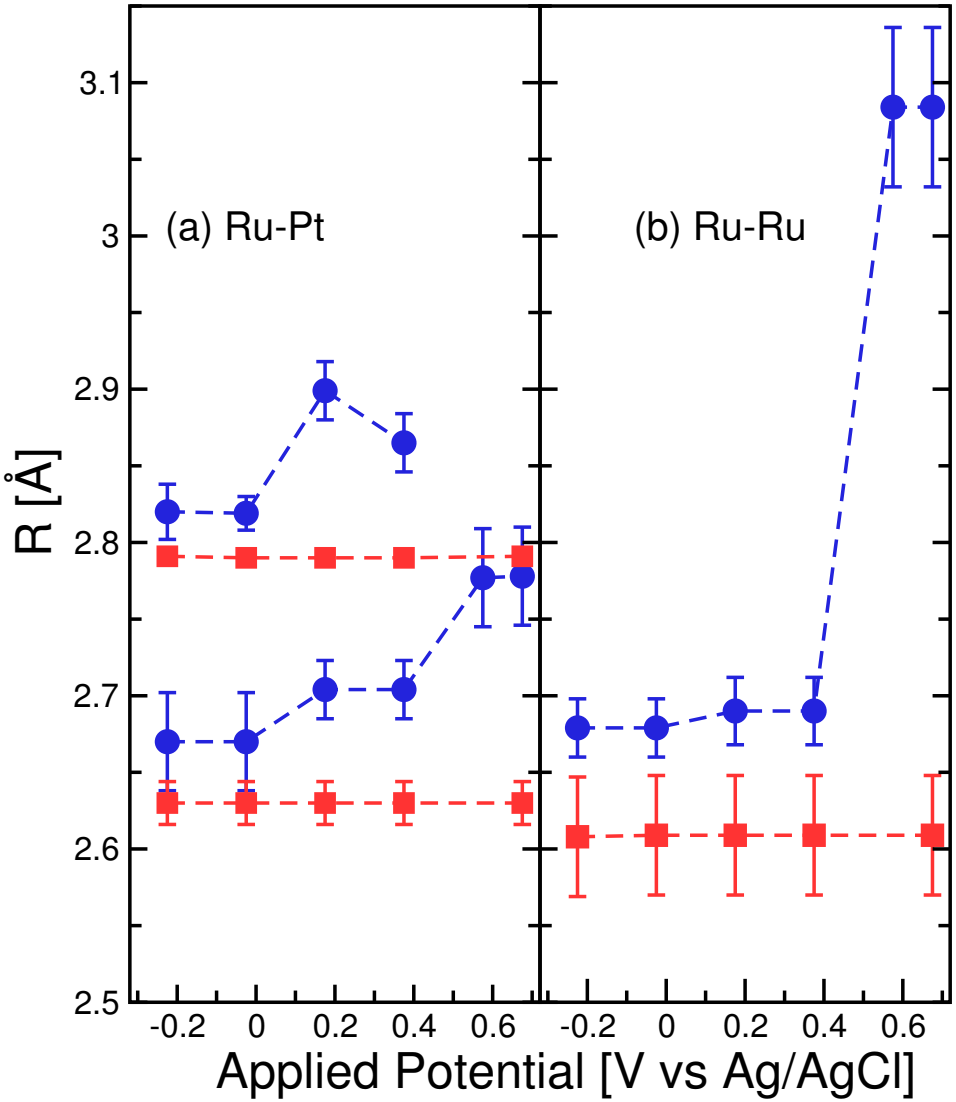


Fit example: 675 mV with methanol





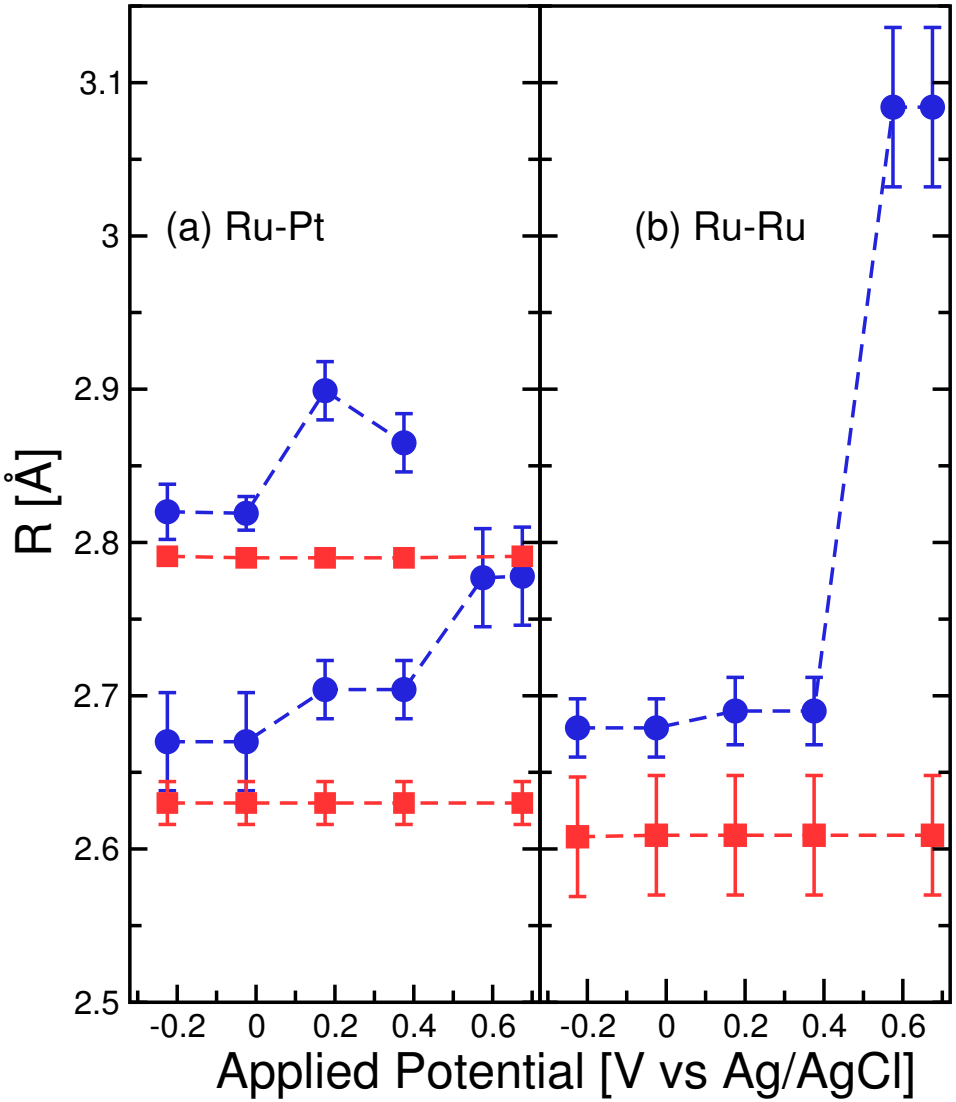
Ru-M paths



Without methanol

With methanol

Ru-M paths

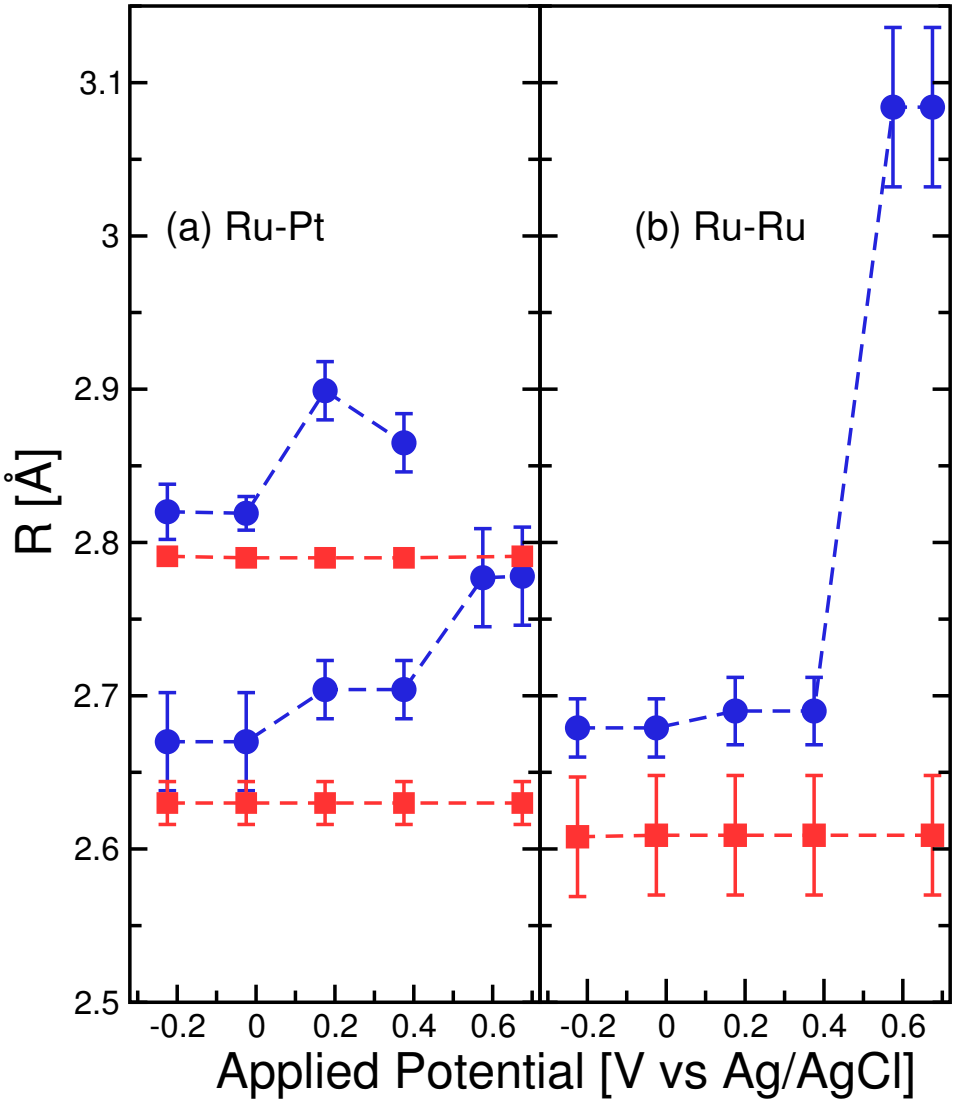


Without methanol

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

With methanol

Ru-M paths



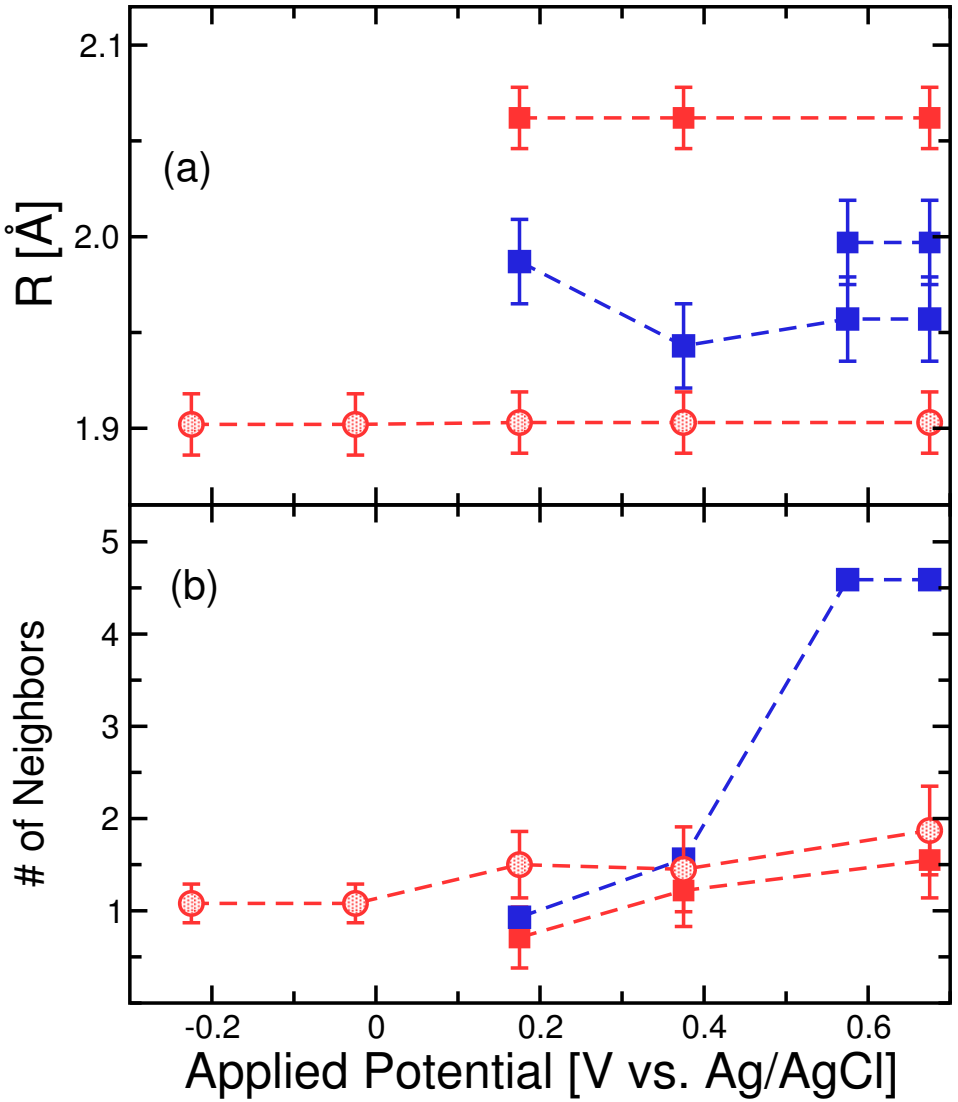
Without methanol

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

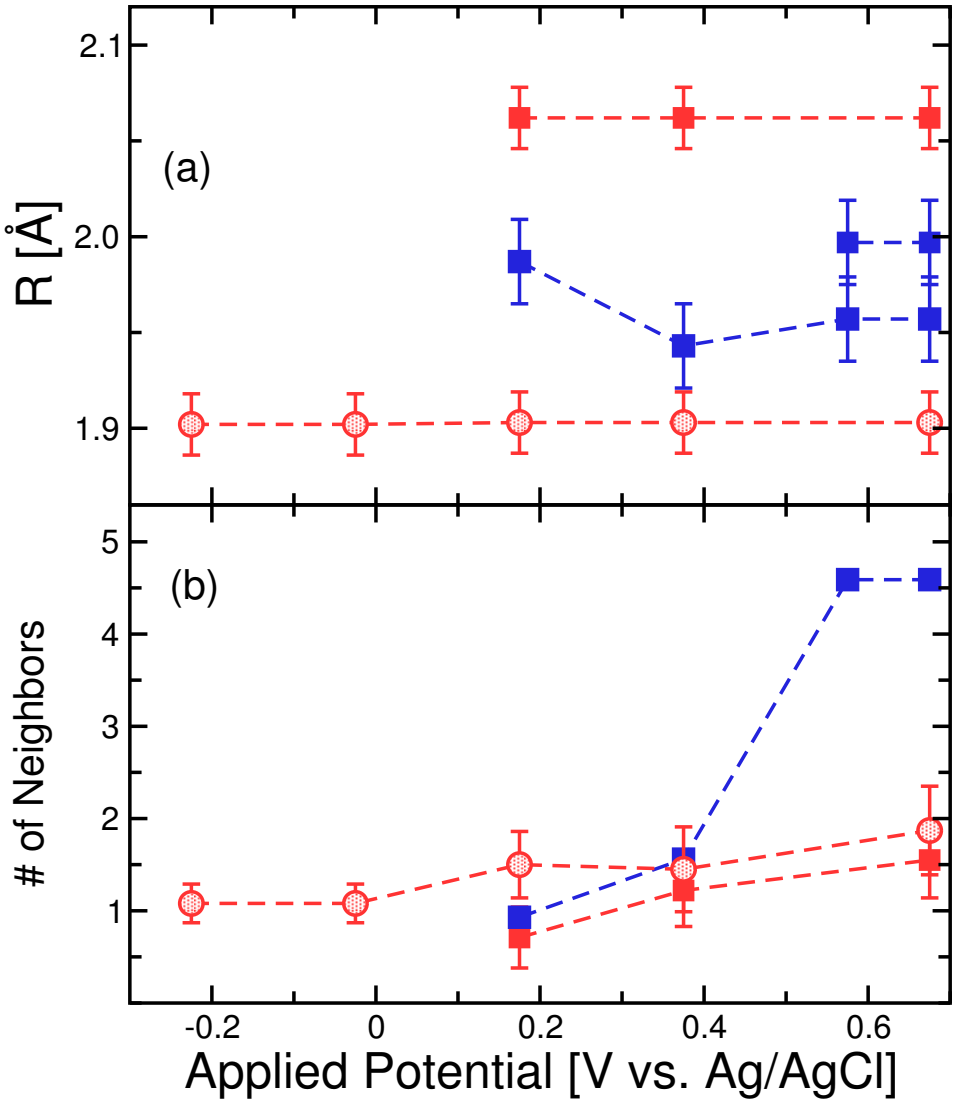
Ru-O/C paths



Without methanol

With methanol

Ru-O/C paths

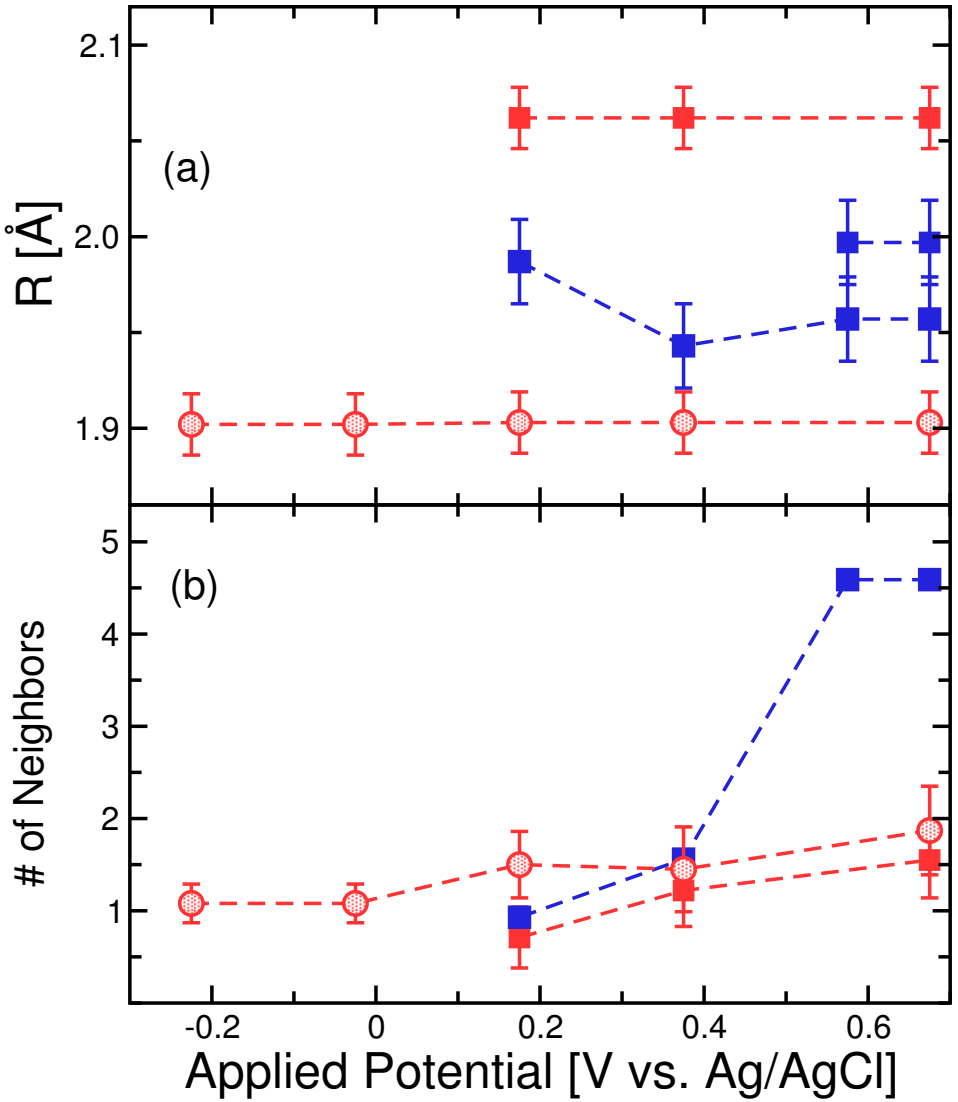


Without methanol

Above 375 mV Ru-O paths appear and total number of Ru-O neighbors increases to that of RuO_2

With methanol

Ru-O/C paths



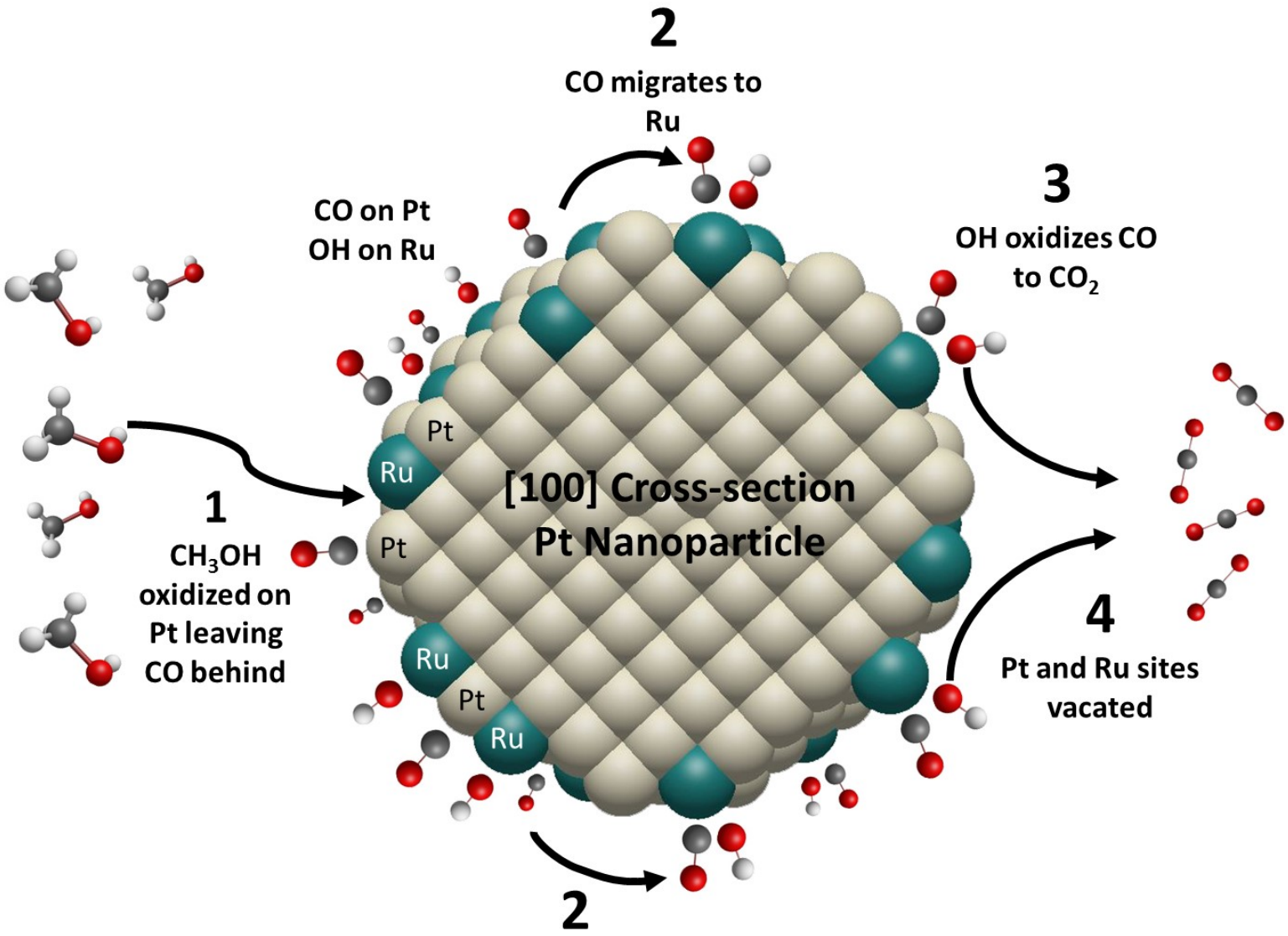
Without methanol

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

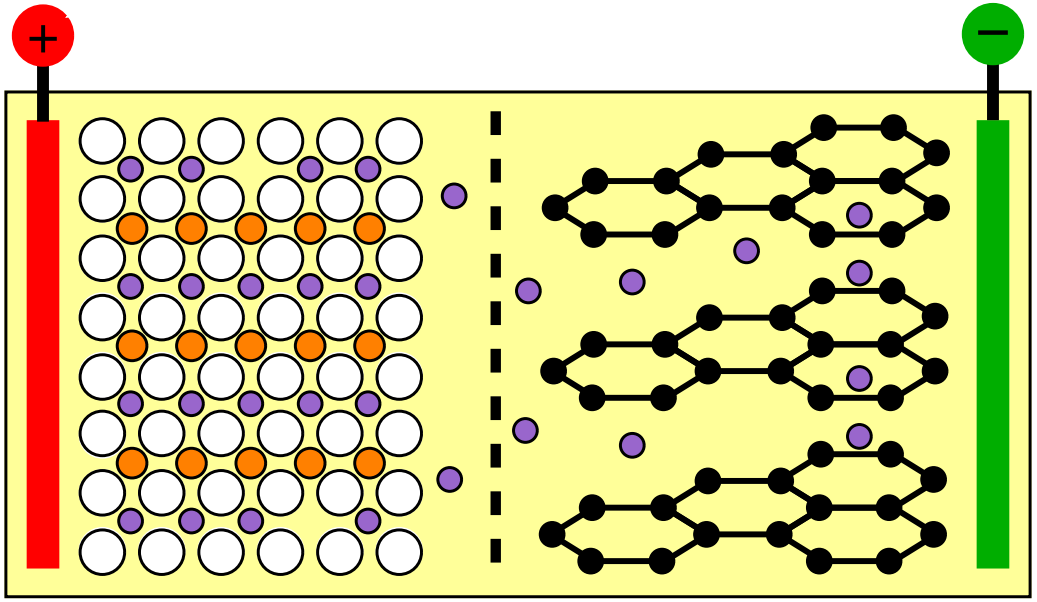
Solid state batteries

Anode - negatively charged electrode

Cathode - positively charged electrode

Separator - allows ions to pass without short circuit

Electrolyte - medium through which ions move



Solid state batteries

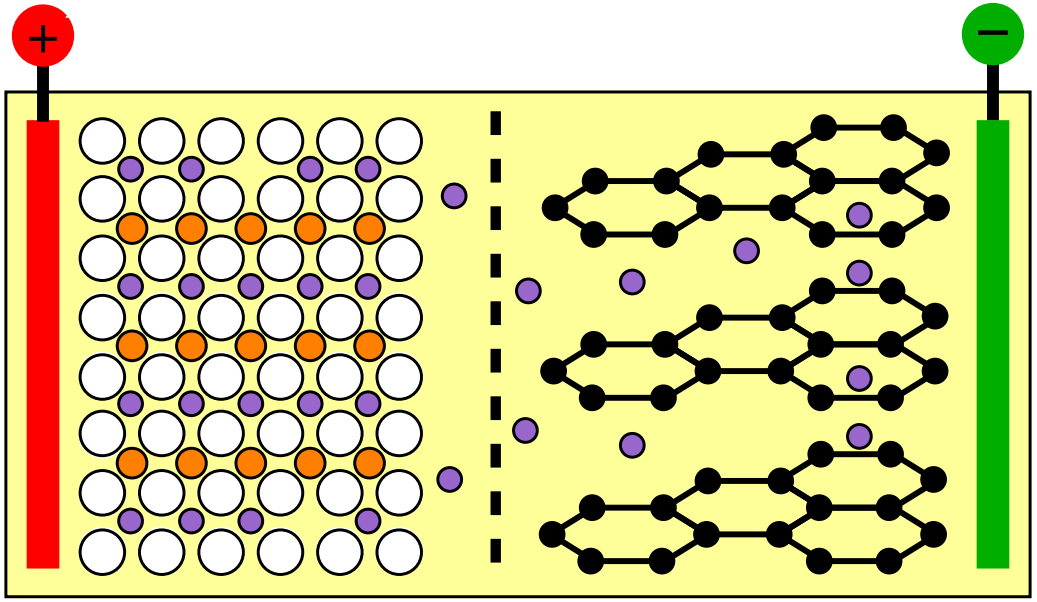
Anode - negatively charged electrode

Cathode - positively charged electrode

Separator - allows ions to pass without short circuit

Electrolyte - medium through which ions move

Consider a Li-ion battery



Solid state batteries

Anode - negatively charged electrode

Cathode - positively charged electrode

Separator - allows ions to pass without short circuit

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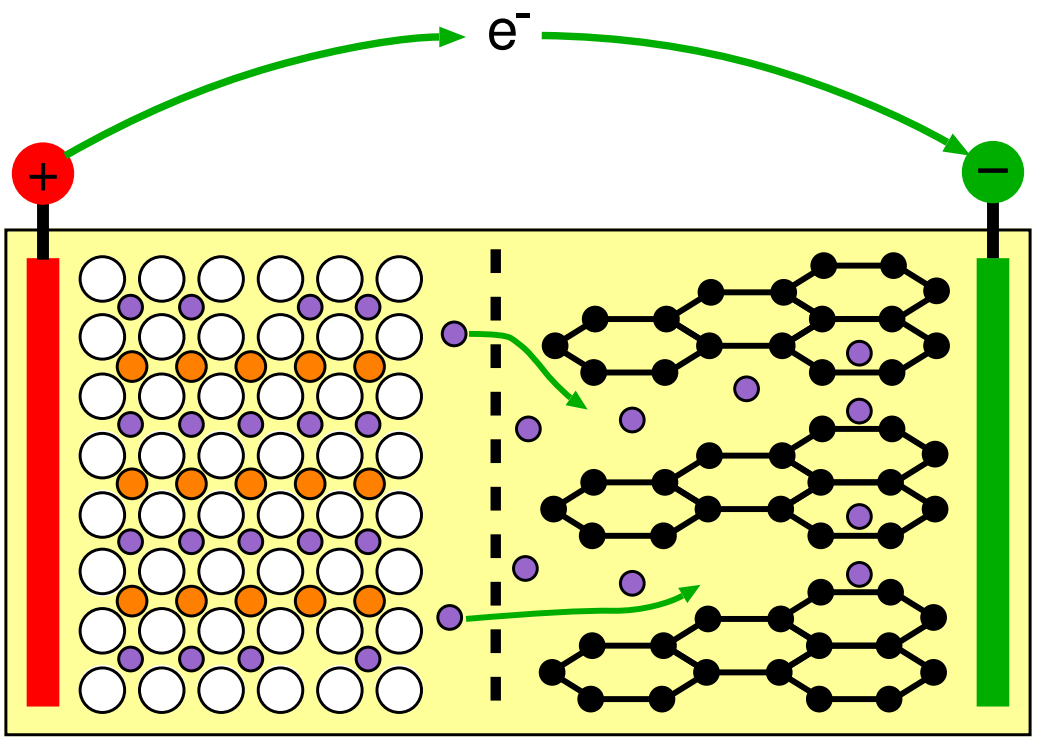

Charge - Li^+ ions move from cathode to anode and electrons also flow to the anode externally, anode is reduced

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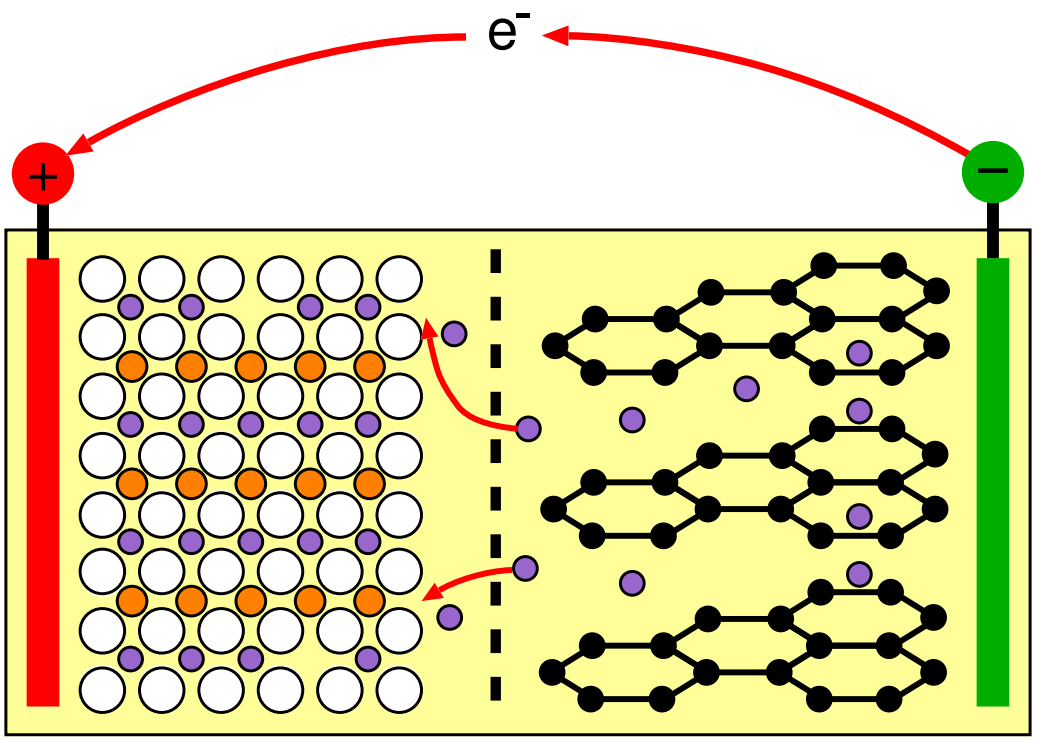

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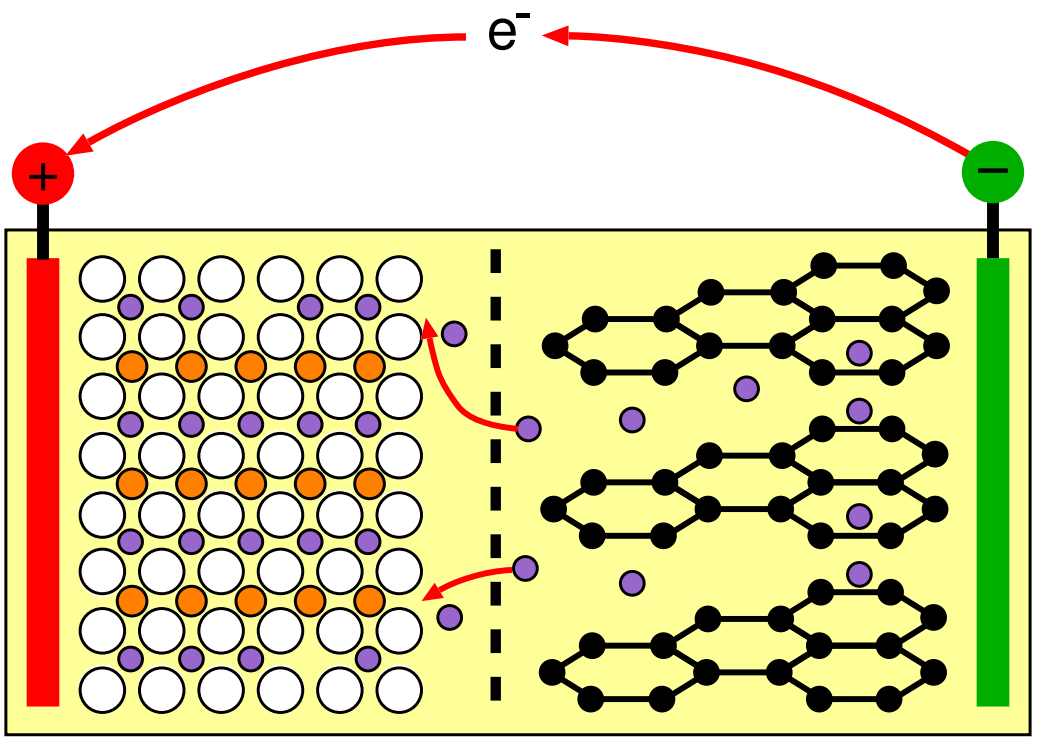

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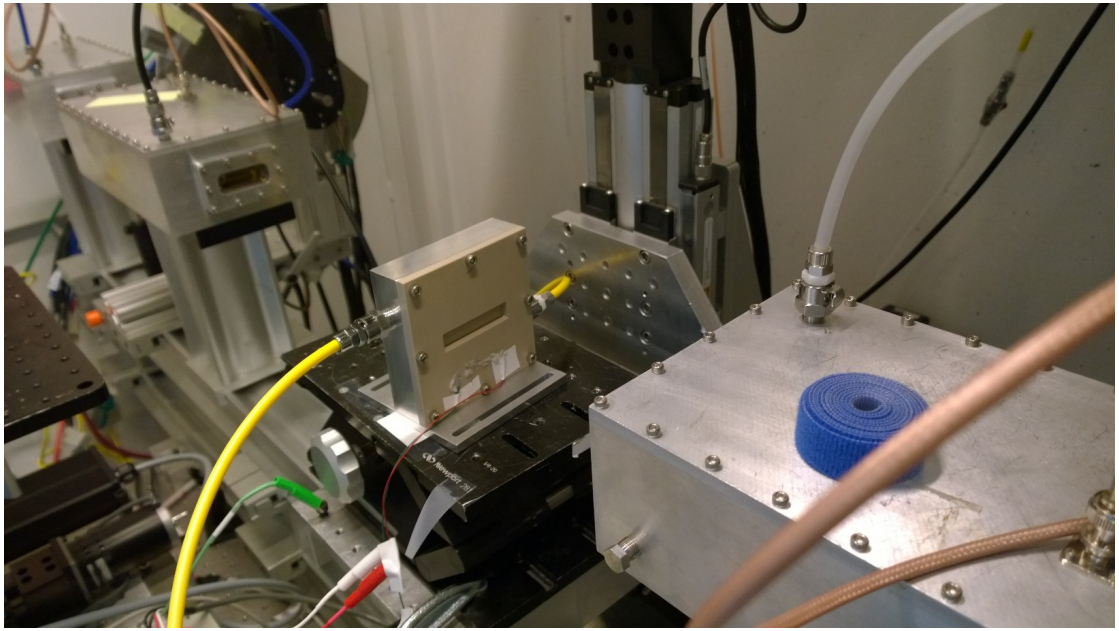
Potential, energy density, and power determined by the chemistry

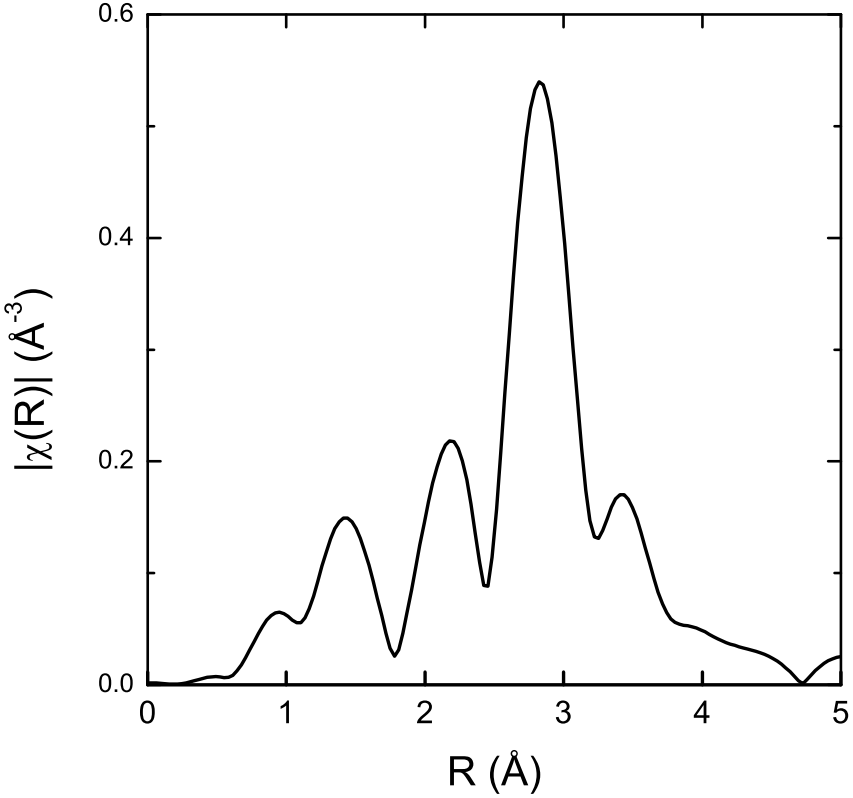
In situ lithiation of Sn

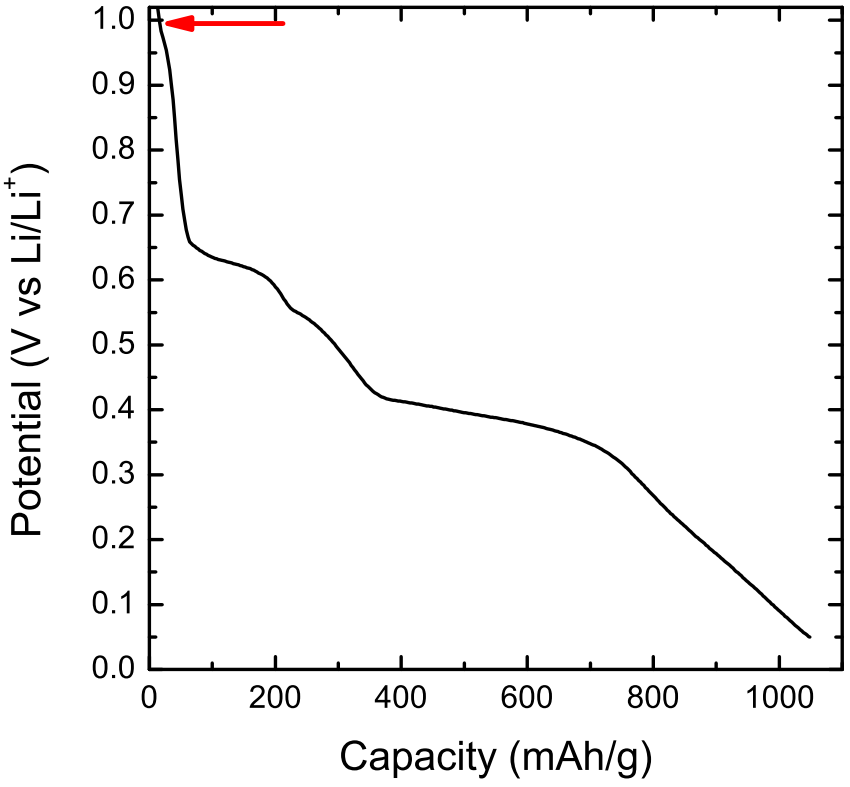
- In situ box for non-aqueous experiments
- Have measured $Sn_3O_2(OH)_2$, SnO_2, Sn, ZnO, MoO_2 ...
- Pouch cell simplifies experiment



- 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

Sn EXAFS versus potential

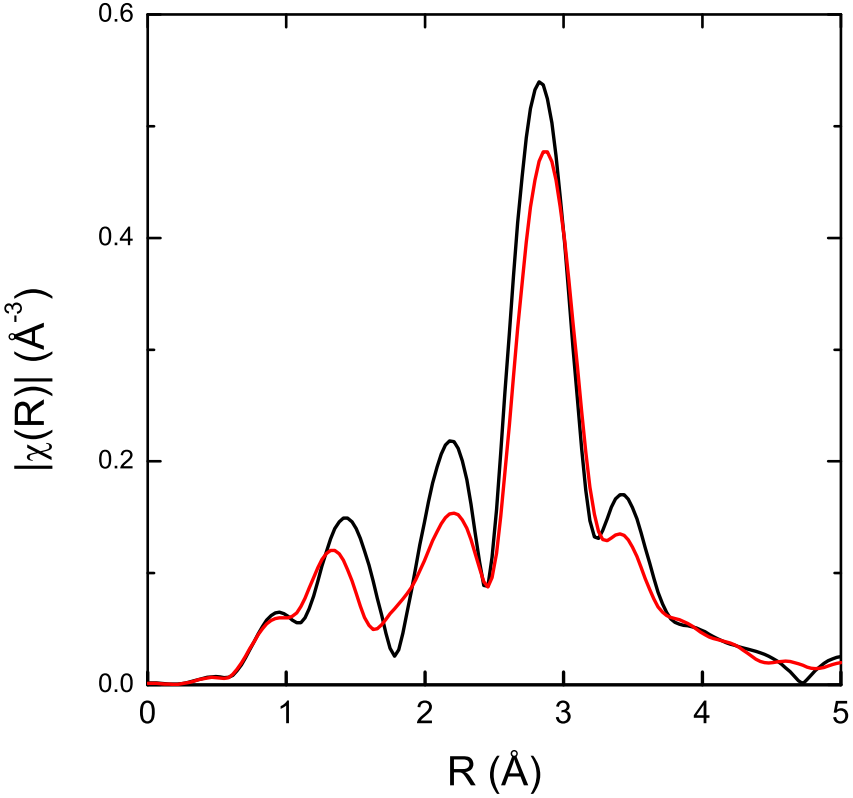


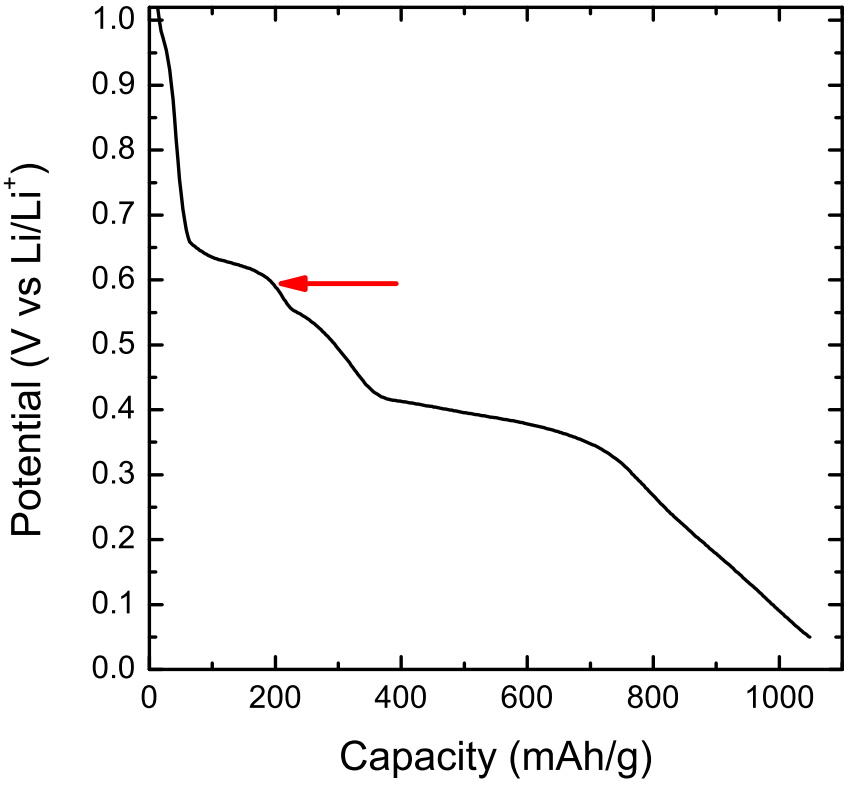


$Li_{22}Sn_5$ has 14 Sn-Li paths with distance 3.4Å or less

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

Sn EXAFS versus potential





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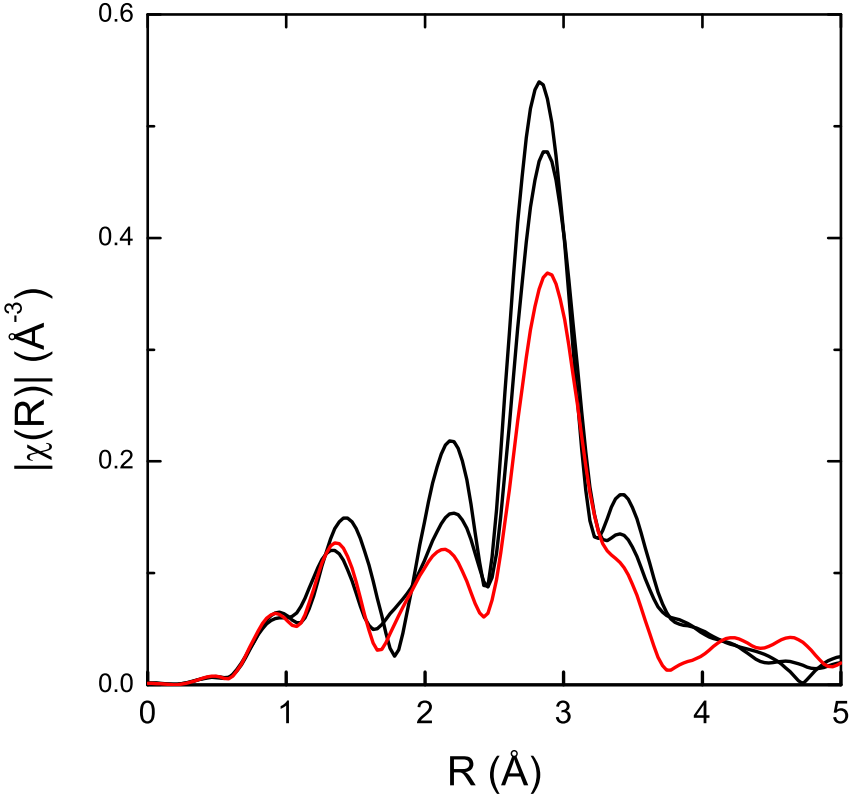

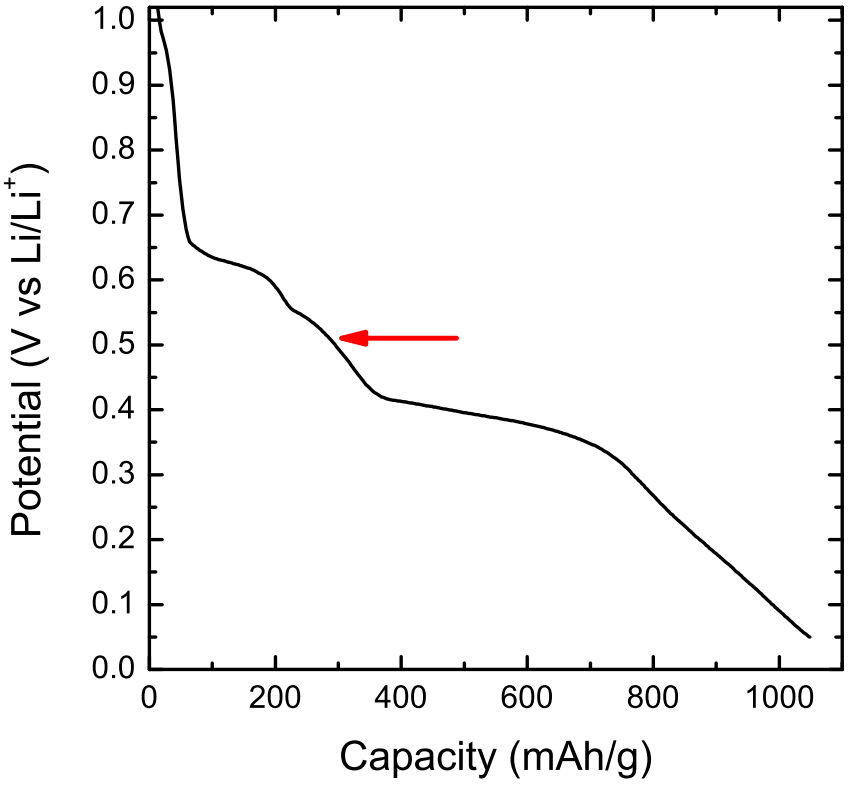

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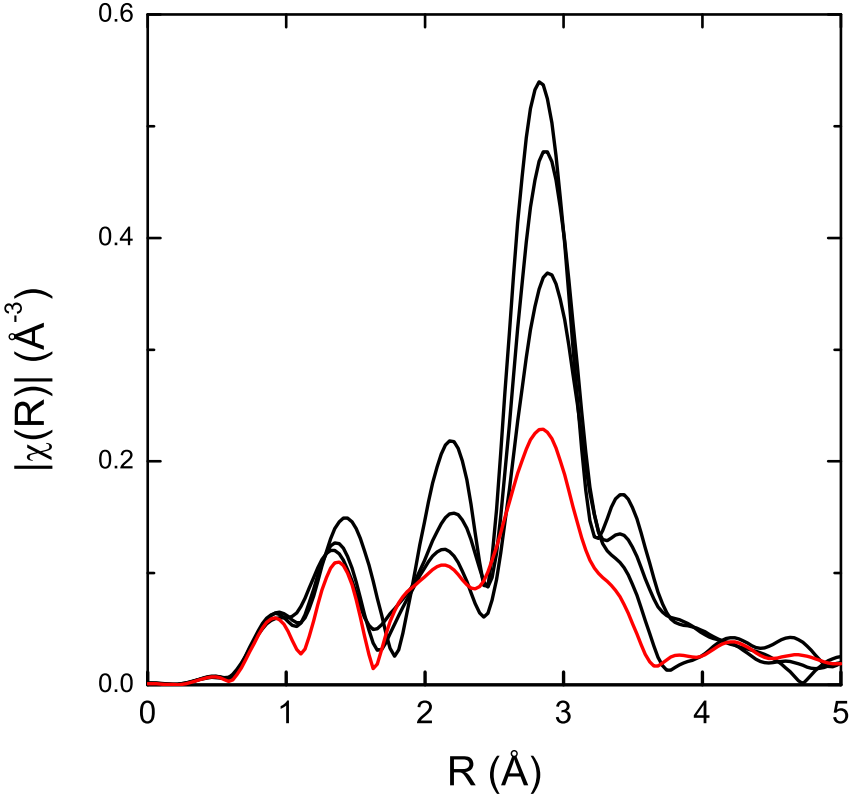

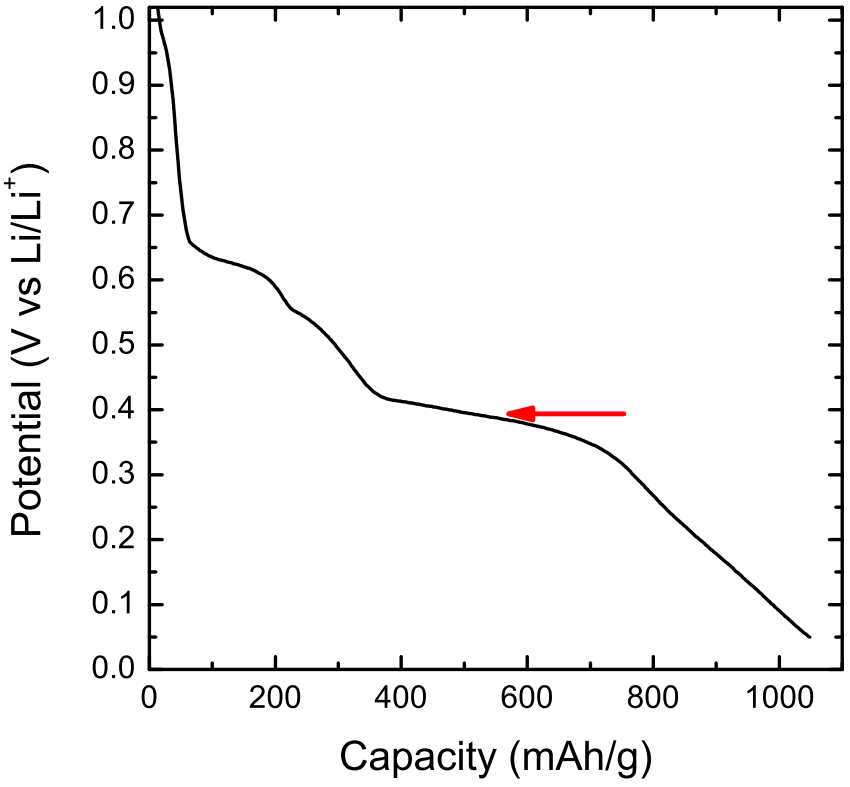

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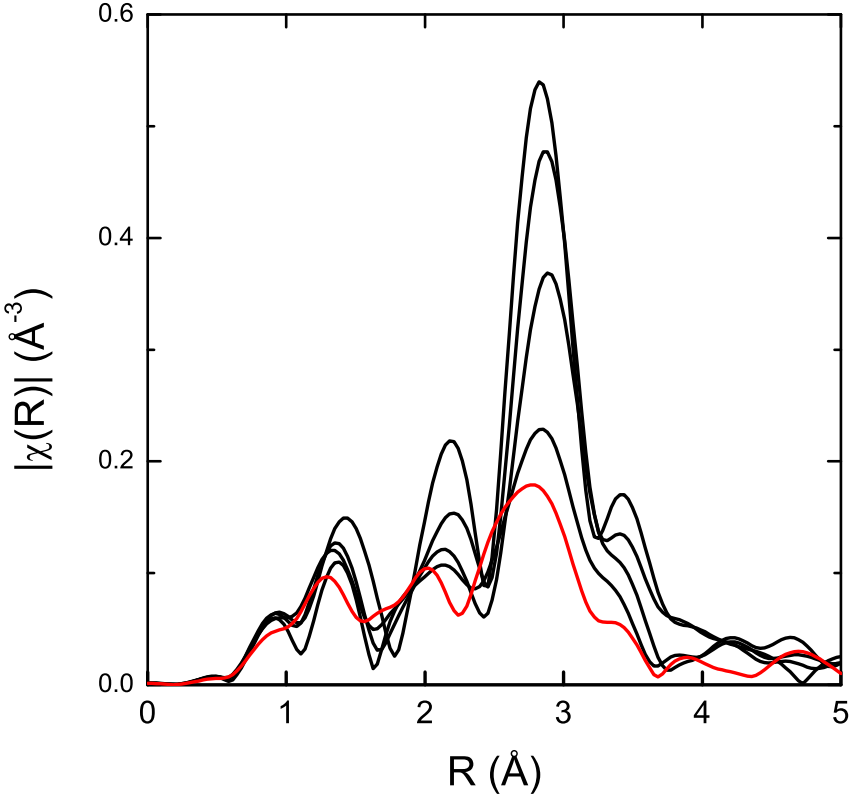

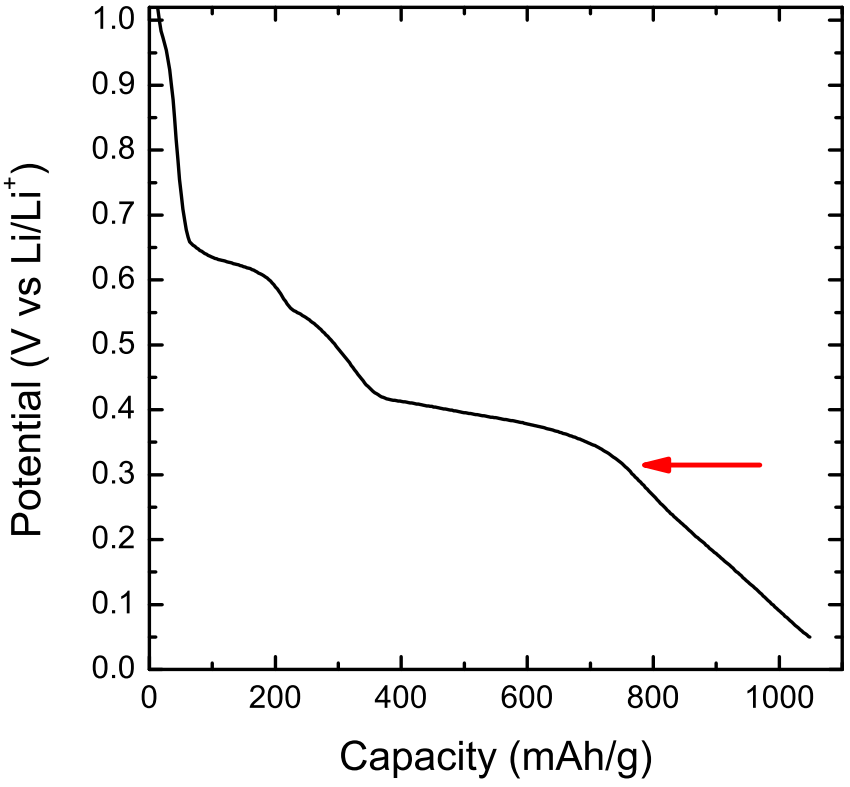

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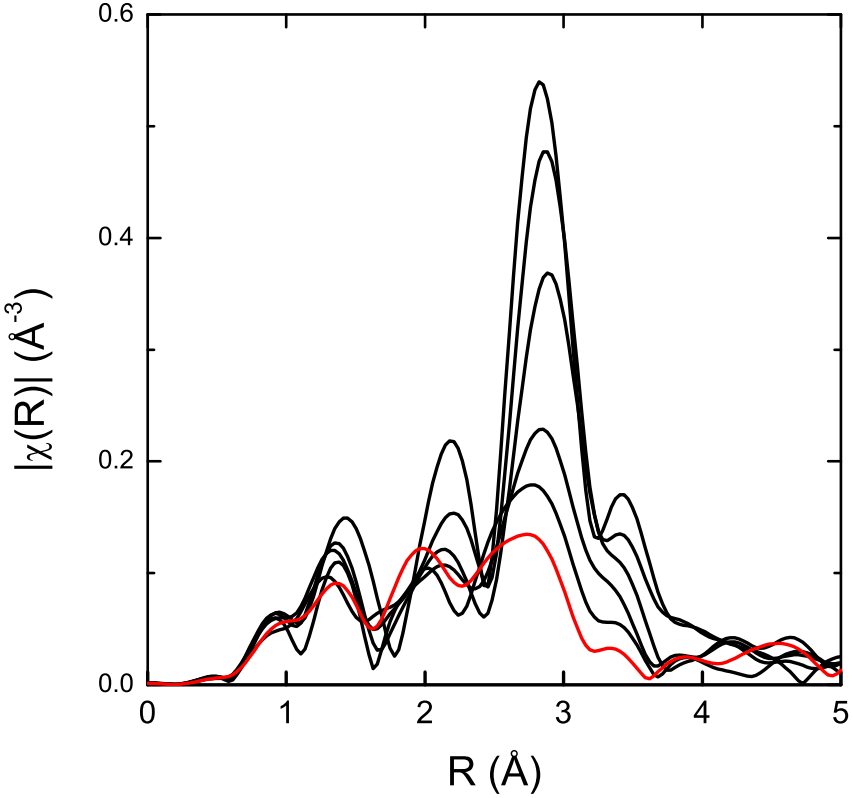

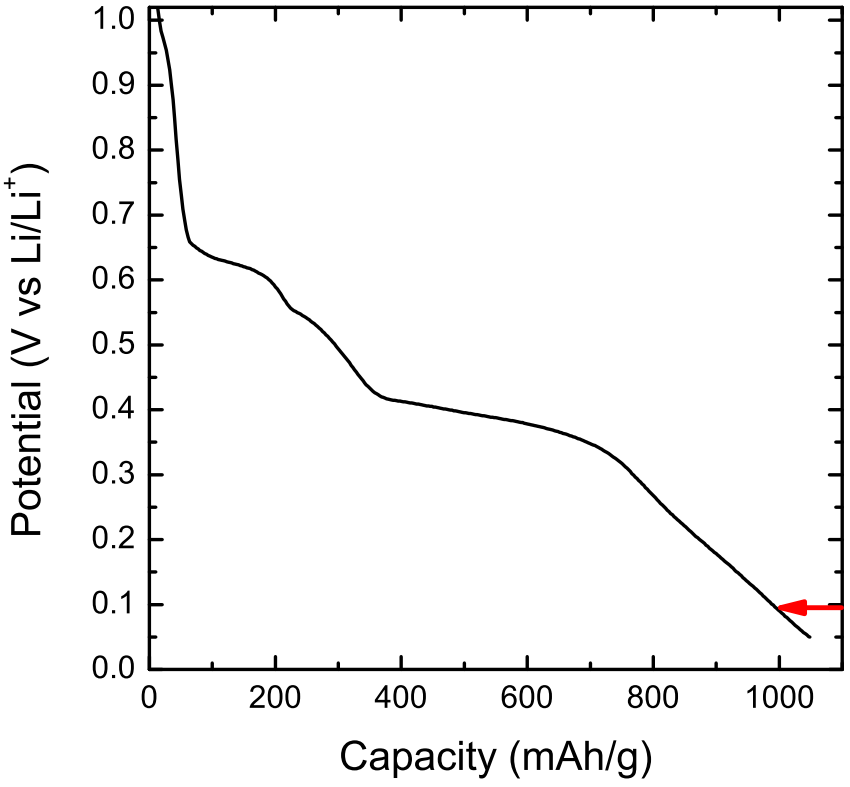

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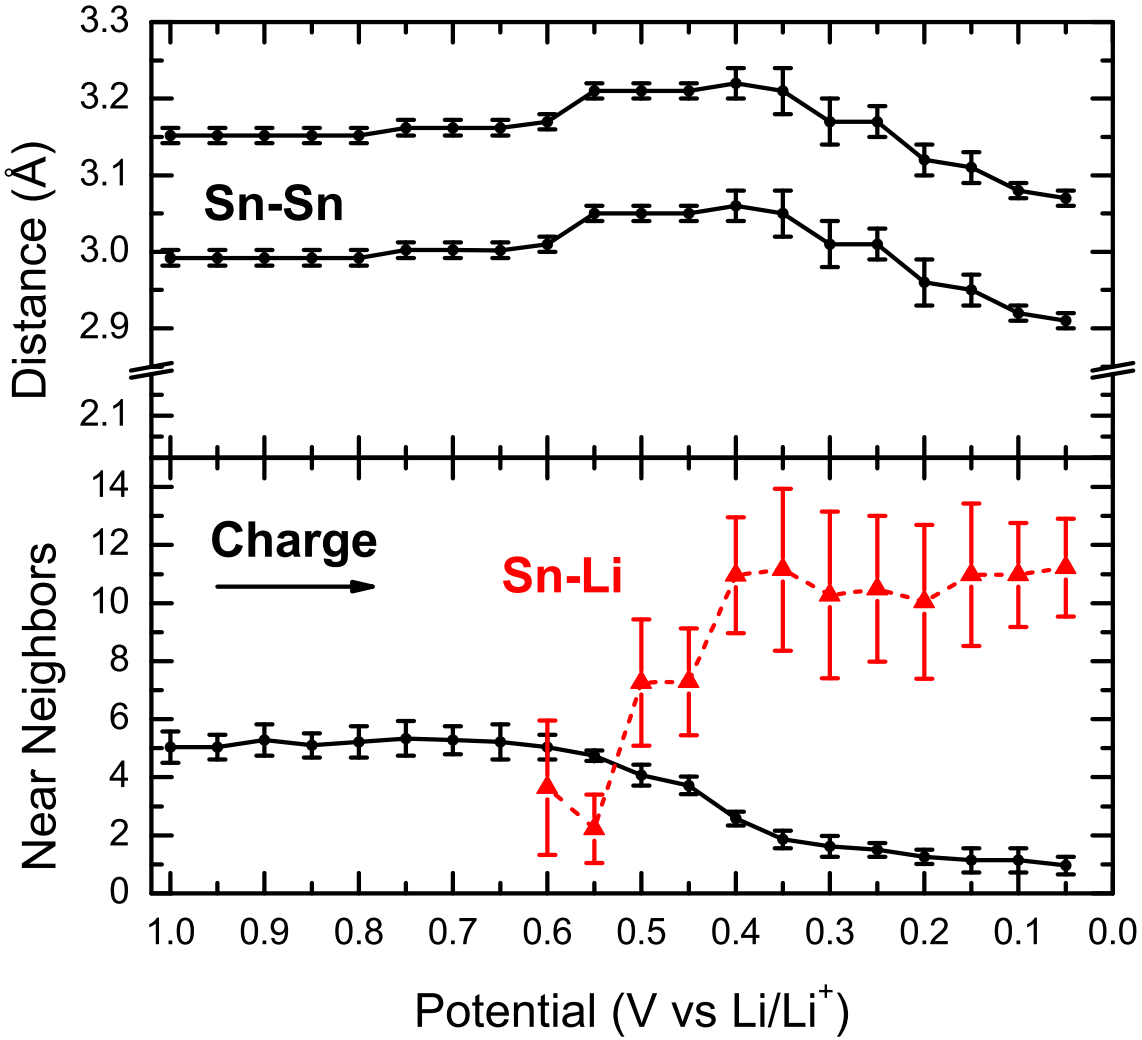
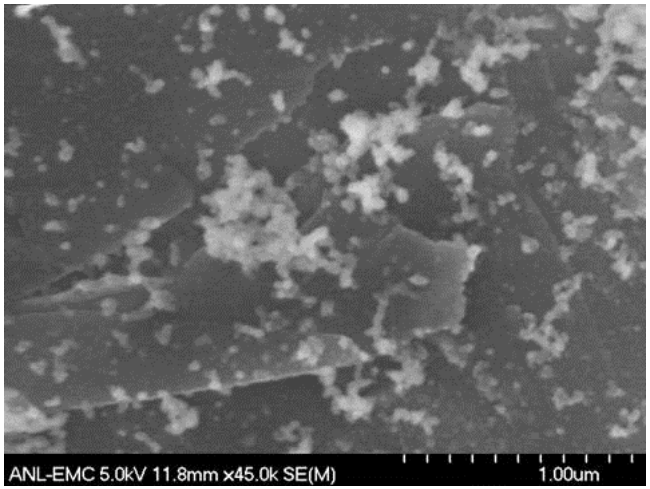
The Sn lithiation process



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

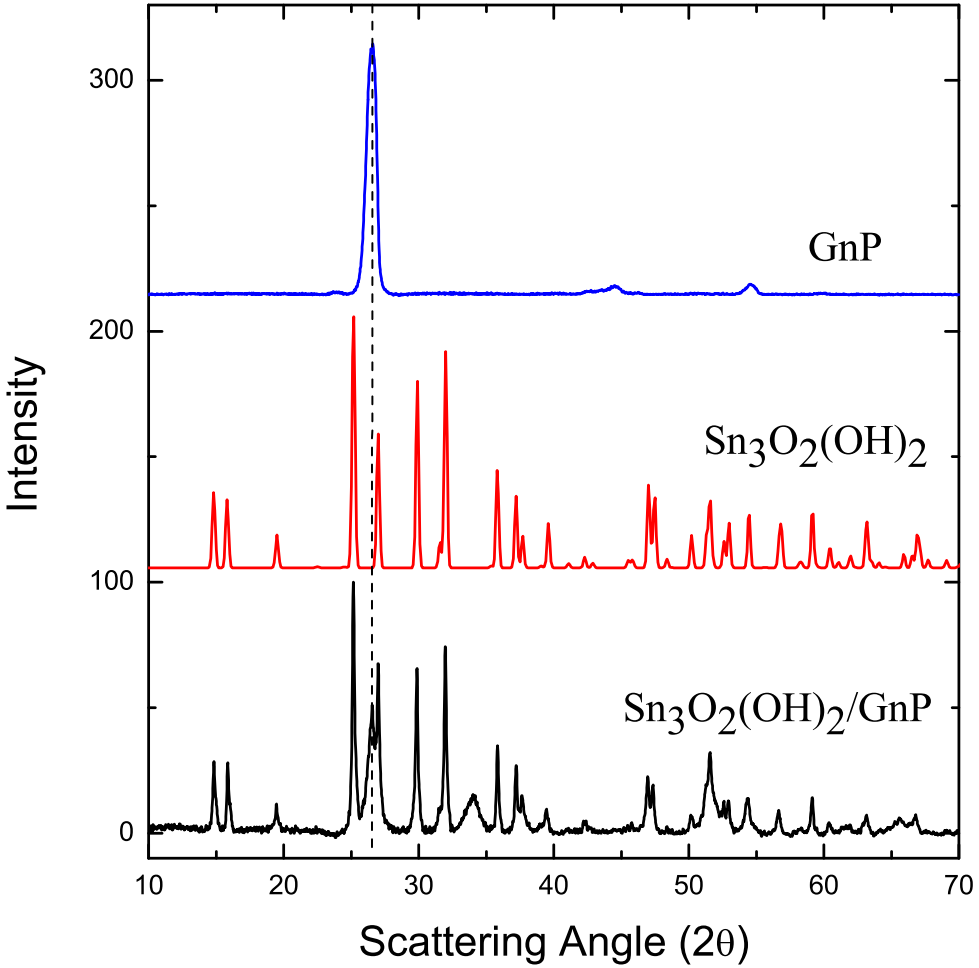
0.45V – number of Li reaches 11 and stabilizes at near full $Li_{22}Sn_5$

Synthesis of Sn-graphite nanocomposites

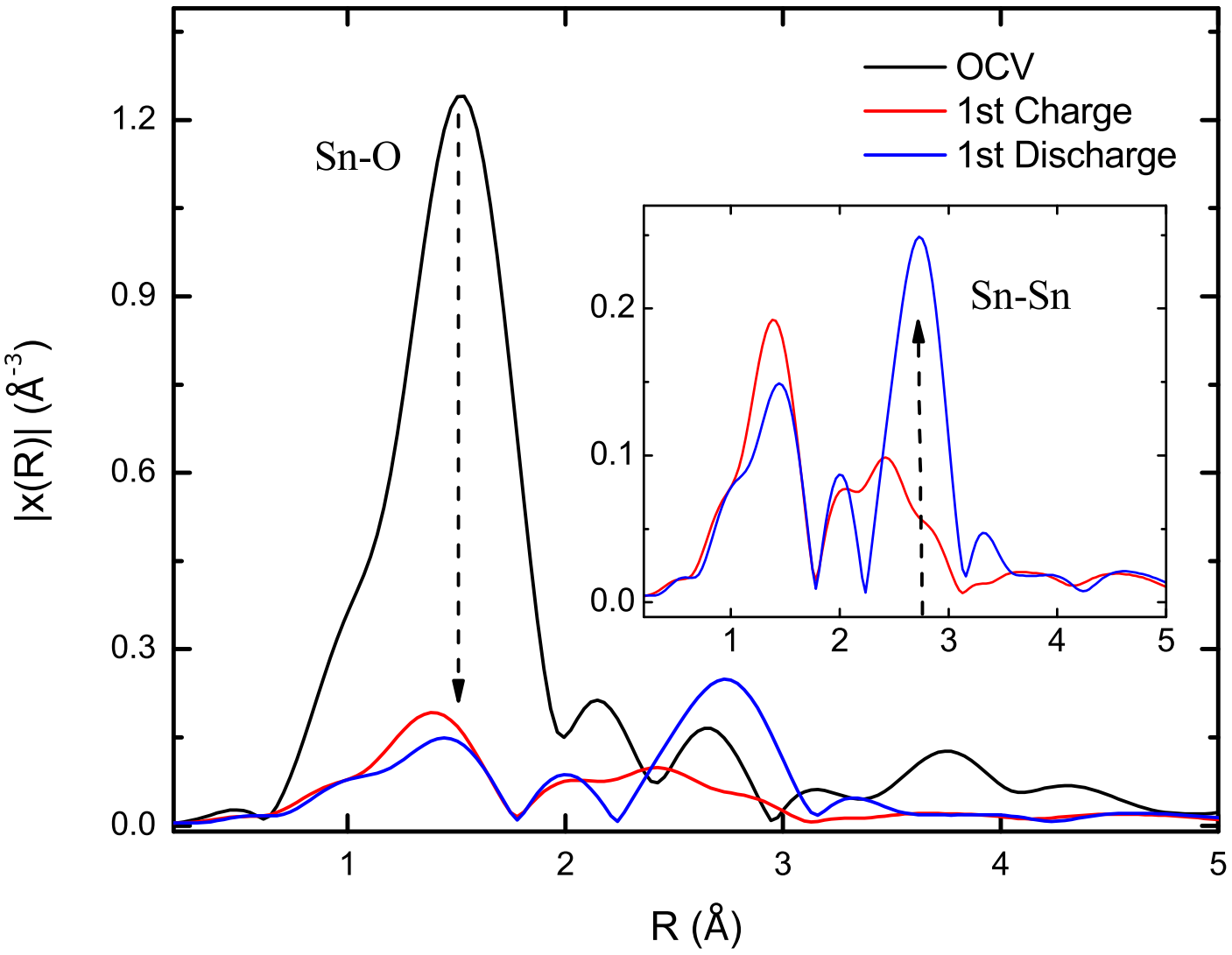


One-pot synthesis produces evenly distributed $Sn_3O_2(OH)_2$ nanoparticles on graphite nanoplatelets

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



In situ XAS studies of lithiation



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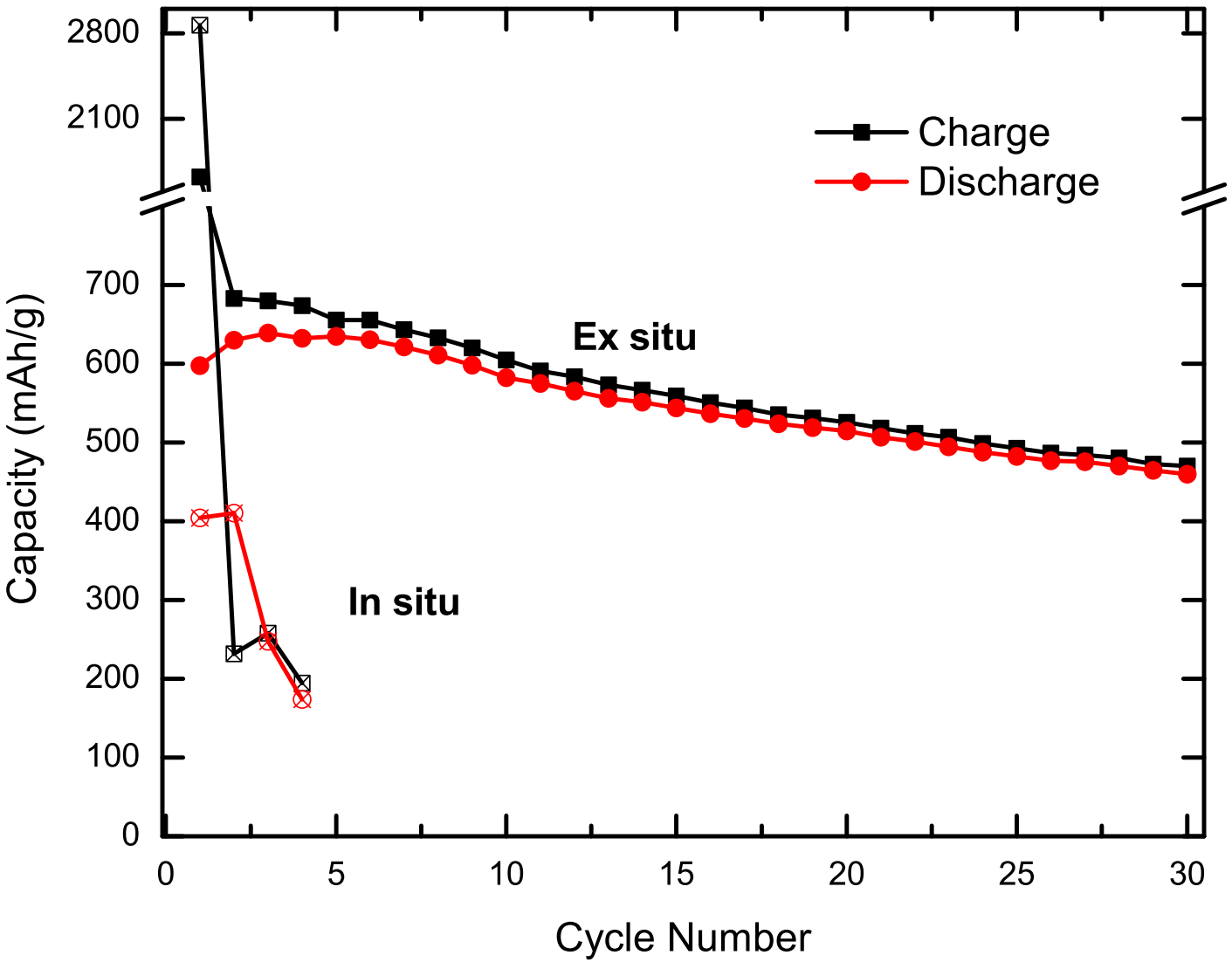

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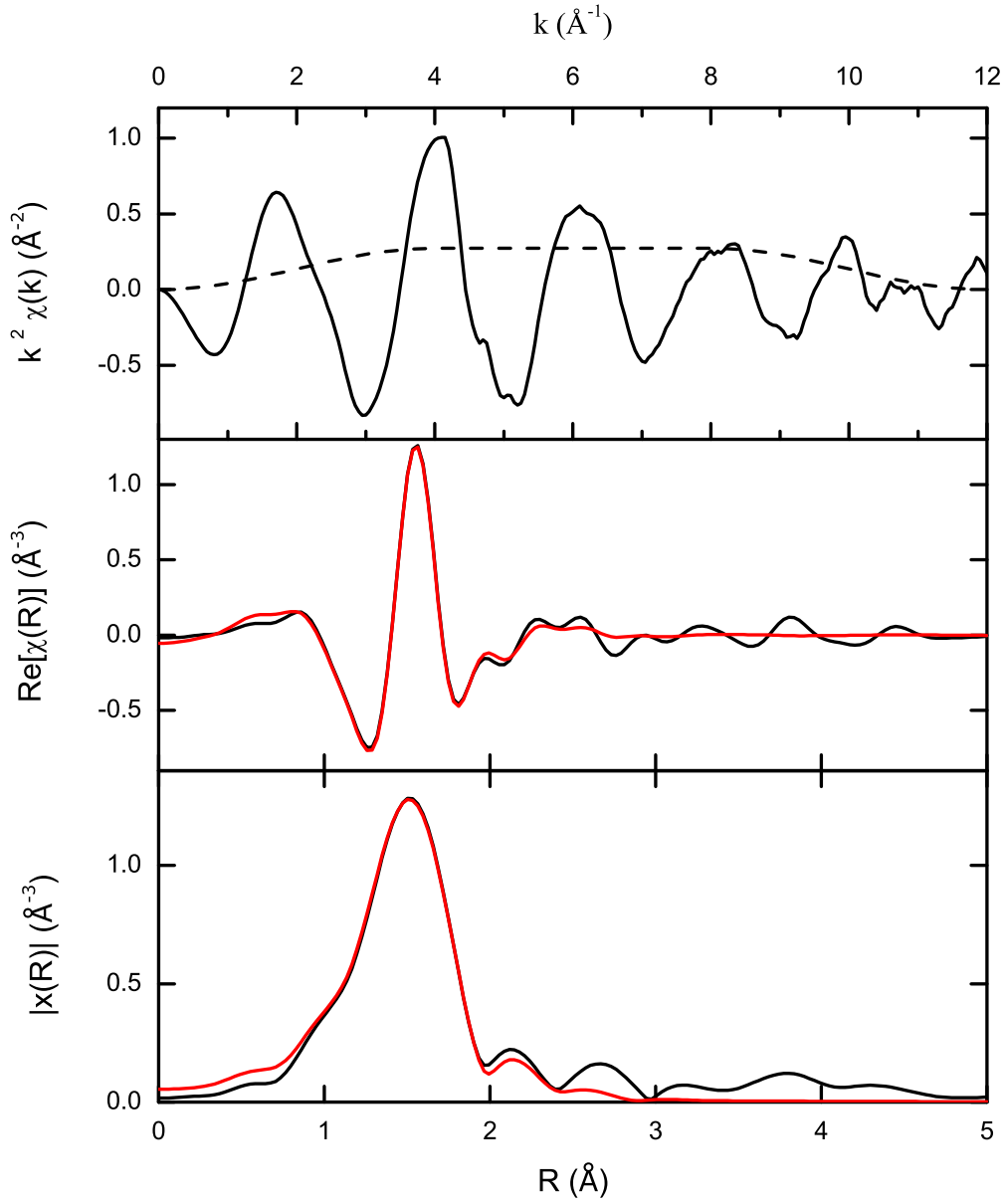

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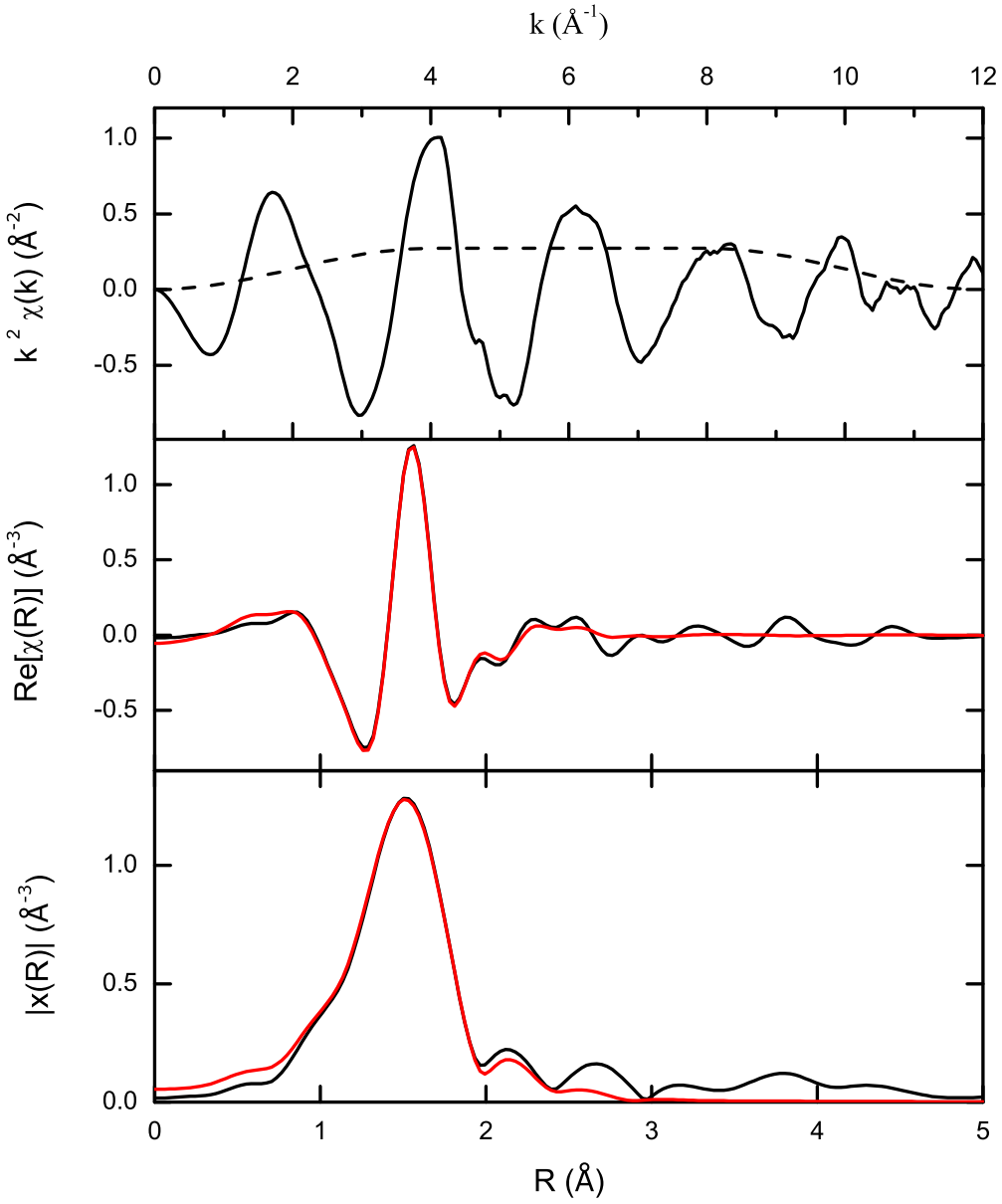

Fresh electrode can be fit with $Sn_3O_2(OH)_2$ structure which is dominated by the near neighbor Sn-O distances

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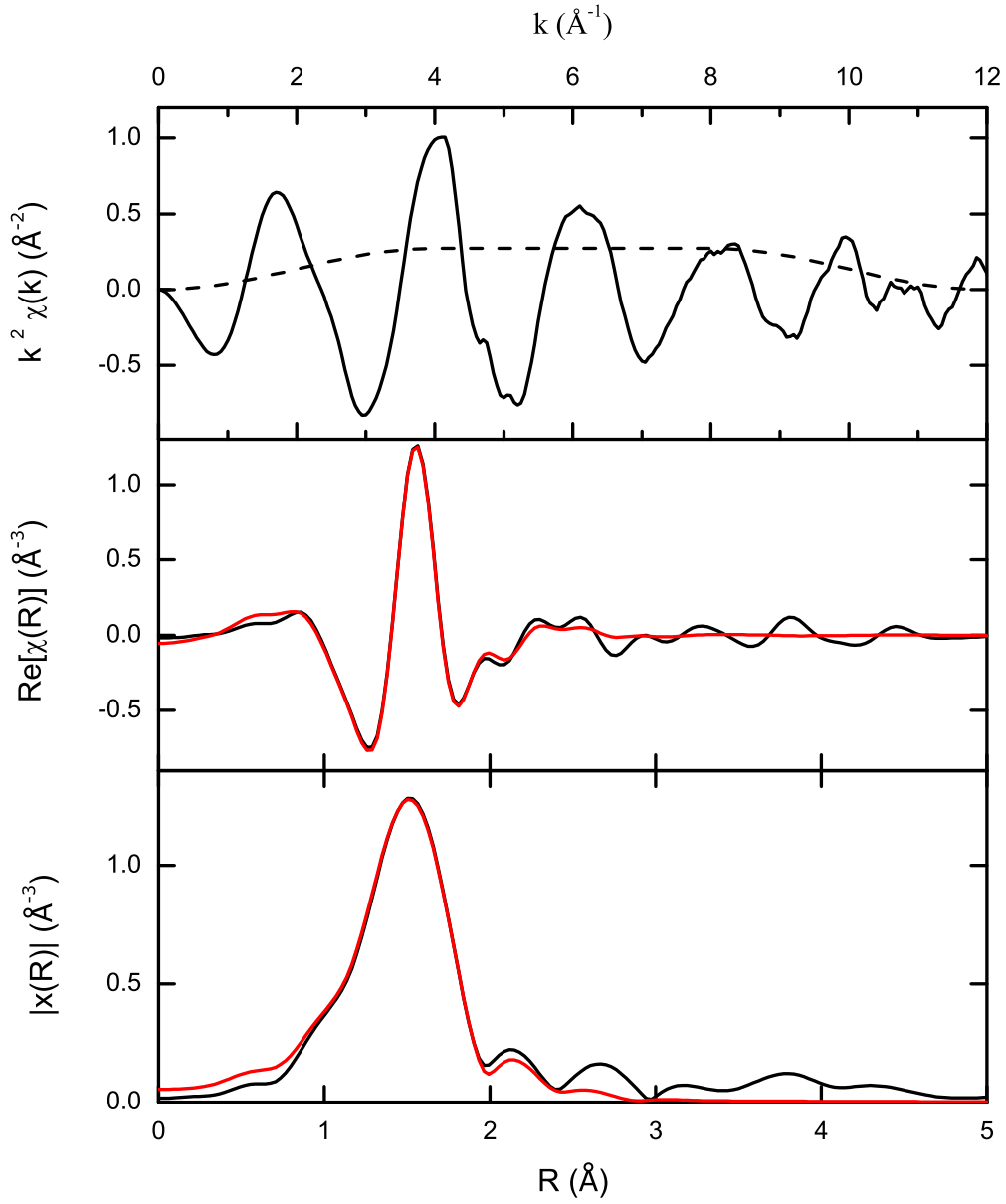

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Only a small amount of metallic Sn-Sn distances can be seen

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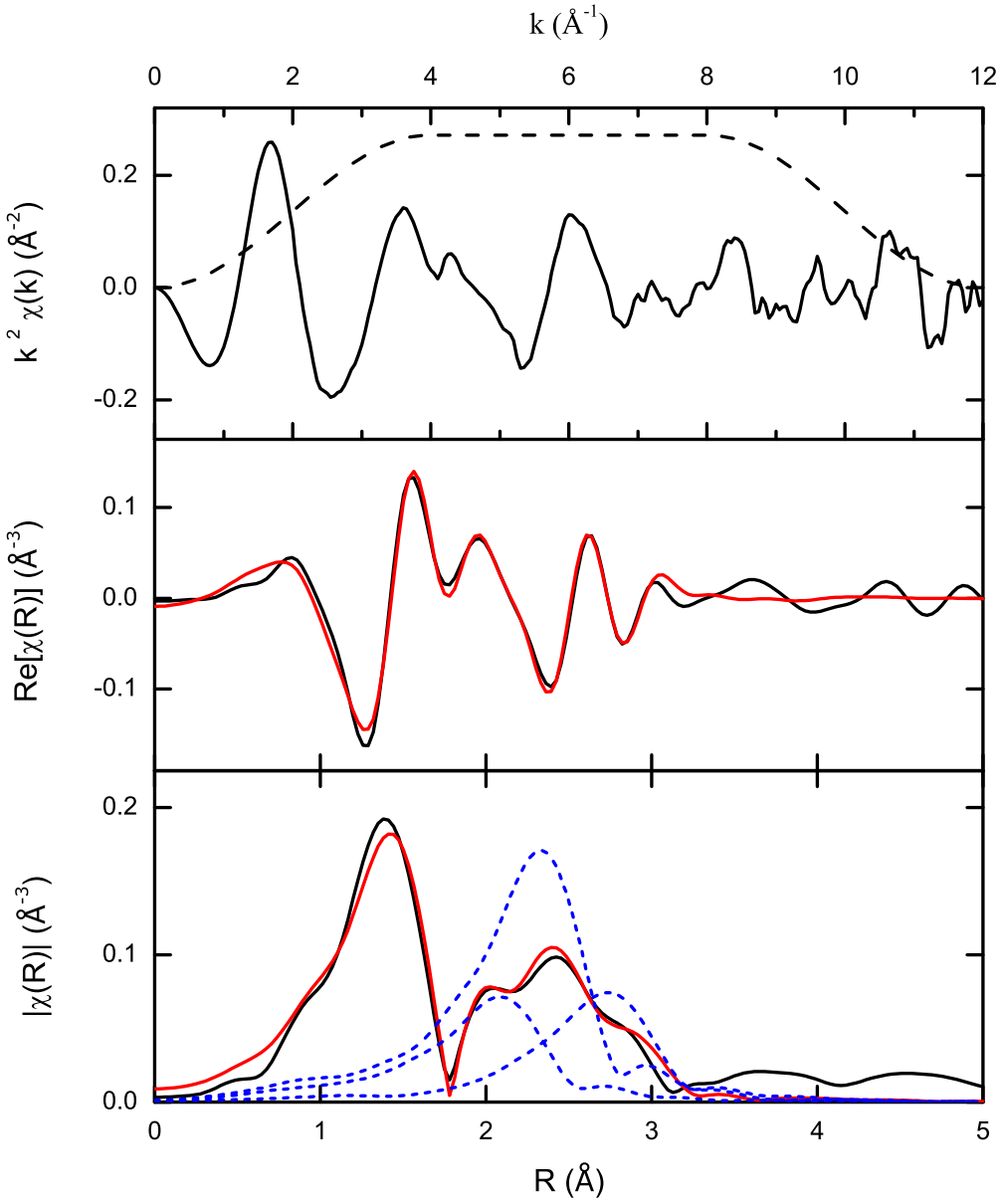

Reduction of number of Sn-O near neighbors and 3 Sn-Li paths characteristic of the $Li_{22}Sn_5$ structure

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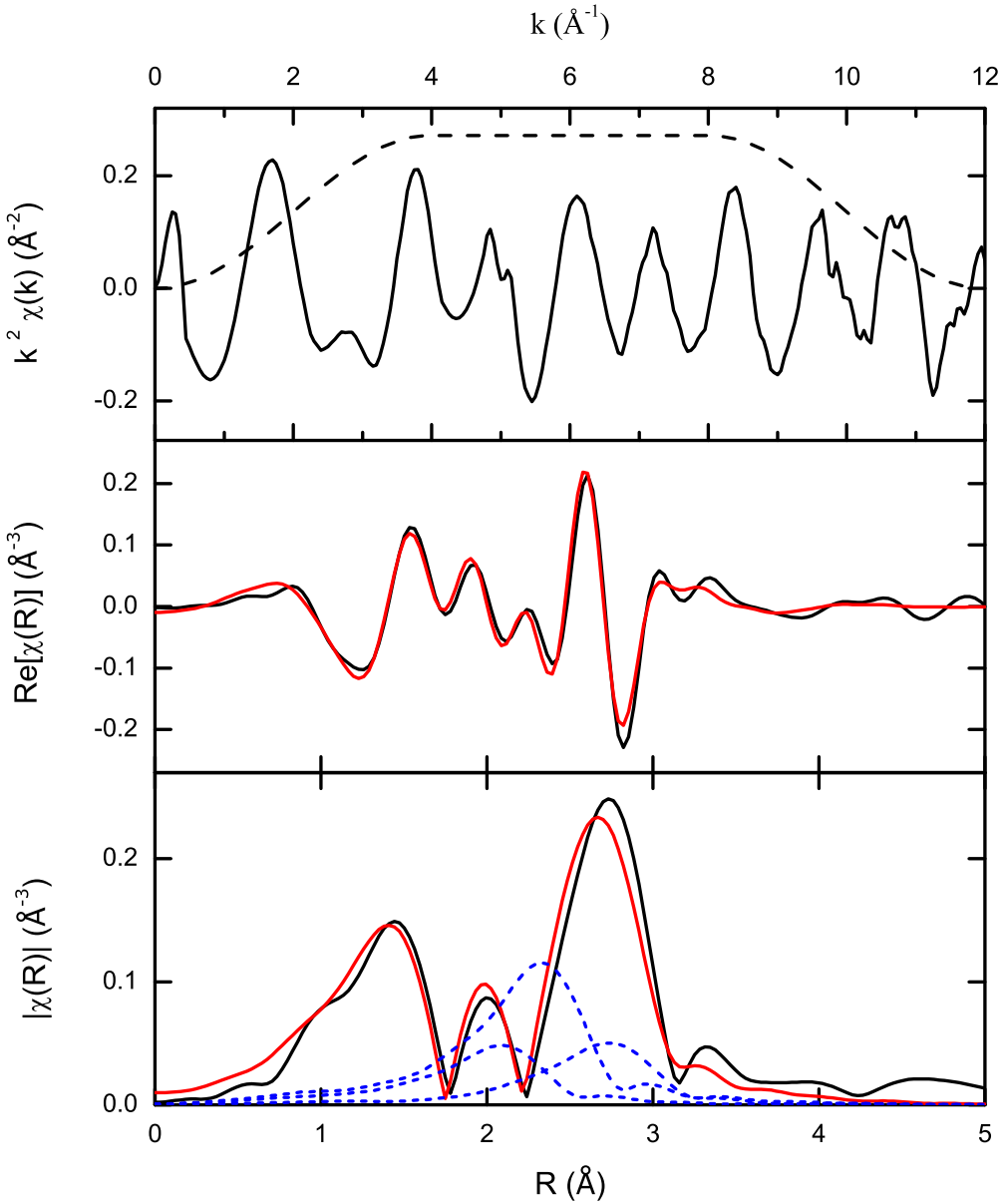
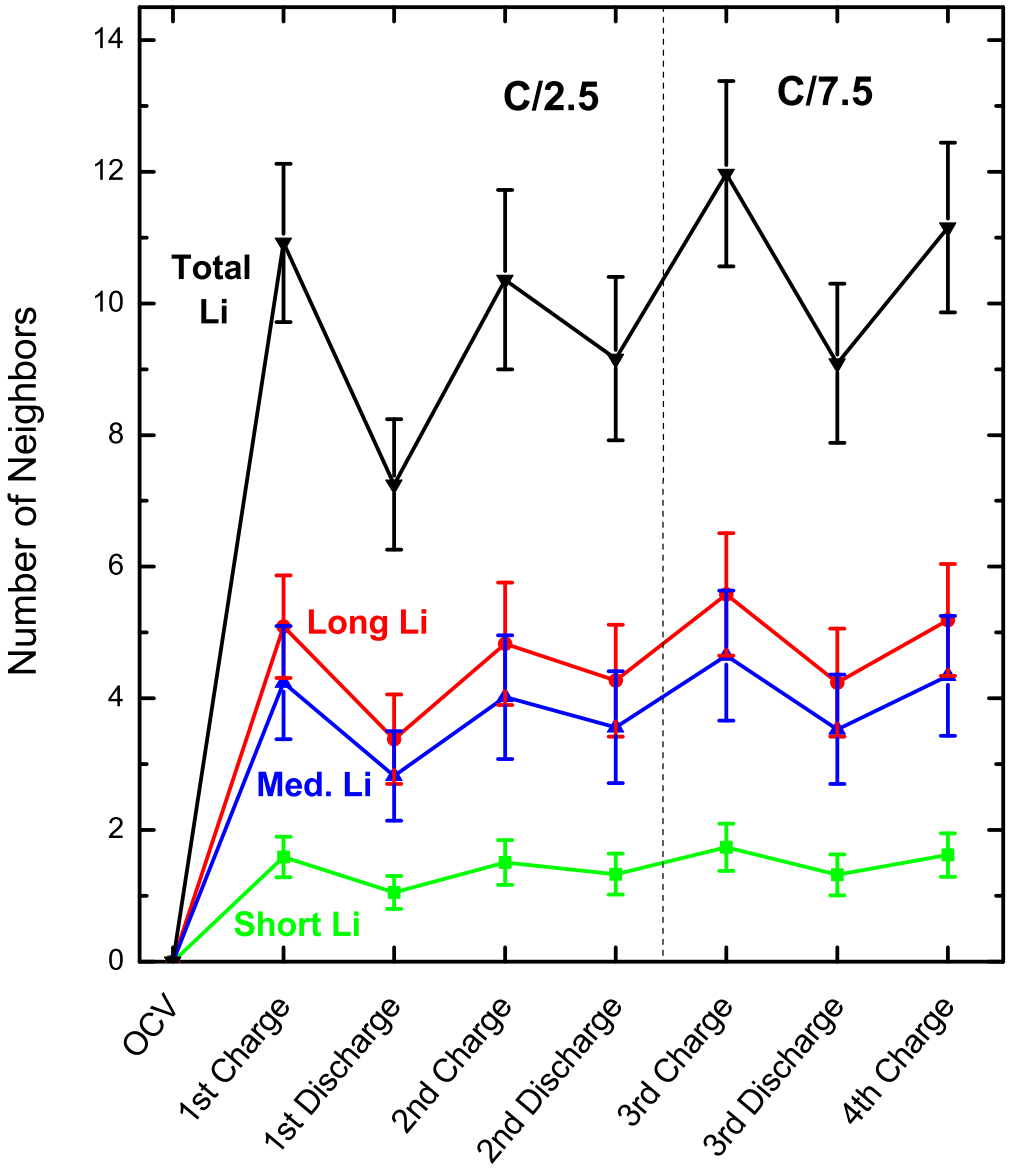


Metallic Sn-Sn distances appear but Sn-Li paths are still present, further reduction in Sn-O near neighbors.

In situ XAS studies of lithiation



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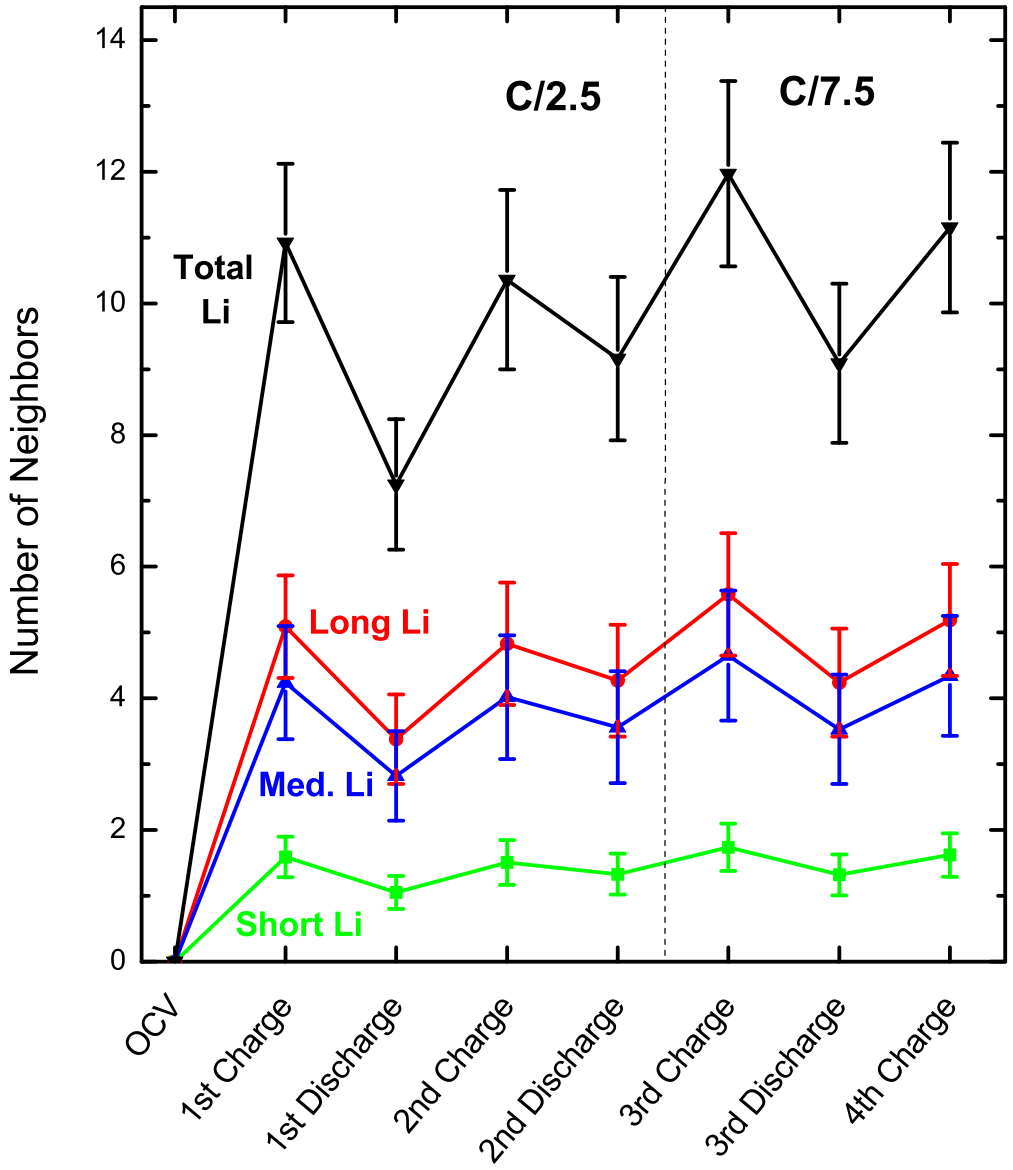

Number of Li near neighbors oscillates with the charge/discharge cycles but never returns to zero

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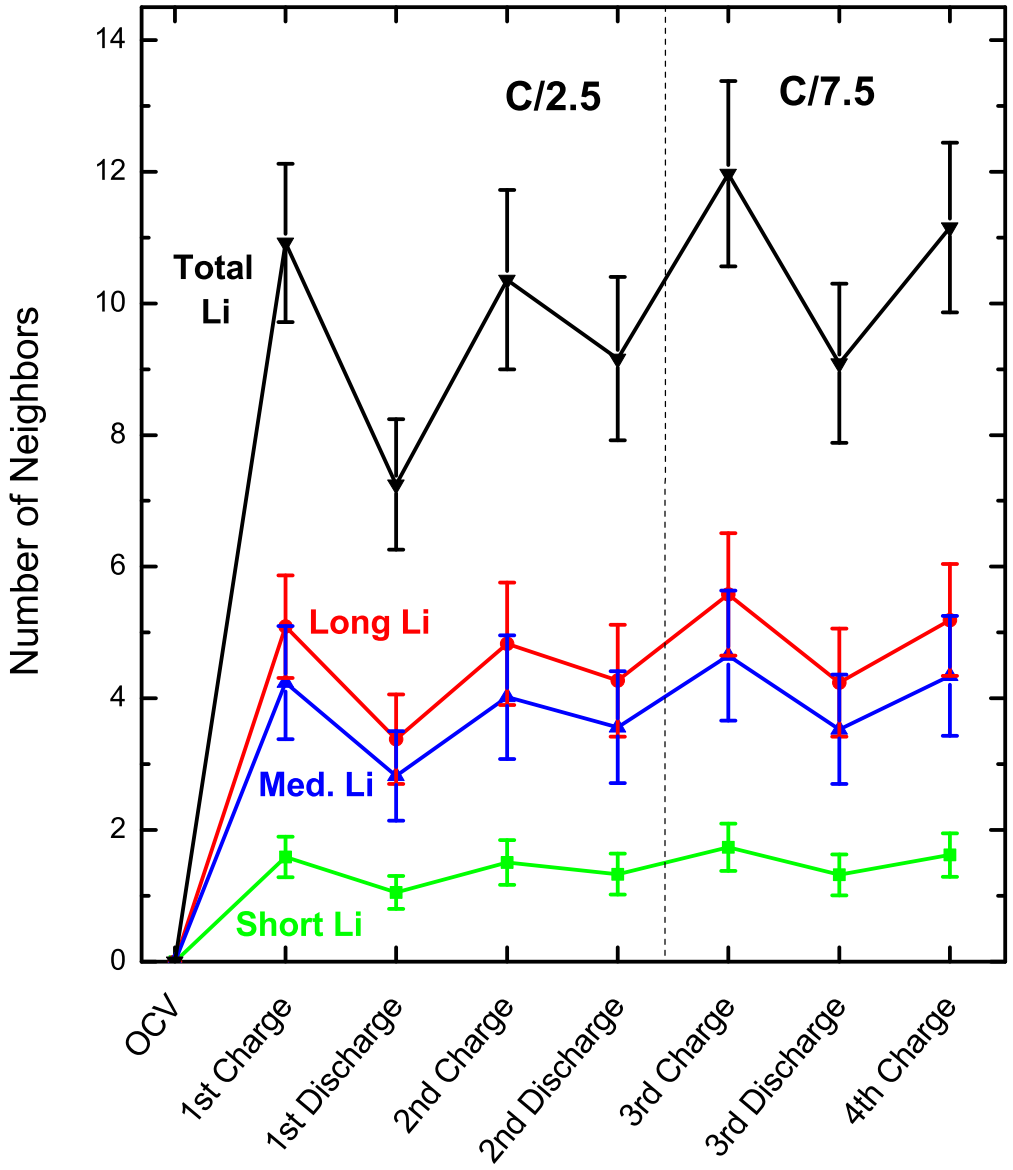

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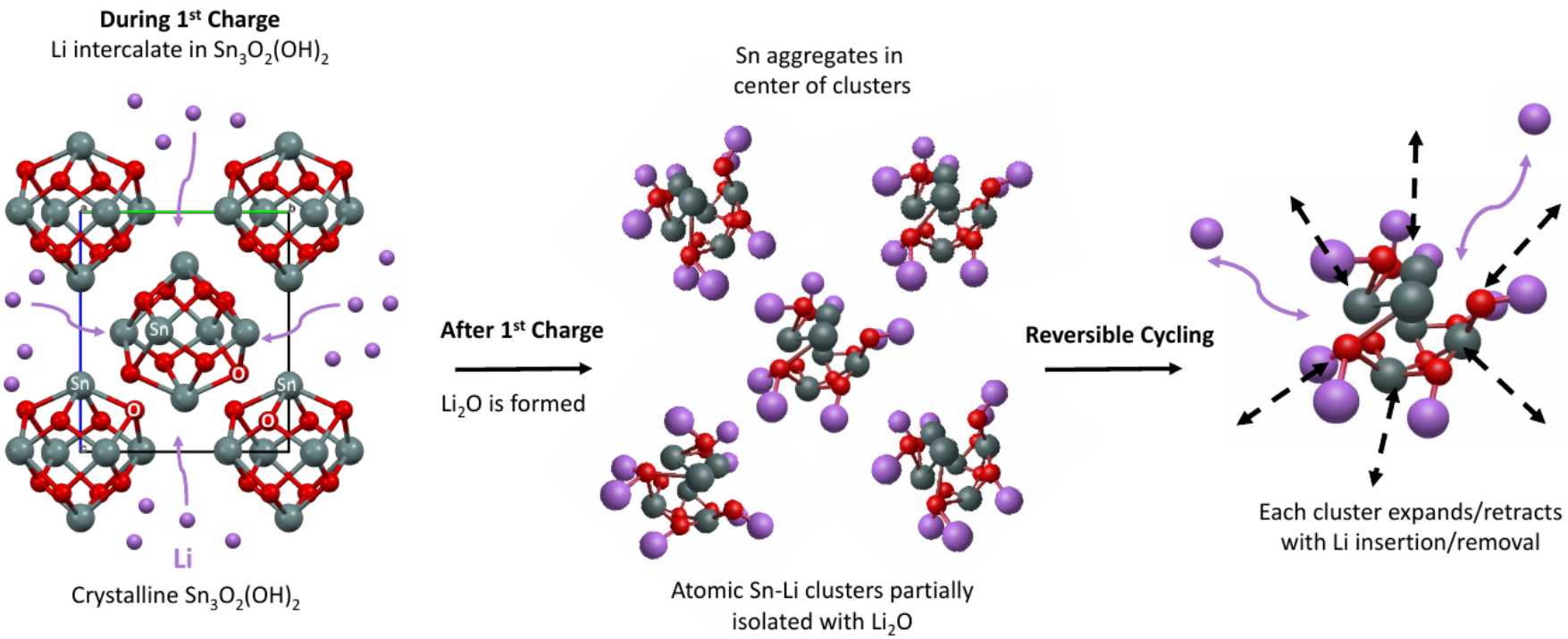
In situ cell promotes accelerated aging because of Sn swelling and the reduced pressure of the thin PEEK pouch cell assembly

In situ XAS studies of lithiation



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).

Principal collaborators - Thank you!

- Christopher Pelliccione – IIT (Ph.D. student)
- John Katsoudas – IIT (MRCAT staff)
- Elena Timofeeva – Argonne, Energy Systems

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Abstract

X-ray absorption spectroscopy using synchrotron radiation has become an essential tool for operando studies of catalysts and batteries where nanoparticles and amorphous materials preclude the use of x-ray diffraction to study structural changes. I will discuss the fundamentals of synchrotron radiation and x-ray absorption spectroscopy along with examples of how it is applied to the study of polymer electrolyte fuel cell catalysts and lithium ion battery materials.