How do we design improved materials for electrochemical energy applications?

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Opening remarks

Challenges for electrochemical energy systems

- Fuel cells - reduce overpotential losses and use of expensive materials
- Batteries - increase volumetric & gravimetric energy density while reducing costs by $\sim 50\%$

Will present three examples of how we can probe fundamental mechanisms at play and use this information to design better materials

Opening remarks

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Will present three examples of how we can probe fundamental mechanisms at play and use this information to design better materials

- Aside: a brief introduction to XAS
- Methanol oxidation catalysts
- Sn-based lithium ion battery anodes
- Nanofluid battery electrodes
- Final thoughts

Acknowledgements

Illinois Institute of Technology

- John Katsoudas – Physics & CSRRI
- Vijay Ramani - Chemical Engineering
- Elena Timofeeva – Chemistry & CSRRI

Argonne National Laboratory

- Sujat Sen – Energy Systems Division

IIT Graduate Students

- Chris Pelliccione – Physics
- Yujia Ding – Physics
- Yue Li – Chemical Engineering
- Nathaniel Beaver – Physics
- Shankar Aryal – Physics
- Elahe Moazzen – Chemistry

Supported by DOE ARPA-e

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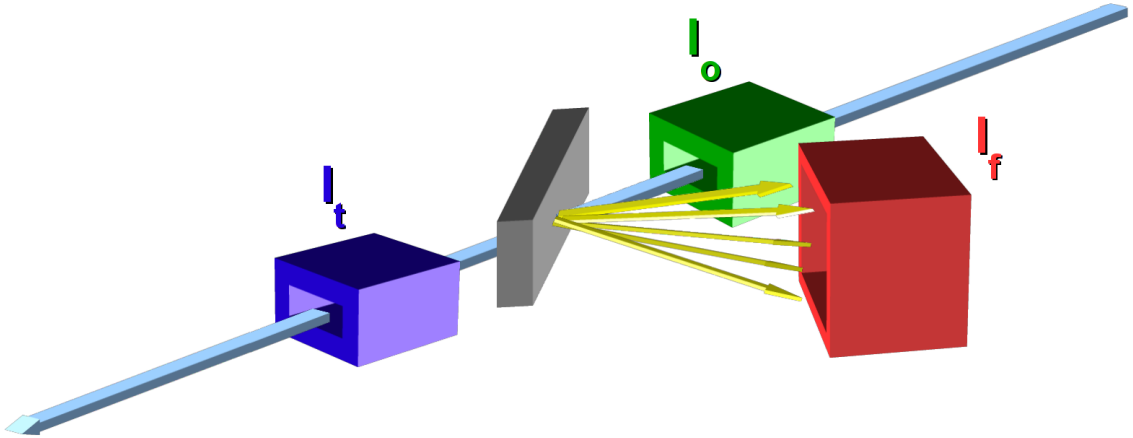
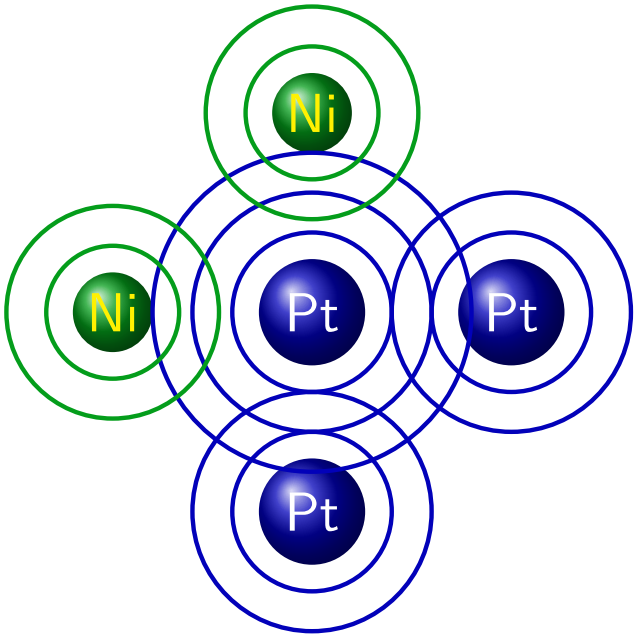
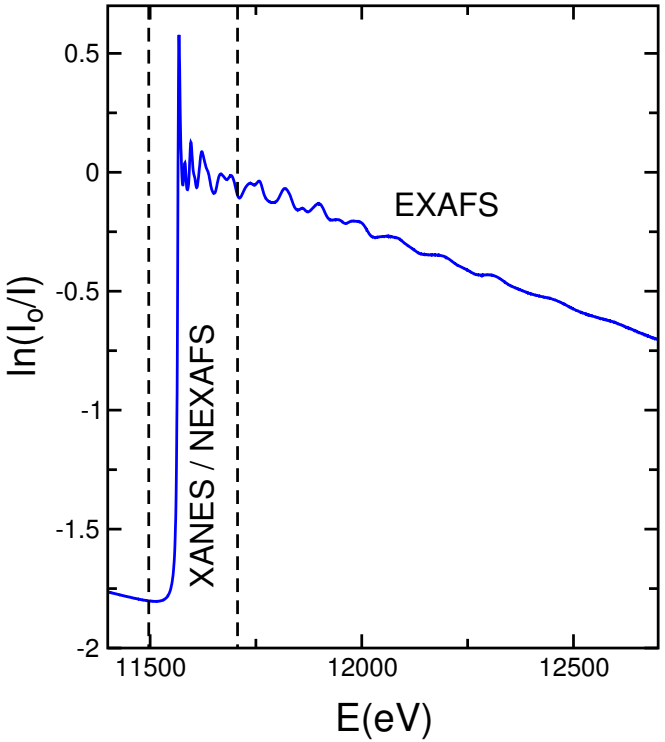
The EXAFS experiment

- Conceptually simple
- Transmission or fluorescence
- "Sees" amorphous phases & local structural distortions







The EXAFS equation

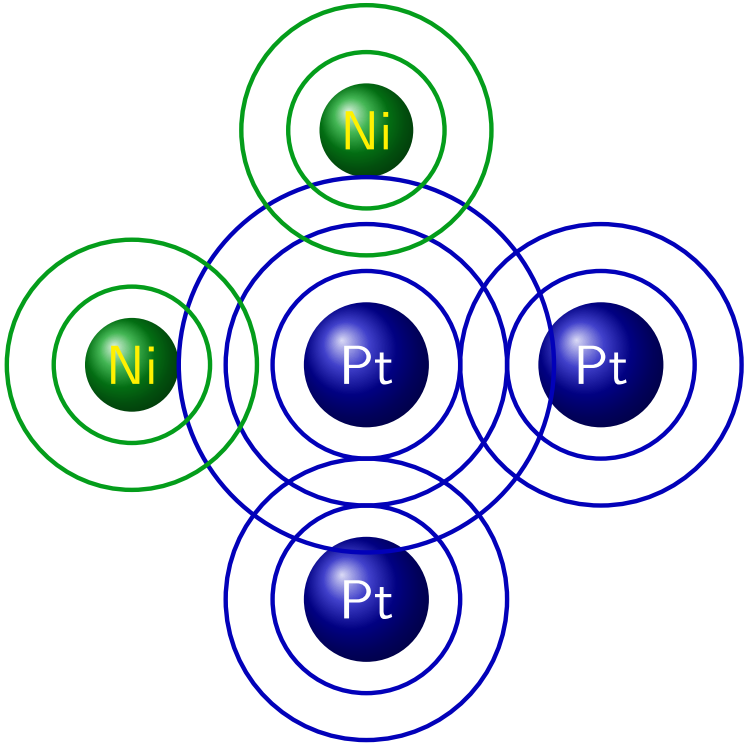
The EXAFS oscillations can be modelled and interpreted using a conceptually simple equation (the details are more subtle!)

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k)}{k R_j^2} e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin\left[2R_j + \delta_j(k)\right]$$

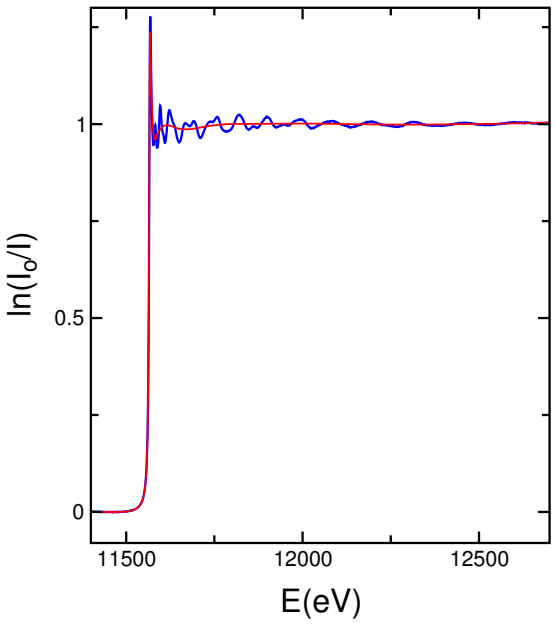
The sum could be over shells of atoms (Pt-Pt, Pt-Ni) or over scattering paths for the photo-electron.

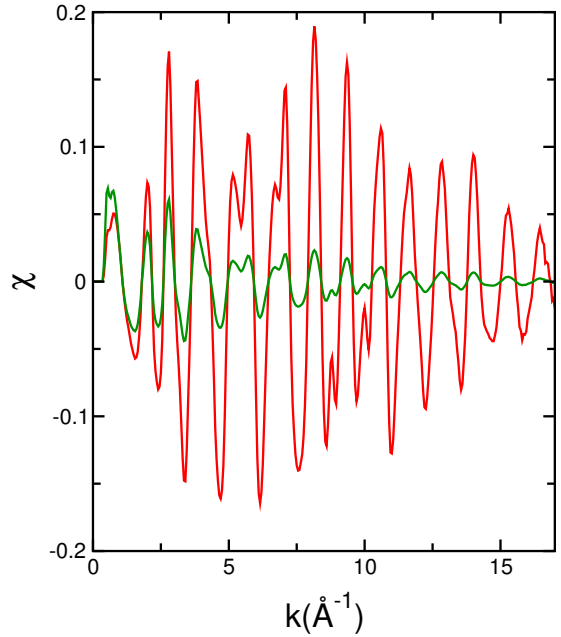
$f_j(k)$: scattering factor for the path
$\lambda(k)$: photoelectron mean free path
$\delta_j(k)$: phase shift for the jth path

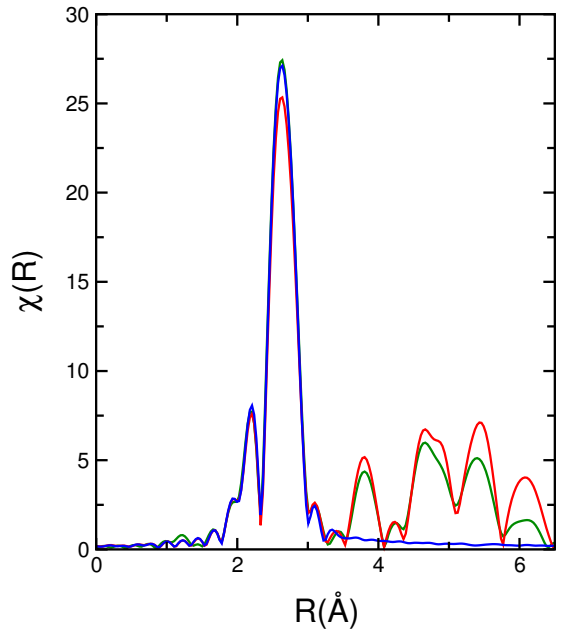
N_j: number of paths of type j
R_j: half path length
σ_j: path "disorder"



EXAFS challenges







normalize edge jump

remove background

apply Fourier transform

model to extract structural parameters:
N_j, R_j, σ_j

- General Challenges

  Sample optimization

  Careful experimentation

  Physical model

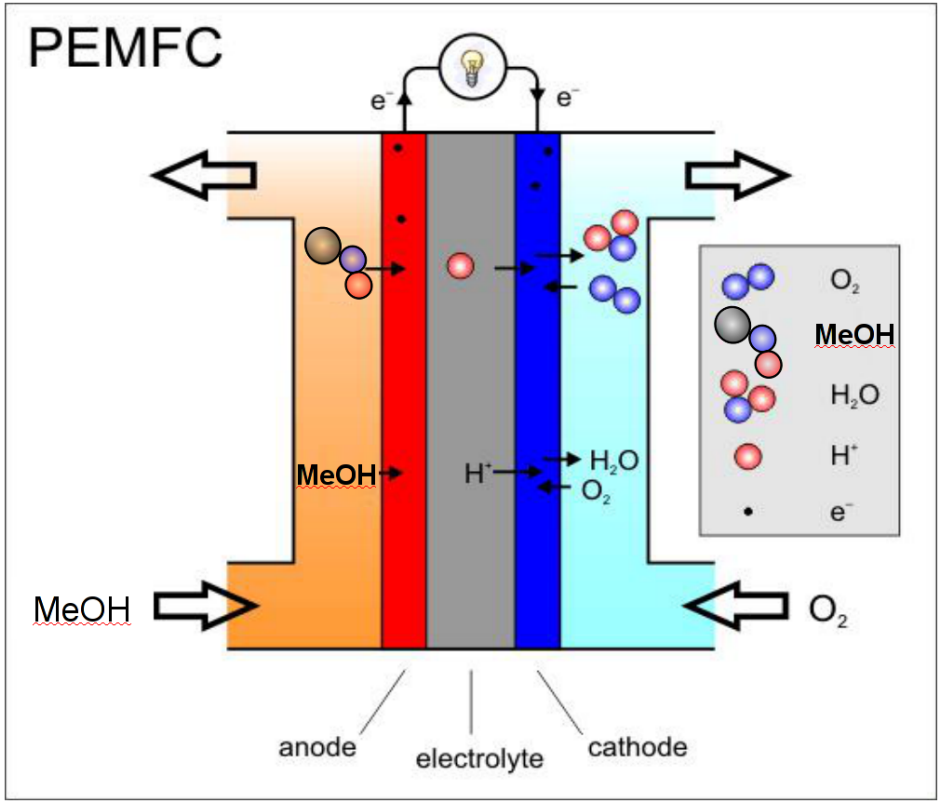
- *In situ* electrocatalyst & battery EXAFS

  Making it work!

  Heterogeneous systems

  Asking the right questions

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

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

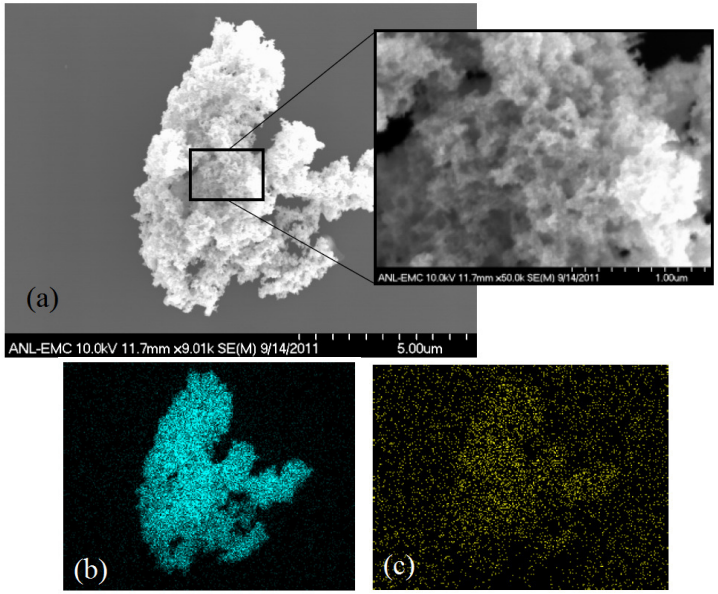
Pt surface poisoned by CO

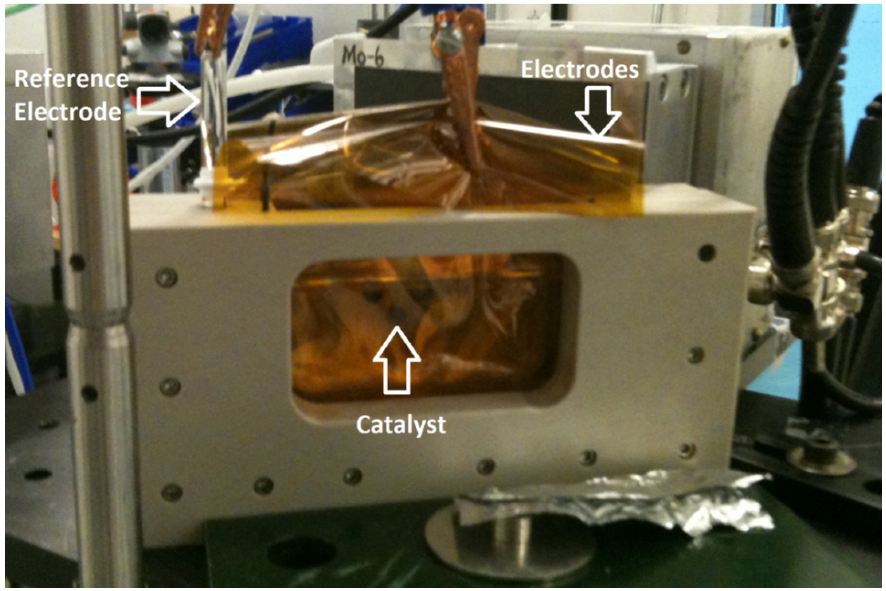
Ru promotes CO oxidation through a "bi-functional mechanism"

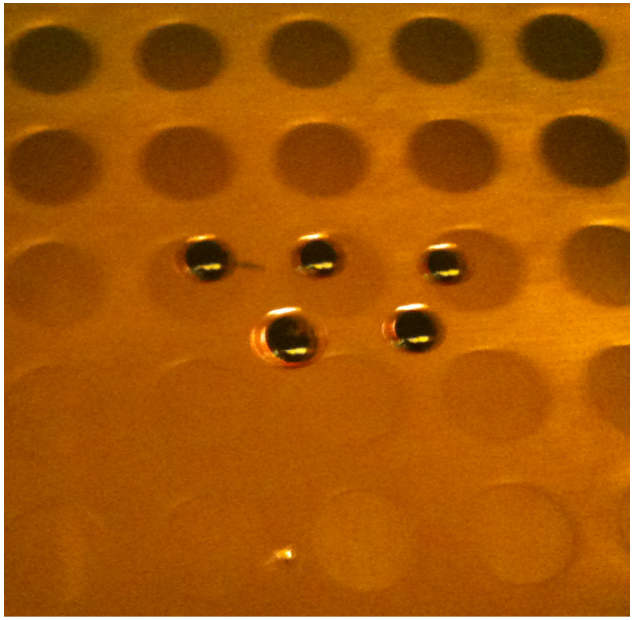
$$Pt{-}(CO)_{ads} + Ru{-}OH \longrightarrow Pt + RuCO_2 + H^+ + 2\,e^-$$

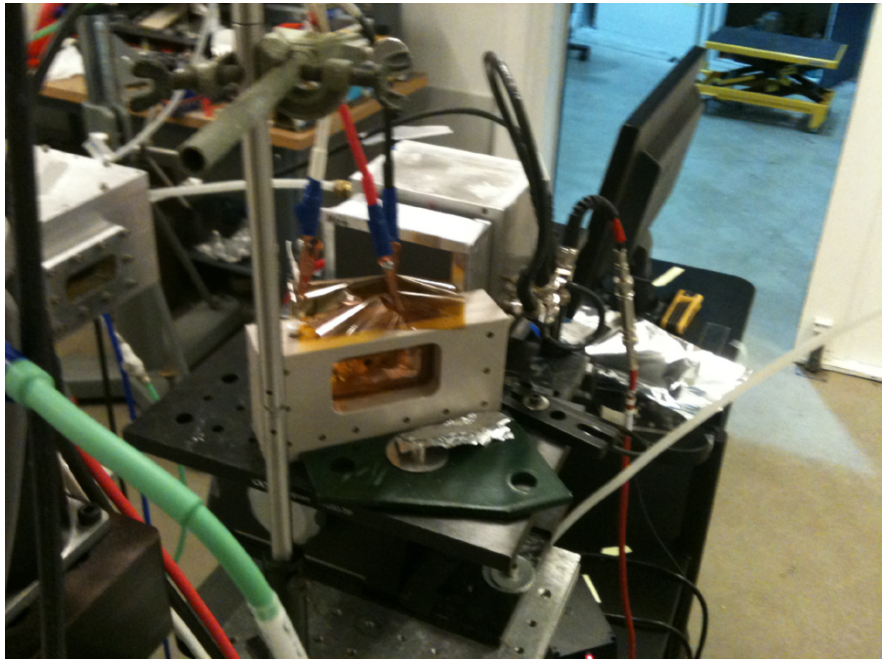
Further improvements require fundamental understanding of the mechanism

Ru-decorated Pt nanoparticles

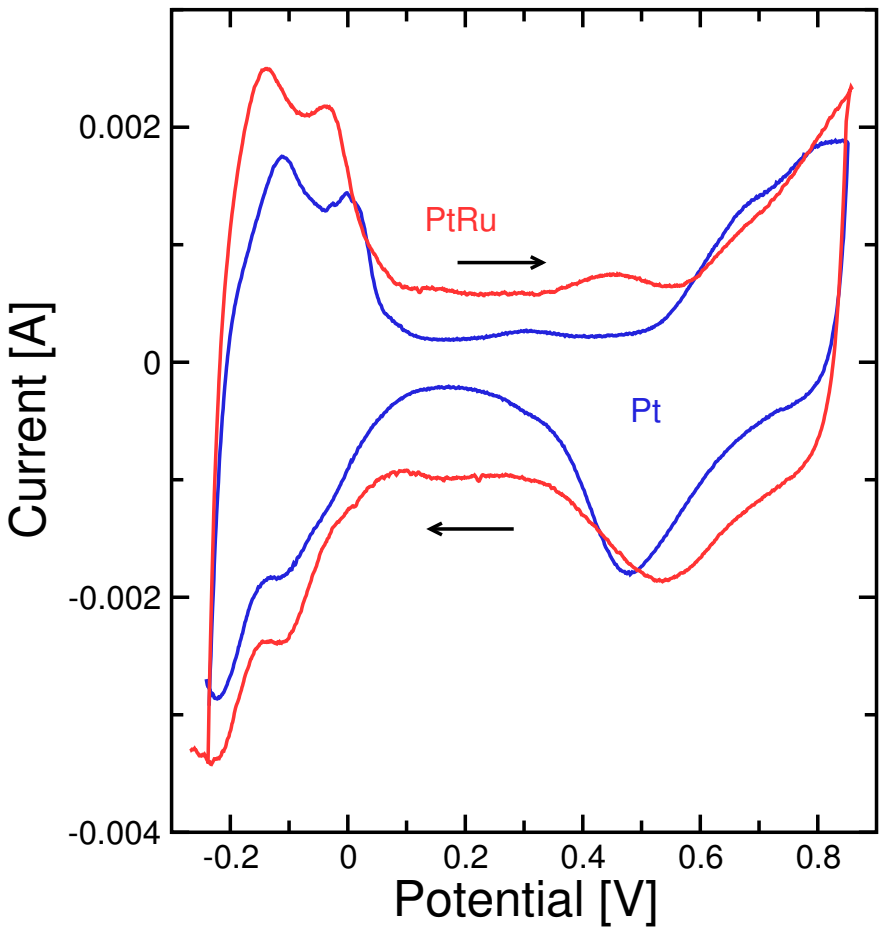








Electrochemical performance



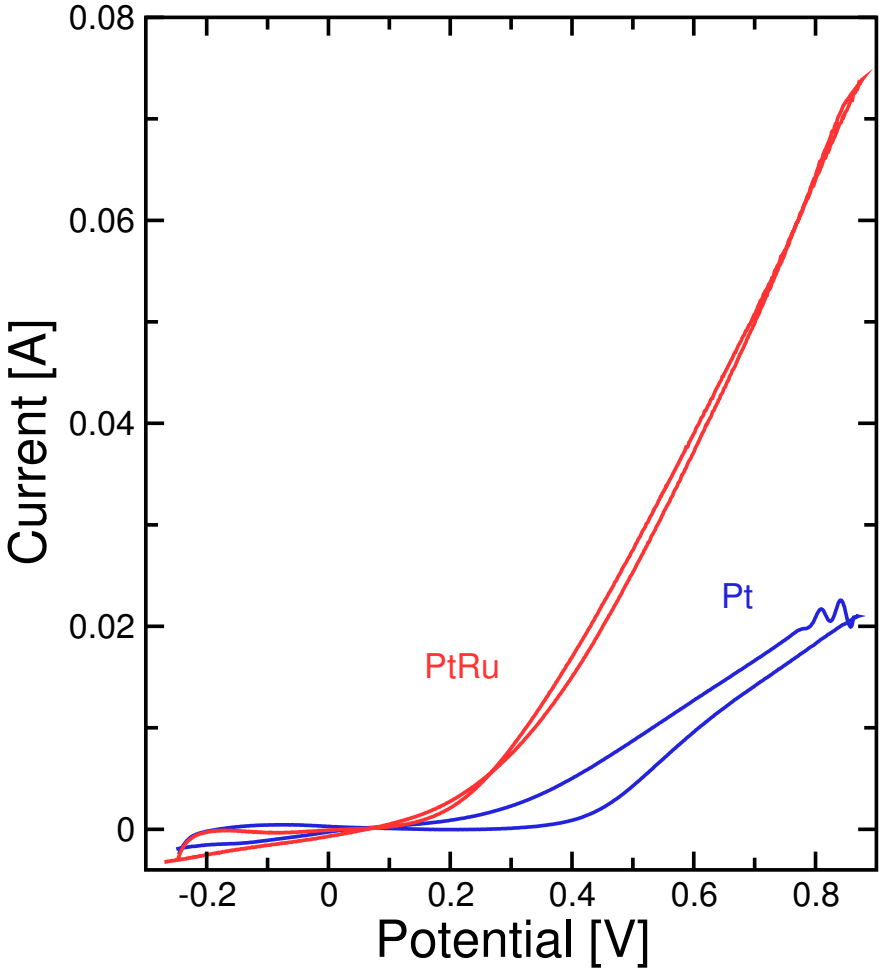
Without Methanol

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

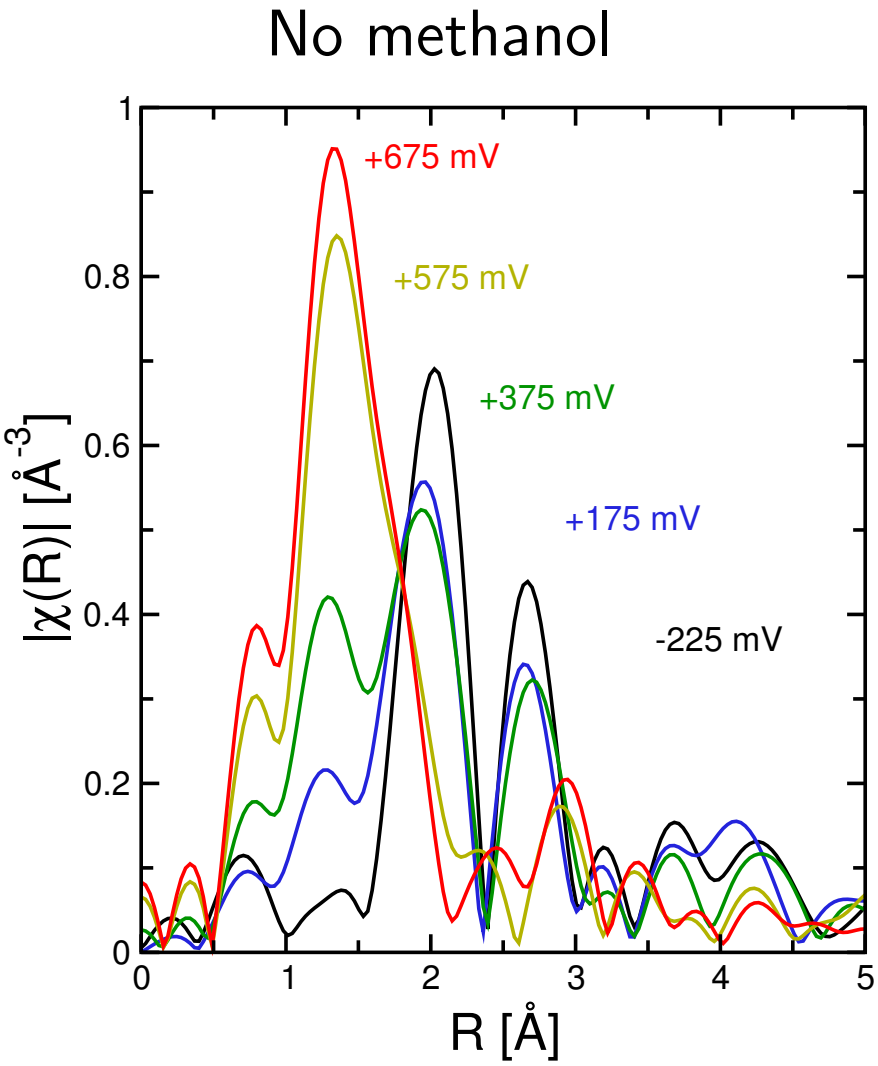
Ru shifts potential on all peaks

With Methanol

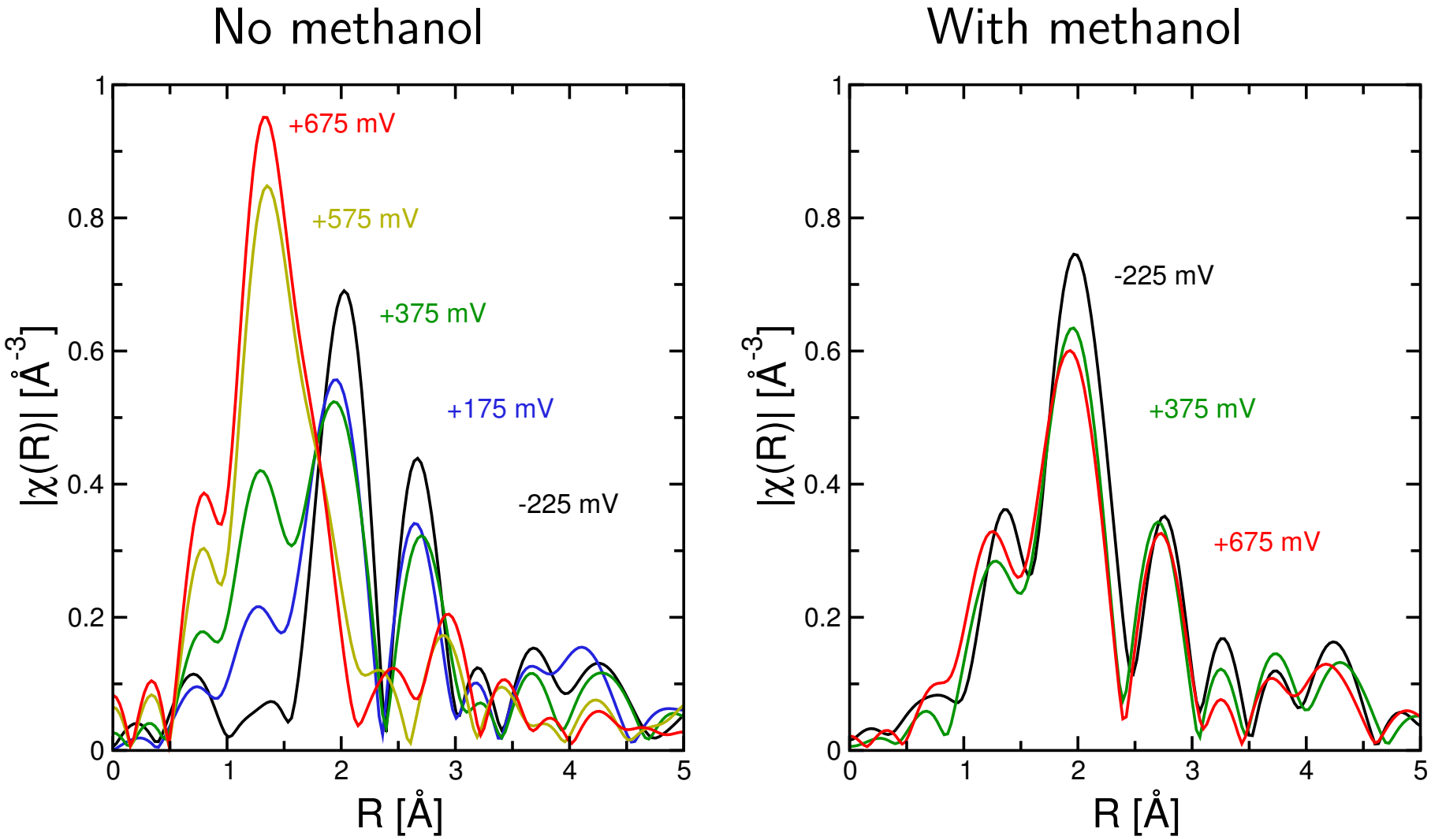
Ru lowers activation potential from $\sim$ 400mV to $\sim$ 175mV

Ru improves current output by over 3.5$\times$

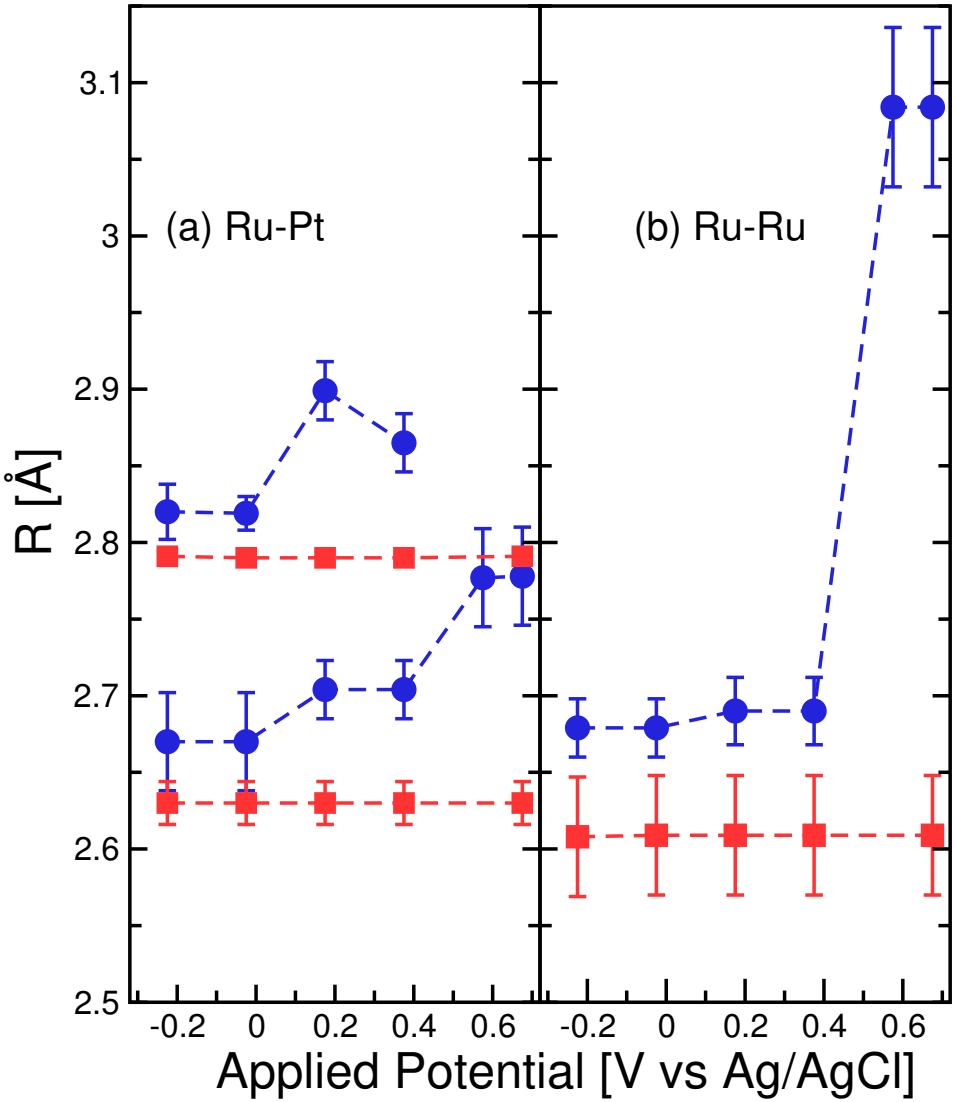
Ru EXAFS


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
+375 mV
+675 mV
|χ(R)| [Å^-3]
R [Å]

Ru-M paths



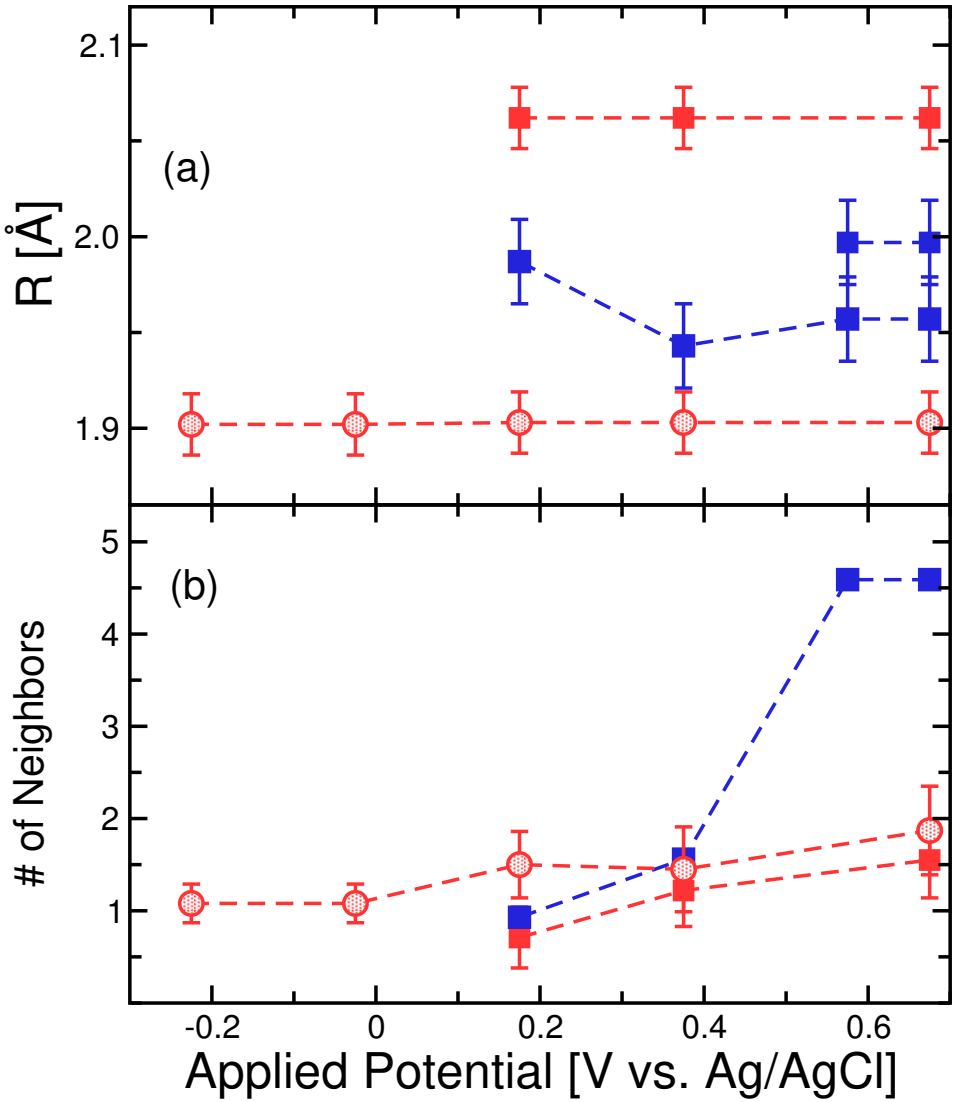
Without methanol

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



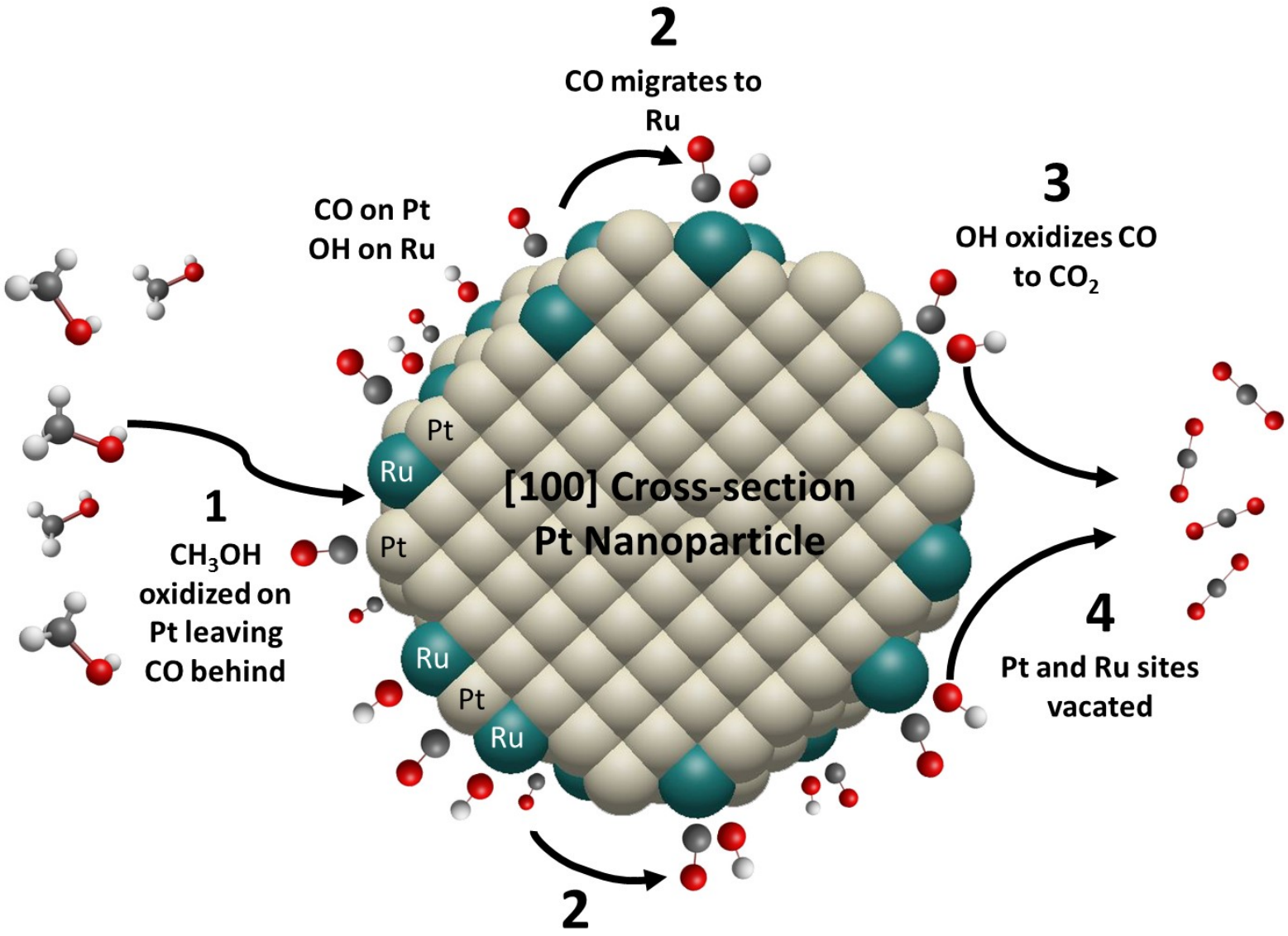
Without methanol

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

With methanol

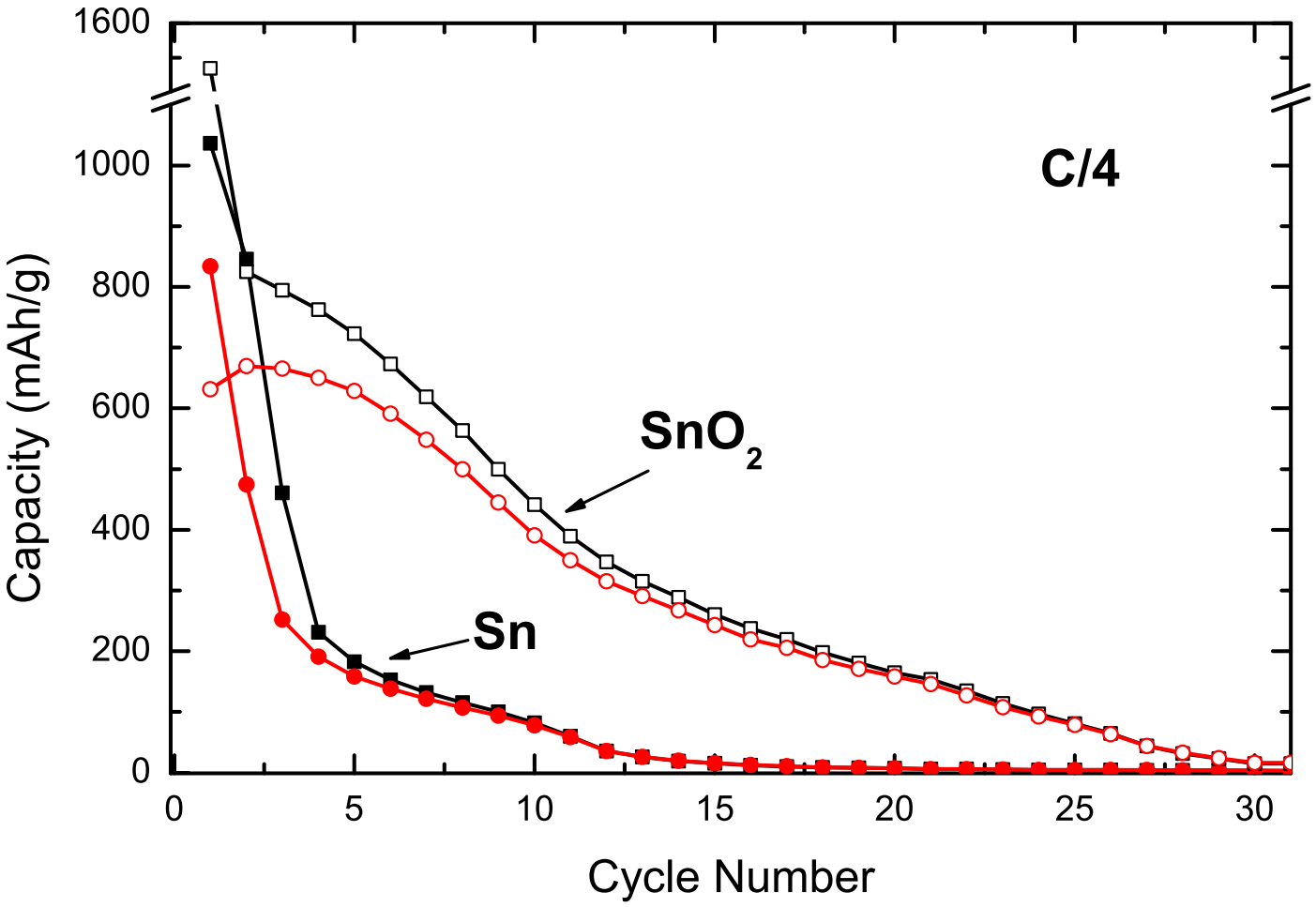
Ru has one low Z neighbor at all potentials (carbon); a second above 175 mV (oxygen) with constant bond lengths and slightly increasing numbers

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**, 18904-18912 (2013).

High capacity Sn-based battery anodes

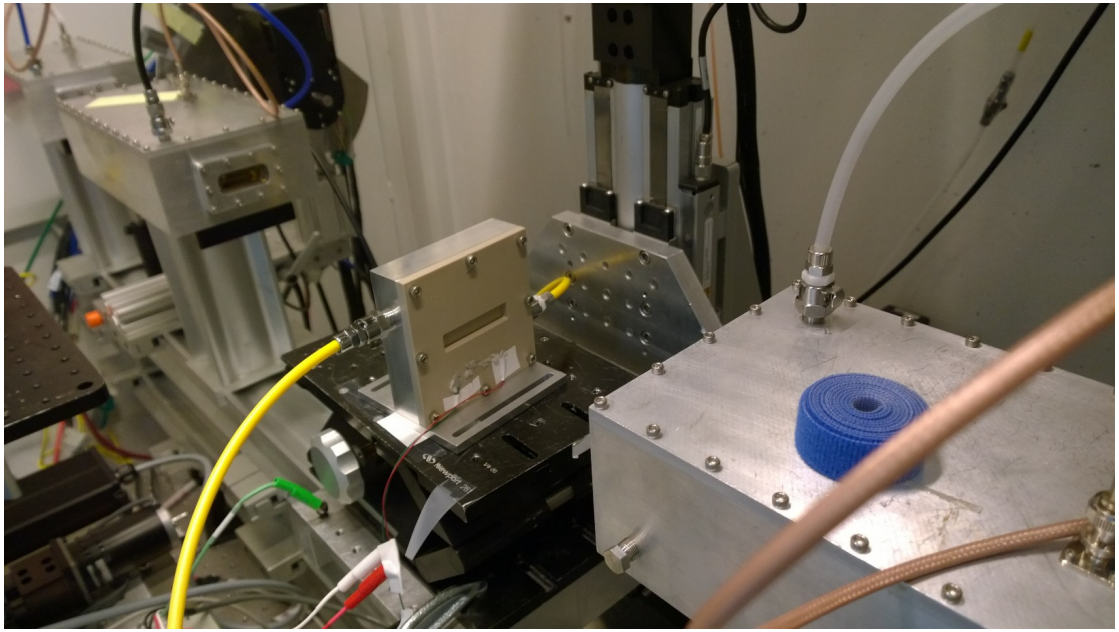


Sn-based anodes have high initial capacity but poor cyclability

In situ EXAFS can help to understand the details of lithiation

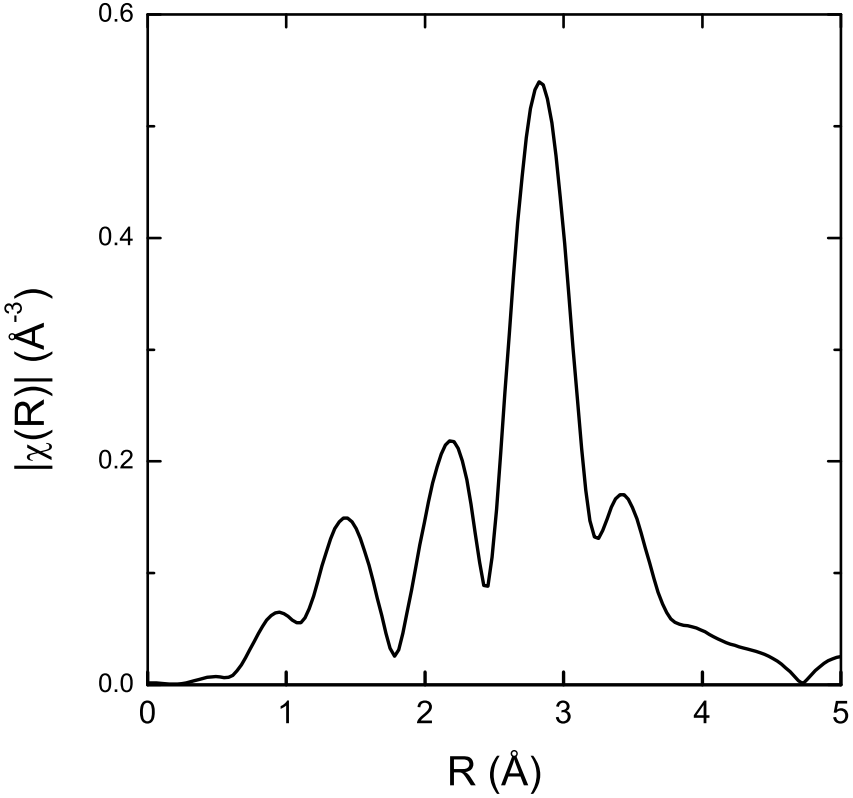
In situ lithiation of Sn

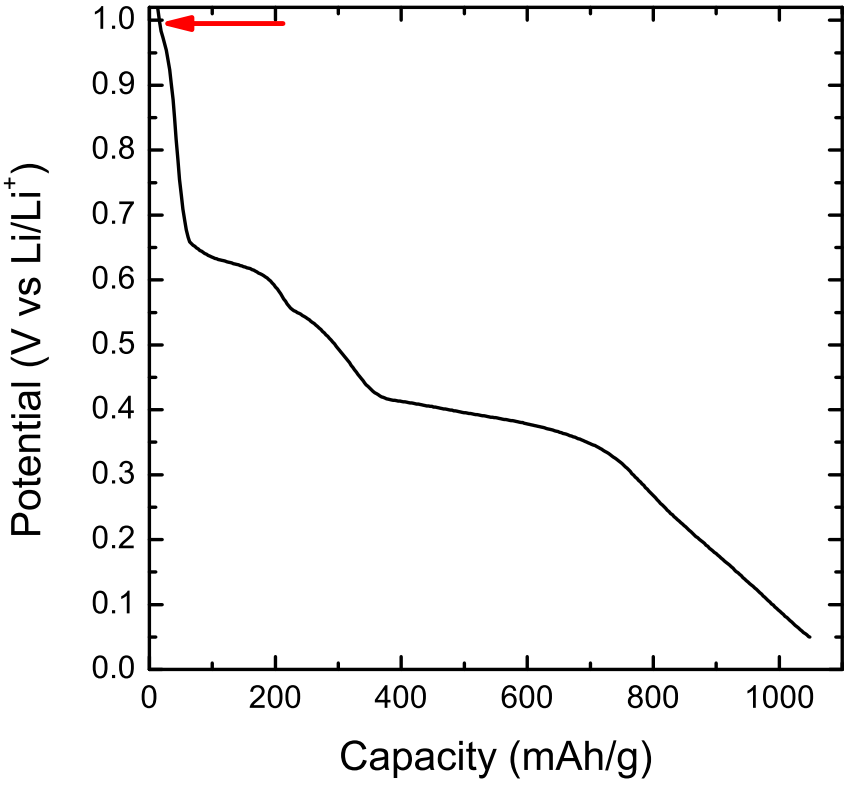
- In situ box for non-aqueous experiments
- Have measured $Sn_3O_2(OH)_2$, SnO_2, Sn, ZnO, MoO_2 ...
- Pouch cell simplifies experiment



- 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 using 3 composite paths

Sn EXAFS versus potential

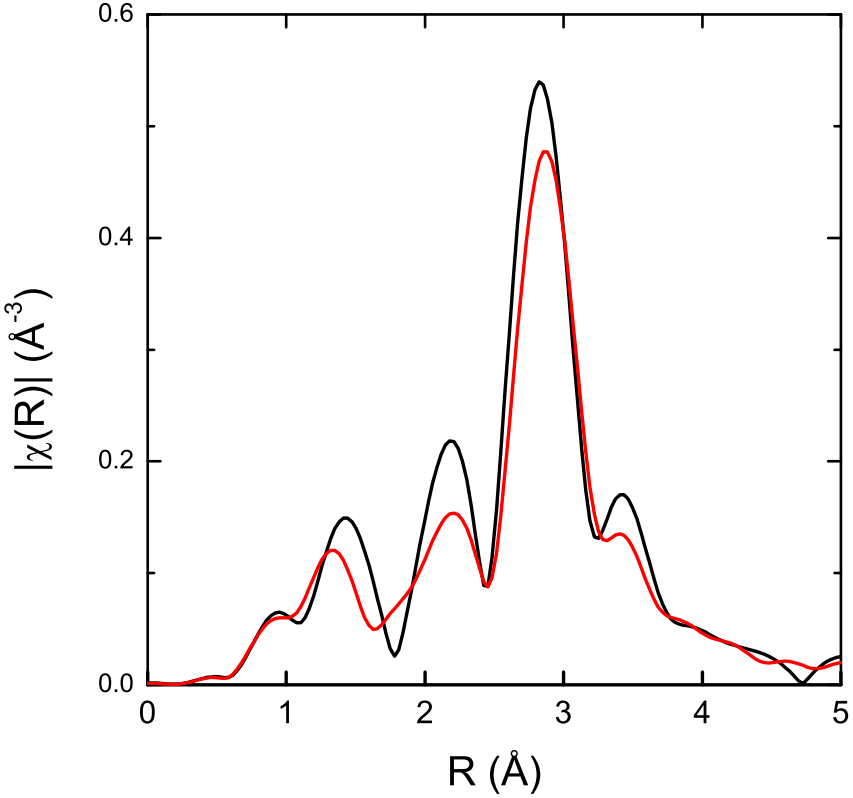


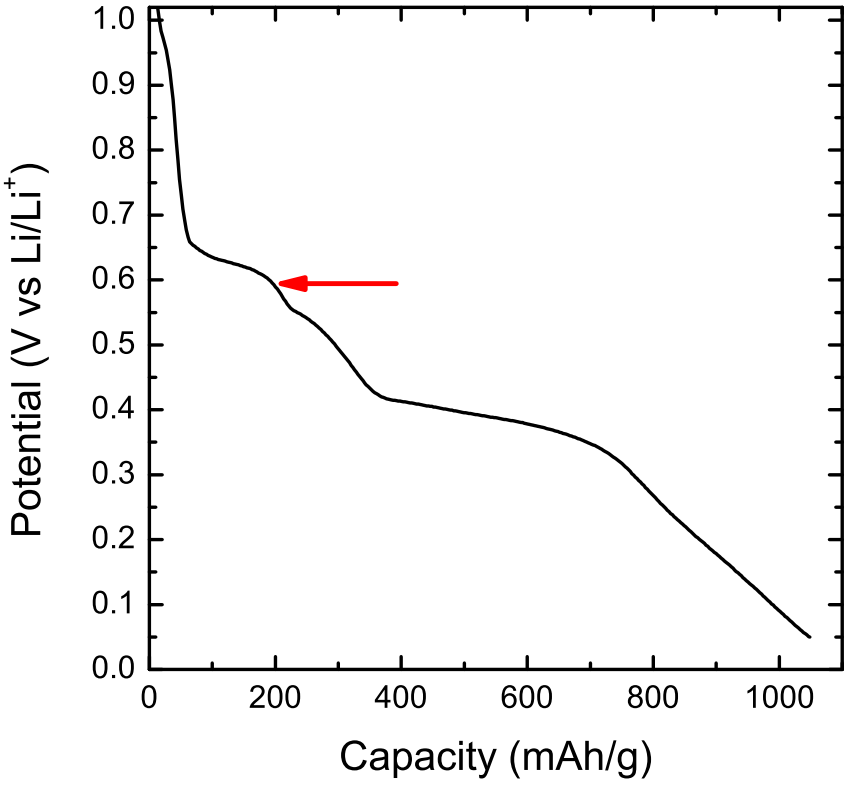


$Li_{22}Sn_5$ has 14 Sn-Li paths with distance 3.4Å or less

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

Sn EXAFS versus potential





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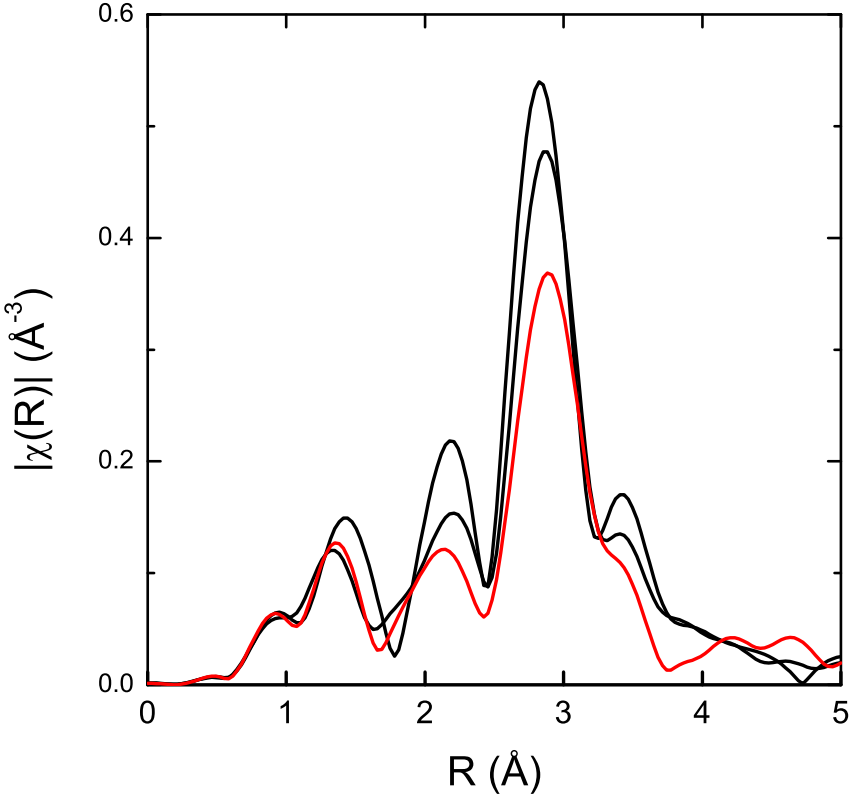

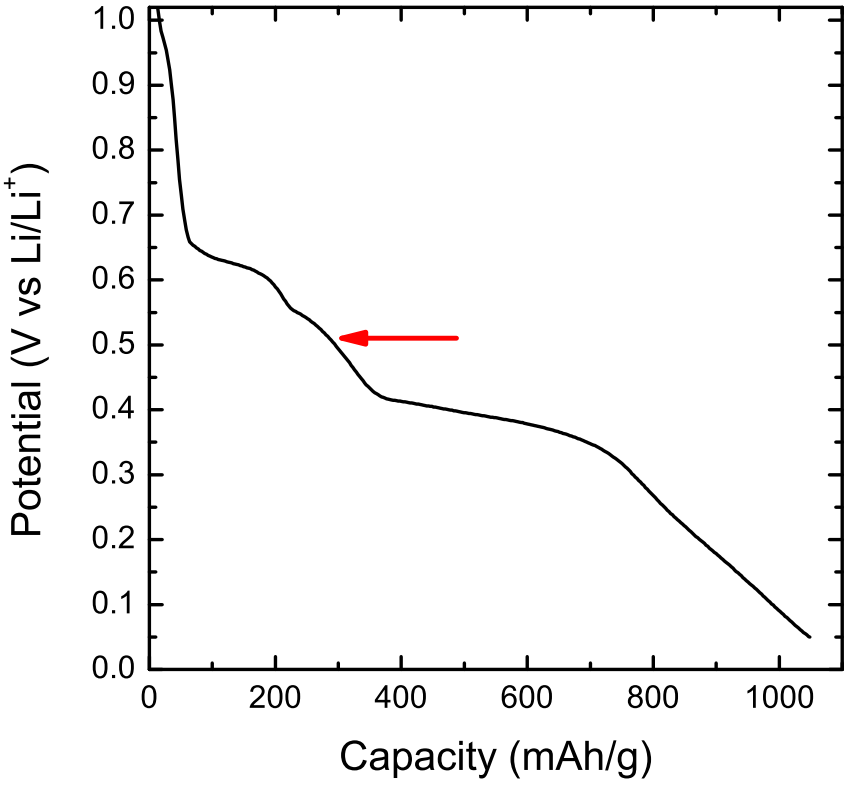

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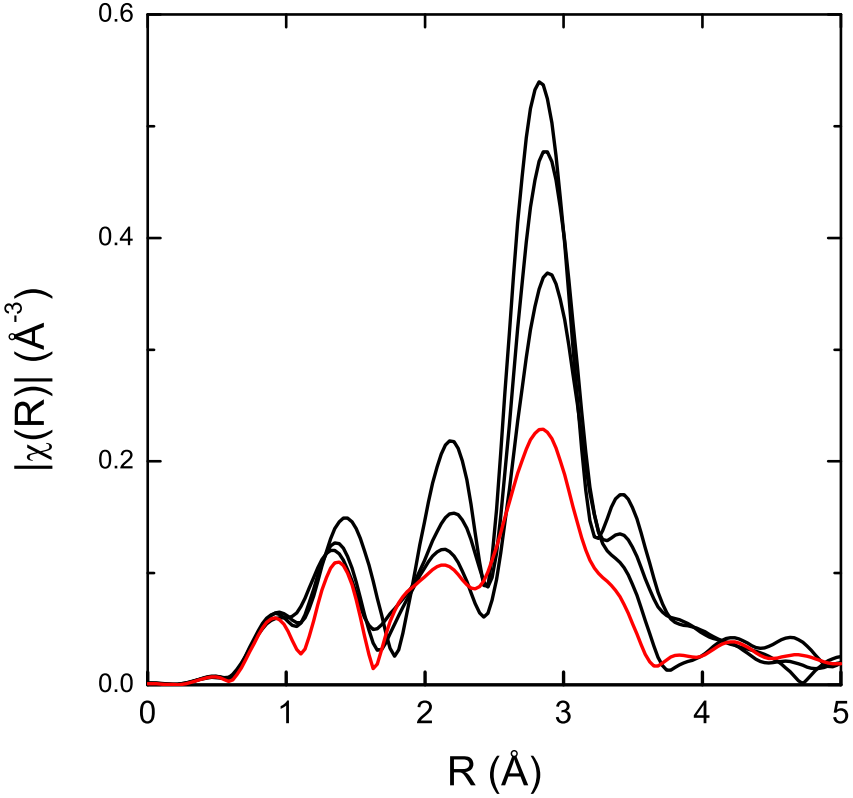

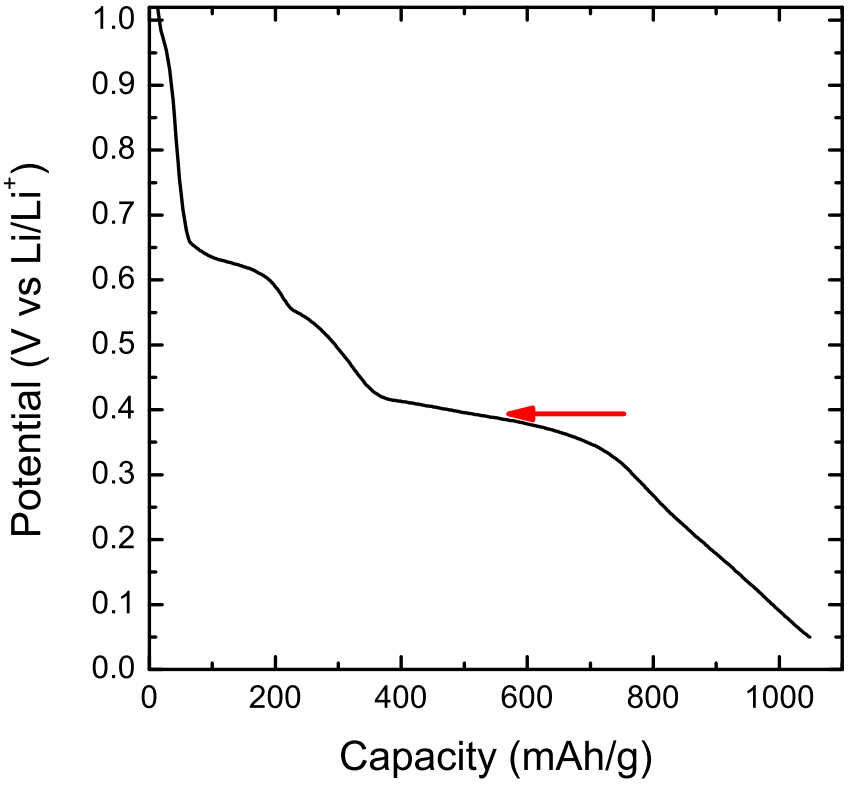

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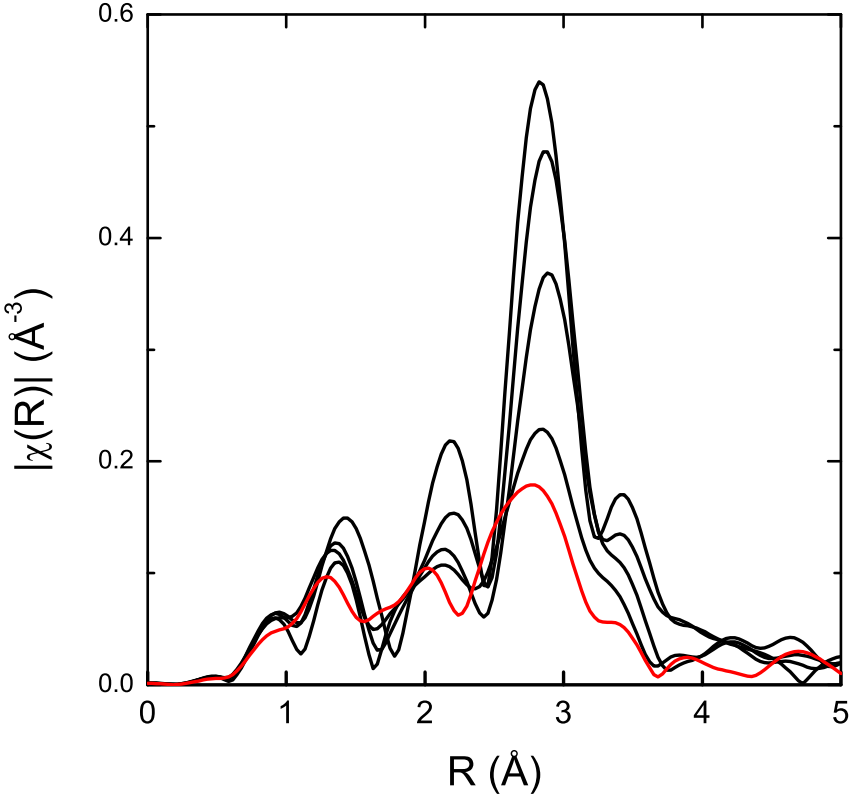

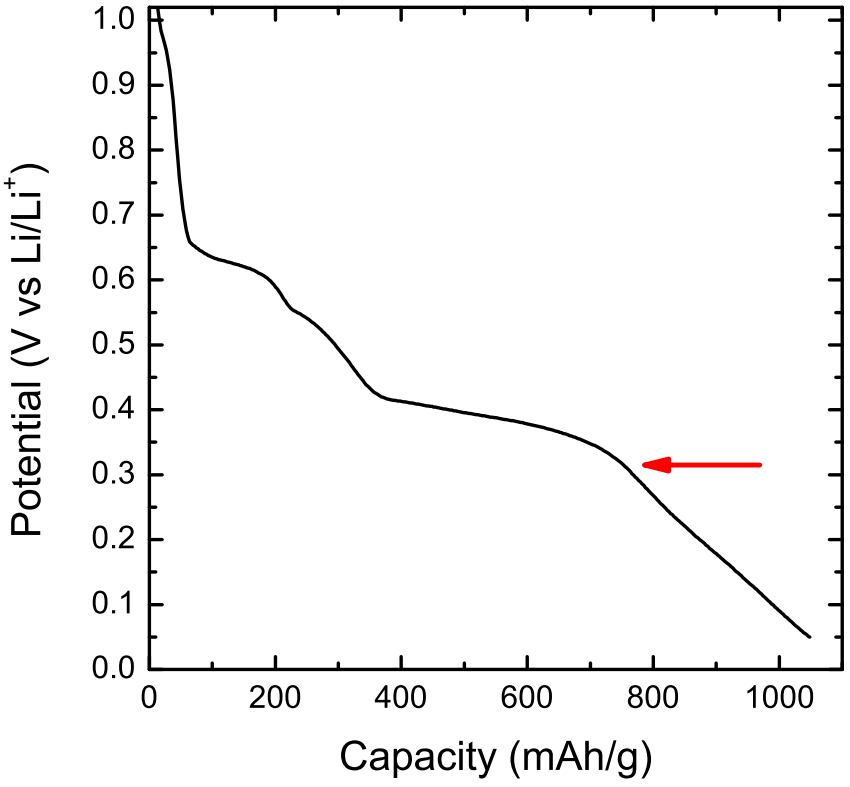

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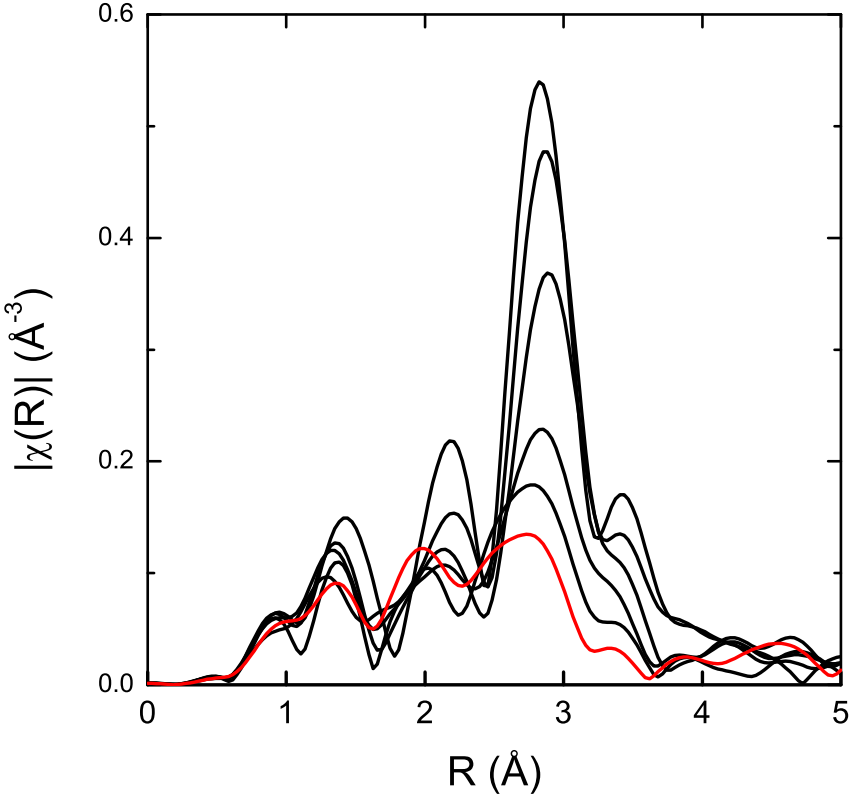
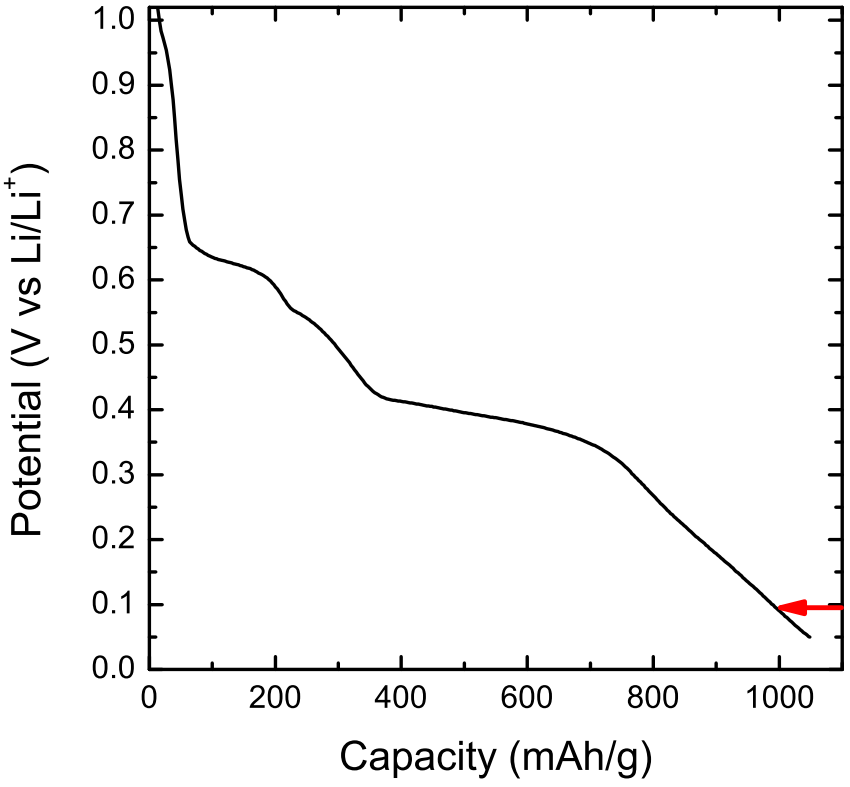
Sn EXAFS versus potential





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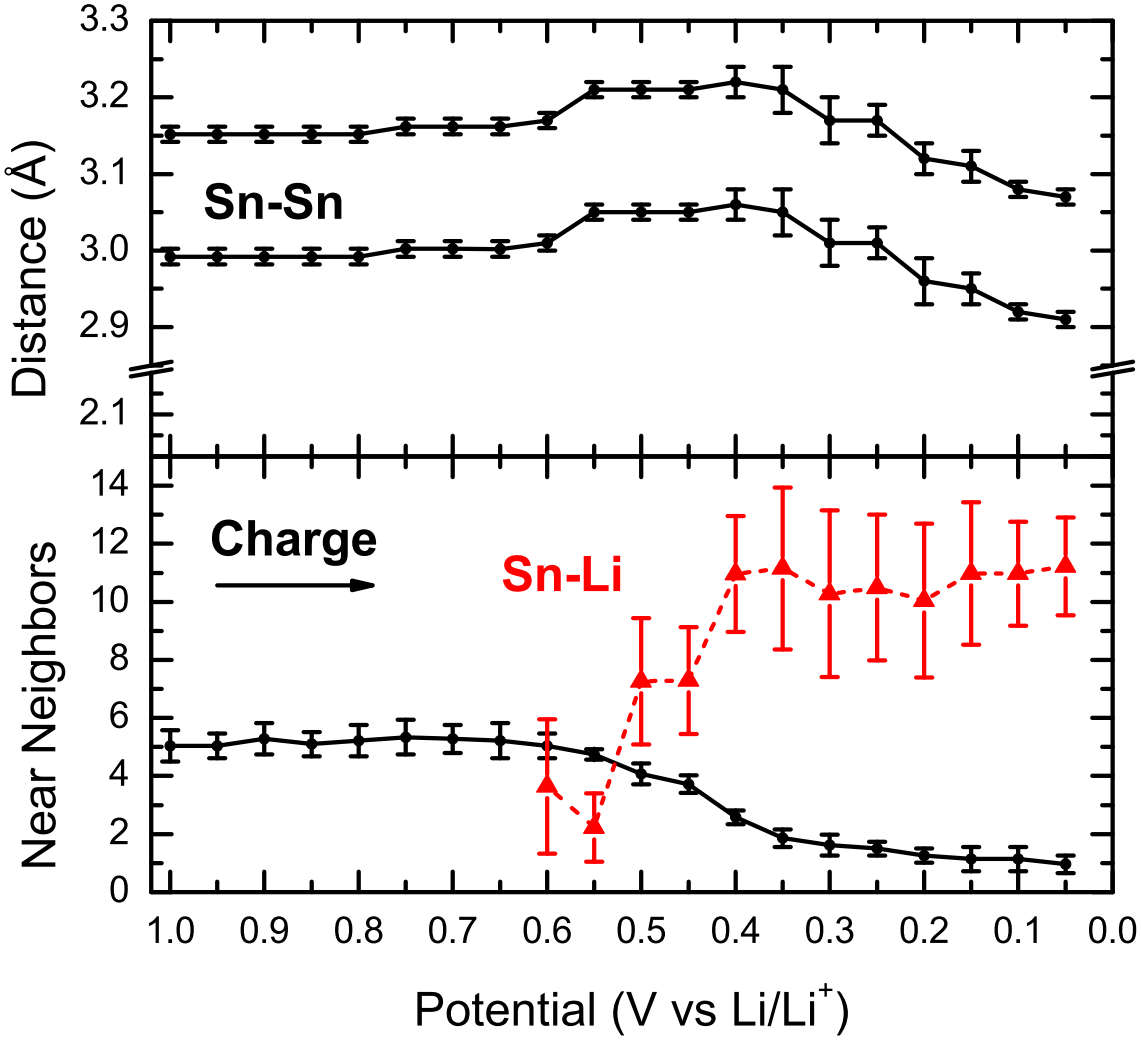
The Sn lithiation process



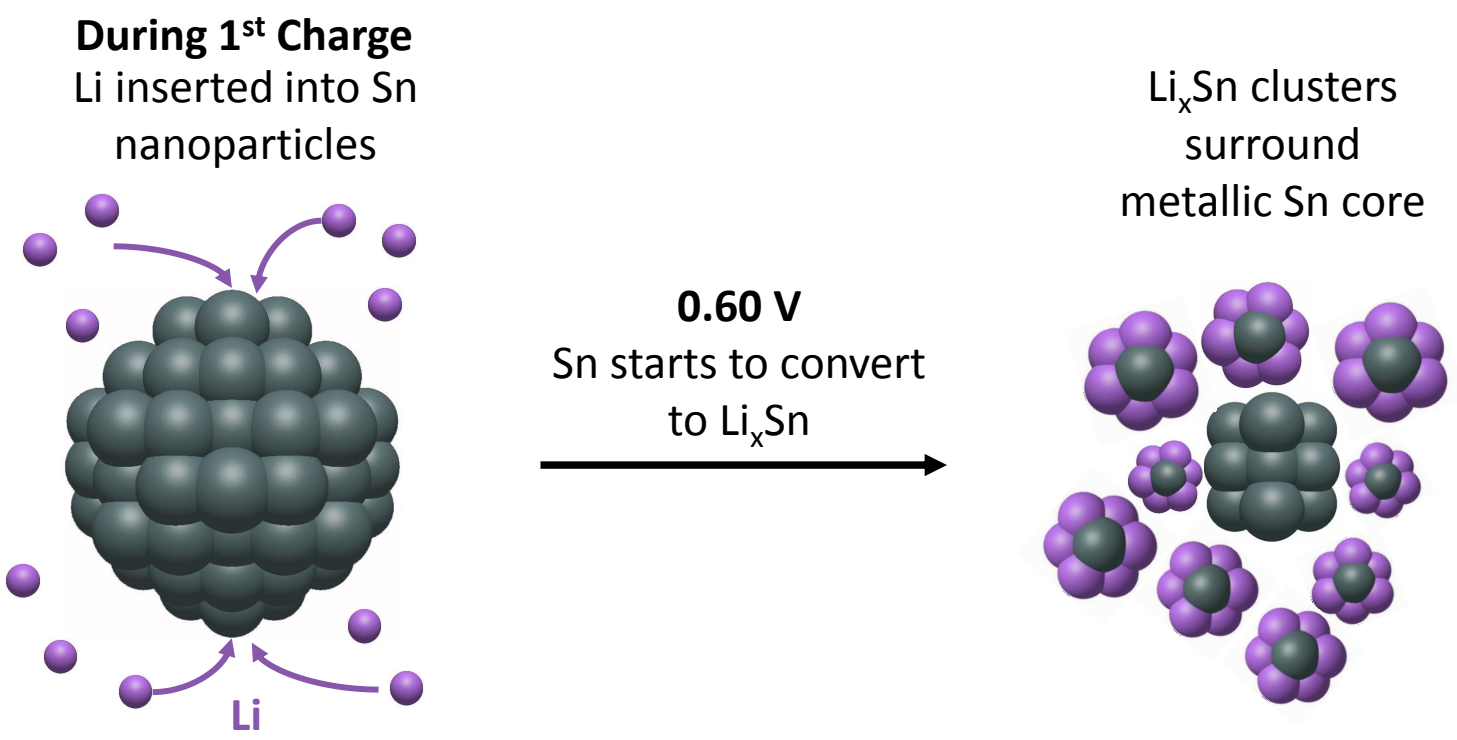
0.60V – Sn metal begins to break down and Li appears

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

Sn-Sn bonds (Sn metal) never completely disappear

On subsequent delithiation and lithiation cycles, the total number of incorporated Li continues to decrease.

Sn nanoparticle degradation mechanism

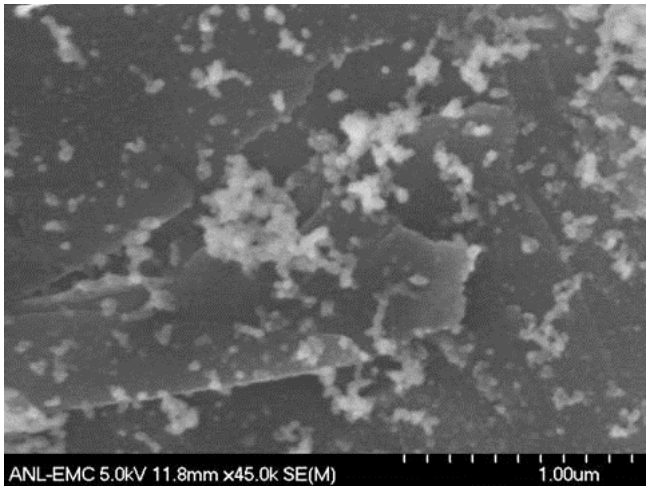


The Sn nanoparticles do not fully lithiate, the conversion on the outside of the particle electrically isolates the clusters and the metallic core

SnO_2 is somewhat better but still shows the effects of electrical isolation

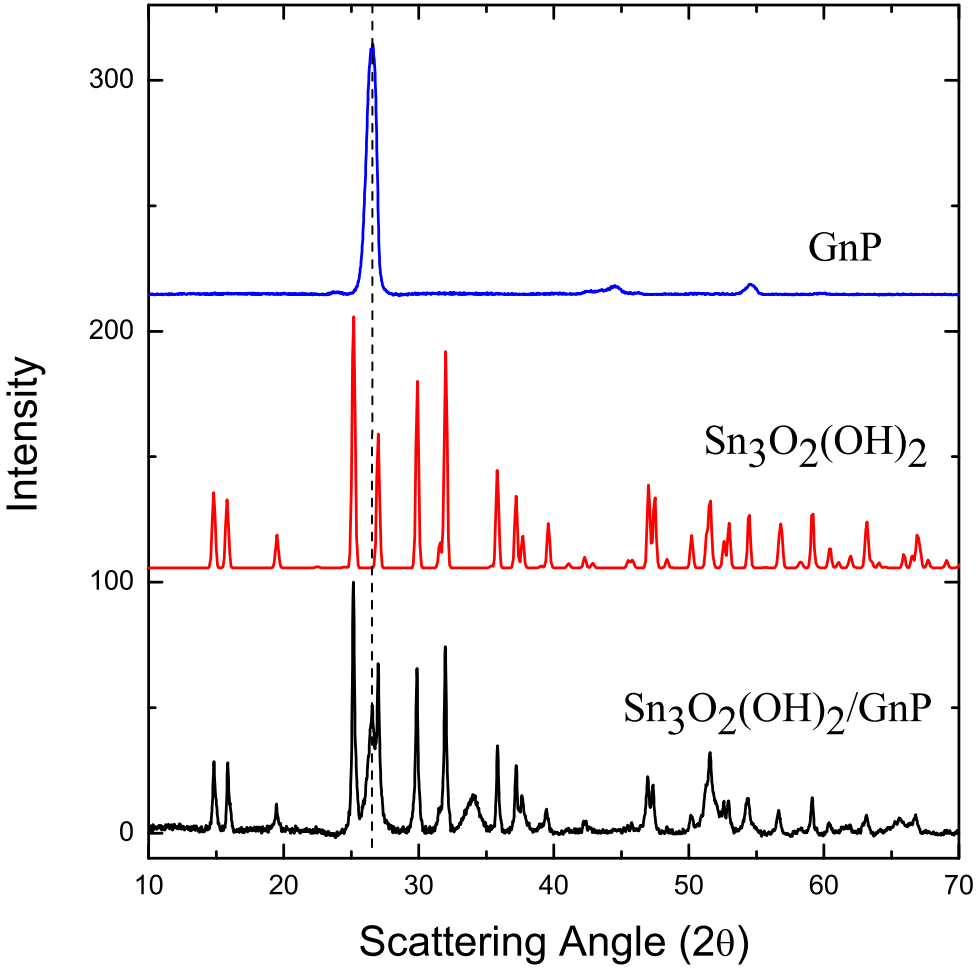
C. Pelliccione et al. "Potential-resolved in situ x-ray absorption spectroscopy study of Sn and SnO_2 nanomaterial anodes for lithium-ion batteries," *J. Phys. Chem.* **C 120**, 5331-5339 (2016).

Synthesis of Sn-graphite nanocomposites

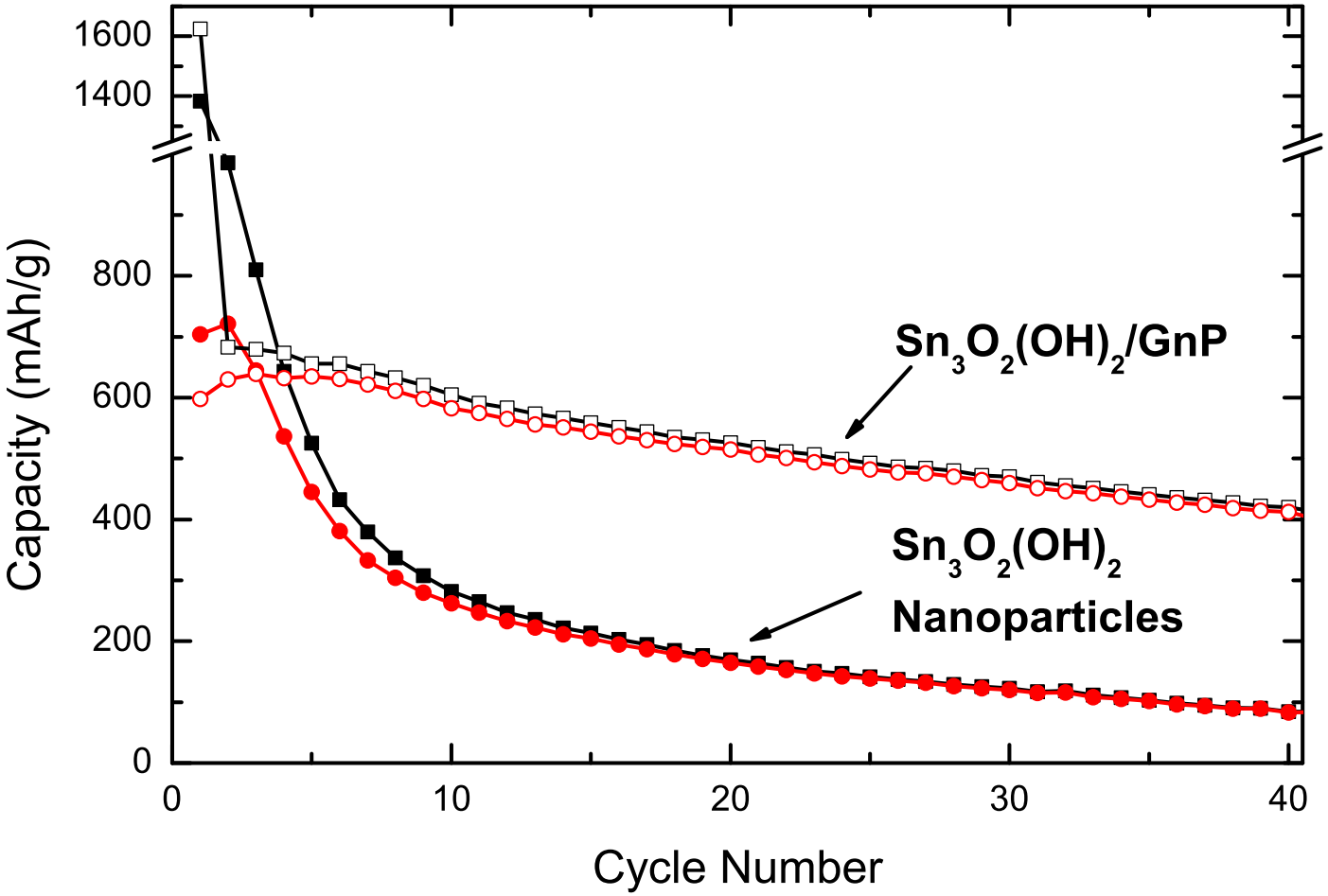


One-pot synthesis produces evenly distributed $Sn_3O_2(OH)_2$ nanoparticles on graphite nanoplatelets

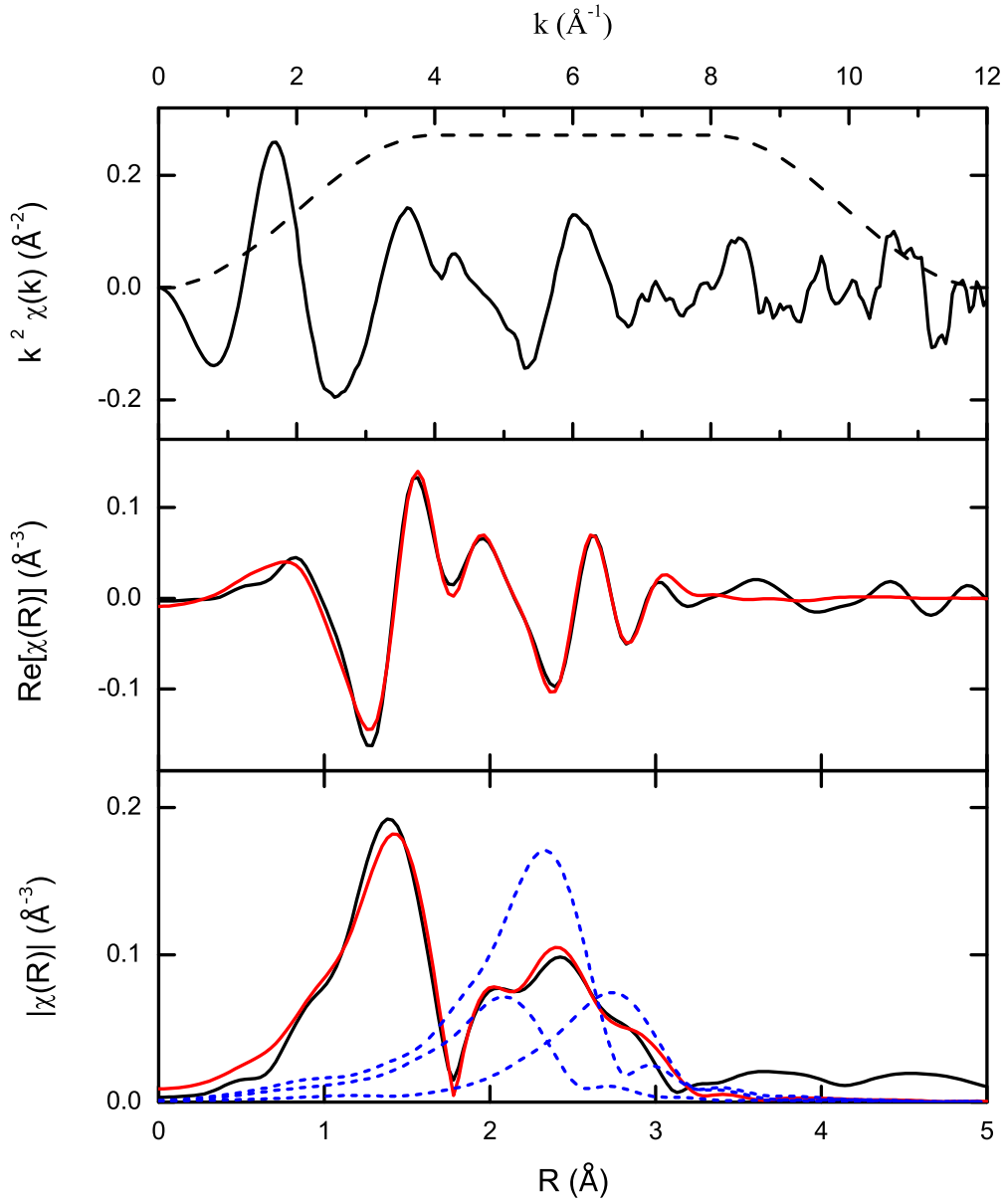
XRD shows a small amount of Sn metal in addition to $Sn_3O_2(OH)_2$



$Sn_3O_2(OH)_2$ capacity comparison



In situ XAS of $Sn_3O_2(OH)_2$

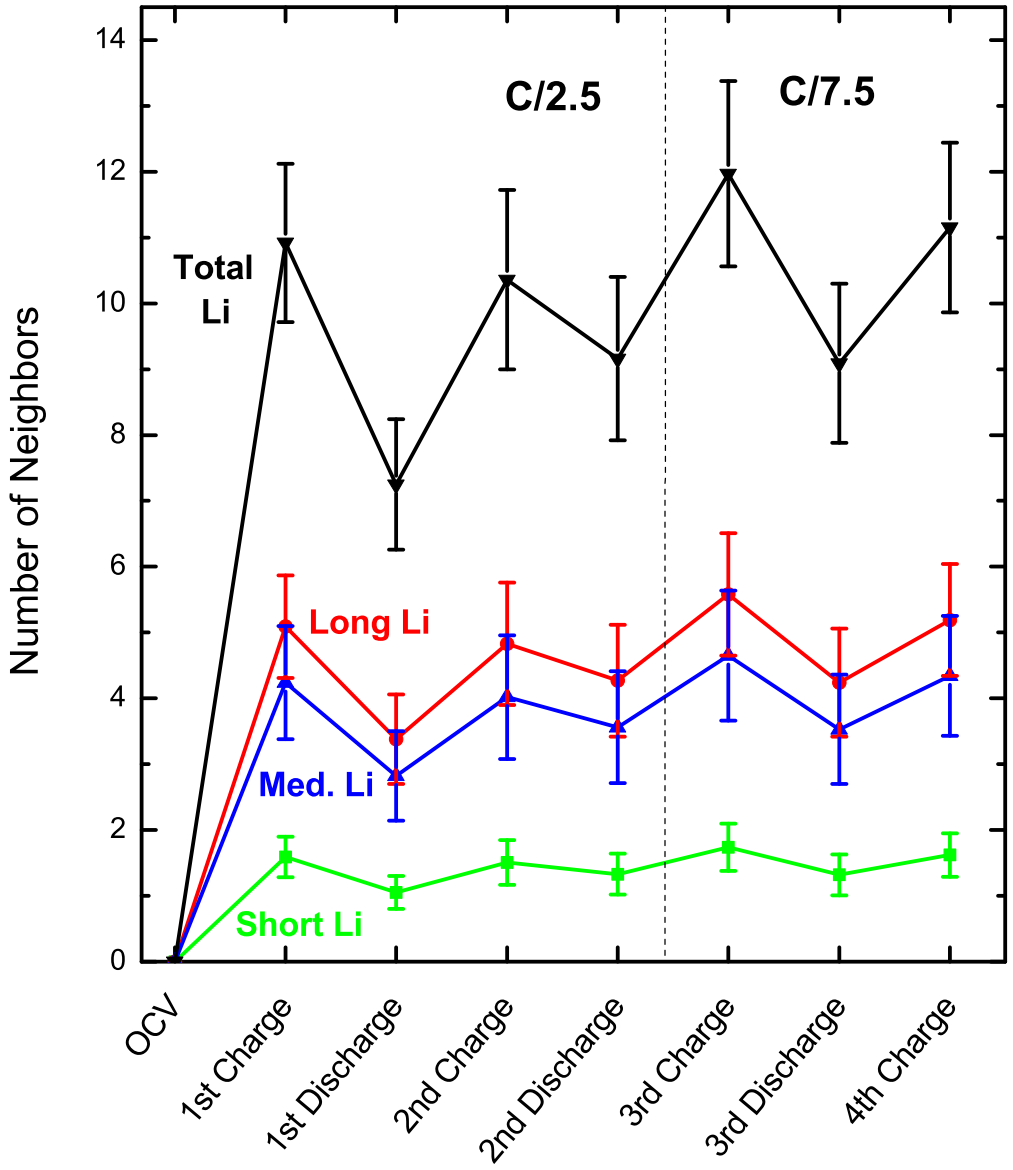


After first lithiation, Sn-O near neighbors significantly reduced

3 Sn-Li paths characteristic of the $Li_{22}Sn_5$ structure are prominent

No Sn-Sn paths typical of metallic Sn are present

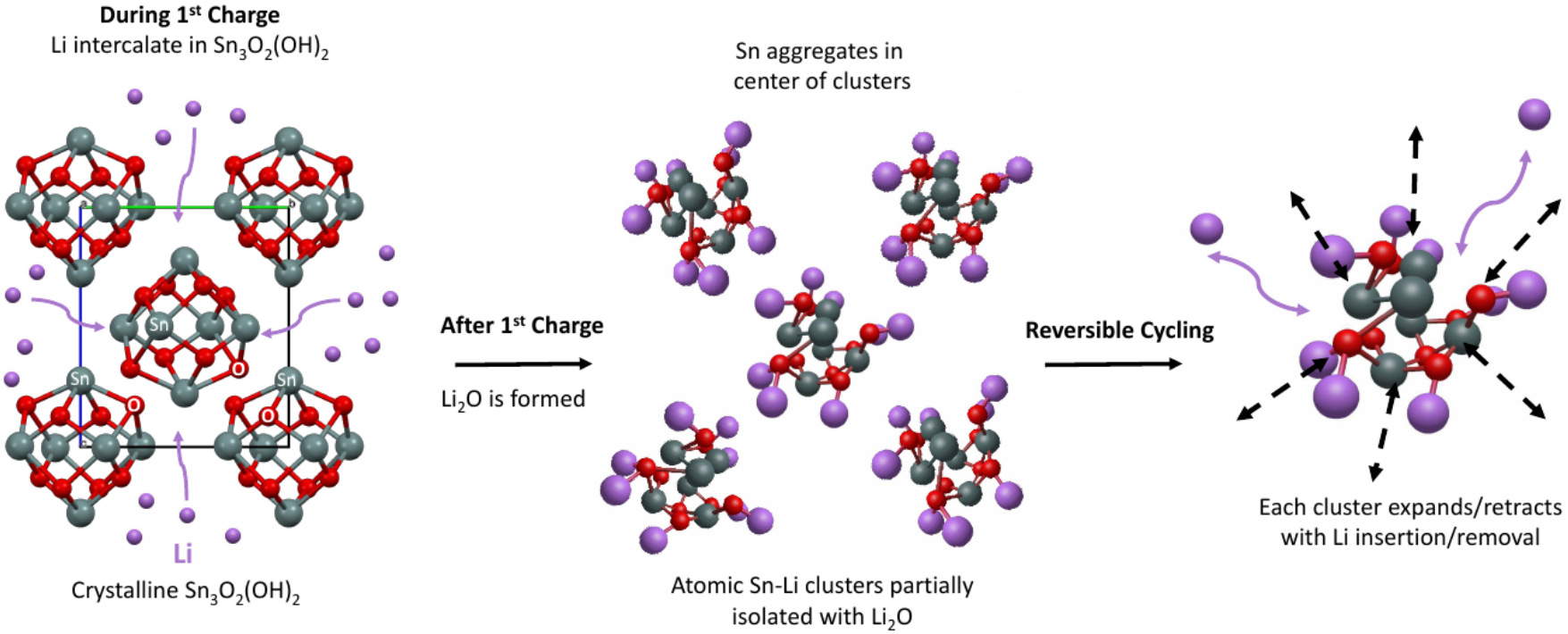
$Sn_3O_2(OH)_2$ lithium content



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

In situ cell promotes accelerated aging because of the reduced pressure of the thin PEEK pouch cell assembly. New cell designs can significantly improve *in situ* cyclability.

$Sn_3O_2(OH)_2$ lithiation mechanism

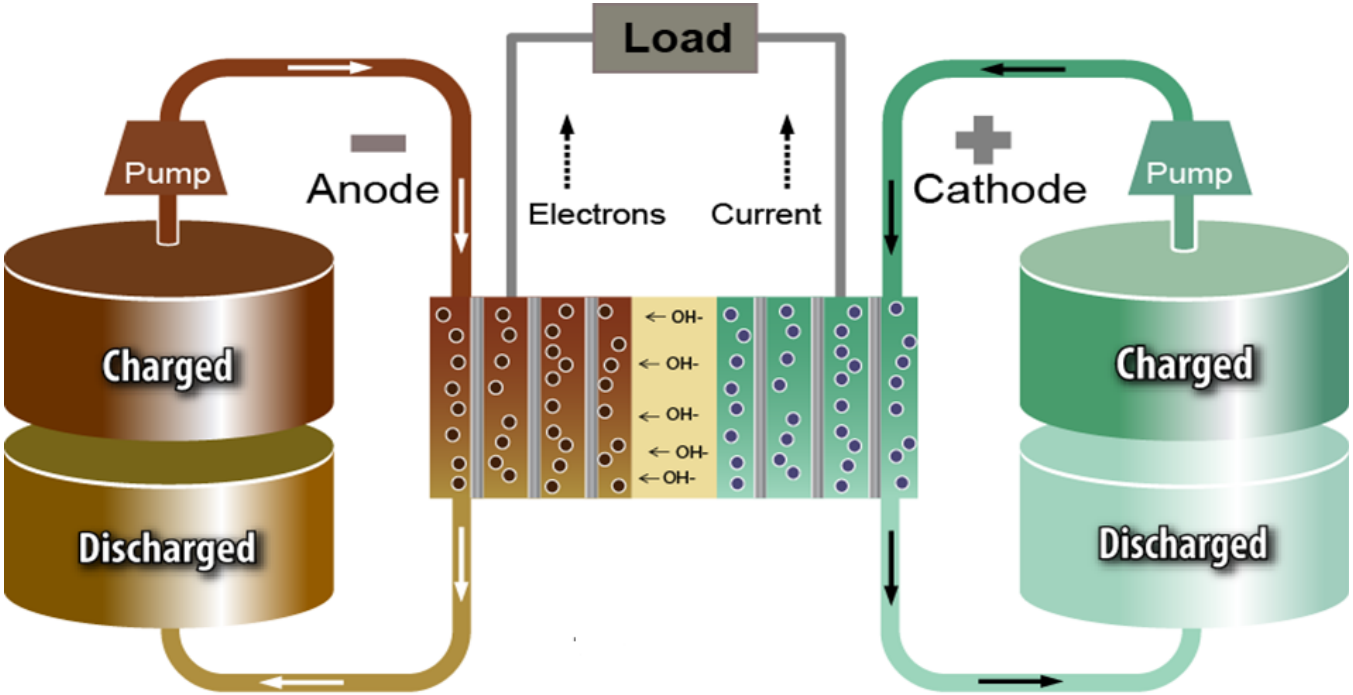


$Sn_3O_2(OH)_2$ provides ideal-sized clusters for Sn-lithiation and composite with graphite nanoplatelets gives superior cyclability

Such composites may be best path to high capacity and cycle life

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).

Nanofluid battery electrodes



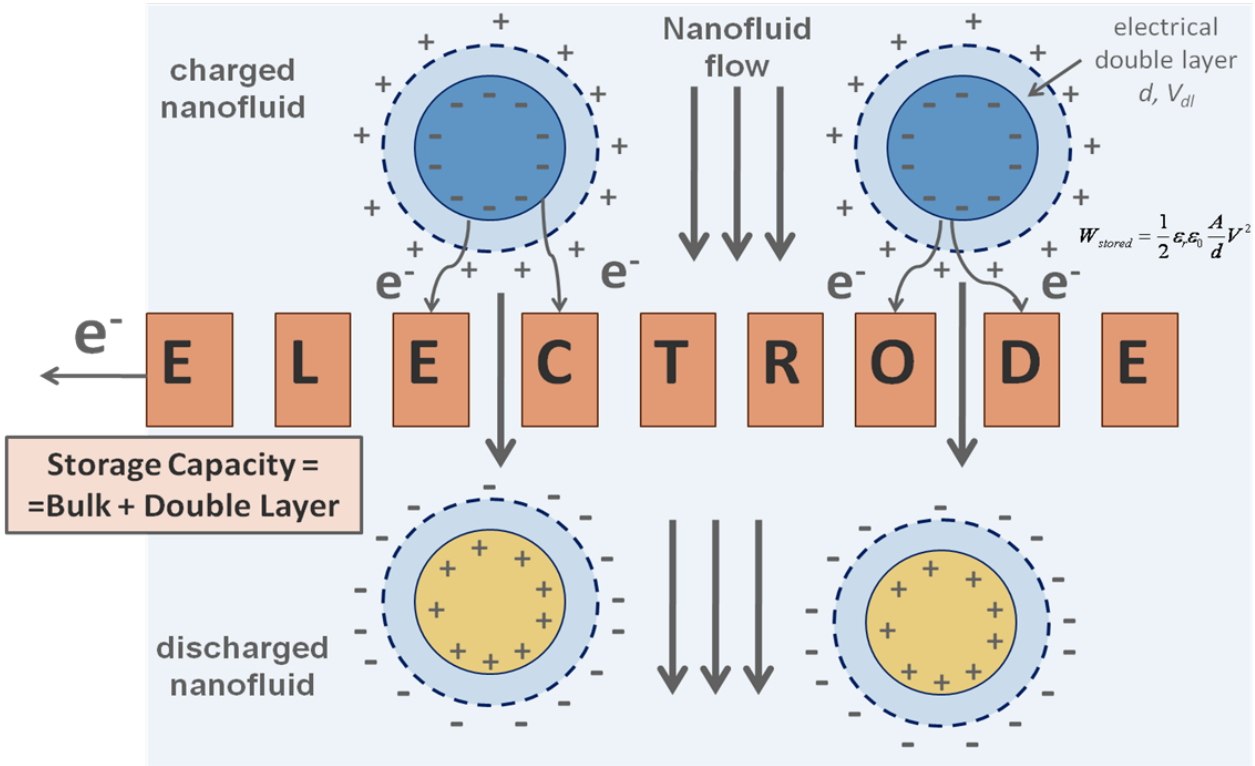
Solid-state batteries have high energy density but large fraction of inactive packaging materials and high cost

Flow batteries have low energy density but decouple energy storage from power generation

A number of groups across the country working on fluidic electrodes with suspended electroactive particles which combine the advantages of both

Charging & discharging nanoelectrofuel

Charging and discharging in a flow can be achieved by proper design of the electrode but all these ideas have to be validated through computation and experiment.



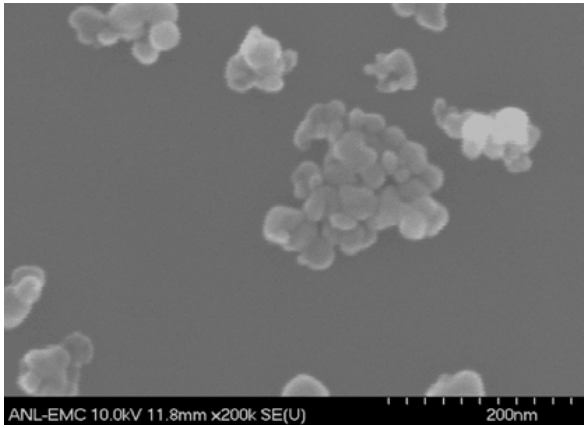
- Porous electrode for high contact probability
- Turbulent flow to maximize electrode contact
- Moderate pressure drop across the cell
- Must have electron transfer with transient contact

NEF anode: Fe_2O_3

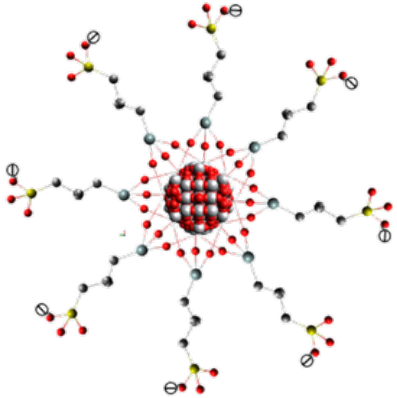
Start with commercially available Fe_2O_3 suspended in water with $\sim$ 5M LiOH

The goal is to reduce Fe^{+3} to Fe^{+2} and there are three reactions present which compete with each other

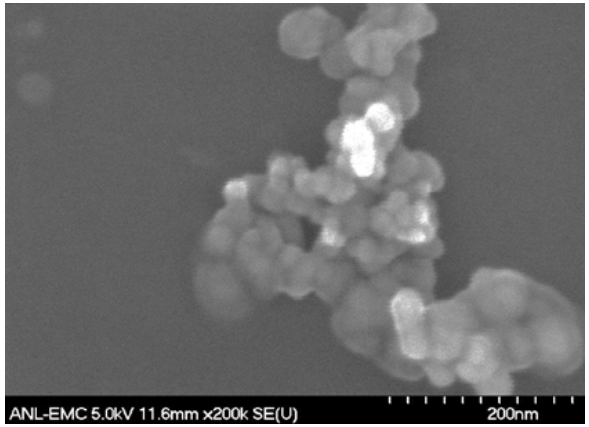
$Fe_2O_3 + 3\,H_2O + 2\,e^- \longrightarrow 2\,Fe(OH)_2 + 2\,OH^-$	$E_0 = -0.9V$	$\sim$ 335 mAh/g
$Fe(OH)_2 + 2\,e^- \longrightarrow Fe + 2\,OH^-$	$E_0 = -1.0V$	$\sim$ 670 mAh/g
$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$	$E_0 = -0.9V$	Bad!



pristine Fe_2O_3

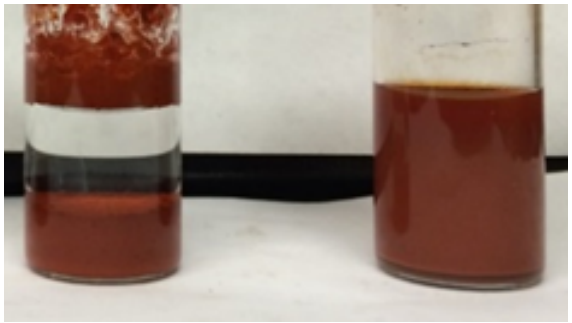


treat with $\sim$ 3 wt% $(OH)_3{-}Si{-}(CH)_3{-}SO_3$



sulfonated Fe_2O_3

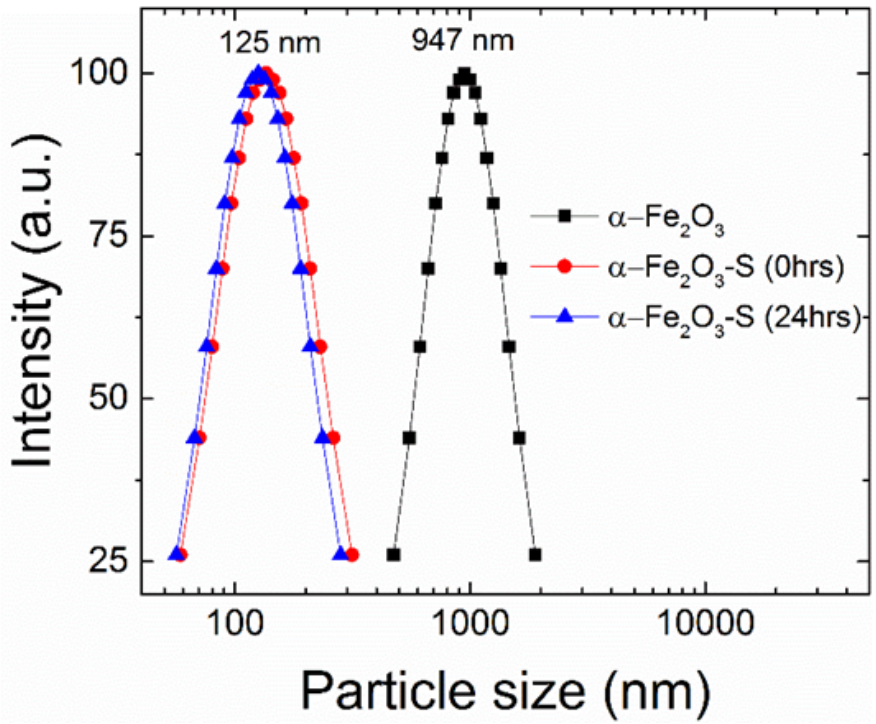
Fe_2O_3 rheology

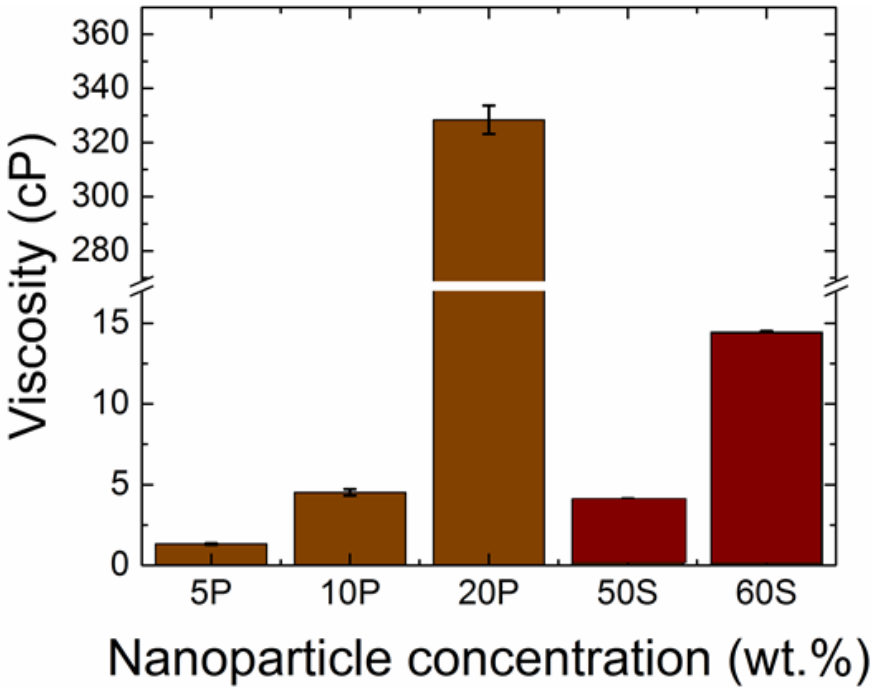


5 wt% pristine (left) vs. modified (right) nanofluid after 2 weeks

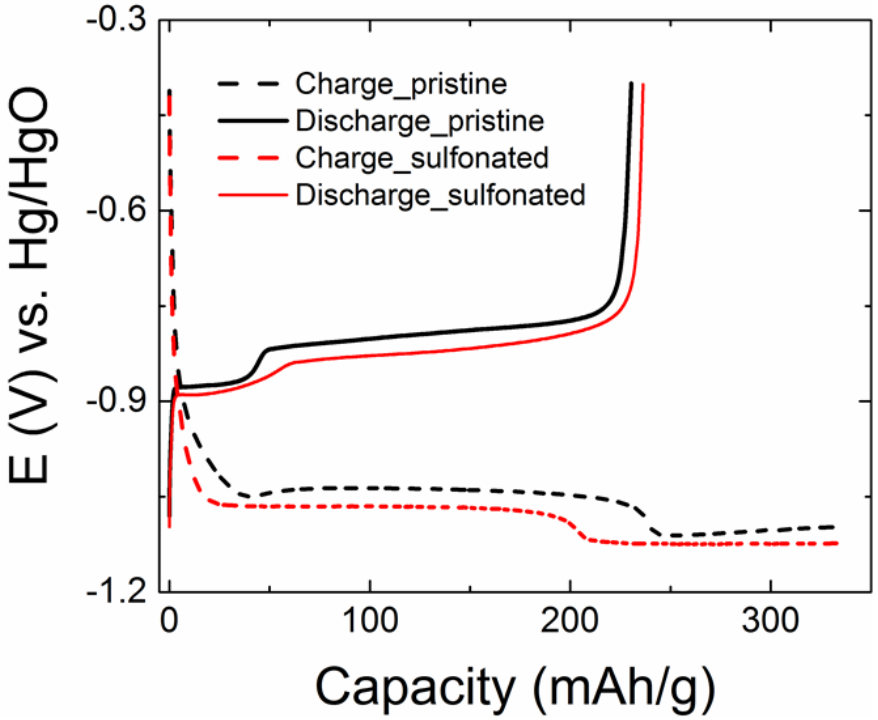
Dynamic light scattering measurements of Fe_2O_3 nanofluids

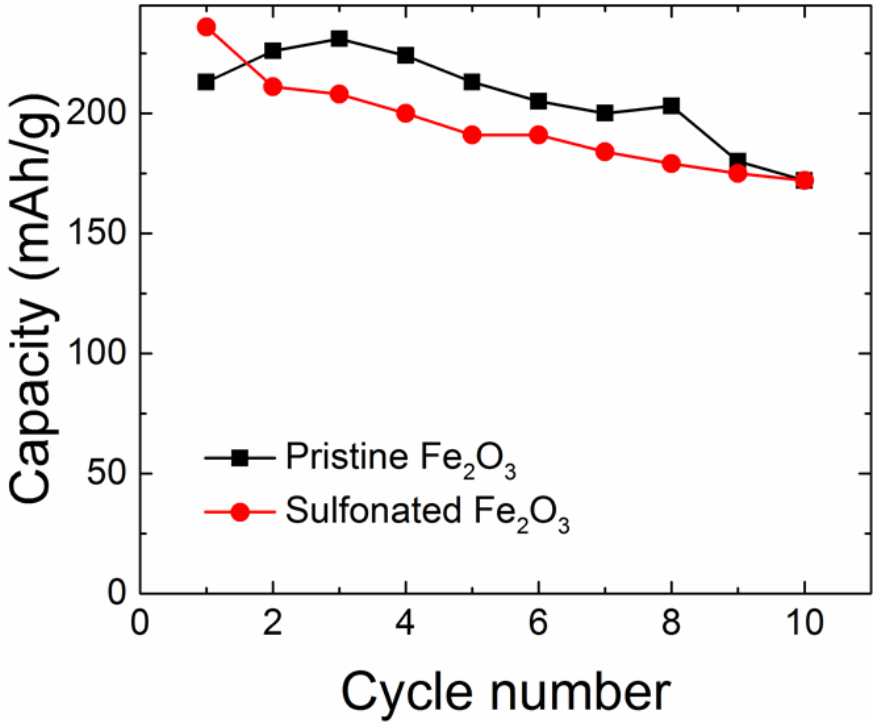
Viscosity comparision of pristine (P) and modified (S) Fe_2O_3 nanofluids





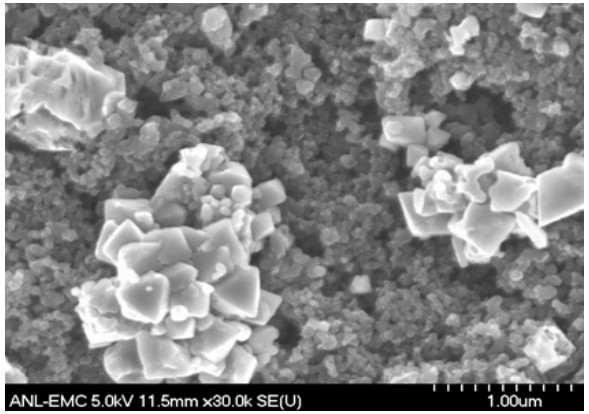
Solid state performance



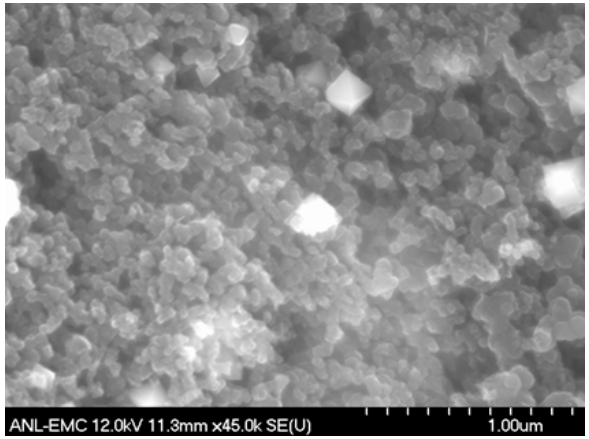


Performance of sulfonated nanoparticles very similar to pristine

Morphology of pristine electrode changes

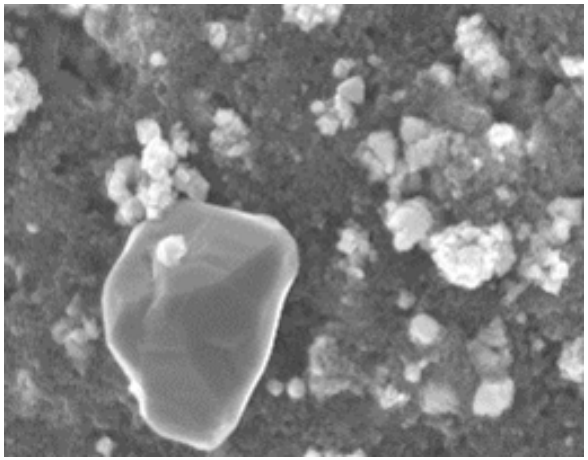
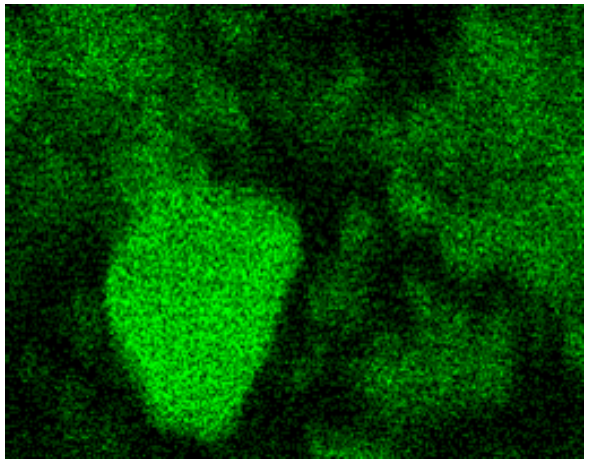
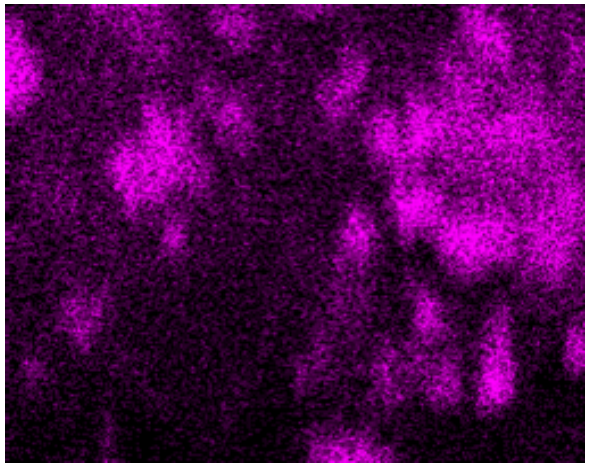


pristine

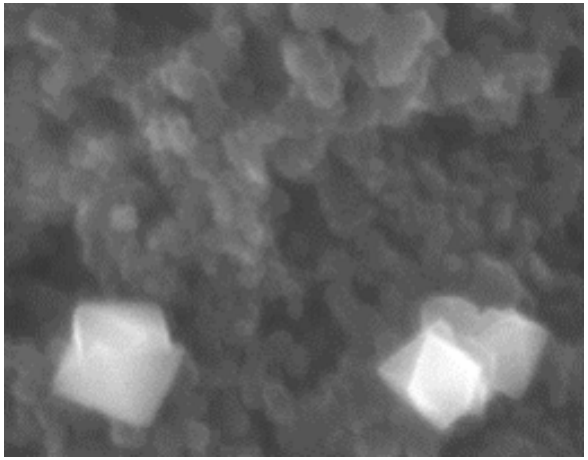
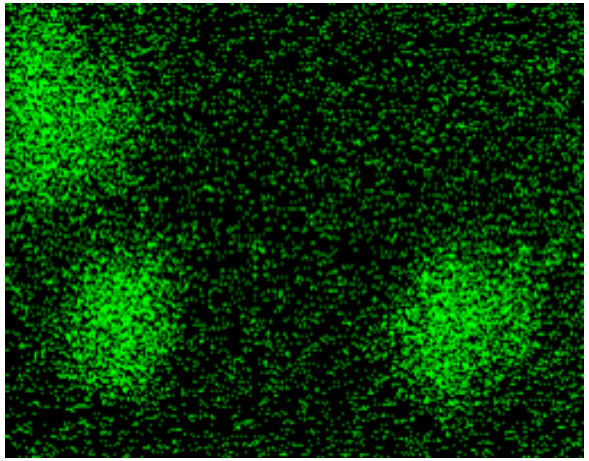
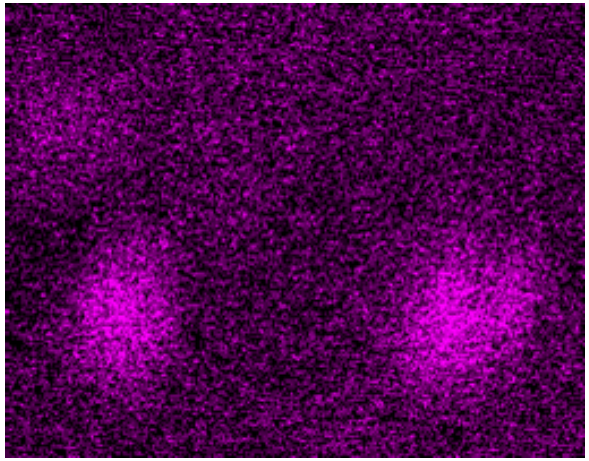


sulfonated

Fe_2O_3 post-cycling analysis

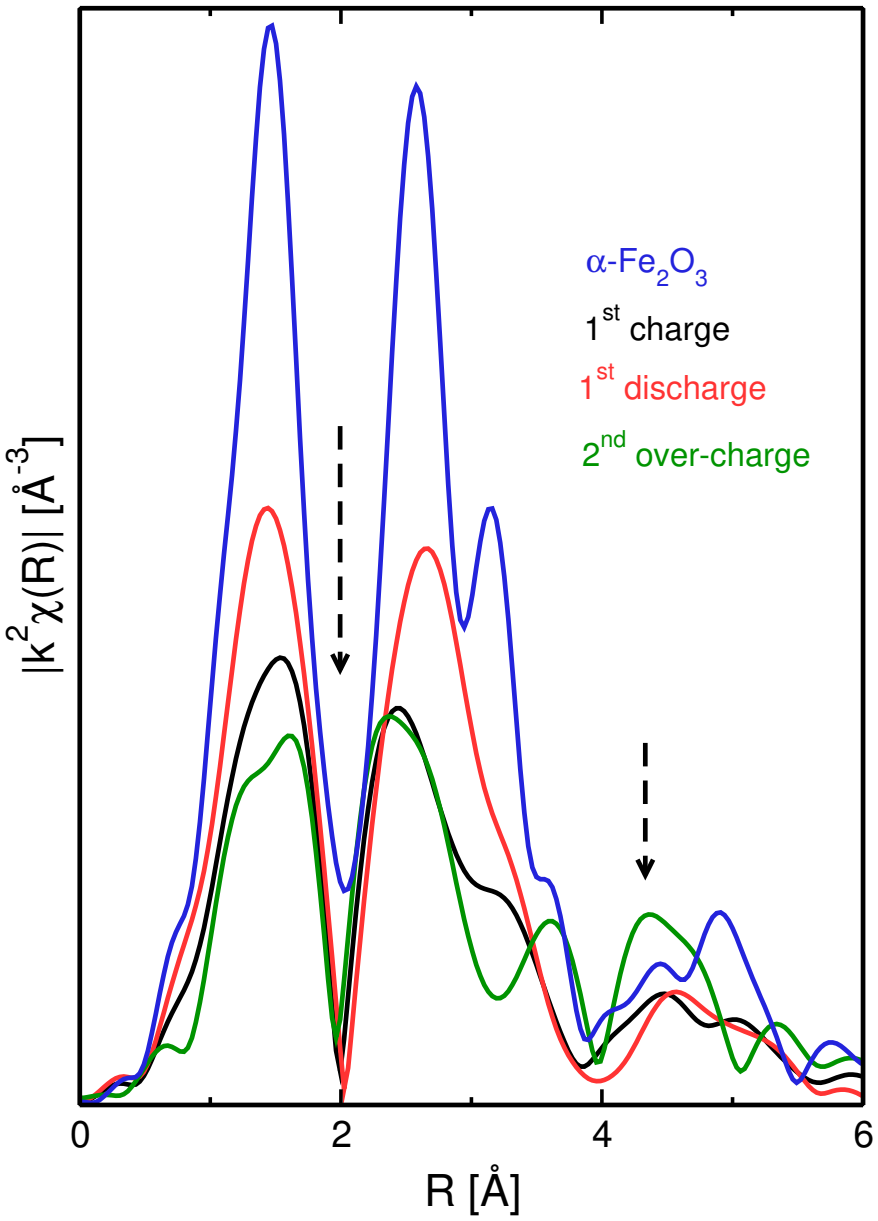
Pristine Fe_2O_3 electrodes show recrystallized Fe metal particles

Sulfonated Fe_2O_3 electrodes show only oxide particles

S. Sen et al., "Engineering nanofluid electrodes: controlling rheology and electrochemical activity of γ-Fe_2O_3 nanoparticles," *J. Nanopart. Res.* **17** 437 (2015).

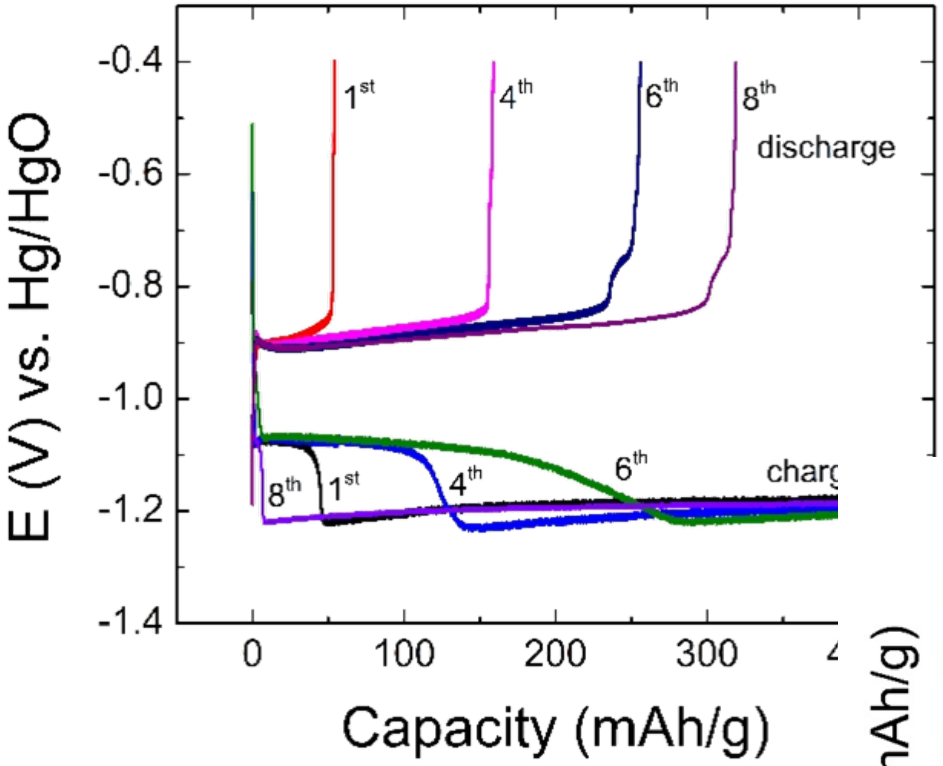
α – Fe_2O_3 *in situ* EXAFS

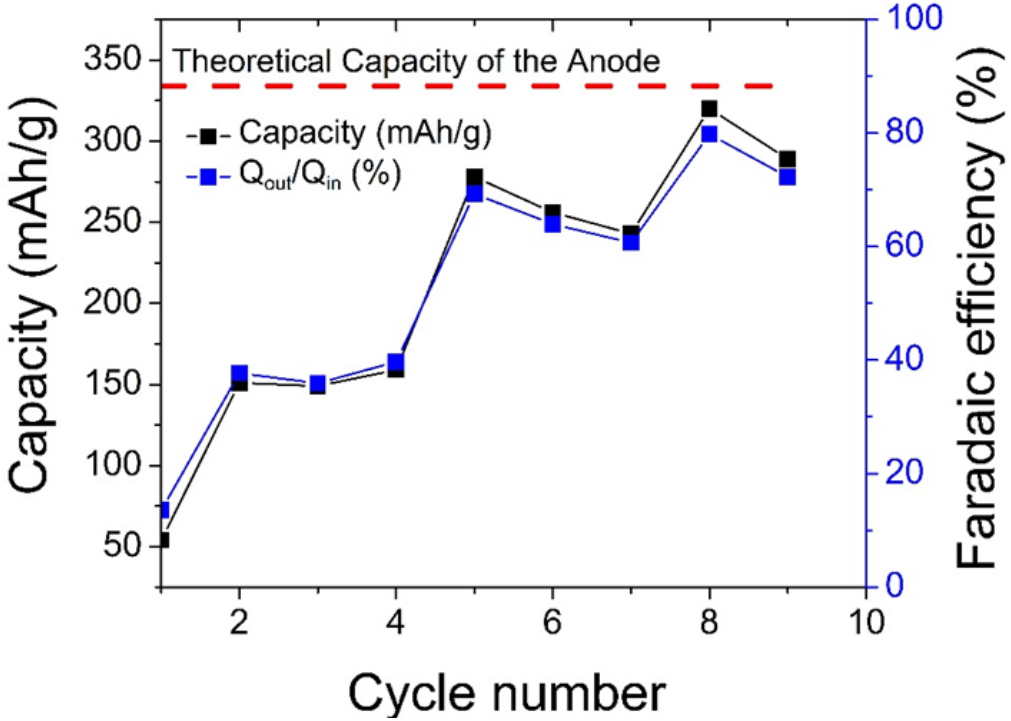


- Clear evidence of metallic Fe but no $Fe(OH)_2$ seen
- Discharge does not return electrode to α-Fe_2O_3
- Over-charge pushes system toward metallic Fe
- Fitting reveals mixture of Fe and/or Fe_3O_4/γ-Fe_2O_3 in all spectra.

	Fe_3O_4	metallic Fe
1st charge	85%	15%
1st discharge	100%	
2nd charge	83%	17%
1st over-charge	82%	18%
2nd over-charge	67%	33%

Fe_2O_3 NEF performance





With repeated cycling, the performance of the NEF is increasing with a capacity of up to 300 mAh/g

Final thoughts

A fruitful, but complex, direction for development is composite materials where the complementary properties of two or more materials are expressed

Successful design of new materials for electrochemical energy systems can be inspired by information obtained from *in situ* characterization

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Thank You