Making a nanoelectrofuel flow battery

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Outline

- Batteries 101
- Nanoelectrofuel concept
- Prototype design
- Electrochemical characterization
- EXAFS studies
- Conclusions

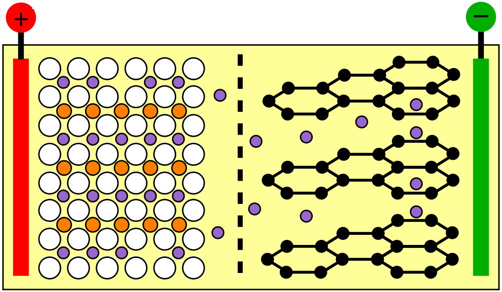
Solid state batteries

Anode - negatively charged electrode

Cathode - positively charged electrode

Separator - allows ions to pass without short circuit

Electrolyte - medium through which ions move



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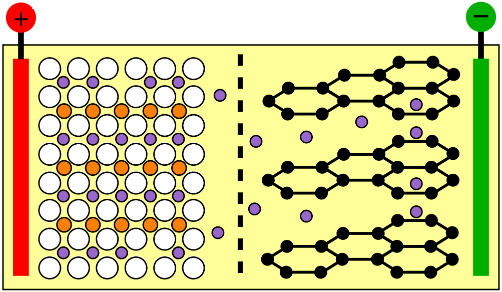

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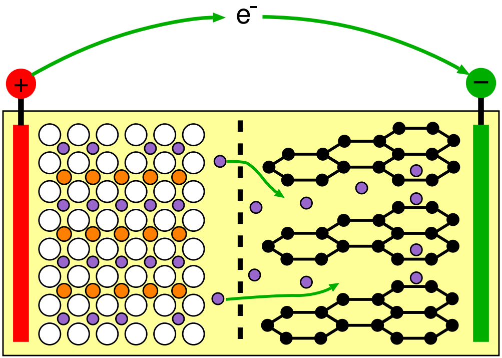

Charge - Li^+ ions move from cathode to anode and electrons also flow to the anode externally, anode is reduced

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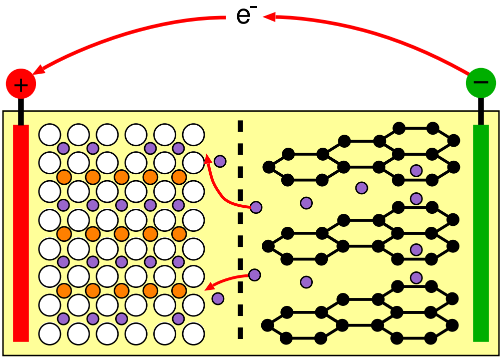

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Discharge - Li^+ ions move back to cathode and electrons flow through the external load, anode is oxidized

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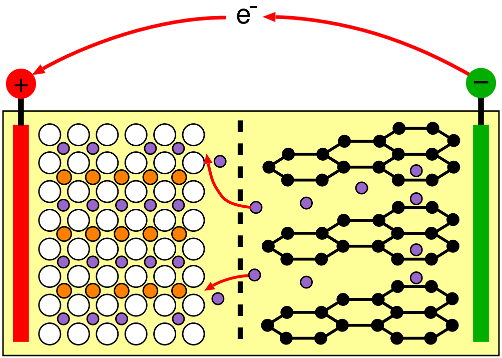

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Potential, energy density, and power determined by the chemistry

Common solid state battery chemistries

Lead-acid battery: $E_{oc} = 2.05$ V

Cathode: $PbO_2 + SO_4{}^{2-} + 4H^+ + 2\,e^- \longleftrightarrow Pb_2SO_4 + 2\,H_2O$

Anode: $PbSO_4 + 2\,e^- \longleftrightarrow Pb + SO_4{}^{2-}$

NiMH battery: $E_{oc} = 1.28$ V

Cathode: $NiOOH + H_2O + e^- \longleftrightarrow Ni(OH)_2 + OH^-$

Anode: $M + H_2O + e^- \longleftrightarrow MH + OH^-$

Li-ion battery: $E_{oc} = 4.00$ V

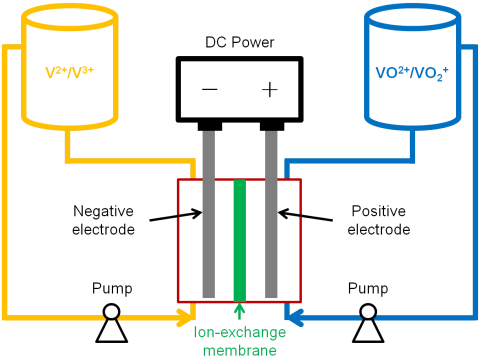
Cathode: $CoO_2 + Li^+ + e^- \longleftrightarrow LiCoO_2$

Anode: $Li^+ + C_6 + e^- \longleftrightarrow LiC_6$

Characteristics

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

Flow batteries



Characteristics

- Low packaging overhead
- Unlimited cycle life
- Low energy density

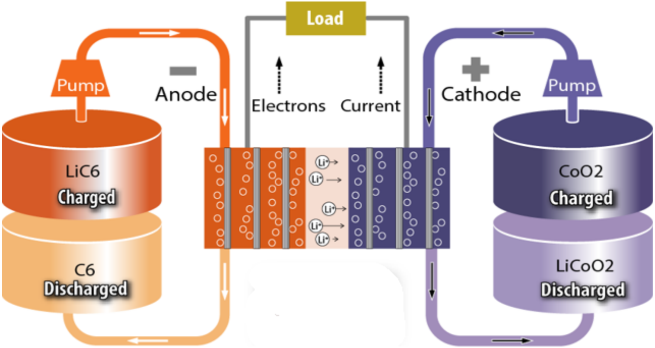
Vanadium: $E_{oc} = 1.26$ V

Cathode:	$V^{3+} + e^-$	$\longleftrightarrow$	V^{2+}
Anode:	$VO_2{}^+ + 2\,H^+ + e^-$	$\longleftrightarrow$	$VO^{2+} + H_2O$

Zinc-Bromine: $E_{oc} = 1.67$ V

Cathode:	$Br_2(aq) + 2\,e^-$	$\longleftrightarrow$	$2\,Br^-_{(aq)}$
Anode:	$Zn^{2+}_{(aq)} + 2\,e^-$	$\longleftrightarrow$	$Zn_{(s)}$

Nanoelectrofuel battery



Suspended electroactive nanoparticles

Advantages of flow batteries

Energy density of solid state

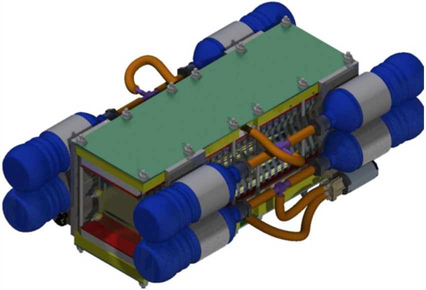
Chemistry agnostic
 aqueous or non-aqueous

3 year arpa·e funded program

Prototype: 1 kWh total energy stored
 40 V, C/3 discharge rate

Develop commercialization plan

Nanoelectrofuel challenges



40 V aqueous chemistry stack

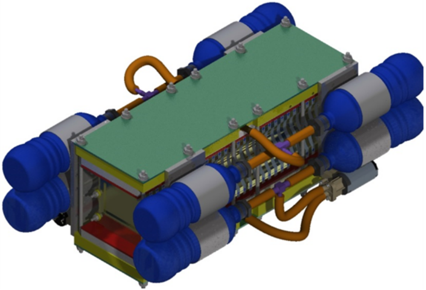
25 kWh using 4.5 L of nanoelectrofuel

26 kg stack, 10 kg 50% loaded fluid

70 Wh/kg (compare to 40 Wh/kg for Pb-acid)

Nanoelectrofuel challenges

- What is the intrinsic performance of active materials in nanoparticle form?



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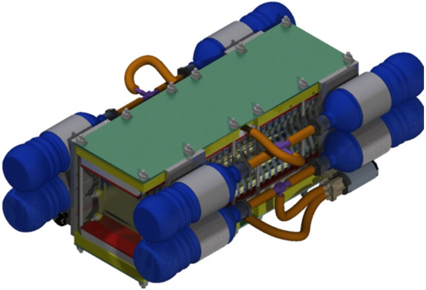

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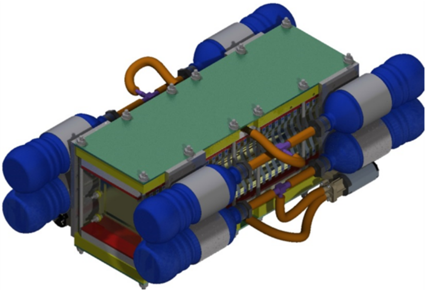

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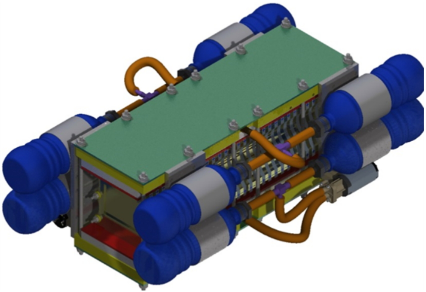
- Will these nanoelectrofuels be pumpable and not destroy the enclosure materials?



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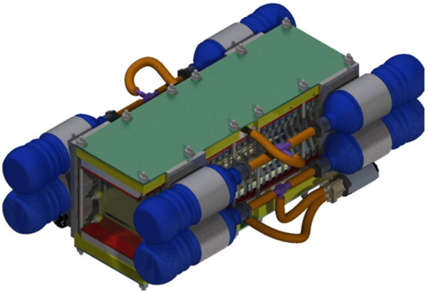
- Will these nanoelectrofuels be pumpable and not destroy the enclosure materials?
- Can physics graduate students on the project get a Ph.D. doing this very applied project?



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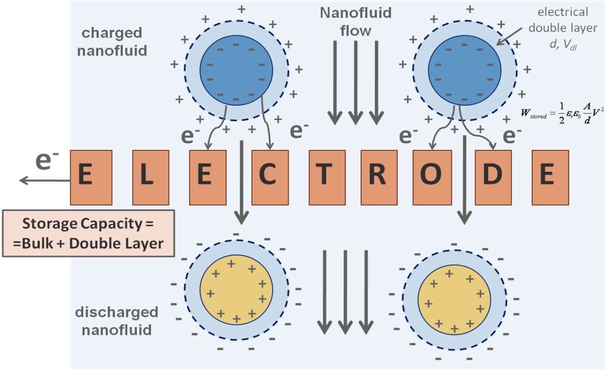
Charging & discharging nanoelectrofuel

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.



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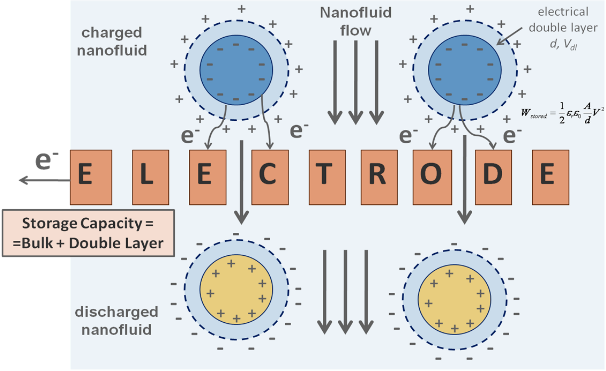
- Porous electrode for high contact probability



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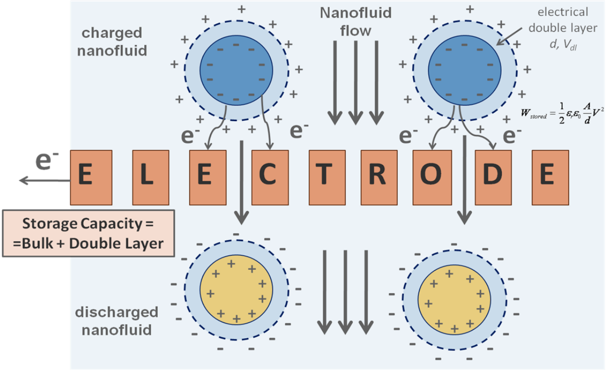

- Porous electrode for high contact probability
- Turbulent flow to maximize electrode contact

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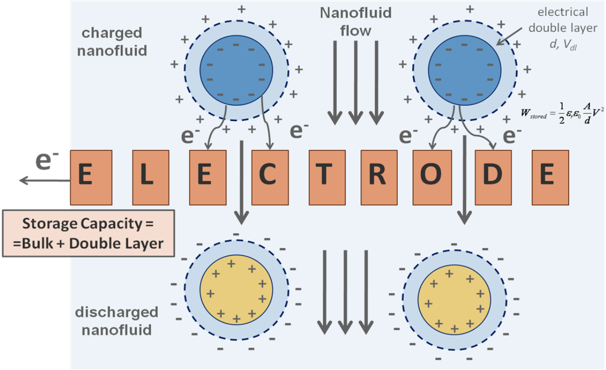

- Porous electrode for high contact probability
- Turbulent flow to maximize electrode contact
- Moderate pressure drop across the cell

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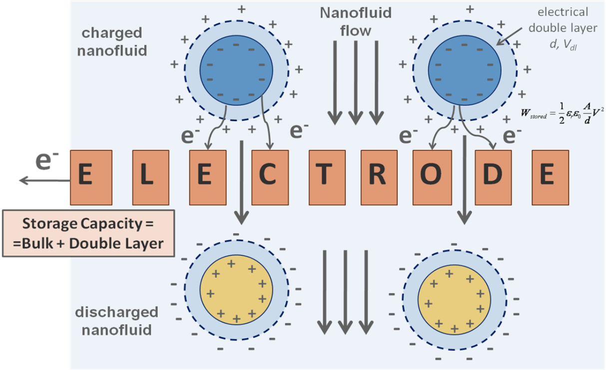
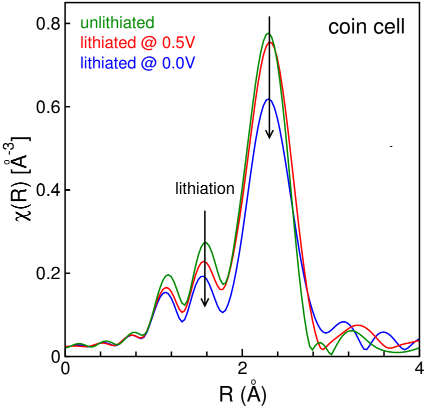
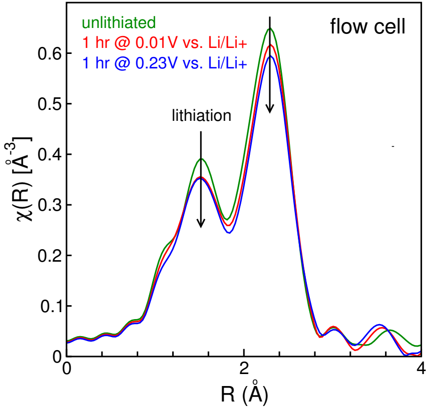


- Porous electrode for high contact probability
- Turbulent flow to maximize electrode contact
- Moderate pressure drop across the cell
- Must have electron transfer with transient contact

First charging results

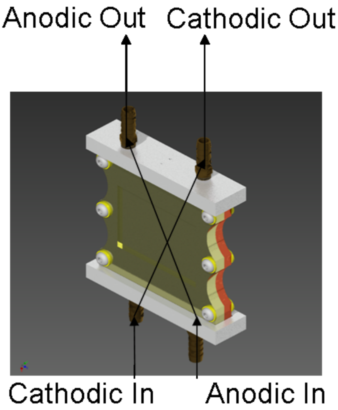
December 2012 data comparing x-ray absorption spectroscopy results on Cu_6Sn_5 anode material in a coin cell and flowing through a metal frit.

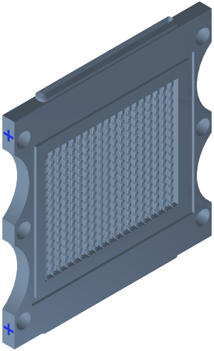


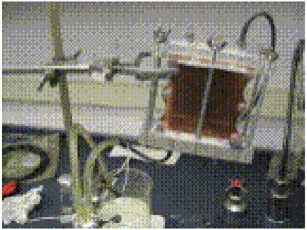


Similar trends indicate that nanoparticles in the flow cell are charging, albeit slowly and inefficiently.

Initial prototype cell



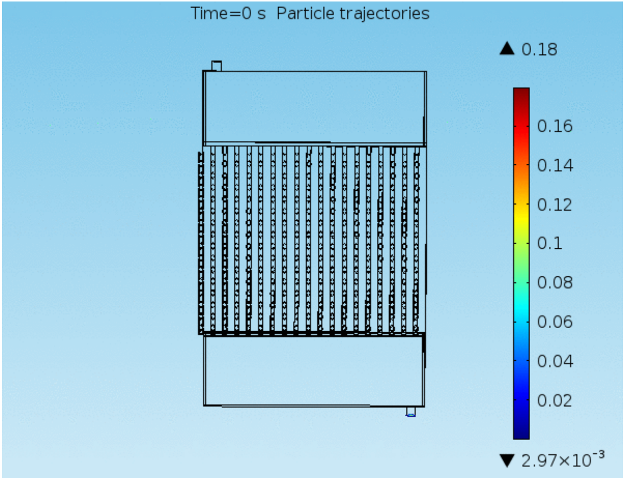




Made from metal with machined posts for increased contact area

Future designs manufactured with 3D printing & metal electrode inserts

CFD modeling

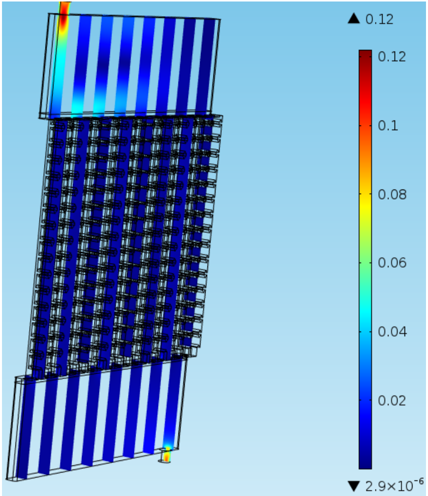


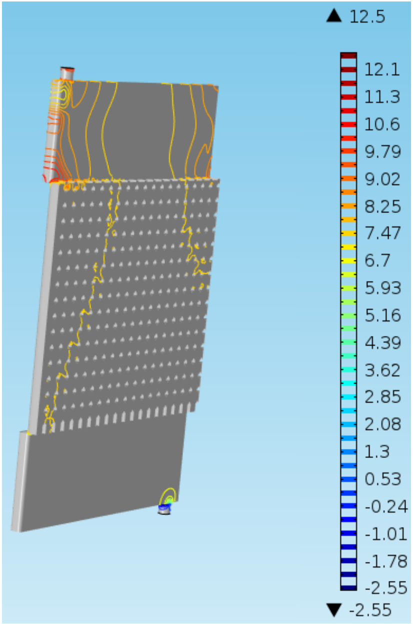
Inject 5000 particles and evolve for 15 s

Extend to repeated injections of 5000 particles and add electrochemical modeling

Initial CFD results

Pressure field ⟶

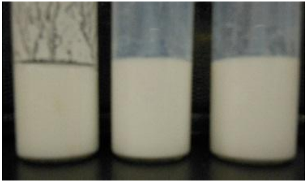




Velocity field ↑

Nanofluid settling

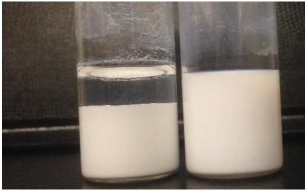
TiO_2 pristine (left & center) and sulfonated (right) in 0.4M KOH/LiOH (left) and 0.04M KOH/LiOH (center & right)



0 hours

18 hours

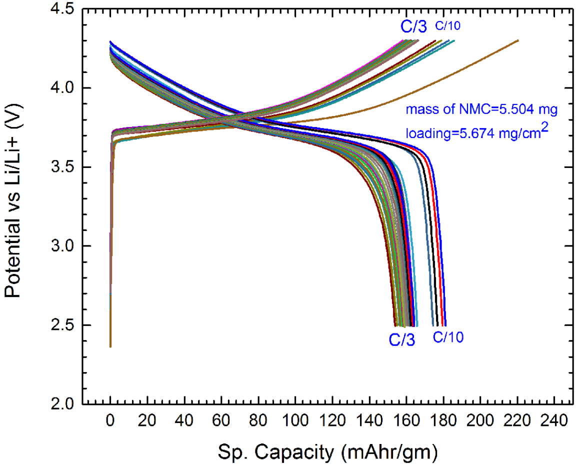
45 hours



1 month

Nanoparticle electrochemical performance

$LiNi_xMn_yCo_zO_2$ non-aqueous cathode material



As received micron-sized particles (MTI Inc.)

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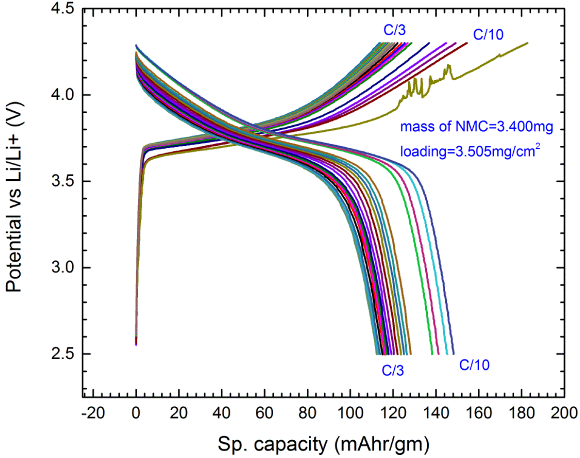
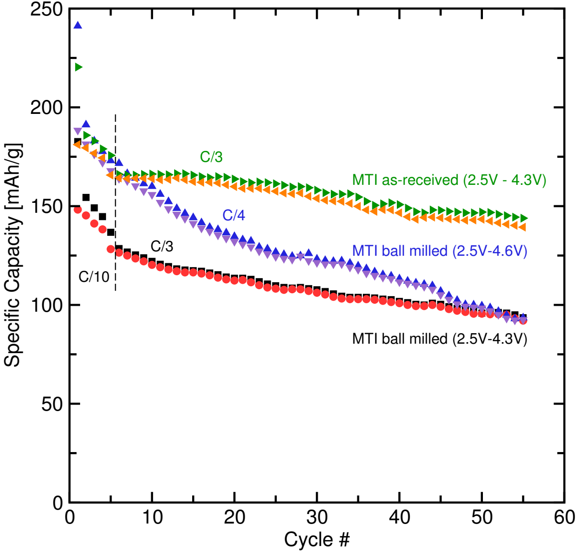


Ball milled ∼400 nm particles (MTI Inc.)

Nanoparticle electrochemical performance

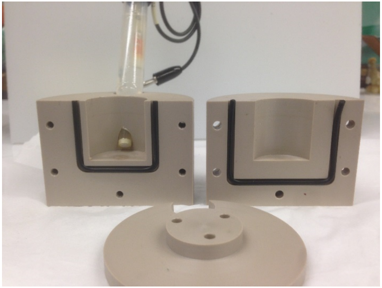


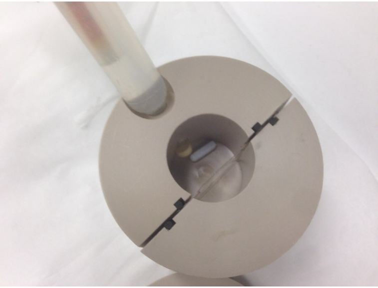
Nanoparticle-sized $LiNi_xMn_yCo_zO_2$ has lower capacity and more fading

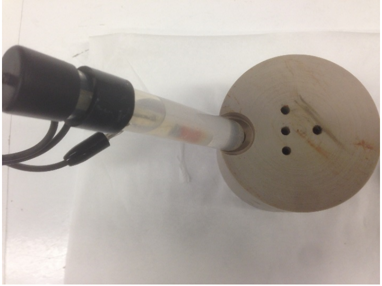
Cycling to 4.6 V yields slightly higher initial capacity but faster fading

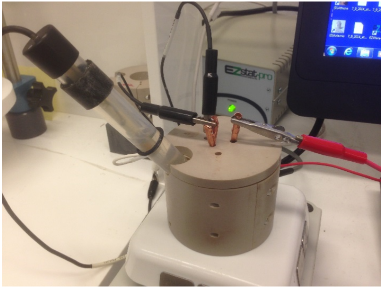
Solid electrolyte interface (SEI) layer is a significant problem at high potentials and for nanoparticles

Initial nanofluid charging tests

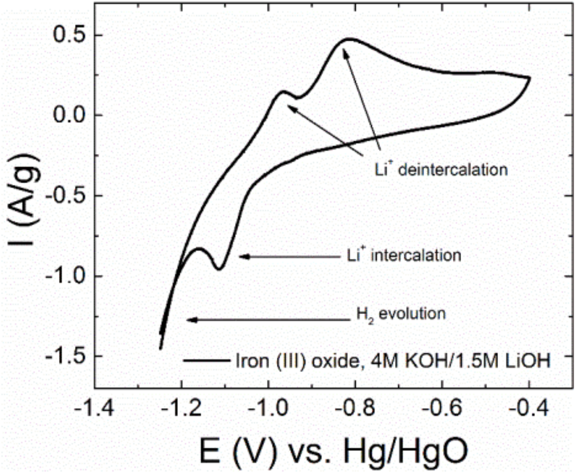








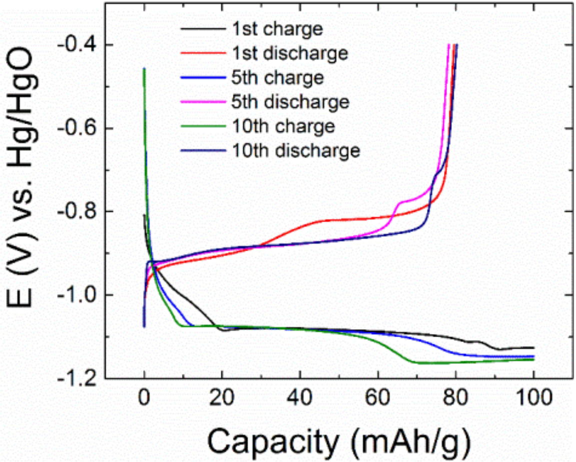
Fe_2O_3 coin cell



Hydrogen evolution at potentials below -1.0V

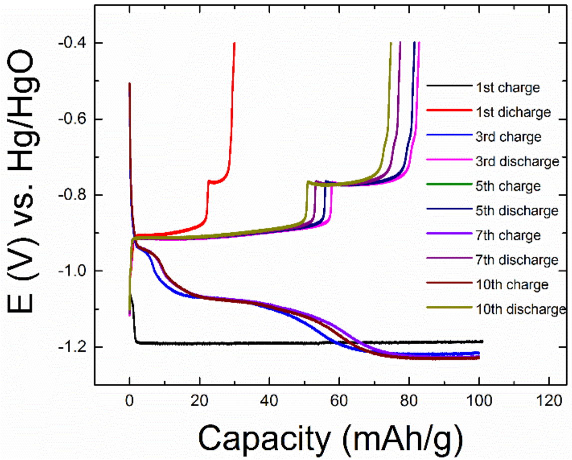
Fe_2O_3 cyclic voltammetry shows Li intercalation

Fe_2O_3 coin cell



Theoretical capacity for $Fe^{+3} \rightarrow Fe^{+2}$ is $\sim$335 mAh/g

Fe_2O_3 nanofluid



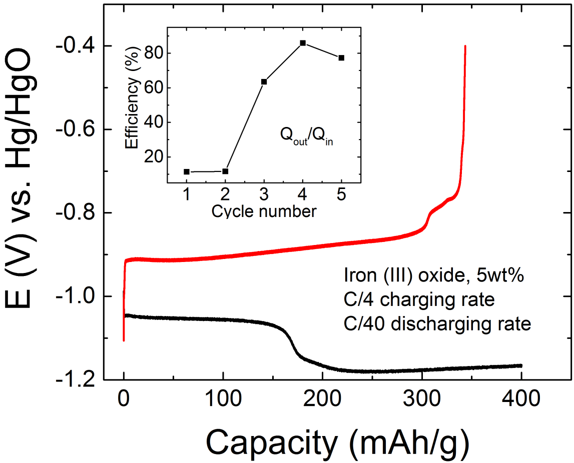
5% wt suspension of Fe_2O_3 nanoparticles in KOH/LiOH solution

Performance of nanofluid equivalent or to solid nanoparticle electrode

Capacity increase with cycles indicates that it is limited by suboptimal current collector

Need to move to flow-through current collector design

Fe_2O_3 nanofluid – overcharged



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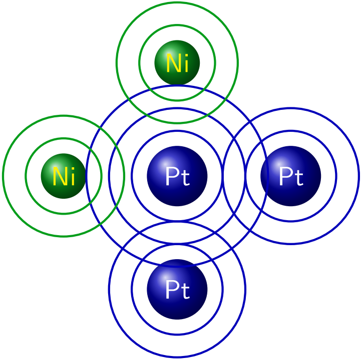
The EXAFS equation

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

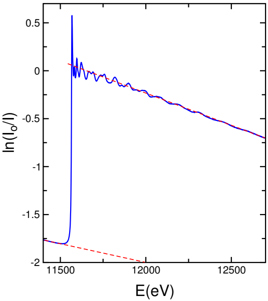
$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k)}{k R_j^2} e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin\left[2R_j + \delta_j(k)\right]$$

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 analysis



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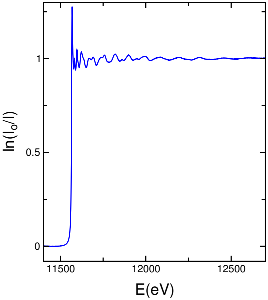

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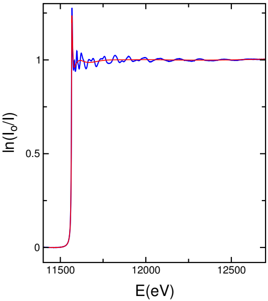

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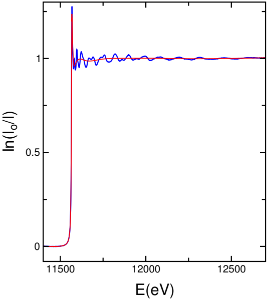
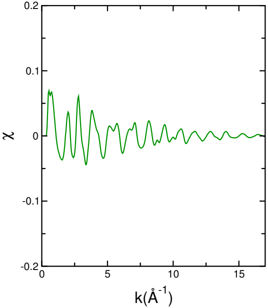


remove background



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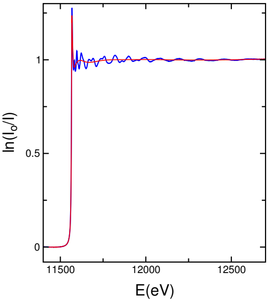
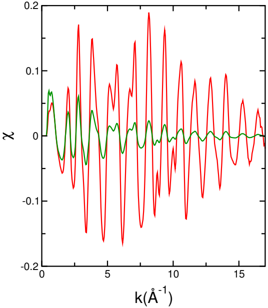


remove background and apply k-weighting



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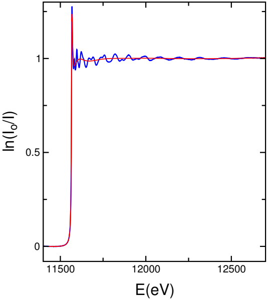

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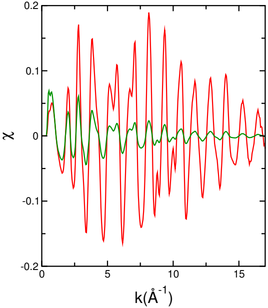
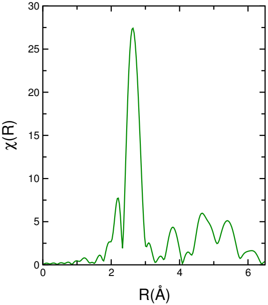
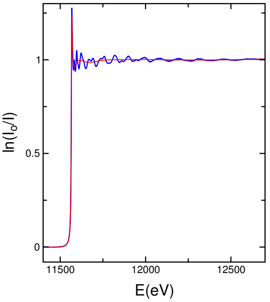


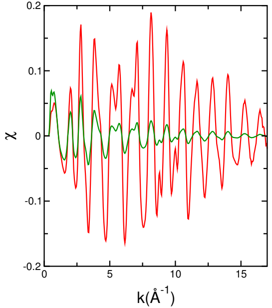


take Fourier Transform

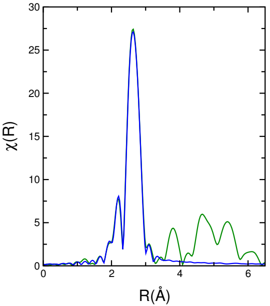
EXAFS analysis



remove background and apply k-weighting

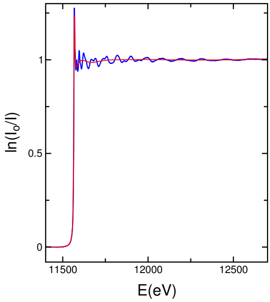


take Fourier Transform and fit with a structural model

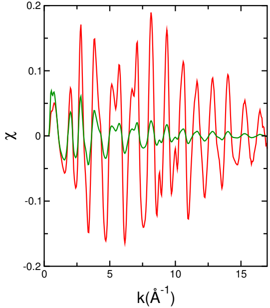


extract structural parameters for first shell

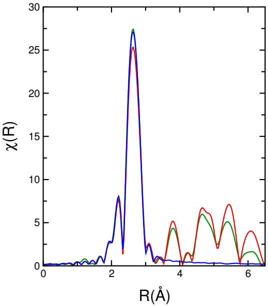
EXAFS analysis



remove background and apply k-weighting

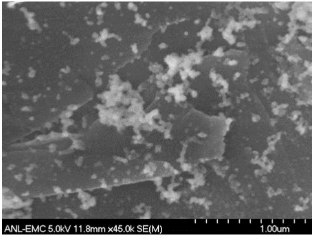


take Fourier Transform and fit with a structural model



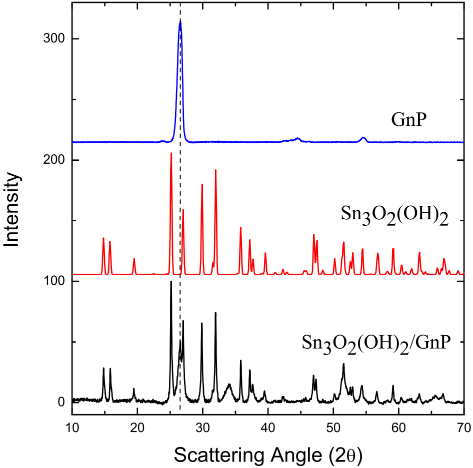
extract structural parameters for first shell or more distant atoms as appropriate

Synthesis of Sn-graphite nanocomposites

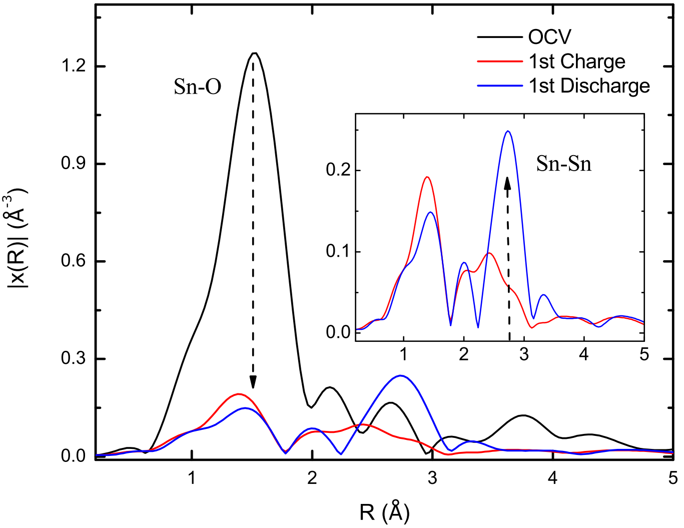


One-pot synthesis produces evenly distributed $Sn_3O_2(OH)_2$ nanoparticles on graphite nanoplatelets

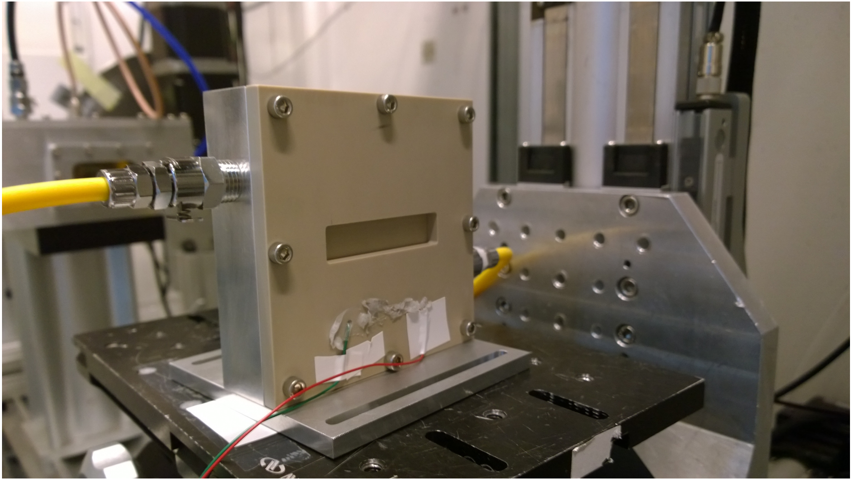
XRD shows a small amount of Sn metal in addition to $Sn_3O_2(OH)_2$



In situ XAS studies of lithiation

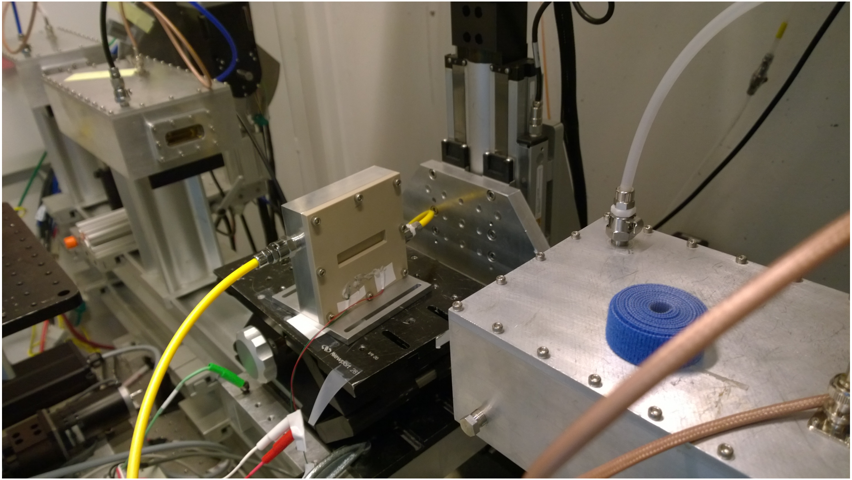


In situ battery box



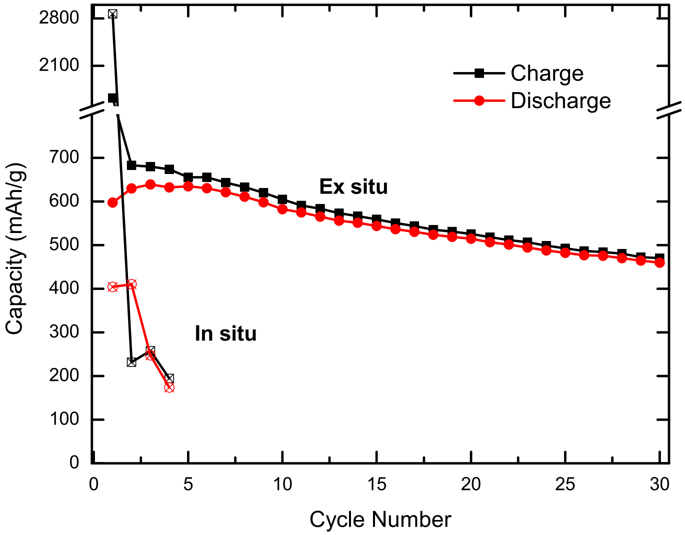
Pouch cell clamped against front window in helium environment

In situ battery box

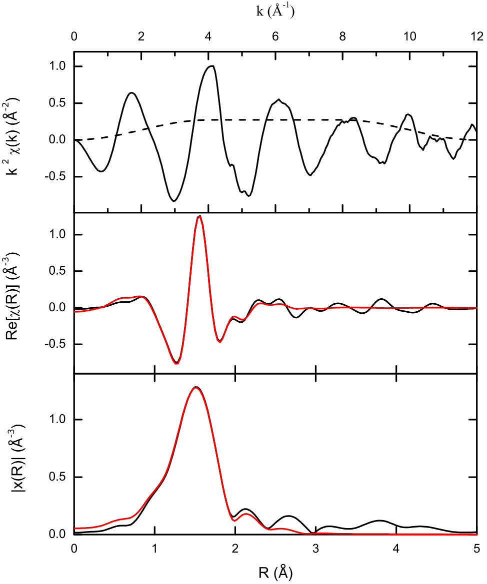


Suitable for both transmission and fluorescence measurements

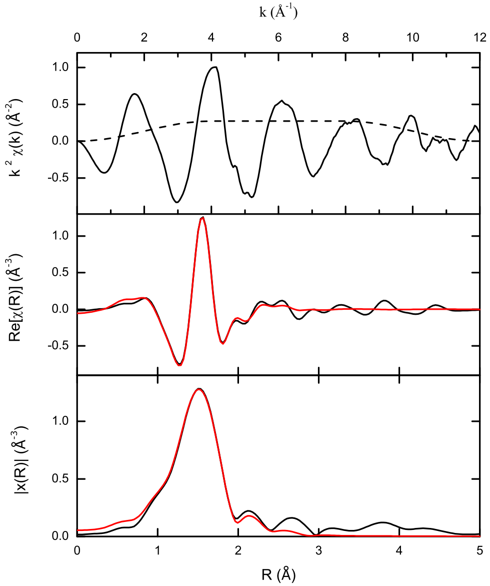
In situ XAS studies of lithiation



In situ XAS studies of lithiation

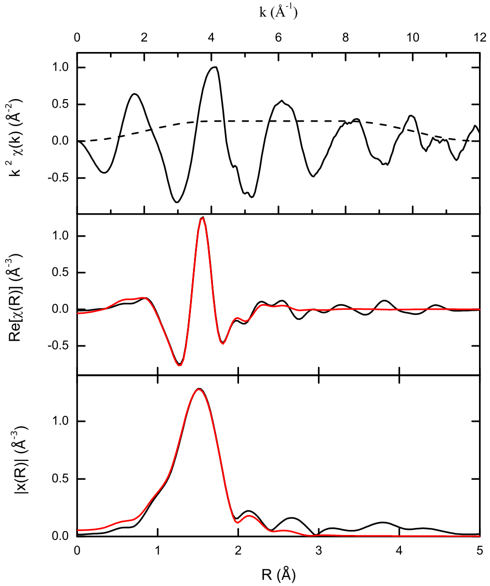


In situ XAS studies of lithiation



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

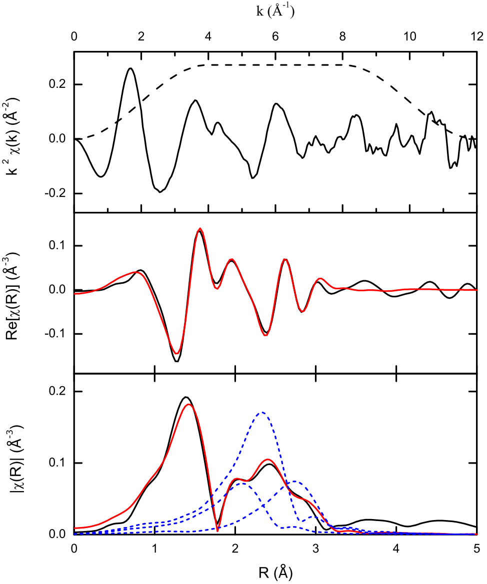
In situ XAS studies of lithiation



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

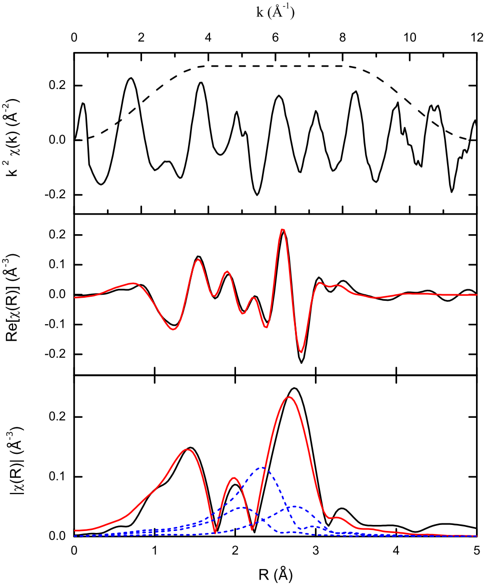
Only a small amount of metallic Sn-Sn distances can be seen

In situ XAS studies of lithiation



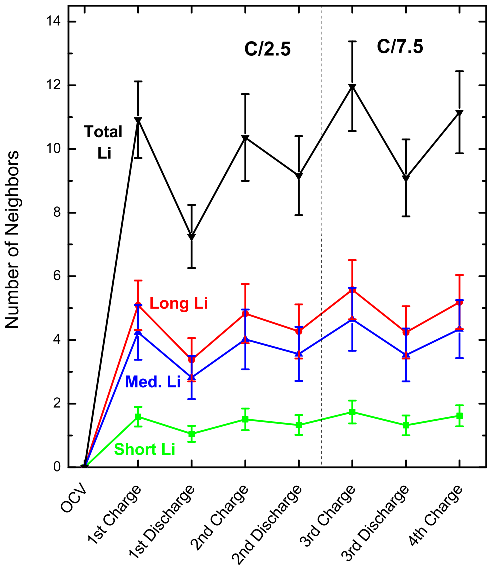
Reduction of number of Sn-O near neighbors and 3 Sn-Li paths characteristic of the $Li_{22}Sn_5$ structure

In situ XAS studies of lithiation

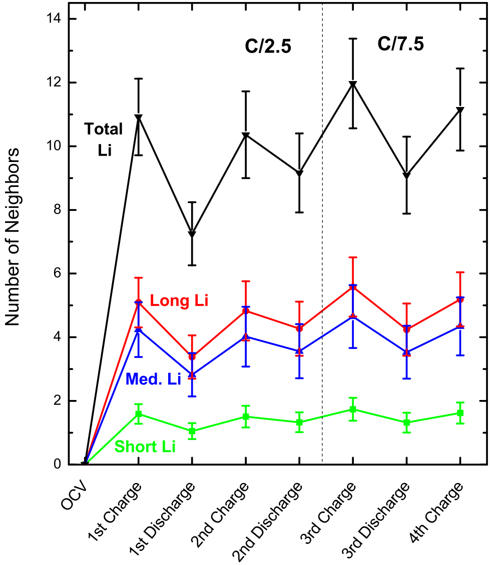


Metallic Sn-Sn distances appear but Sn-Li paths are still present, further reduction in Sn-O near neighbors.

In situ XAS studies of lithiation

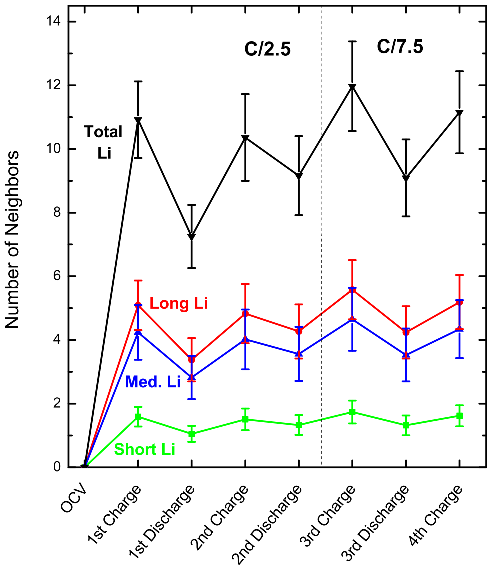


In situ XAS studies of lithiation



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

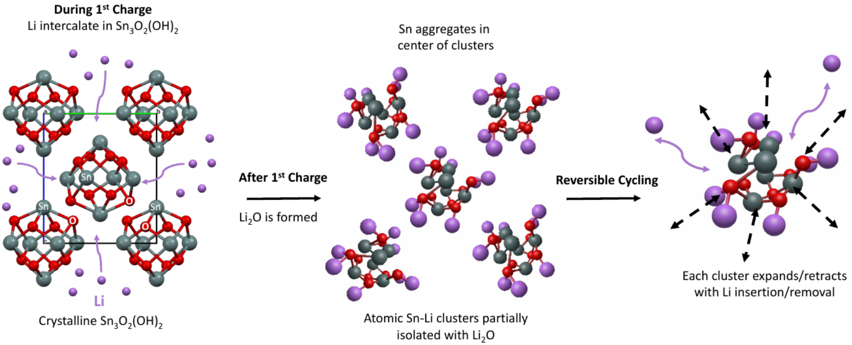
In situ XAS studies of lithiation



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

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



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- Yue Li – Ph.D. Chemical Engineering
- Nathaniel Beaver – Ph.D. Physics
- Shankar Aryal – Ph.D. Physics

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Abstract

We are currently in the first year of an ARPA-e project to produce a prototype nanoelectrofuel flow battery. This new battery concept marries the traditional solid state battery with a flow battery to obtain higher energy densities and reduction in packaging weight. Successful development of this new battery format requires the ability to charge and discharge nanoparticle suspensions by transient contact with the current collectors. While the basic effect has been demonstrated, many challenges lie ahead. Notably the ability to make efficient and high capacity battery materials in nanoparticle form. In order to understand the differences between battery materials in macroscopic (micron-sized) and nanoparticle form, we are using x-ray absorption spectroscopy to probe the structure of materials as they are electrochemically cycled. I will present some initial results on our in-situ studies of anode lithiation and discuss our future plans.