High Energy Density Nanoelectrofuel Flow Batteries for Transportation and Renewables: Development, Prospective and Challenges

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Outline

- The nanoelectrofuel concept
- Challenges for prototype design
- How to make nanoelectrofuel
- Fe_2O_3 anode characterization
- Fe_2O_3 nanoelectrofuel characterization
- Synchrotron radiation studies
- Lessons from I-Corps

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
- Kamelsh Suthar – Advanced Photon Source

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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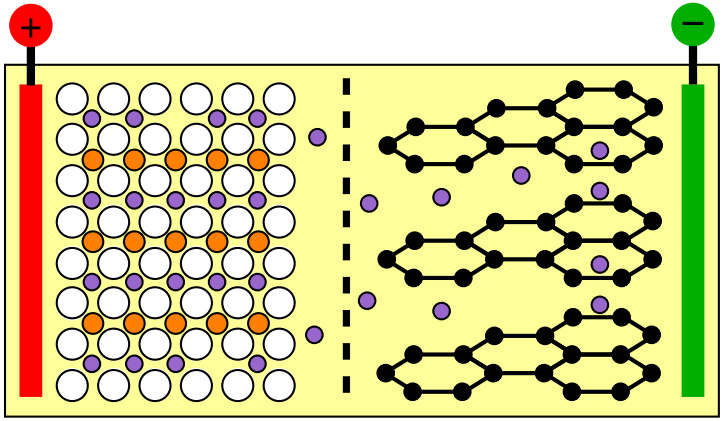
Common solid state battery chemistries



Characteristics

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

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

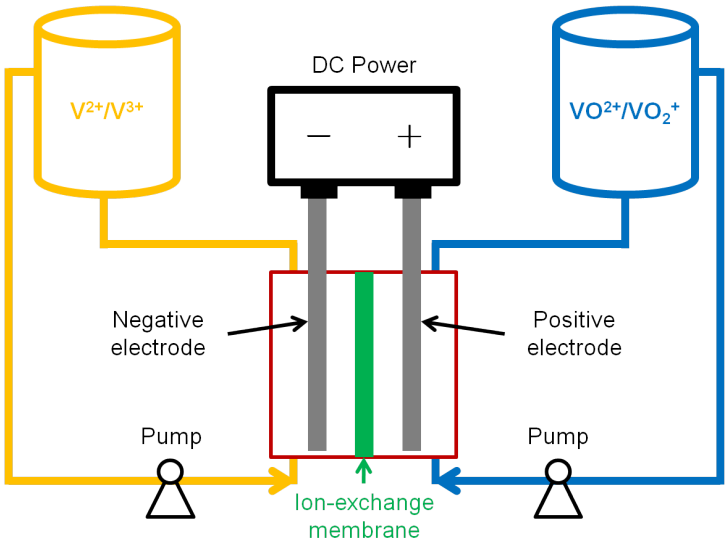
Anode: $M + H_2O + e^- \longleftrightarrow MH + OH^-$

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

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

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

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

What if. . .

The advantages of solid state and flow batteries could be combined?

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The range of an electric vehicle could be extended to 500 or even 1000 miles?

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Refueling stations could replace spent energy storage media and provide a full charge in a few minutes?

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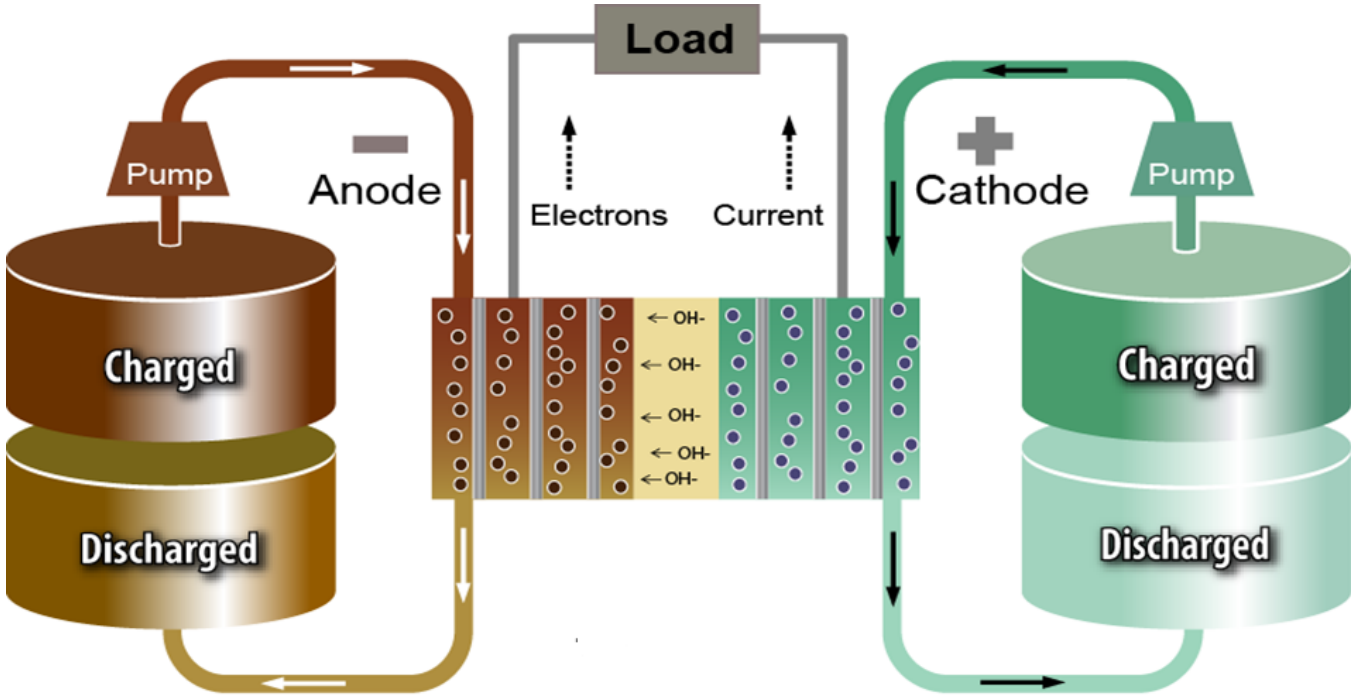
The range of an electric vehicle could be extended to 500 or even 1000 miles?

Refueling stations could replace spent energy storage media and provide a full charge in a few minutes?

This is the original idea behind Nanoelectrofuel!

Nanoelectrofuel flow battery



Suspended electroactive nanoparticles

Advantages of flow batteries

Energy density of solid state

Chemistry agnostic
aqueous or non-aqueous

Initial arpa·e funding

IIT/Argonne collaboration

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

Develop commercialization plan

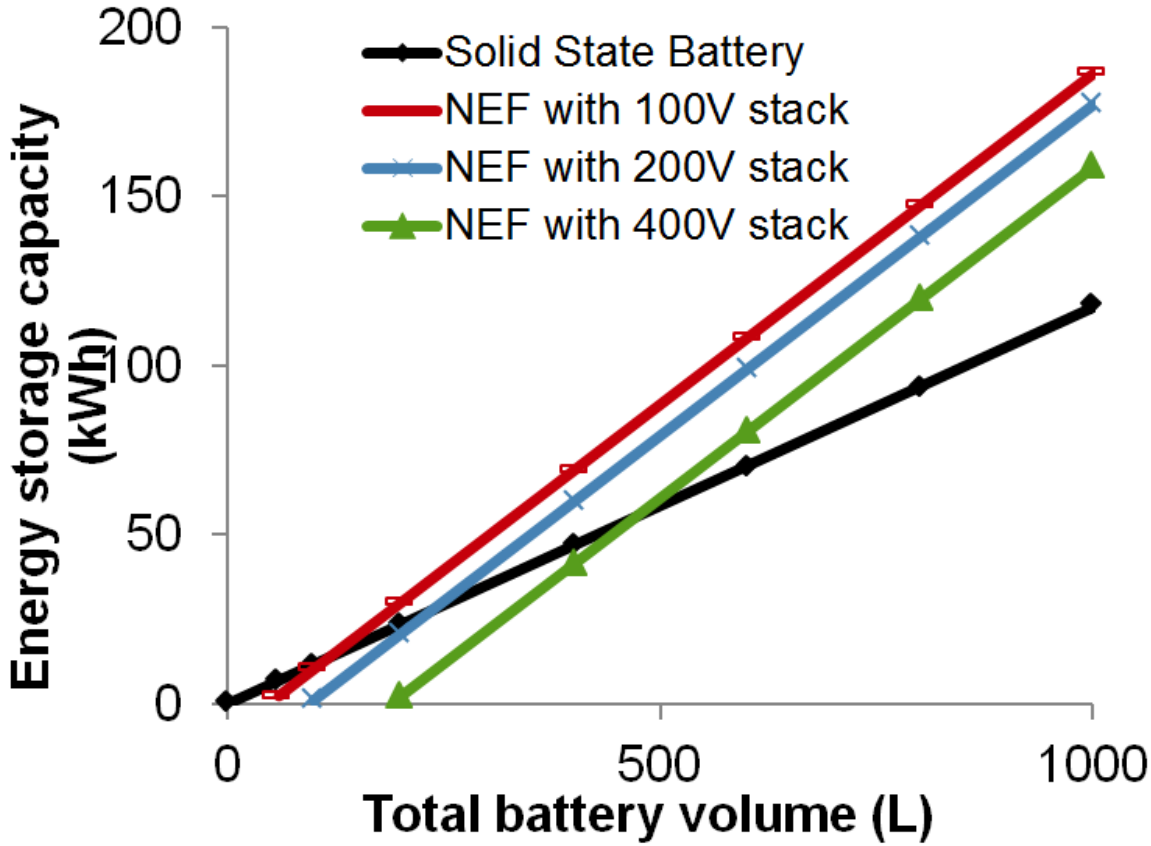
Advantages of nanoelectrofuel

of active material in solid batteries

of active material in NEF flow batteries

initial overhead for power stack depends on desired voltage

active material fraction depends on loading (50% shown)



Advantages of nanoelectrofuel

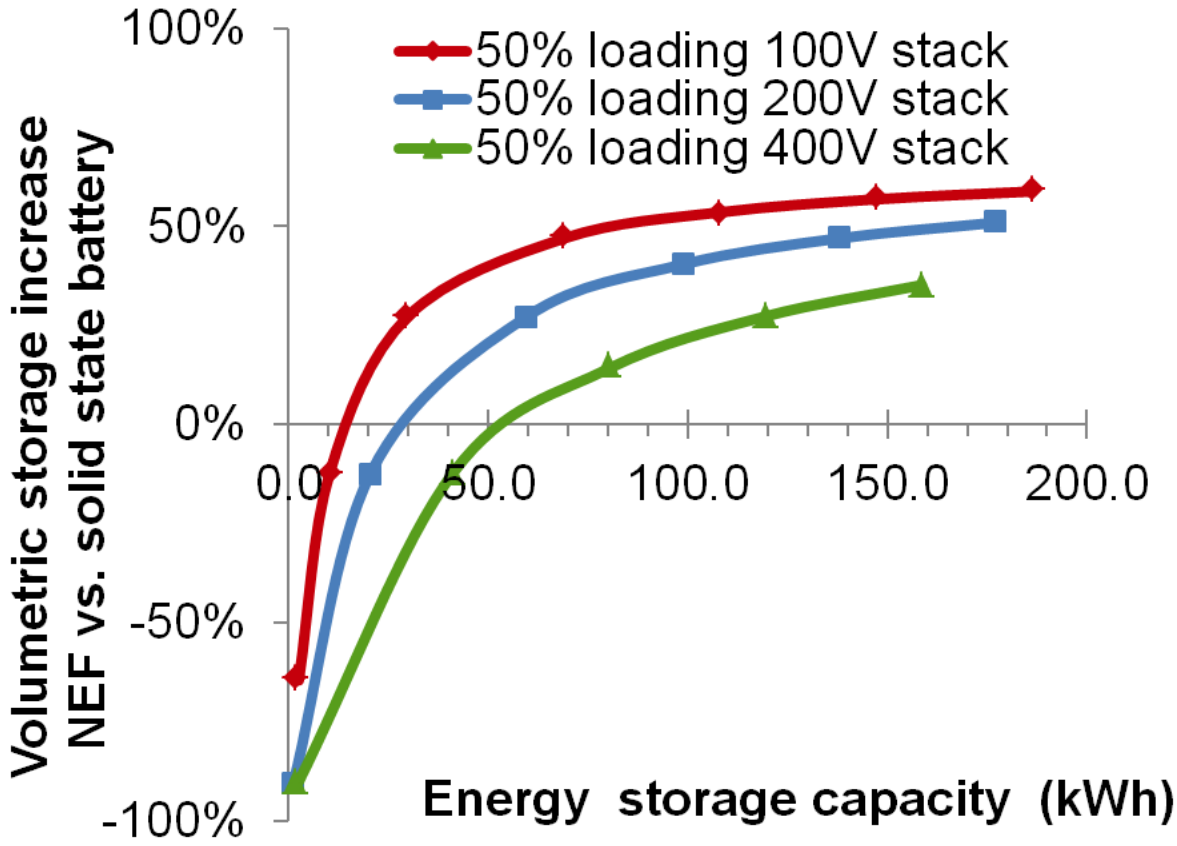
of active material in solid batteries

of active material in NEF flow batteries

initial overhead for power stack depends on desired voltage

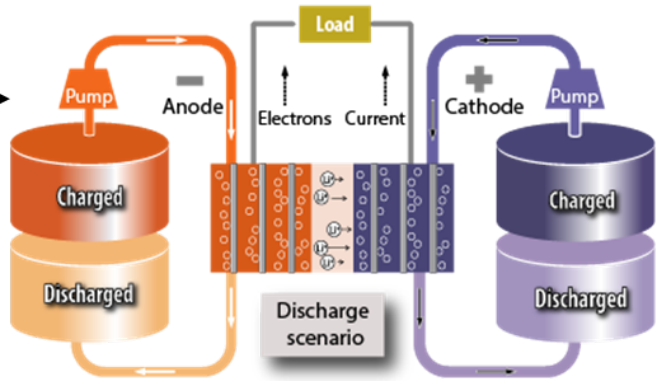
active material fraction depends on loading (50% shown)

beyond 50 kWh, NEF has higher volumetric capacity



Long term vision

Energy Generation Avenues



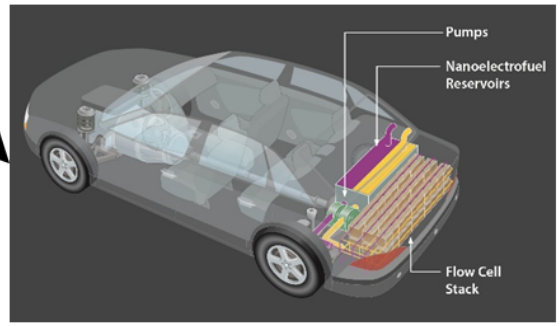
Nanoelectrofuels Charging

Enables Rate Shifting and Grid Leveling

Charged suspension to markets

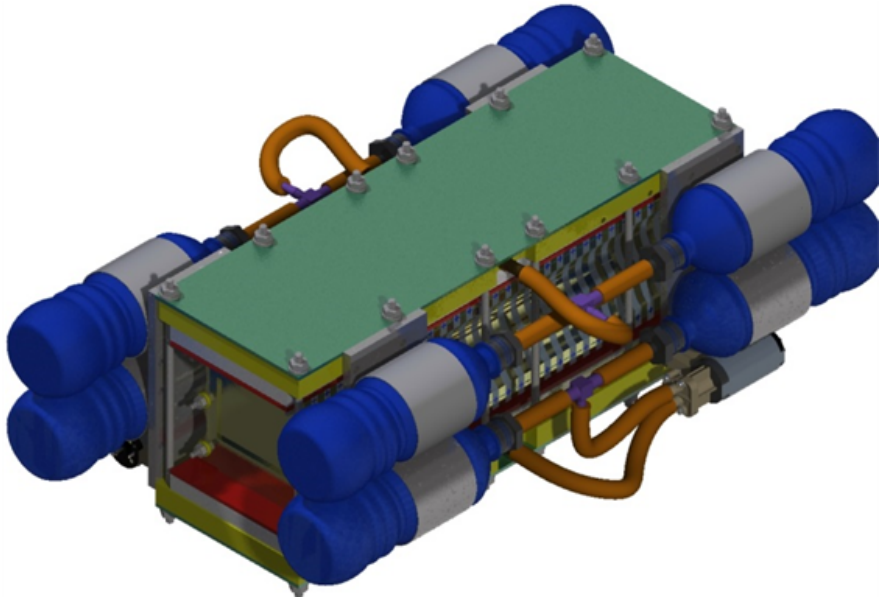
Enables V2H macro and micro grid applications

Rapid pump EV refueling



Nanoelectrofuel challenges

- What is the intrinsic performance of active materials in nanoparticle form?
- Can suspended nanoparticles be effectively charged and discharged during flow?
- How much loading can be stabilized in suspension?
- Will these nanoelectrofuels be pumpable and not destroy the enclosure materials?
- Can the technology be econmical enough to compete with more established technologies?



40 V aqueous chemistry stack

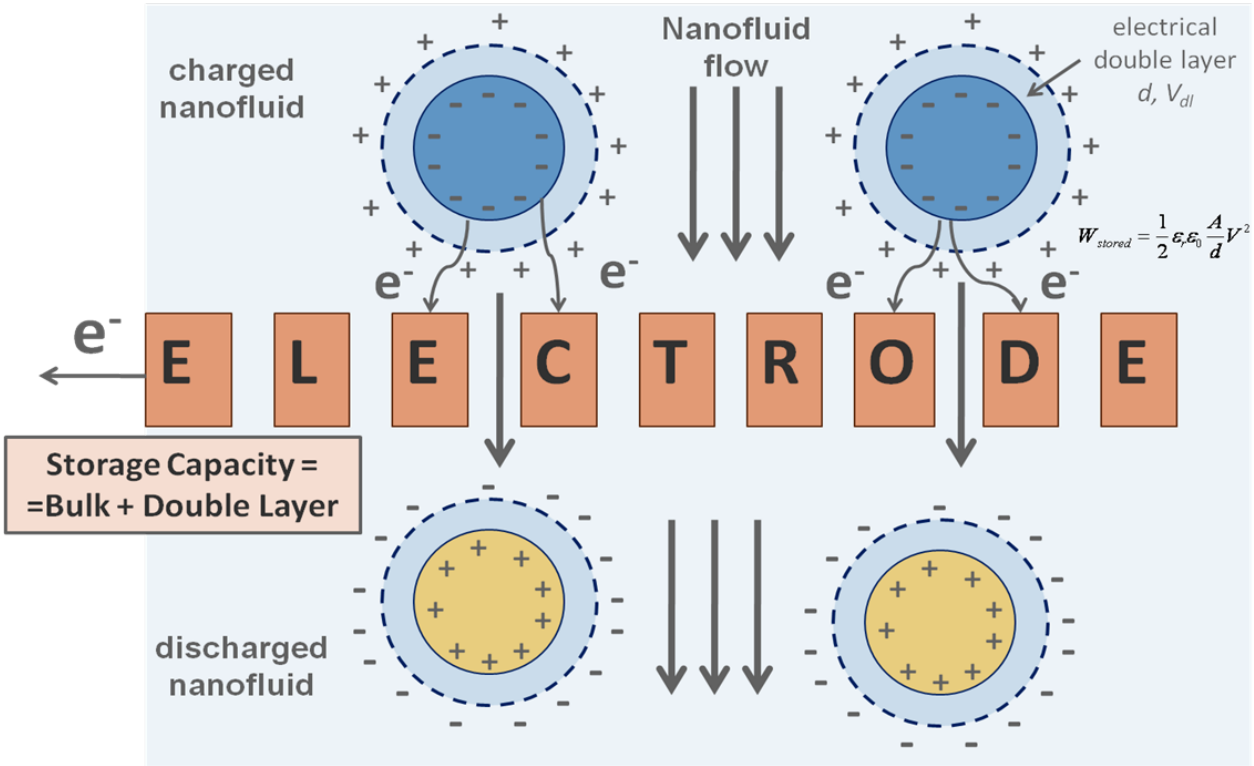
25 kWh using 4.5 L of nanoelectrofuel

26 kg stack, 10 kg 50% loaded fluid

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

Charging & discharging nanoelectrofuel

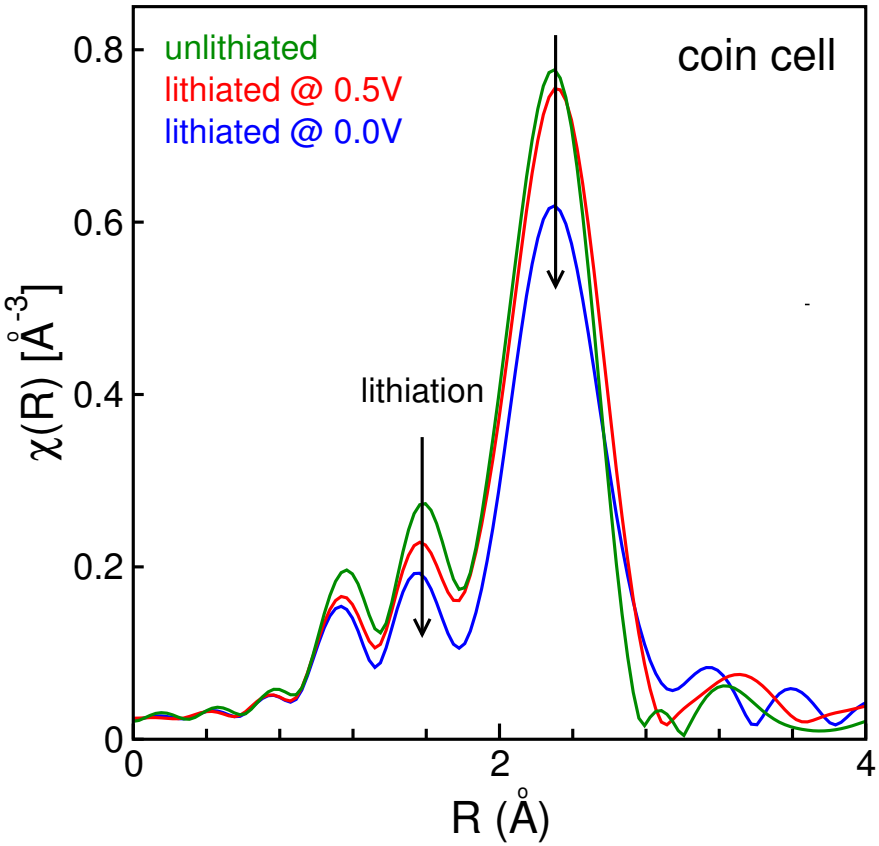
Charging and discharging in a flow can be achieved by proper design of the electrode but all these ideas have to be validated through computation and experiment.

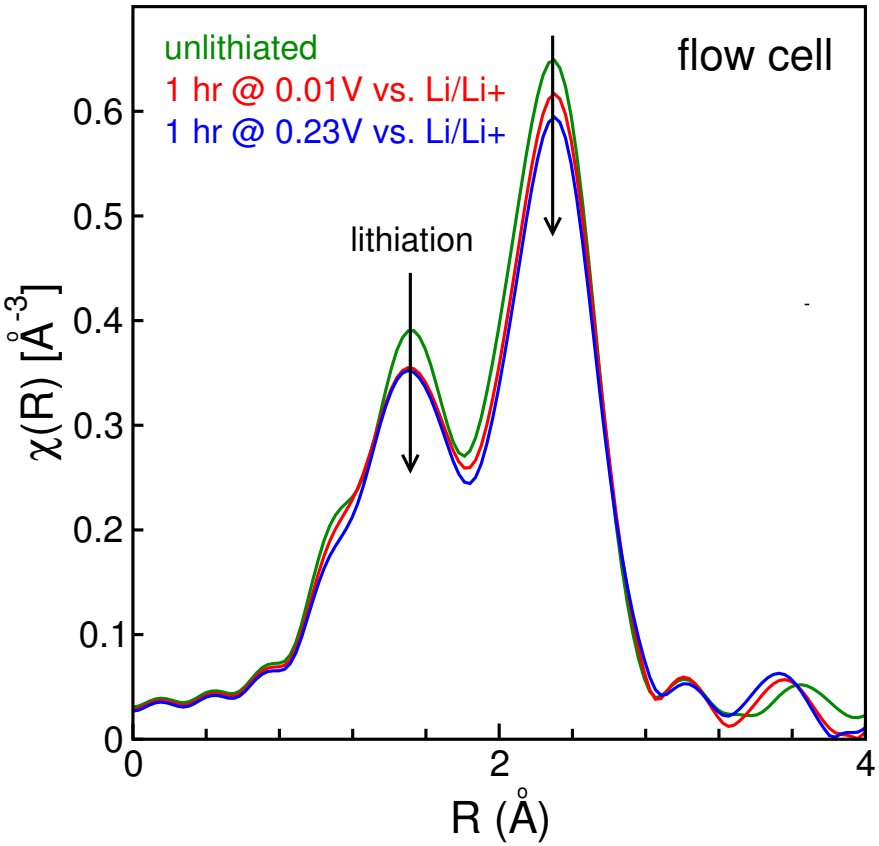


- Porous electrode for high contact probability
- Turbulent flow to maximize electrode contact
- Moderate pressure drop across the cell
- Must have electron transfer with transient contact

First charging results

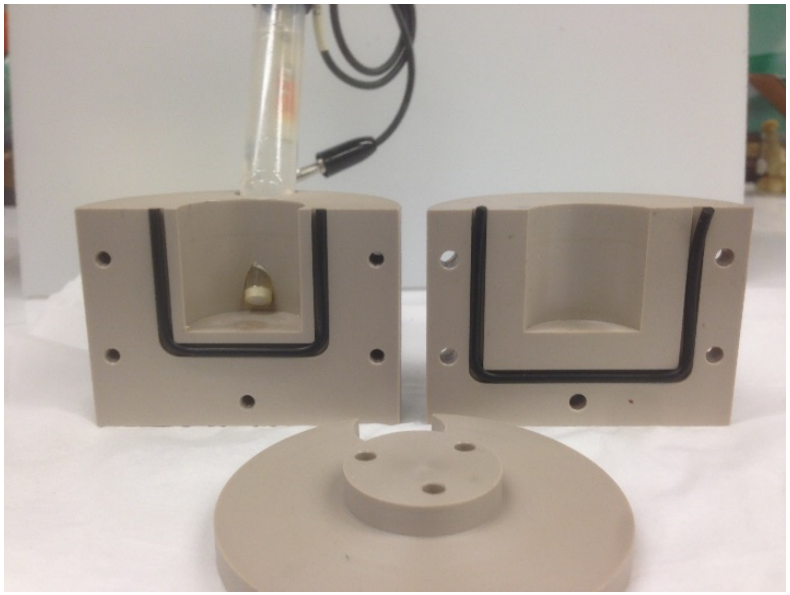
December 2012 data comparing x-ray absorption spectroscopy results on Cu_6Sn_5 anode material in a coin cell and flowing through a metal frit.

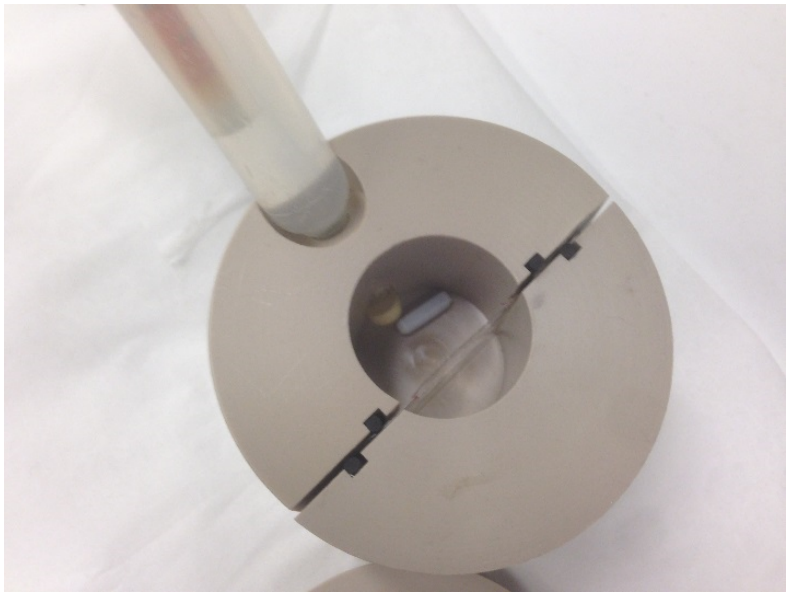


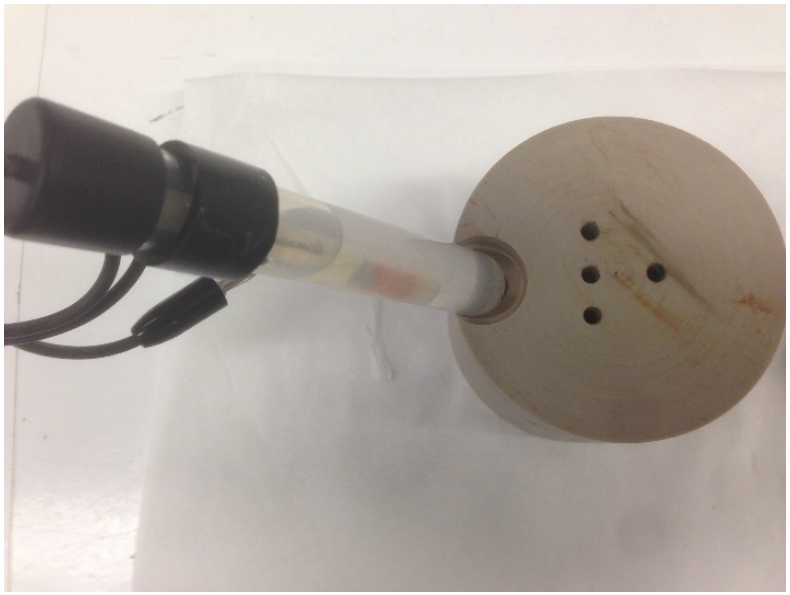


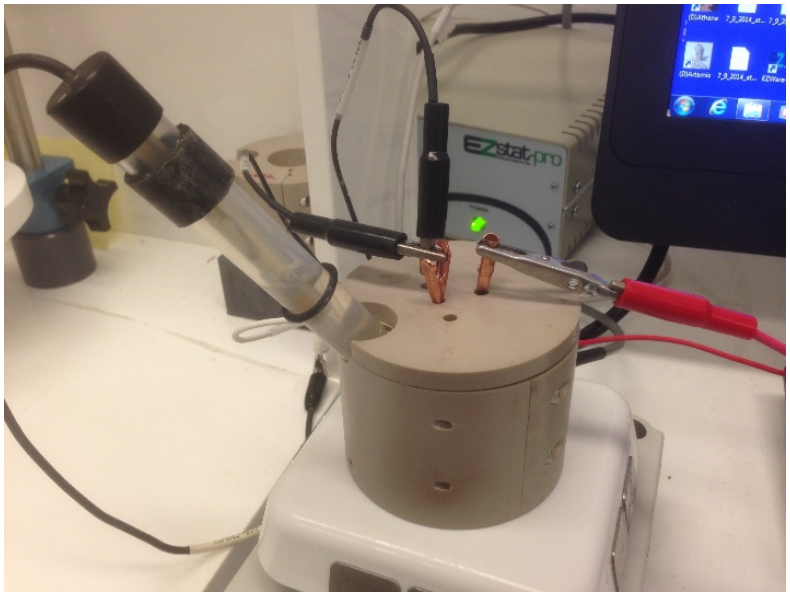
Similar trends indicate that nanoparticles in the flow cell are charging, albeit slowly and inefficiently.

Beaker cell for initial charging tests

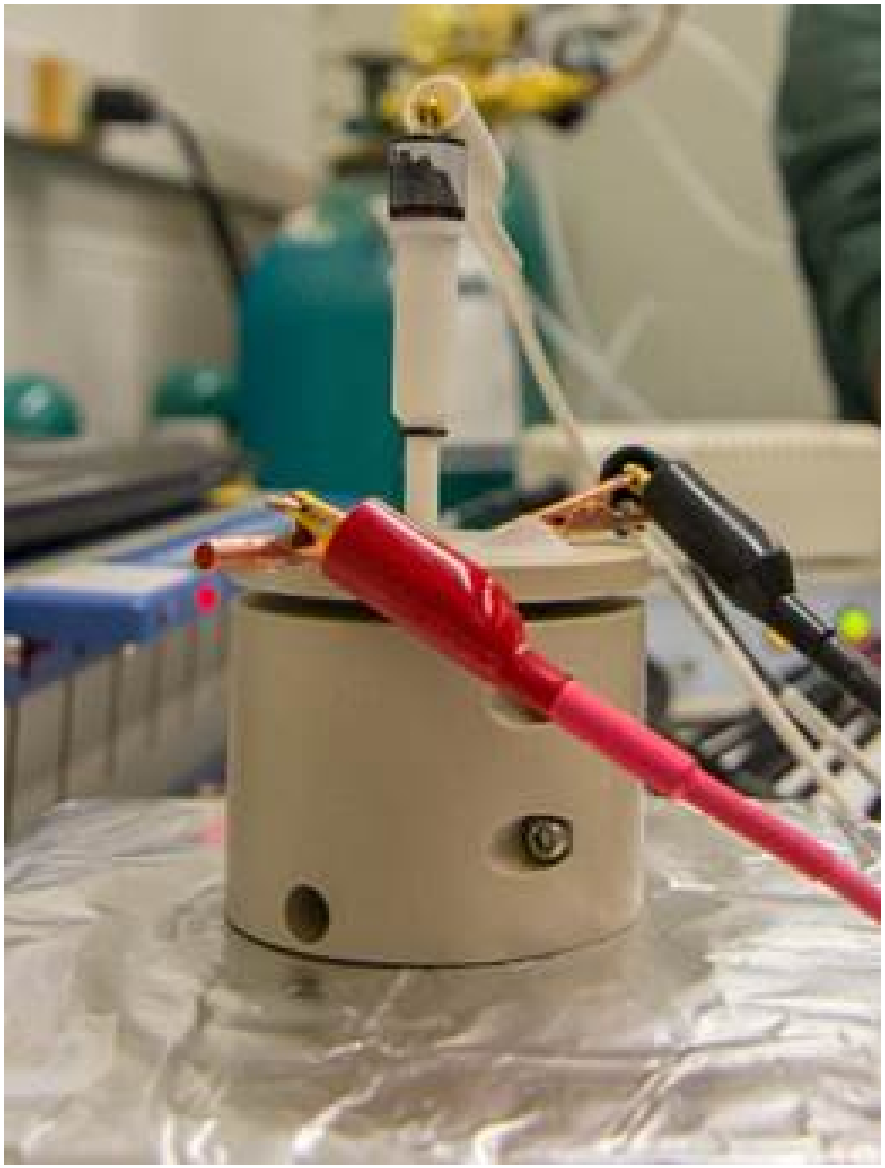








Initial nanofluid charging



Initial nanofluid charging using a beaker cell

Agitation using a magnetic stir bar with a wire mesh current collector immersed in fluid

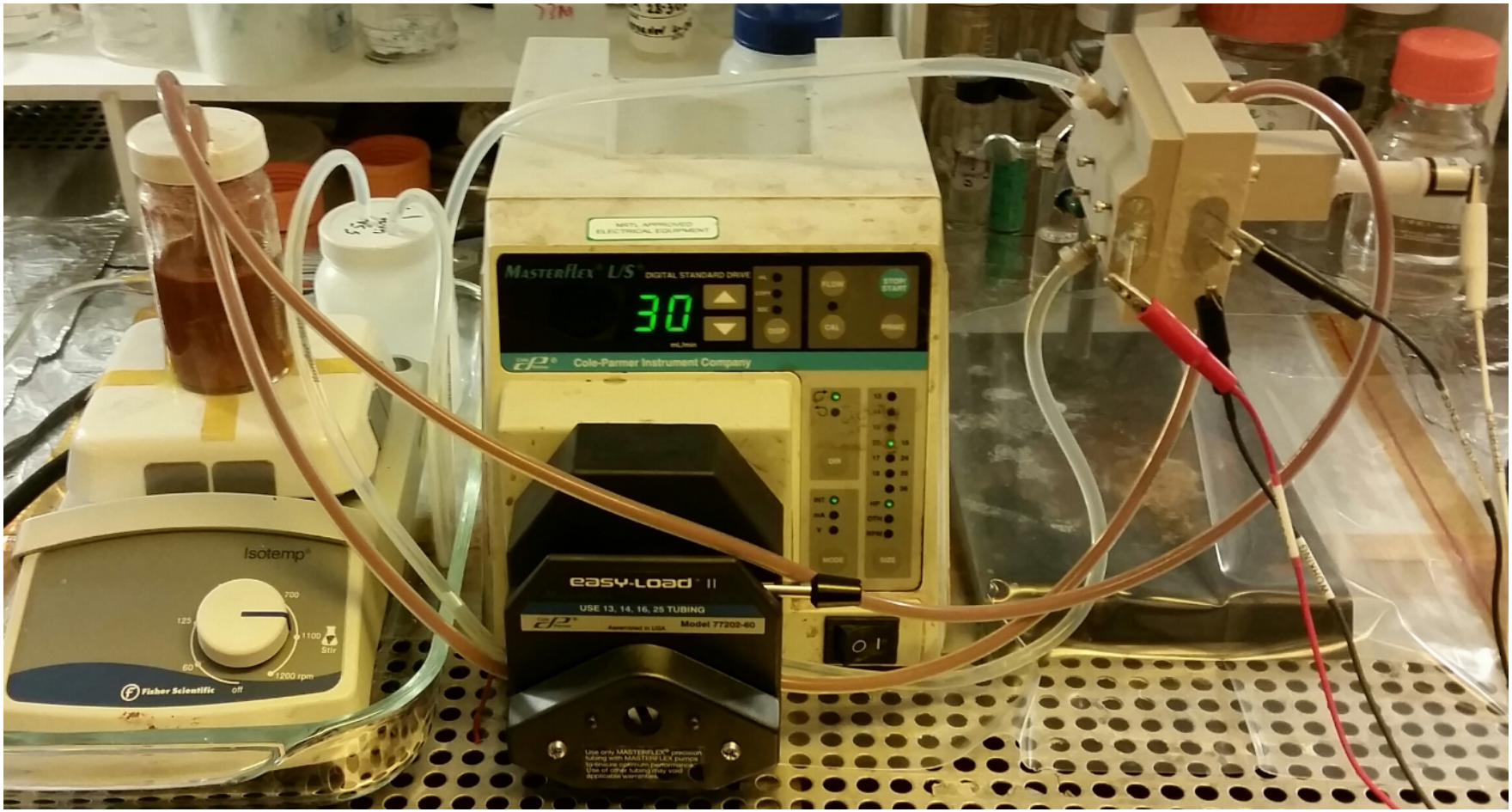
Non-aqueous (Li-ion) chemistries have very low conductivity and require significant research to move forward

Aqueous chemistries easier to charge and more compatible with "real" world

Charge/discharge times still 10× too slow!

Need a flow-through system to improve charge/discharge times

Test flow cell



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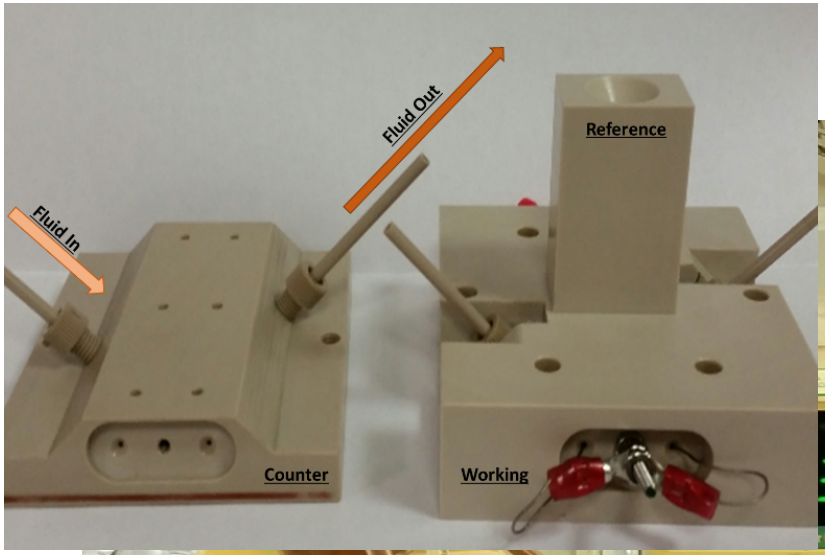

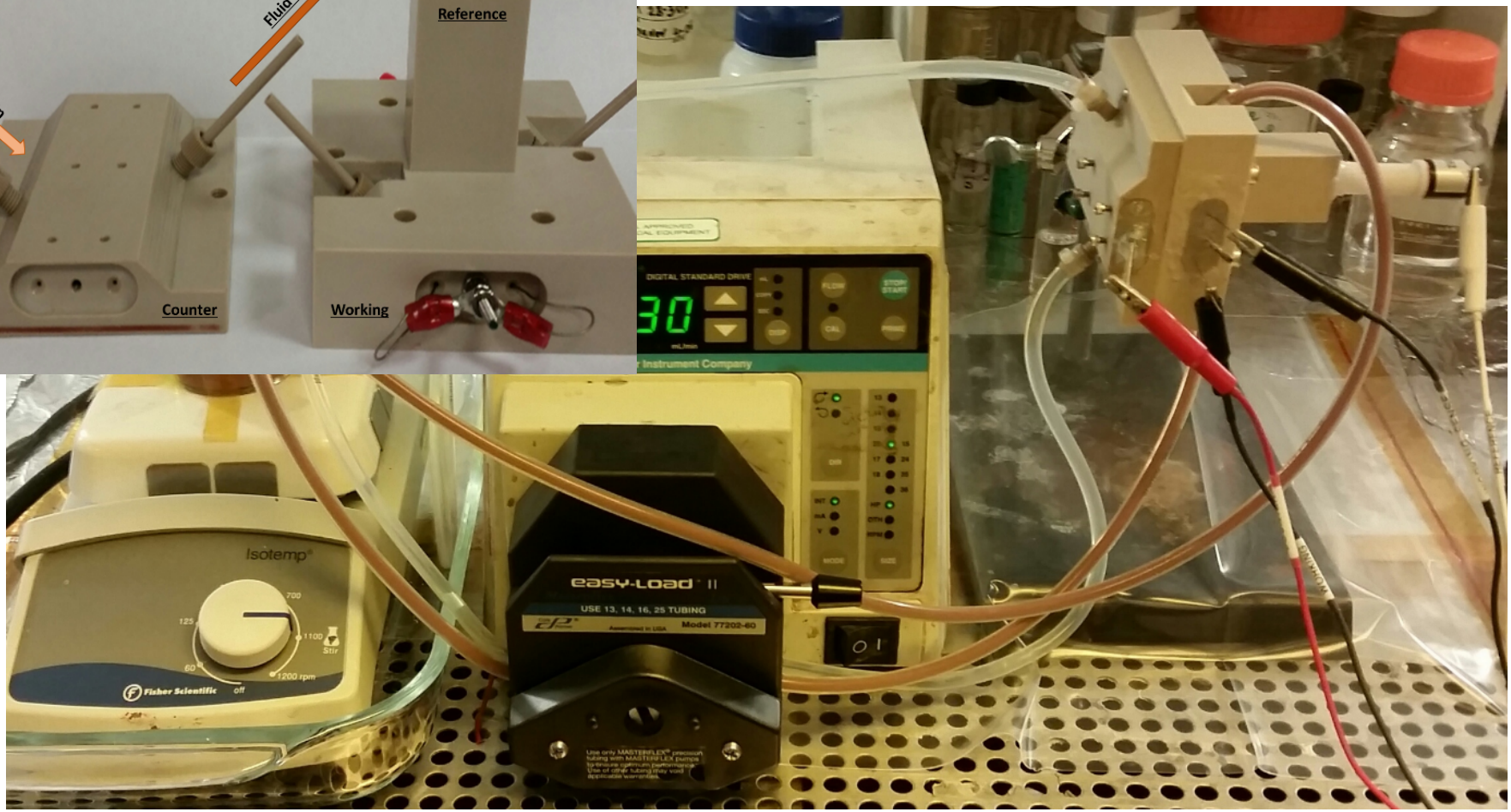

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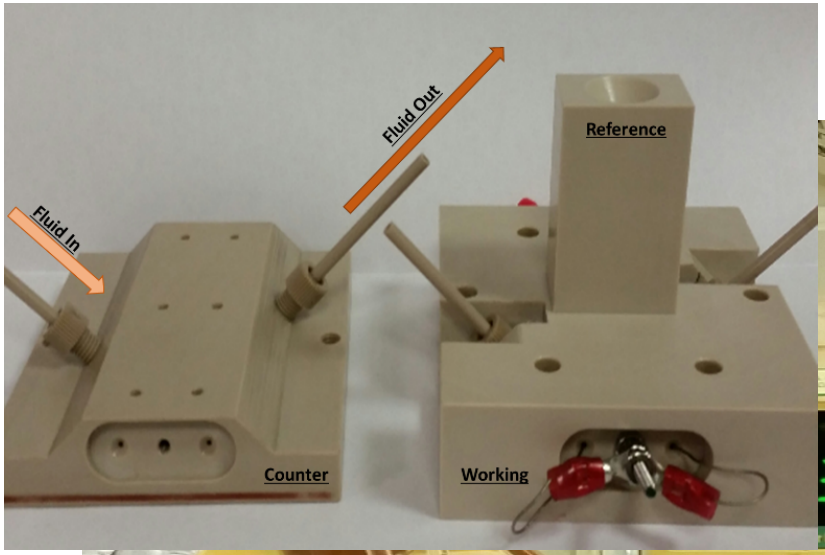
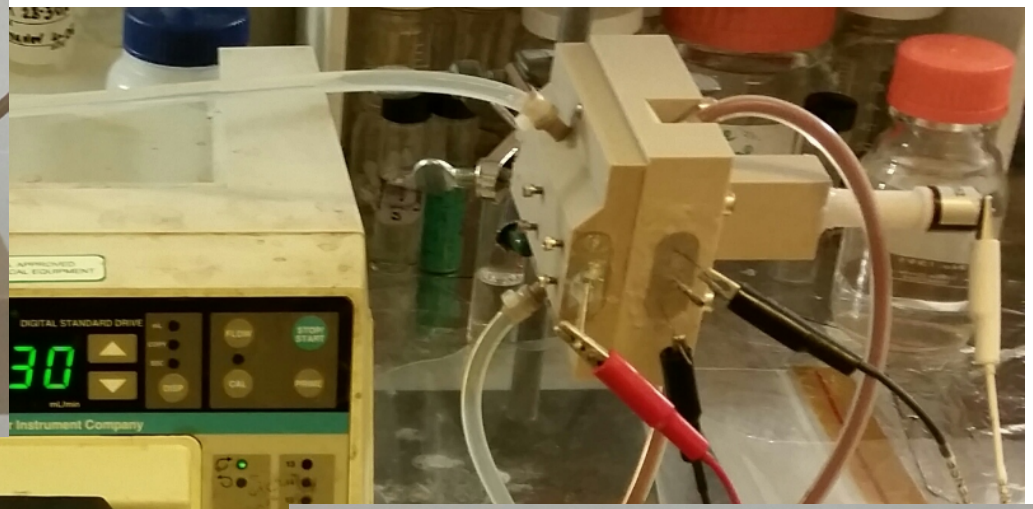
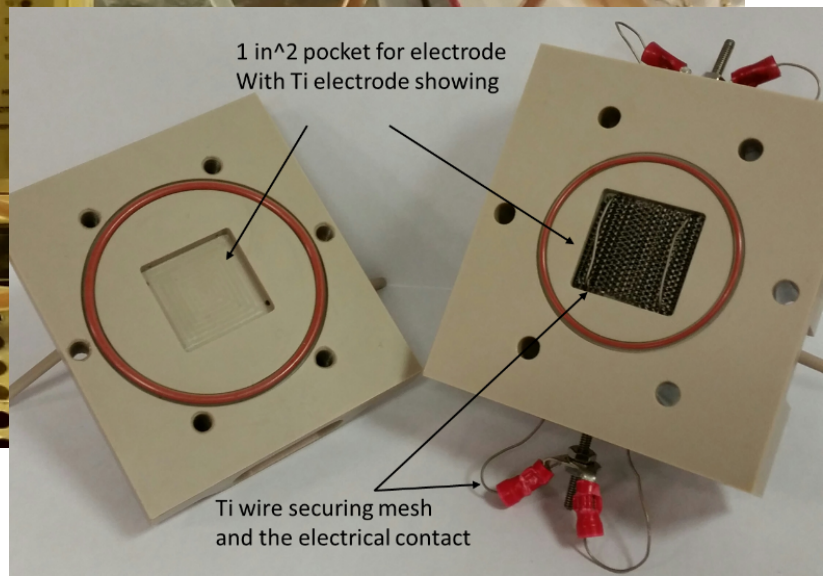




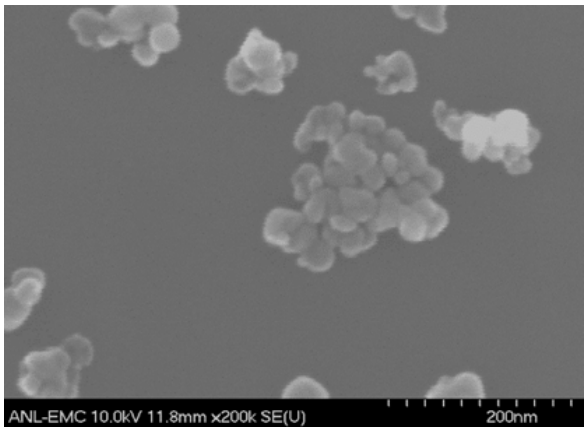


NEF anode: Fe_2O_3

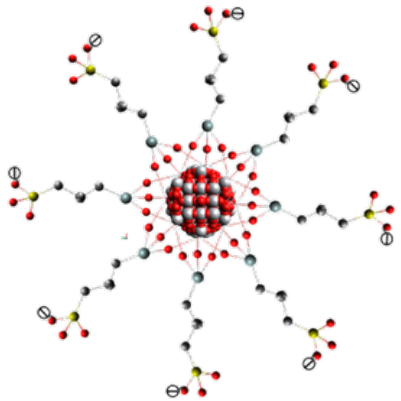
Start with commercially available Fe_2O_3 suspended in water with $\sim$ 5M LiOH

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

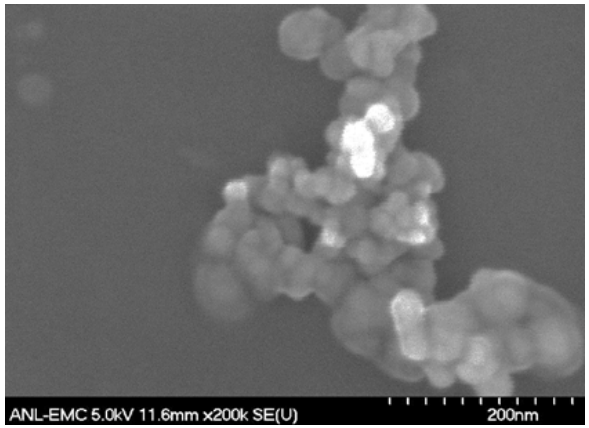
$Fe_2O_3 + 3\,H_2O + 2\,e^- \longrightarrow 2\,Fe(OH)_2 + 2\,OH^-$	$E_0 = -0.9V$	$\sim$ 335 mAh/g
$Fe(OH)_2 + 2\,e^- \longrightarrow Fe + 2\,OH^-$	$E_0 = -1.0V$	$\sim$ 670 mAh/g
$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$	$E_0 = -0.9V$	Bad!



pristine Fe_2O_3

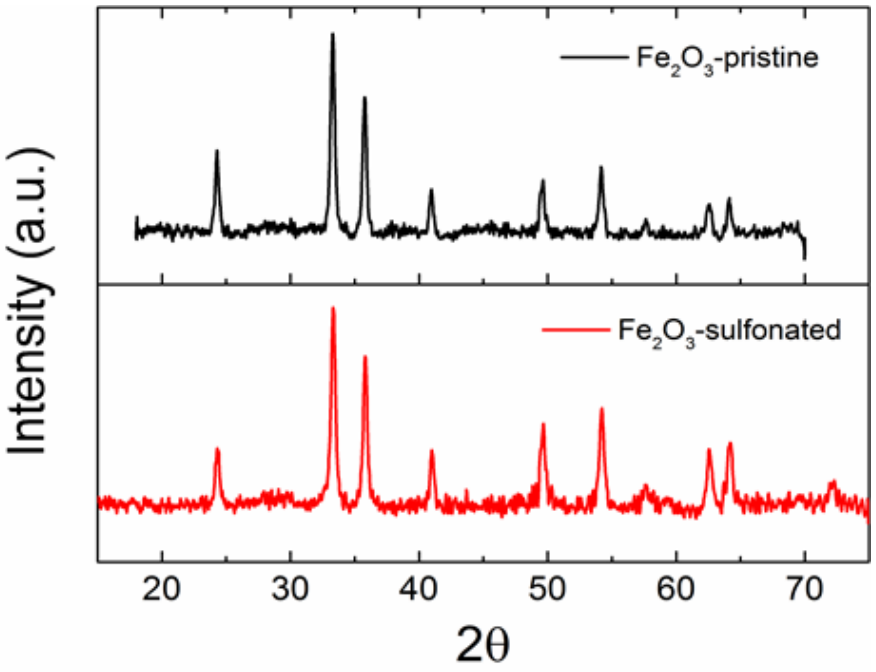


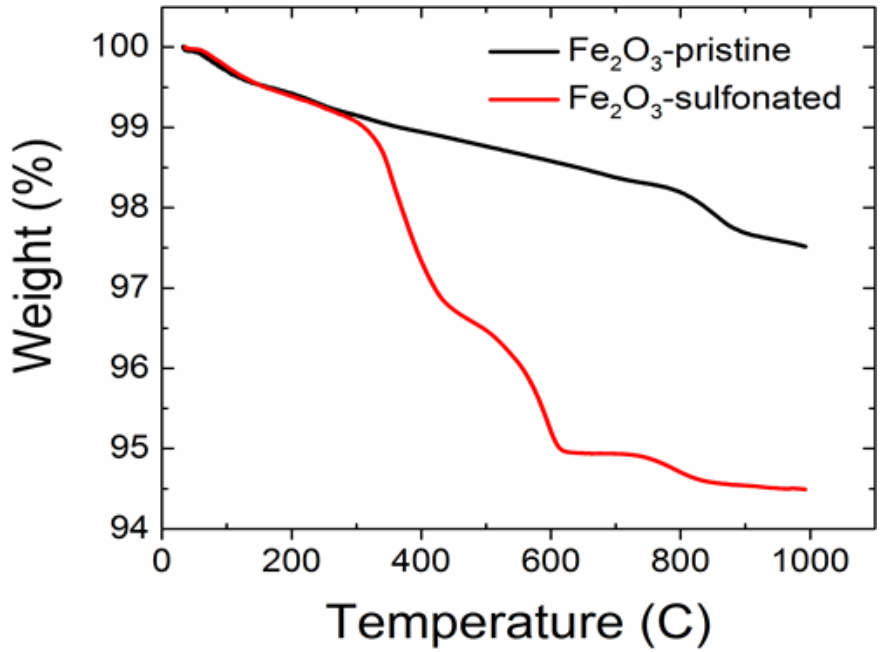
treat with $\sim$ 3 wt%
$(OH)_3{-}Si{-}(CH)_3{-}SO_3$



sulfonated Fe_2O_3

Fe_2O_3 nanoparticle characterization

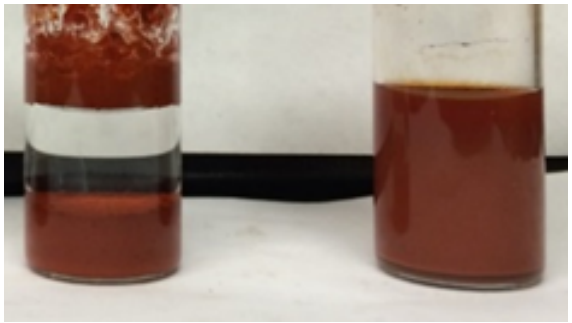




X-ray diffraction shows no structural changes with sulfonation

TGA measurement shows $\sim$3 wt% due to surface treatment, about 1 monolayer on a typical nanoparticle

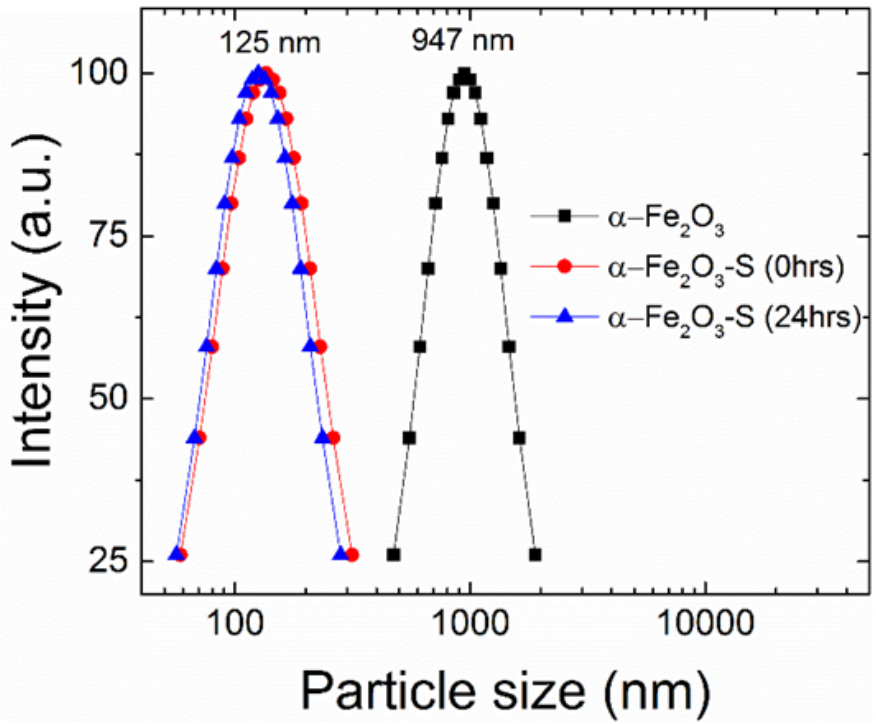
Fe_2O_3 rheology

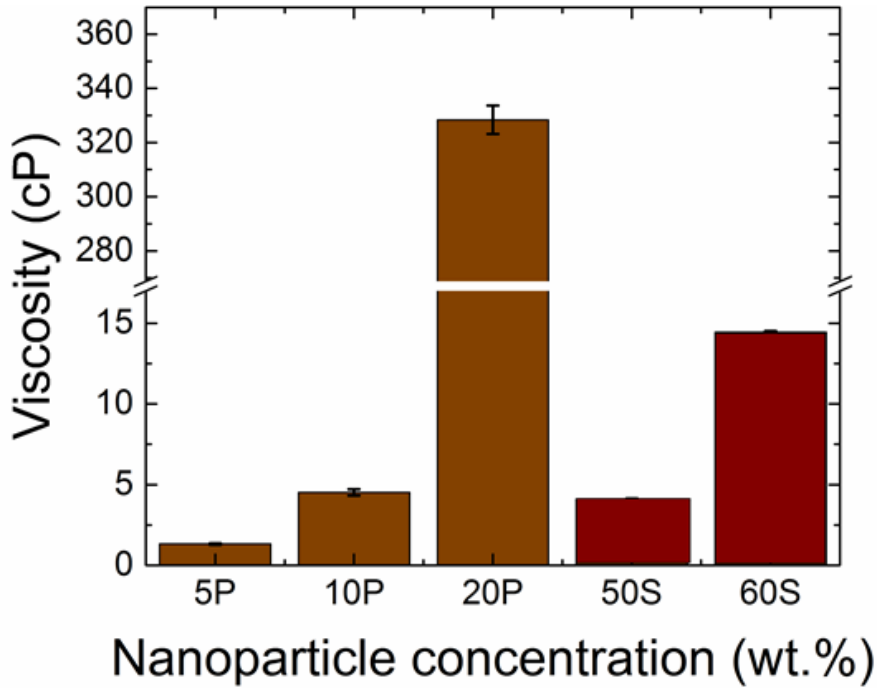


5 wt% pristine (left) vs. modified (right) nanofluid after 2 weeks

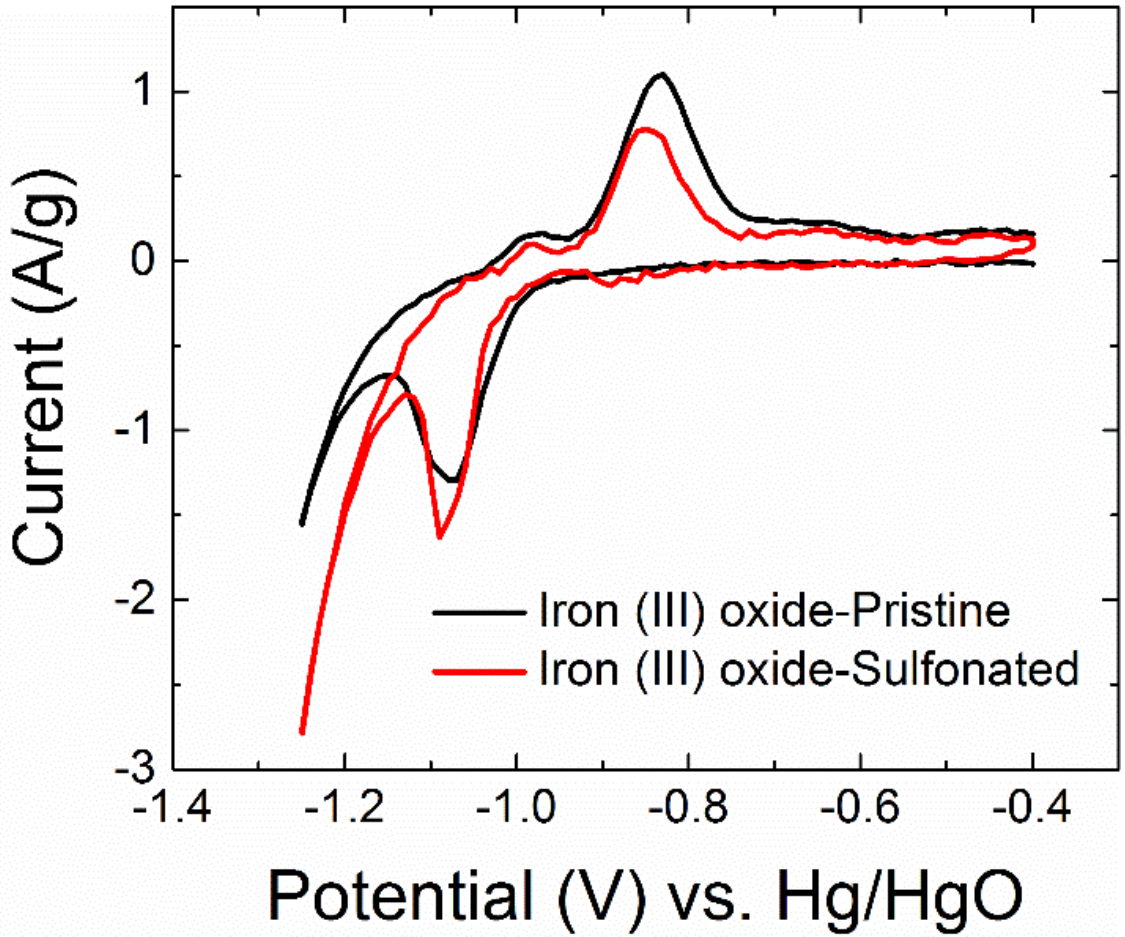
Dynamic light scattering measurements of Fe_2O_3 nanofluids

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





Fe_2O_3 solid electrode electrochemistry

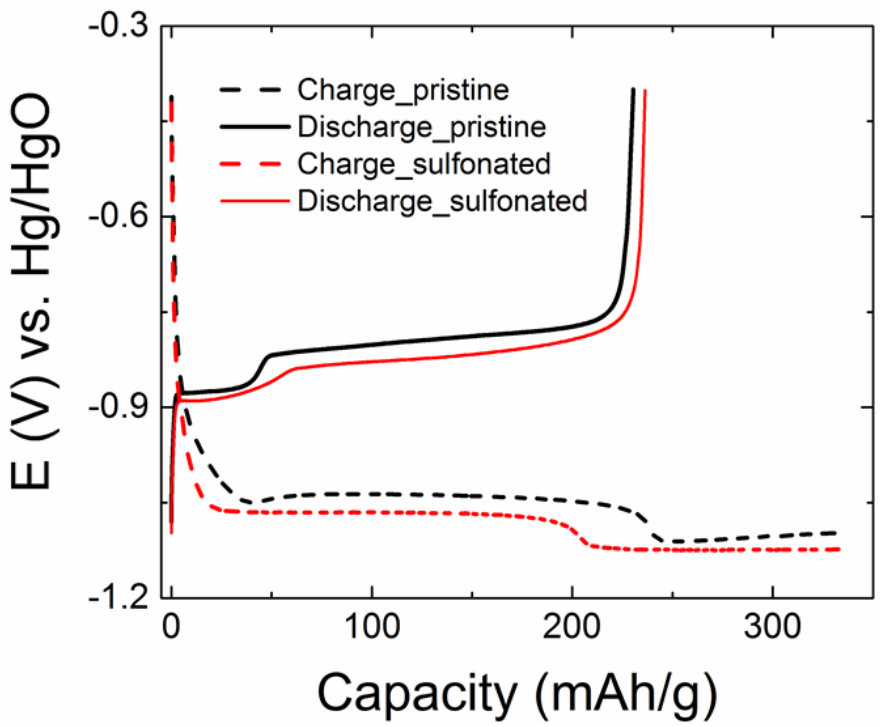


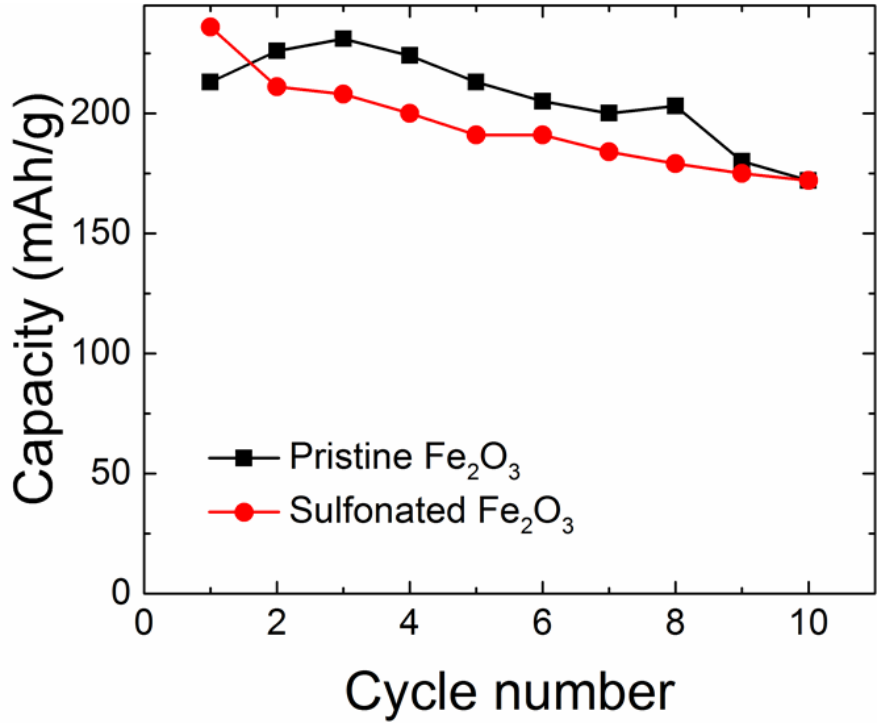
Casted electrodes on Ni foam in alkaline pouch cell

Hydrogen evolution at potentials below -1.2V

Fe_2O_3 cyclic voltammetry shows redox reactions of Fe in both pristine and sulfonated nanoparticles

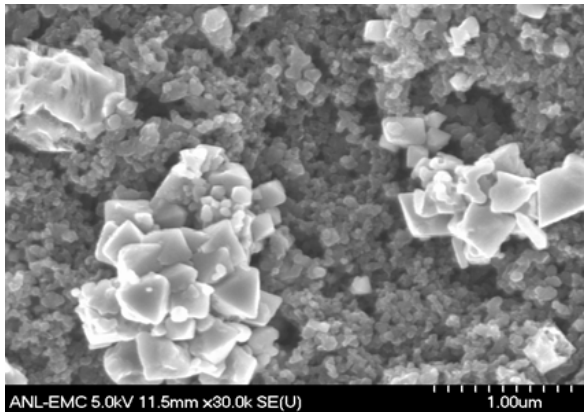
Solid state performance



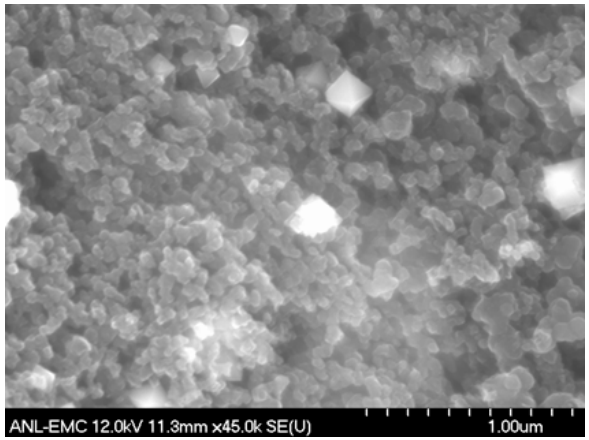


Performance of sulfonated nanoparticles very similar to pristine

Morphology of pristine electrode changes

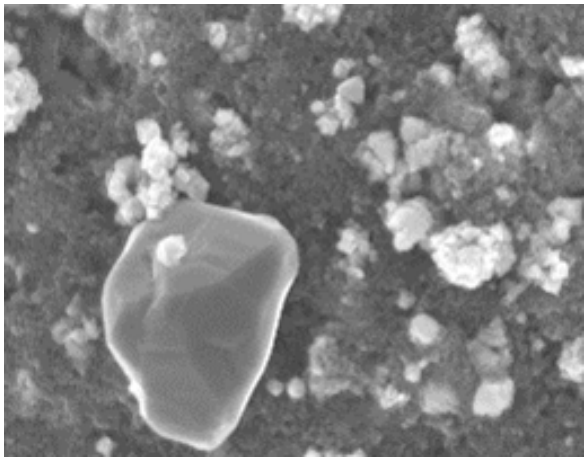
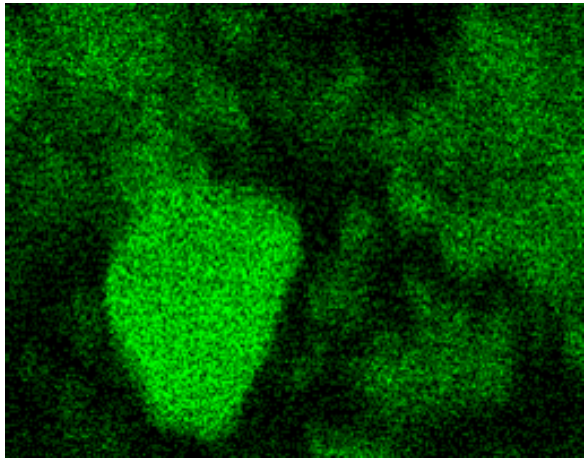
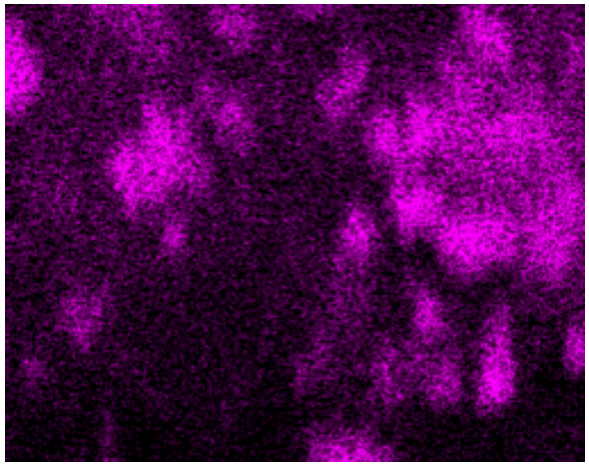


pristine

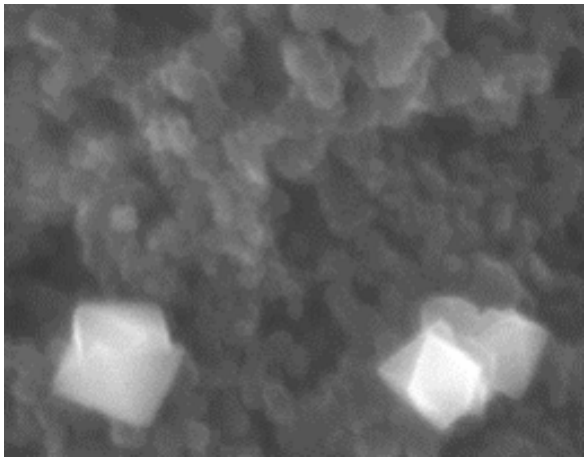
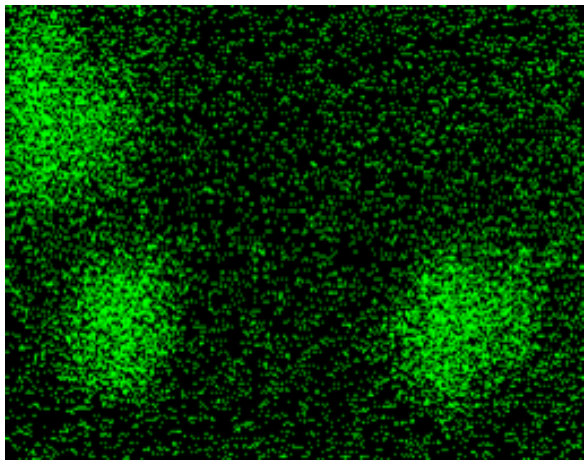
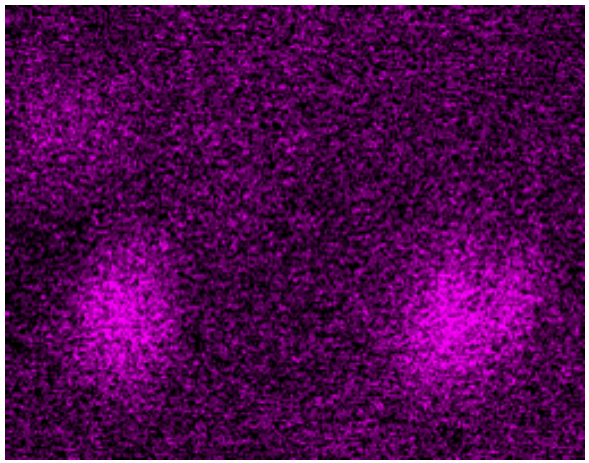


sulfonated

Fe_2O_3 post-cycling analysis

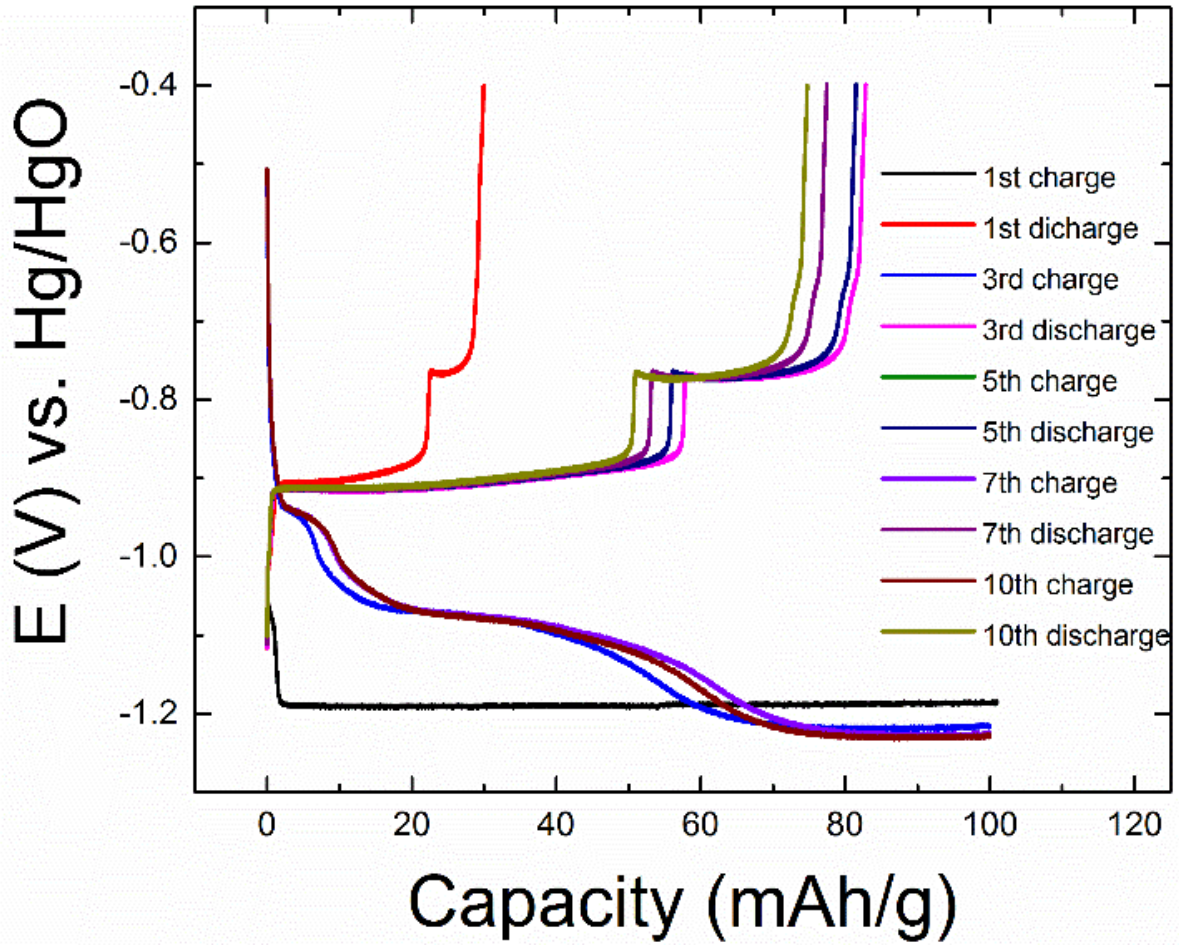




Pristine Fe_2O_3 electrodes show recrystallized Fe metal particles

Sulfonated Fe_2O_3 electrodes show only oxide particles

Fe_2O_3 nanofluid

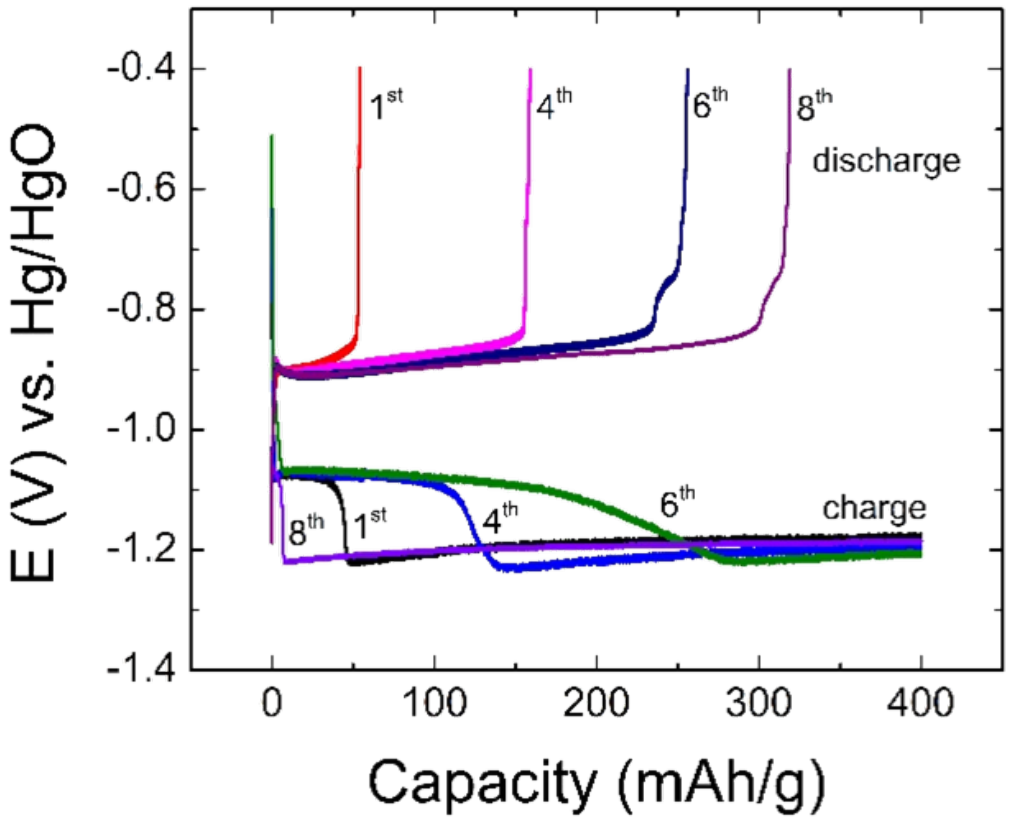


5% wt suspension of Fe_2O_3 nanoparticles in KOH/LiOH solution

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

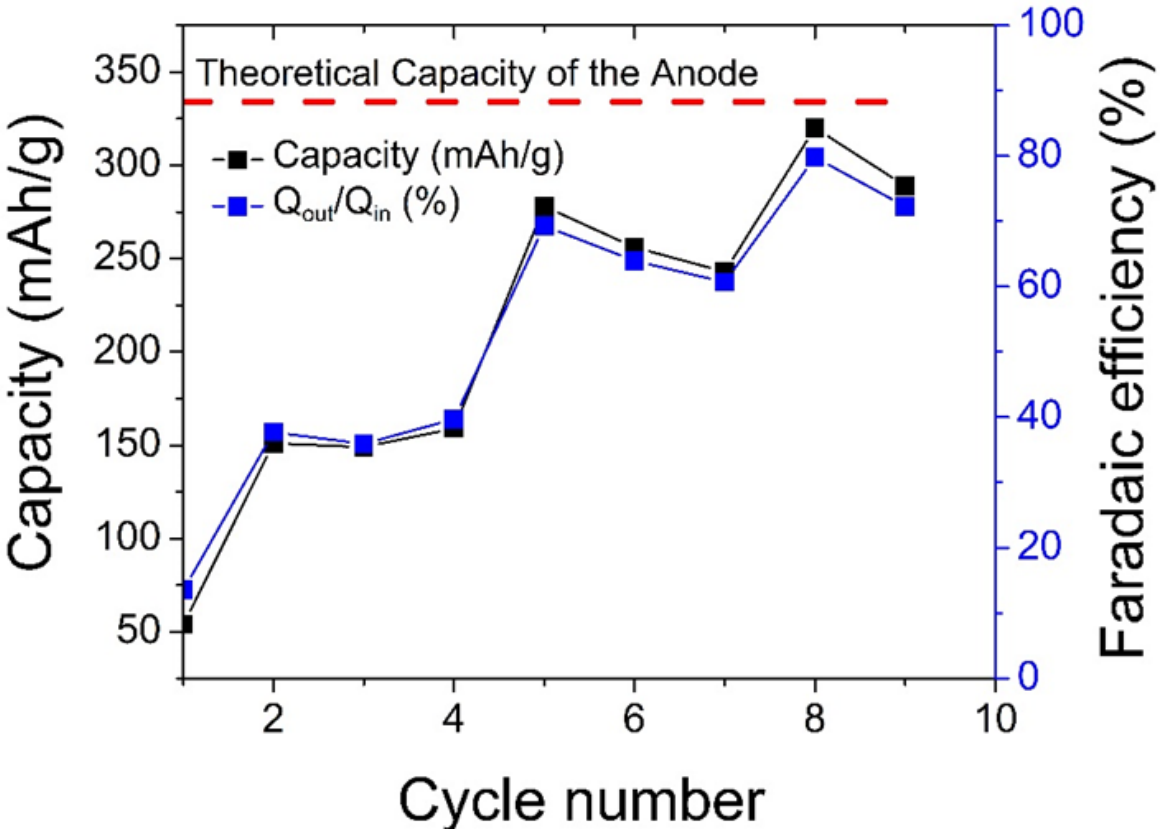
Need to move to flow-through current collector design

Pristine Fe_2O_3 NEF performance



5% suspension of pristine Fe_2O_3, over-charged and discharged at C/33 with improved electrode

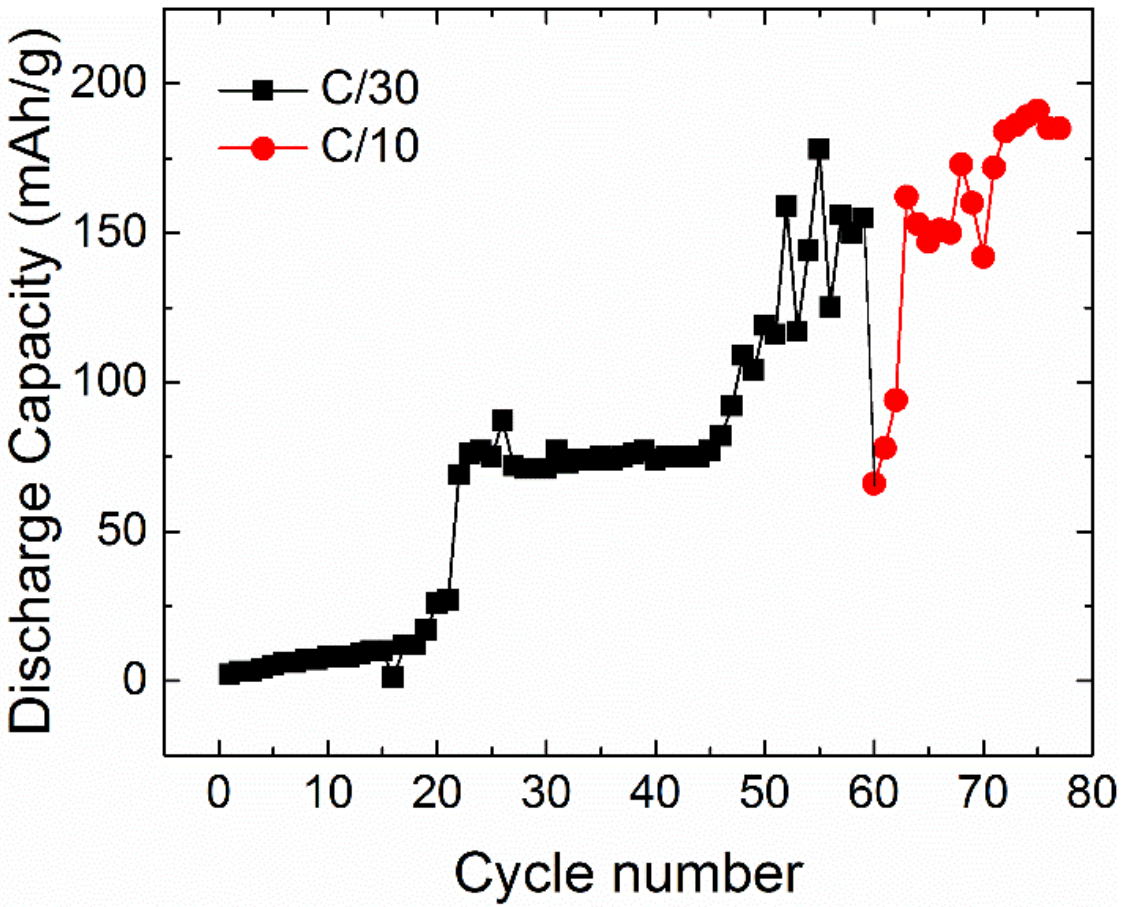
Pristine Fe_2O_3 NEF performance



5% suspension of pristine Fe_2O_3, over-charged and discharged at C/33 with improved electrode

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

Sulfonated Fe_2O_3 NEF performance

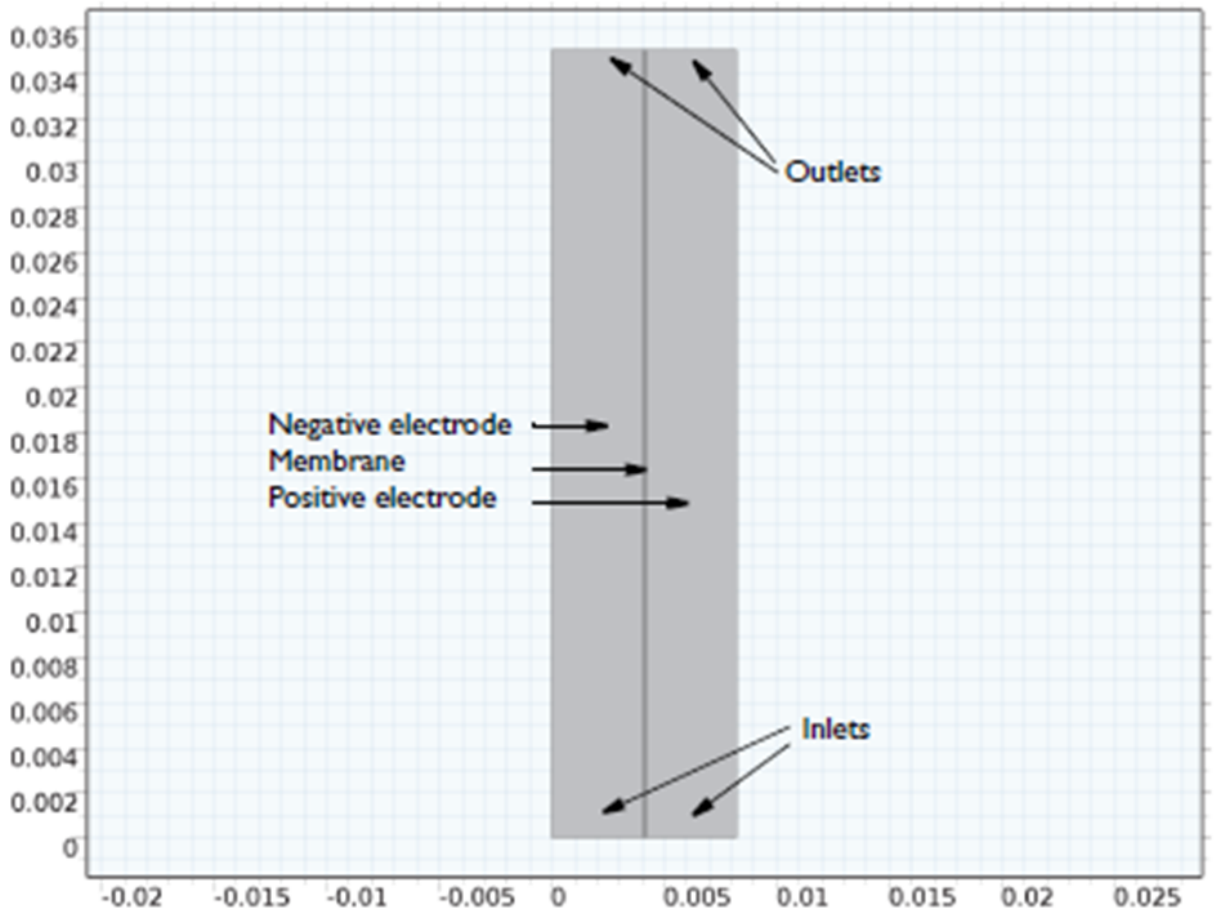


5% suspension of sulfonated Fe_2O_3, overcharged and discharged at C/30 and C/10 with improved electrode

Capacity lower than pristine Fe_2O_3 but improving with training

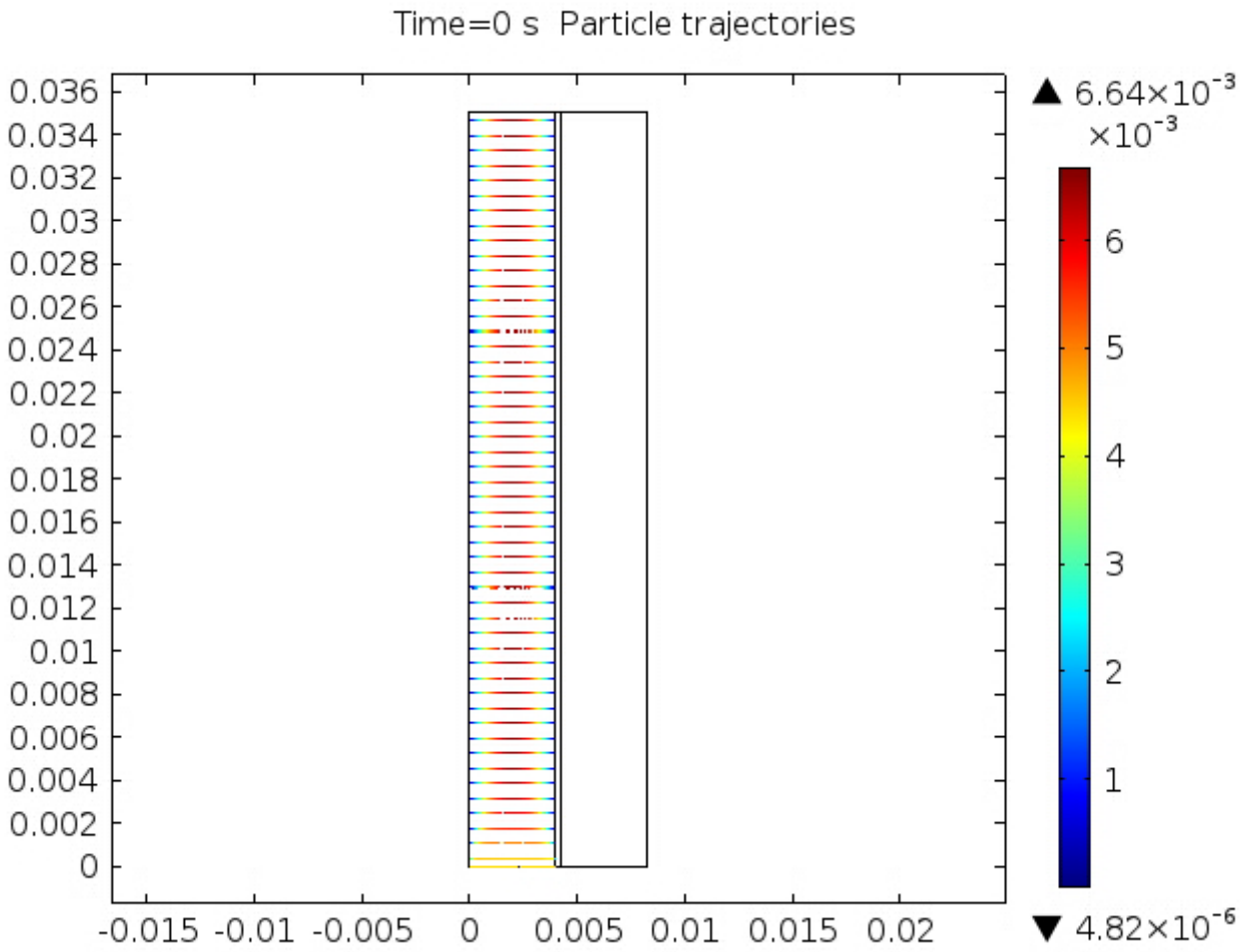
Surface treatment may be preventing conversion to metallic Fe, thus lower "capacity"

Microscopic modeling of NEF



Initial model includes charged particle-particle interaction, interaction with electrode, and particle-fluid interaction

Microscopic modeling of NEF



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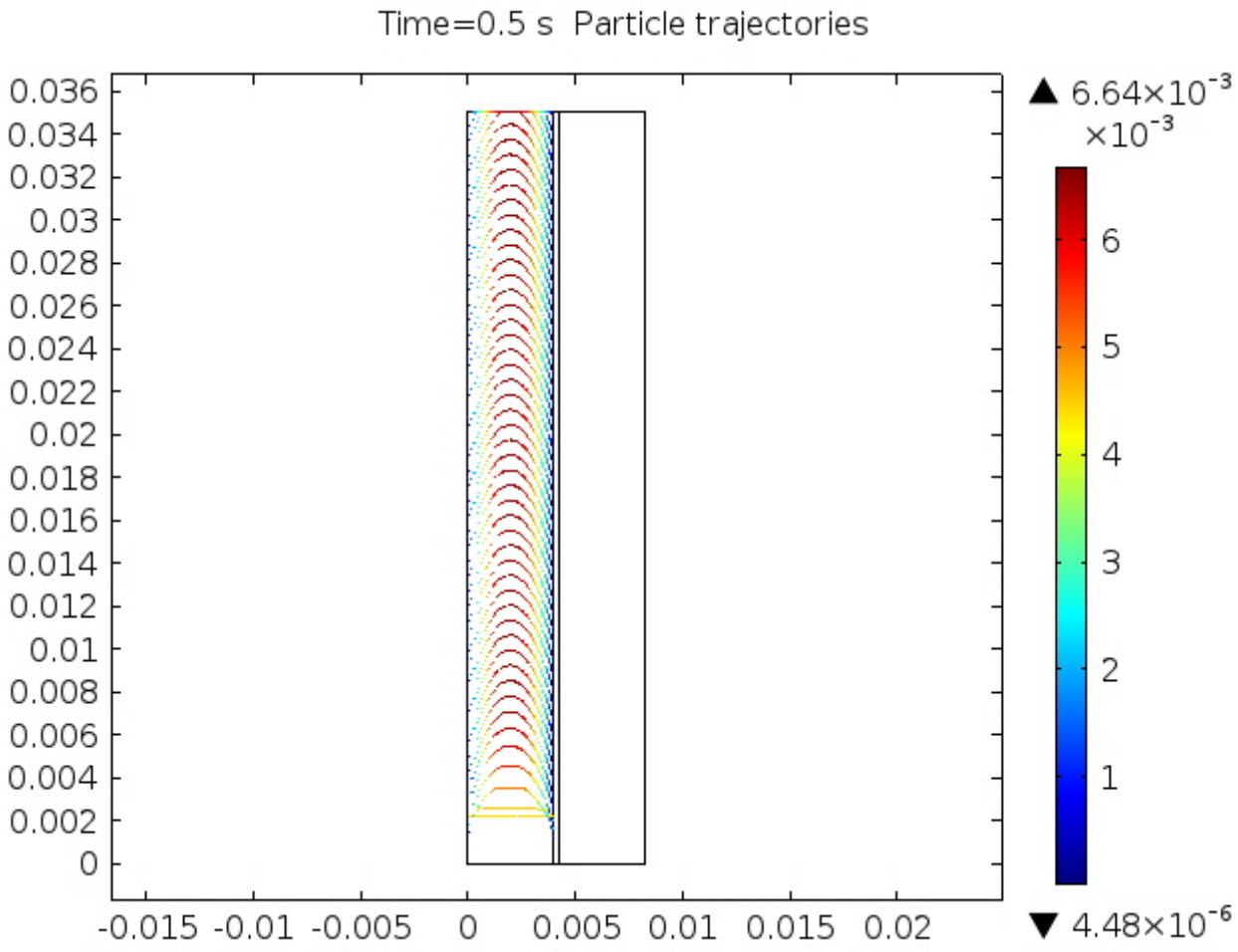

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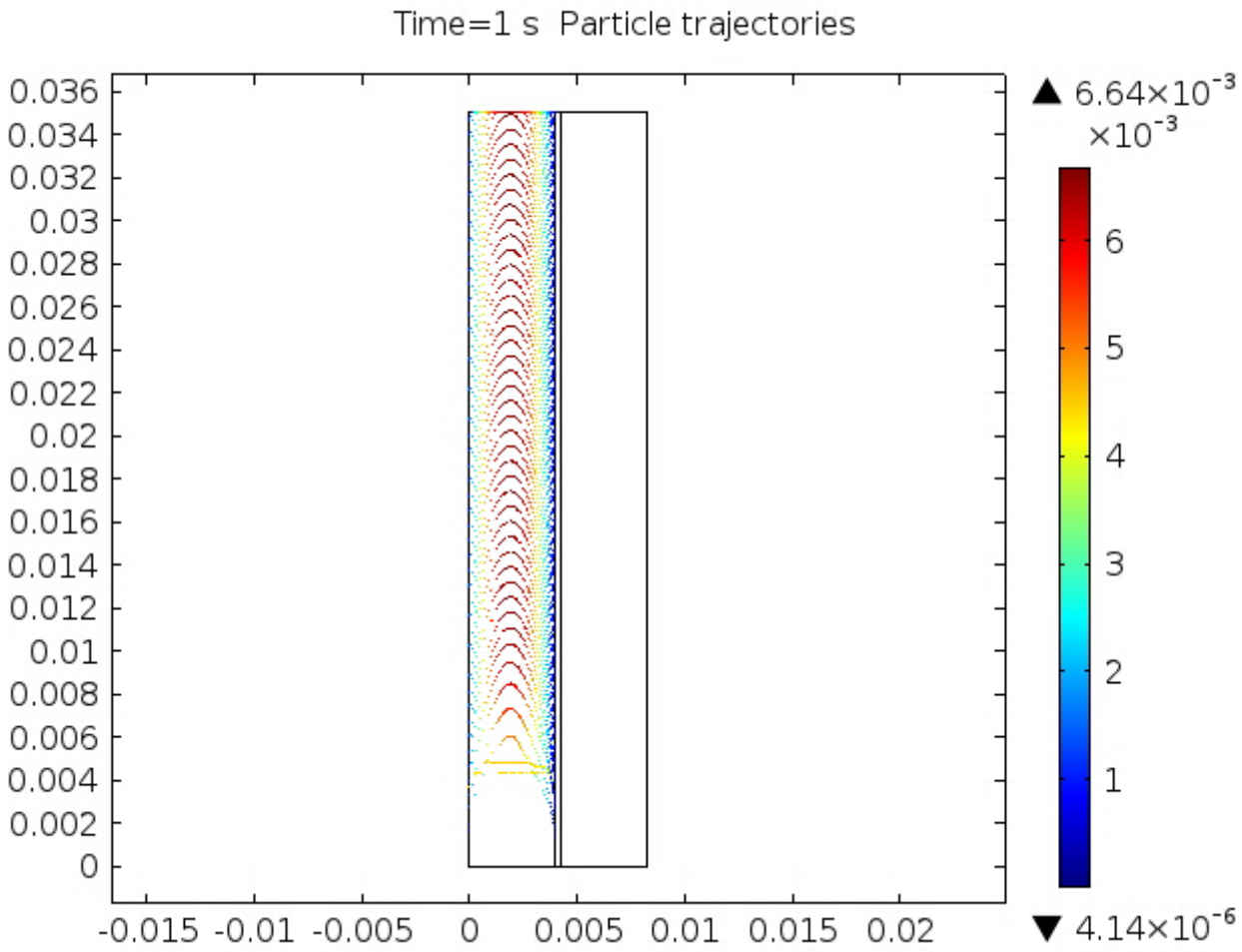
Microscopic modeling of NEF



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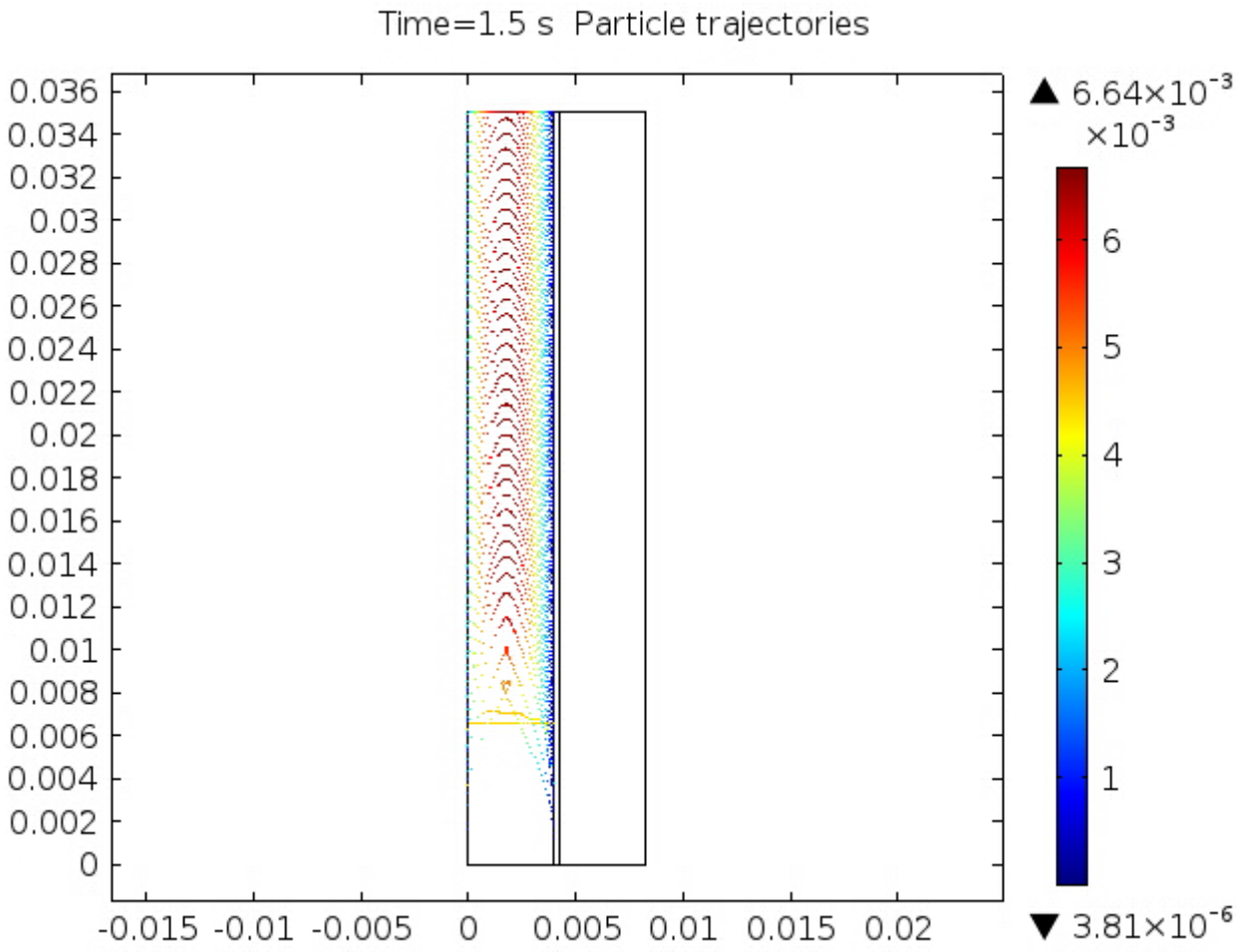
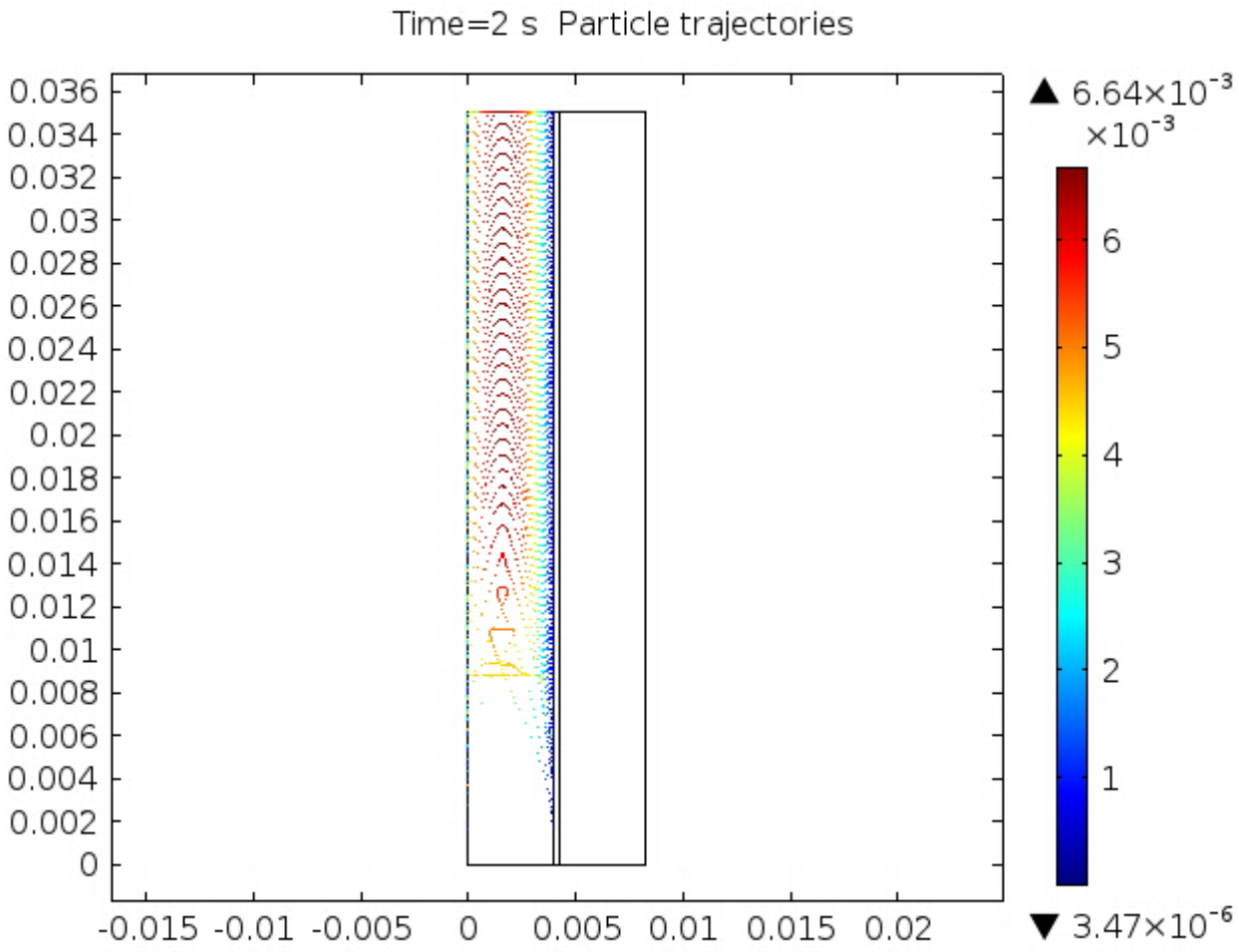
Microscopic modeling of NEF



Initial model includes charged particle-particle interaction, interaction with electrode, and particle-fluid interaction

Microscopic modeling of NEF



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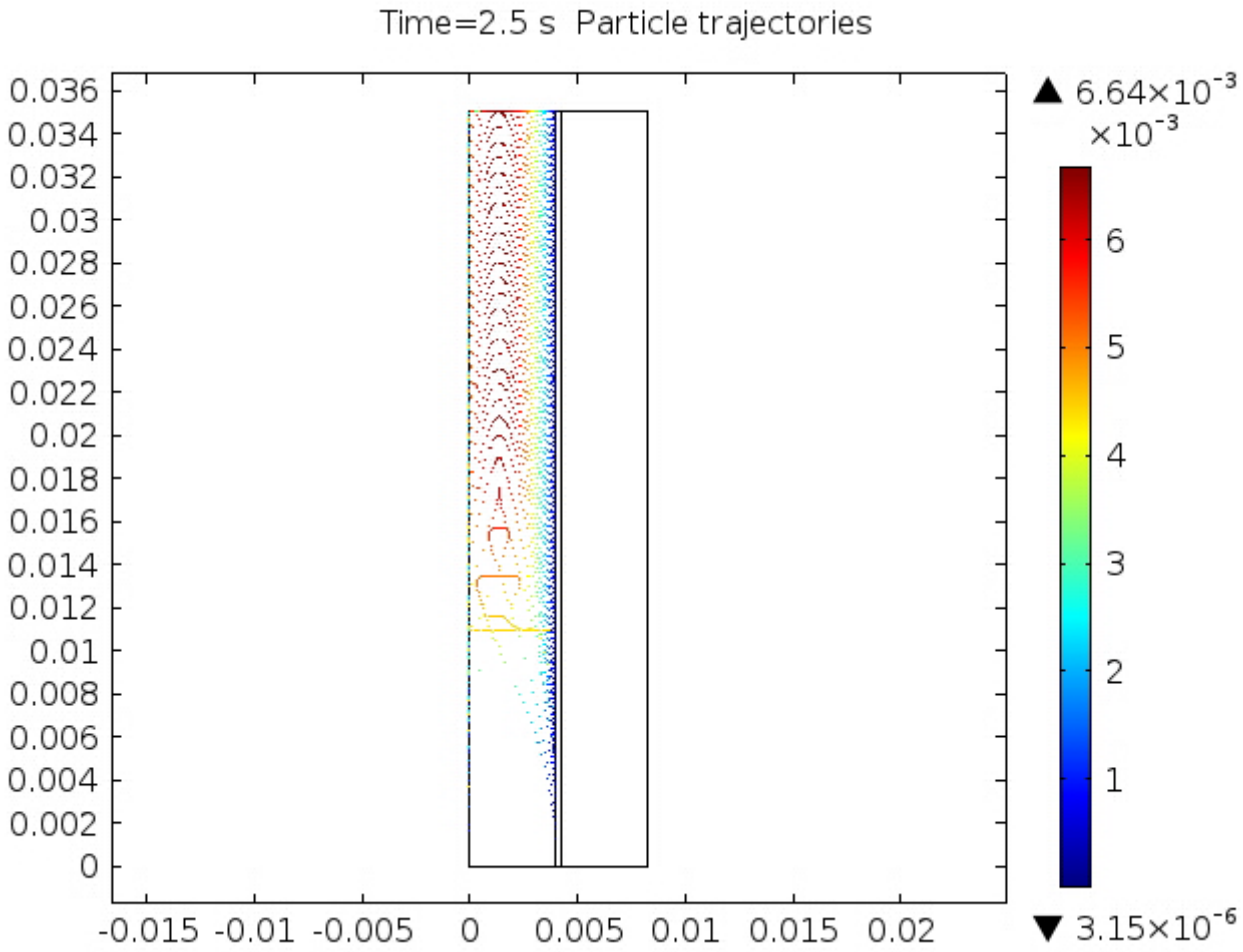
Microscopic modeling of NEF



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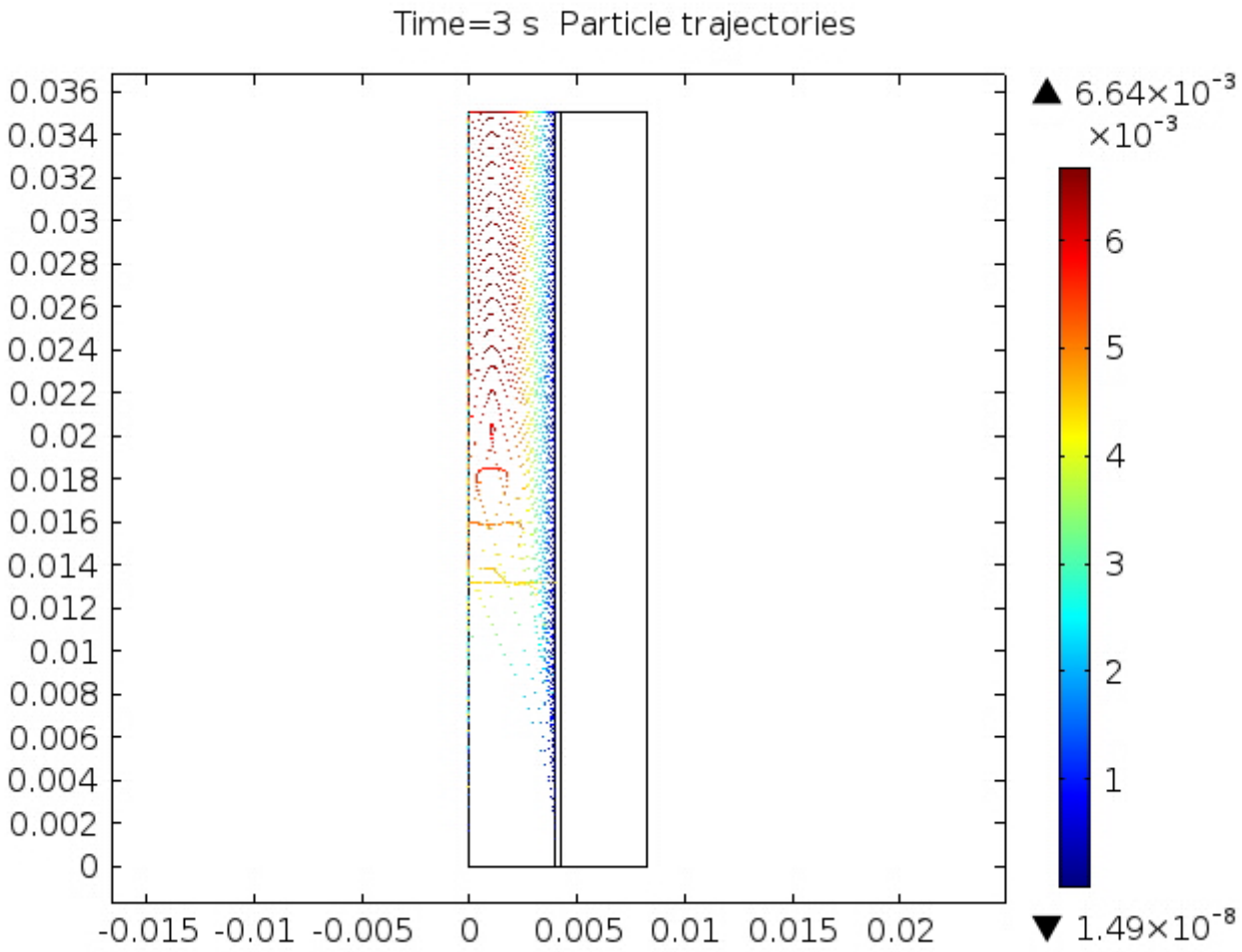
Microscopic modeling of NEF



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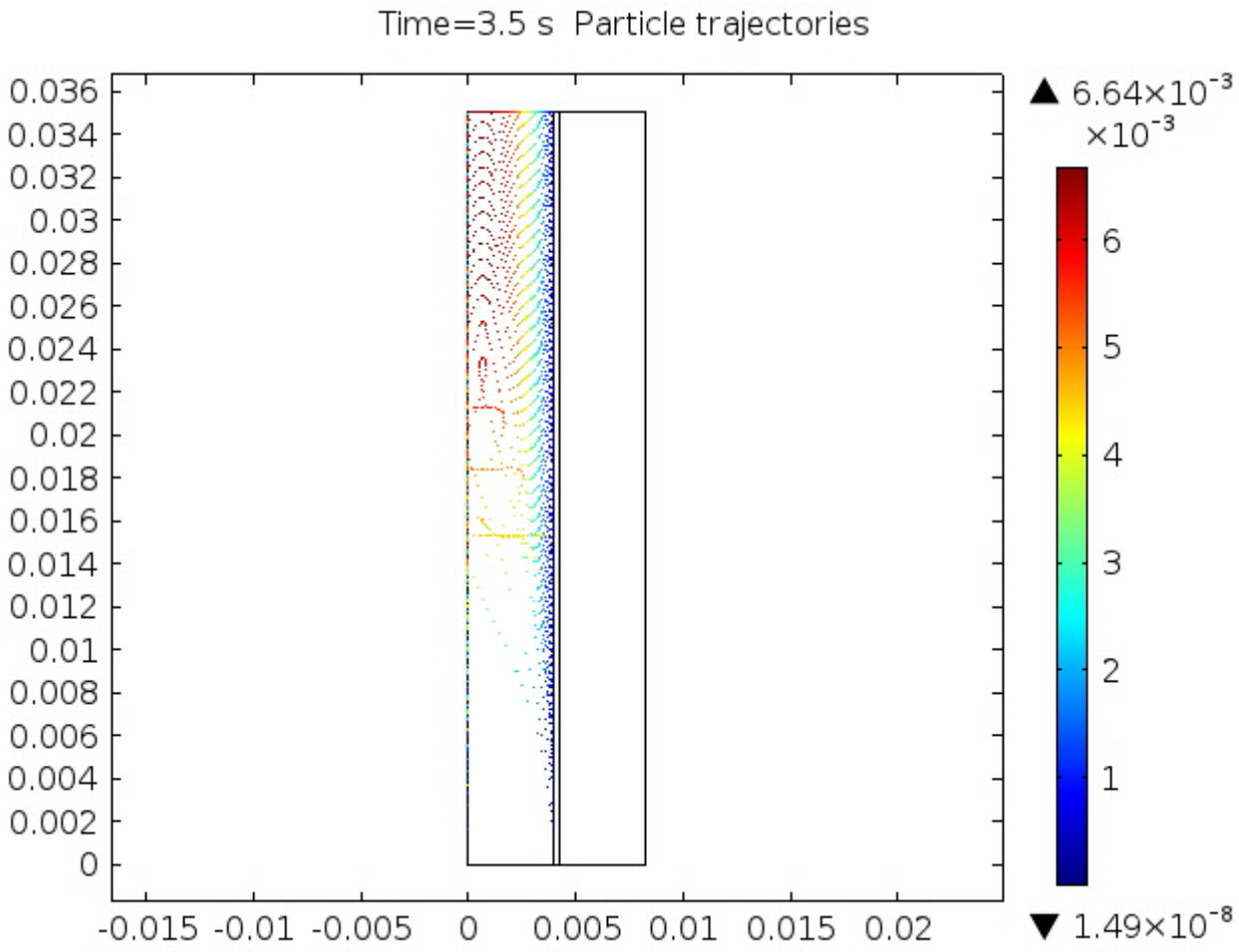
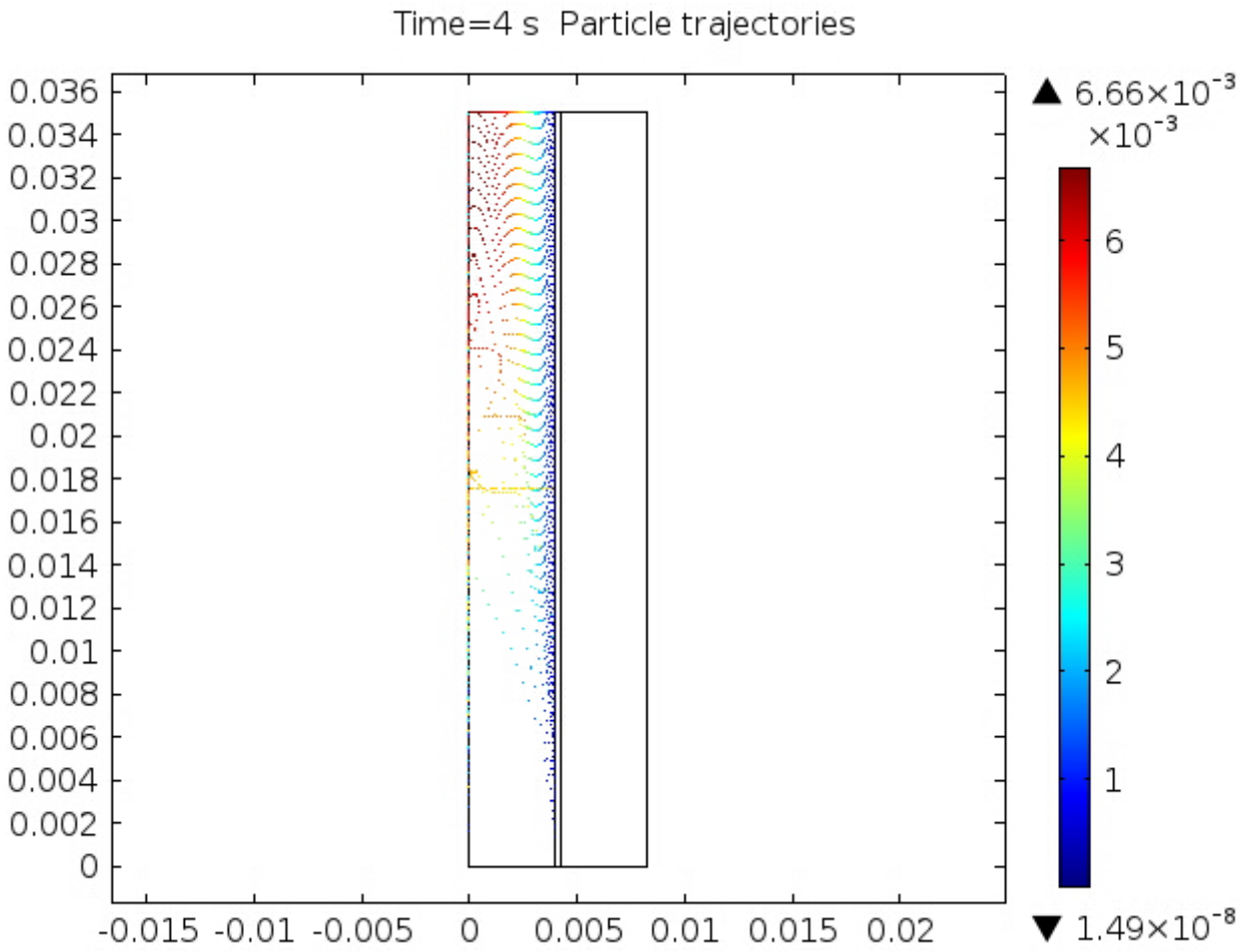
Microscopic modeling of NEF



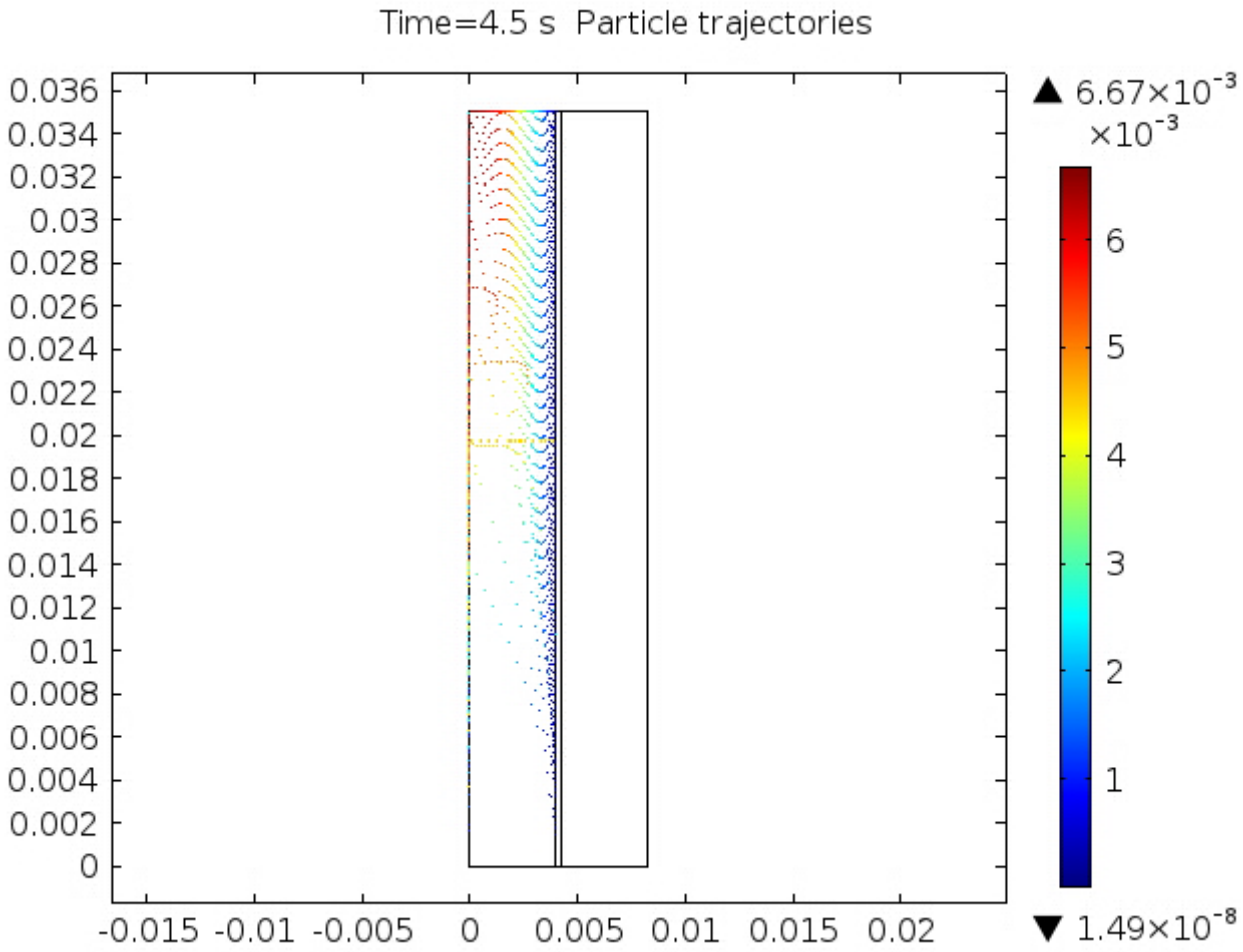
Initial model includes charged particle-particle interaction, interaction with electrode, and particle-fluid interaction

Microscopic modeling of NEF



Initial model includes charged particle-particle interaction, interaction with electrode, and particle-fluid interaction

Microscopic modeling of NEF



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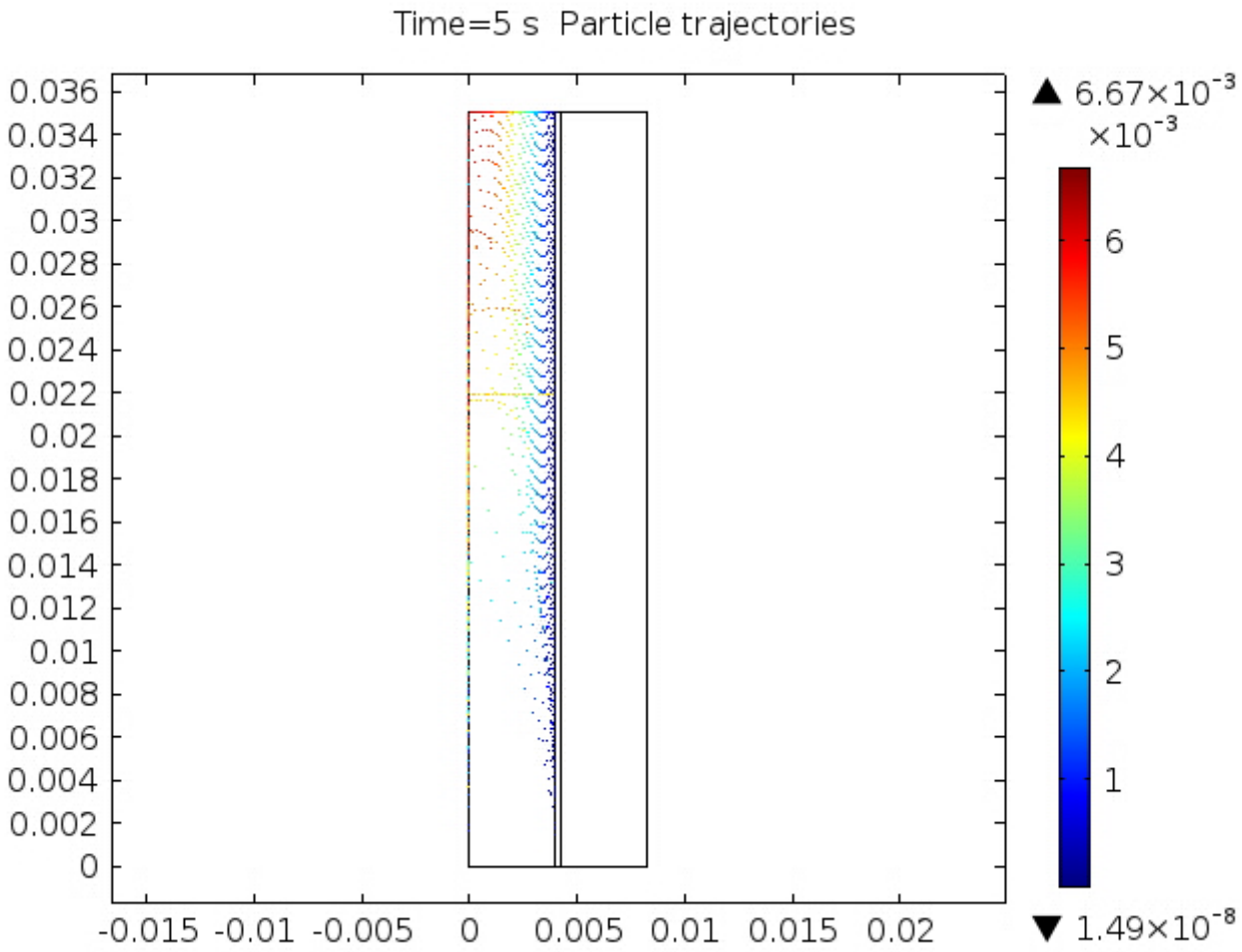
Microscopic modeling of NEF



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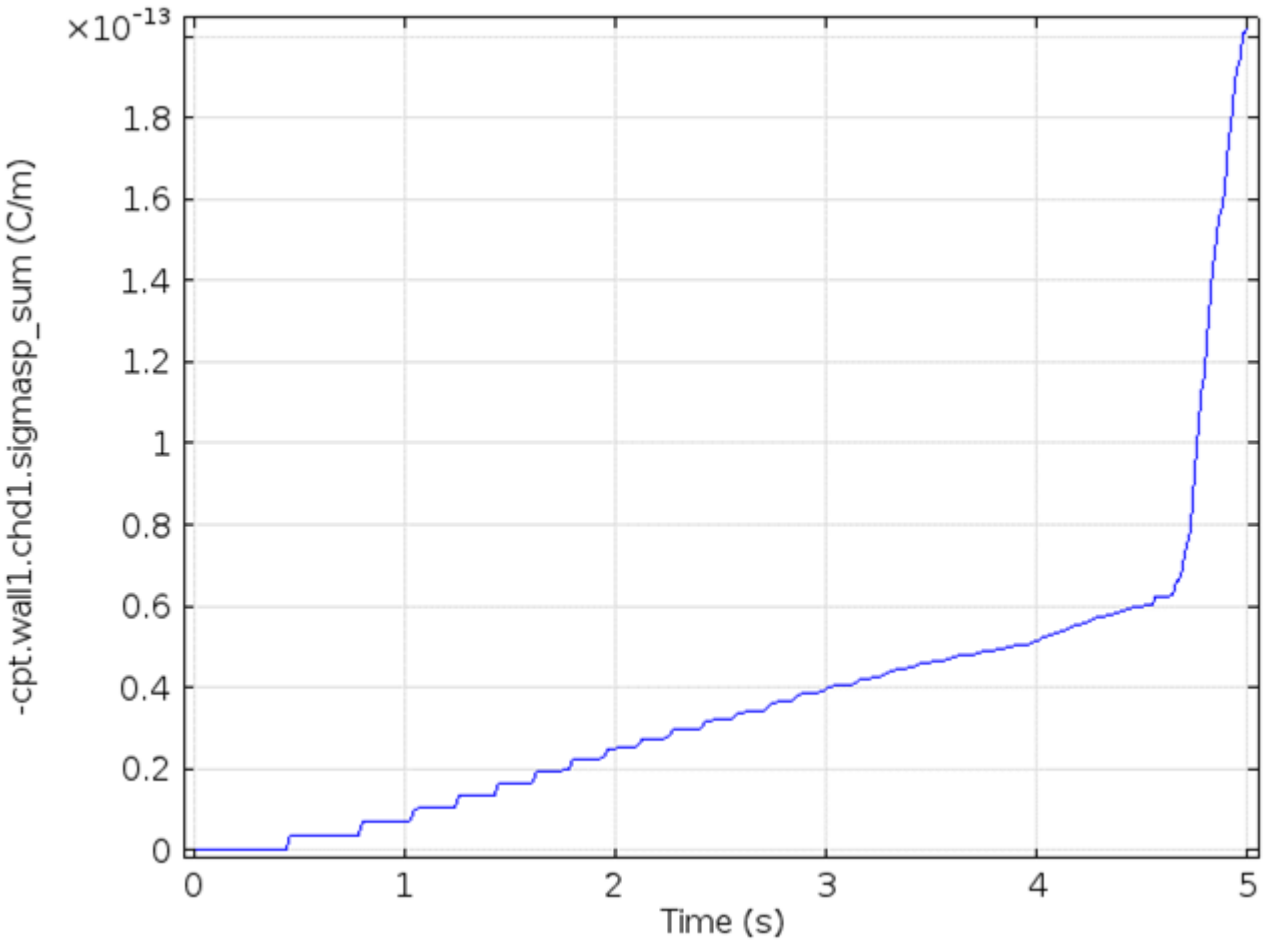
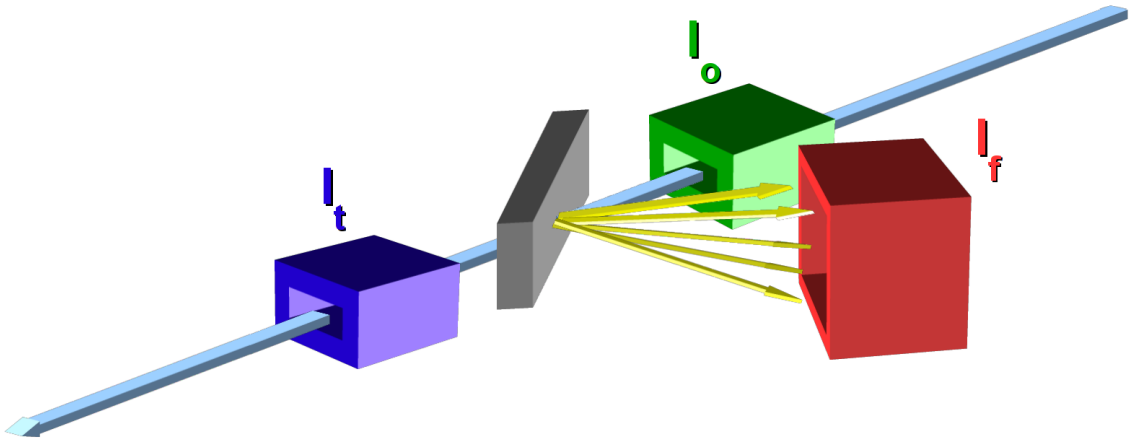
Microscopic modeling of NEF

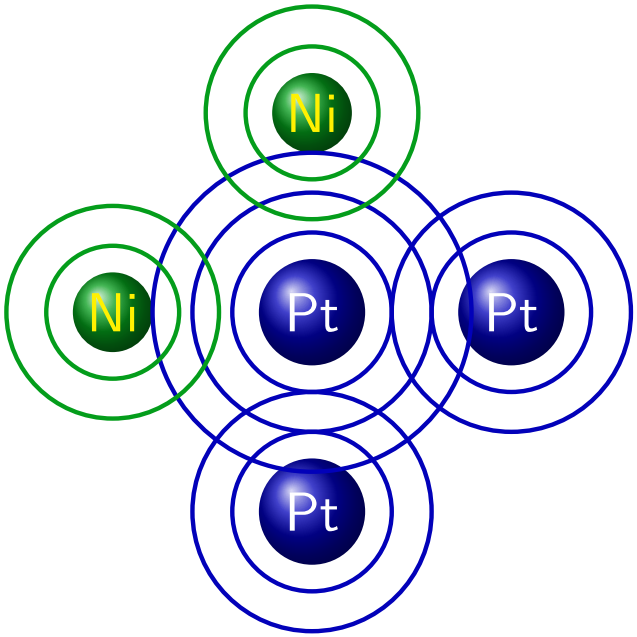


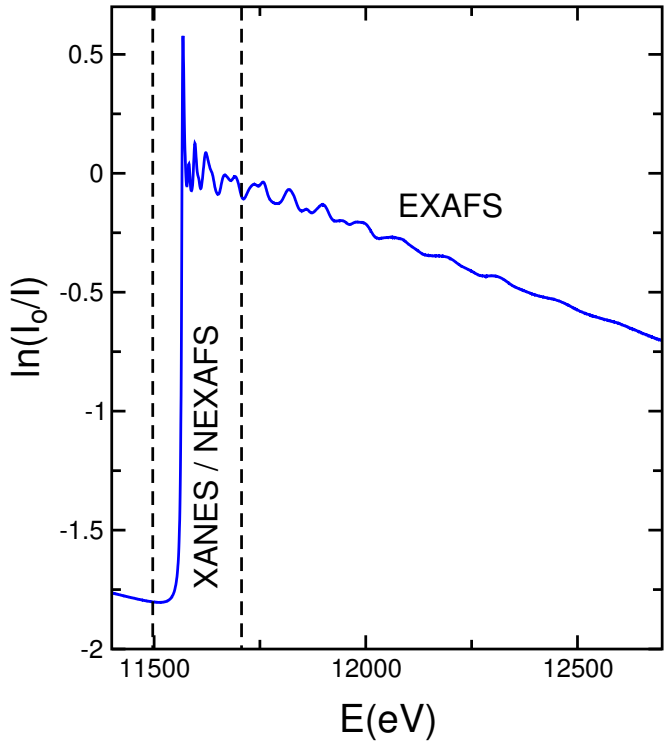
Initial model includes charged particle-particle interaction, interaction with electrode, and particle-fluid interaction

The EXAFS experiment

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







The EXAFS equation

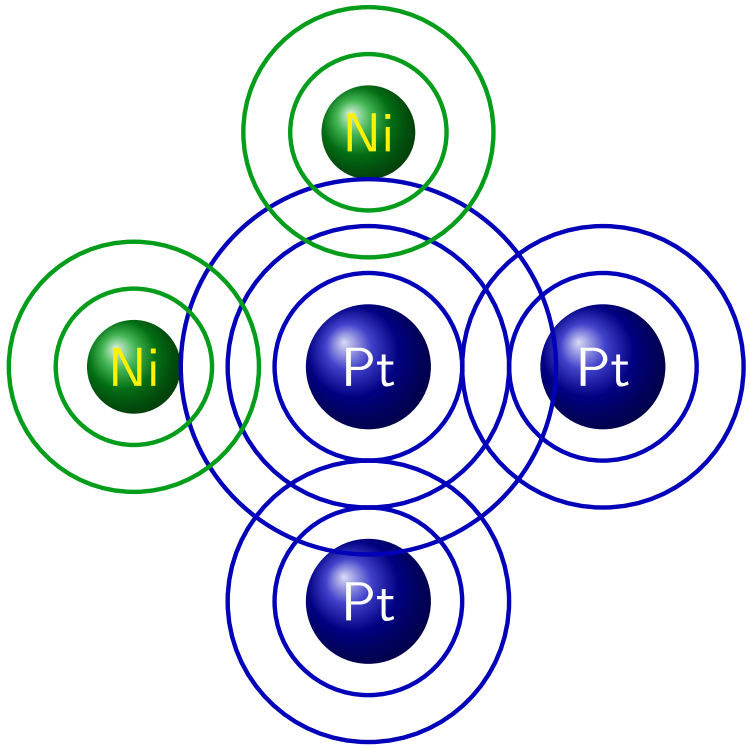
The EXAFS oscillations can be modelled and interpreted using a conceptually simple equation (the details are more subtle!)

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

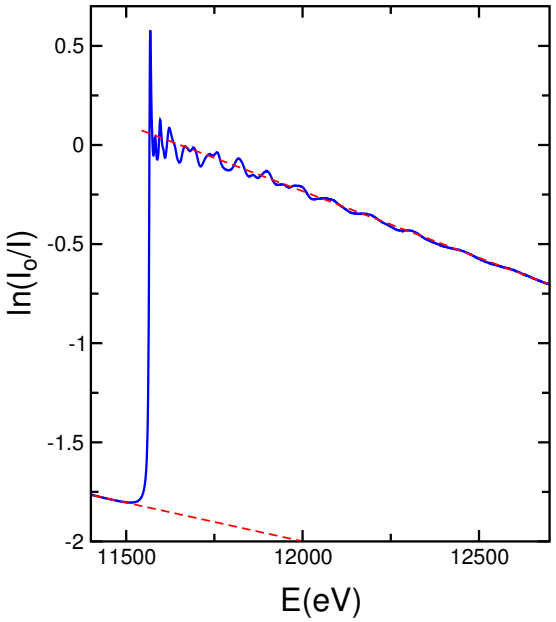
The sum could be over shells of atoms (Pt-Pt, Pt-Ni) or over scattering paths for the photo-electron.

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

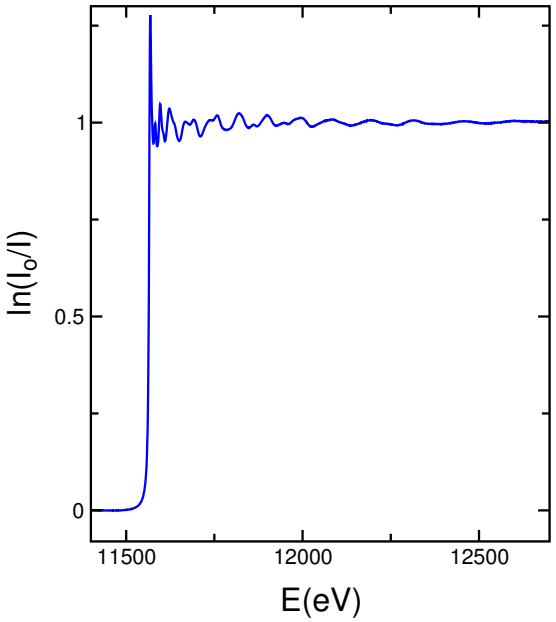
N_j: number of paths of type j
R_j: half path length
σ_j: path "disorder"



EXAFS analysis



EXAFS analysis



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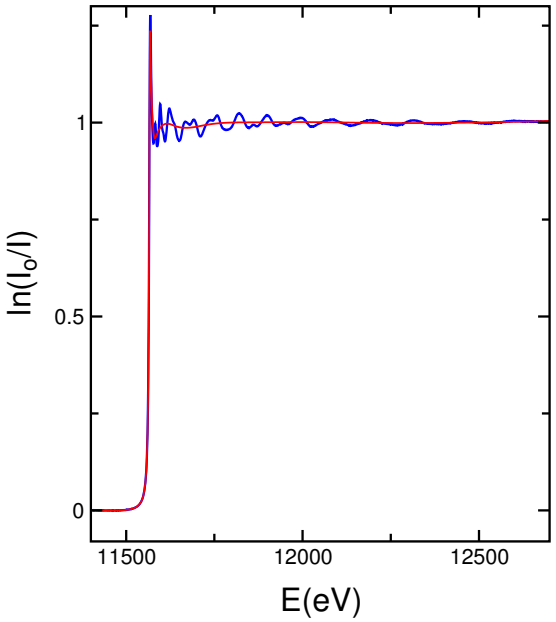

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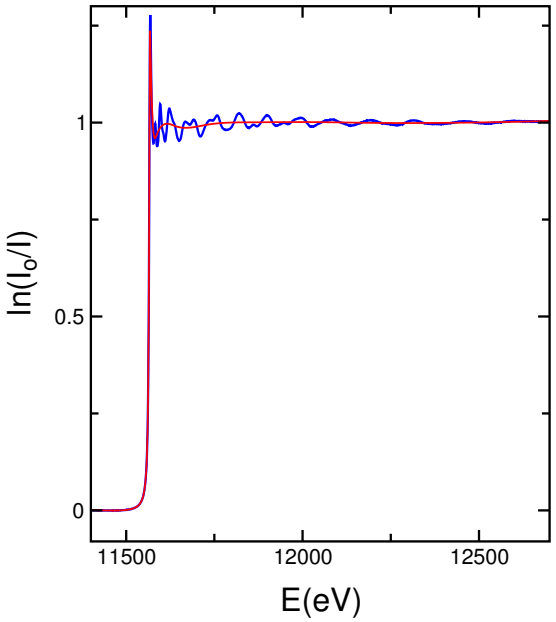
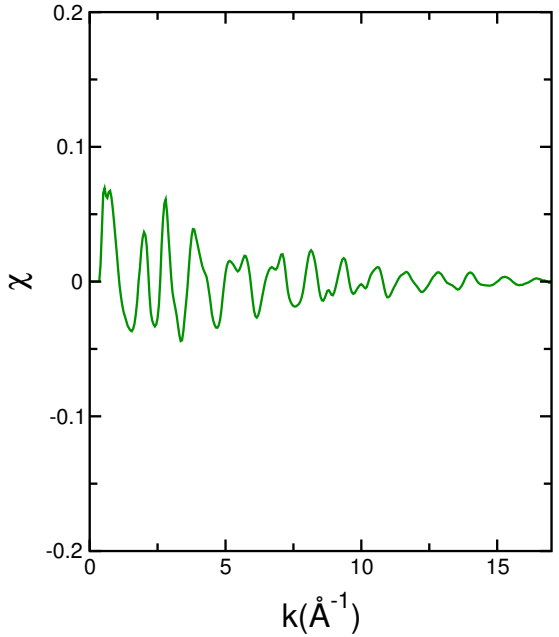
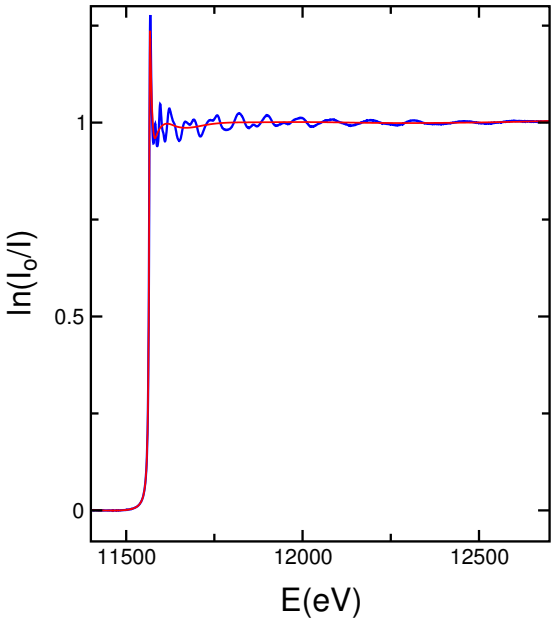


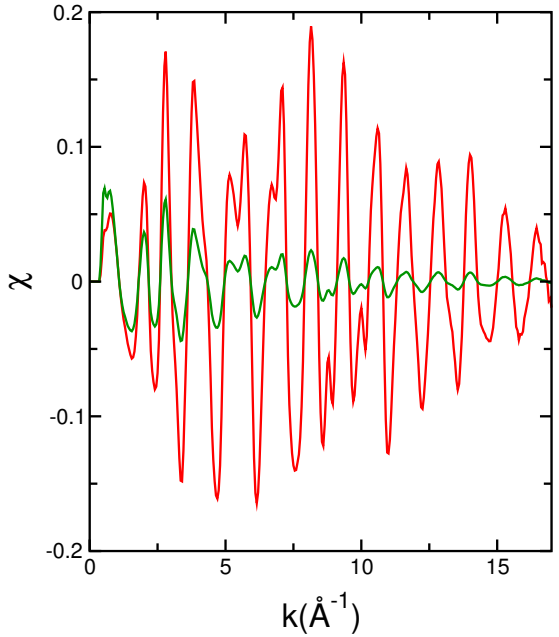
remove background



EXAFS analysis



remove background and
apply k-weighting



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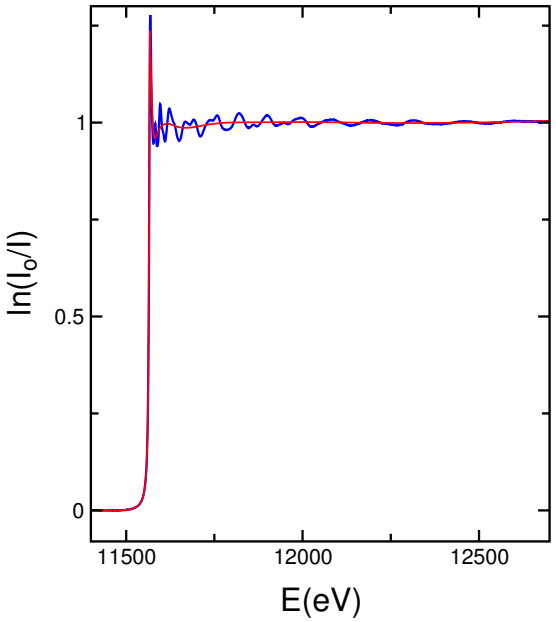

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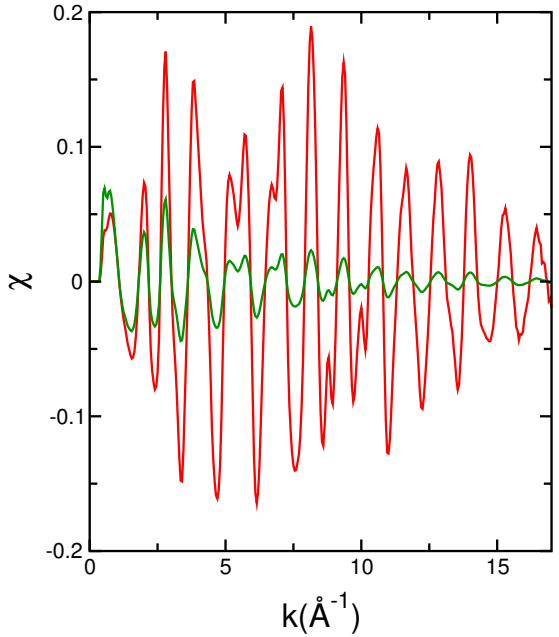
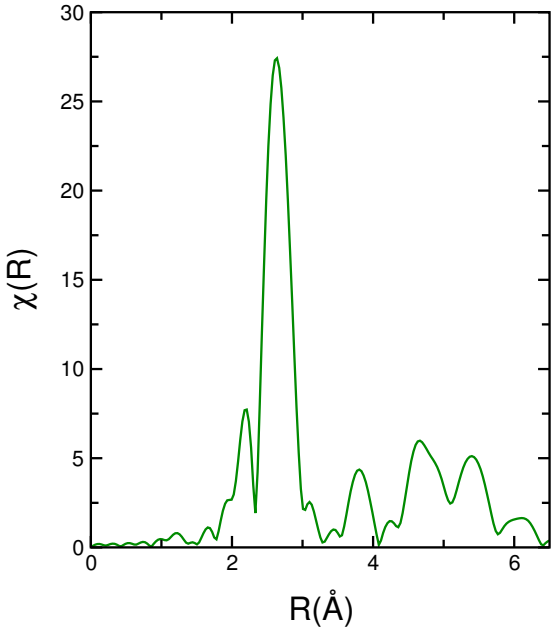
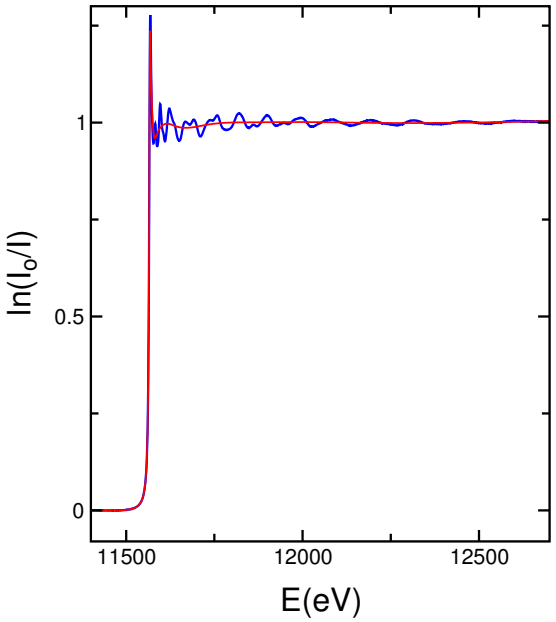


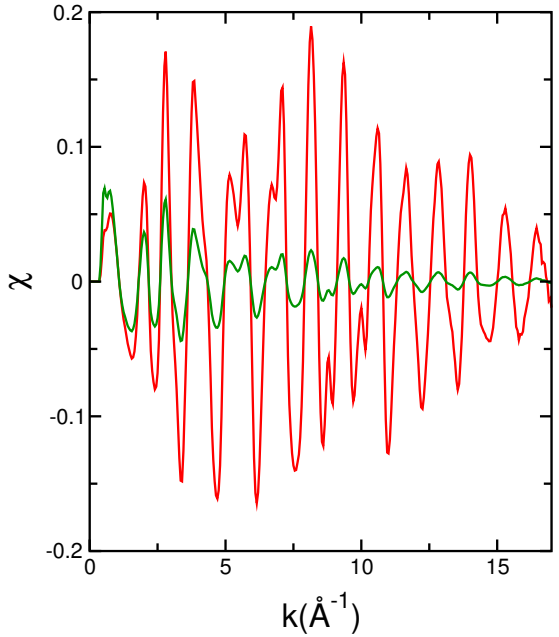
take Fourier Transform



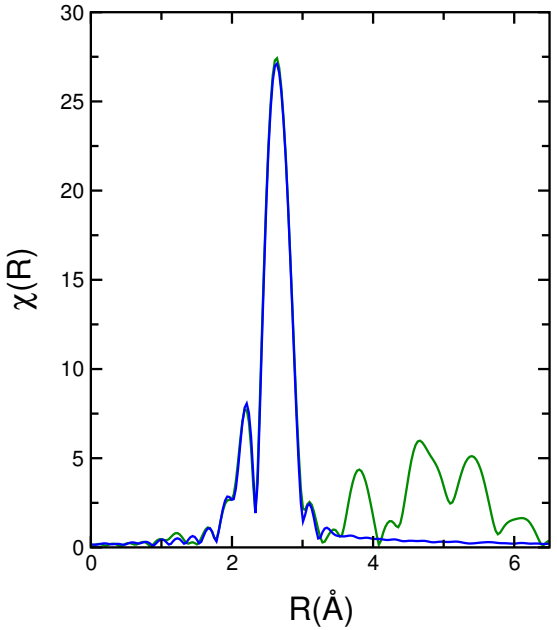
EXAFS analysis



remove background and apply k-weighting

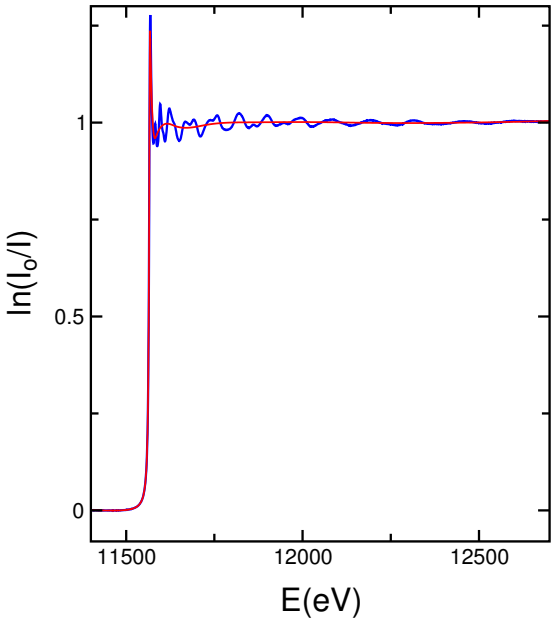


take Fourier Transform and fit with a structural model



extract structural parameters for first shell

EXAFS analysis



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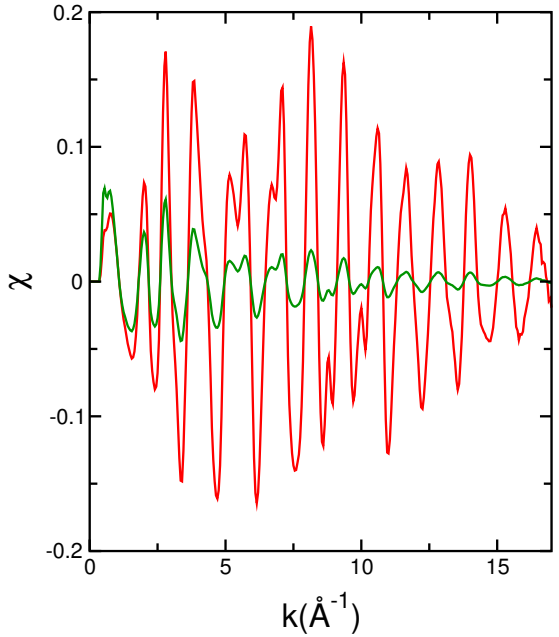

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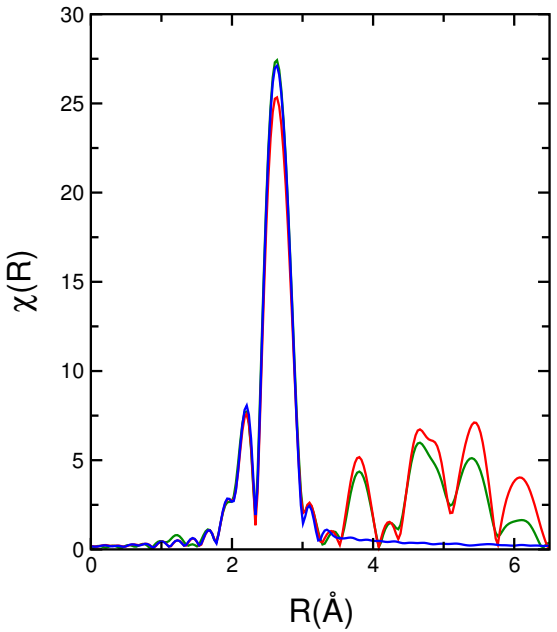


extract structural parameters for first shell or more distant atoms as appropriate

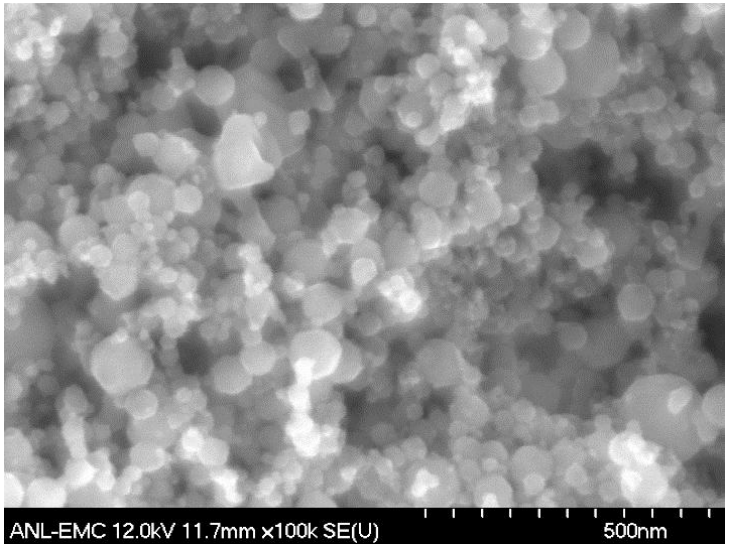
Fe_2O_3 *in situ* studies

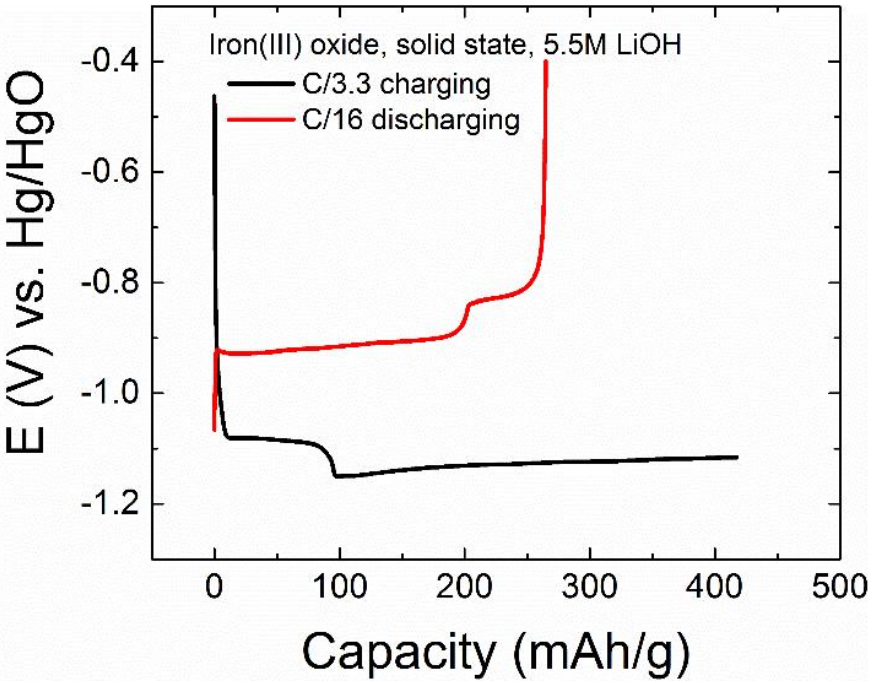
Charging reaction: 335 mAh/g

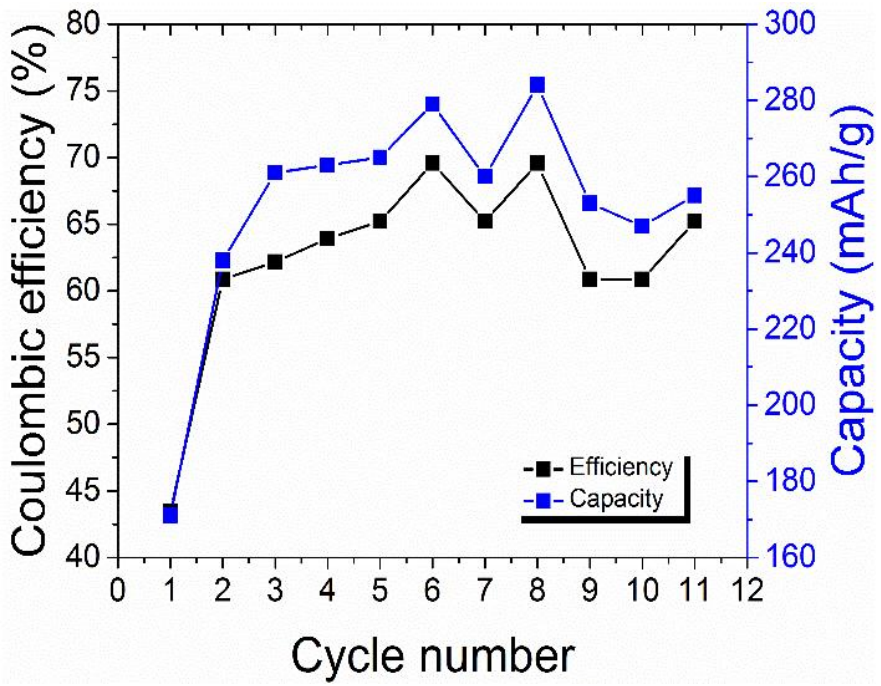
$$Fe_2O_3 + 3\,H_2O + 2\,e^- \longrightarrow 2\,Fe(OH)_2 + 2\,OH^-$$

Over-charging reaction: 670 mAh/g

$$2\,Fe(OH)_2 + 4\,e^- \longrightarrow 2\,Fe + 4OH^-$$

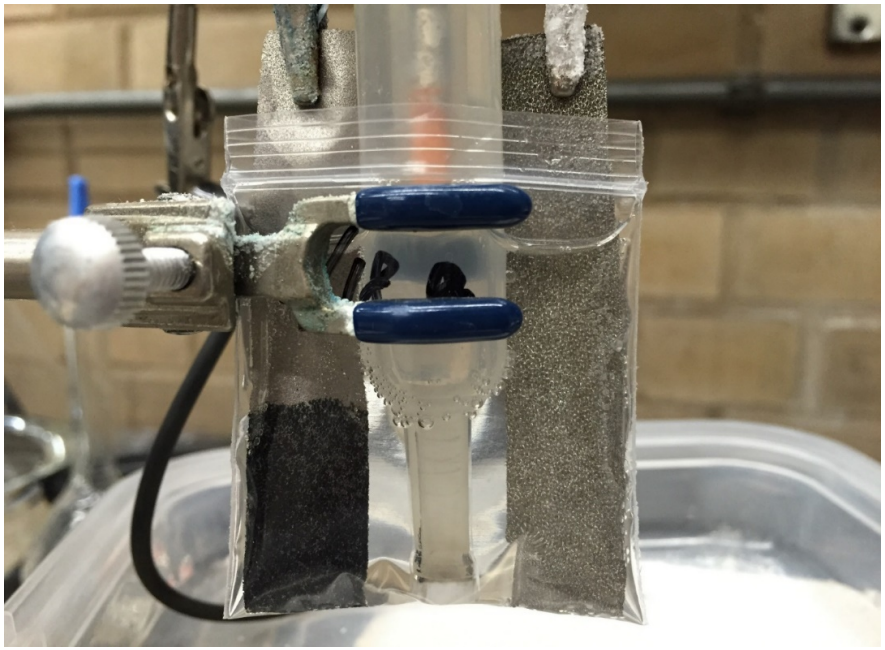






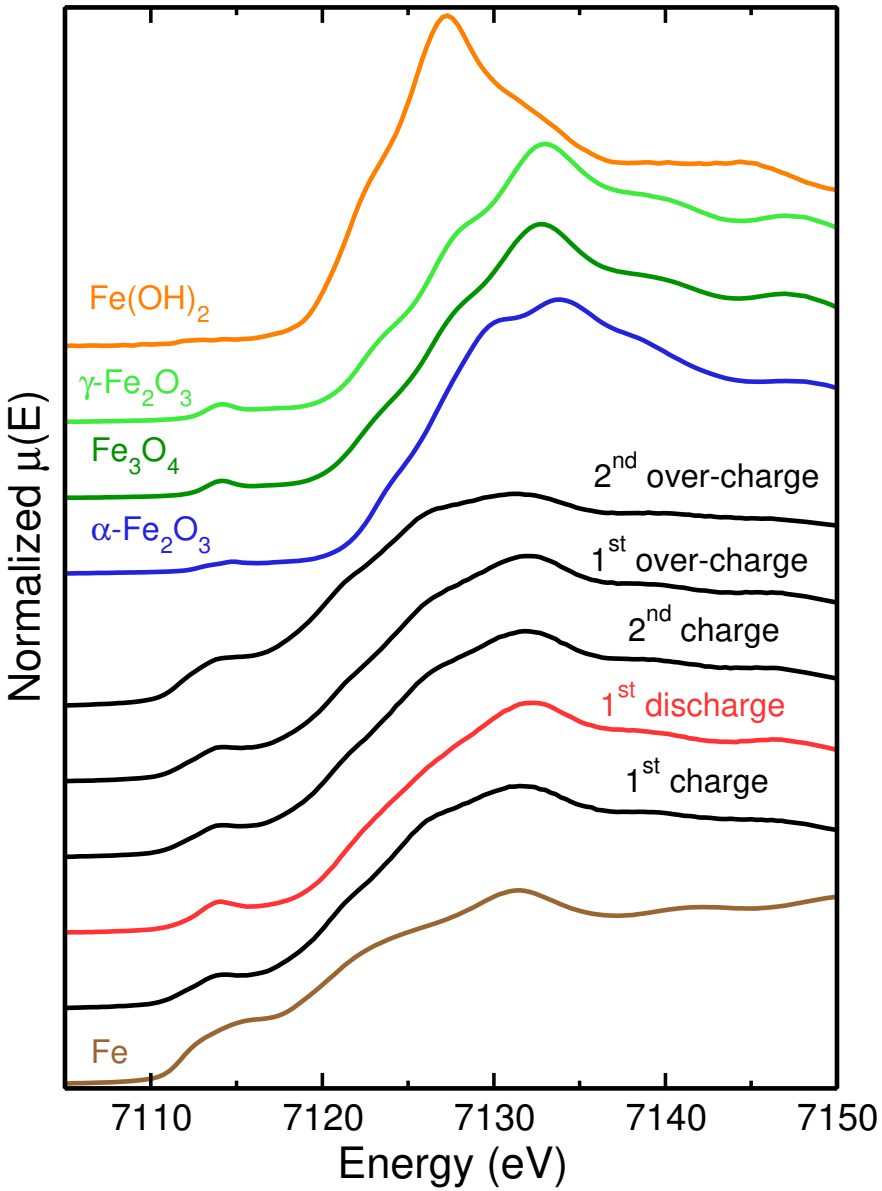
In situ Fe_2O_3 charging

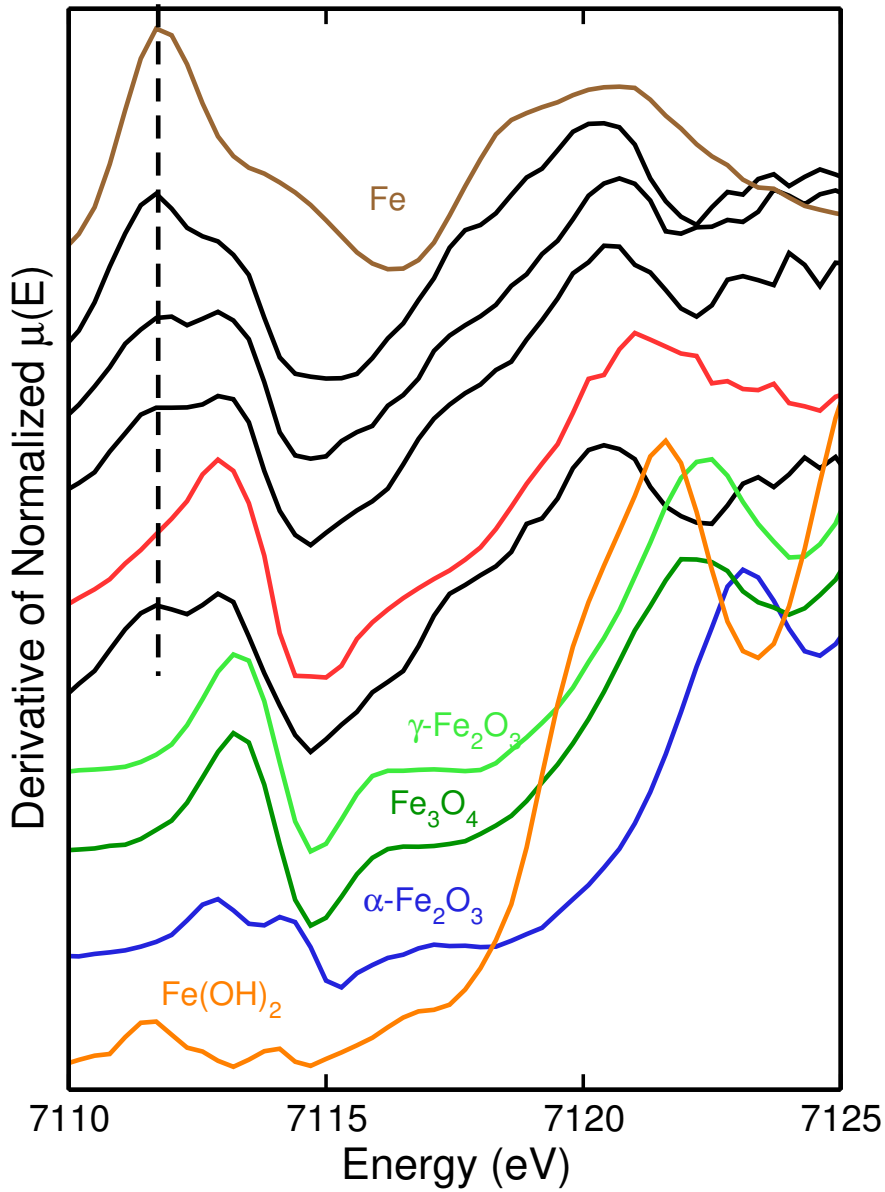
- Aqueous pouch cell
- Ni-mesh electrode
- MRCAT 10-BM beam line
- Fluorescence mode data acquisition
- ∼45 min per data set



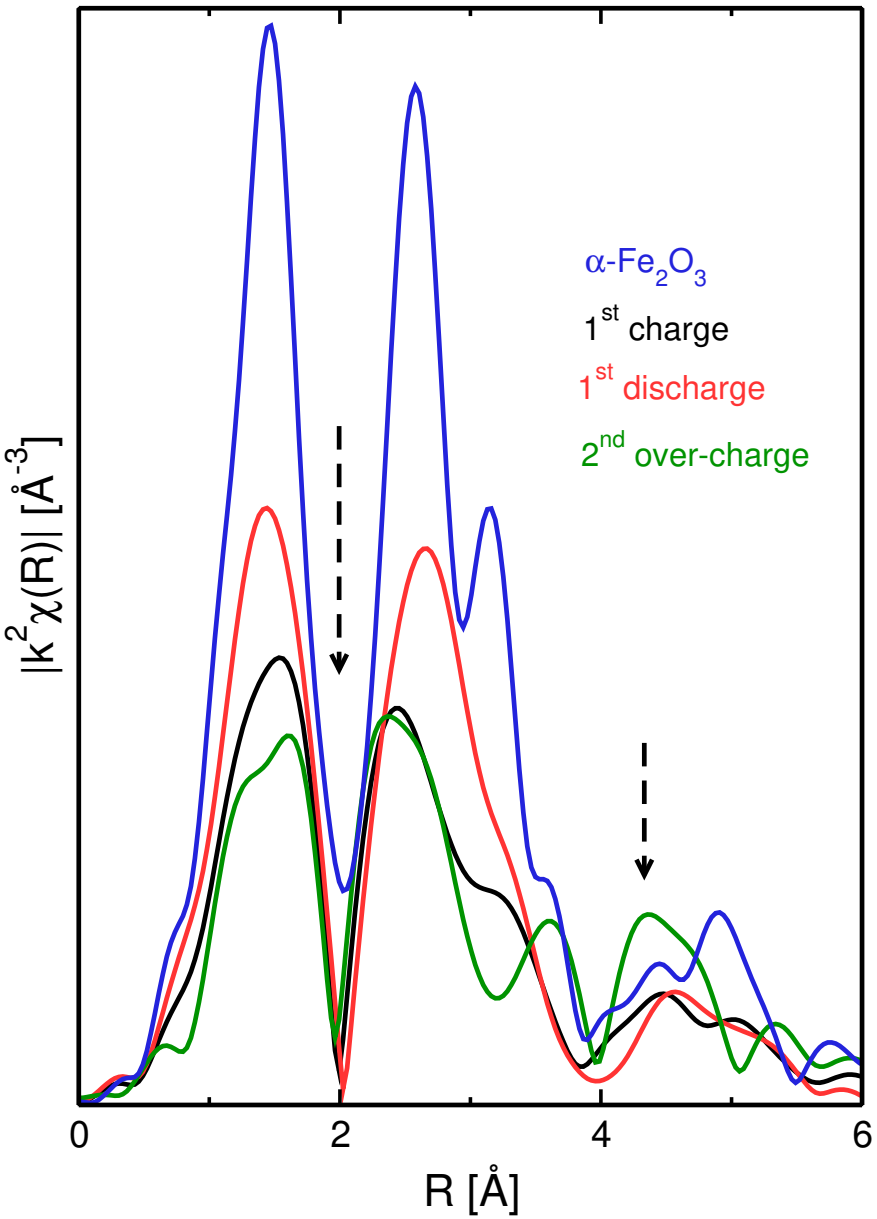
- Only take data at end of charge/discharge
- First & second charges to 335 mAh/g
- Discharges only produce 150 mAh/g
- Two over-charges to 1005 mAh/g

Fe_2O_3 XANES


Fe(OH)2
γ-Fe2O3
Fe3O4
α-Fe2O3
2nd over-charge
1st over-charge
2nd charge
1st discharge
1st charge
Fe
Normalized μ(E)
7110
7120
7130
7140
7150
Energy (eV)


Fe
γ-Fe2O3
Fe3O4
α-Fe2O3
Fe(OH)2
Derivative of Normalized μ(E)
7110
7115
7120
7125
Energy (eV)

Fe_2O_3 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
1^{st} charge	85%	15%
1^{st} discharge	100%	
2^{nd} charge	83%	17%
1^{st} over-charge	82%	18%
2^{nd} over-charge	67%	33%

Initial funding: the RANGE program

Robust **A**ffordable **N**ext **G**eneration **E**nergy Storage Systems

Develop transformational electrochemical energy storage technologies for electric vehicles (EVs)

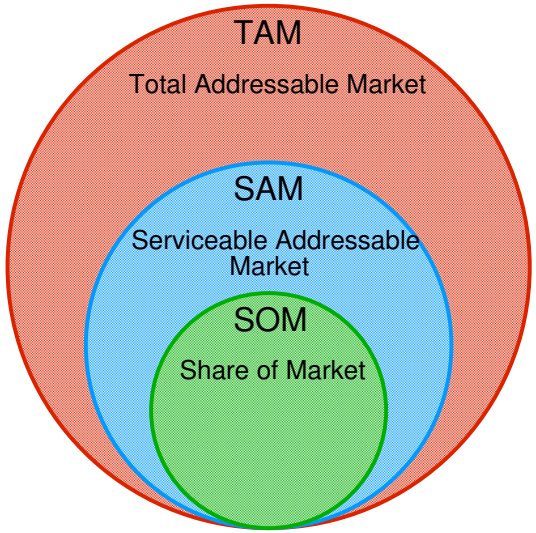
- provide greater EV driving range
- reduce overall weight of the vehicle
- maximize the overall energy stored in a vehicle
- enhance safety
- minimize manufacturing costs
- enable greater design flexibility for manufacturers

22 projects across the United States

The I-Corps experience

The I-Corps experience

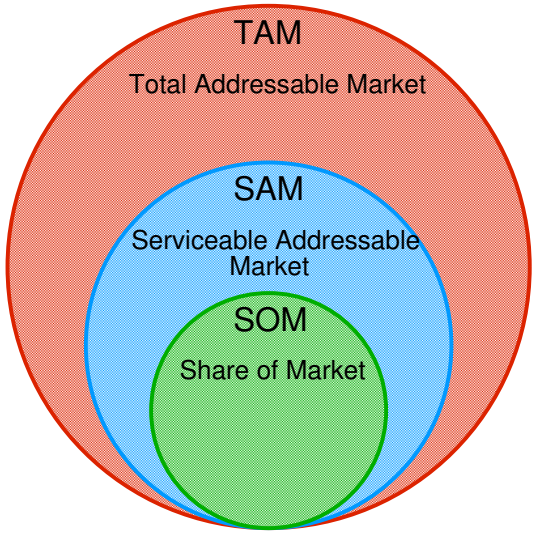
Participated in the I-Corps Energy & Transportation program sponsored by Next Energy in Detroit



The I-Corps experience

Participated in the I-Corps Energy & Transportation program sponsored by Next Energy in Detroit

- initial goal to grow the EV market by providing a better battery



Total Automotive Market

TAM – $40B

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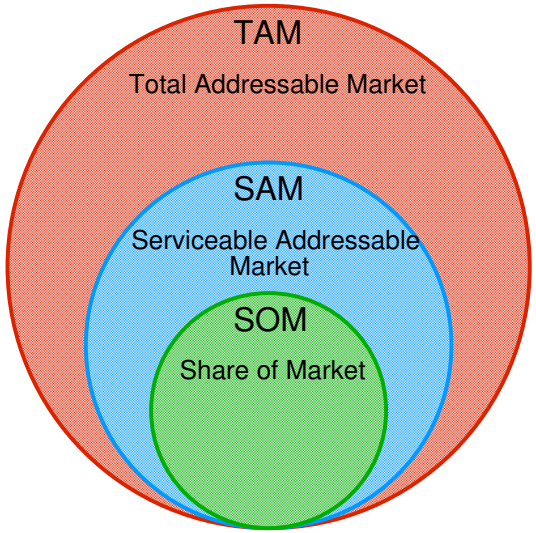
The I-Corps experience



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NEXTENERGY
ask us what's next

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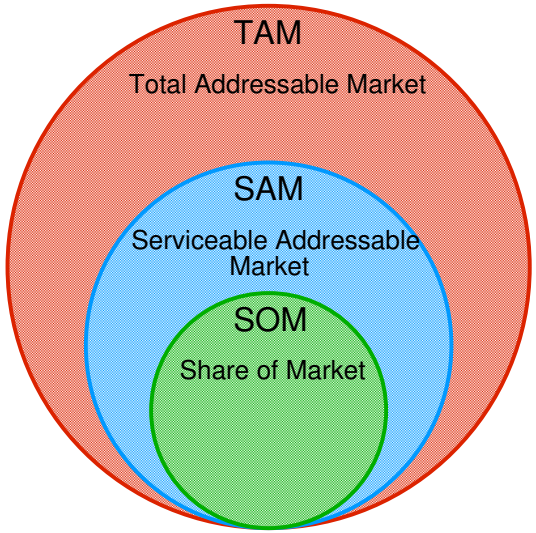

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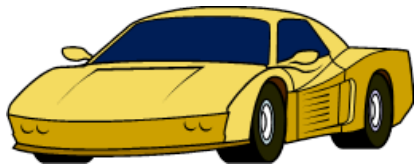

TAM – $720M

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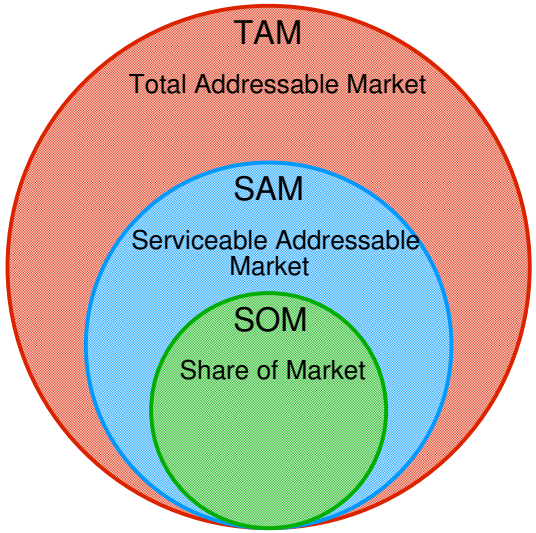

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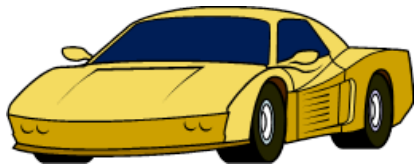

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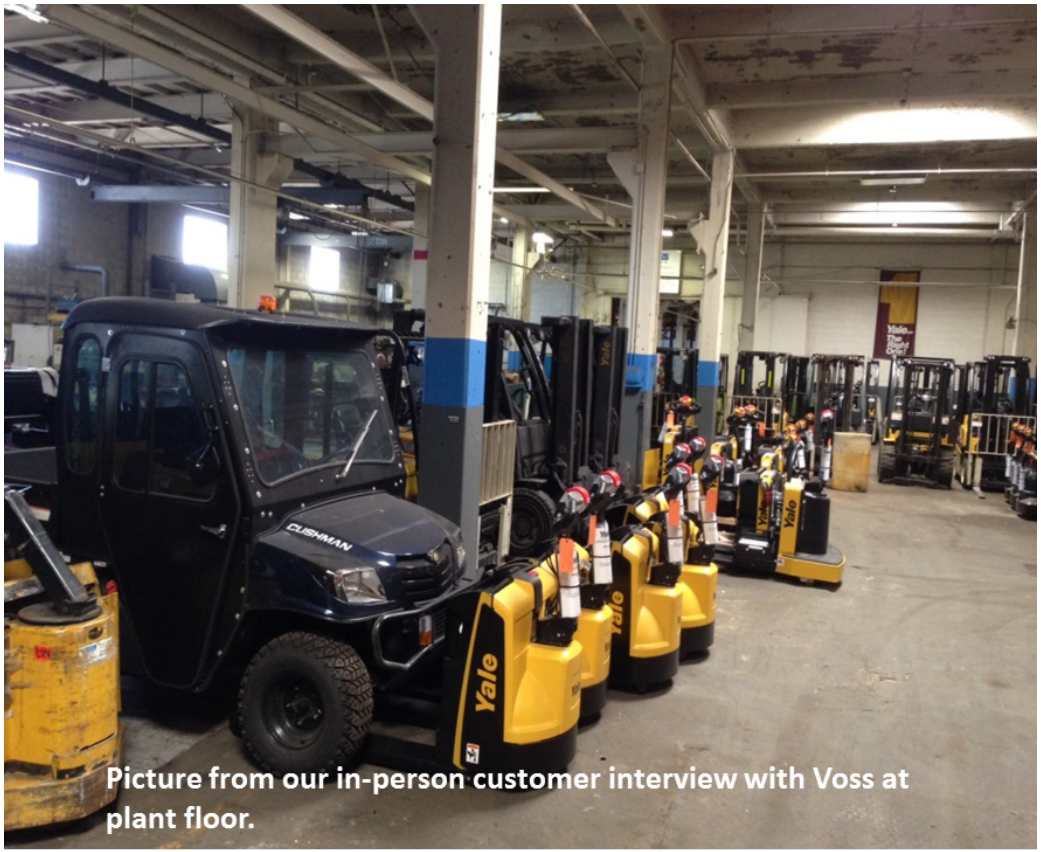

Picture from our in-person customer interview with Voss at plant floor.

EUVs and fork lifts are already predominantly electric

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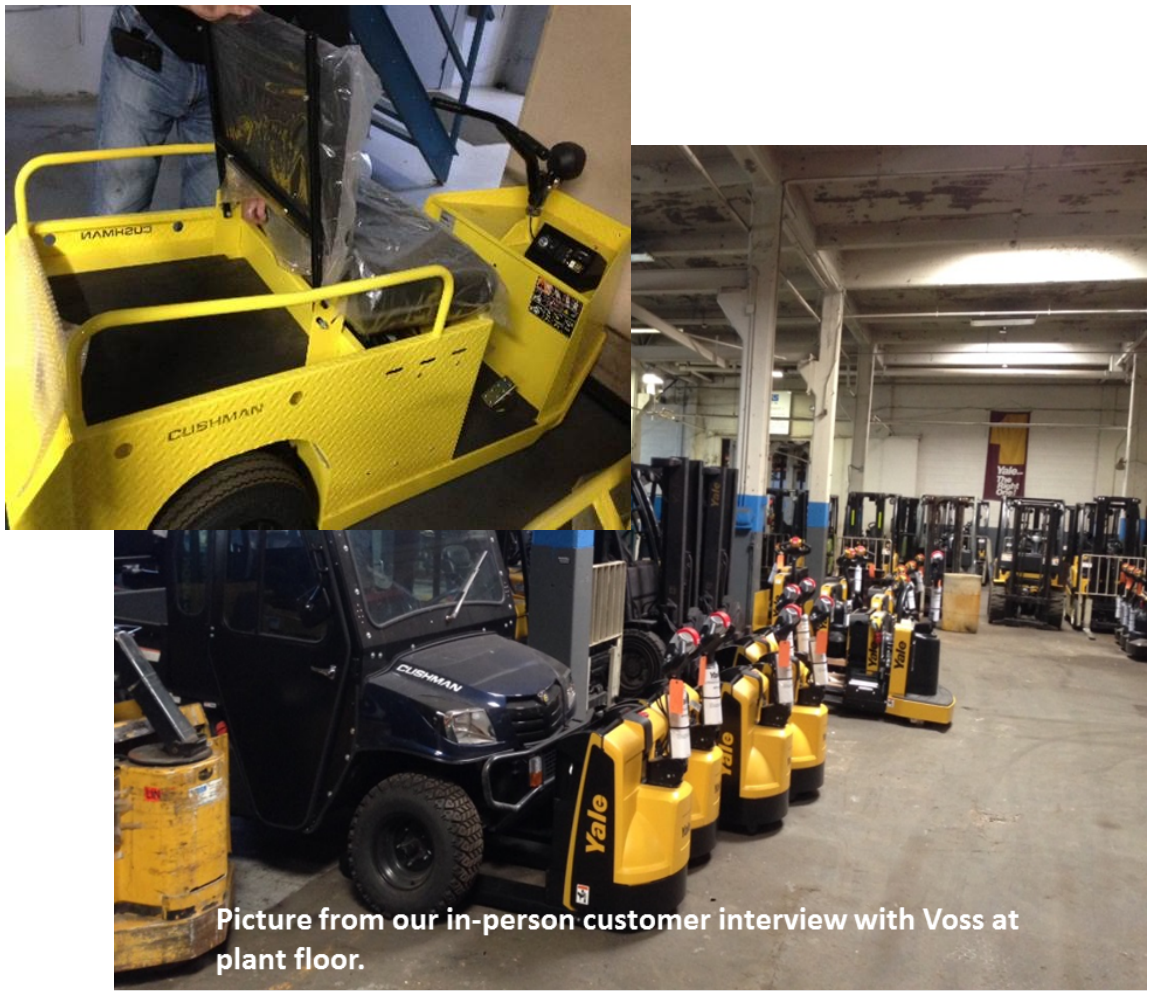

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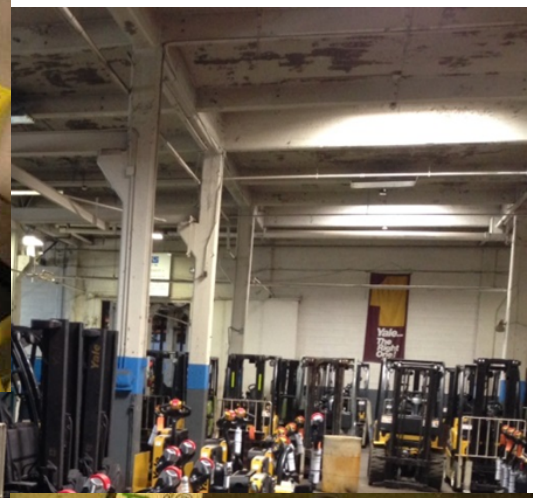

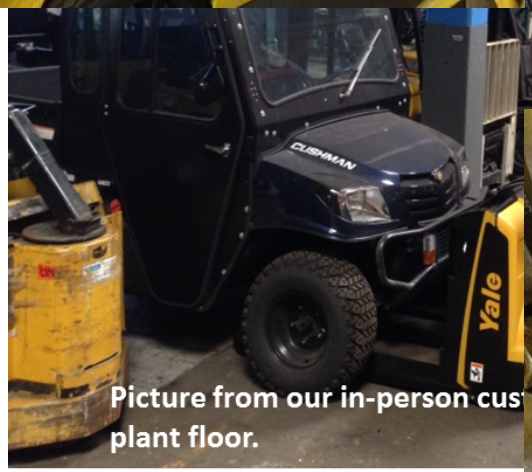

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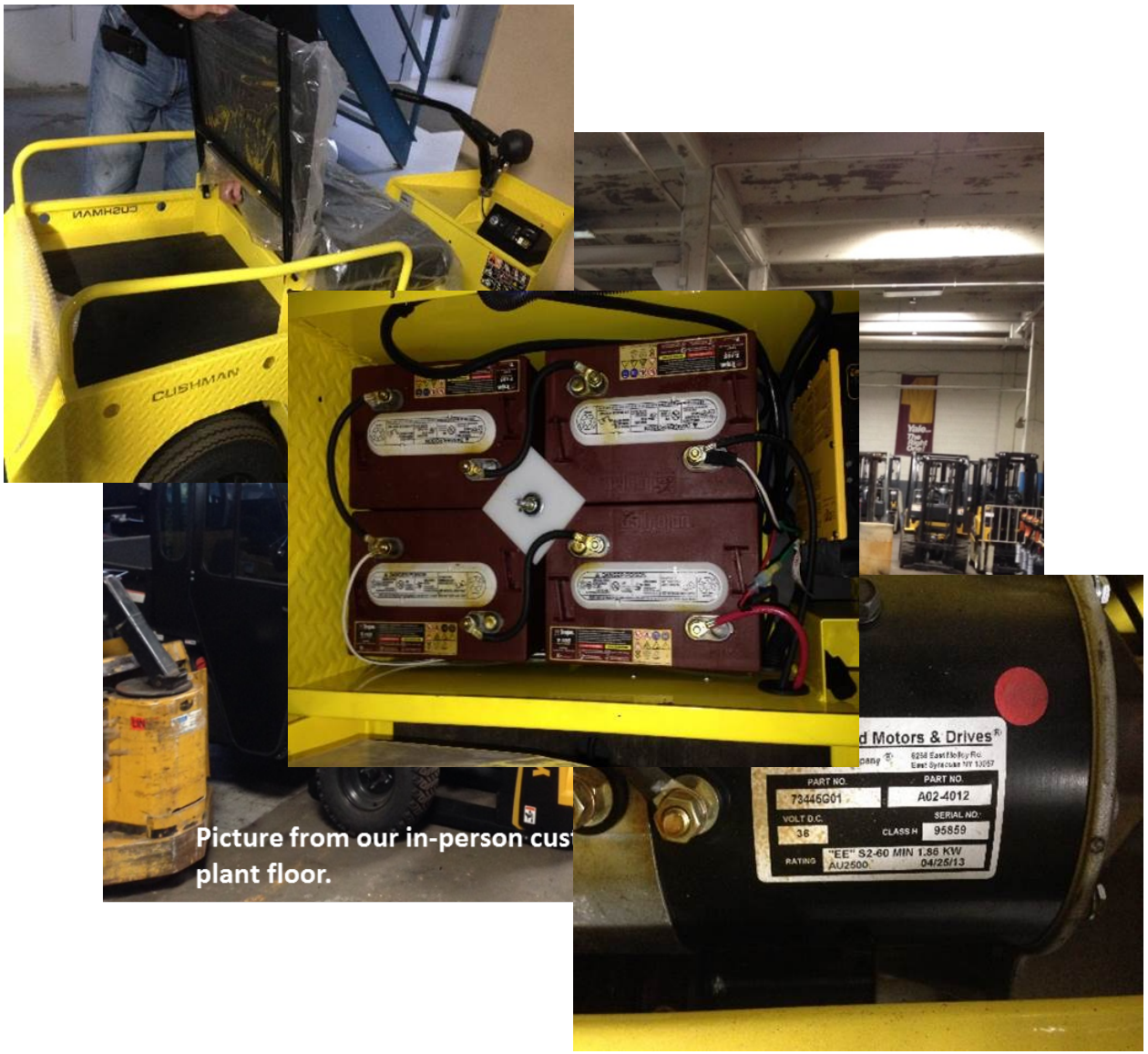

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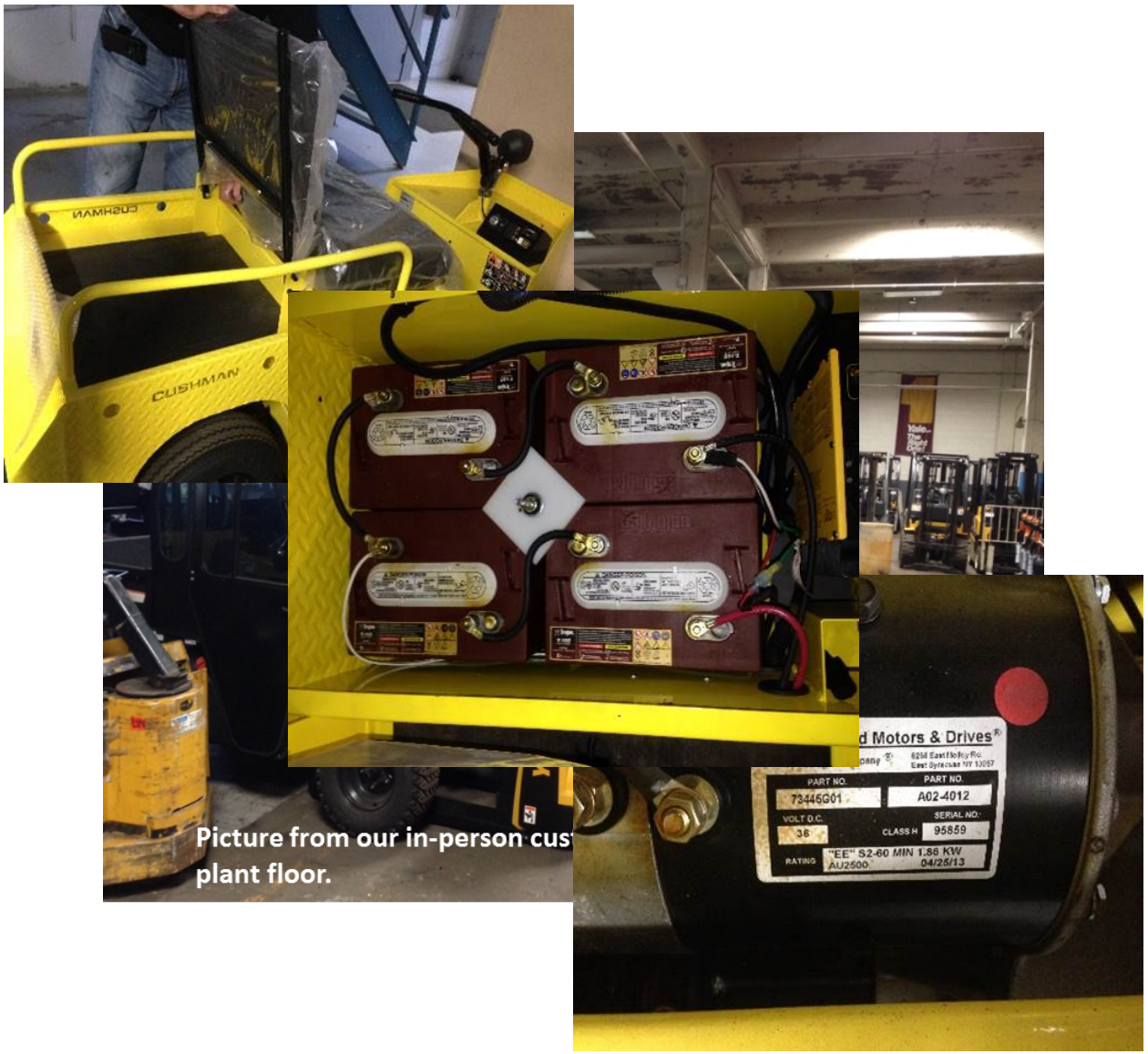

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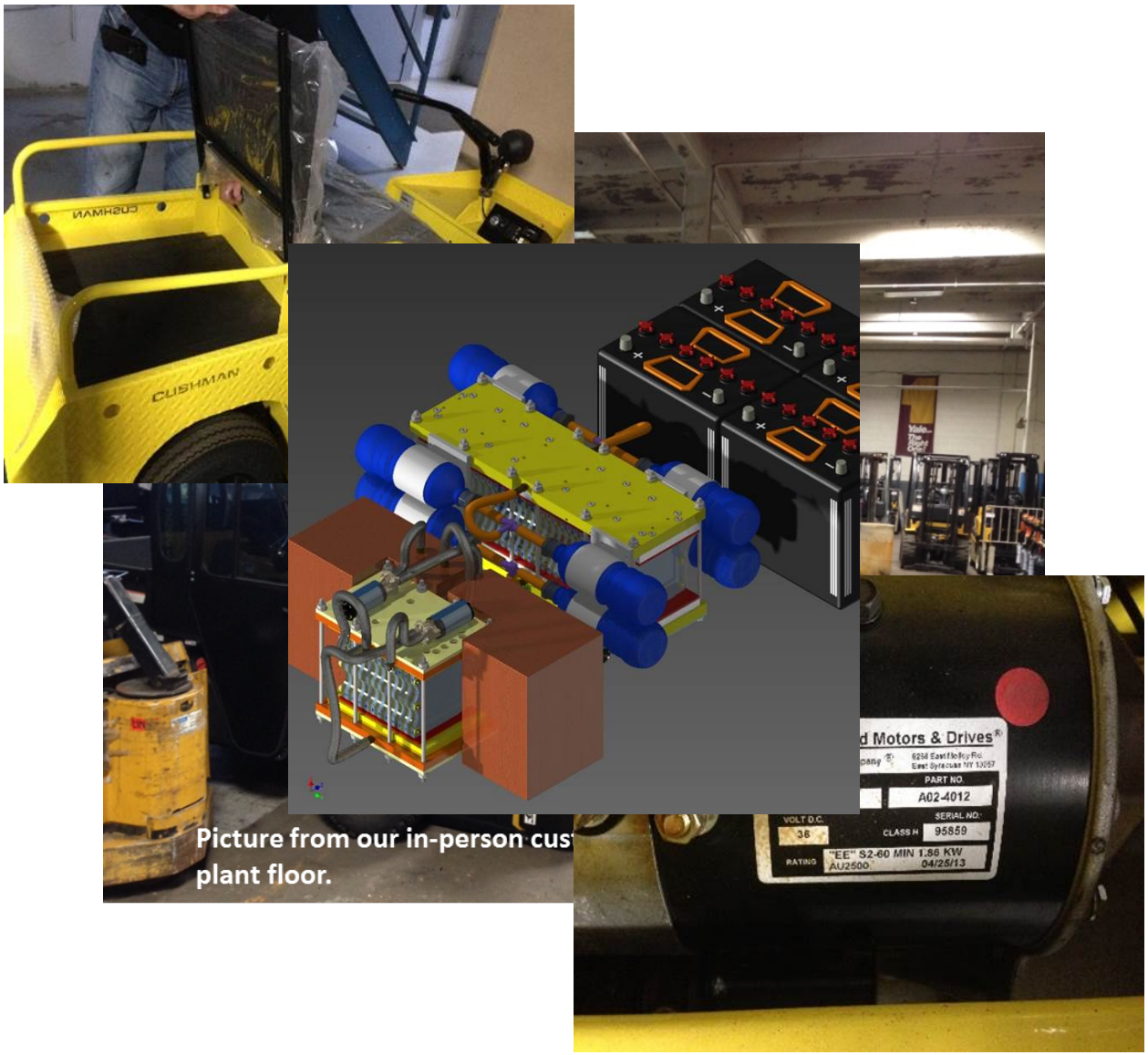

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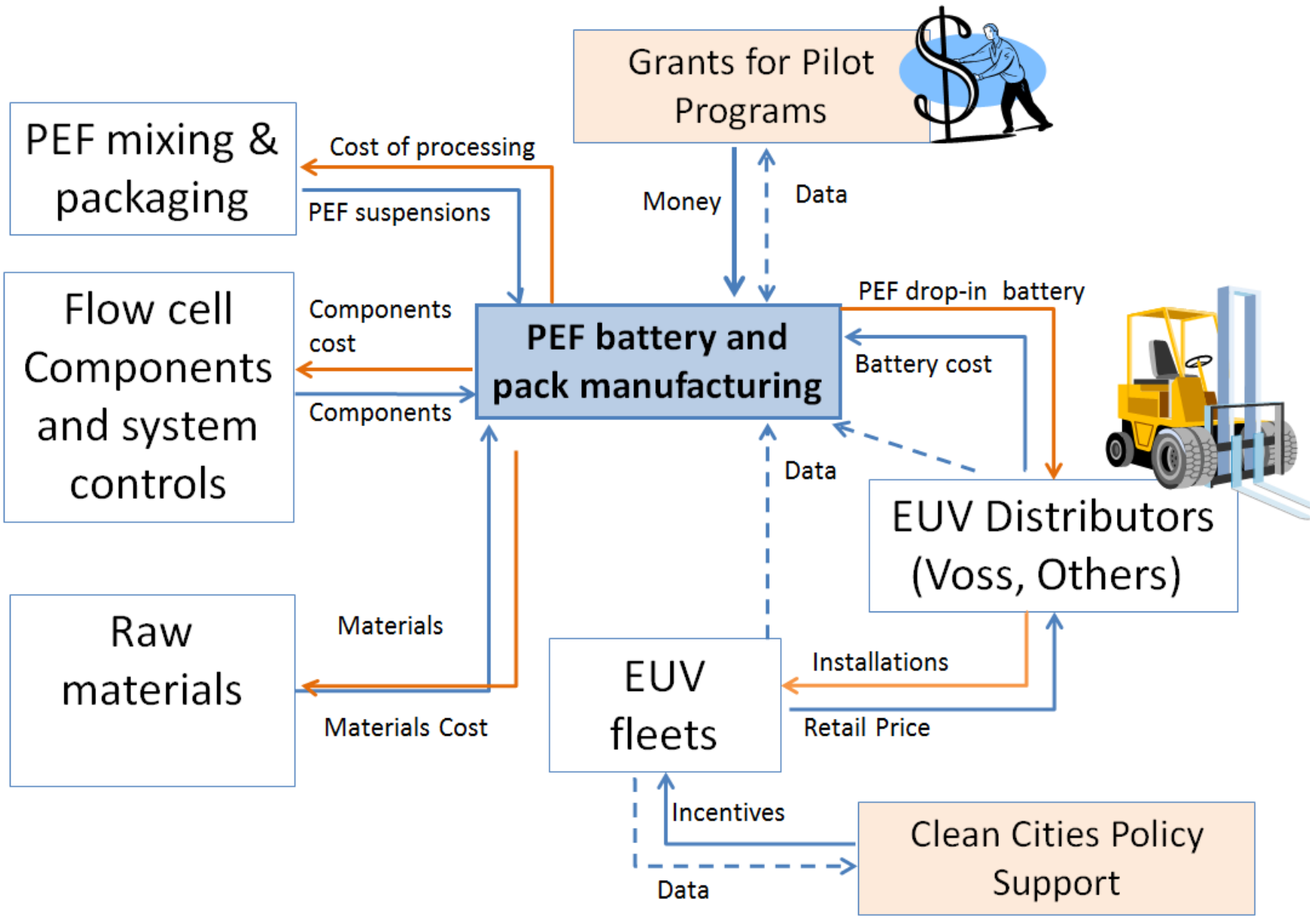
a perfect match for our nanoelectrofuel prototype battery

What a startup might look like



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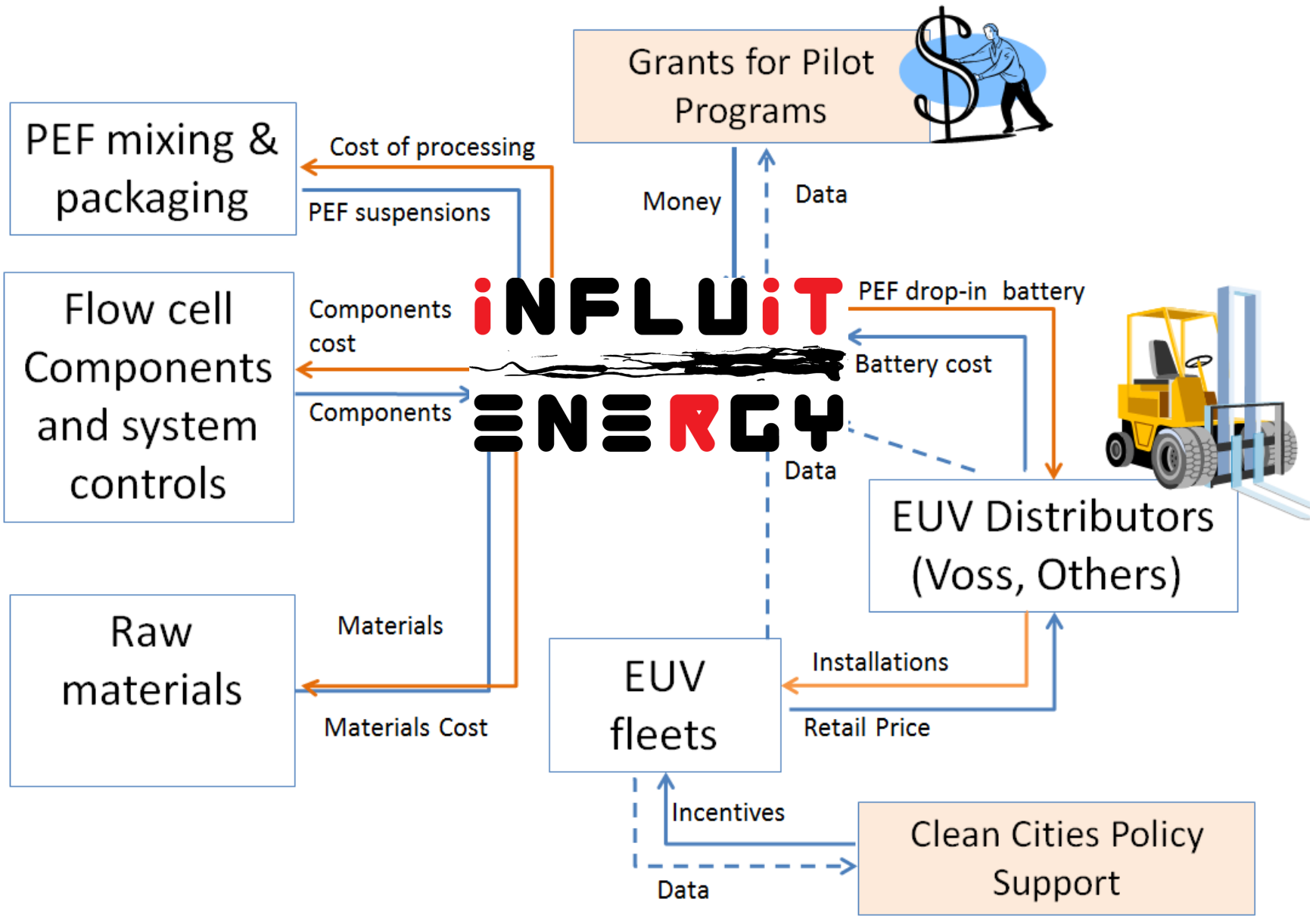

Thank You!