The challenges of making flow batteries with nanoelectrofuel

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Outline



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



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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- Consider a Li-ion battery





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- Charge ${\rm Li}^+$ ions move from cathode to anode and electrons also flow to the anode externally, anode is reduced
- Discharge ${\rm Li^+}$ ions move back to cathode and electrons flow through the external load, anode is oxidized



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Potential, energy density, and power determined by the chemistry

Common solid state battery chemistries



Lead-acid bat Cathode: Anode:	$\frac{\text{tery:}}{\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2 \text{ e}^-}{\text{PbSO}_4 + 2 \text{ e}^-}$	$\begin{array}{l} E_{\mathit{oc}} = 2.05 \ V \\ \longleftrightarrow & Pb_2SO_4 + 2 \ H_2O \\ \longleftrightarrow & Pb + SO_4^{2-} \end{array}$
NiMH battery Cathode: Anode:	: NiOOH + $H_2O + e^-$ M + $H_2O + e^-$	$\begin{array}{l} E_{oc} = 1.28 \ V \\ \longleftrightarrow & Ni(OH)_2 + OH^- \\ \longleftrightarrow & MH + OH^- \end{array}$
Li-ion battery: Cathode: Anode:	$\begin{array}{c} CoO_2 + Li^+ + e^- \\ Li^+ + C_6 + e^- \end{array}$	$\begin{array}{l} E_{oc} = 4.00 \ V \\ \longleftrightarrow & LiCoO_2 \\ \longleftrightarrow & LiC_6 \end{array}$

Characteristics

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

Flow batteries





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Nanoelectrofuel battery





Suspended electroactive nanoparticles

Advantages of flow batteries

Energy density of solid state

Chemistry agnostic aqueous or non-aqueous 3 year ana e funded program

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

Develop commercialization plan

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- How much loading can be stabilized in suspension?
- 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?









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





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





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- 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.

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Initial prototype cell



Anodic Out Cathodic Out



.

Anodic In

Made from metal with machined posts for increased contact area

Future designs manufactured with 3D printing & metal electrode inserts

Cathodic In

CFD modeling



Inject 5000 particles and evolve for 15 s

Extend to repeated injections of 5000 particles and add electrochemical modeling

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Wichita State University

Initial CFD results





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Nanofluid settling



 ${\rm Li}_{4}{\rm Ti}_{5}{\rm O}_{12}$ coated with a variety of organic molecules



0 hours



0.5 hours



1 hour



1.5 hours



2 hours



18 hours



LiNi_xMn_yCo_zO₂ non-aqueous cathode material



As received micron-sized particles (MTI Inc.)

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LiNi_xMn_yCo_zO₂ non-aqueous cathode material



Ball milled ~400 nm particles (MTI Inc.)







 Nanoparticle-sized LiNi_xMn_yCo_zO₂ has lower capacity and more fading





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- Nanoparticle-sized LiNi_xMn_yCo_zO₂ 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









Fe₂O₃ cyclic voltammetry shows Li intercalation

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 Fe_2O_3 nanoparticle anode in a coin cell





 Fe_2O_3 nanoparticles in fluid





• Performance of nanofluid equivalent to solid nanoparticle electrode

Fe₂O₃ nanoparticles in fluid





 Performance of nanofluid equivalent to solid nanoparticle electrode

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

 Fe_2O_3 nanoparticles in fluid





- Performance of nanofluid equivalent 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

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 $\delta_i(k)$: phase shift for the jth path
- N_j : number of paths of type j R_i : half path length
- σ_j : path "disorder"





































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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 battery box





Pouch cell clamped against front window in helium environment

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In situ battery box





Suitable for both transmission and fluorescence measurements

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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





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





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





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





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





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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





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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. Successful development of this new battery format requires the ability to charge and discharge nanoparticle suspensions by transient contact with the electrodes. 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.