# The science and engineering of Nanoelectrofuel flow battery development

#### Carlo Segre

#### Physics Department & Center for Synchrotron Radiation Research and Instrumentation Illinois Institute of Technology

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#### Outline



- The nanoelectrofuel concept
- Challenges for prototype design
- How to make nanoelectrofuel
- Fe<sub>2</sub>O<sub>3</sub> anode characterization
- Synchrotron radiation studies
- Fe<sub>2</sub>O<sub>3</sub> nanoelectrofuel characterization
- Ni(OH)<sub>2</sub> cathode
- Lessons from I-Corps

#### Acknowledgements



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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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Potential, energy density, and power determined by the chemistry

#### Common solid state battery chemistries



Lead-acid battery:		$E_{oc} = 2.05 V$
Cathode:	$PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$	$\leftrightarrow$ Pb <sub>2</sub> SO <sub>4</sub> + 2 H <sub>2</sub> O
Anode:	$PbSO_4 + 2 e^-$	$\leftrightarrow$ Pb <sup>2</sup> + SO <sub>4</sub> <sup>2-</sup>
NiMH battery		E., = 1.28 V
Cathode:	. NiOOH $\pm$ H O $\pm$ e <sup>-</sup>	$L_{0c} = 1.20$ V
An e des	$M + H_2 O + e^{-1}$	$\longrightarrow$ $MU + OU=$
Anode:	$M + H_2O + e$	$\leftrightarrow$ MH + OH
Li-ion battery:		$E_{oc} = 4.00 V$
Cathode:	$CoO_2 + Li^+ + e^-$	$\leftrightarrow$ LiCoO <sub>2</sub>
Anode:	$L\bar{i^{+}} + C_{6} + e^{-}$	$\leftrightarrow$ LiC <sub>6</sub>
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#### Characteristics

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

#### Flow batteries





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#### Nanoelectrofuel flow battery





Suspended electroactive nanoparticles Advantages of flow batteries Energy density of solid state Chemistry agnostic aqueous or non-aqueous Initial anpare funding

IIT/Argonne collaboration

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

Develop commercialization plan

# Advantages of nanoelectrofuel





initial

pacity

#### Long term vision





#### 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

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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

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December 2012 data comparing x-ray absorption spectroscopy results on  $\rm Cu_6Sn_5$  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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#### 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  $10\times$  too slow!

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

#### Test flow cell





#### Test flow cell





#### Test flow cell





# NEF anode: Fe<sub>2</sub>O<sub>3</sub>



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

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

$$\begin{split} & \operatorname{Fe}_2 \operatorname{O}_3 + 3\operatorname{H}_2 \operatorname{O} + 2\operatorname{e}^- \longrightarrow 2\operatorname{Fe}(\operatorname{OH})_2 + 2\operatorname{OH}^- & E_0 = -0.9V & \sim 335 \text{ mAh/g} \\ & \operatorname{Fe}(\operatorname{OH})_2 + 2\operatorname{e}^- \longrightarrow \operatorname{Fe} + 2\operatorname{OH}^- & E_0 = -1.0V & \sim 670 \text{ mAh/g} \\ & 2\operatorname{H}_2 \operatorname{O} + 2\operatorname{e}^- \longrightarrow \operatorname{H}_2 + 2\operatorname{OH}^- & E_0 = -0.9V & \operatorname{Bad!} \end{split}$$



pristine  $Fe_2O_3$ 





sulfonated  $Fe_2O_3$ 

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 $(OH)_3 - Si - (CH)_3 - SO_3$ 

treat with  $\sim 3 \text{ wt}\%$ 

# Fe<sub>2</sub>O<sub>3</sub> 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  $\mathrm{Fe_2O_3}$  nanofluids

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



#### Fe<sub>2</sub>O<sub>3</sub> 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

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# Fe<sub>2</sub>O<sub>3</sub> post-cycling analysis





Pristine Fe<sub>2</sub>O<sub>3</sub> electrodes show recrystallized Fe metal particles



Sulfonated Fe<sub>2</sub>O<sub>3</sub> electrodes show only oxide particles

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# The EXAFS experiment

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- 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  $\delta_i(k)$ : phase shift for the j<sup>th</sup> path
- $N_j$ : number of paths of type j  $R_i$ : half path length
- $\sigma_i$ : path "disorder"































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#### **EXAFS** analysis





## $Fe_2O_3$ in situ studies

Charging reaction: 335 mAh/g  $Fe_2O_3+3H_2O+2e^- \longrightarrow 2Fe(OH)_2+2OH^-$ 

Over-charging reaction: 670 mAh/g  $2 \operatorname{Fe}(OH)_2 + 4 \operatorname{e}^- \longrightarrow 2 \operatorname{Fe} + 4 OH^-$ 







# In situ $Fe_2O_3$ charging

- Aqueous pouch cell
- Ni-mesh electrode
- MRCAT 10-BM beam line
- Fluorescence mode data acquisition
- $\sim$ 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<sub>2</sub>O<sub>3</sub> XANES





- First charge shows edge similar to Fe metal
- Discharged electrode never returns to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> but seems to be in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>
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- Derivatives show these features even more clearly

## Fe<sub>2</sub>O<sub>3</sub> EXAFS





- Clear evidence of metallic Fe but no Fe(OH)<sub>2</sub> seen
- Discharge does not return electrode to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>
- Over-charge pushes system toward metallic Fe
- Fitting reveals mixture of Fe and/or  $Fe_3O_4/\gamma$ -Fe $_2O_3$  in all spectra.

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

## Fe<sub>2</sub>O<sub>3</sub> 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 flowthrough current collector design

# Pristine Fe<sub>2</sub>O<sub>3</sub> NEF performance





5% suspension of pristine  $Fe_2O_3$ , overcharged and discharged at C/33 with improved electrode

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5% suspension of pristine Fe<sub>2</sub>O<sub>3</sub>, overcharged 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<sub>2</sub>O<sub>3</sub> 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"

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The goal is to oxidize  $\mathrm{Ni}^{+2}$  to  $\mathrm{Ni}^{+3}$ 

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 $Ni(OH)_2 + OH^- \longrightarrow NiOOH + H_2O + e^- \sim 289 \text{ mAh/g}$ 

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Capacity (mAh/g)

E (V) vs. Hg/HgO



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#### $Ni(OH)_2$ is a poor conductor, lots of challenges still ahead



# Initial funding: the RANGE program



#### Robust Affordable Next Generation Energy 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









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







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Total Automotive Market



TAM – \$40B

- SAM \$10B
- SOM \$ 2B





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Electric utility vehicles (EUVs) can bridge the "valley of death"

#### Current EUV Market



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SOM - \$ 75M







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a perfect match for our nanoelectrofuel prototype battery

#### What a startup might look like





#### What a startup might look like





## Thank You!

