Recent Progress and Challenges of the Iron Flow Battery for Large Scale Energy Storage

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Beyond Lithium Ion IX
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Grid Energy Storage Requirements

- High efficiencies- >75% round trip energy storage
- Capital cost <$250 /kW or <$100 / kWh (installed)
- Large number of deep discharges: 10+ year life, LCoS < $0.02/kWh
- Flexible capacity / power capabilities
- Long Duration (6 – 10 hrs at rated power)

Grid Scale Storage

Without Storage	With Storage
Grid is load following	Producers decoupled from consumers
Production is centralized, inefficient, and potentially unreliable	Peak shaving and load leveling increases efficiency and reliability
Limited penetration of renewables	Renewables can be used reliably

Why don't we have grid scale storage?

Cost

Generation is much cheaper than existing Storage technology

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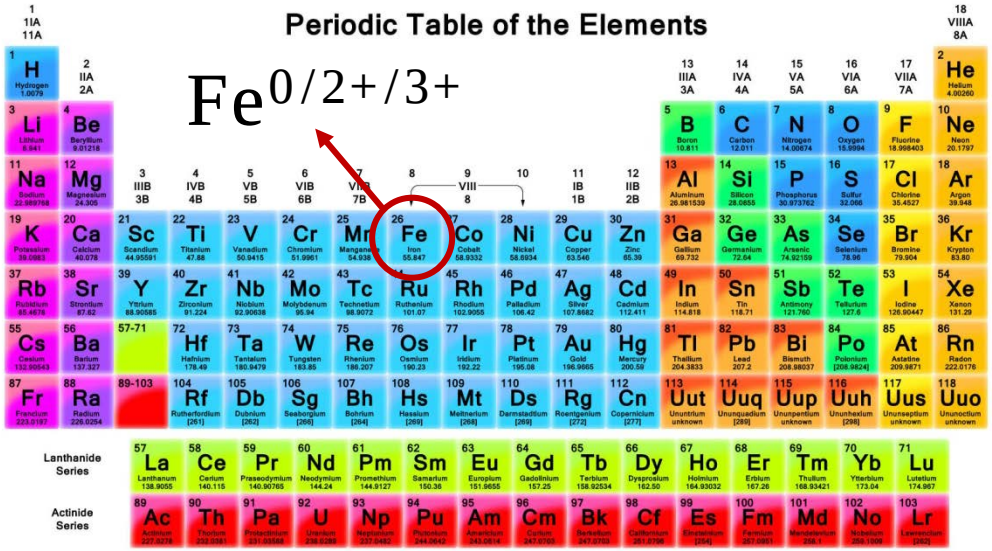
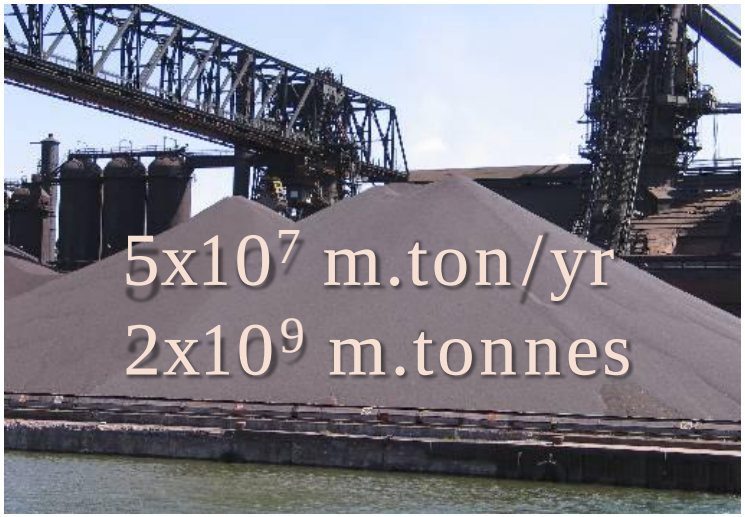
EEE @ CWRU

All-Iron Flow Batteries

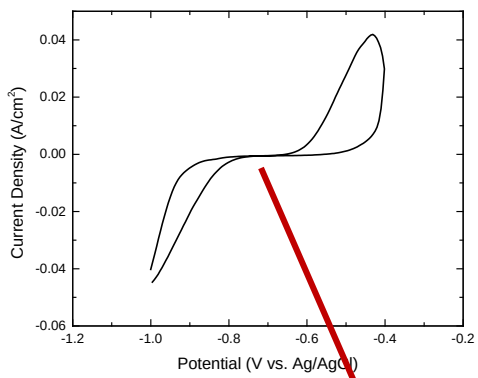
- Iron is cheap and widely available
- Iron is non-toxic
- Iron electrolyte is mildly acidic, non-flammable
- Low cost (non-perfluoro, non-ionomer) separators



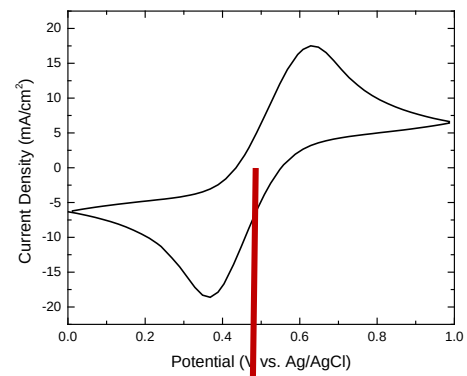


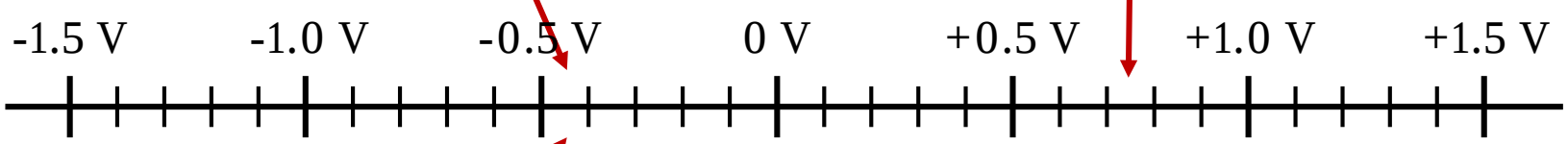
All-Iron Flow Battery Chemistry

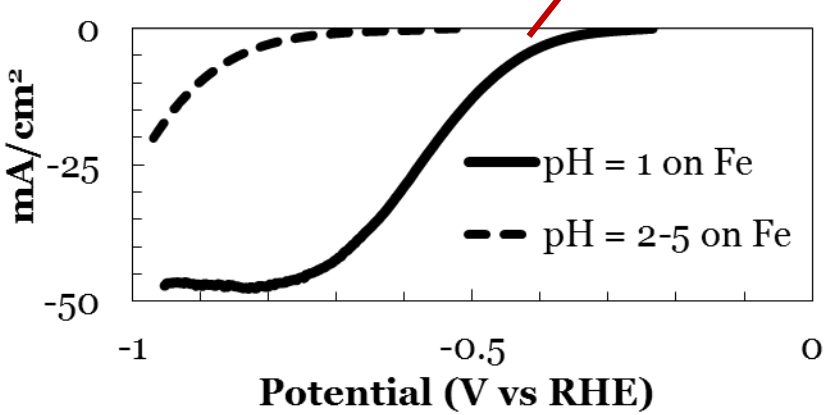
$Fe^{2+} + 2e \rightarrow Fe^{o}$



$Fe^{2+} \rightarrow Fe^{3+} + e$







Technical Challenges

- High Plating Efficiency
  - Hydrogen evolution
- Plating Density – Energy Storage

DOE – Office of Electricity Program

2011-2015

'Hybrid' battery

- Conventional $Fe^{+2/+3}$ solution redox positive electrode
- Plate iron within the stack at negative electrode

Electrolyte chemistry to minimize H_2 evolution

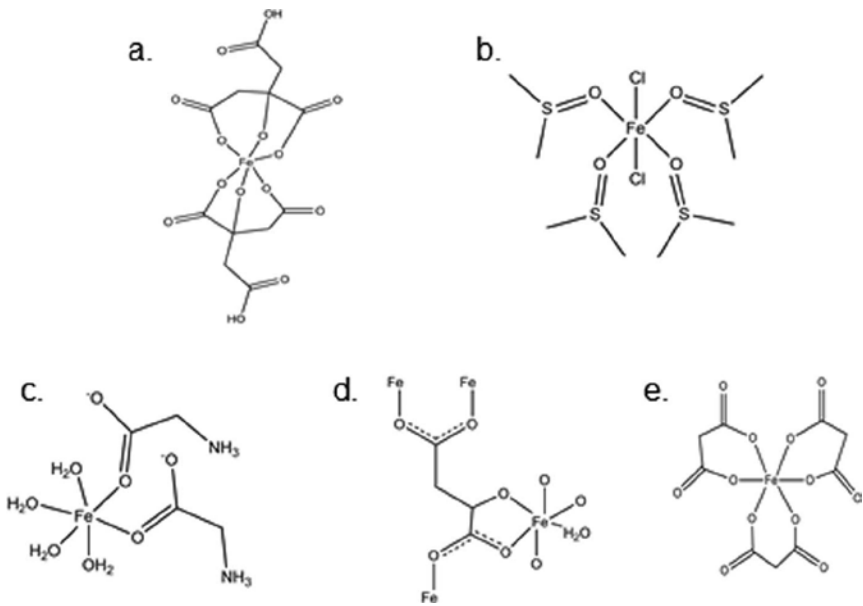
- Raise pH
- Use ligand complexes to prevent Fe(OH)3 ppt

Negative electrode structures

- Minimize overpotentials
- Acceptable plating density 200 - 600 mAh/cm^2

Program extended to include

- Hydrogen recombination reactor – electrolyte rebalancing
- Copper chemistry (Cu^0 / Cu^{+1} / Cu^{+2})



Iron-ligand complexes:
a) citrate, b) DMSO, c) glycine
d) Malic acid, e) malonic acid

ARPA-E Program

- 1 year proof of concept program (2013)
  Using chemistry developed in DOE program
- Program given 2 year extension
  March 2014 – March 2016
- In negotiations for 18 month extension
  Scale up to 1 kW/ 6 kWh prototype

- Slurry electrodes to de-couple energy/power
  Plate on dispersed conductive particles
  Plated iron is carried out of the stack to reservoir
  True ‘flow battery’ behavior
    Energy stored limited only by tank size

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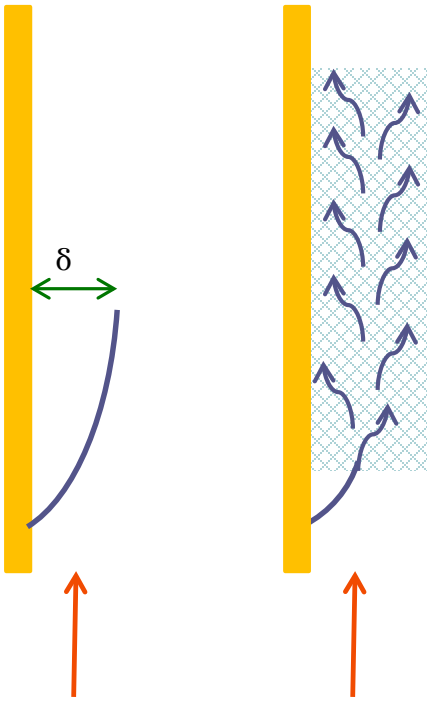
OE Project - Hybrid Electrode Design

Flow Assisted Plating Reaction

- Iron stored in battery
- Limited energy to power ratios possible
- Trade-offs
  - Voltaic efficiency vs plating density
  - Pressure drop vs plating density

J. Electrochem. Soc., **161**, A1662 (2014)
J. Power Sources, **269,** 216 (2014)
J. Electrochem. Soc., **162,** A1 (2015)
J. Electrochem. Soc., **163,** A5041 (2016)



FLAT PLATE

- Low limiting c.d. <30 mA/cm^2
- Large ohmic loss due to gap

POROUS FLOW THROUGH

- non-uniform current distribution
- Properties vary with metal loading

Thanks to Dr. Krista Hawthorne and Dr. Nathan Hoyt

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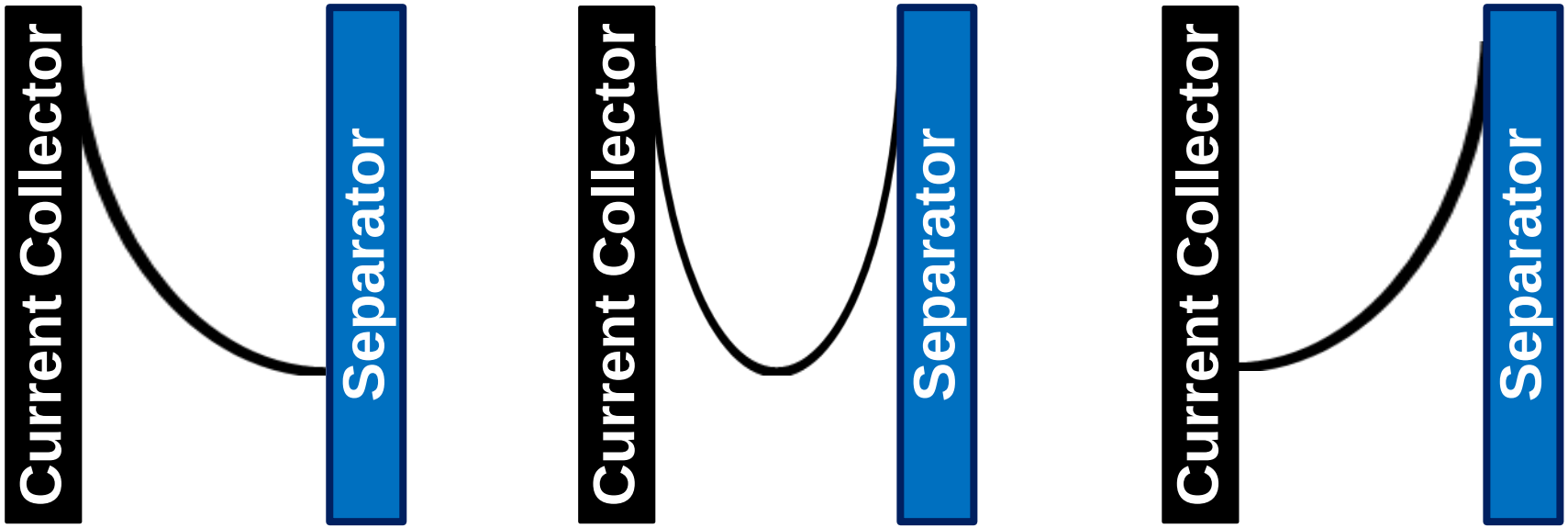
Porous Electrodes
Primary Current Distribution

σ= electronic conductivity, K =solution conductivity (~0.1 S/cm)

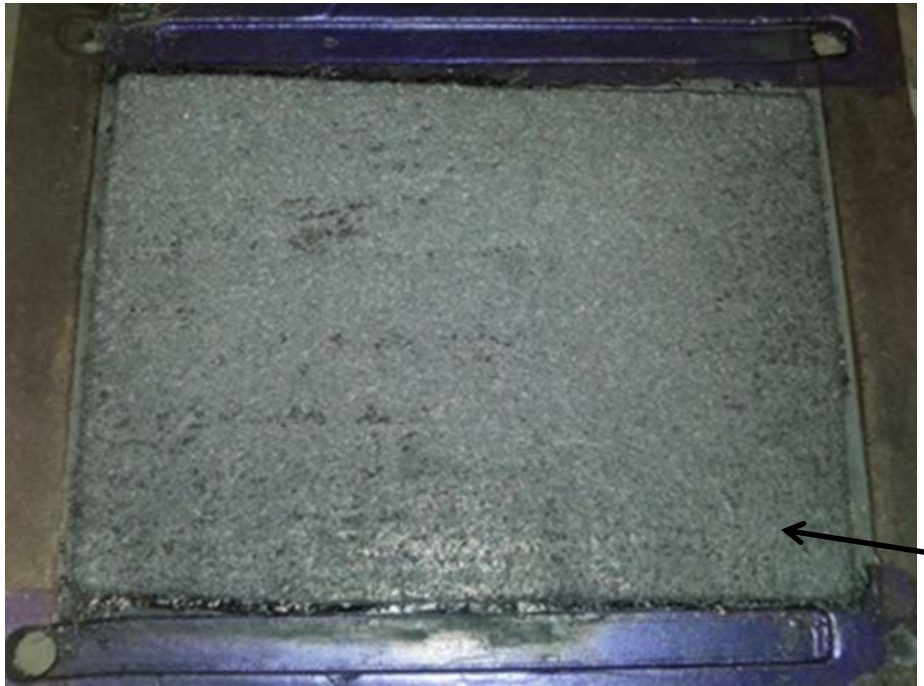
- If $\sigma \ll \kappa$
- If $\sigma \approx \kappa$
- If $\sigma \gg \kappa$



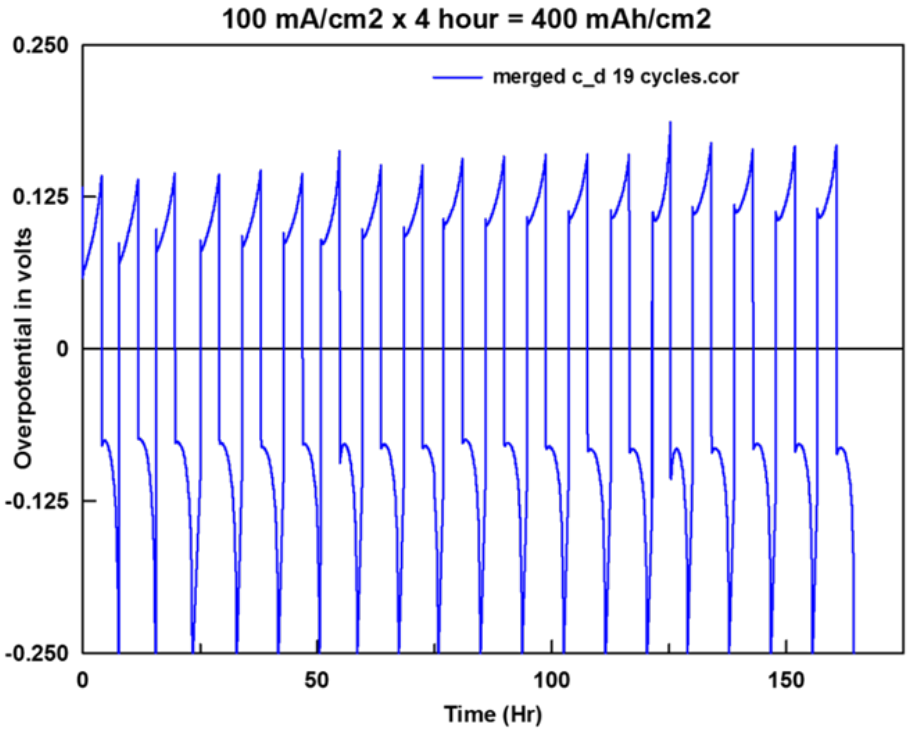
- To plate uniformly throughout a porous electrode
  - need kinetics or mass transfer to be controlling
  - Limits power density, voltaic efficiency

OE Project - Hybrid Electrode Designs

- Tailored electronic conductivity
  - Similar to ionic conductivity
  - Plating inward from both faces
  - 400 – 600 mAh/cm^2 useful capacity
    - 3 – 6 hr at useful c.d.
  - Dendrite free growth



Iron Deposit

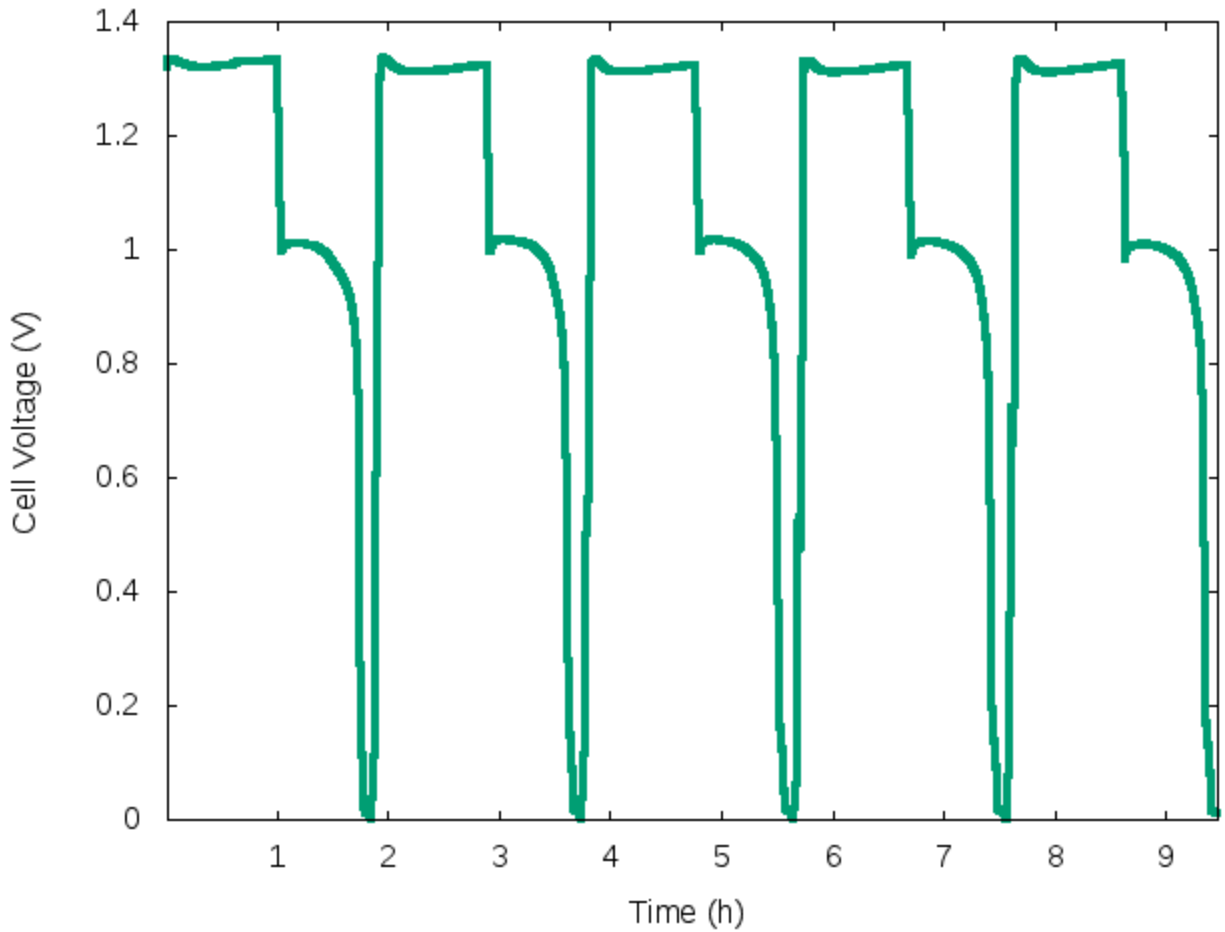


OE Project - Hybrid Electrode Designs

Optimized electrode

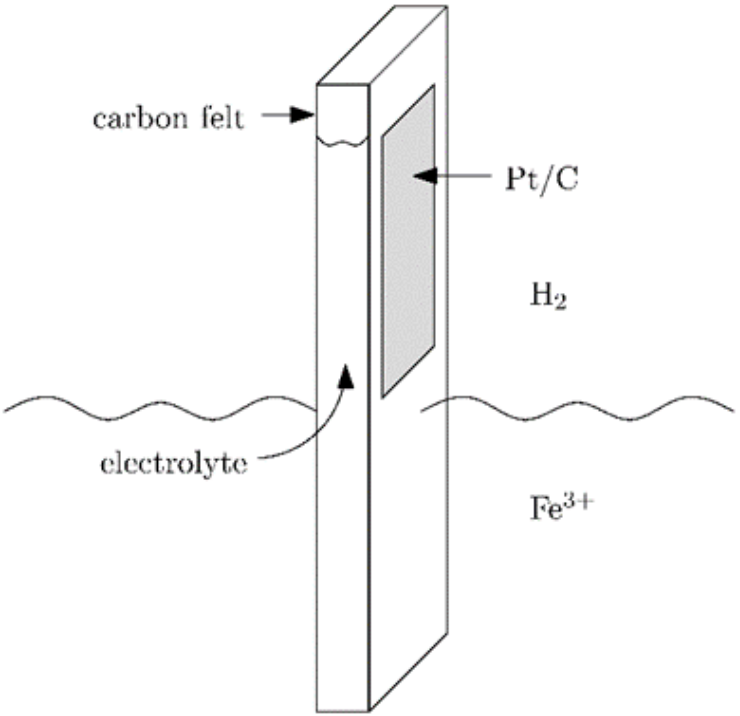
- Balances capacity and voltaic efficiency
- 400 mAh/cm^2
- 75% VE @ 100 mA/cm^2
  - 1.32V charge
  - 1.0 V discharge

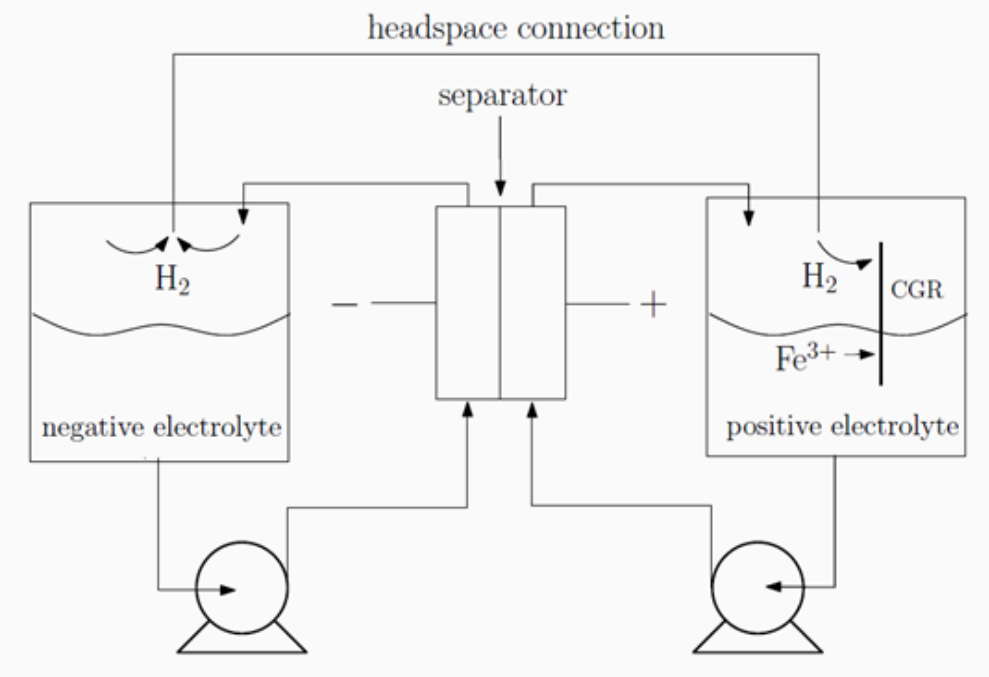
1 hr cycles with exhaustive discharge shown



OE Project - Electrolyte rebalancing:

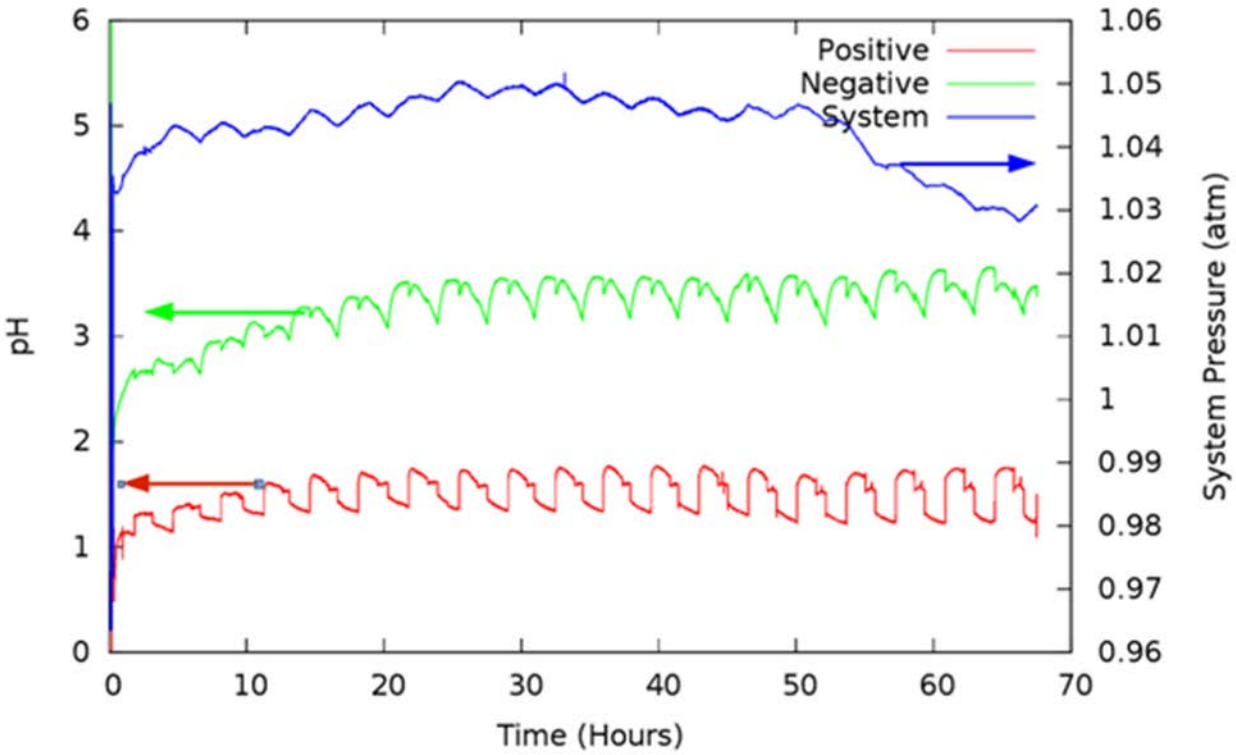
- Floating, membrane-less galvanic reactor
- Passive control of pressure, pH
- Design avoids flooding of H_2 electrode
- *J Power Sources*, in press





OE Project - Electrolyte rebalancing:

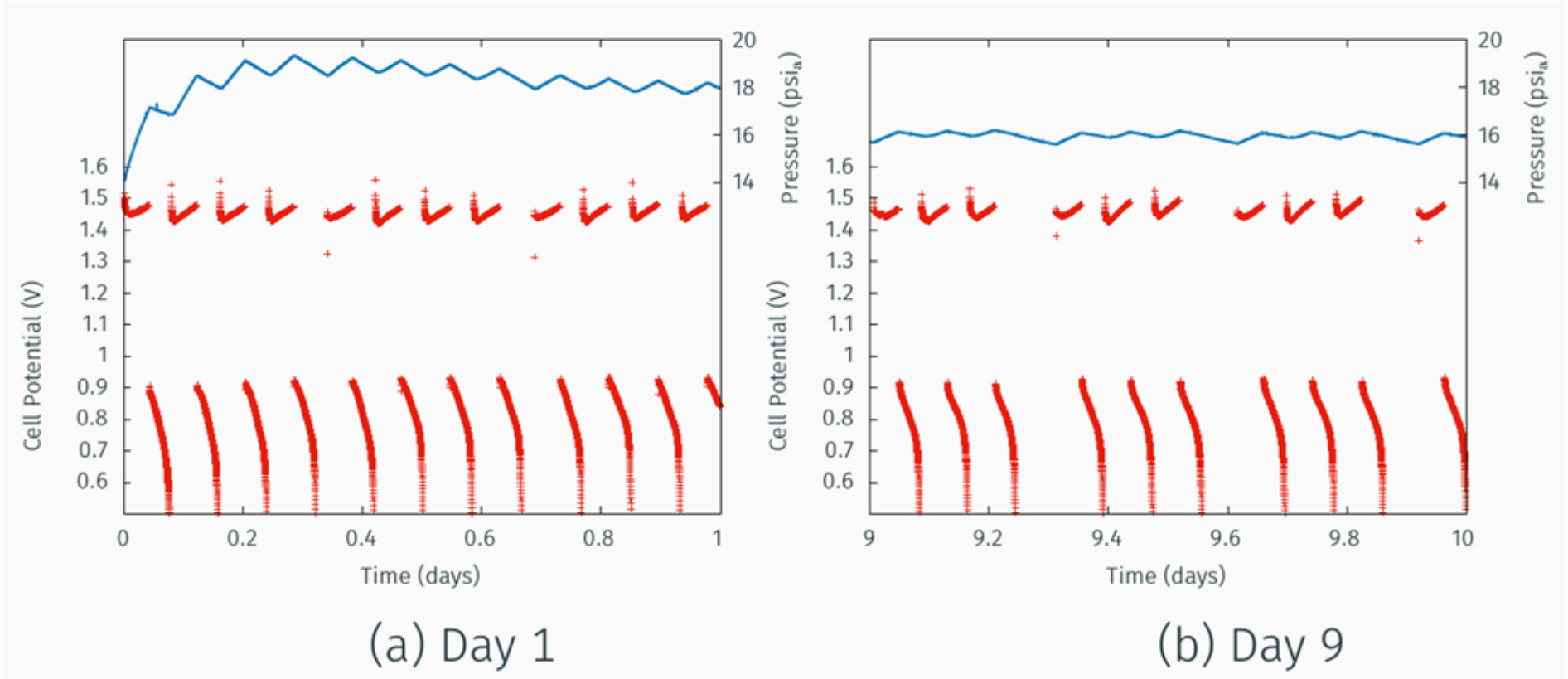
- re-oxidize H_2 that is evolved on charge
- maintains stable pH, $[Fe^{+3}]$



Example of pH and pressure control with electrolyte rebalancing in hybrid iron cells

OE Project - Electrolyte rebalancing:

- 10 day test – completely passive
- maintains stable potentials
- Electrolyte clear, no ppt, stable pH



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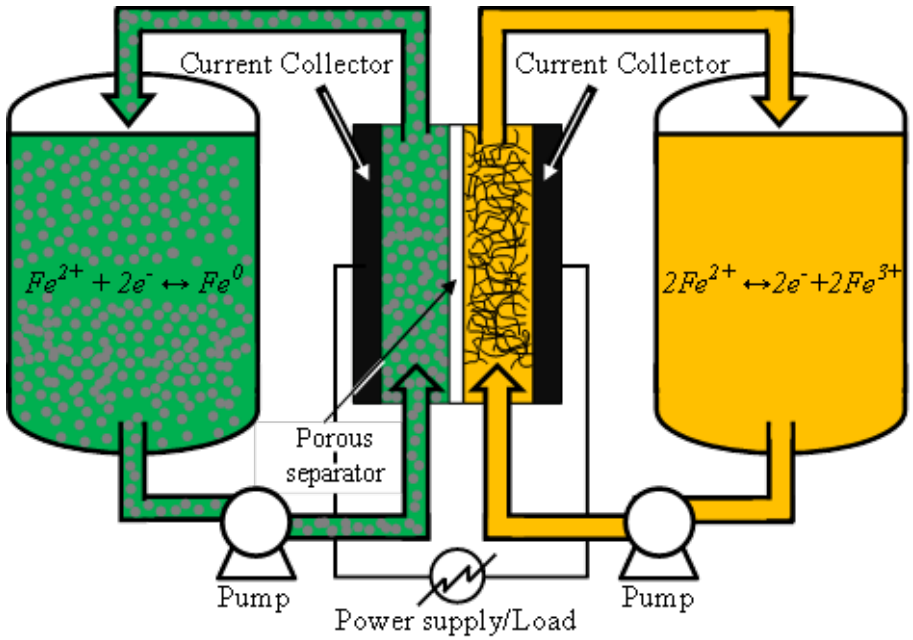
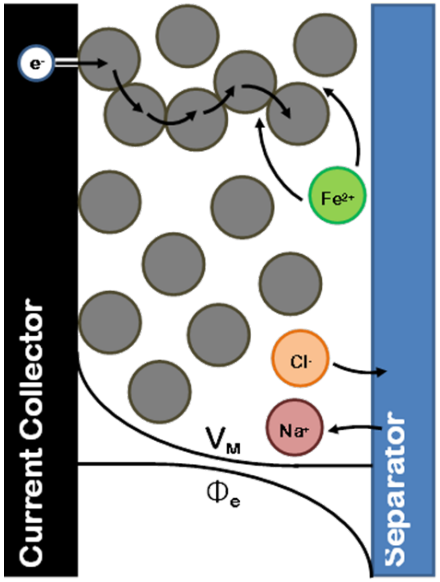
Decoupled All-Iron Battery - Slurry electrodes





$$Fe^{2+} + 2e \longleftrightarrow Fe^0$$

- Iron plates onto particles
- Particles carry plated iron out of the cell
- **Decouples energy capacity and power density**
- Enables long duration operation

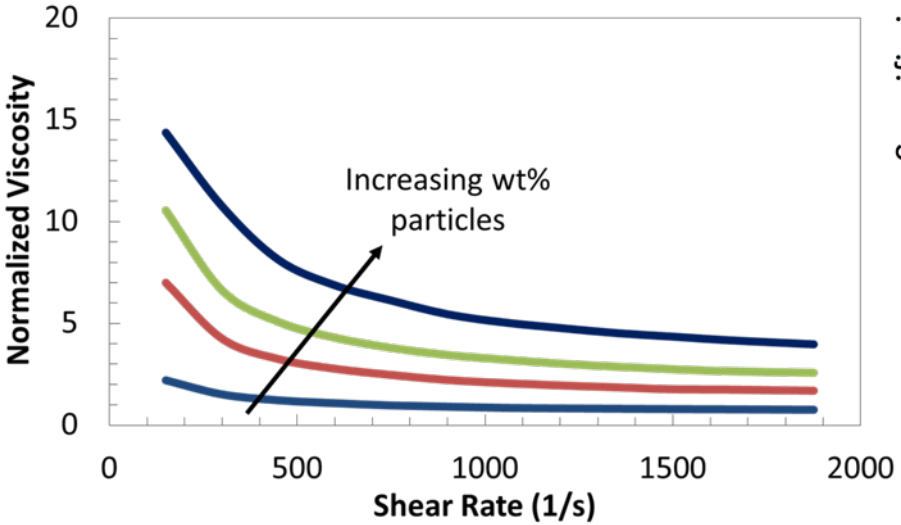
SLURRY REQUIREMENTS

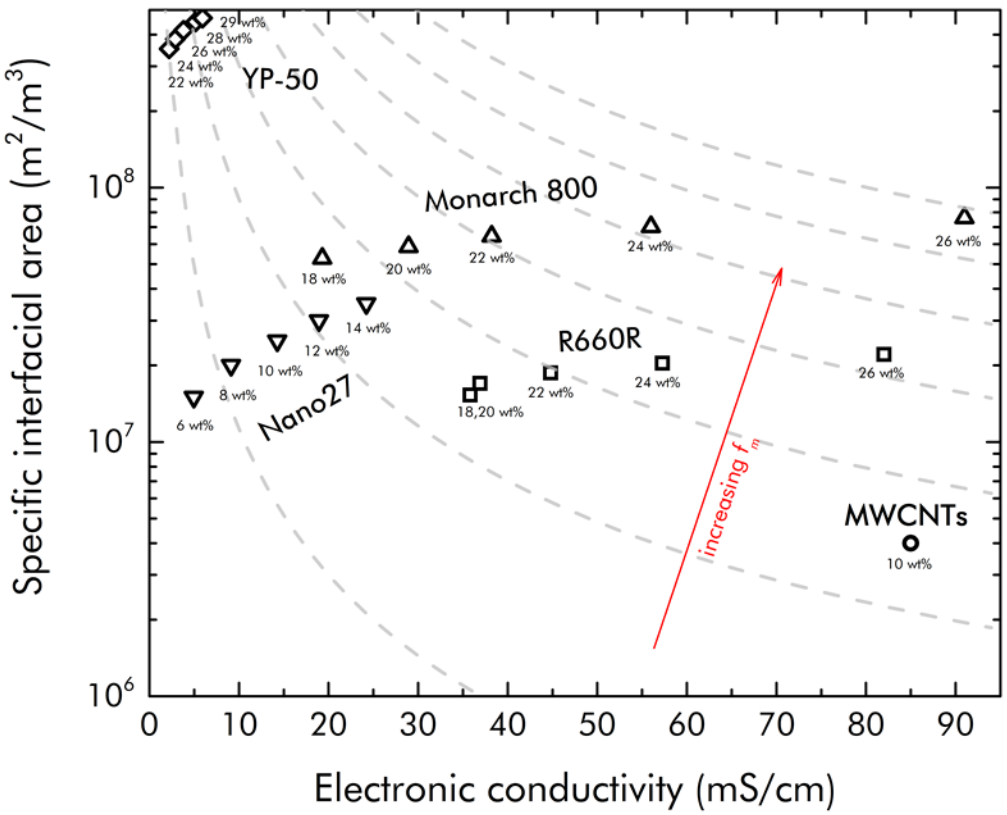
- electronic conductivity - percolation
- Stable in suspension
- Acceptable parasitic losses
- Low cost

Decoupled All-Iron Battery - Slurry electrodes

Slurries are …

- shear-thinning
  - 5X base electrolyte when flowing
- modestly conductive
- Performance figure of merit
  - Higher surface area
    - lower Rct, Rmt
  - Higher conductivity
    - Lower ohmic losses

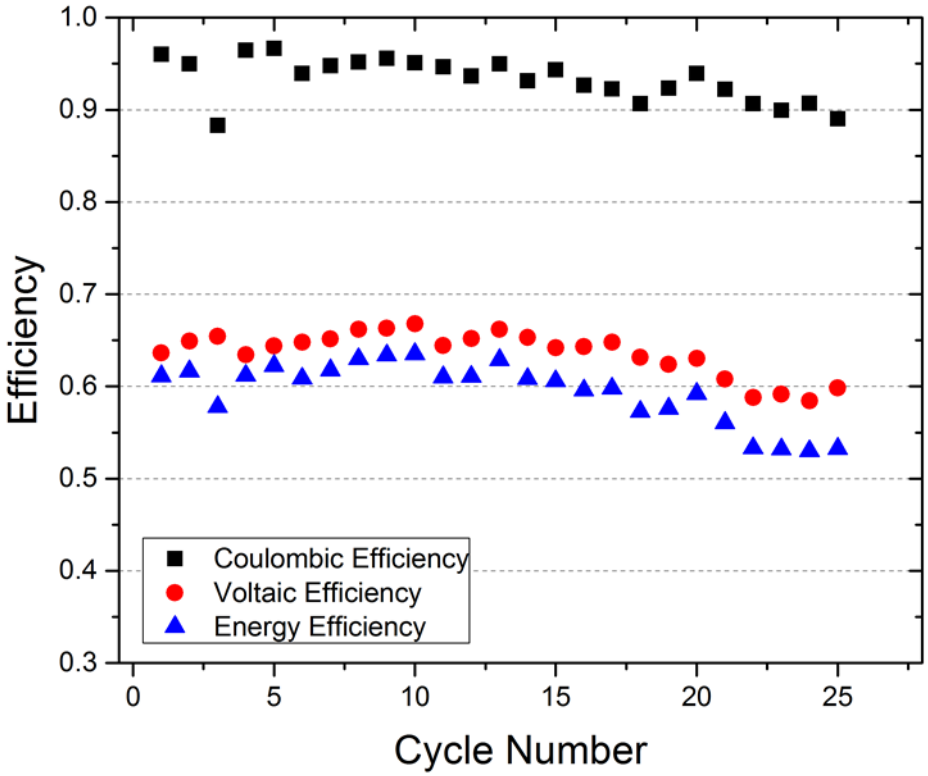


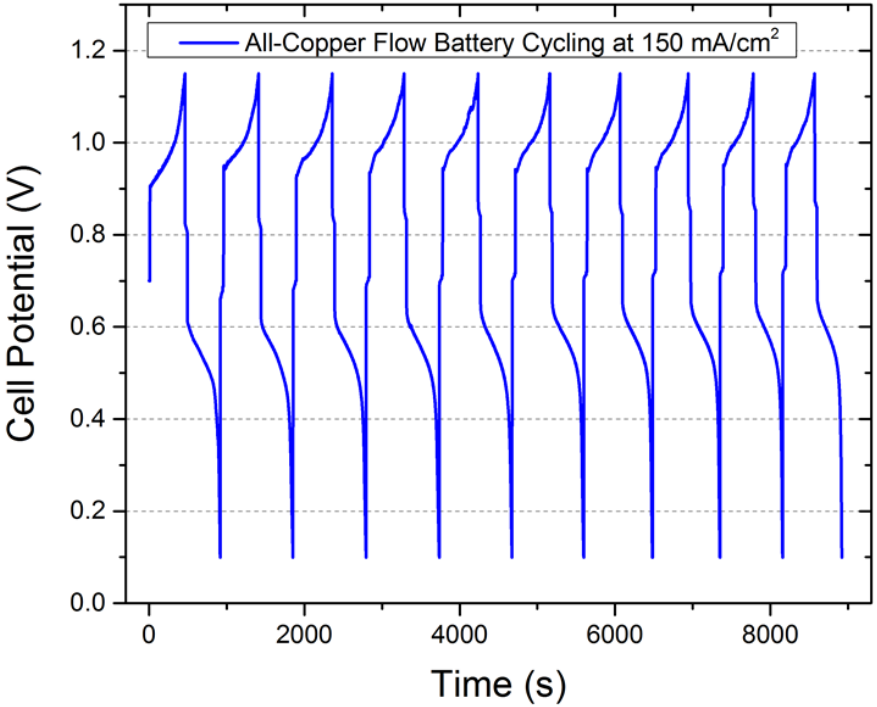


Thanks to Dr. Tyler Petek and Dr. Nathan Hoyt

Slurry electrode Battery – $Cu^{0/+1/+2}$

- 150 mA/cm^2
- Nafion 212





Thanks to Dr. Ertan Agar

Slurry Electrode Approaches for Different Applications

Large scale storage vs High energy density

CWRU All-Iron Slurry	MIT Li-ion Slurry*
• Aqueous electrolyte ▫ High ionic conductivity • Surface plating reaction • Electronic conductivity ▫ 10 – 100 mS/cm • Operating current density ▫ ≥ 100 mA/cm^2 • Power density at 1.2 V ▫ 150 mW/cm^2 • Continuous flow ▫ Low conversion per pass	• Non-aqueous electrolyte ▫ Low ionic conductivity • Intercalation – solid state diffusion • Electronic conductivity ▫ 0.01 – 0.06 mS/cm • Operating current density ▫ < 6 mA/cm^2 • Power density at 3.5 V ▫ 20 mW/cm^2 • Intermittent flow ▫ High conversion per pass

•M Duduta and YM Chiang, et al., *Adv. Energy Mater.*, **1**, 511-516 (2011)

Decoupled All-Iron Battery - Slurry electrodes

"Mathematical Modeling of Electrochemical Flow Capacitors"
J. Electrochem. Soc., **162**, A652 (2015)

“Current Density Scaling in Electrochemical Flow Capacitors”
J.Electrochemical Society, **162,** A1102 (2015)

“Slurry Electrodes for Iron Plating in an All-Iron Flow Battery”
J.Power Sources, **294**, 620, (2015)

“Characterizing Slurry Electrodes Using Electrochemical Impedance Spectroscopy”
J. Electrochem. Soc. **163**, A5001, (2016)

“Modeling of Flowable Slurry Electrodes with Combined Faradaic and Nonfaradaic Currents”
Chemical Engineering Science (2016), pp. 288-297

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Summary

- Hybrid battery
  - 75% VE, 95% CE
  - 4 hr capacity at 100 mA/cm^2
  - $230/kW (1 hr duration, stack, pumps, tanks, etc but no power electronics)
  - $9 each additional hour ($64/kWh @ 4 hrs)
  - Conventional stack construction/operation
- Slurry battery based on carbon blacks
  - 65% VE, 95% CE at 100 mA/cm^2
  - 6-10 hr capacity - Longer durations limited only by carbon cost
  - $200/kW (1 hr duration, no power electronics)
  - $14 each additional hour ($44/kWh @ 6 hrs, $32/kWh @ 10 hrs)
  - Pumping and shunt current losses acceptable
  - Novel stack design may be required
- Ligands can be used to shift redox reaction solubility, pH, and potential

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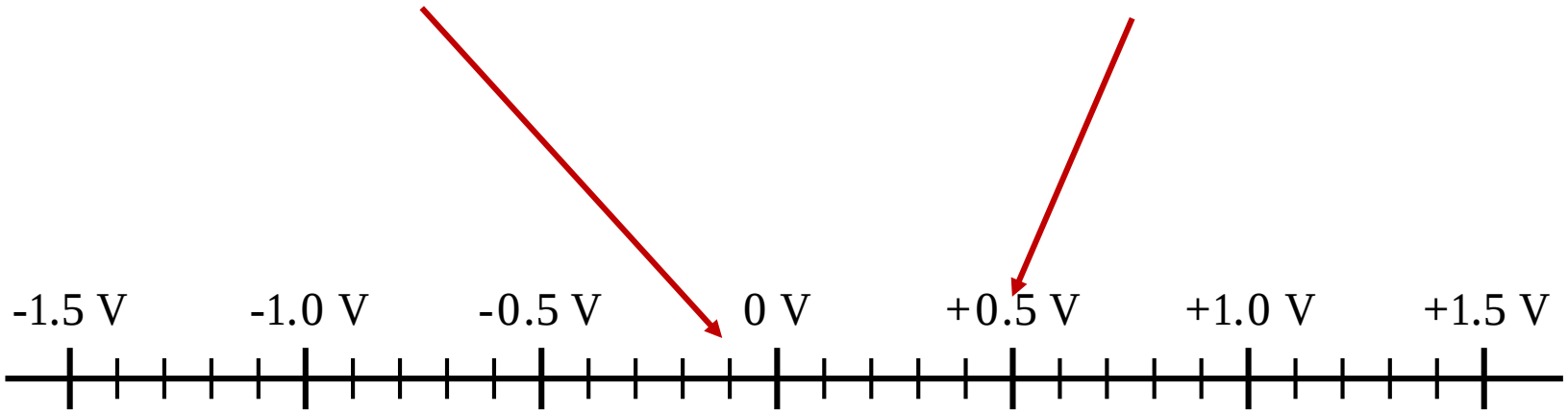
Future All-Iron Flow Battery Chemistries All-redox, multiple ligand systems

$Fe^{3+} \bullet EDTA + e \rightarrow Fe^{2+} \bullet EDTA$

$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e$



Advantages

- Single metal
- All soluble reactants, no plating
- avoids H_2 evolution

Technical Challenges

- Cell voltage
- Solubility
- Compatible pH values
- Ligand Crossover

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EEEJ @ CWRU

Electrochemical Engineering and Energy Labs @ CWRU

Principal Investigators

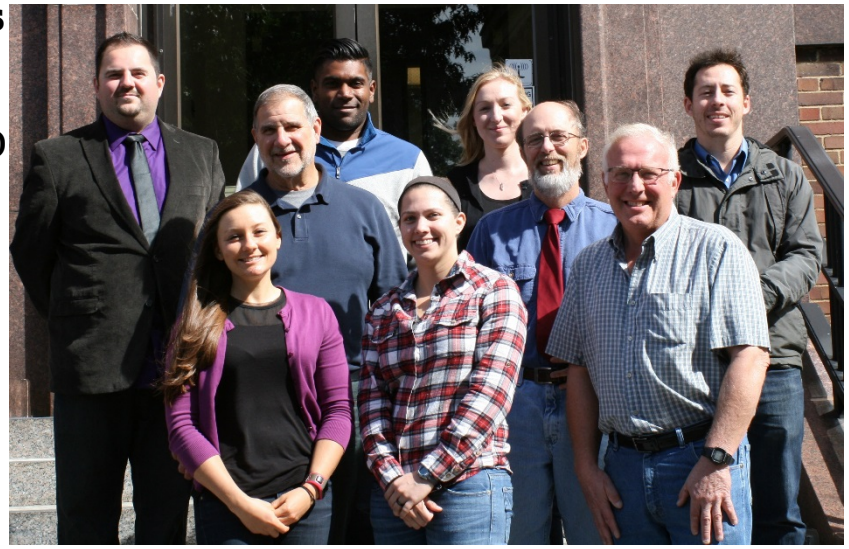
- Robert F. Savinell, PhD
- Jesse S. Wainright, PhD

Research Staff

- Mirko Antloga
- Nicholas Sinclair
- Enoch Nagelli, PhD
- Andrea Bourke, PhD

Doctoral Candidates

- Steve Selverston
- Elizabeth Freund
- Mallory Miller
- Xinyou Ke



U.S. DEPARTMENT OF ENERGY

Office of Electricity

arpa·e CHANGING WHAT'S POSSIBLE

NSF

Fundamentals

- Electrocatalysis and kinetics
- Electrode and cell design
- Membrane transport processes
- Mathematical modeling

Device Innovation

- Energy storage, conversion and efficiency
- Chemical synthesis and separation
- Device prototyping and cost analysis

Thank you!

Questions?

Backup slides

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Other Flow Battery Research at CWRU

Project	Features/Issues	Partners/Sponsors
STTR Phase II: Flow battery structures to enhance performance and reduce manufacturing cost	• Bipolar plate structures to replace carbon felt/paper electrodes • Low cost manufacturing and highly reproducible • Validate electroetching process	Faraday Technology DOE Office of Electricity -Dr. Imre Gyuk
Sustainable Energy Program: Non-aqueous flow battery	• High voltage for high energy density • Low cost transition metals and ligands, membranes, power density	U. Michigan NSF