DOE Peer Review
Iron Based Flow Batteries for Low Cost, Grid Level Energy Storage

Jesse S. Wainright

Department of Chemical Engineering

Great Lakes Energy Institute

Cleveland, Ohio

26 September 2014

U.S. DEPARTMENT OF ENERGY

Office of Electricity

CASE WESTERN RESERVE UNIVERSITY EST. 1826

CASE WESTERN RESERVE UNIVERSITY EST. 1826

The All-Iron Flow Battery

Purpose: Develop an efficient, cost-effective grid level storage capability based on iron

- Low cost electrolyte ($7/kWh)
- Domestic supply of Fe
- Environmentally benign, mild pH, non-toxic
- Cap cost below $150/kW if c.d. > 100 mA/cm^2

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ +0.77 V

$Fe^{2+} + 2e^- \rightarrow Fe^0$ -0.41V

Technical Challenges

- High plating efficiency
  - Minimize H2 evolution
  - pH, Ligand chemistry
- High Plating Density (Ah/cm^2)
  - Electrode Structures
- High Current Density

CASE WESTERN RESERVE UNIVERSITY EST. 1826

Research Plan

Year 1: COMPLETE

- Ligand Screening – demonstrated [Fe^{+3}] >0.5M @ pH>2
- H_2 evolution suppression – effect of pH, anions evaluated

Year 2: COMPLETE

- Effect of Ligands on Fe plating efficiency, morphology
  - Plating density >500 mAh/cm² demonstrated
    > 99% coulombic efficiency

Year 3: COMPLETE

- Negative Electrode Design
  optimize plating capacity, power density
- Separator studies – Fe^{+3}, Ligand crossover

Year 4: in progress

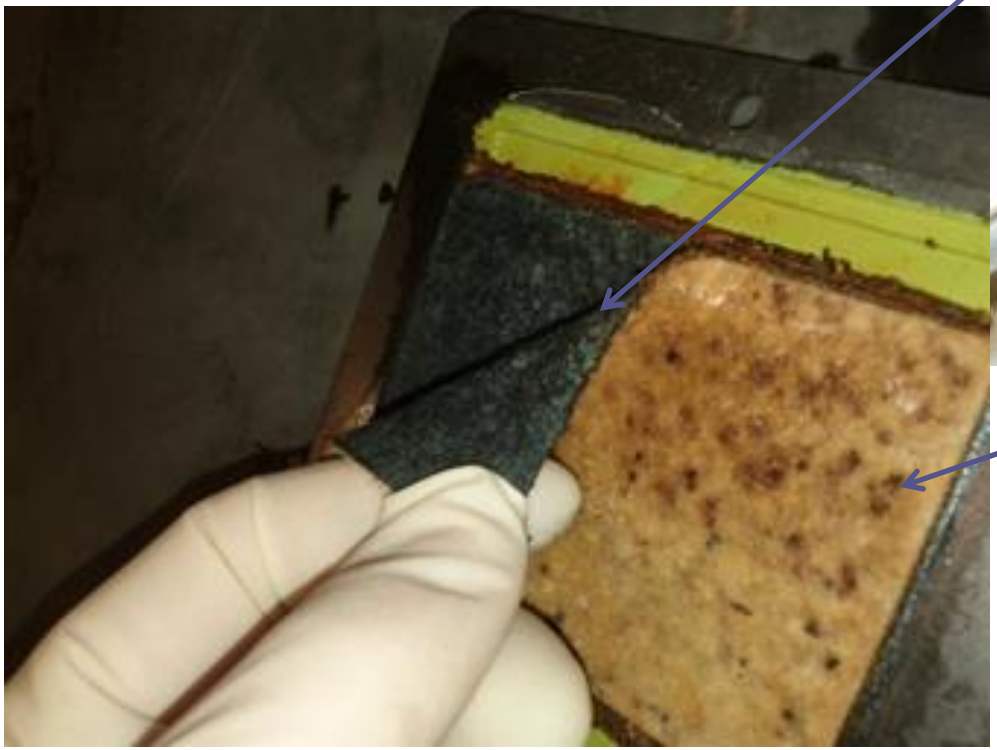
- Extended cycle testing / scale-up of all-Fe battery
- Alternative chemistries

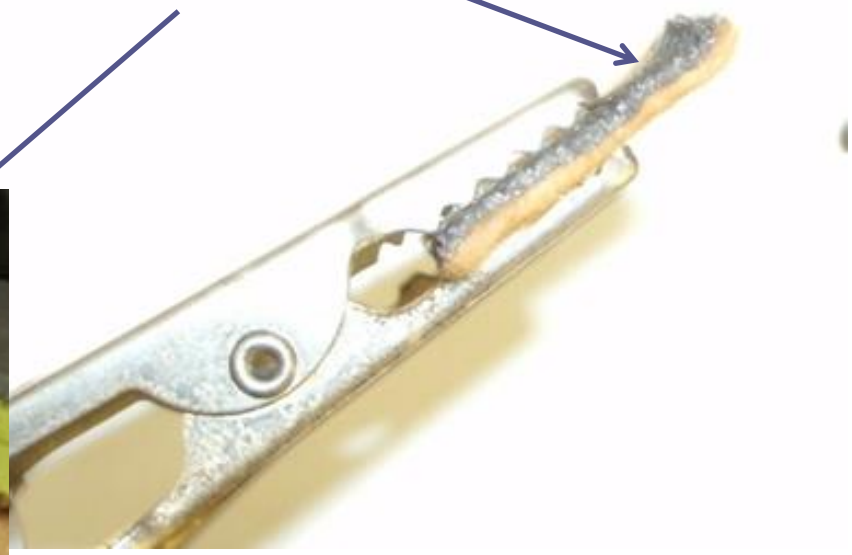
CASE WESTERN RESERVE UNIVERSITY EST. 1826

Hybrid Electrode Designs

Porous, Non-conductive spacer

- Acceptable mass transfer
  - $i_L \approx 200$ mA/cm²
- Large plating density
  - 200 - 500 mAh/cm²





Dark spots are Dendrites

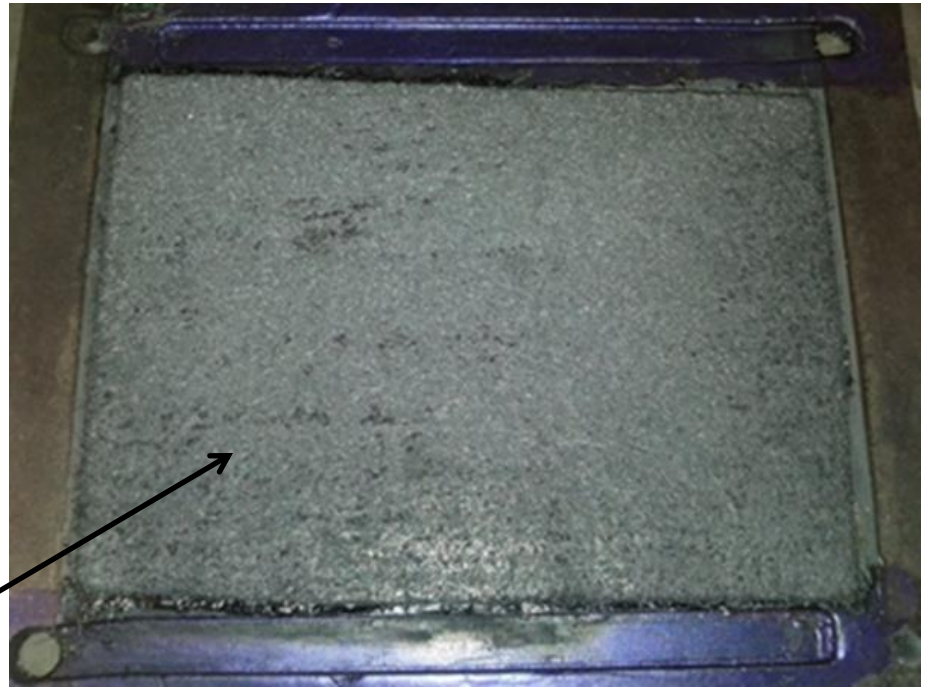
- Plating at Current Collector
- Dendrite growth is an issue
- Kinetic and Ohmic Losses significant

CASE WESTERN RESERVE UNIVERSITY EST. 1826

Hybrid Electrode Designs

Porous, Conductive Felt

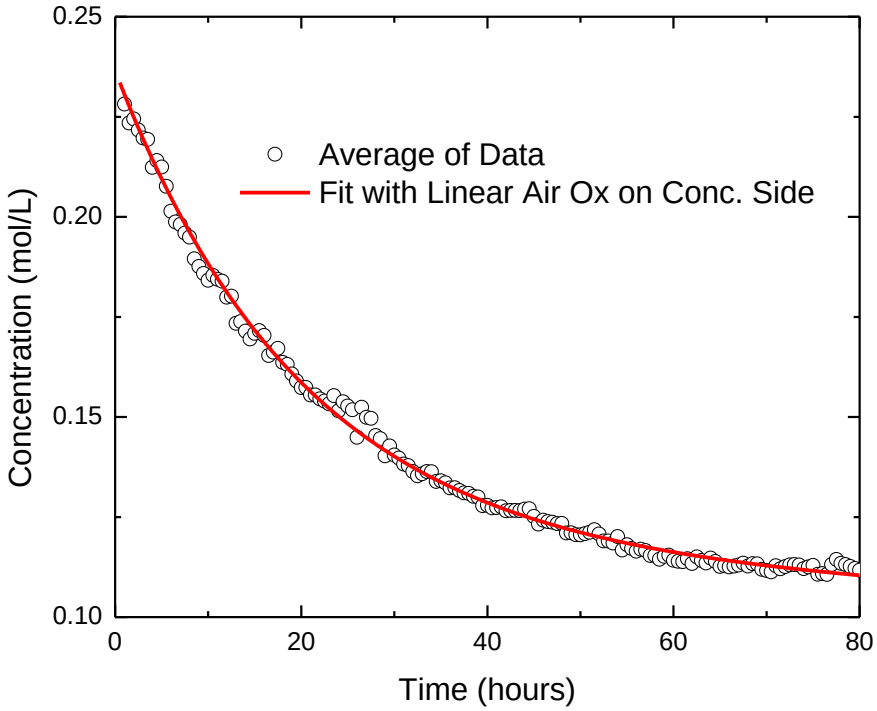
- Plating near membrane
- Increased mass transfer
  - $i_L \approx 1{,}000$ mA/cm²
- Acceptable plating density
  - 100 - 200 mAh/cm²
  - 1 - 2 hr cycles feasible
- Dendrite growth not an issue
- Kinetic & Ohmic Losses minimized
  - High surface area electrode
  - Electrically conductive up to membrane
- 70% VE, 95% CE



Crossover Measurements

Experimental Parameters

- Gradient in Fe^{+2} or Fe^{+3}, not both
- Na^{+} gradient in opp. direction
- Constant anion concentration
- Constant proton concentration (1M)
- Fe concentration probed by voltammetry
- Quasi-steady state solution
  - linear gradient across membrane
  - constant partition coefficient
- Oxidation of Fe^{+2} by air included



Fe^{3+} crossover in Nafion 117

- $D_{eff} = 3.2 \times 10^{-7}$ cm²/s

Iron Crossover
Impact on Battery Size /Efficiency

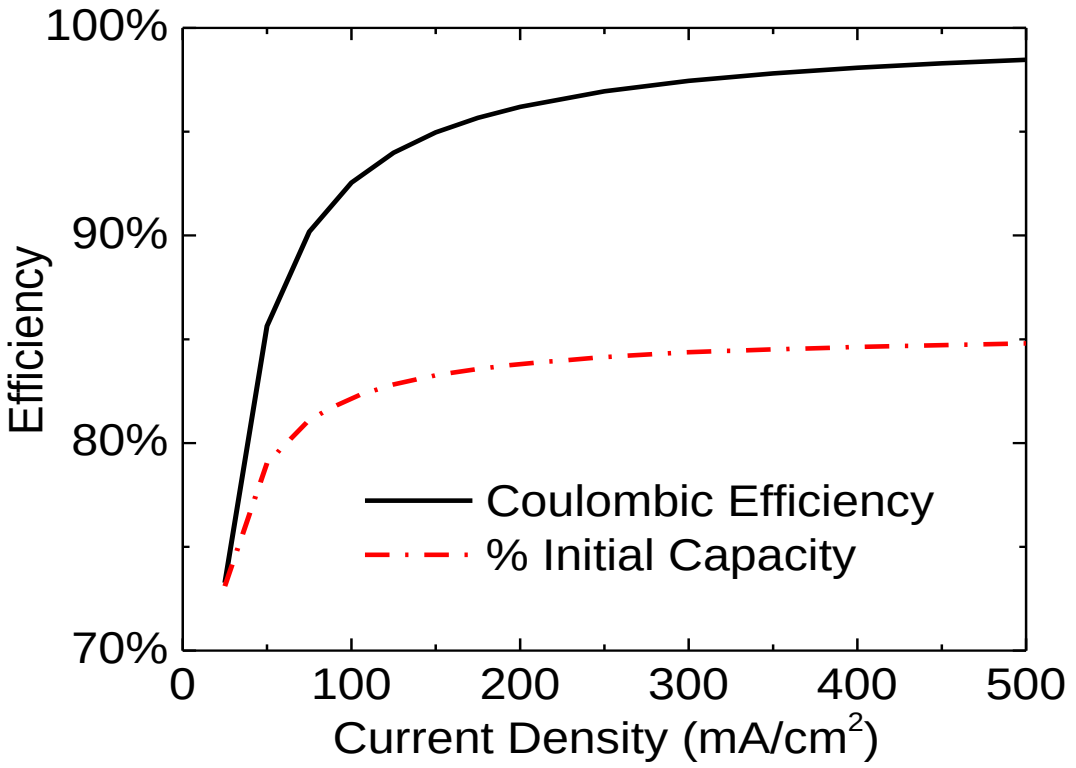
Transport of Fe^{+3} to negative
Reaction w/ Fe^{0} produces Fe^{+2}

Steady State after ≈20 cycles

Coulombic efficiency loss
• due to reaction of Fe^{0} and Fe^{+3}

Capacity Loss
- build-up of Fe^{+2} on negative side
- decrease in Fe^{+2} on positive side

Losses mitigated > 200 mA/cm²



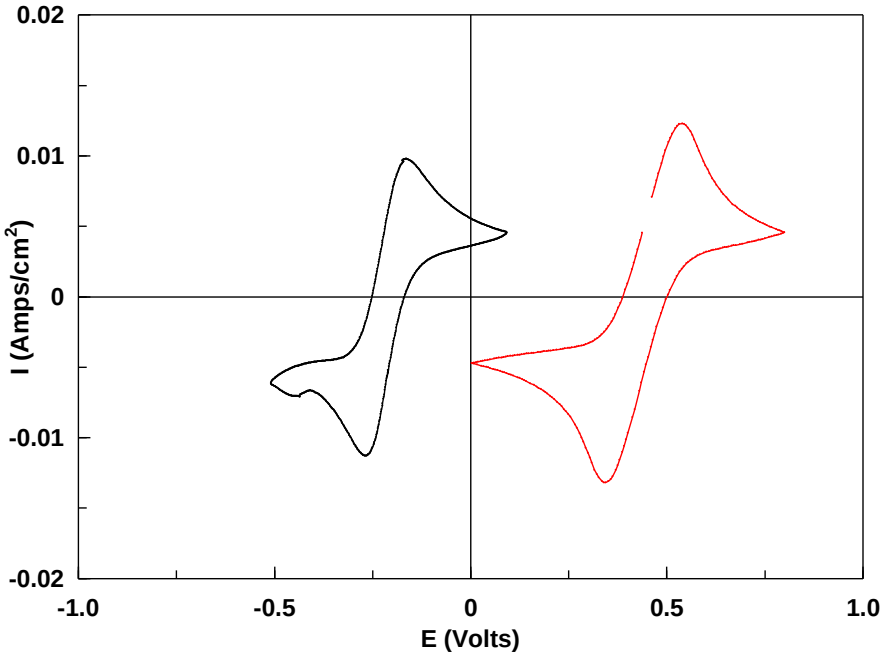
Battery Chemistry – looking ahead

Iron – "Double Redox"

Use Ligands to Shift Fe+2/+3 Redox Potential

- True Flow Battery –
  - All reactants in solution
- Eliminates H_2 Evolution

- Cost of Ligands
  - High concentrations required
- Solubility of Fe:Ligand complexes
  - pH dependence
- Lower Cell Potential
  - Impact on Voltaic Efficiency

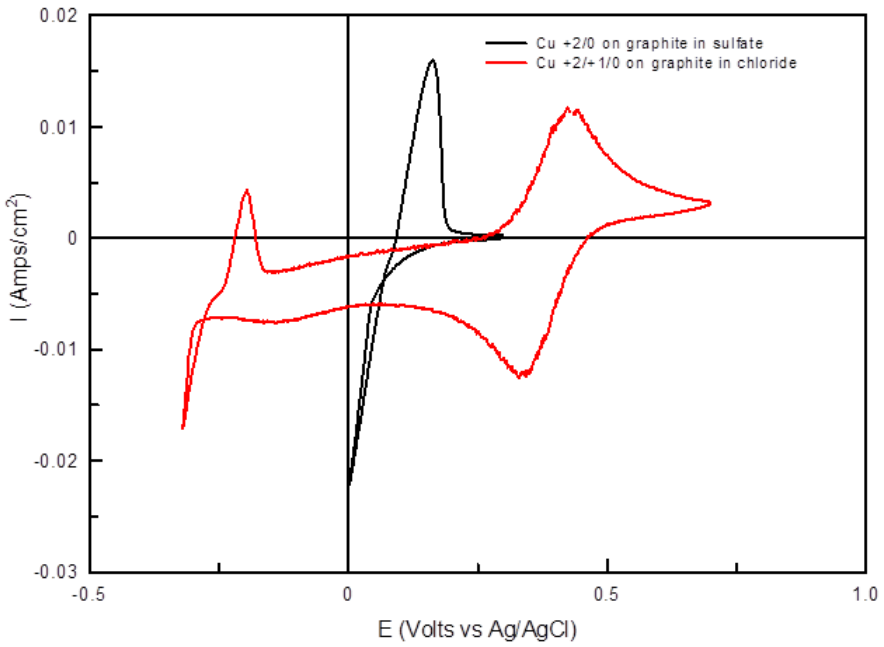


Battery Chemistry - looking ahead

All - Copper (Cu^0 / Cu^{+1} / Cu^{+2})

Electrochemistry of Cu changes dramatically w/ excess halide ions

- Form Cu – $4X^-$ complexes
- Cu^{+1} stabilized, much more soluble
  - mM to > 1 M w/ 10:1 Cl^-:Cu^+



Advantages of Cu-Halide chemistry :

- Eliminates H_2 evolution,
- More facile plating reaction
  - But only 1e- per Cu, not 2
- Acid electrolyte possible (pH <1)
  - High ionic conductivity
- Cu costs higher, but not prohibitive
  - Need low overpotentials to offset lower cell voltage
- Patent application submitted in 2014

$Cu^+ \rightarrow Cu^{2+} + e^-$ +0.35 – +0.5 V

$Cu^+ + e^- \rightarrow Cu^0$ -0.25V

All - Cu Battery Efficiencies

		Voltaic (%)	Coulombic (%)
2nd Cycle	Nafion	67.8	98.8
	Daramic	71.3	92.5
5th Cycle	Nafion	67.9	97.8
	Daramic	72.6	92.3

5% - 80% SOC
±100 mA/cm²

OCV = 0.75V
100 mAh/cm²

CWRU Iron Flow Battery Project

Dr. Krista Hawthorne completed her Ph.D. in July 2014

Papers related to her dissertation:

- "Studies of Iron-Ligand Complexes for an All-Iron Flow Battery Application"
  - *J. Electrochem. Soc.*, **161** (10) A1662-A1671 (2014)

- "Maximizing plating density and efficiency for a negative deposition reaction in a flow battery"
  - *J. Power Sources* **269,** 216 (2014)

- "An Investigation into Factors Affecting the Iron Plating Reaction for an All-Iron Flow Battery"
  - Submitted to *J. Electrochem. Soc.*

CWRU Iron Flow Battery Project

- ***Draft papers in progress:***
- *"Iron Crossover in Flow Battery Separators"*
  - *Part 1: Effective Diffusivity Measurements*
  - *Part 2: Optimizing battery performance and cost*
  - *T. Petek, 1st author, (J. Electrochem. Soc.)*

- *"In-Line Reference Electrodes in Flow Batteries with Porous and Slurry Electrodes"*
  - *N. Hoyt, 1st author, (J. Electrochem. Soc.)*

- *"Plating utilization of carbon felt in a hybrid flow battery"*
  - *N. Hoyt, 1st author (J. Power Sources)*

CASE WESTERN RESERVE UNIVERSITY EST. 1826

E3EJ @ CWRU

Electrochemical Engineering and Energy Labs @ CWRU

Principal Investigators

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

Research Staff

- Mirko Antloga
- Nicholas Sinclair
- Nathaniel Hoyt, PhD
- Enoch Nagelli, PhD

Doctoral Candidates

- Ismailia Escalante-Garcia
- Krista Hawthorne
- Mallory Miller
- Tyler Petek
- Liz Freund
- Steve Selverston

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 and generation
- Chemical synthesis and separations
- Electrodes for neural stimulation
- Device prototyping and cost analysis

CASE WESTERN RESERVE UNIVERSITY EST. 1826

EECS @ CWRU

Thank you!

Questions?