Flow Batteries
A Historical Perspective

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OUTLINE

- The first flow cell?
- Review articles- documented progress
- Early NASA Work- some learning
- Fuel Cell and Flow Battery Similarities (and differences)
- What my group is working on at CWRU
- Acknowledgements

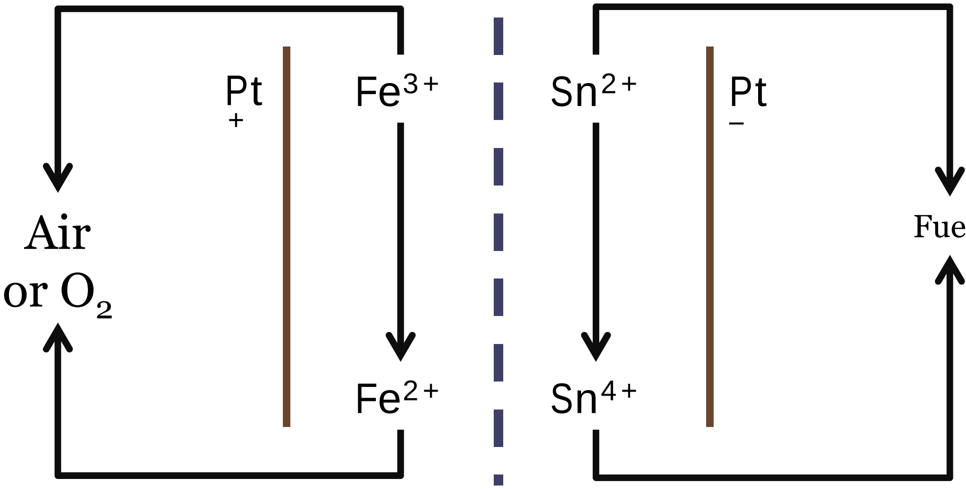
Redox Flow Batteries: Earliest?

Fuel, V. 34, pp. 330-338, 1955

Redox Fuel Cell

A. M. POSNER

Concept:



Air
or O_2

Pt
+

Fe^{3+}

Fe^{2+}

Sn^{2+}

Sn^{4+}

Pt
–

Fuel

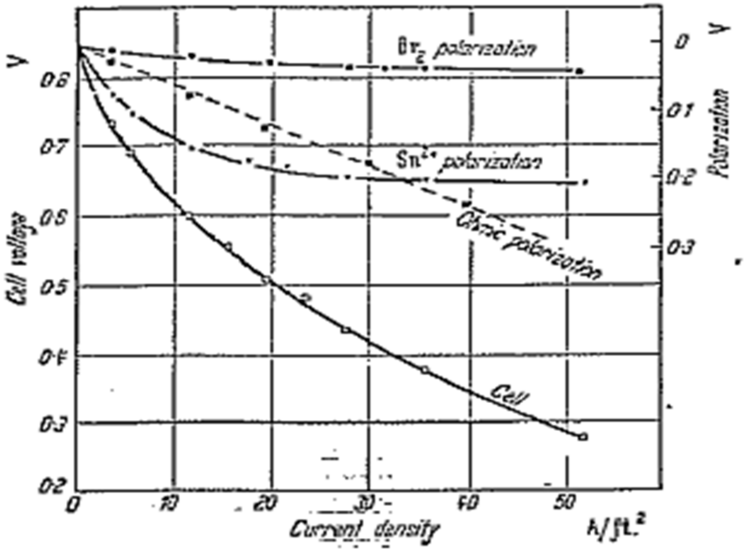


Figure 4. Current-voltage and polarization characteristics of cell: anolyte—1·2N Br_2 in 0·7N HBr, *3N* HCl, *1·2N* $SNCl_4$; *catholyte—1·2N* $SnCl_2$ *in 1·9N* HBr, *3N* HCl; *flow rate 3 and 8 ml/min*

Also $Br_2 + 2e^- \leftrightarrow 2Br^-$

$Sn^{2+} \leftrightarrow Sn^{4+} + 2e^-$

Excellent Review Articles on Flow Batteries

•M. Bartaozzi, “Development of redox flow batteries: A historical bibliography”, J. Power Sources, 27, 219-234 (1989)

•J. Jorne, “Flow Batteries”, American Scientist”, 71 (5), 507-513 (1983)

•C. Ponde de Leon, et al, “Redox flow cells for energy conversion”, J. Power Sources, 160, 716-732 (2006)

•A.Z. Weber, et al., “Redox flow batteries: a review”, J. Appl. Electrochem., 41, 1137-1164 (2011)

•M. Skyllas-Kazacos, et al., “Progress in flow battery research and development’, J. Electrochem. Soc., 41, 1137-1164 (2011)

Early NASA RFB Program

Fe/Ti System

- 1975 Cost estimates \$190-\$330/kW, \$10/kW-H, Marvin Warshay
- 1976 Shunt Current Model, Paul Prokopius
- 1976 Interfaced an RFB with solar cells
- 1977 Electrode-Membrane-Flow Battery Testing
    - Largest polarization @ negative electrodes
    - Significant performance decay with cycle number
    - Membrane transports more H^+ than Cl^-

Early NASA RFB Program

1977 NASA TM-79067

Redox Couple Screening

$Fe^{2/3}$ on C
$Cr^{2/3}$ on C and on B_4C
$V^{2/3/4/5}$ on C and on B_4C
$Fe(O)_3^{-3/-4}$ on Pt and on C
Br^{-1}/Br_2 on B_4C

NASA effort moved to $Cr^{2/3}$ system because of attractiveness of cost and cell potential

Electrode Screening

Graphite- cloth, felt, foam, chips
Screens- Ag, AgCl, Hg-Ag, Nb, Ta, W-Re, Hg-Cu
Granules- Pb, Hg-Pb, Bi

Early NASA RFB Program- Fe/Cr

NASA TM-79067 (DOE/NASA/1002-78/2)

ANION MEMBRANE SCREENINGS

Areal Resistivity

Commercial/Inhouse *	2 – 10 Ω-cm^2
Nafion 117	~0.2 Ω-cm^2

Resistivity increases with time caused by fouling of charged sites and pore plugging

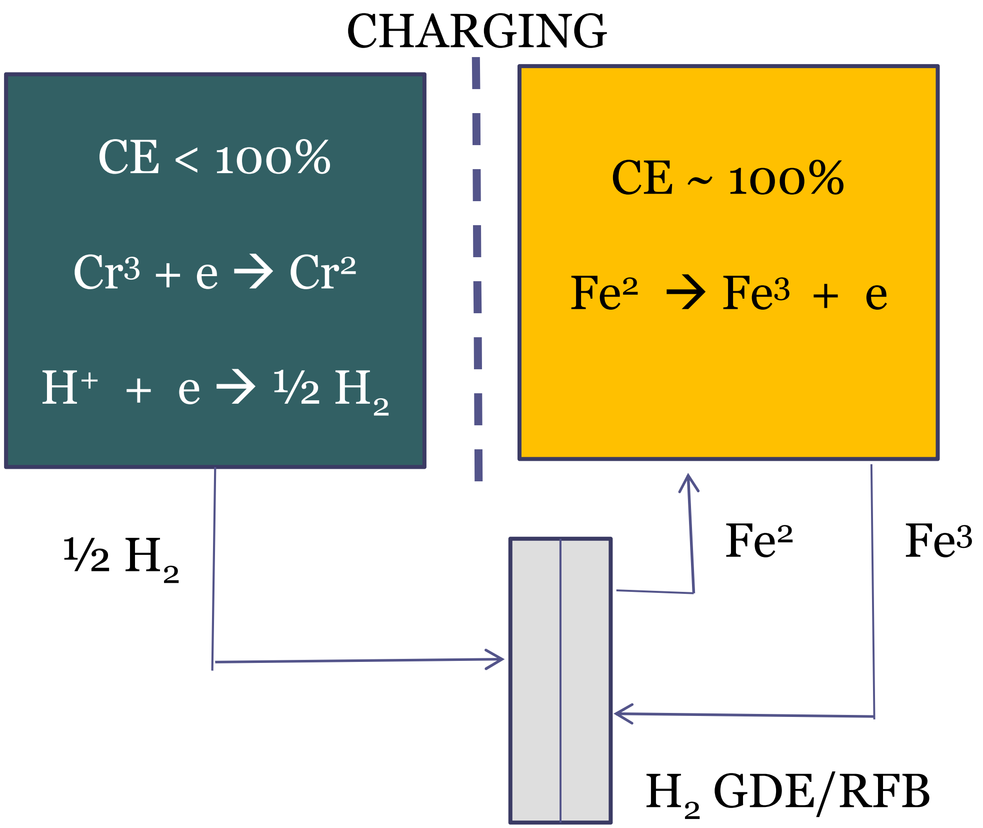
Cross-over continues to be an issue

*most promising co-polymers of vinylpyridines, vinylbenzenes, vinylbenzylchloride, divinylbenzes, and dimethylamine-ethylmethacrylate

NASA 1979

AIAA Terrestrial Energy Systems Conference, Orlando, Fl

Introduction of the Rebalance Cell Concept



CHARGING

CE < 100%

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

$H^{+} + e \rightarrow \frac{1}{2} H_2$

CE ~ 100%

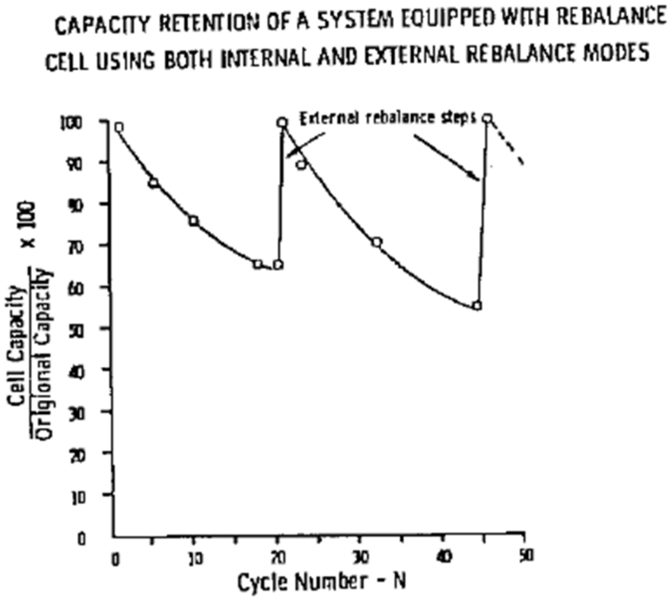
$Fe^{2} \rightarrow Fe^{3} + e$

$\frac{1}{2} H_2$

Fe^{2}

Fe^{3}

H_2 GDE/RFB



CAPACITY RETENTION OF A SYSTEM EQUIPPED WITH REBALANCE CELL USING BOTH INTERNAL AND EXTERNAL REBALANCE MODES

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J. Giner and K. Cahill
Feb 1980 NASA CR-159738

Cr^3/Cr^2 Reaction
Electrode Materials Screening

Five Step Screening

1. H_2 evolution in HCl
2. Cr^3 reduction activity
3. Anodic corrosion in HCl
4. Cr^2 oxidation activity
5. Further detailed studies

Metals and metalloid materials tested:

As, Au, Br, Vitreous C, Graphite C, Cd, Cu, In, Pb, Sb, SiC, Sn, Ti, W, WO, Ag/Hg, Cu/Hg, Pb/Sn, TaC, TaN, TiC, TiN, ZrC, ZrN, B_4C, Cu/Pb, WC, Ag/Pb, Au, Au/Pb

Au/Pb

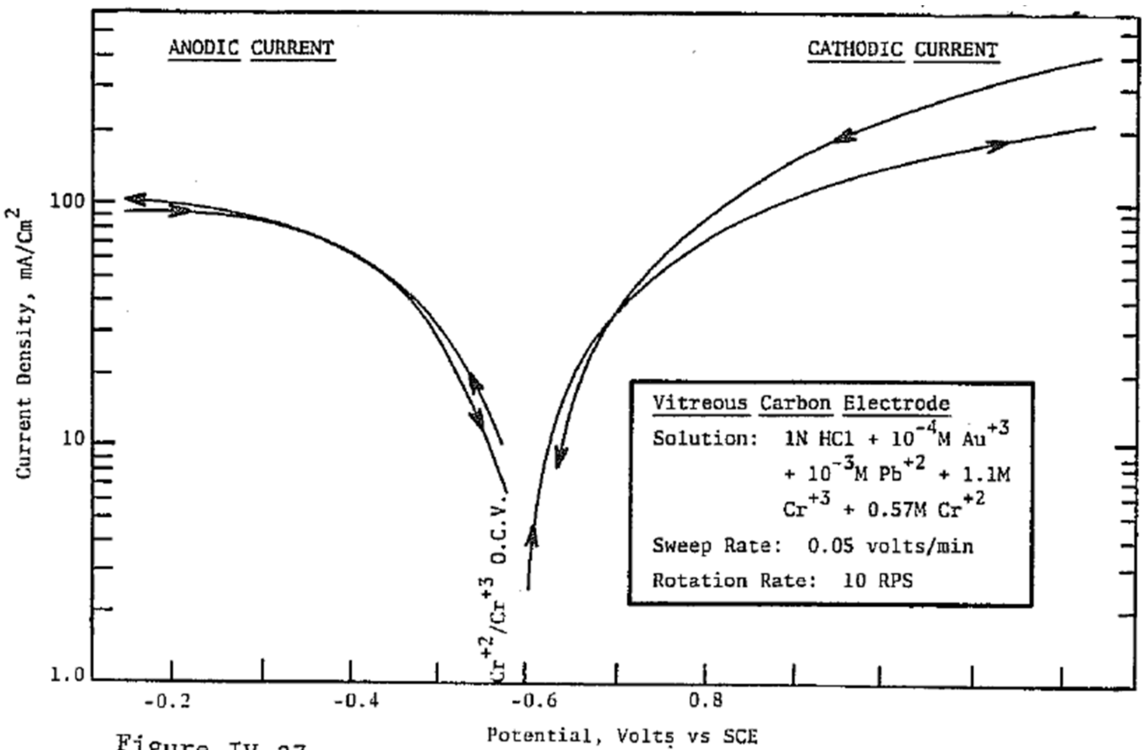


Figure IV-37

Replace with fig 37

Electrocatalyst- In situ Bi deposition with added salt to electrolyte

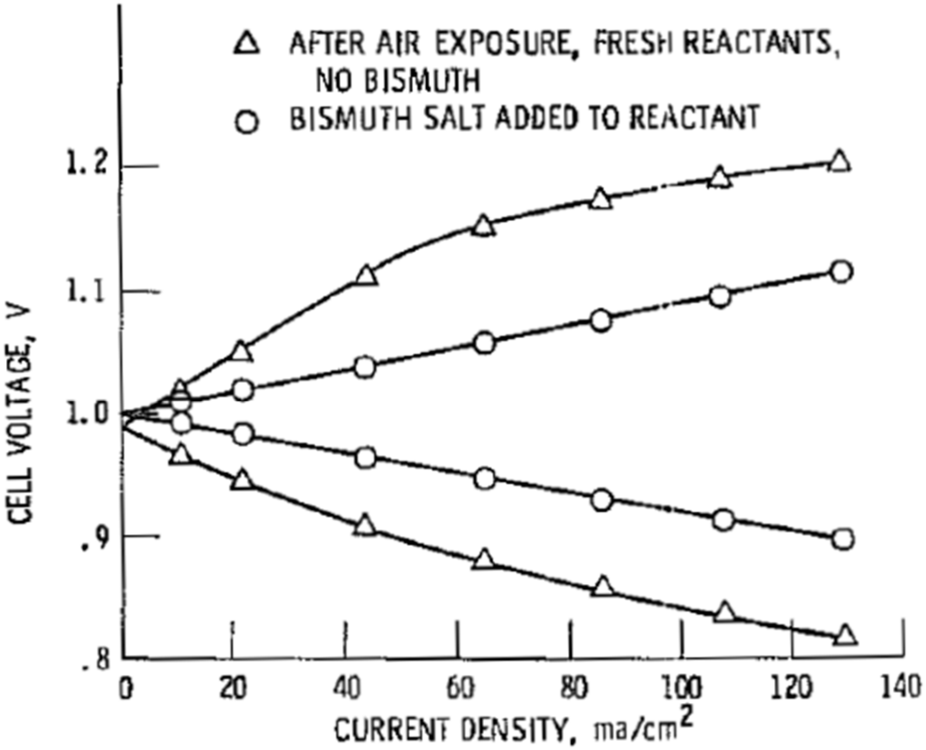
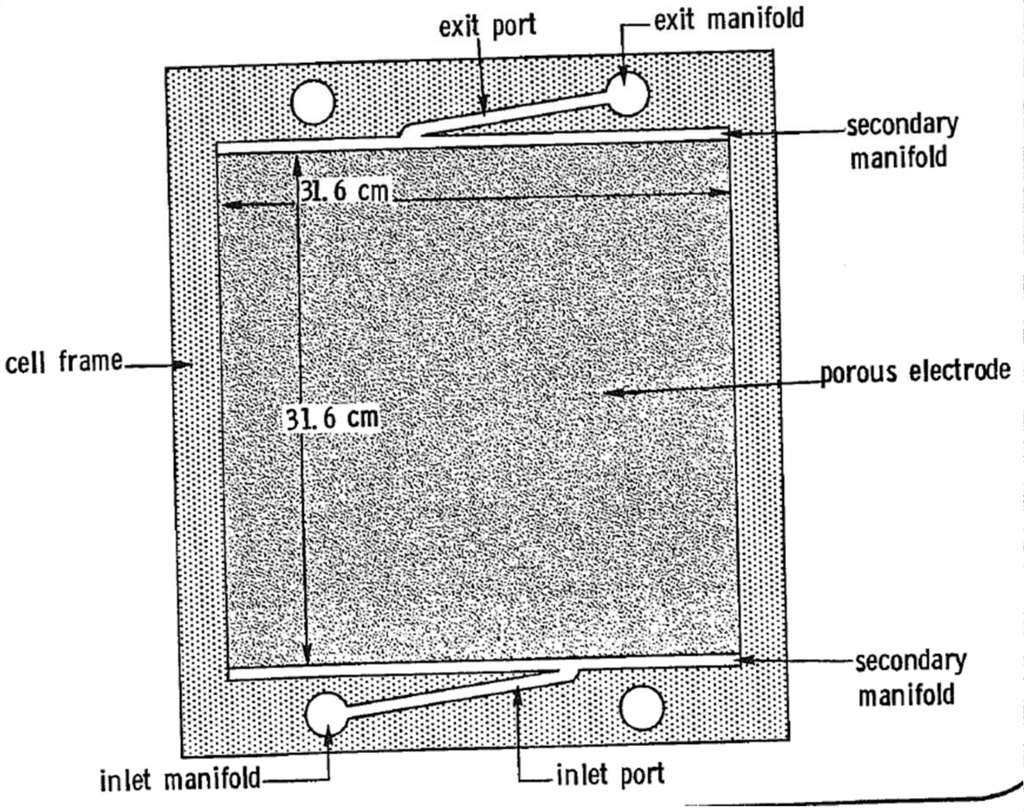


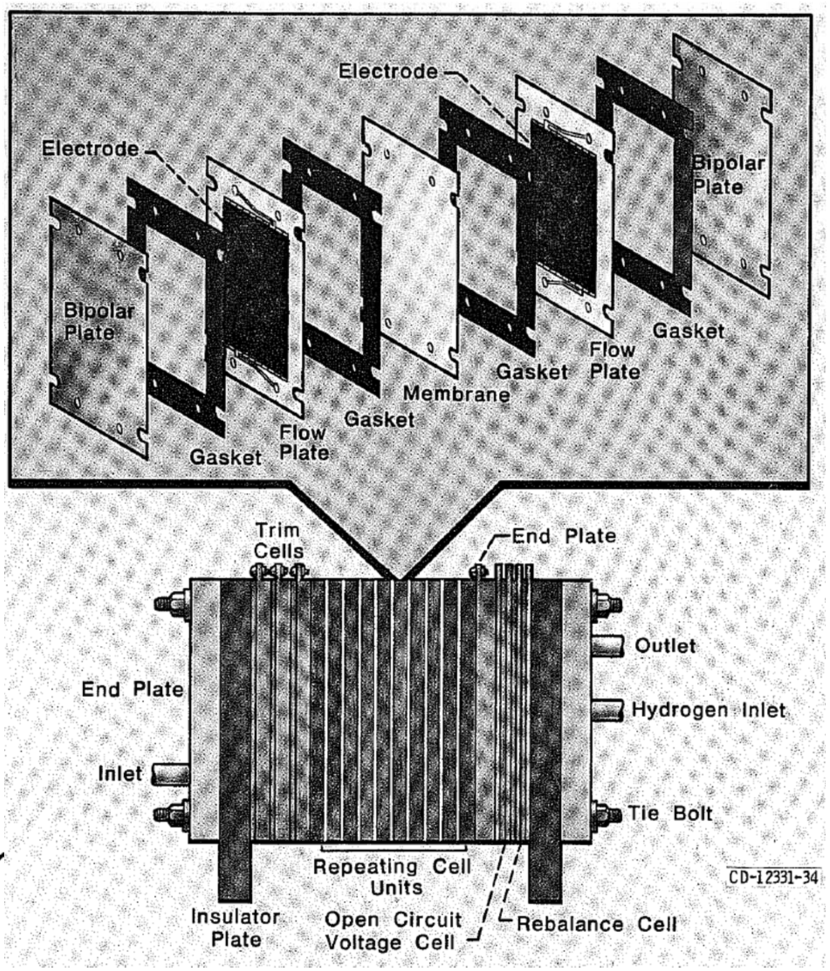
Figure 12. - Effect of re-catalyzing the chromium electrode after air exposure.

NASA RFB Later Work

•1980-82	Cell stacks and integration with solar cells NASA TM-81464, TM-82607
•1982	Cost prediction for production of redox chemicals NASA CR-167882
•1982	Pumping Losses and Shunt Current Losses NASA TM-82686
•1982	Introduction of mixed reactants, elevated temperatures and additive electrocatalyst NASA TM-83401

NASA Cell Structures-modern performance and cost improvements?





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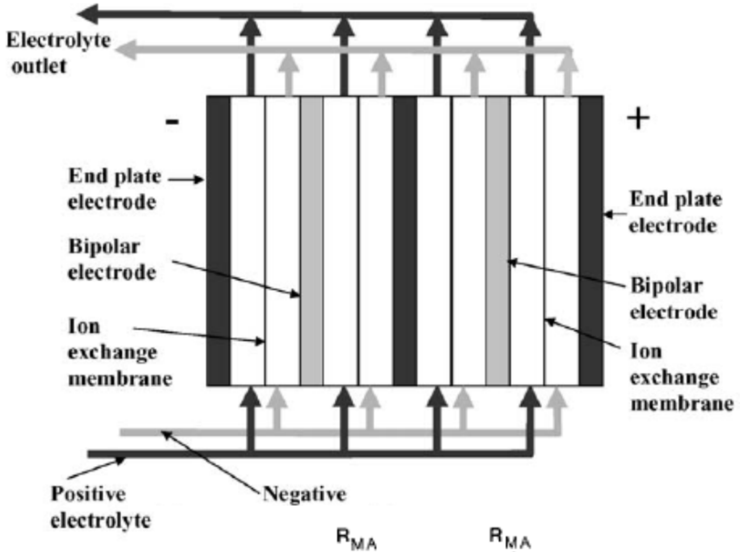
NASA 1982 Pumping and Shunt Current Losses

TM-82686



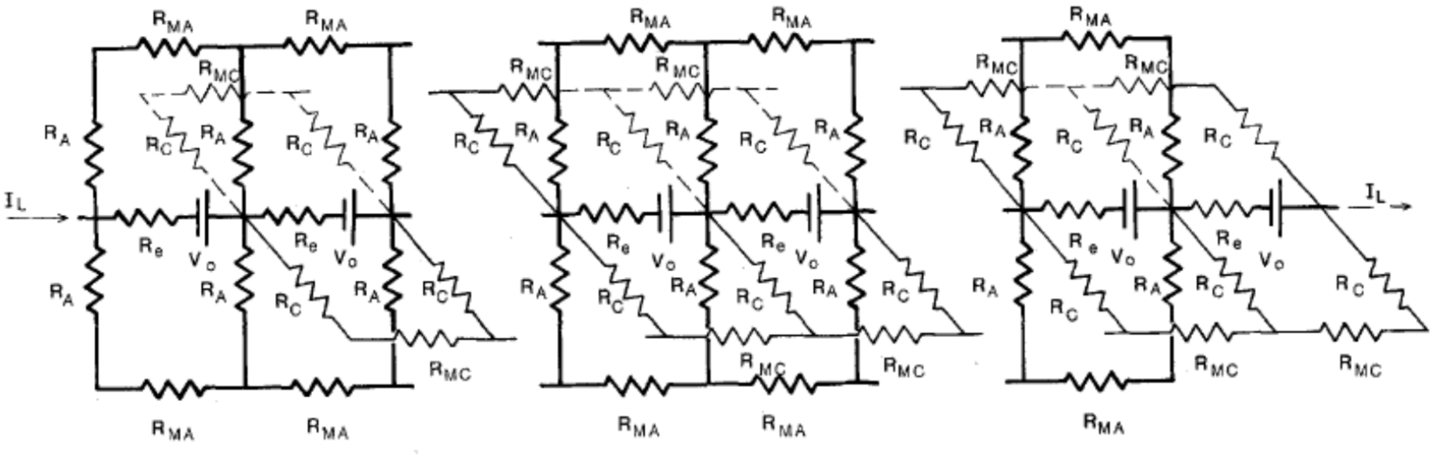
Pumping Losses

0.5 – 1% variable flow

4.6- 8.8% Constant flow (1.5-2 SF @90% DOD)

Shunt Current Losses

40 cell stack ~ 2% (at 65 mA/cm²)



Aug 1983 NASA TM-83385

Fe/Cr RFB Mixed Reactant Solution

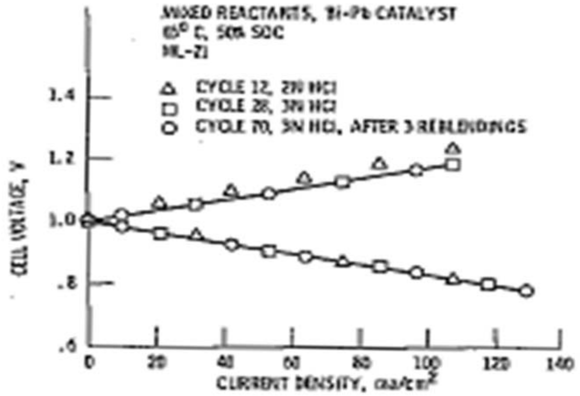


Figure 13. - Charge and discharge polarization curves for mixed reactant system.

Advantages:

- Improved voltaic efficiency due to low resistance cation membranes
- Less selective, less costly membranes can be used
- Remixing electrolyte to correct for imbalances from cross-over and counter movement
- Smaller cell stacks due to higher power densities
- Lower chemical costs

Disadvantages:

- Lower coulombic efficiency due to cross-over
- Larger masses of chemicals needed
- Lower open-circuit voltage due to dilution

CD, mA/cm²	**Resist,** ohm-cm²	**Coul eff,** percent	**W-H eff,** percent	**H_2 evol,** percent
43	0.74	92	86	0.3
65	.99	95	83	1.0
86	.88	95	81	.3
108	1.00	96	76	.3
129	.94	97	75	.6

Cell area: 14.5 cm²

Membrane resistivity: 0.45- 0.70 ohm-cm²

Membrane selectivity: 1000 μg Fe/hr/cm²/mole/liter

Chrome Redox Chemistry Details

1982 TM-82913

(A) $Cr(H_2O)_6^{3+}$ + HCl $\leftarrow\rightarrow$ $Cr(H_2O)_5Cl^{2+}$

Elevated temperature drives equilibrium to right

(B) $Cr(H_2O)_5Cl^{2+} + e \rightarrow Cr(H_2O)_5Cl^{+}$ fast

(C) $Cr(H_2O)_6^{3+} + e \rightarrow Cr(H_2O)_6^{2+}$ slow

Inner Sphere electron transfer with pentahydrate-monochloro (JACS, 97:15/July 23, 1975)

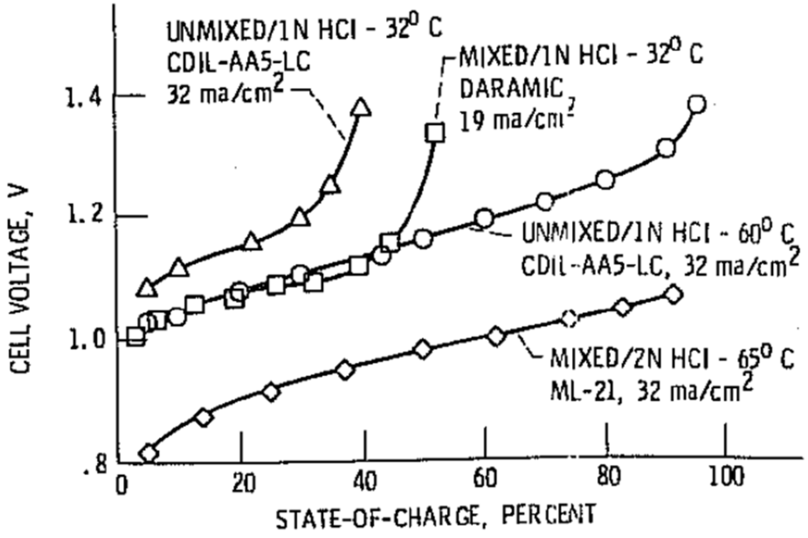


Figure 3. - Charging performance comparison for mixed and unmixed reactant systems as a function of temperature.

Other Flow Battery Systems

HALIDE POSITIVE ELECTRODE-very fast and reversible reactions
Chlorine: ADVANTAGES: high potential, low corrosion, membrane-less
DISADVANTAGES; RuO_2 electrocatalyst, Ti substrates, low temp hydrate storage
Bromine: ADVANTAGES: low cost graphite electrodes, bromine complex storage
DISADVANTAGES: high corrosion rates, membrane required, low potential

ZINC NEGATIVE ELECRODE ADVANTAGES high hydrogen overpotential, fast reaction, large negative potential, high energy density
DISADVANTAGES: dendrites, cell shorting, coupled power-energy

HYDROGEN NEGATIVE ELECTRODE ADVANTAGES : fast reaction
DISADVANTAGES: Pt catalyst, GDE required, Hydrogen storage

COMPONENT	FUEL CELL	FLOW BATTERY
REACTANTS	GAS	MOSTLY LIQUIDS, UNDERSTANDING SPECIATION
ELECTRODES	Pt/C THIN LAYER, DURABILITY, SUBSTRATE STABILITY	GRAPHITE THICK LAYER FELT, CATALYST, DURABILITY, SUBSTRATE STABILITY
ELECTRODE DESIGN	THIN LAYER MEA Low C (concentration), high D (diffusivity)	FLOW THROUGH High C, low D
MEMBRANE	CATION PERMSELECTIVE IN GAS PHASE, LOW REACT SOLUBILITY	CATION, ANION, OR MICROPOROUS IN LIQUIDS, HIGH REACT SOLUBILITY
BIPOLAR PLATES	GRAPHITE, METALS, COMPOSITES	SAME
CELL STRUCTURE	PLATE AND FRAMES WITH FLOW FIELDS	SAME, LIQUID HYDROSTATIC EFFECTS, SHUNT CURRENT PATHS
BALANCE OF PLANT	H2 STORAGE, WATER BALANCE, THERMAL CONTROL, POWER CONDITIONING	TANKS, PUMPS, POWER CONDITIONING, C/D control

FRB Research at CWRU

Mechanistic and kinetic studies of electrocatalyst, electrode supports, and durability

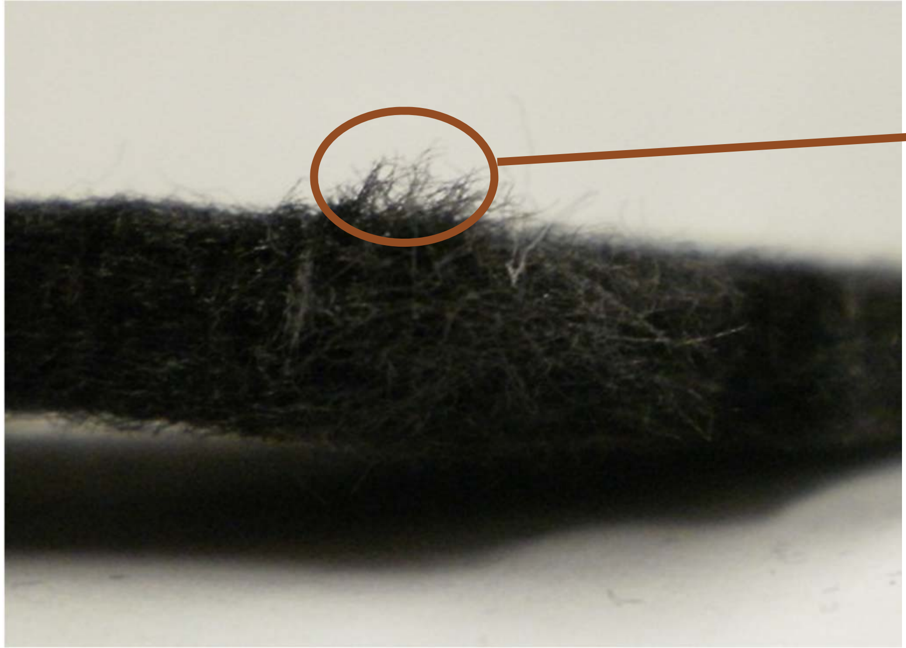
All Iron Flow Battery Approach

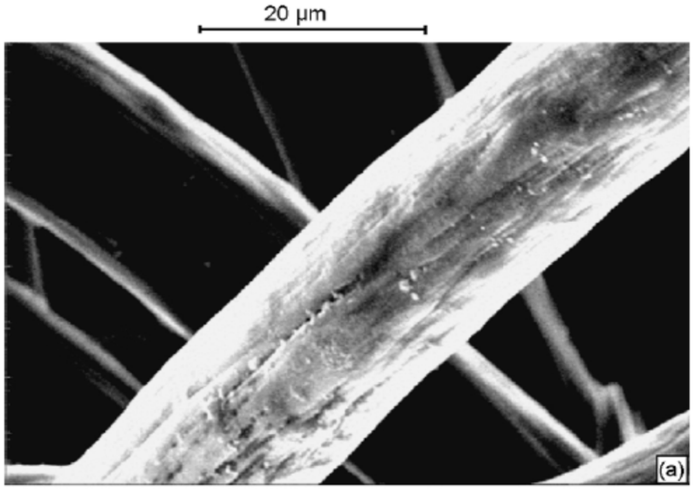
Low cost bi-polar plates with engineered structures for low cost RFBs
collaboration with Faraday Technology

Membranes with high conductivity, long durability, and low cost
collaboration with Hossein Gossemi

Non-aqueous RFB approaches for high power and energy density
collaboration with Levi Thompson of UM

Kinetic and Reaction Mechanism Studies, electrocatalysts, electrode supports, durability

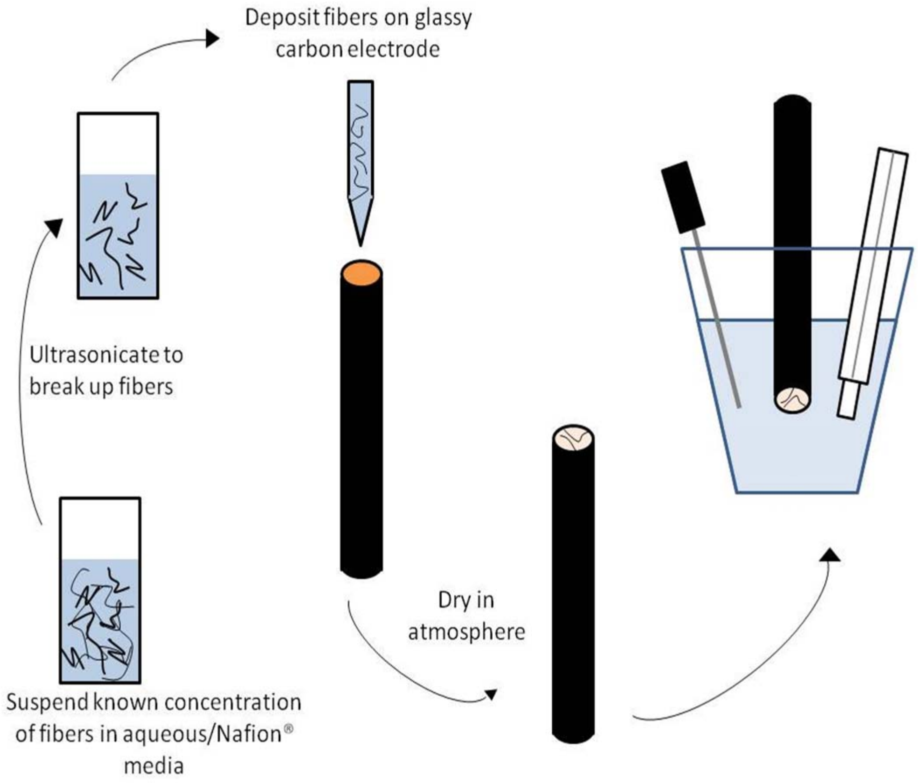


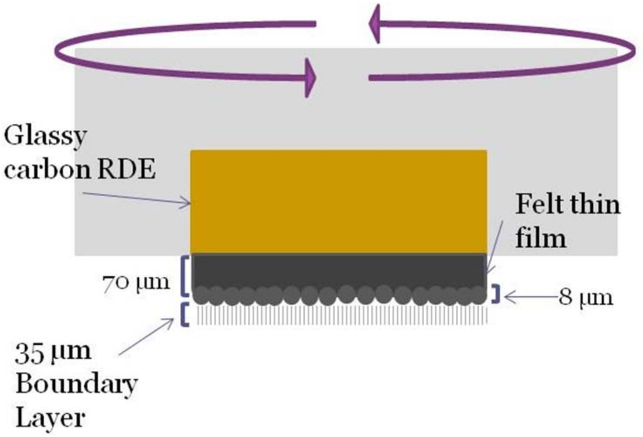


Separate out ohmic and mass transfer comlications

Wang, W. H. and X. D. Wang (2007). Electrochimica Acta 52(24): 6755-6762.

Approach: Thin Fiber Film RDE –based on FC electrocatalyst testing experience



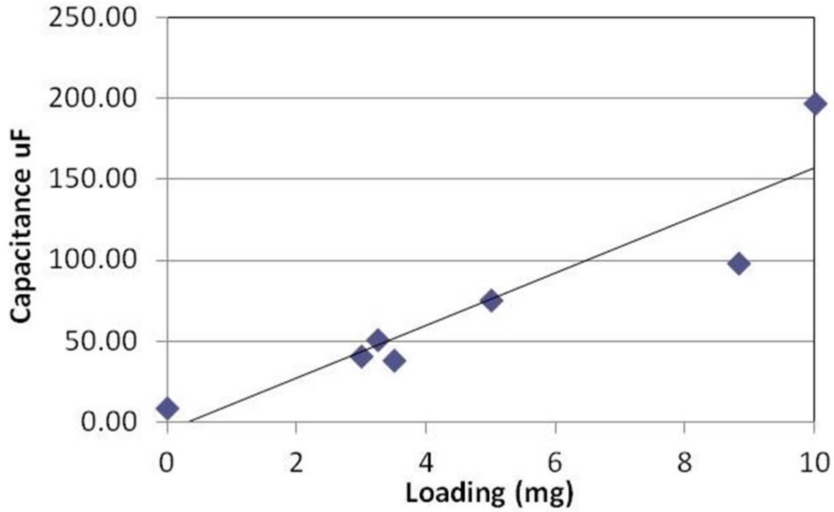


Diffusion layer (200 rpm) = 35 µm

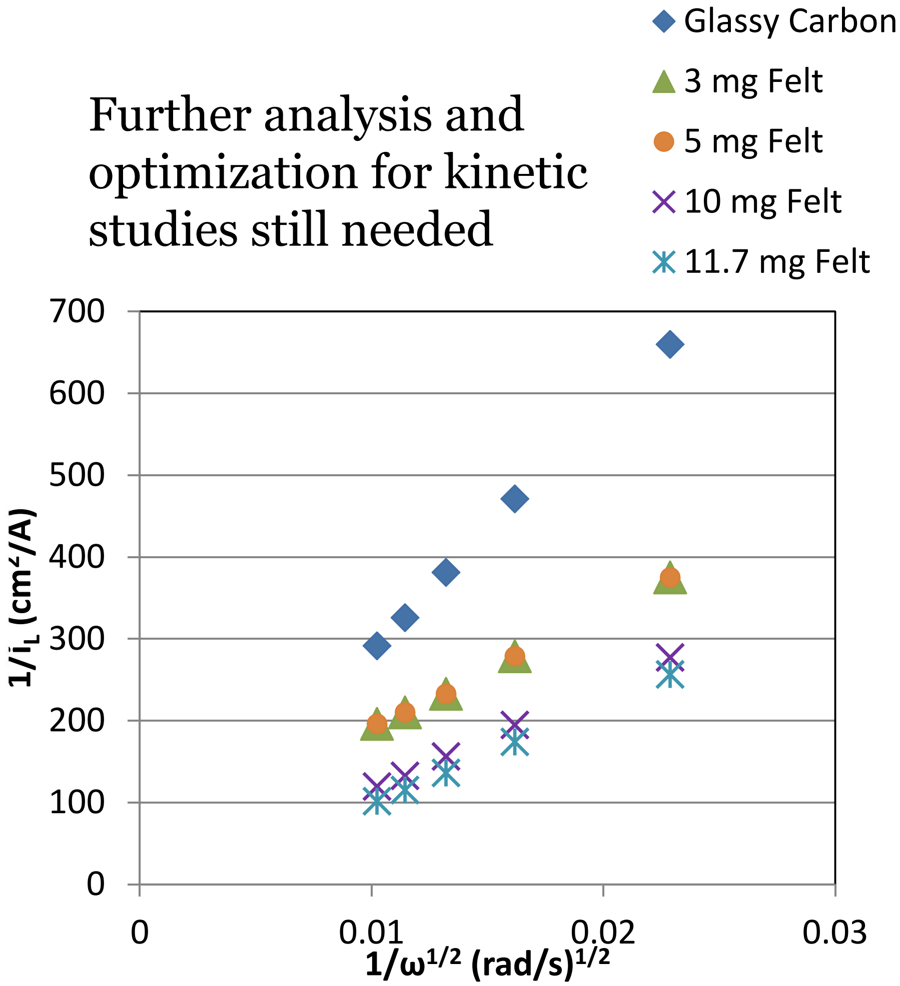
Thin film height (3 mg) = 70 µm

Preliminary Results: RDE experiments with the TFFRDE

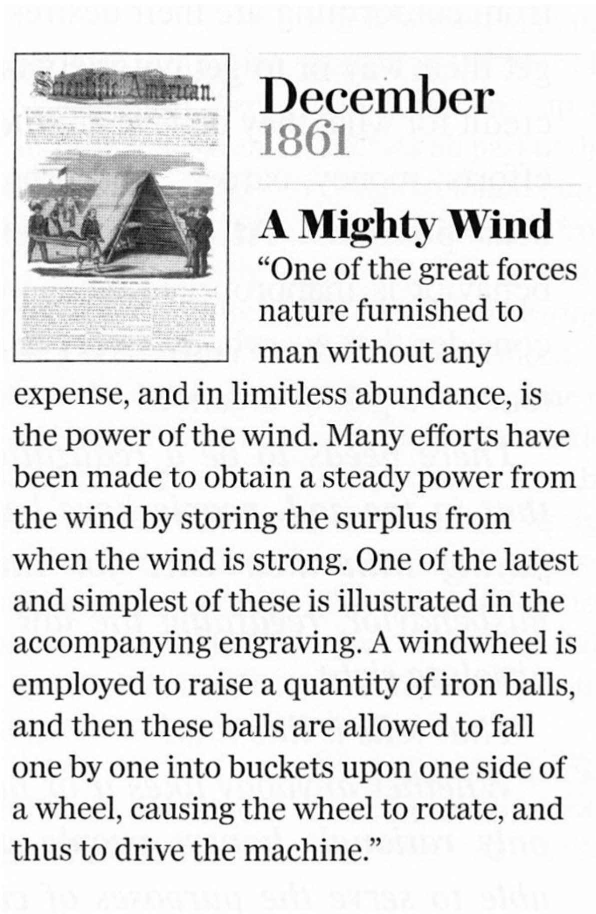
Fibers are electronically connected and accessible



Further analysis and optimization for kinetic studies still needed



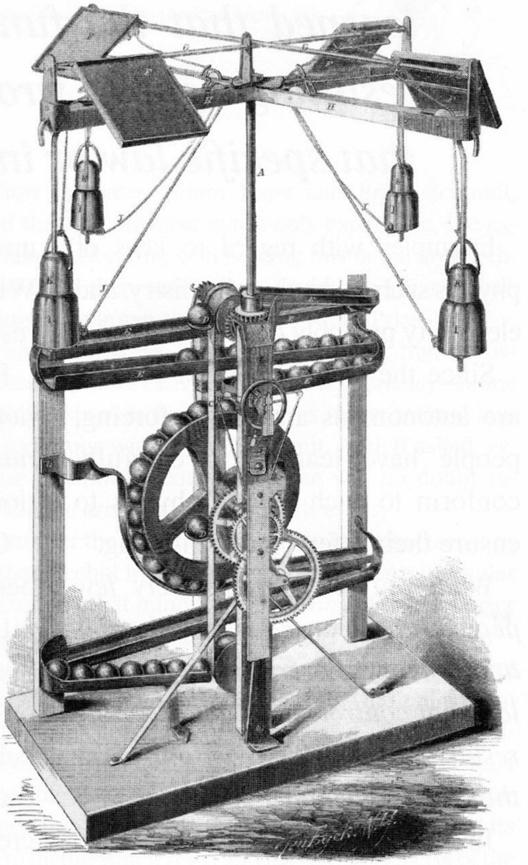
The First Flow All-Iron Energy Storage System-1861



December
1861

A Mighty Wind

"One of the great forces nature furnished to man without any expense, and in limitless abundance, is the power of the wind. Many efforts have been made to obtain a steady power from the wind by storing the surplus from when the wind is strong. One of the latest and simplest of these is illustrated in the accompanying engraving. A windwheel is employed to raise a quantity of iron balls, and then these balls are allowed to fall one by one into buckets upon one side of a wheel, causing the wheel to rotate, and thus to drive the machine."



Harness the wind: Rube Goldberg in form, basic physics in function, 1861. The iron balls the machine used would have made a fearsome din.

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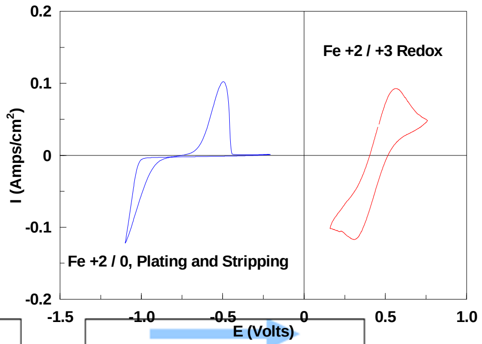
CWRU Iron Flow Battery Technology

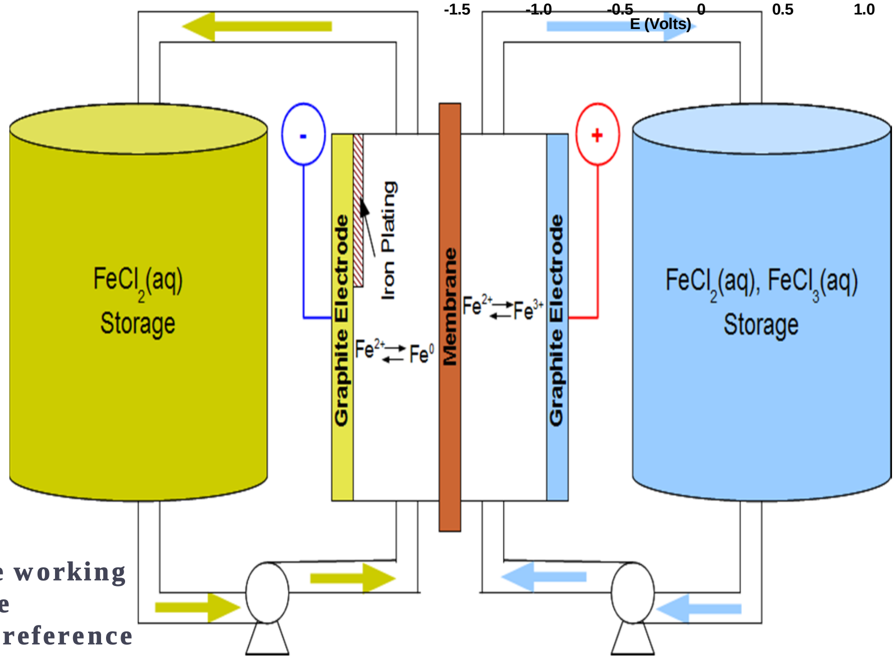
CHARGE

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

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

$E^{0} = 1.21$ volts





Graphite working electrode
Ag/AgCl reference electrode
pH=2

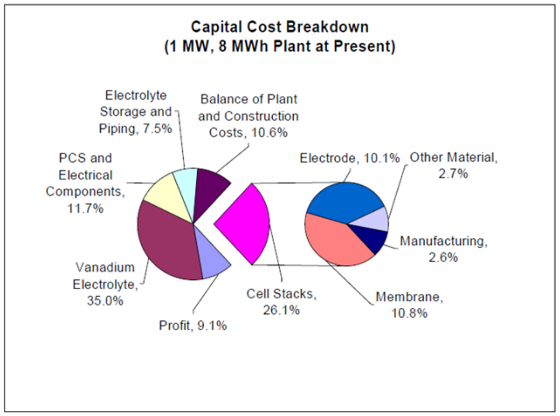
Advantages:

Low Cost Active Element (Iron)

Inexpensive Separator
common electrolyte for
positive/negative electrodes

Safety
non-toxic materials,
moderate pH

Motivation-eliminate V



Provisional patent filed by CWRU

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The Next All-Iron Energy Storage System-1981

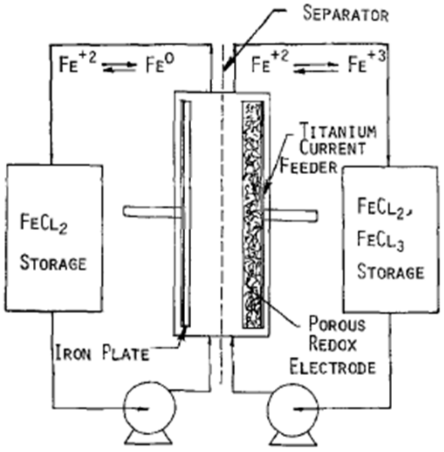

Fig. 1. Schematic of iron-redox laboratory cell and electrolyte circuit.

FINDINGS

- Capable of RT energy storage, 90% CE, 50% EE
- 100 cycles @ 60 mA/cm^2
- Low pH for redox, high pH for plating reaction
- Plating on Ti

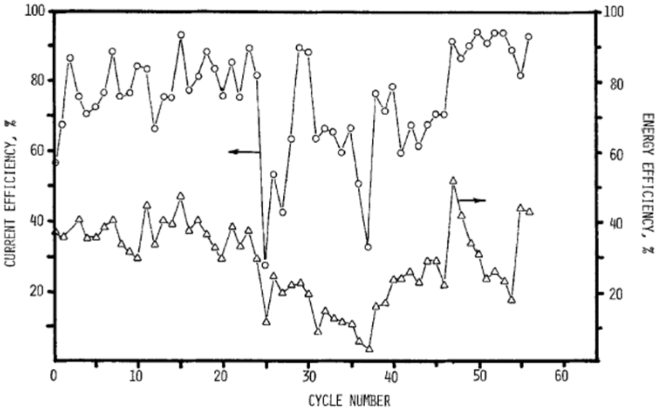

Fig. 13. Measured efficiency during cycling of a 100 cm^2 iron-redox cell. Details of operating conditions are given in Table II.

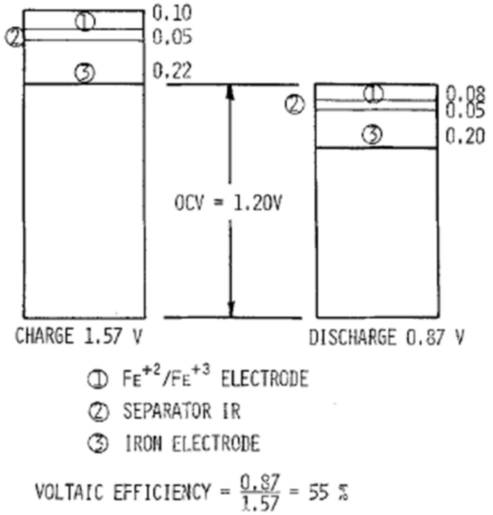

Fig. 14. Measured voltage breakdown for the initial cycle of a 100 cm^2 laboratory cell at 60 mA/cm^2, 60°C, and pH = 1.

L.W. Hruska and R. Savinell, J. Electrochem Soc, 128, 18- 25 (1981)

Iron Flow Battery Positive Electrode Overview

- Fast reaction kinetics ($i_o \approx 10$ mA/cm^2)
- At low pH Fe^{+2} and Fe^{+3} highly soluble (e.g., $FeCl_2$, 4.9M at 20C)
- Goal to raise pH with high ferric ion solubility while maintaining kinetics and positive potential

Iron Flow Battery Negative Electrode Overview

- Increase pH and use additives to minimize hydrogen evolution
- Must be compatible with positive electrolyte with minimal membrane requirements
- Reversible kinetics for iron dissolution

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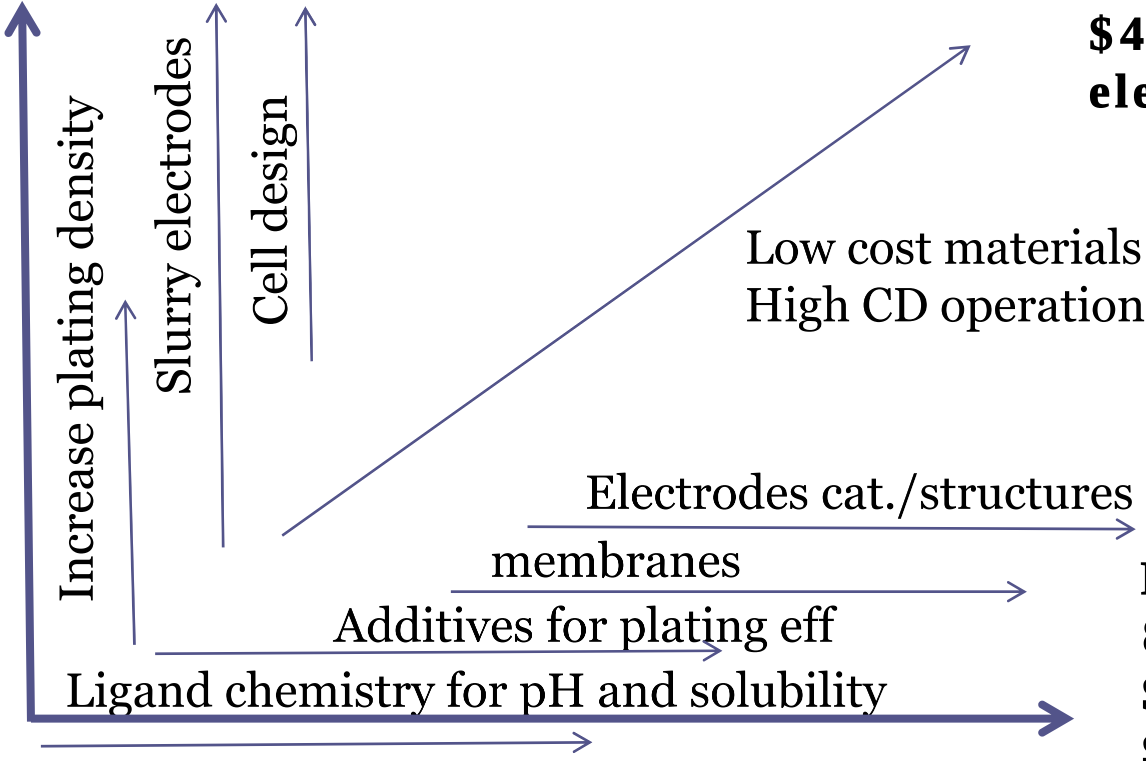
CWRU All-Fe FB R&D Strategy



De-coupled power and energy

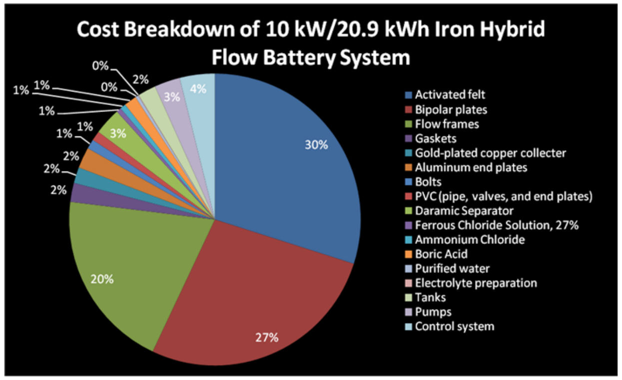
Increase plating density

Slurry electrodes

Cell design

$45/kW-H electrolyte

Low cost materials
High CD operation



Electrodes cat./structures

membranes

Additives for plating eff

Ligand chemistry for pH and solubility

Performance
80% EE
$250/kW
$125/kW-H

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Electrochemical Engineering and Energy Lab @ Case

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DOE Golden Office
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Great Lakes Energy Institute