Component Research for Redox Flow Batteries and ‘Open’ Batteries

Tom Zawodzinski and Zhijiang Tang

With help from Che-Nan (Josh) Sun,
Alan Pezeshki (UTK)
Cy Fujimoto (SNL)

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Team at UTK; Bredesen Center
Goals and Tasks

1. Demonstrate improved performance of RFBs in pre-competitive work
   - Chemistry agnostic; we look at *key representative processes*—VRBs + New directions

2. Develop rational diagnostics to guide component selection
   - Component selection refers to our tests being used to pinpoint key requirements, guiding development

3. New ‘Open’ Battery Directions for Higher Energy Density
   - Metal/air
   - Non-aqueous system
Approach

Working at Component, Cell Level

What limits performance of an RFB?

1. Membranes
   a. Comparing effects in PEMs, AEMs

2. Electrodes
   a. Effect of electrode structure on performance
   b. Concentration polarization issues

3. Broadened scope to other types of open battery systems (Metal/air, Non-aqueous)
Increasing Performance
A Multi-level Issue

First Level: Improve Power Density
We are satisfied with our work on this.

Second Level: Cycling
New challenges not found in steady state
Mass transport/concentration polarization, Capacity fade
This year: develop data to understand effects of different materials

Third Level: Durability and Side Reactions
Work ongoing but slowed due to budget issues
Key Components

- Negative electrode: V(II)/(III)
- Positive electrode: V(IV)/(V)
- Membrane
- Bipolar Plate with flow field

Fuel Flow

Oxidizer Flow

External Circuit
MEMBRANES
Membranes: Recent Work

- Focus on comparing membranes
- Tested more than 20 membranes of a wide variety of types (PFSA, Hydrocarbon, AEM); strong collaborations with SNL, 3M

Here:

- Comparison of PEM, AEM reveals previously unreported phenomenon
- Transference effects different
QDAPP and SDAPP
courtesy of Cy Fujimoto, SNL

Same backbone, different ionogens

QDAPP

SDAPP
Polarization at 100% SoC
AEM behaves differently from PEM

Within each box different curves are for membranes with different SoC

Performance minus Resistance
Performance
Resistance

QDAPP  SDAPP
Polarization at 50% SoC
AEM behaves differently from PEM

Within each box different curves are for membranes with different SoC
Relative Mobility of Anion is Key to Membrane Transference Effects

**PEM**

\[ T_H > T_V >> T_X \]

**AEM**

\[ T_X \sim T_H >> T_V \]
ELECTRODES
Performance in Flow Systems
Polarization Curves
not normally used in battery work!

We separate and measure (both charge, discharge):

- Electrode polarization for each electrode
- Separator/Membrane resistance
- Electrode ionic/reagent mass transport resistance
- Mass transport resistance
- Augmented by impedance tests as well as ex situ component tests

Voltage evolution during cycling

What’s going on here? Same rate is demanded but voltage efficiency drops

Onset of concentration polarization
Concentration Polarization Effects also Reflected in Pol Curves with Lower SoC

**Test conditions**
Electrode thickness ~ 1200µm per side, Membrane : Nafion 117
Solution : 0.8MV, 4MH₂SO₄ ,Single pass, Flow rate ~ 22mL/min
Temp. : 21°C, Same cell hardware
SoC Dependence of Pol Curves
Single Pass, High Flow Rate Isolates Effects

Pol Curve measured with low utilization but at fixed, lowered SoC

Allows us to separate effects of intrinsic lower SoC from those driven by lower reagent concentration along channel

This is what we are working to overcome
Managing this Effect
Electrode Properties are Critical
Transport at Flow Field/Electrode Interface

Flow-by Configuration

Cell Efficiency @ 500 mA/cm²

Now cycling between 20% and 80% SoC
Conclusions from Component Study

Two types of concentration polarization identified

- One due to transference effects in membrane
- One from slow transport within electrode

Minimizing concentration polarization:

- Use cation exchange membrane
- Improve electrode/flow field interface
Recent Results (2012: Basis for Analysis)
We have reached an ohmic limit

Graph showing the relationship between voltage [V] and current density [mA/cm^2] with power density [mW/cm^2] on the y-axis. The graph includes a legend with the following conditions:
- 5 cm^2 cell
- SGL-4412 A5C5
- Nafion 211 x 1 (ASR~0.3 Ohm·cm^2)
- 1.7M V 5M SO_4
- 90 mL/min Single pass
- OCV: 1.64V
- 30°C

Key points:
- 1341 mW/cm^2 at 2866 mA/cm^2
This leads us to ask the question...

Can Non-aqueous Flow Batteries ever Meet these Requirements?
We will focus on only one facet here

Performance
Properties of Non-aqueous Solvents
A Few Salient Properties for Our Analysis

1. High voltage window
2. Relatively low electrolyte conductivity
3. Transference numbers not guaranteed to be high

Also

More expensive than water!

Flammability is a big issue
A Word or Two About Our Analysis

This is designed to show UPPER LIMITS
Based on REAL DATA
NARFBs get credit for perfect kinetics and other advantages
Performance is the only consideration
IN SHORT: THIS IS THE BEST ONE CAN DO!!!!
Not just my contrary opinion, but facts
We can only downgrade from this position!!!
Base Case:
Ohmic limited, electrolyte only, typical lit value of conductivity

- Dashed line: voltage
- Solid line: power density

**Fixed parameters**
- OCV: 3V
- Kinetics:
  - $j_0 = 10^{-3} \text{ A/cm}^2$
  - $\alpha = 0.5$
  - Temperature: 298°K
  - Electrode area: 6800 cm$^2$
- Ohmic:
  - Conductivity: $10^{-3} \text{ S/cm}$
  - Thickness: 25µm

NRFB
ARFB
Effect of Changing Electrolyte Conductivity
Ohmic limited, electrolyte only

Electrolyte conductivity [S/cm] is changing

Fixed parameters
OCV: 3V
Kinetics
alpha: 0.5
Temperature: 298°K
Electrode area: 6800 cm²
j_s = 10^5 A/cm²

Ohmic
Electrolyte thickness: 25.4 micron

dash: voltage
solid: power density

Voltage [V]

Power density [mW/cm²]

Current density [mA/cm²]
Adding in Ohmic Loss in Electrodes

Note the scale
Conclusions

NARFBs fundamentally lag in performance unless one posits the best known conductivity

– Even then, it will be heroic to make them competitive

On top of that, one must consider electrolyte cost and safety issues

May be niches that take advantage of high energy density

**BUT:** we have a way out of this conundrum

**STAY TUNED!**
PROGRAMMATICS
Summary of Accomplishments

1. Analysis of Concentration Polarization Effects; Improvements in Cycling expected to follow.

2. New Directions based on studying key components
   - Strategy identified for high performance NA-RFBs
   - Another ‘open’ system-metal-air batteries: studying Zn processes to quantitate key equilibria; air electrode catalysts and structures for Hi Perf

3. Built necessary interactions with component producers and researchers to connect COMMERCIALLY AVAILABLE (and experimental) materials to developers

4. Translating research to WattJoule

5. Reporting results via publications: 6 submitted/published in FY15
ORNL Research Plan for RFBs
Interactions

Continue to interact with component manufacturers

- 8 different sources of membranes and separators in play; NDAs in negotiation, some new materials tested
- 3 different sources of electrode materials

Ongoing close collaborations with SNL, 3M, electrode makers

- Cy Fujimoto: feedback from our testing driving synthesis
- 3M: visited to discuss, implement test methods; testing of membranes
Next Steps

1. Continue component studies to help identify key chemistry and structure aspects for improved membranes and electrodes
   – Improve cycling capabilities

2. Developing new diagnostics for failure modes and durability, exploiting available work plus new techniques

3. Strengthen and grow interactions
   – Continue to disseminate findings to industry

4. Moving on to promising chemistries beyond VRB, H-Br
   – Metal electrodes, air electrodes