Component Research for Redox Flow Batteries

Tom Zawodzinski and Che-Nan (Josh) Sun

With help from Jamie Lawton, Zhijiang Tang, Doug Aaron, Alex Papandrew, Qinhua Liu, Matt Mench (UTK)

Frank Delnick (SNL)

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Approach

This project is a little different from many others in the portfolio

We are not looking into alternative battery chemistries per se

We are doing work to guide you in choices of materials and hardware designs to make all RFBs better!

Focus on components, diagnostics to drive understanding how to improve
Goals and Tasks

1. Demonstrate improved performance of RFBs in pre-competitive work
   - Chemistry agnostic; we look at key representative processes. However, results here focus on VRBs
   - Pre-competitive means that we will tell you details

2. Develop rational diagnostics to guide component selection
   - ‘Rational diagnostics’ means:
     • We are defining standard tests that are
     • supported by an underpinning of rigorous theory and
     • testing protocols that are meaningful, addressing actual operational questions
   - Component selection refers to our tests being used to pinpoint key requirements, guiding choices and development
Component Selection

Understanding of Properties drives Connection

Our work supports this bridge
Highlights: Performance Enhancement Met Milestone

Power Density over 6X higher vs previous best!
*We are now at ~10x.*

Step by Step on Performance Increase

Initial Figure of Merit: Peak Power Density*

Step one: change cell design

Step two: improve on existing materials
  - Two focus areas: resistance (ASR) and electrode performance

Lowering ASR has dramatic effect; trade-off with cross-over

Working on kinetics, mass transport effects (see diagnostics section of this talk)
### Approach: Membrane Characterization

**Ultimate question:** what goes where, when and how fast?

**Developing extensive tools to comprehensively and systematically unravel performance limitations and their root causes in component properties**

<table>
<thead>
<tr>
<th><em>Ex situ</em> Membrane Property (fundamental)</th>
<th><em>In situ</em> Cell Property (net)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>ASR</td>
</tr>
<tr>
<td>Active Species Diffusion</td>
<td>Cross-over, Cell Balance</td>
</tr>
<tr>
<td>Water Transport</td>
<td>Water Pumping</td>
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</tbody>
</table>

**All Properties are controlled by underlying composition**

**Some of these mappings are very complex**
Membrane/Separators: Uptake & Conductivity

Ultimate question: How does membrane structure and composition impact performance of the membrane in the cell?

Acid uptake, membrane dehydration leads to Major drop in conductivity
Membrane/Separators: Uptake & Conductivity

Ultimate question: How does membrane structure and composition impact performance of the membrane in the cell?

$\text{VO}^{2+}$ uptake leads to Major drop in conductivity
Membranes/Separators: Transport

Solutions are concentrated—fluxes coupled

Our approach: SIMPLIFY—try to isolate some species, multiple measurements

Example: VO$^{2+}$ diffusion measurement

We have choices…

- **Constant Ionic Strength**
  - Limits water transport
- **Constant Acid Concentration**
  - Limits acid transport, initially

Simplest possible measurement—*already complex!*
However!

Note that flux is inversely related to $\text{VO}^{2+}$ concentration!

Clear indicator of complex transport!
Apparent Diffusivity vs. [acid,\( \text{VO}^{2+} \)] (Constant Ionic Strength)

Mostly depends on acid concentration

We are developing an interpretive framework for these types of measurements.
Apparent Diffusivity: Constant Ionic Strength vs. Constant Acid

Take home point: Strong dependence of what you get on how you measure!

Think of these as ‘rate constants’ for diffusion; more detailed interpretation needed in terms of coupling of fluxes.
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
Electrodes

Inserting Reference Electrode Allow us to Measure Kinetics at Each Side Separately

At 40°C

Rxn Kinetics on Negative much worse than on Positive

Cell
0.1 M vanadium, 5.0 M H₂SO₄
1 x10 AA paper each side; 2x N117
V⁵⁺/⁺ WE, V³⁺/⁺ CE, DHE- RE
Electrodes
Impedance Measurements allow us to pinpoint exact sources of loss in cell
Electrodes
Improvements via better materials

High SOC

50% SOC

1.7 x increase in the peak power density-- not yet optimized!

Test conditions
Electrode thickness ~ 1200 µm per side, Membrane: Nafion 117
Solution: 0.8MV, 4MH₂SO₄, Single pass, Flow rate ~ 22mL/min
Temp.: 21°C, Same cell hardware
Electrodes
Improvements via better materials

Polarization

Power

900 mW/cm²

570 mW/cm²

1.7 x increase in the peak power density-- not yet optimized!
Electrodes Kinetic Region

4 to 5 times increase in current density at 1.4 V!!!
ORNL Research Plan for RFBs

Interactions

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 Communication with other labs
- December 2010: First Working Group meeting at SNL
- Phone meetings and e-mail exchanges with PNNL and SNL
- Material exchange starting
- Exchanging best practices by researcher interaction, visits
Summary of Accomplishments

1. Major test beds for component studies and cell testing in place
2. Path to significant performance gains mapped
3. Substantial new insights into membrane performance factors and underlying chemistry
4. State of the Art *in situ* electrode test methods evolved including interpretative tools to isolate areas to target for improvement
5. Built necessary interactions with component producers and researchers to connect COMMERCIALLY AVAILABLE (and experimental) materials to developers
Next Steps

1. Continue component studies to help identify key chemistry and structure aspects for improved membranes and electrodes
   - Improve current density at high cell voltage

2. Develop new diagnostics for failure modes and durability, exploiting available work plus new techniques
   - Localized current and chemistry

3. Strengthen and grow interactions
   - Provide platform to disseminate findings to industry

4. Move on to other chemistries beyond VRB, H-Br
   - Metal electrodes, air electrodes