Component Research for Redox Flow Batteries

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Coming Soon!

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Previous Highlights

Unprecedented VRB Power Density:  ~2600 W/cm²
Cycling at 500mA/cm² between 20 and 80% capacity with 90% efficiency

Technology is being Patented

WattJoule LLC
This is their Core Cell Technology

• Previously elucidated electrode kinetics, membrane effects
Approach

Working at Component, Cell Level

This Year’s Efforts

1. Cell cycling studies
   a) Baseline
   b) Integrating our cells with PNNL’s electrolyte to support WattJoule

2. Components
   a) Membranes
   b) Electrodes
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

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
Key Components

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

Fuel Flow

Oxidizer Flow

External Circuit

e−

B−

Managed by UT-Battelle for the Department of Energy
CELL CYCLING
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

Fundamental stability of materials

Hydrogen Evolution, Chlorine Evolution in Mixed Acids
Voltage Efficiency at low, high rates (one data set)

100 mA/cm²

500 mA/cm²

The value of high rate…
Long Cycling: Efficiency of 1513232B (500 mA/cm$^2$)

Some capacity fade; working now to understand origin
PNNL Electrolyte has higher capacity and capacity stability in 500 mA/cm$^2$ cycling (specific mat’l set)

Significant corrosion, chlorine evolution issues were addressed.
COMPONENTS
## 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>Ex situ Membrane Property (fundamental)</th>
<th>In situ 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>
</tr>
</tbody>
</table>

All Properties are controlled by underlying composition. Some of these mappings are very complex.
Membranes: Recent Work

- We are now testing membranes for uptake/composition, conductivity, vanadium species permeation and in cells
- Tested more than 20 membranes of a wide variety of types (PFSA, Hydrocarbon, AEM); strong collaborations with SNL, 3M

Key findings

- AEM performance is systematically less than PEM
- Mechanical properties of membrane play a key role
- Donnan effects are less important than expected
- In cell, voltage decay measurements do not correlate perfectly with fundamental performance
**VO^{2+} Permeability**

Interdiffusion with $H^+ > VO_2^{+} > V^{3+}$

![Graph showing the permeability of VO^{2+} with respect to [H_2SO_4] (M). The graph includes data for $H^+$, $V^{3+}$, and $VO_2^{+}$ counter ions, indicating a decrease in permeability with increasing [H_2SO_4] concentration.]
Uptake Effects: from P to D

Uptake in 0.1M V ion and 0.5M Sulfuric Acid:

<table>
<thead>
<tr>
<th>Ion</th>
<th>$V/\text{SO}_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{VO}^{2+}$</td>
<td>0.097</td>
</tr>
<tr>
<td>$\text{VO}_2^+$</td>
<td>0.022</td>
</tr>
<tr>
<td>$\text{V}^{3+}$</td>
<td>0.076</td>
</tr>
</tbody>
</table>

Partition Competition?

Both $\text{VO}^{2+}$ and $\text{V}^{3+}$ show increased permeability when crossing against $\text{VO}_2^+$ and decreased permeability crossing against each other. $\text{VO}_2^+$ shows less partitioning into the membrane.

Possibly, increased permeability in the presence of $\text{VO}_2^+$ could be a result of lack of competition for ‘space’ in the membrane.
We now can comprehensively track species transport across operating cell

Experimental Results
1700mV charge, 1100 mV discharge

Calculated Results
Electrodes: Recent Work

- We are now testing electrodes of various types
- Tested more than 5 electrodes of a wide variety of types
- Key findings
  - No catalyst is needed with appropriate carbon electrodes
  - Electrode stability is a major issue for many types
  - Wetting behavior of electrode is important
  - Electrode thickness is critically important for high performance
- We are now exploring making our own…
PROGRAMMATICS
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
Summary of Accomplishments

1. Major test beds for component studies and cell testing in place

2. Substantial cycling data obtained; using it to trouble shoot and gain understanding of how to optimize components

3. Total analysis of mass transfer during cell operation

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

5. Translating research to WattJoule

6. Reporting results via publications
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
   - Improve cycling capabilities

2. Develop 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. Move on to promising chemistries beyond VRB, H-Br
   - Metal electrodes, air electrodes