Component Research for Redox Flow Batteries

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Coming Soon!

FBOB Conference

Padua, Italy

Summer 2015

Previous Highlights

Unprecedented VRB Power Density: ~2600 W/cm^2

Cycling at $500 mA/cm^2$ 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

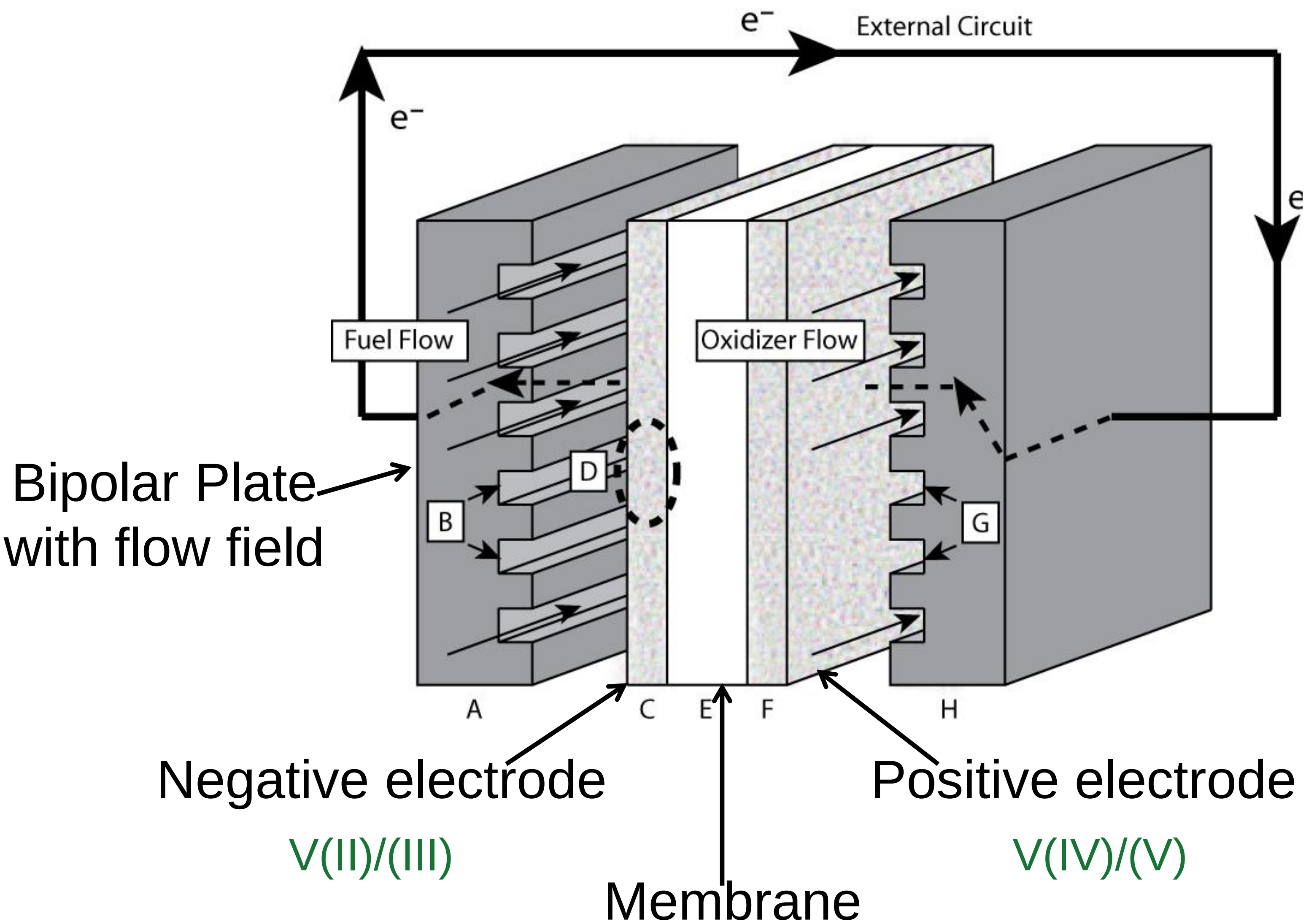
This Year's Efforts

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 <u>standard</u> 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



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

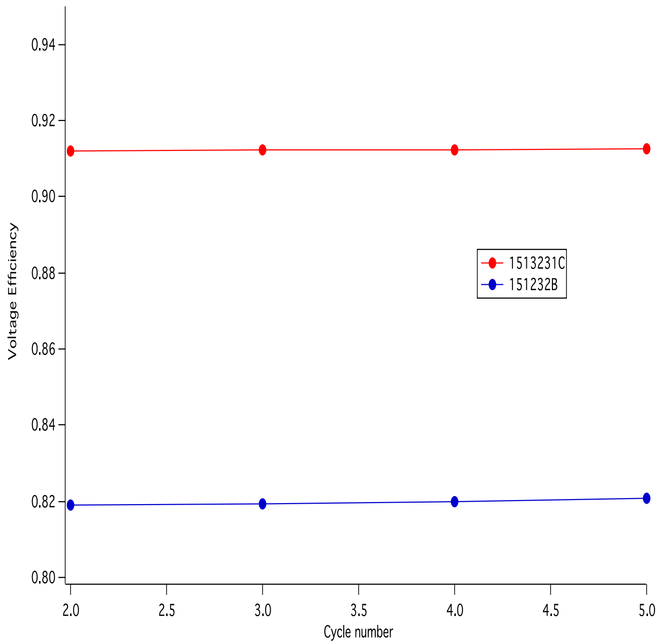
Third Level: Durability and Side Reactions

Fundamental stability of materials

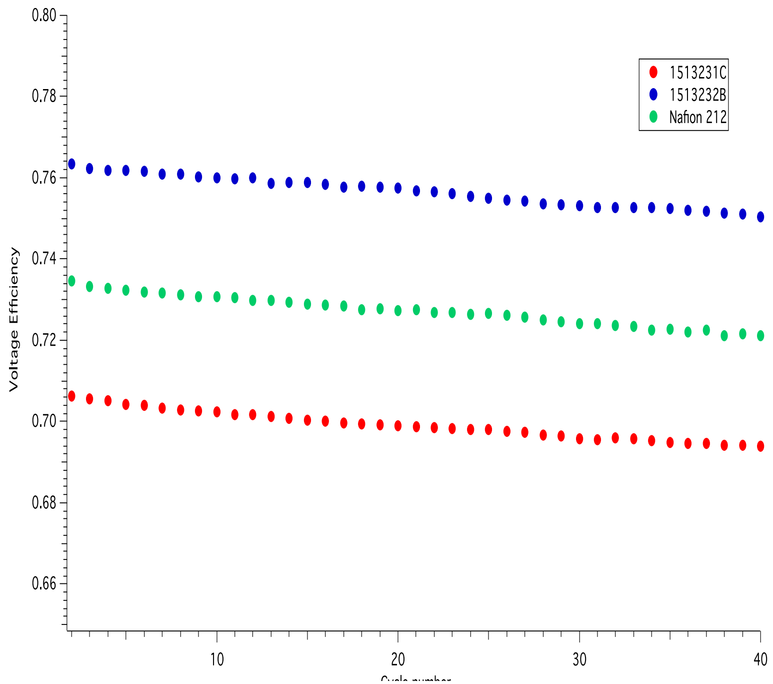
Hydrogen Evolution, Chlorine Evolution in Mixed Acids

Voltage Efficiency at low, high rates (one data set)

100 mA/cm^2

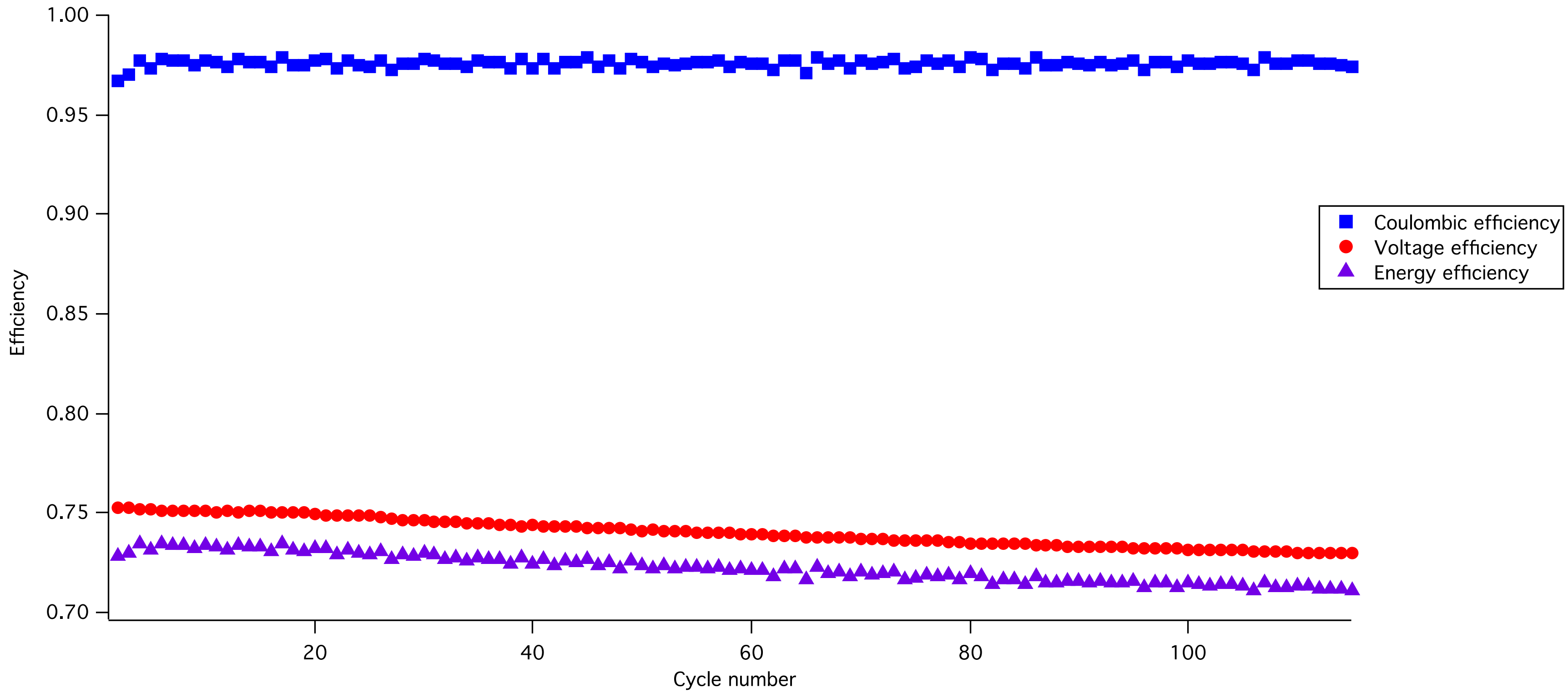


500 mA/cm^2



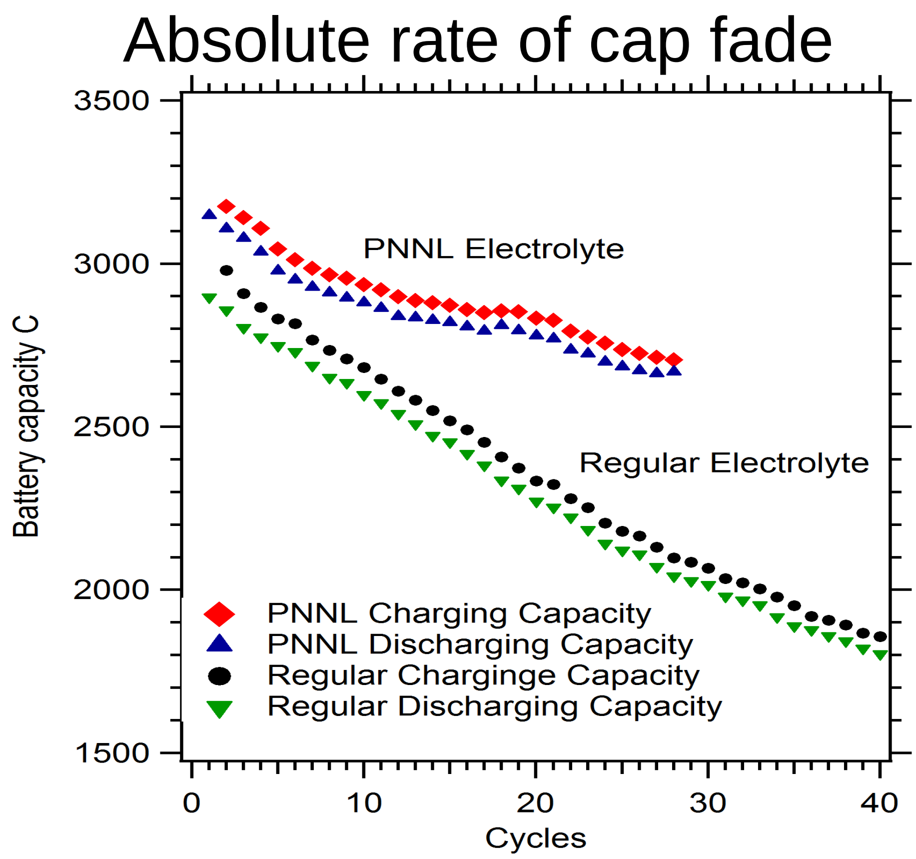
The value of high rate…

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

***Ex situ* Membrane Property (fundamental) maps to**	***In situ* Cell Property (net)**
Conductivity	ASR
Active Species Diffusion	Cross-over, Cell Balance
Water Transport	Water Pumping

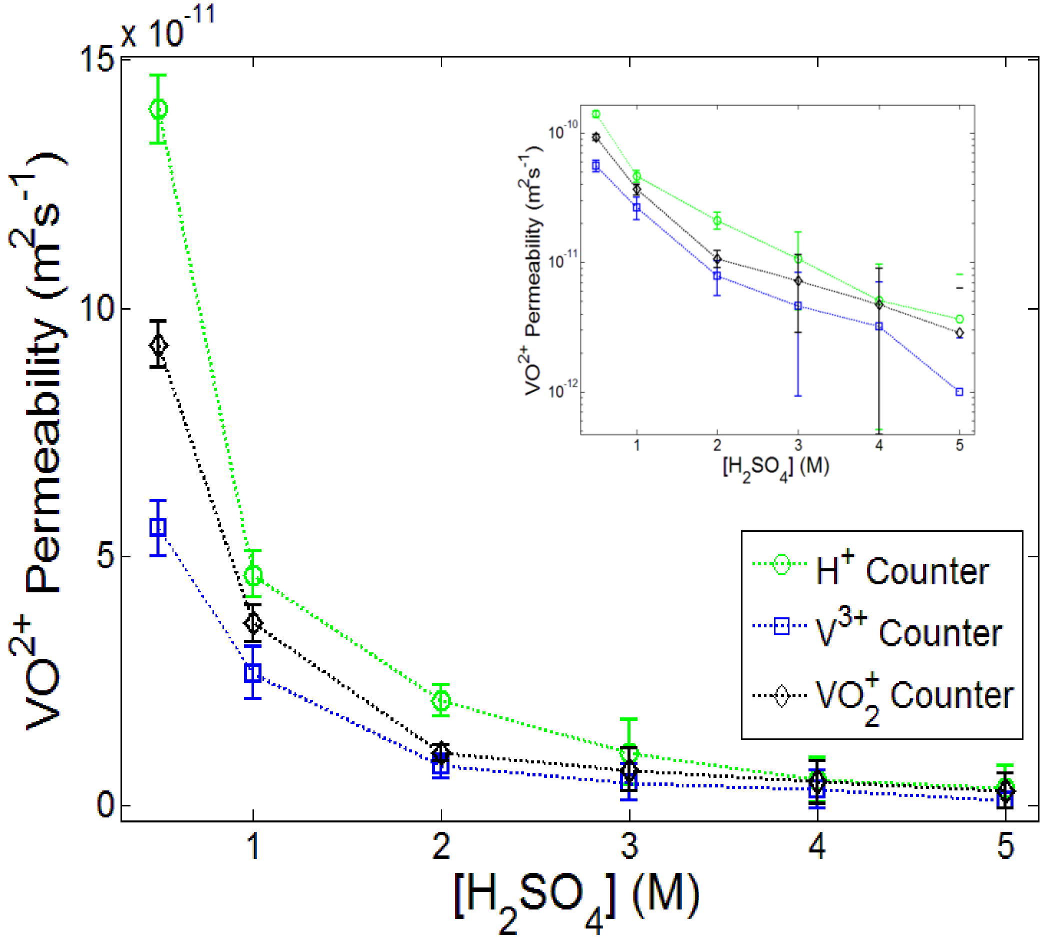
All Properties are controlled by underlying composition
Some of these mappings are very complex

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

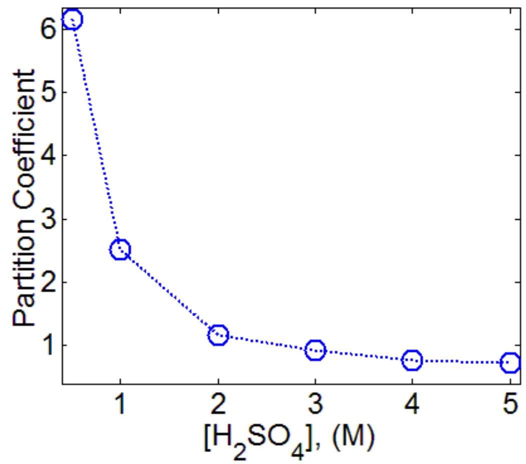
Interdiffusion with $H^+ > VO_2^+ > V^{3+}$

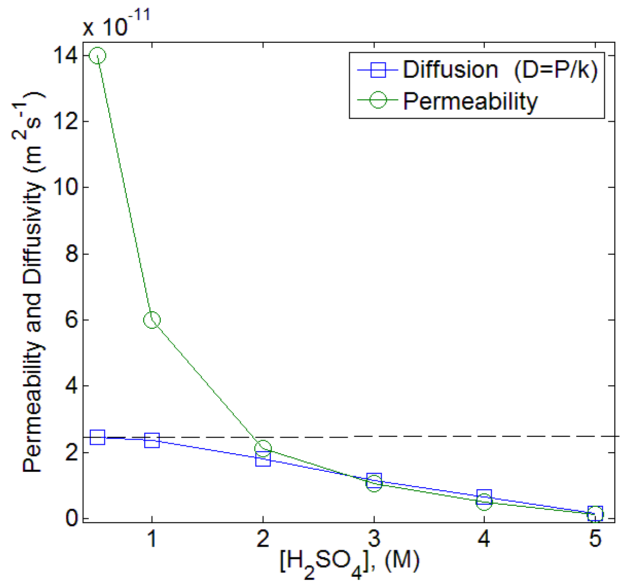


Uptake Effects: from P to D

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

Ion	V/SO_3^-
VO^{2+}	0.097
VO_2^+	0.022
V^{3+}	0.076



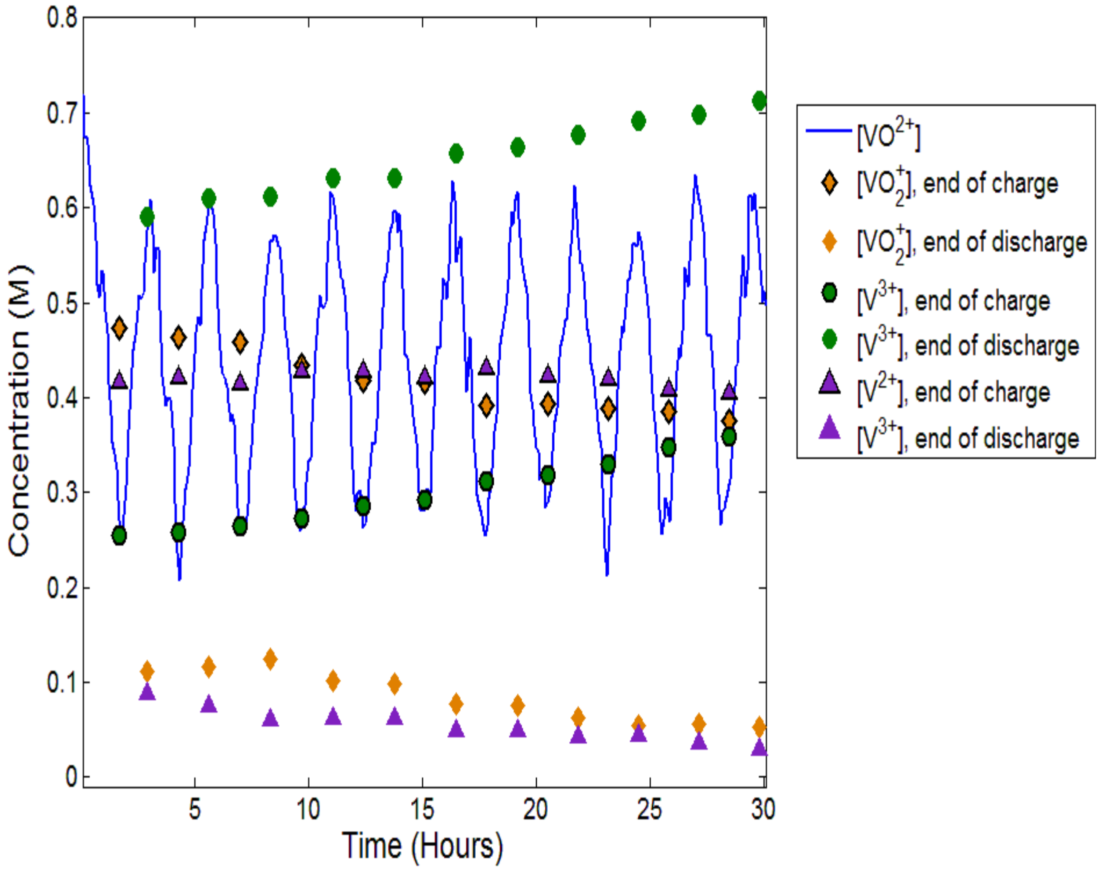


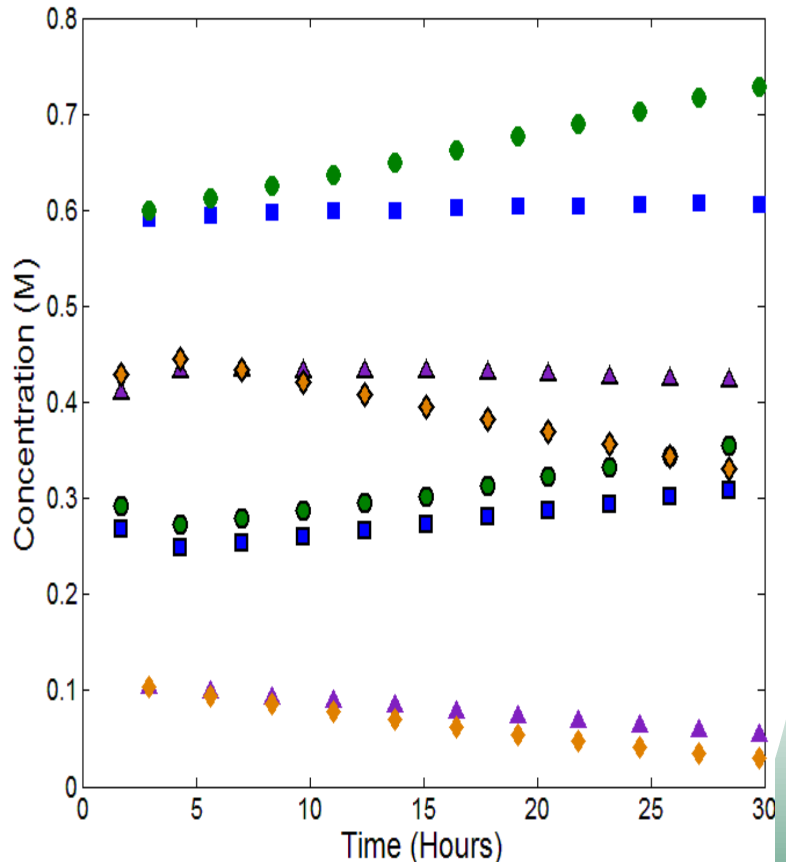
Partition Competition?

Both VO^{2+} and V^{3+} show increased permeability when crossing against VO_2^+ and decreased permeability crossing against each other. VO_2^+ shows less partitioning into the membrane….

Possibly, increased permeability in the presence of 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

Calculated Results

1700mV charge, 1100 mV discharge

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