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)

Thanks to Imre Gyuk (OE) and team at UTK

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

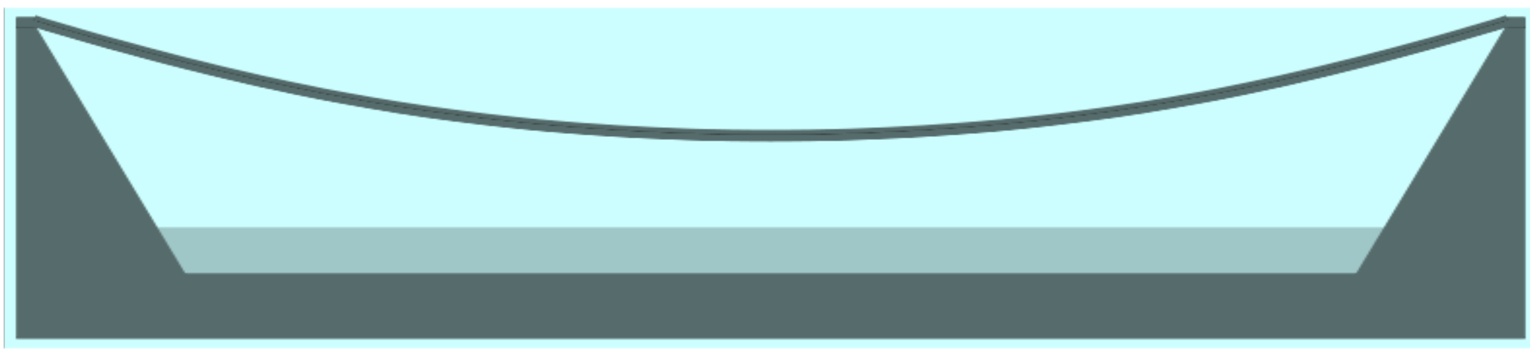
1. Demonstrate improved performance of RFBs in pre-competitive work
   – Chemistry agnostic; we look at key representative processes However, results here focus on VRBs
   – Pre-competitive means that we will tell you details
2. Develop rational diagnostics to guide component selection
   – 'Rational 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

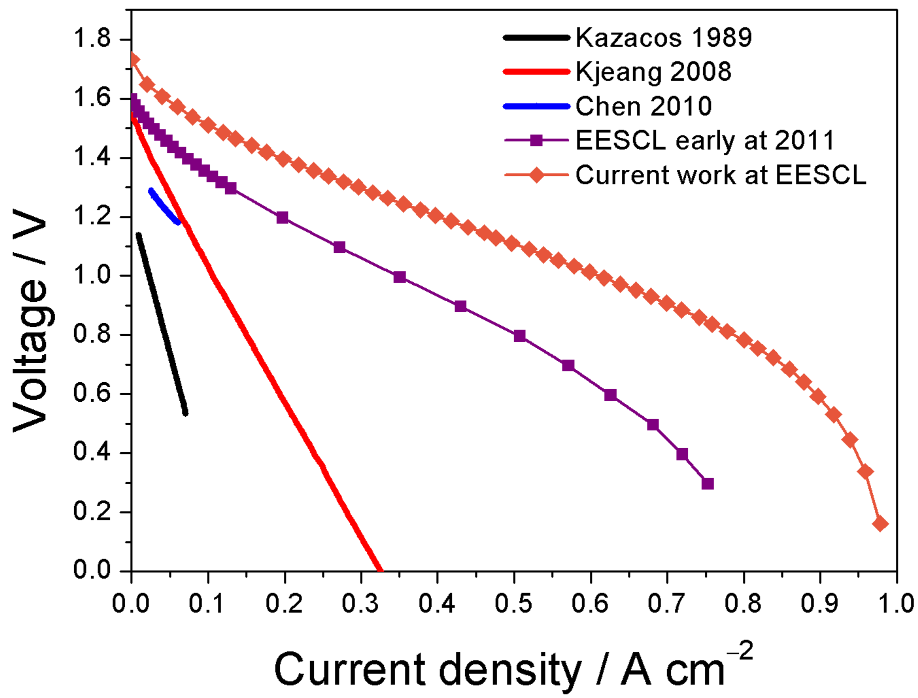
Membrane, electrode suppliers ⟵ **ORNL** ⟶ Flow Battery Makers

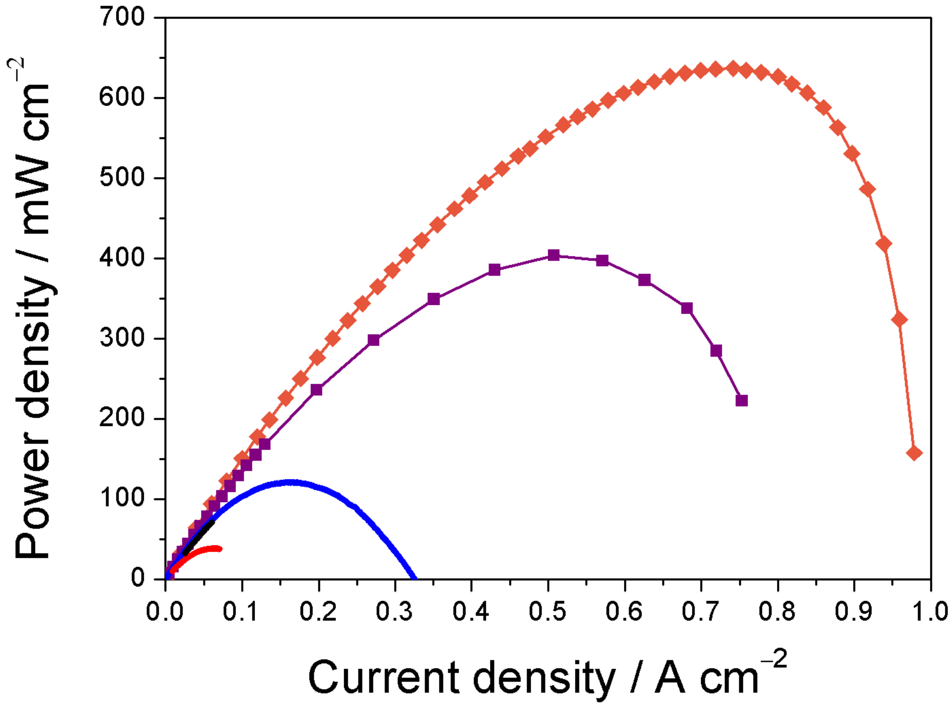
Diagnostics, Materials Properties, Requirements, Cell Testing, Designs



Our work supports this bridge

Highlights: Performance Enhancement Met Milestone





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

D.S. Aaron, Q.-H. Liu, Z. Tang, G.M. Grim, A.B. Papandrew, A. Turhan, T.A. Zawodzinski, M. M. Mench, *Journal of Power Sources, 2012.*

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

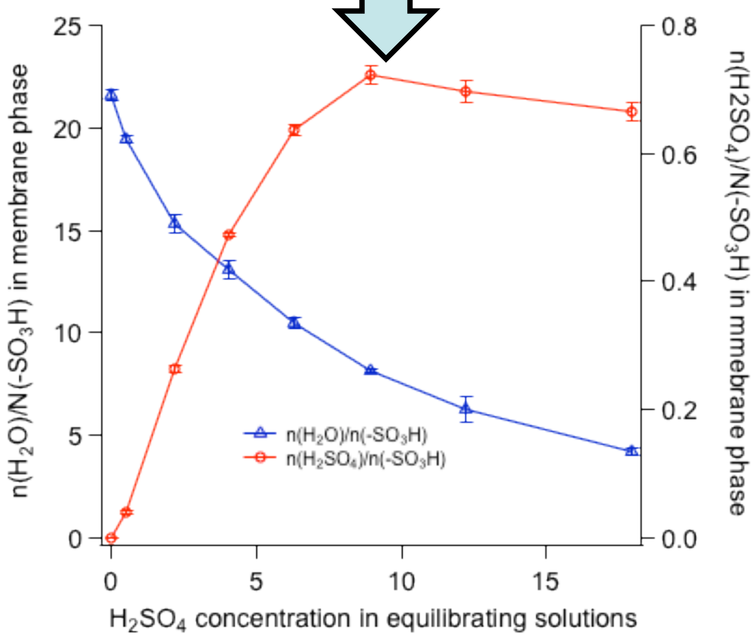
***Ex situ* Membrane Property (fundamental) maps to**	***In situ* Cell Property (net)**
Conductivity	ASR
Active Species Diffusion	Cross-over, Cell Balance
Water Transport	Water Pumping

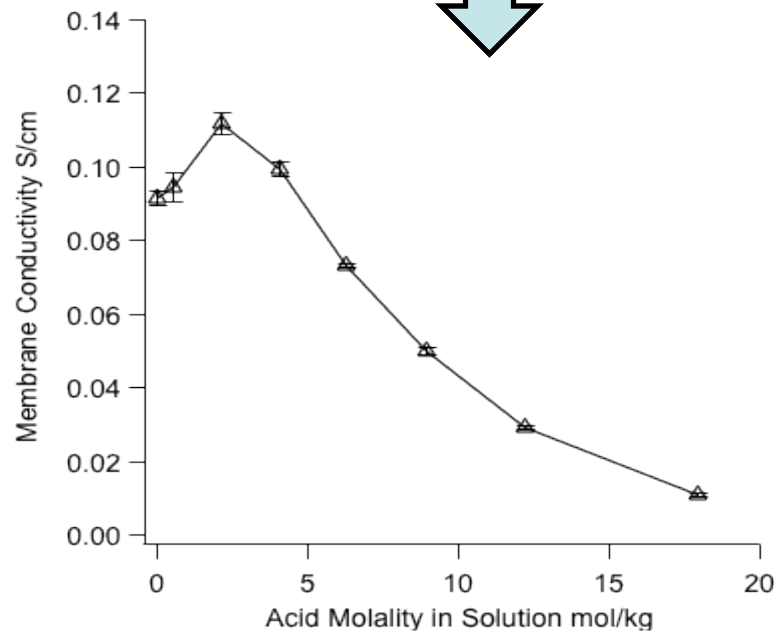
All Properties are controlled by underlying composition
Some of these mappings are very complex

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

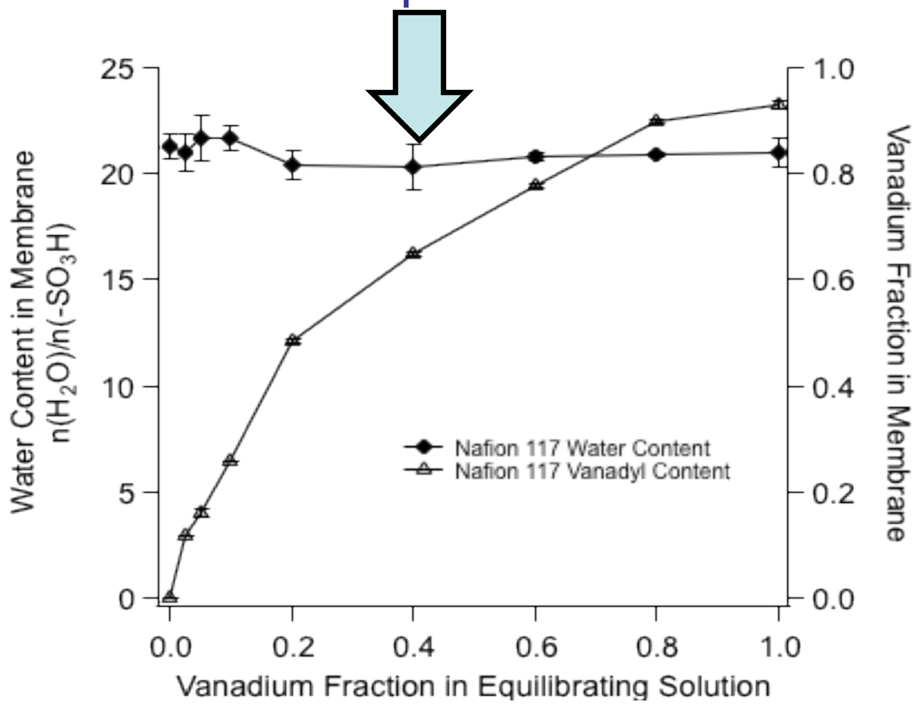


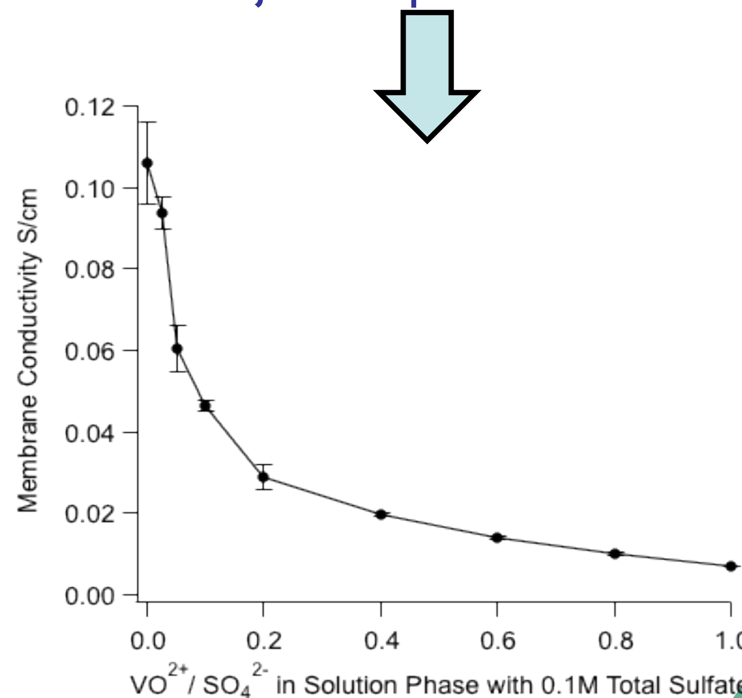


Membrane/Separators: Uptake & Conductivity

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

VO^{2+} uptake leads to Major drop in conductivity

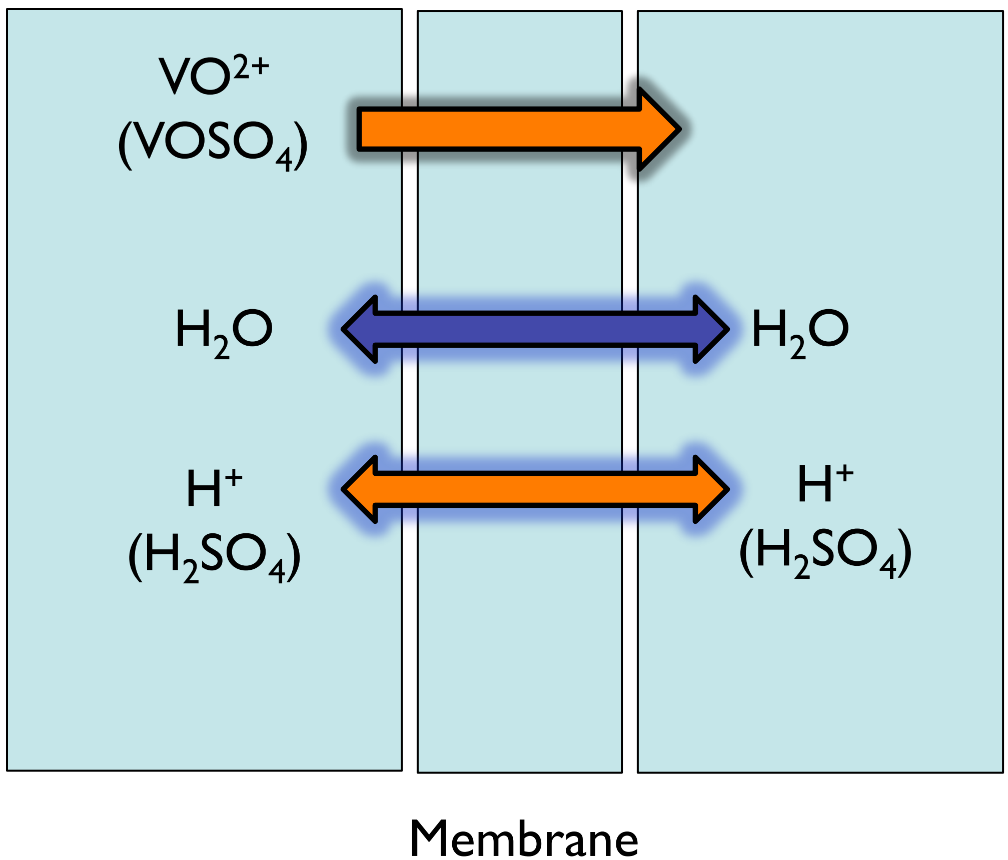




Membranes/Separators: Transport

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

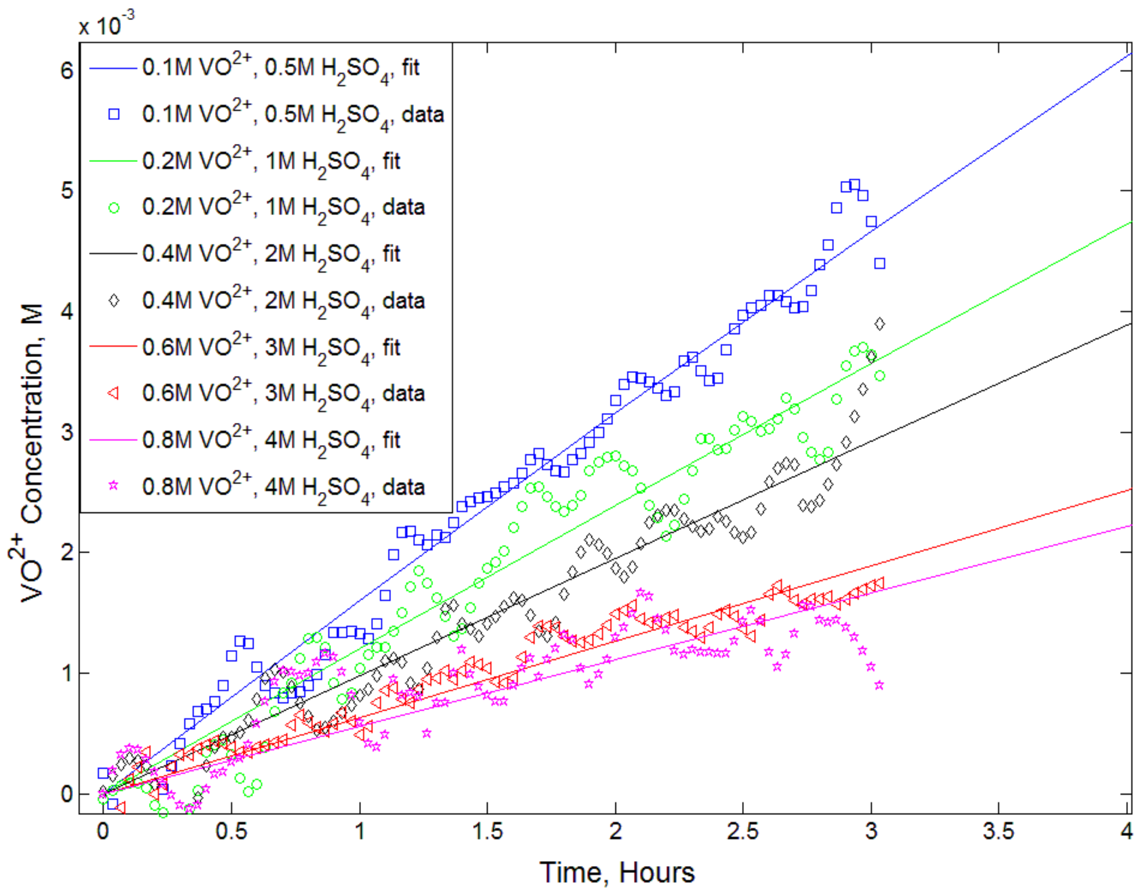
Limits water transport

Constant Acid Concentration

Limits acid transport, initially

Simplest possible measurement—**already complex!**

VO^{2+} Transport Across Membrane from ESR

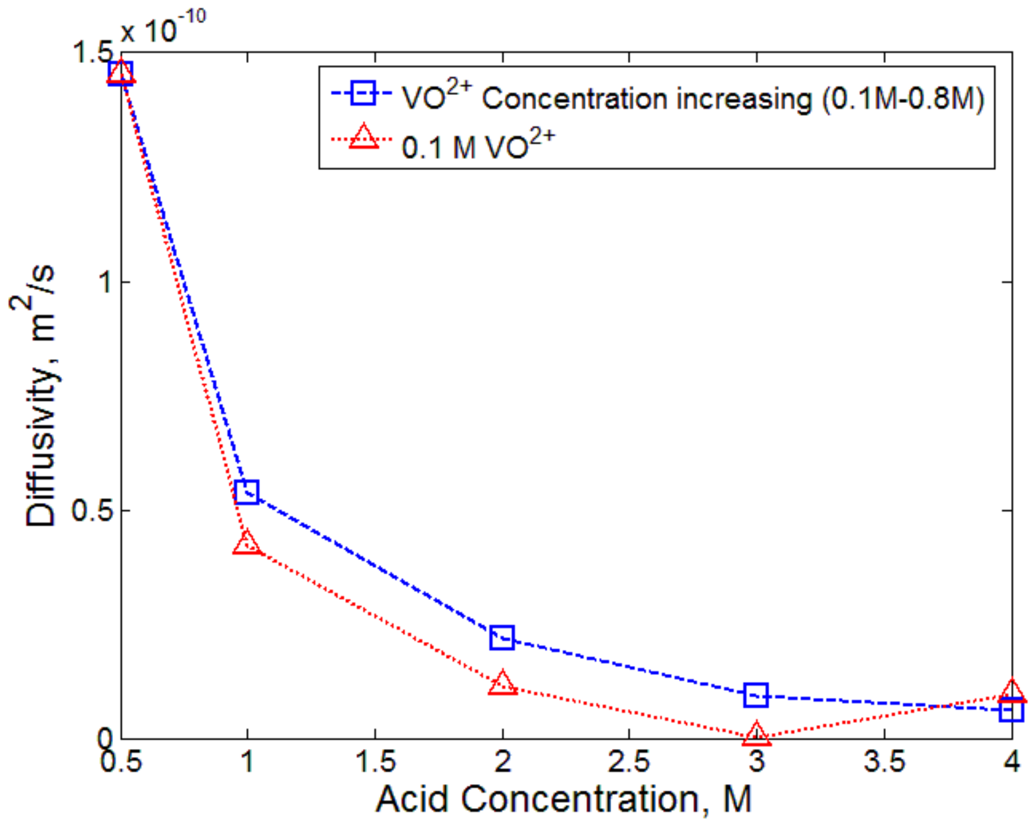


However!

Note that flux Is inversely related to VO^{2+} concentration!

Clear indicator of complex transport!

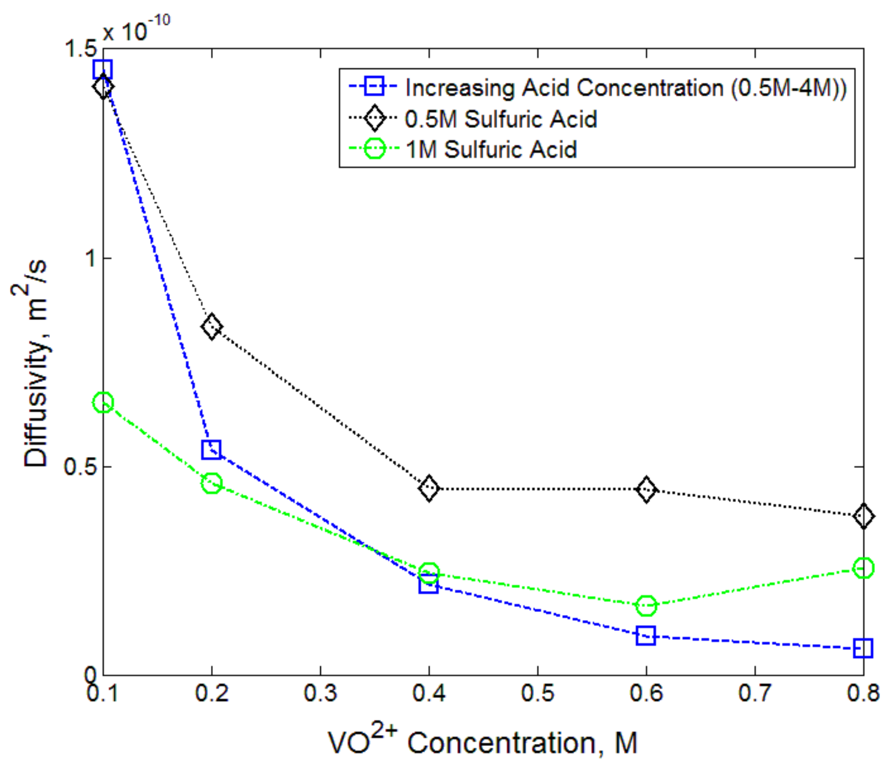
Apparent Diffusivity vs. [acid, VO^{2+}] (Constant Ionic Strength)



Mostly depends on acid concentration

We are developing an interpretive framework for these types of measurements

Apparent Diffusivity: Constant Ionic Strength vs. Constant Acid



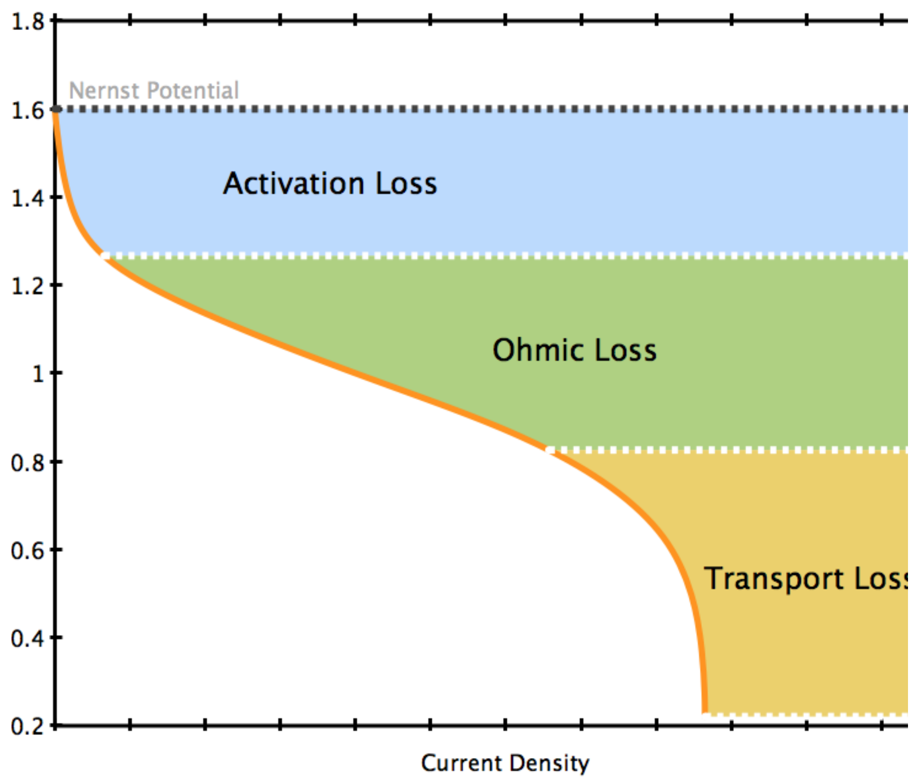
Take home point:
Strong dependence
Of what you get on how you measure!

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!

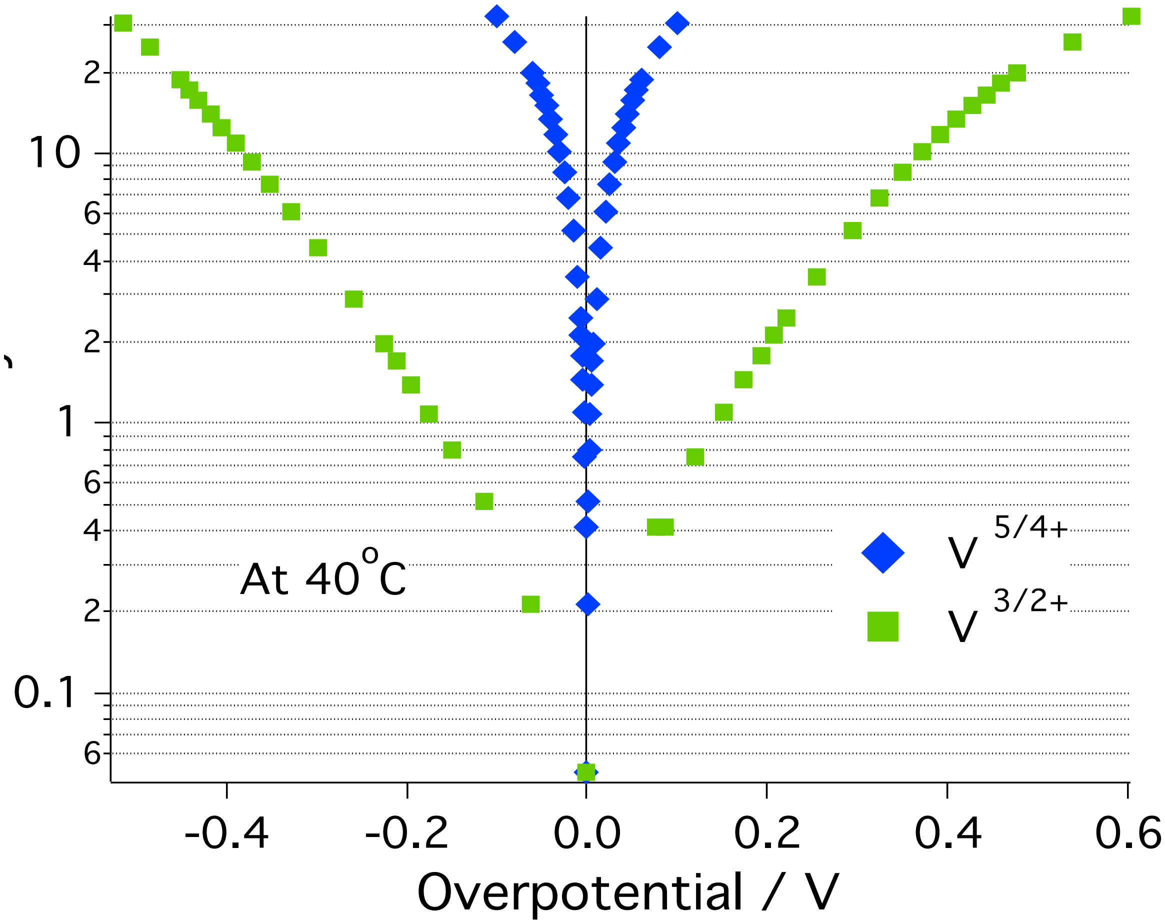


We separate and measure (both charge, discharge):

- **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



Rxn Kinetics on Negative much worse than on Positive

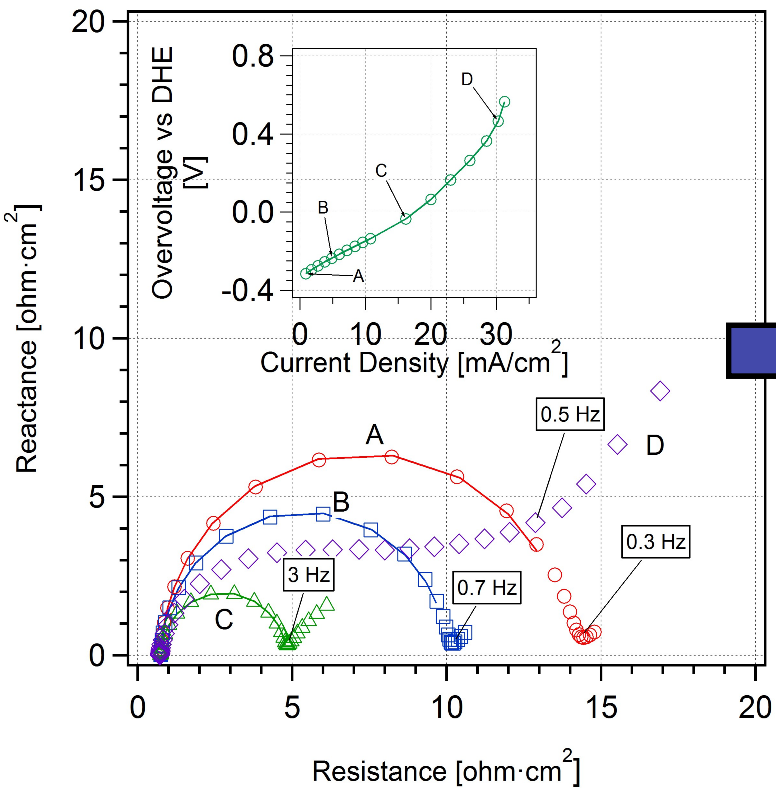
Cell

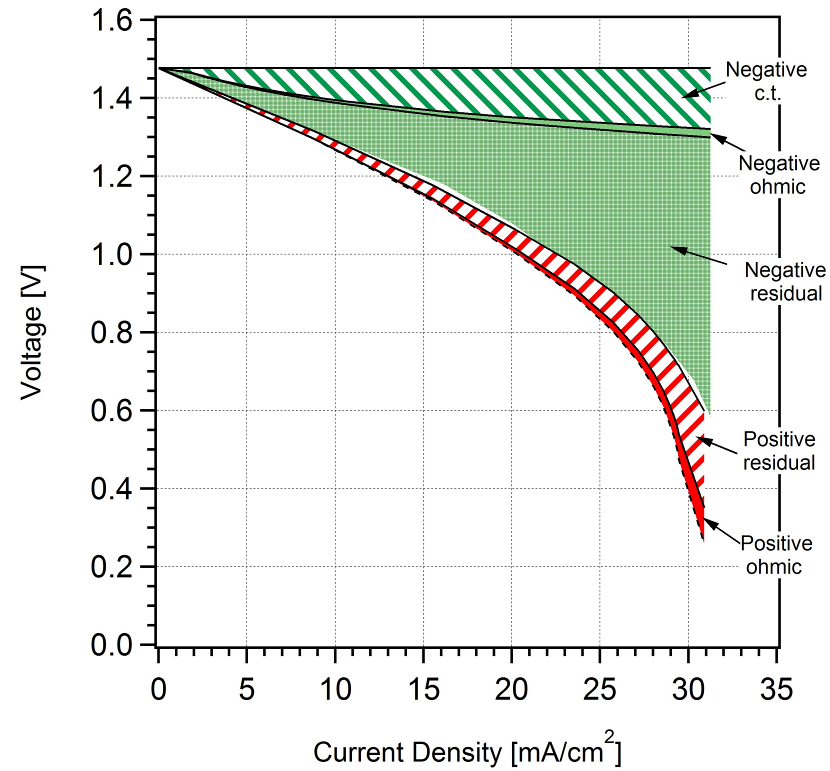
0.1 M vanadium, 5.0 M H_2SO_4

1 x10 AA paper each side; 2x N117

$V^{5/4+}$ WE, $V^{3/2+}$ CE, DHE- RE

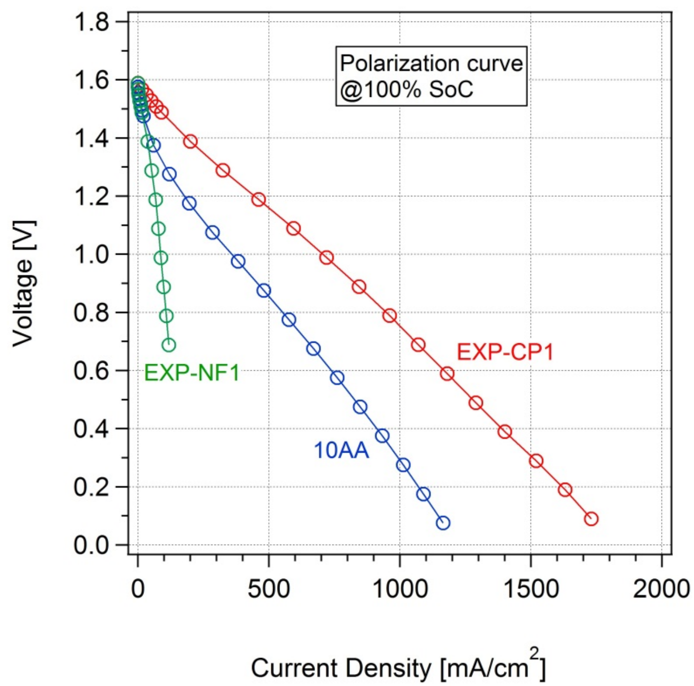
Electrodes
Impedance Measurements allow us to pinpoint exact sources of loss in cell



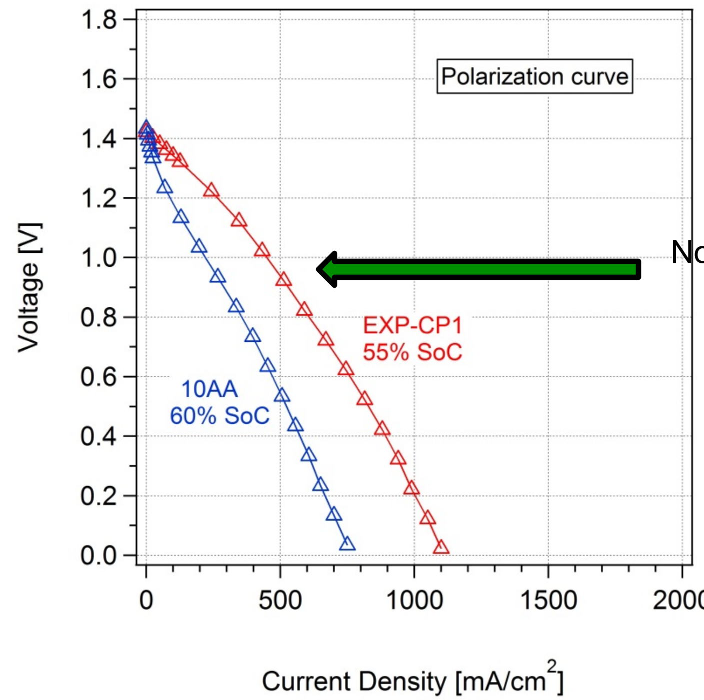


Electrodes
Improvements via better materials

High SOC



50% SOC



Note mt losses, conc polrn

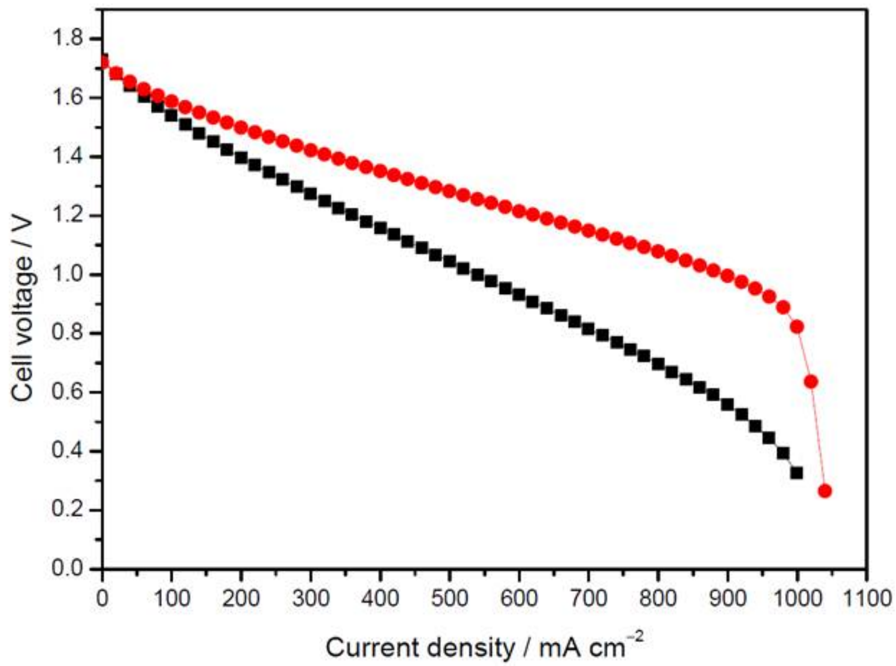
1.7 x increase in the peak power density-- not yet optimized!

Test conditions

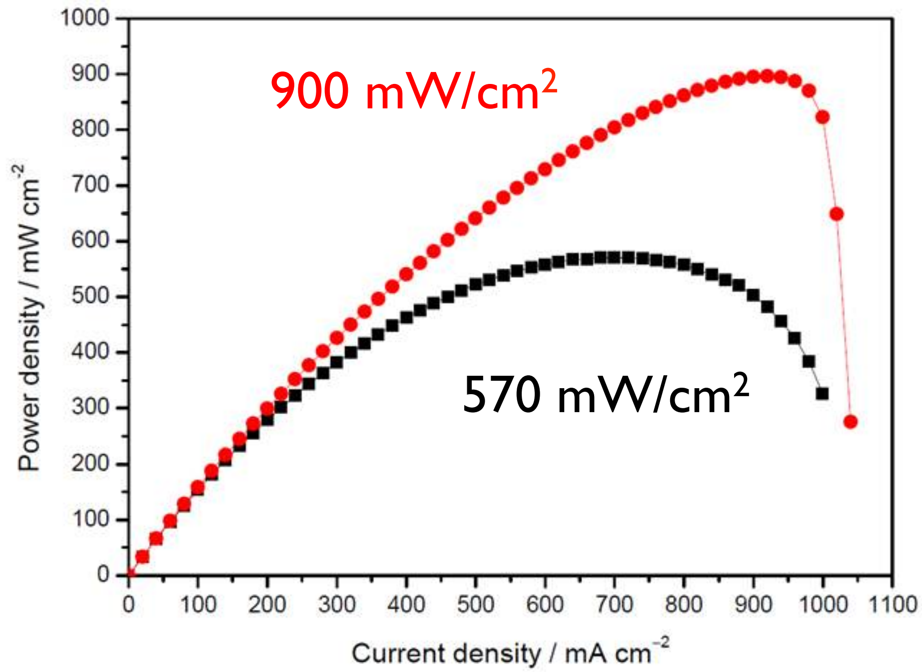
Electrode thickness ~ 1200µm per side, Membrane : Nafion 117
Solution : 0.8MV, 4MH_2SO_4 ,Single pass, Flow rate ~ 22mL/min
Temp. : 21^{o}C, Same cell hardware

Electrodes
Improvements via better materials

Polarization



Power



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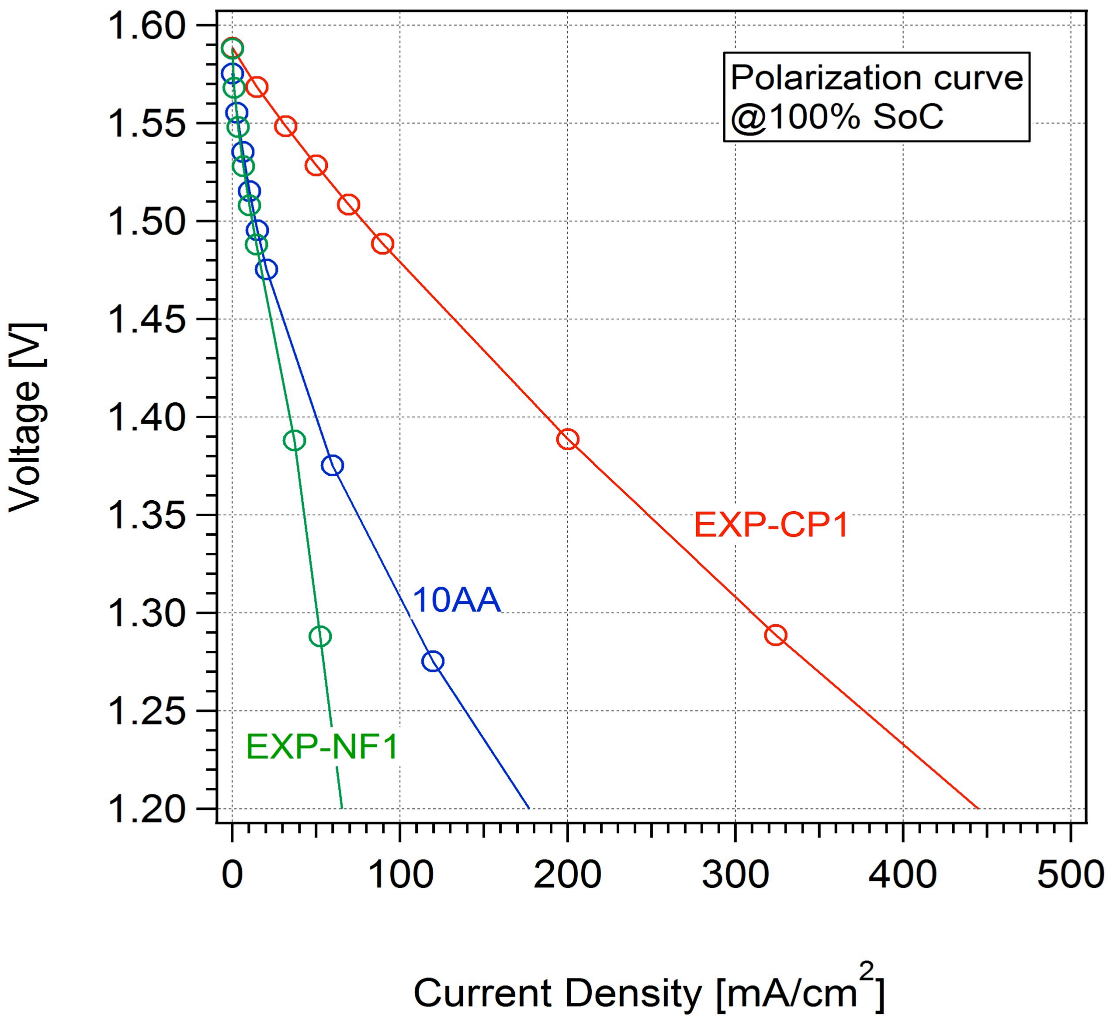
Electrodes
Kinetic Region



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