Transitioning From Fuel Cells to Redox Flow Cells

T. Zawodzinski and Matt Mench
University of Tennessee and ORNL

Acknowledgments

$$

DOE-OE

EPRI

GCEP

NSF EPSCOR (TN SCORE)

UTK Governor's Chair Fund

Partner in Crime

Matt Mench

‘Peeling the Onion’
Personalized History of PEM Fuel Cells

We May Recapitulate This for RFBs

Catalysis

Test System
- Small Single Cell
- Large Single Cell
- Stack
- System

Layers of the Onion Hot Topic *du Jour*
- Water Management, Membranes
  - Late ’80’s, early ’90’s
- Reformate Tolerance, DMFC’s
  - Mid ’90’s
- High Temp Membranes
  - Late ’90’s
- Durability
  - Early ’00’s

Modeling
- Membrane/ Water
- Cathode
- Impedance
- Anode/Whole Cell
- *Stack*

Transitioning to RFBs
What Could Remain the Same

1. **Materials**
   – **Membranes, diffusion media, electrodes, hardware**
2. **Diagnostics**
   – **Flow batteries are a lot like fuel cells**
   – **Polarization curves, ASR, segmented cells**
     - **This is NOT the way battery people test!**

Transitioning to RFBs
What is Different

1. **Battery Chemistry**
   - **Many different chemistries**
   - **Multiple components**
   - **Different reactivity challenges**
2. **Need to account for state of charge**
3. **Energy density, power density concerns different**
4. **Cost drivers different**

Membranes from Fuel Cells to RFBs

1. **The Good**
   - **Many different membranes available**
     - **PFSAs, Hydrocarbons**
2. **The Not so Good**
   - **Starting over to understand durability; multiple chemistries to take into account**
   - **Cross-over is more prevalent and a big issue; lots of water pumping as well**
3. **The Ugly**
   - **Multiple components lead to complex transport**
4. **The Just Plain Different**
   - **Both membranes and porous separators used**

Transitioning Electrodes to RFBs

1. **The Good**
   - **Many different porous carbon materials for electrodes**
   - **Don't always have catalysis**
2. **The Not so Good**
   - **Transport issues are rather different**
   - **Need to sort out the loss mechanisms**
3. **The Ugly**
   - **Air electrodes are real issues**
4. **The Just Plain Different**
   - **All phases used; concentration polarization**

Transitioning Cells and Stacks to RFBs

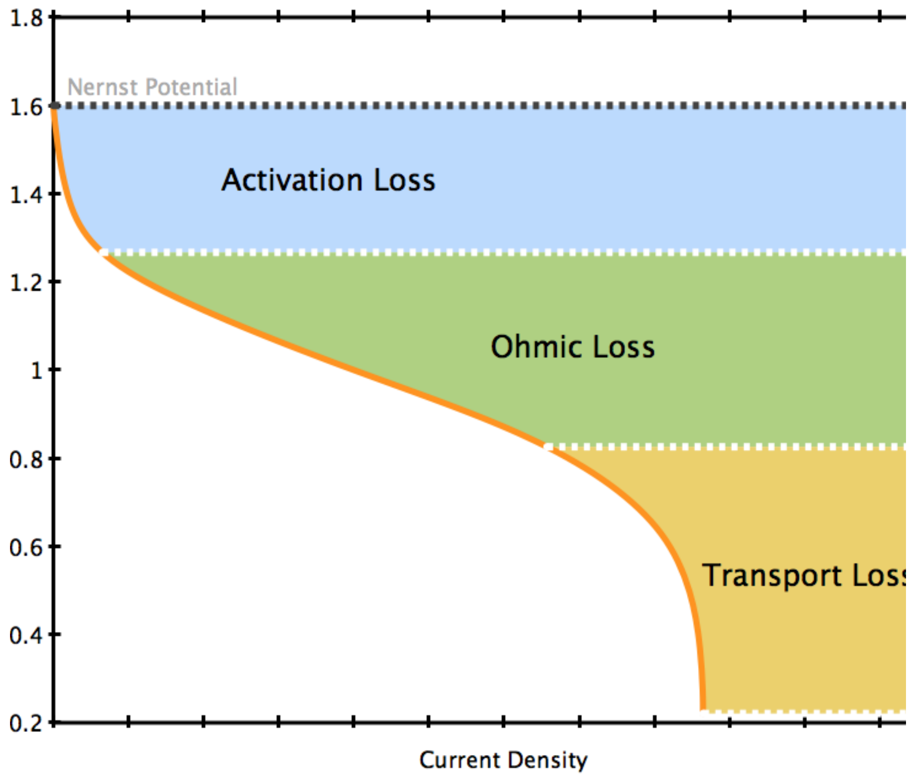
1. **The Ugly**
   - **Typical flow cell design has horrible performance characteristics**
2. **The Good**
   - **Flow-by cells (typical fuel cell architecture) works**
     - **Bipolar plates?**
3. **The Not so Good**
   - **Need to deal with shunt currents**
   - **Multiple phases?**

Diagnostics for RFBs

1. **The Good**
   – **Many standard approaches for battery testing**
2. **The Not so Good**
   – **This has fuel cell characteristics and these FC test methods yield more information**
   – **Significant need to transfer from FCs**
3. **The Ugly**
   – **Simple descriptions often do not exist**
4. **The Just Plain Different**
   – **Complex electrolytes and transport issues**

Performance in Flow Systems: Polarization Curves

not normally used in battery work!



We separate and measure (both charge, discharge):

- **Electrode polarization for each electrode**
- **Membrane resistance**
- **Electrode ionic/reagent mass transport resistance**
- **GDL mass transport resistance**

Augmented by impedance tests as well as ex situ component tests

Needed Improvements and Measurements

We separate and measure (both charge, discharge):

- Electrode polarization for each electrode
  - Reference electrode
- Membrane resistance
  - High frequency resistance at each pol curve point; conductivity
- Electrode ionic/reagent mass transport resistance
  - Analysis of IR-corrected pol curve; impedance
- GDL mass transport resistance
  - Analysis of IR-corrected pol curve; impedance
- PLUS: cross-over measurements, membrane transport studies of all species

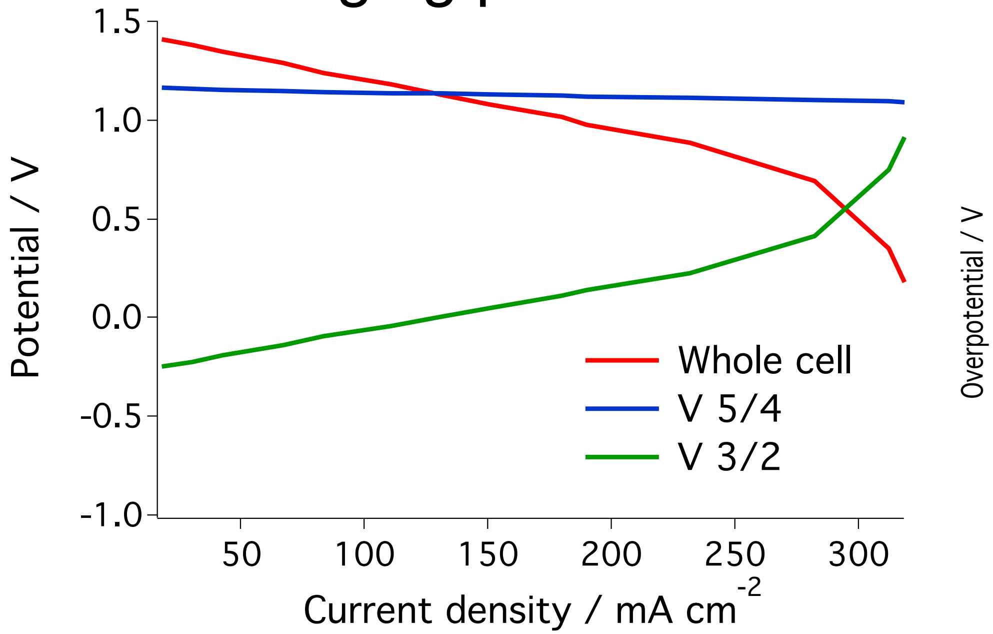
Missing Diagnostics that we enjoy in fuel cells

- ESA measurements
- Detailed understanding of flow and current distribution
- Detailed descriptions of what goes where and how fast
- Life testing/durability methods

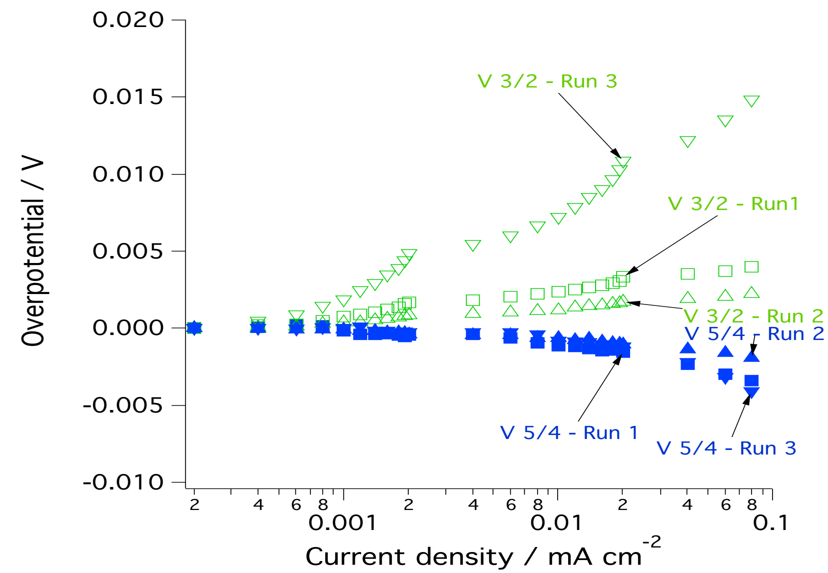
- And one other thing: patience!

Asymmetric Electrode Polarization

Discharging polarization curve



"Kinetic region"

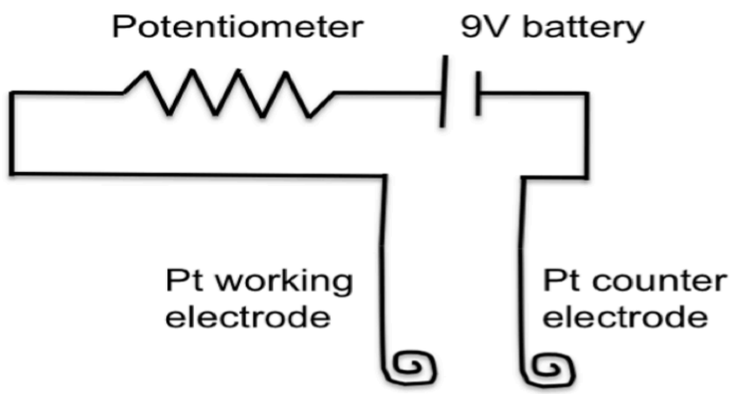


- The V 3/2 electrode also dominated overpotential for a discharging polarization curve.
- Kinetic losses not large…

Reference electrodes

Dynamic hydrogen electrode

- Connected two Pt wires to a 9 V battery and a ~1.5 MΩ resistor, resulting in ~6 μA of current flowing*
- The "working electrode" of the DHE formed a layer of hydrogen bubbles at very little overpotential
- DHE is sandwiched between two N11

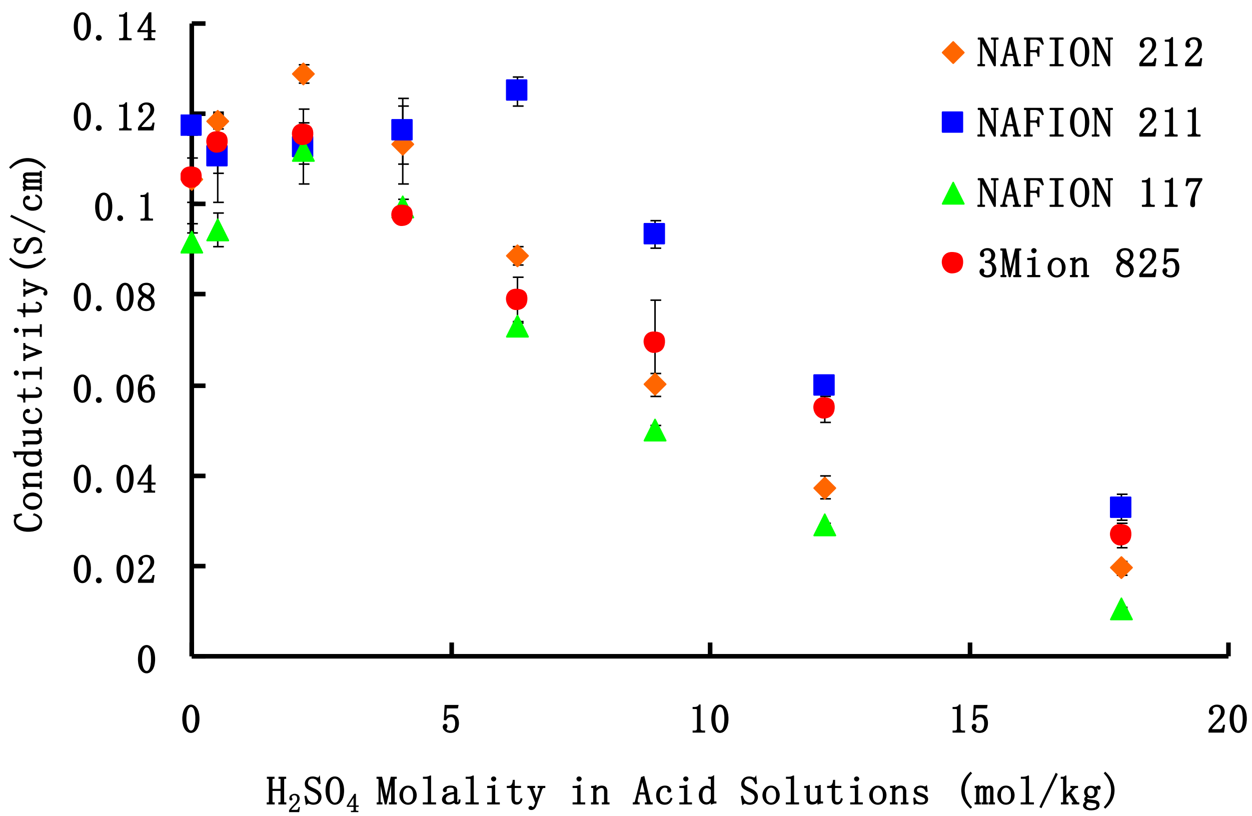


Also tested a commercially-supplied FlexRef DryRef reference electrode, but found vanadium infiltrated the DryRef

- 1/8" PTFE tube filled with proprietary gel and a silver wire
- KONBO liquid junction

*Li, G. & Pickup, P.G. Measurement of single electrode potentials and impedances in hydrogen and direct methanol PEM fuel cells. *Electrochimica Acta* **49**, (2004) 4119-4126.

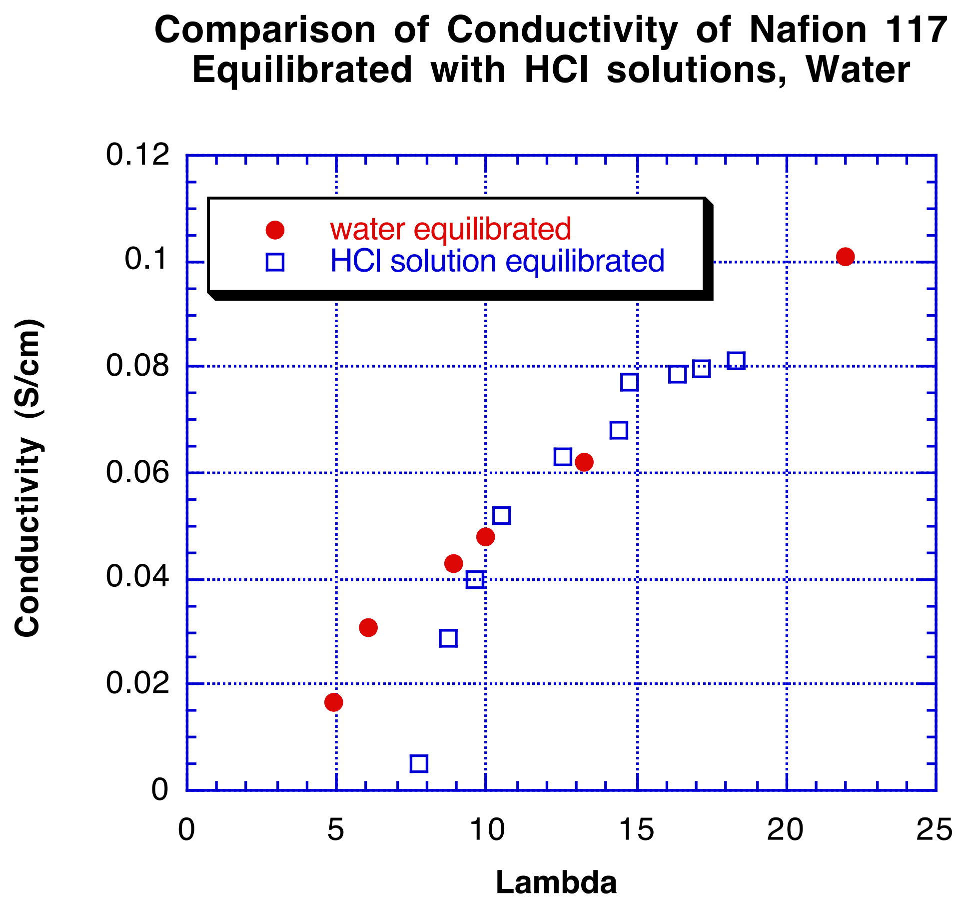
Conductivity of Membrane Equilibrated in Sulfuric Acid Solutions



Highly concentrated sulfuric acid solutions reduce membrane conductivities

Membranes in Contact with Strong Acid Solution

The HCl Case



Vanadium Electron Paramagnetic Resonance

Vanadium

$I_{vanadium} = 7/2$

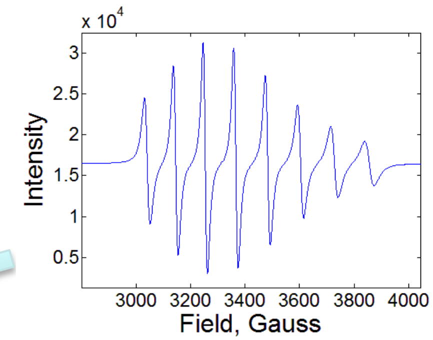
Electron configuration:

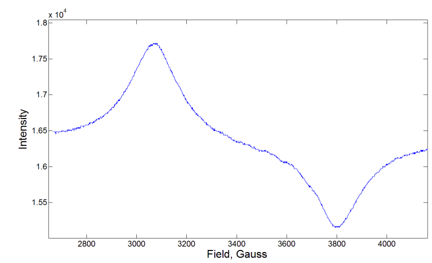
V^{5+}: $1s^2 2s^2 2p^6 3s^2 3p^6$

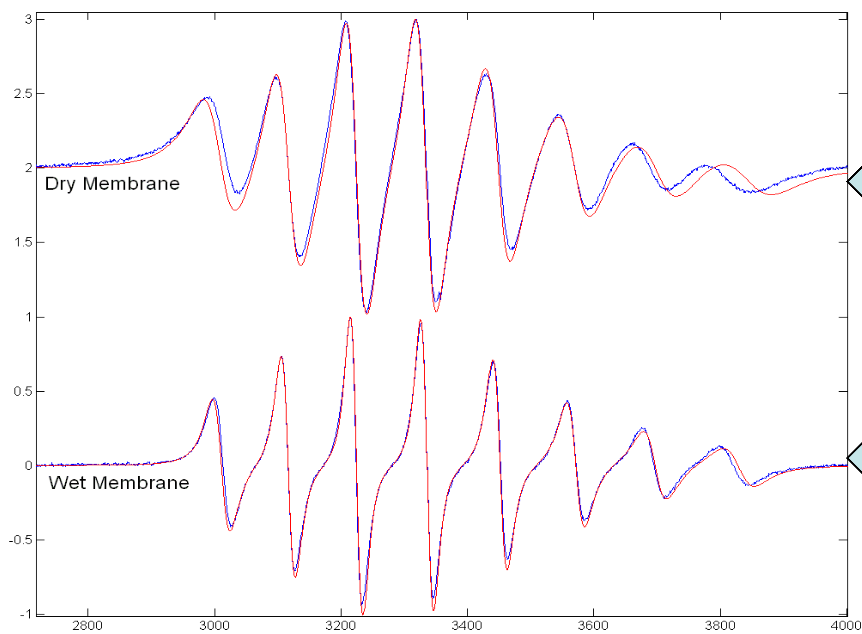
V^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^1$

V^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^2$

V^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^3$





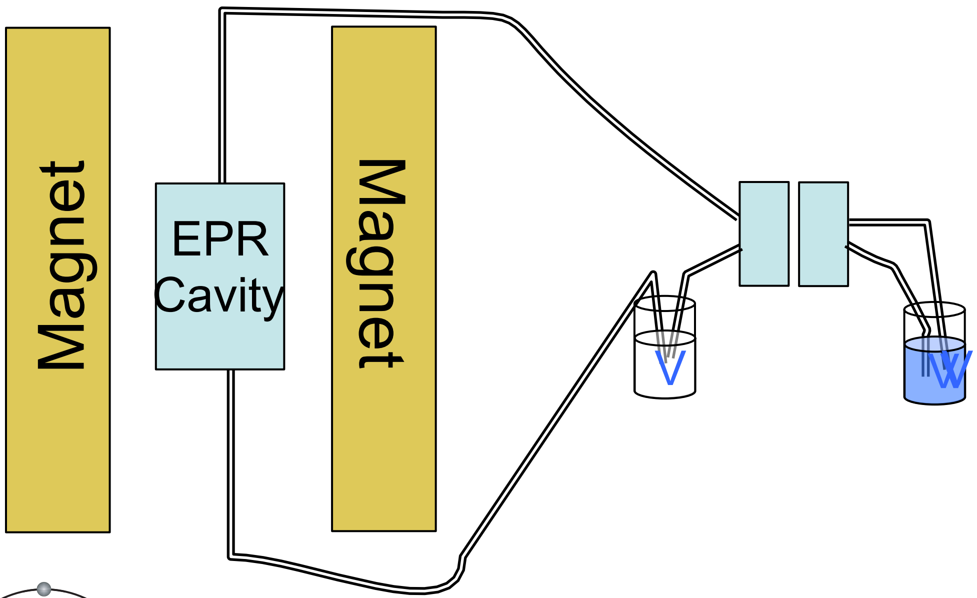


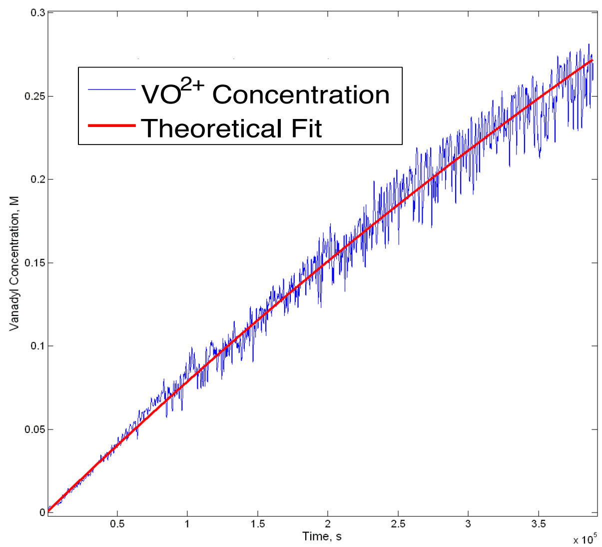
Field, G

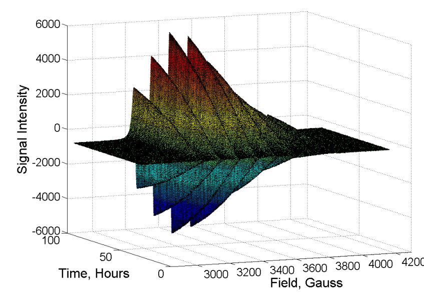
Dry: $R_V = 2.6 \times 10^8\ s^{-1}$

Wet: $R_V = 8.4 \times 10^8\ s^{-1}$

Crossover in Vanadium Redox Flow Batteries (measurements under way)



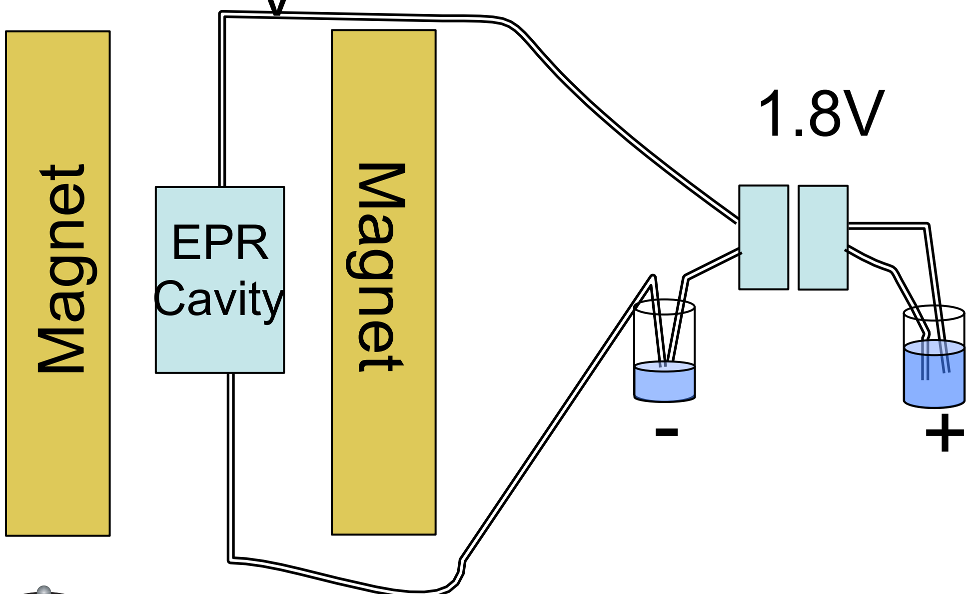




Oxygen crossover from Positive electrolyte solution

Rxn @ positive side: $VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-}$

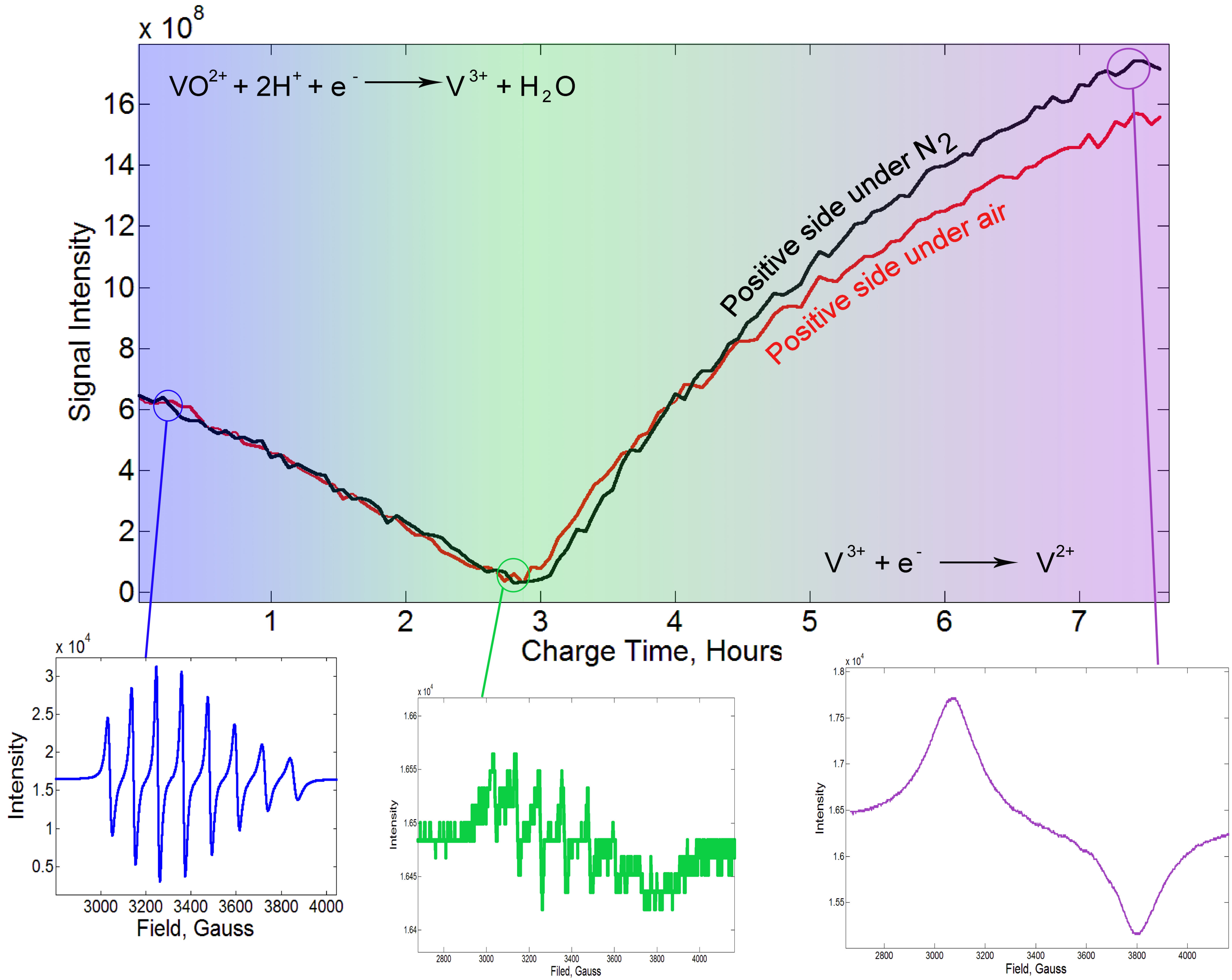
Rxn @ negative side: $VO^{2+} + 2H^{+} + e^{-} \rightarrow V^{3+} + H_2O$ then $V^{3+} + e^{-} \rightarrow V^{2+}$



V2+ reacts quickly with oxygen. The negative side is kept under nitrogen to prevent that.

If O2 crosses the membrane from the positive side:

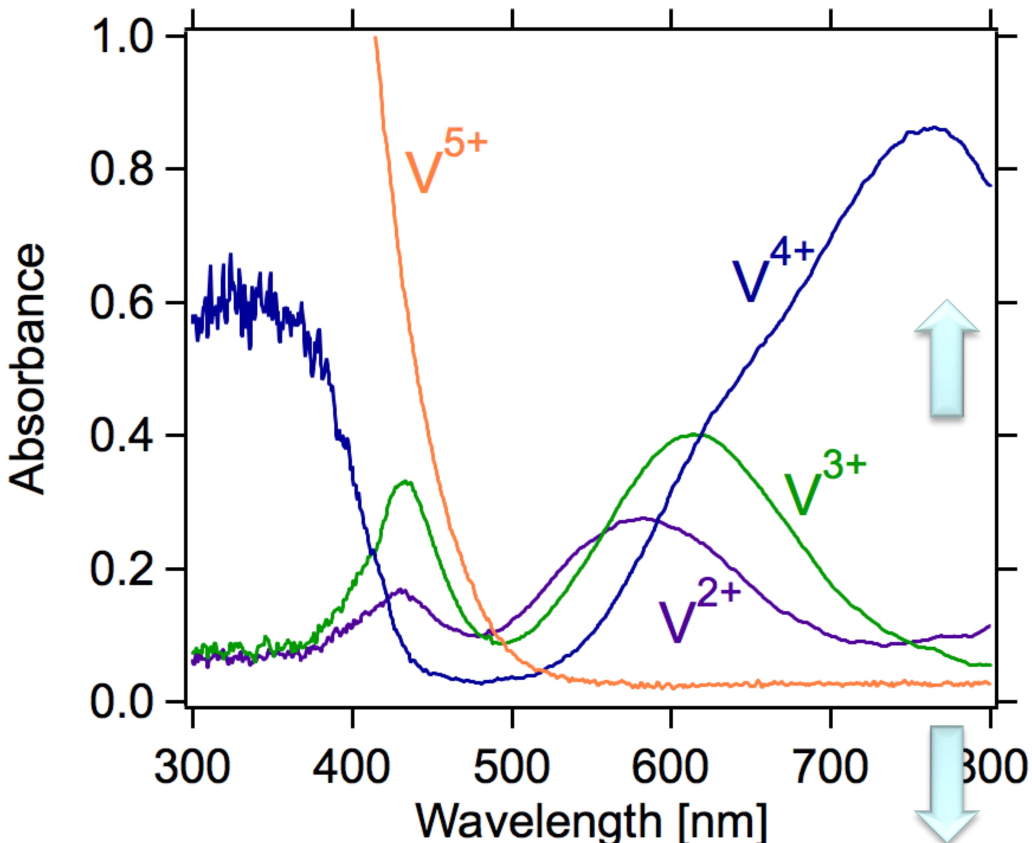
$$4V^{2+} + O_2 + 4H^{+} \rightarrow 4V^{3+} + 2H_2O$$

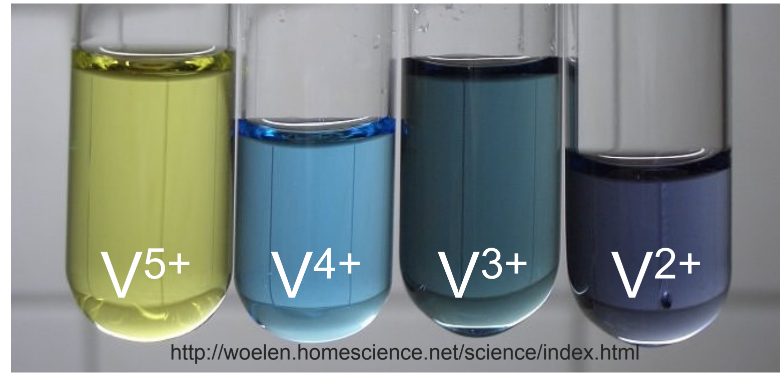


x 10^8
VO^2+ + 2H^+ + e^- → V^3+ + H_2O
Signal Intensity
Positive side under N_2
Positive side under air
V^3+ + e^- → V^2+
Charge Time, Hours
x 10^4
Intensity
Field, Gauss
x 10^4
Intensity
Filed, Gauss
x 10^4
Intensity
Field, Gauss

UV-Vis Spectrometry

Vanadium ions in solution have different colors and distinct UV-VIS spectra





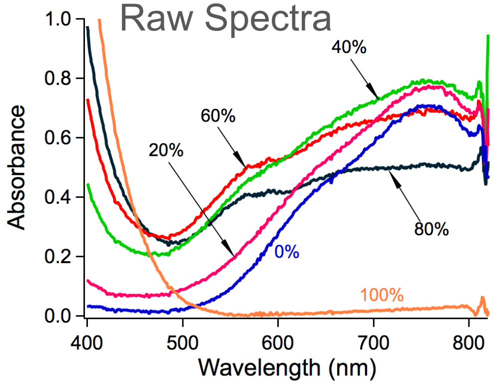
1M Vanadium in aqueous H_2SO_4 solutions / 5M total sulfate

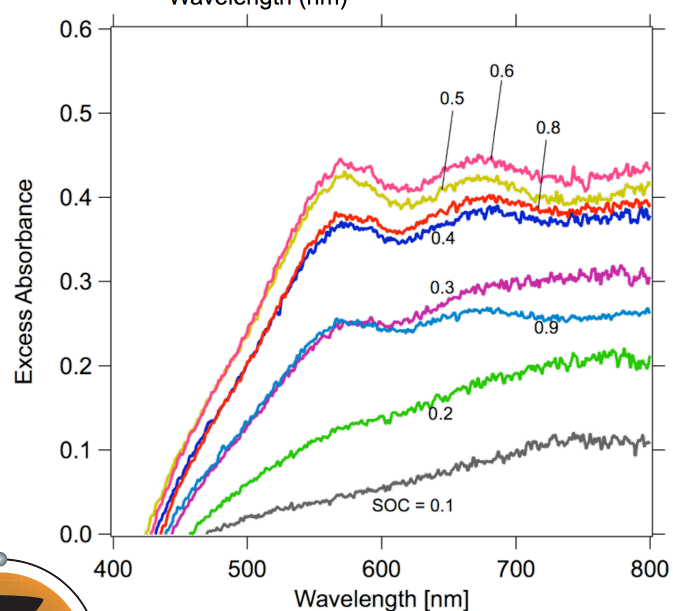
0.5 mm lightpath

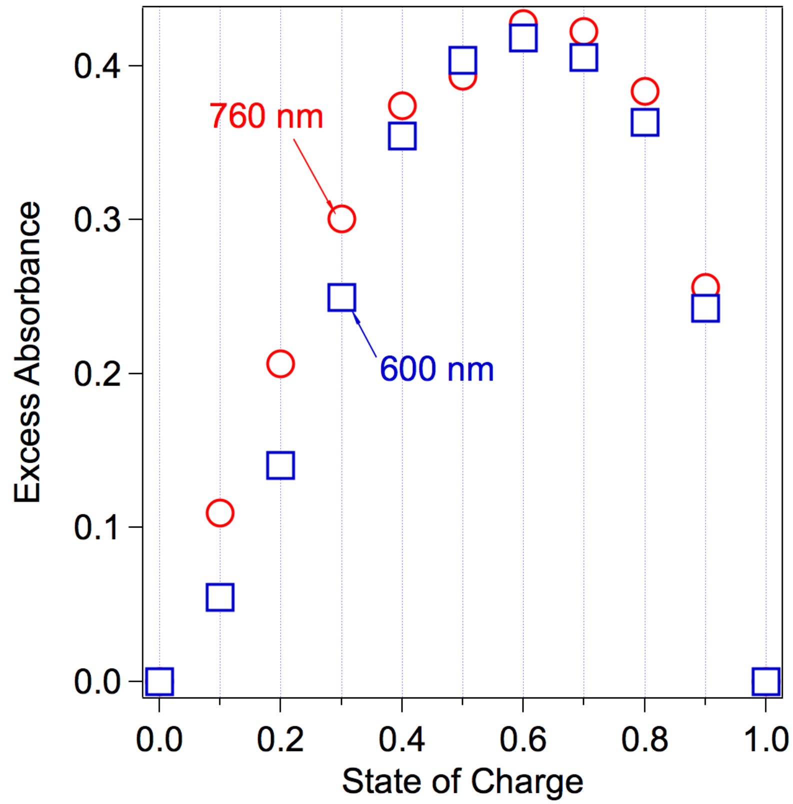
ALS SEC2000 spectrometer

Excess Absorption Suggests a Third Species

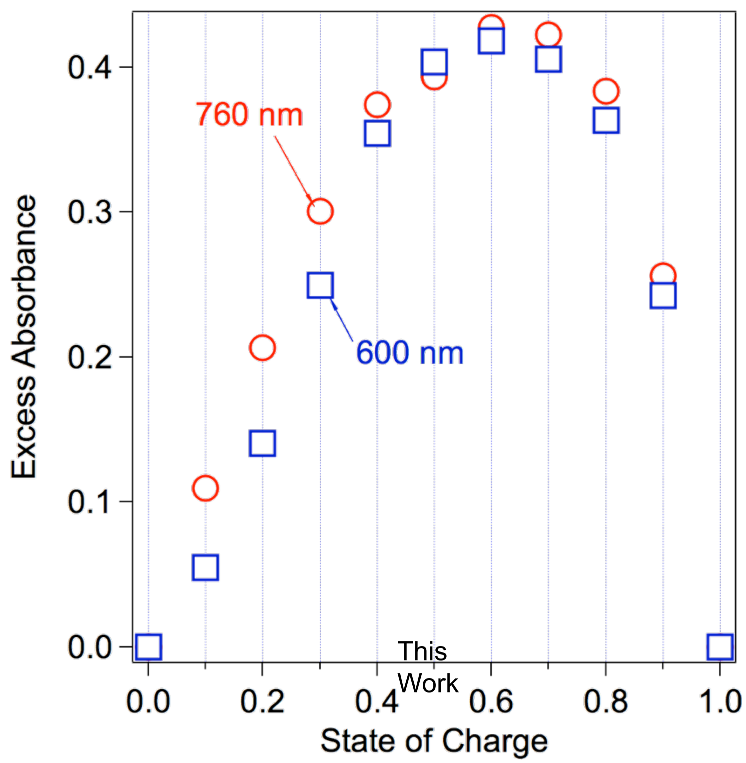
$$ExcessAbsorbance = S_{meas} - \alpha S(VO_2^+) + (1-\alpha)S(VO^{2+})$$

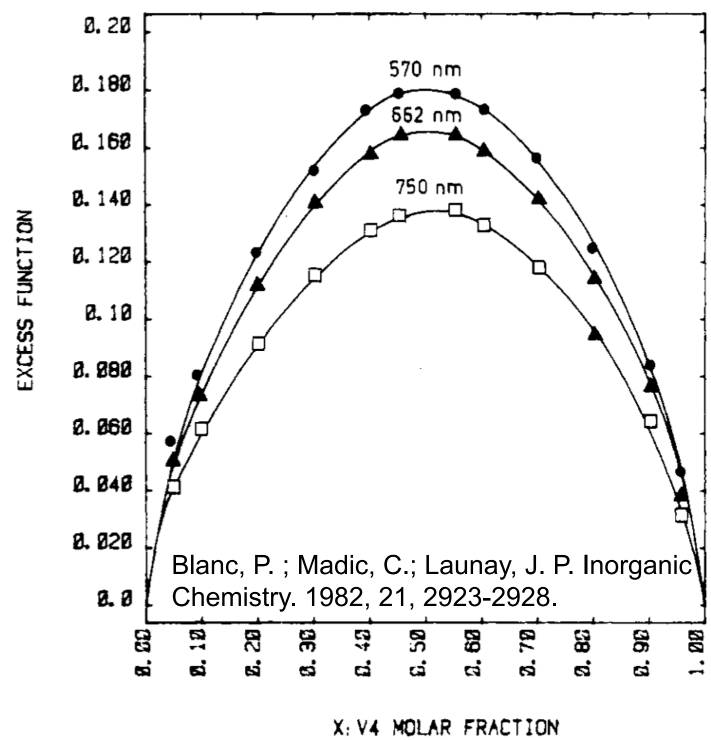






1:1 Complexes Have Been Observed in VO^{2+}/VO_2^+ Solutions in $HClO_4$



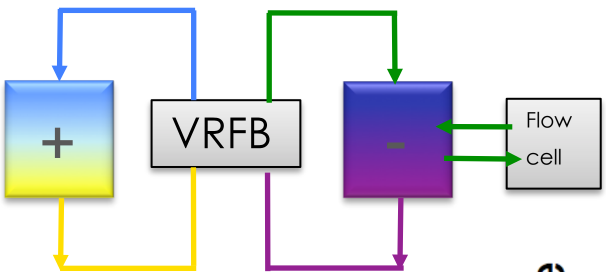


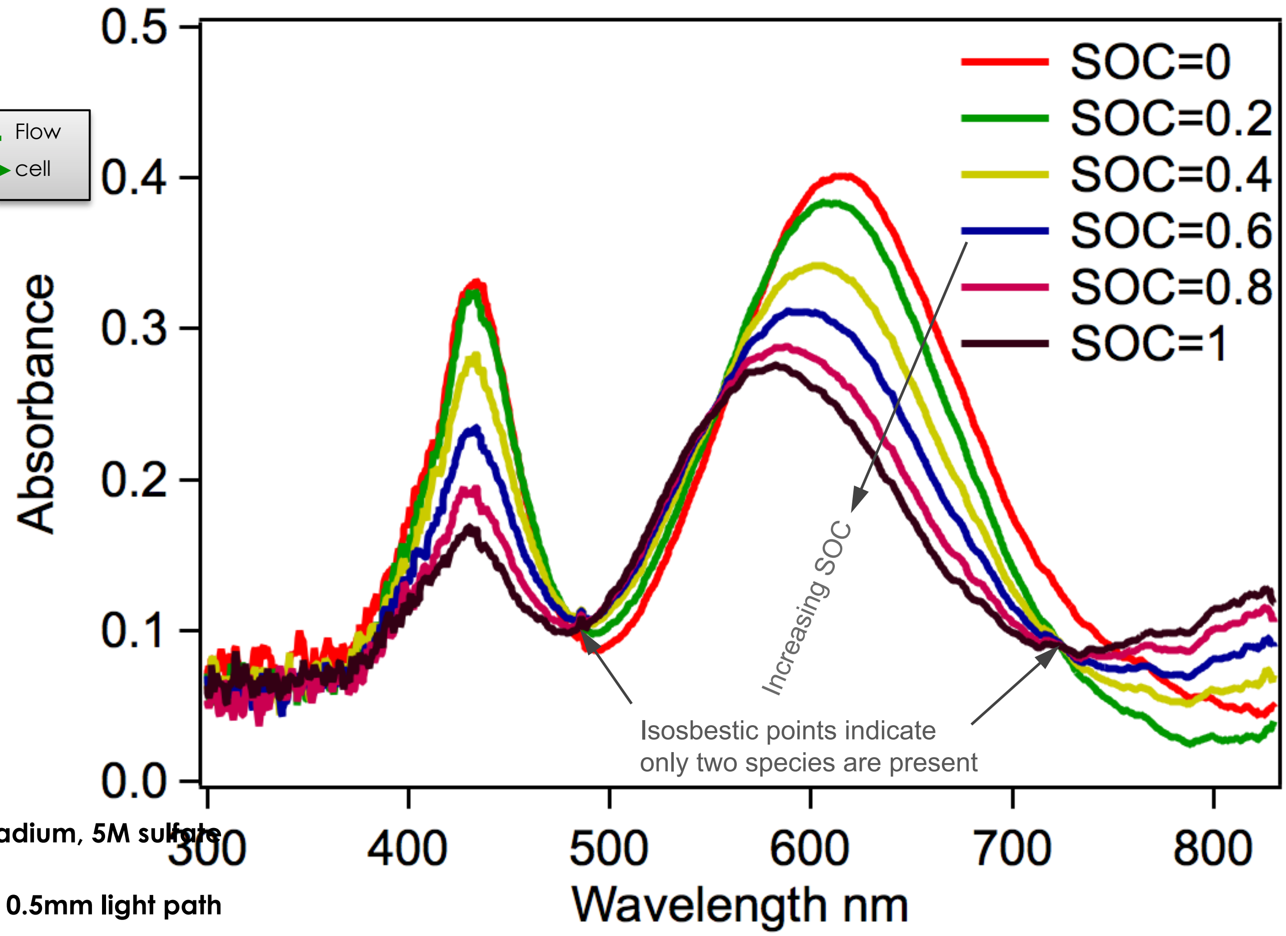
Blanc, P. ; Madic, C.; Launay, J. P. Inorganic Chemistry. 1982, 21, 2923-2928.

- The peak in excess absorbance near 0.5 SOC suggests a 1:1 complex, $VO^{2+} + VO_2^+ \rightarrow V_2O_3^{3+}$
- Also inferred from broadening of ^{51}V NMR peaks*

* (Okamoto, K. Woo-Sik, J. Tomiyasu, H.; Fukutomi, H. Inorganica Chimica Acta. 1988, 143, 217-221.)

Absorbance of V2+/V3+ in an Operating VRFB





1M Vanadium, 5M sulfate

0.5mm light path

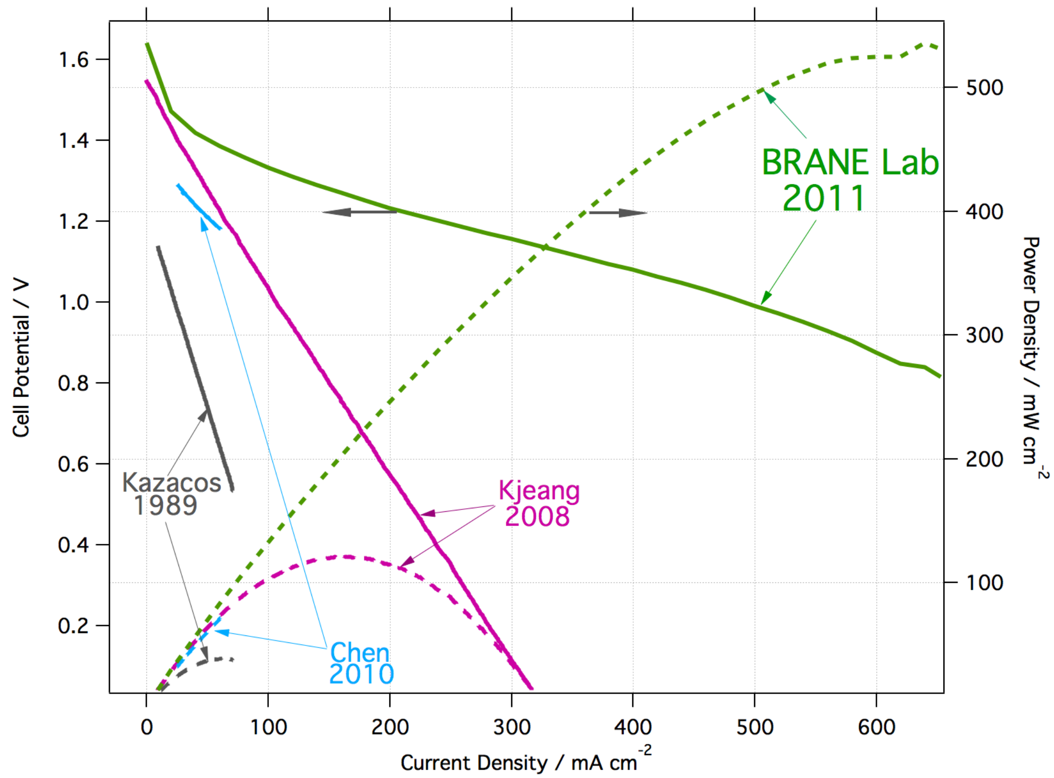
Spectrometer on flow cell bypass

Parallel chronoamperometry on 25 cm² battery

SOC determined by coulometric counting

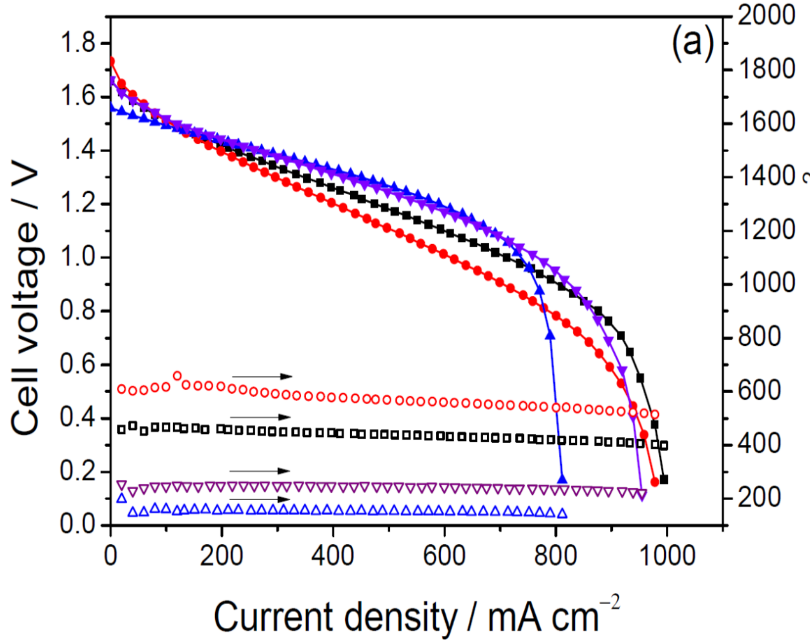
Dramatically Increased Performance

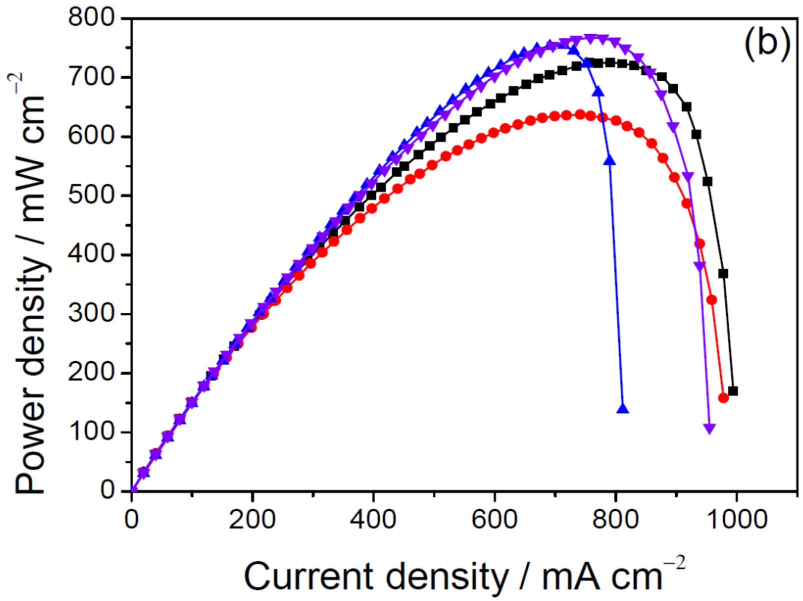
Increased VRB Max Power Density by ~10x



Comparison to literature reports of performance

Performance gain obtained using new architecture, materials





Peak Power density ~ 800 mW/cm^2

Core Issues

It will eventually come back to the membrane!

Cost Modeling is tricky.

As we increase power density/current density, membrane resistance will become limiting again