# Component Research for Redox Flow Batteries and 'Open' Batteries

**Tom Zawodzinski and Zhijiang Tang**

**With help from Che-Nan (Josh) Sun,**

**Alan Pezeshki (UTK)**

**Cy Fujimoto (SNL)**

**Thanks to: Imre Gyuk (OE)**

**Team at UTK; Bredesen Center**

# Goals and Tasks

1. **Demonstrate improved performance of RFBs in pre-competitive work**
   - **Chemistry agnostic; we look at *key representative processes*--- VRBs + New directions**
2. **Develop rational diagnostics to guide component selection**
   - **Component selection refers to our tests being used to pinpoint key requirements, guiding development**
3. **New 'Open' Battery Directions for Higher Energy Density**
   - **Metal/air**
   - **Non-aqueous system**

# Approach

## Working at Component, Cell Level

### What limits performance of an RFB?

1. Membranes
   a. Comparing effects in PEMs, AEMs
2. Electrodes
   a. Effect of electrode structure on performance
   b. Concentration polarization issues
3. Broadened scope to other types of open battery systems (Metal/air, Non-aqueous)

# Increasing Performance
# A Multi-level Issue

**<u>First Level</u>: Improve Power Density**

**We are satisfied with our work on this.**

**<u>Second Level</u>: Cycling**

**New challenges not found in steady state**

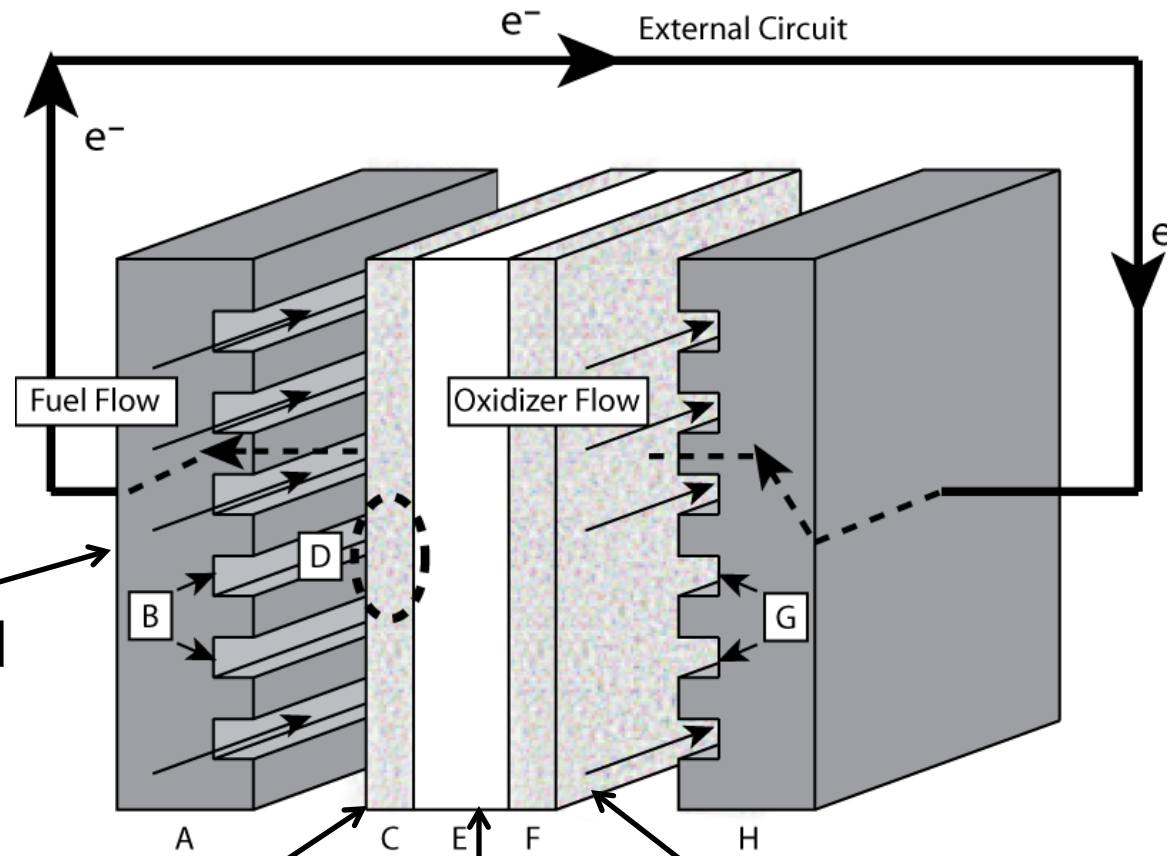
**Mass transport/concentration polarization, Capacity fade**

**This year: develop data to understand effects of different materials**

**<u>Third Level</u>: Durability and Side Reactions**

**Work ongoing but slowed due to budget issues**

# Key Components




Bipolar Plate with flow field

Negative electrode

V(II)/(III)

Membrane

Positive electrode

V(IV)/(V)

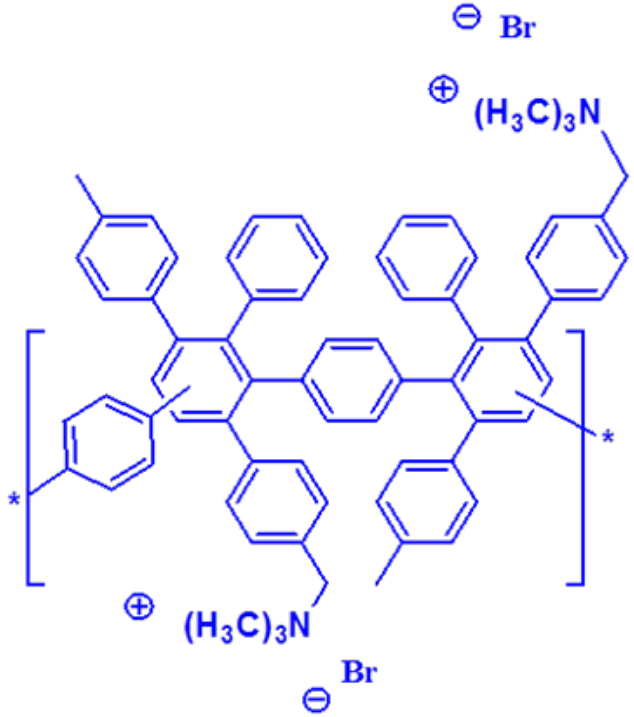
# MEMBRANES

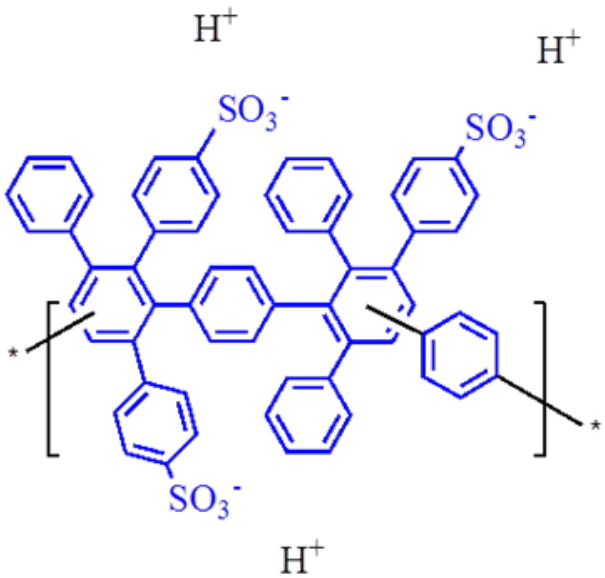
# Membranes: Recent Work

- **Focus on comparing membranes**
- **Tested more than 20 membranes of a wide variety of types (PFSA, Hydrocarbon, AEM); strong collaborations with SNL, 3M**
- **Here:**
  - **Comparison of PEM, AEM reveals previously unreported phenomenon**
  - **Transference effects different**

# QDAPP and SDAPP
# courtesy of Cy Fujimoto, SNL

## Same backbone, different ionogens



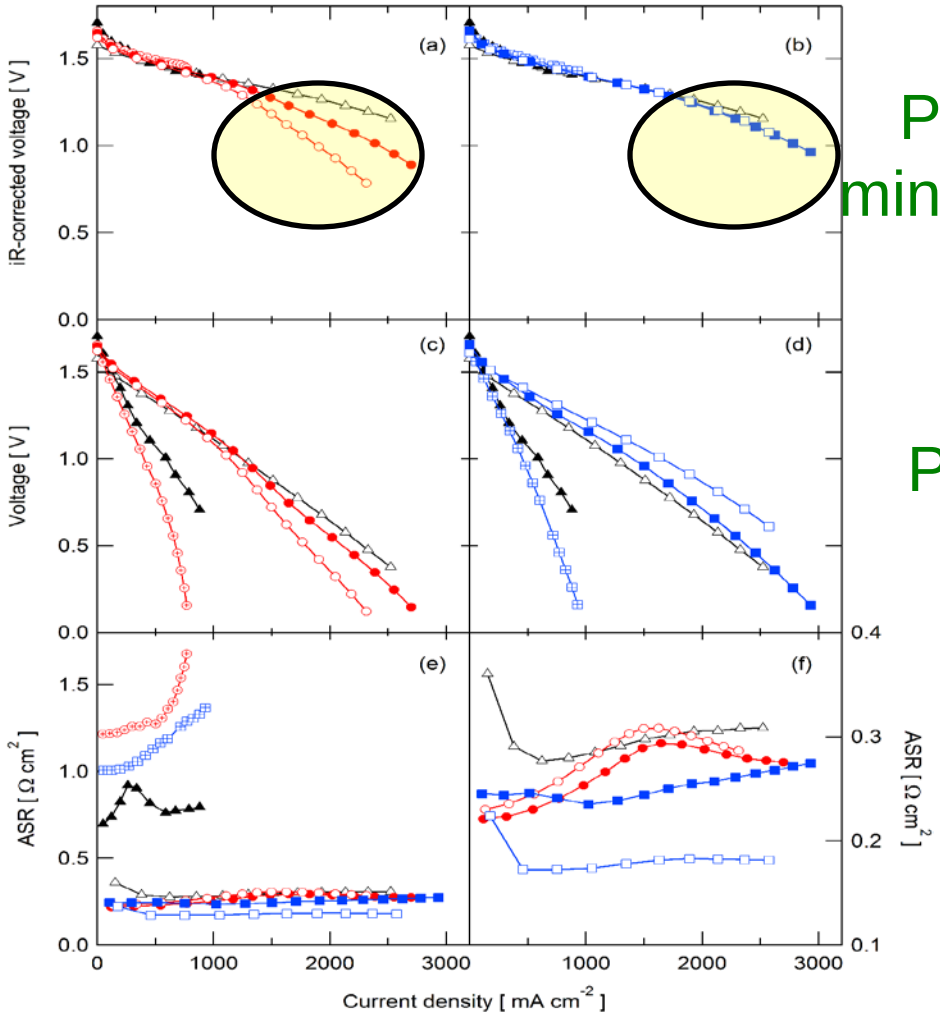




**QDAPP** **SDAPP**

# Polarization at 100% SoC

## AEM behaves differently from PEM

Within each box different curves are for membranes with different SoC




Performance minus Resistance

Performance

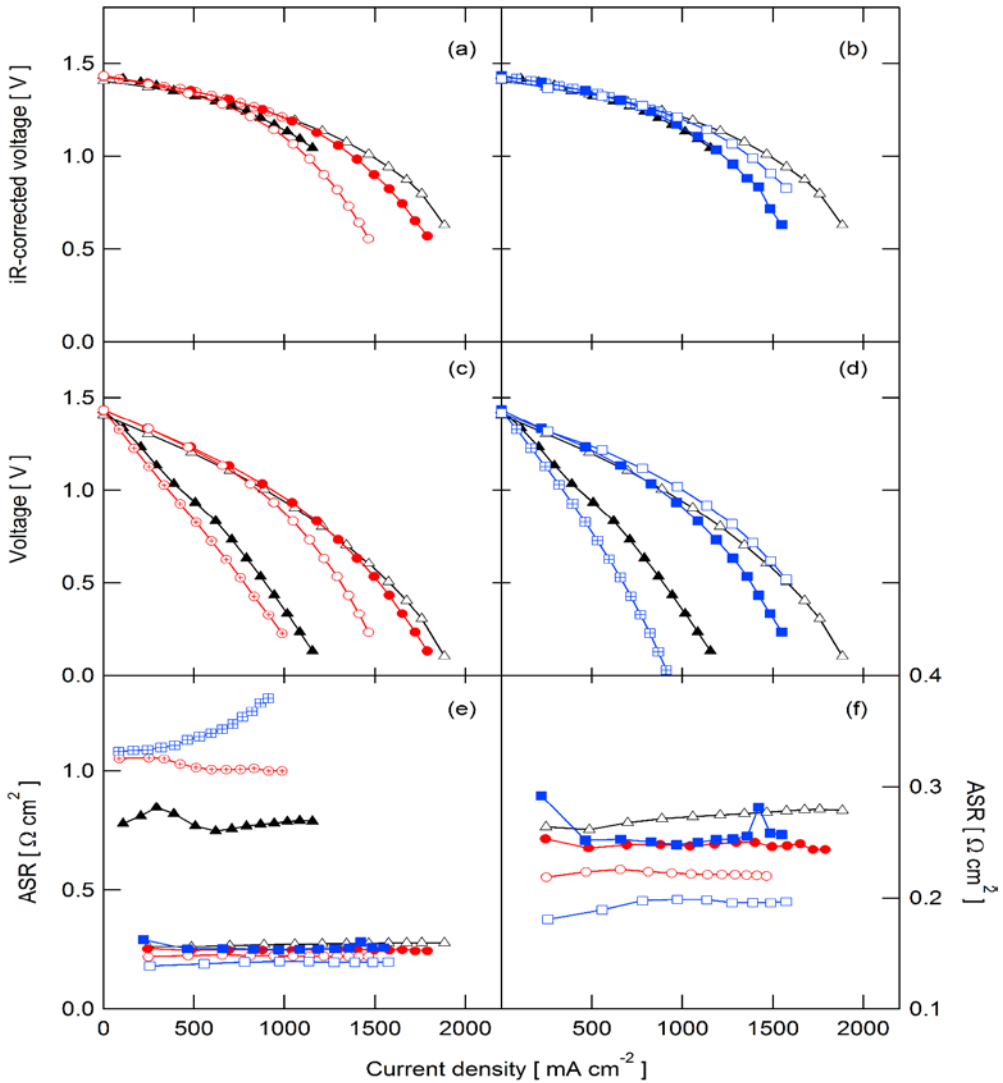
Resistance

**QDAPP** **SDAPP**

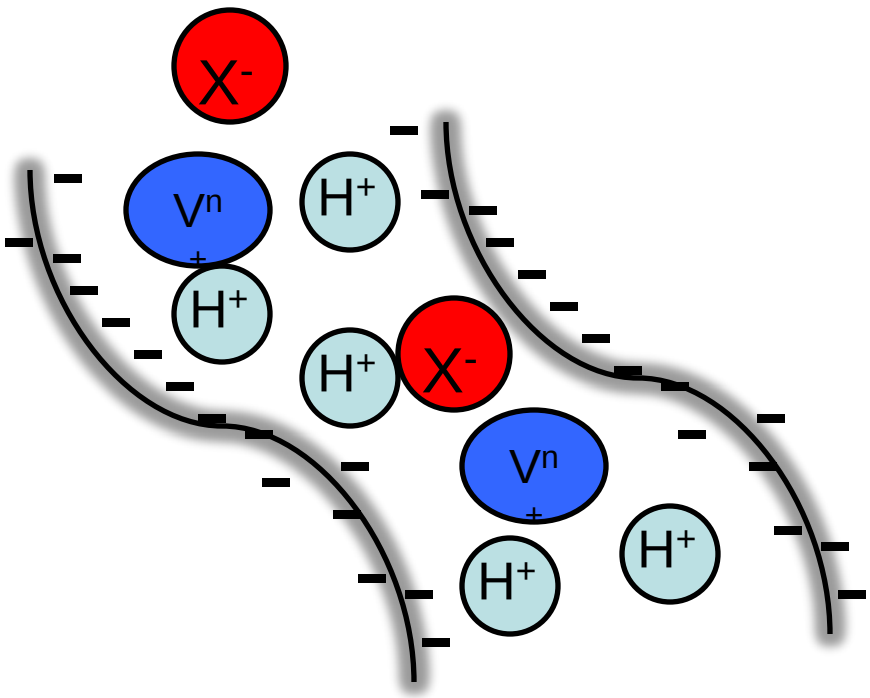
# Polarization at 50% SoC

## AEM behaves differently from PEM

Within each box different curves are for membranes with different SoC

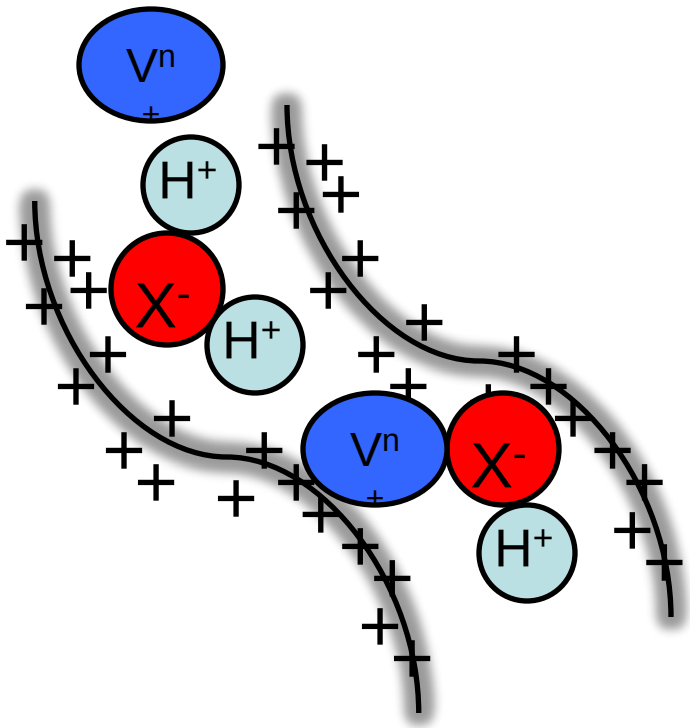


# Relative Mobility of Anion is Key to Membrane Transference Effects




PEM

$T_H > T_V >> T_X$




AEM

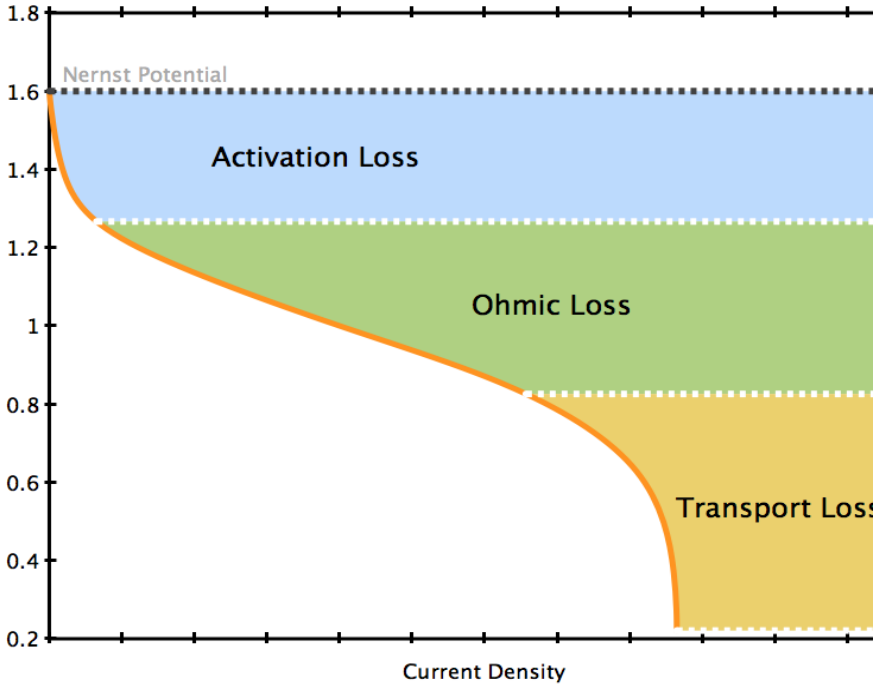
$T_X \sim T_H >> T_V$

# ELECTRODES

# Performance in Flow Systems

## Polarization Curves

not normally used in battery work!

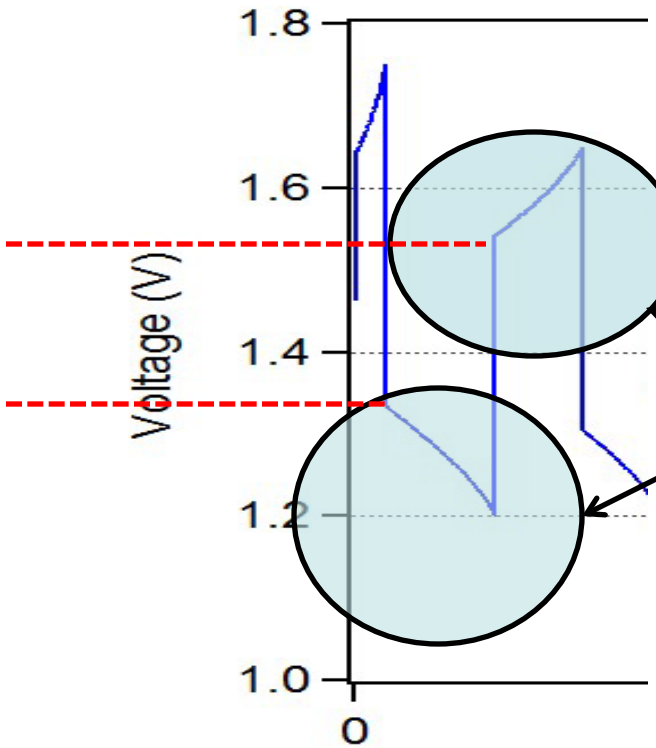


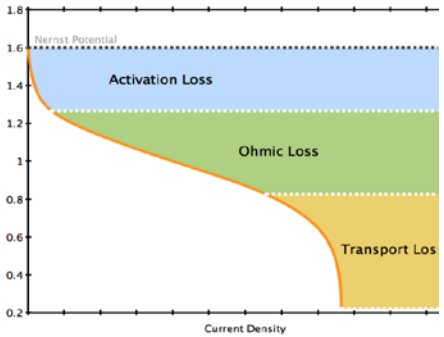

**We separate and measure (both charge, discharge):**

- **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**

Aaron, D. S.; Liu, Q.; Tang, Z.; Grim, G. M.; Papandrew, A. B.; Turhan, A.; Zawodzinski, T. A.; Mench, M. M. Journal of Power Sources 2012, 206, 450–453.

# Voltage evolution during cycling



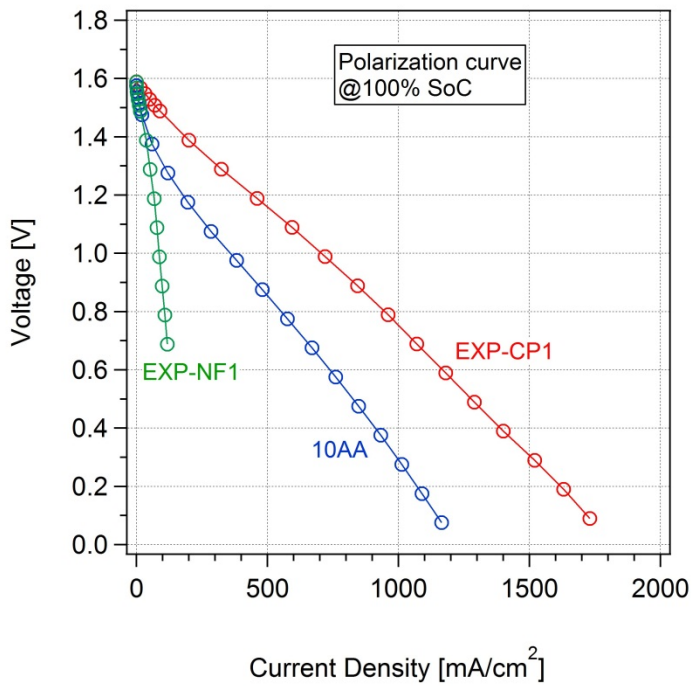




**What's going on here? Same rate is demanded but voltage efficiency drops**

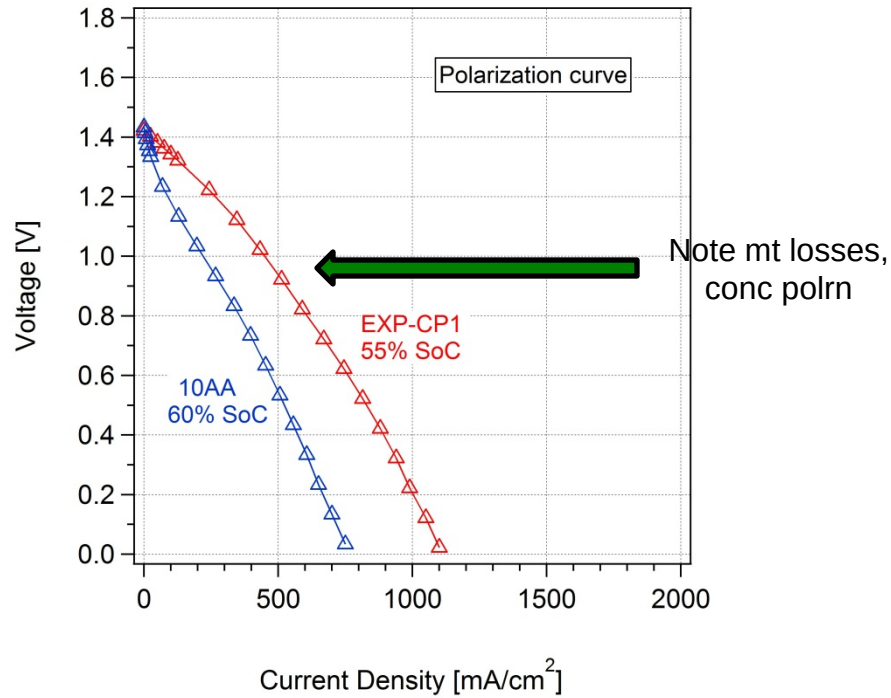
Onset of ***concentration polarization***

# Concentration Polarization Effects also Reflected in Pol Curves with Lower SoC

High SOC




50% SOC




**Test conditions**

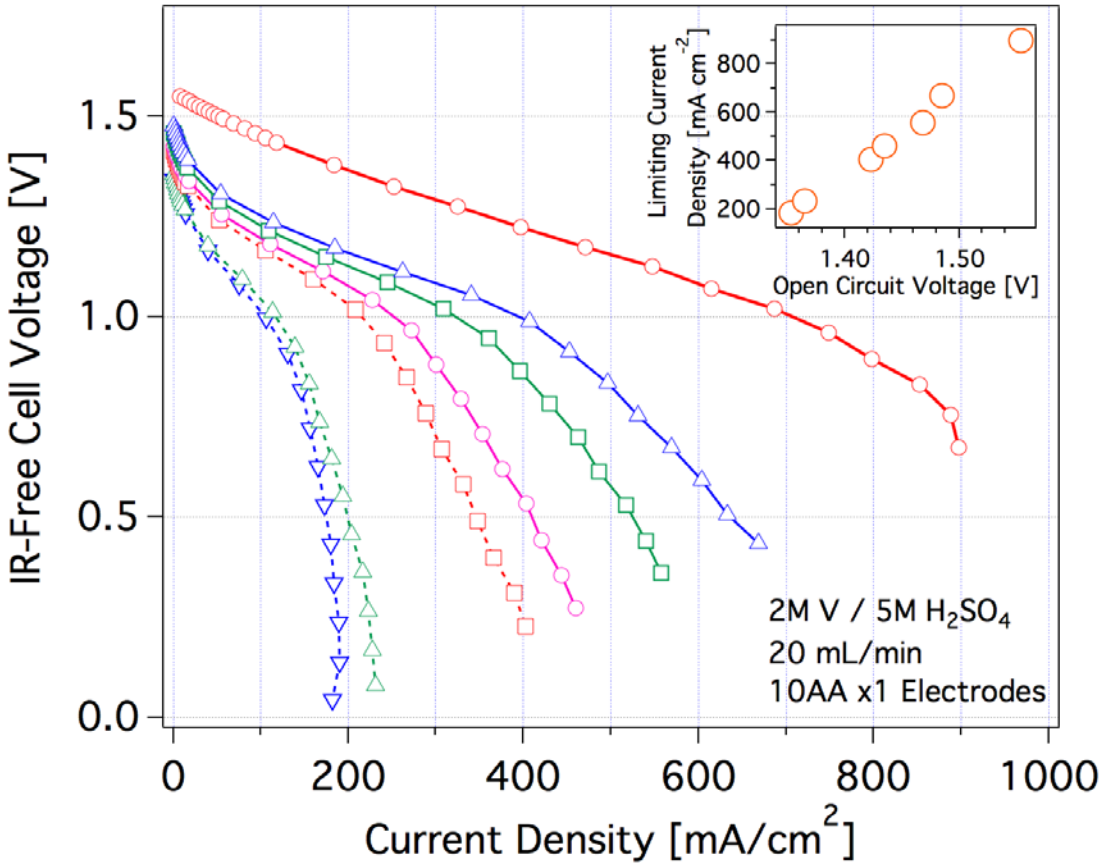
Electrode thickness ~ 1200µm per side, Membrane : Nafion 117

Solution : 0.8MV, 4M$H_2SO_4$ ,Single pass, Flow rate ~ 22mL/min

Temp. : 21$^o$C, Same cell hardware

# SoC Dependence of Pol Curves

## Single Pass, High Flow Rate Isolates Effects




Pol Curve measured with **low utilization** but at **fixed, lowered SoC**

Allows us to separate effects of intrinsic lower SoC from those driven by lower reagent concentration along channel

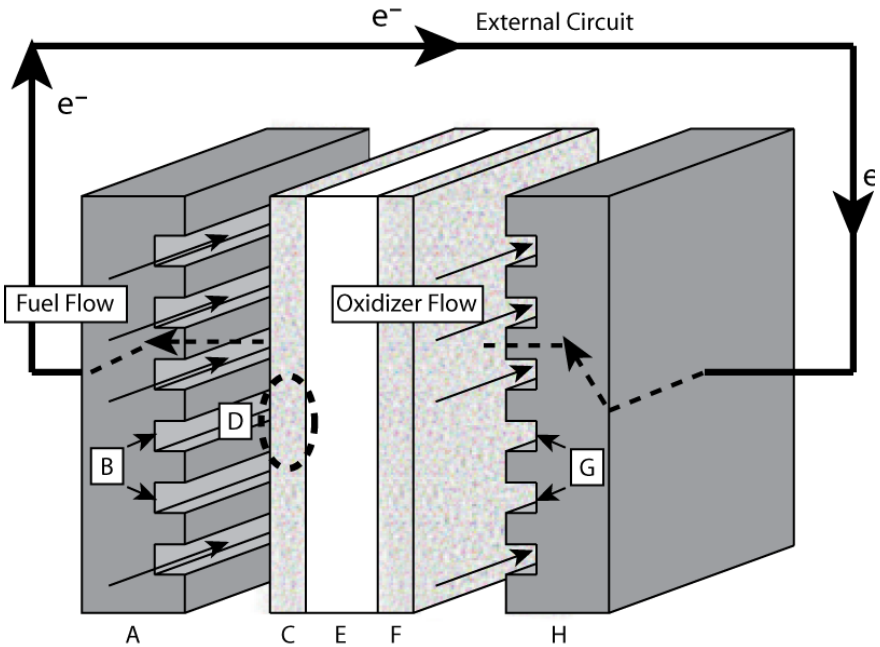
This is what we are working to overcome

# Managing this Effect

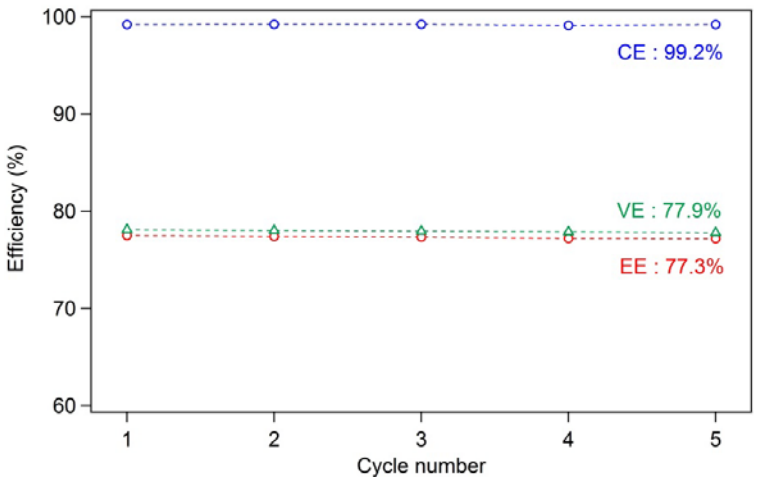
## Electrode Properties are Critical

## Transport at Flow Field/Electrode Interface

Flow-by Configuration




Cell Efficiency @ 500 mA/cm$^2$




Now cycling between 20% and 80% SoC

# Conclusions from Component Study

**Two types of concentration polarization identified**

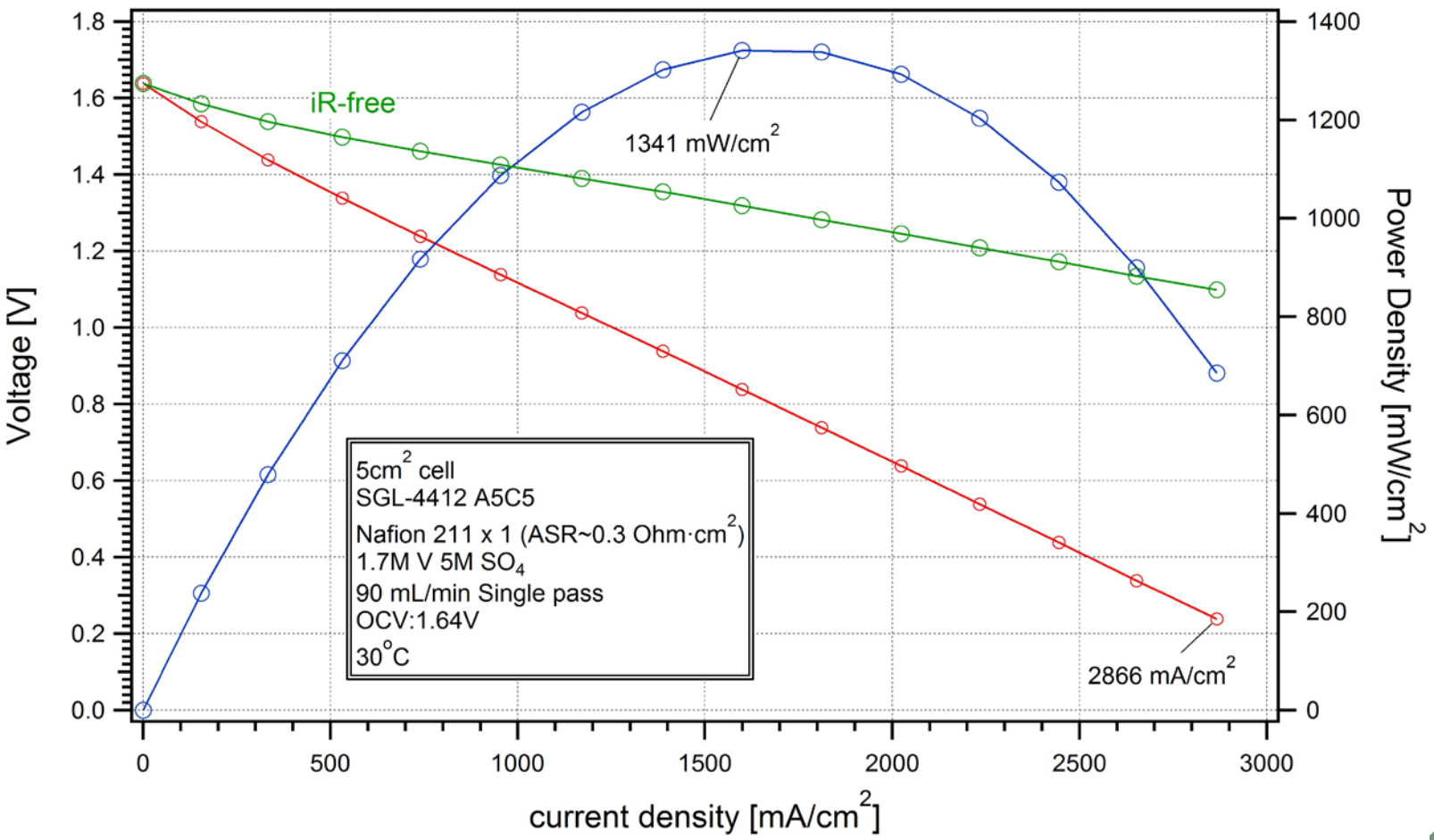
- **One due to transference effects in membrane**
- **One from slow transport within electrode**

**Minimizing concentration polarization:**

- **Use cation exchange membrane**
- **Improve electrode/flow field interface**

# Recent Results (2012: Basis for Analysis)

## We have reached an ohmic limit



This leads us to ask the question…

Can Non-aqueous Flow Batteries ever Meet these Requirements?

## We will focus on only one facet here

Performance

# Properties of Non-aqueous Solvents
# A Few Salient Properties for Our Analysis

1. **High voltage window**
2. **Relatively low electrolyte conductivity**
3. **Transference numbers not guaranteed to be high**

**<u>Also</u>**

**More expensive than water!**

**Flammability is a big issue**

# A Word or Two About Our Analysis

**This is designed to show UPPER LIMITS**

**Based on REAL DATA**

**NARFBs get credit for perfect kinetics and other advantages**

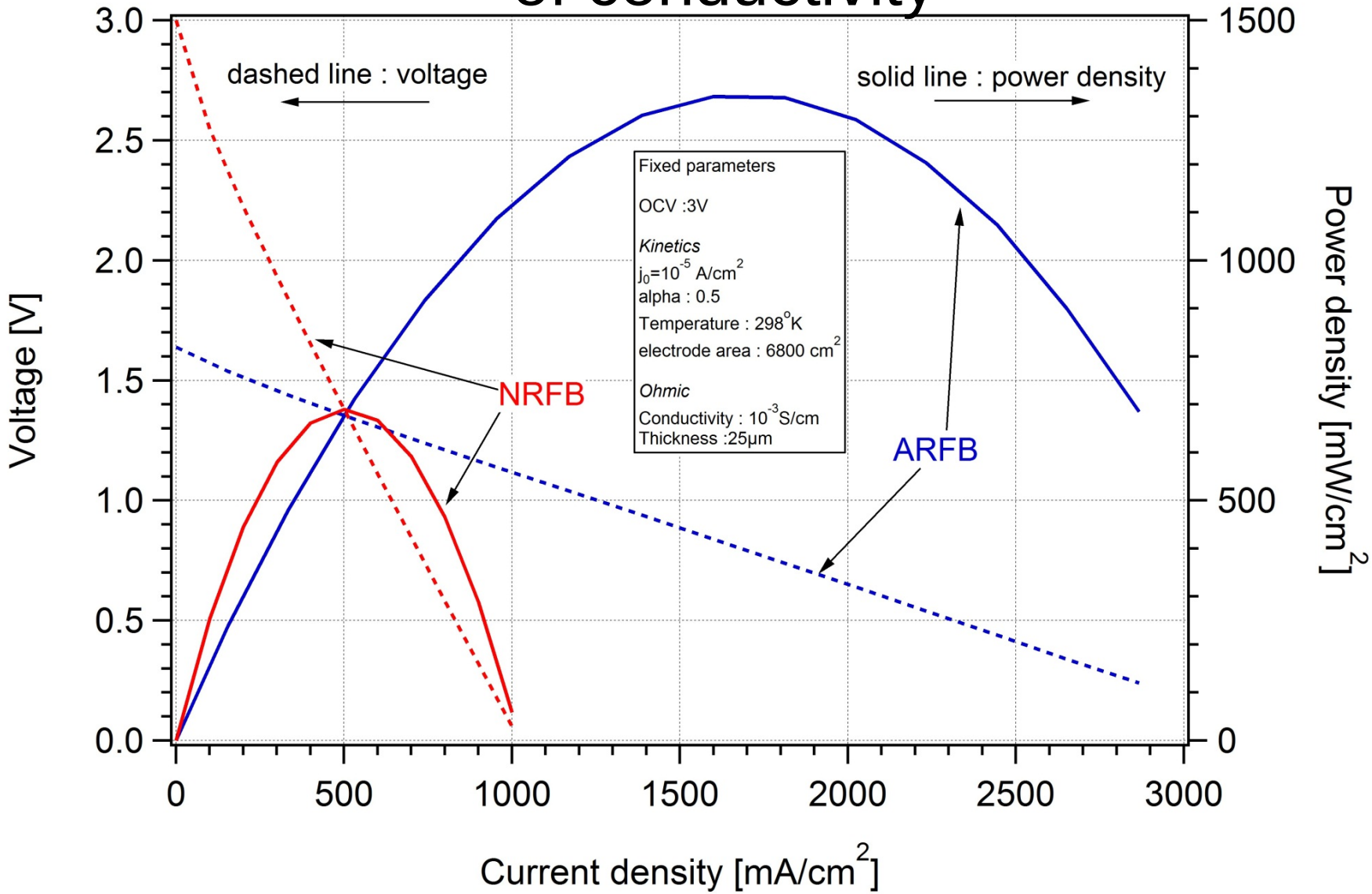
**Performance is the only consideration**

**IN SHORT: THIS IS THE BEST ONE CAN DO!!!!**

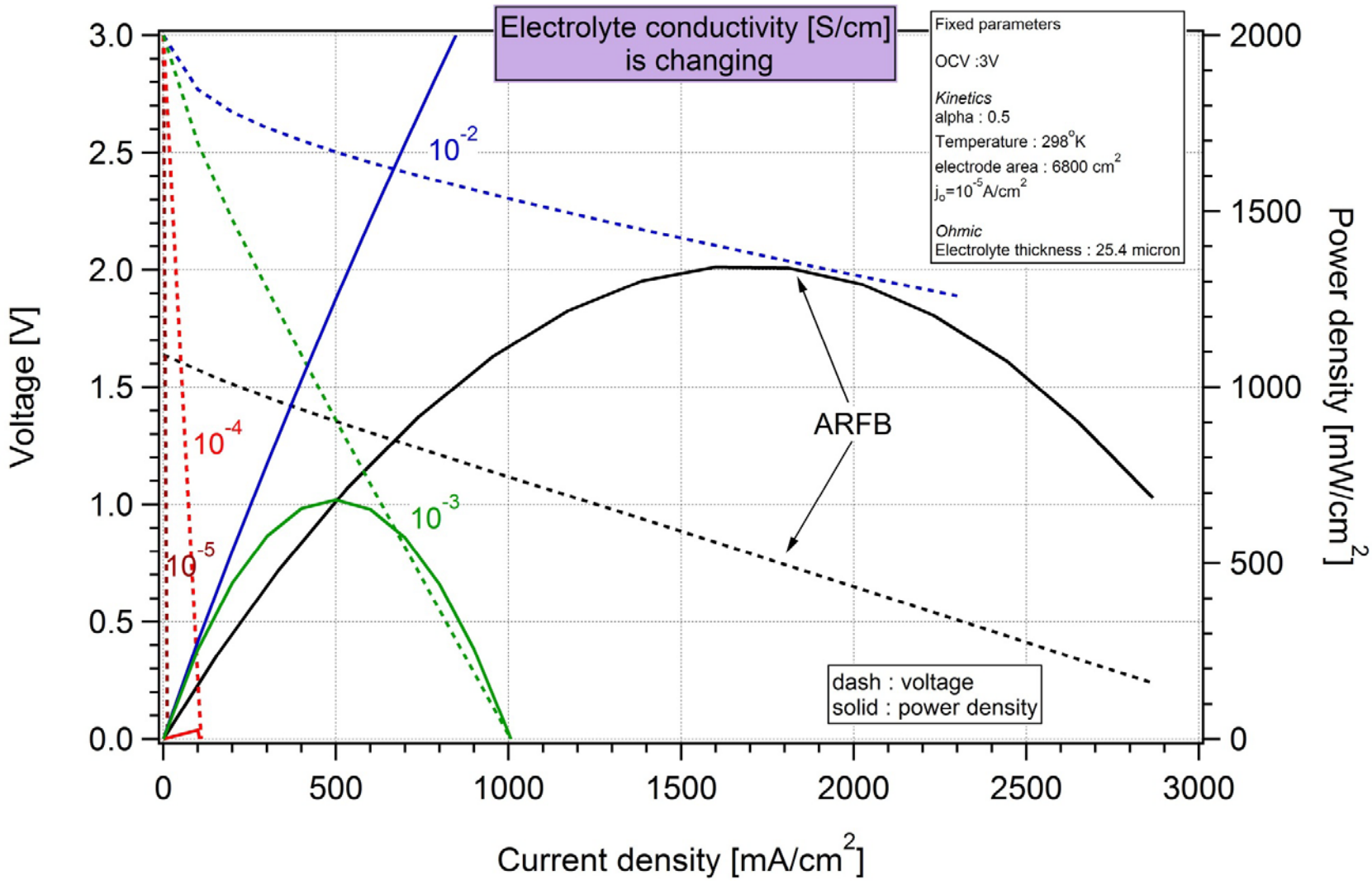
**Not just my contrary opinion, but <u>facts</u>**

**<u>We can only downgrade from this position!!!</u>**

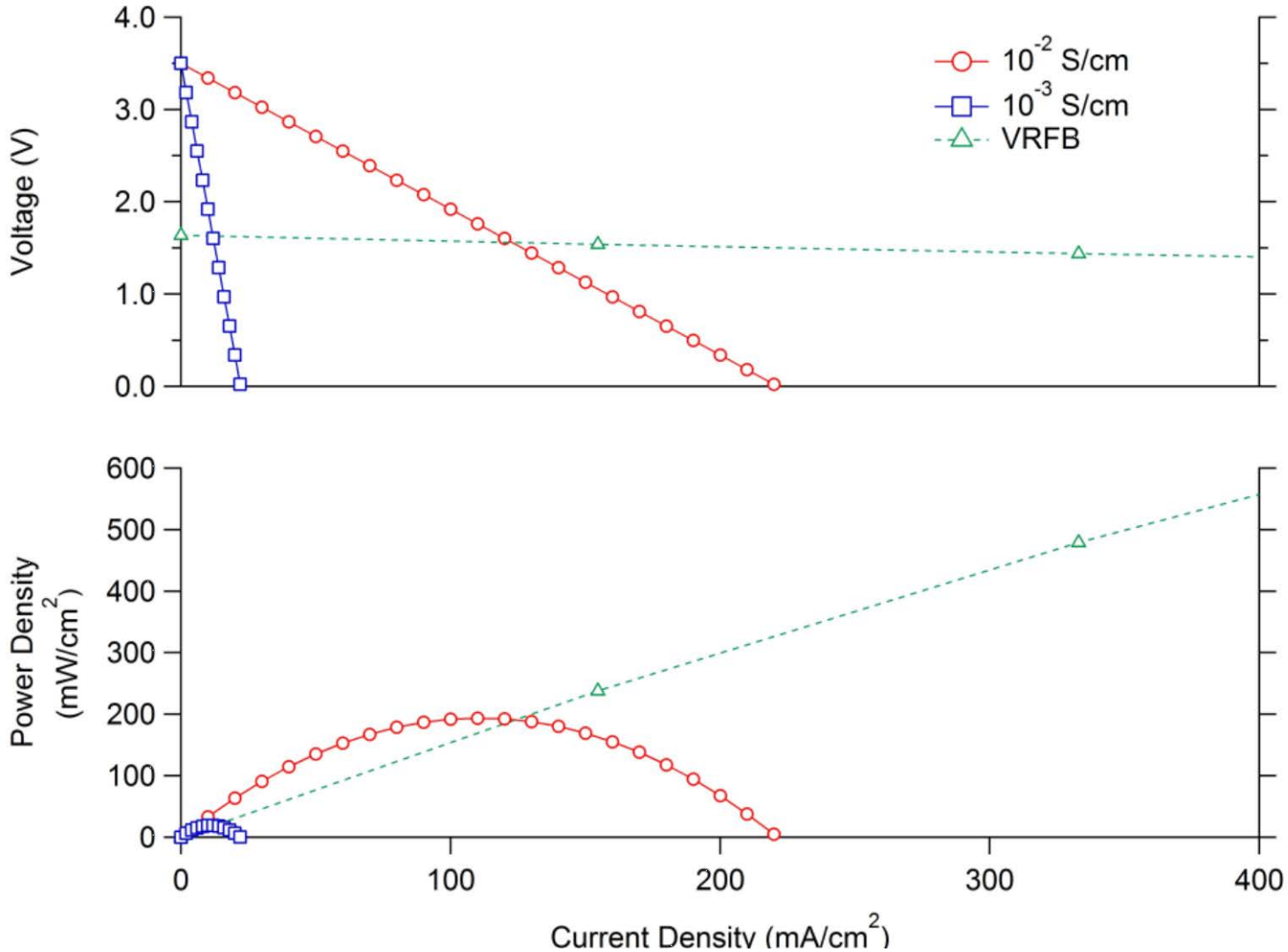
# Base Case:
# Ohmic limited, electrolyte only, typical lit value of conductivity



# Effect of Changing Electrolyte Conductivity Ohmic limited, electrolyte only



# Adding in Ohmic Loss in Electrodes




**Note the scale**

# Conclusions

**NARFBs fundamentally lag in performance unless one posits the best known conductivity**

- **Even then, it will be heroic to make them competitive**

**On top of that, one must consider electrolyte cost and safety issues**

**May be niches that take advantage of high energy density**

**BUT: we have a way out of this conundrum**

**STAY TUNED!**

# PROGRAMMATICS

# Summary of Accomplishments

1. **Analysis of Concentration Polarization Effects; Improvements in Cycling expected to follow.**
2. **New Directions based on studying key components**
   - **Strategy identified for high performance NA-RFBs**
   - **Another 'open' system-metal-air batteries: studying Zn processes to quantitate key equilibria; air electrode catalysts and structures for Hi Perf**
3. **Built necessary interactions with component producers and researchers to connect COMMERCIALLY AVAILABLE (and experimental) materials to developers**
4. **Translating research to WattJoule**
5. **Reporting results via publications: 6 submitted/published in FY15**

# 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**

# Next Steps

1. **Continue component studies to help identify key chemistry and structure aspects for improved membranes and electrodes**
   - **Improve cycling capabilities**
2. **Developing 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. **Moving on to promising chemistries beyond VRB, H-Br**
   - **Metal electrodes, air electrodes**