Non-aqueous RFBs: Notes on Performance and Some Economic Factors

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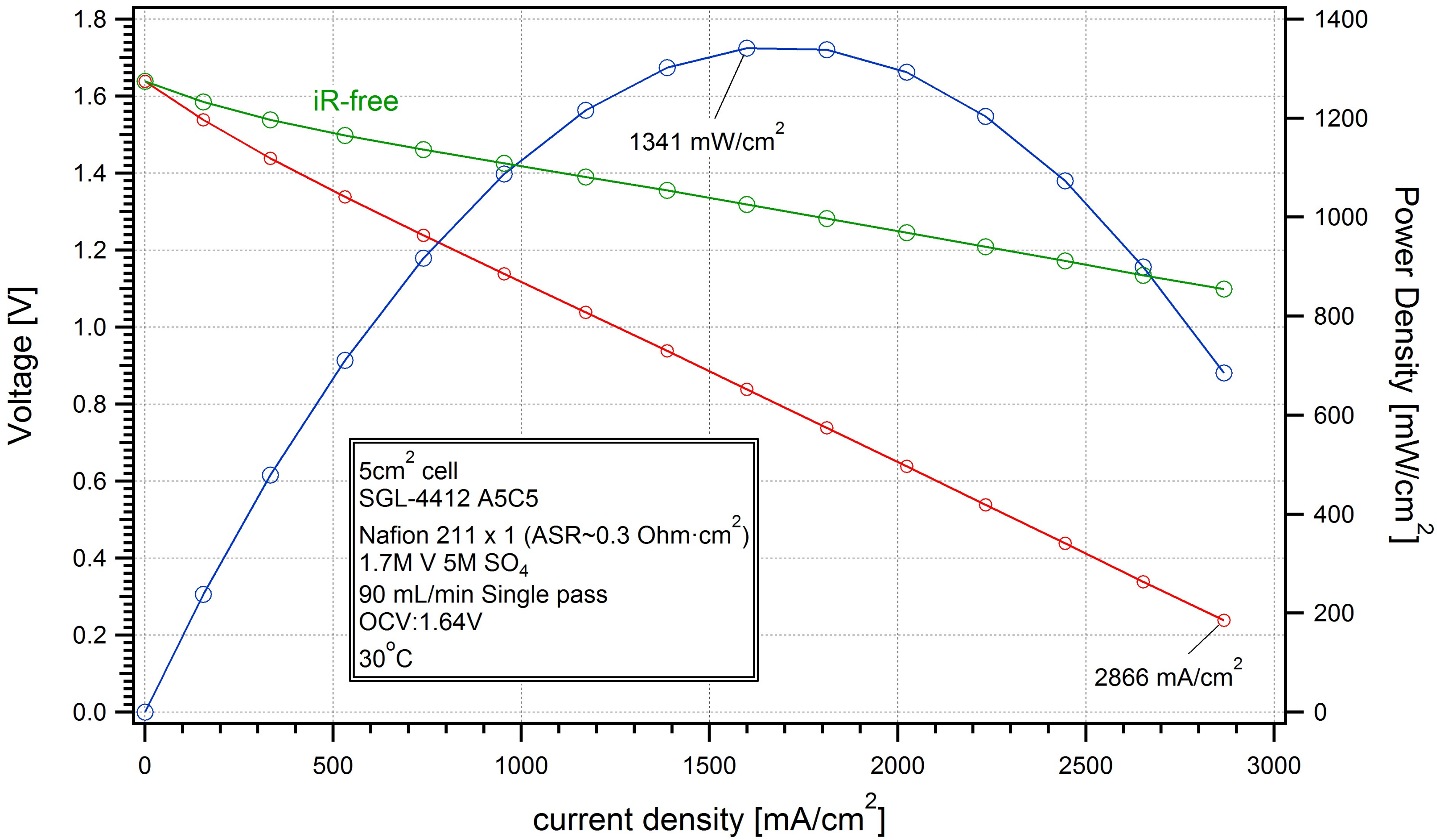
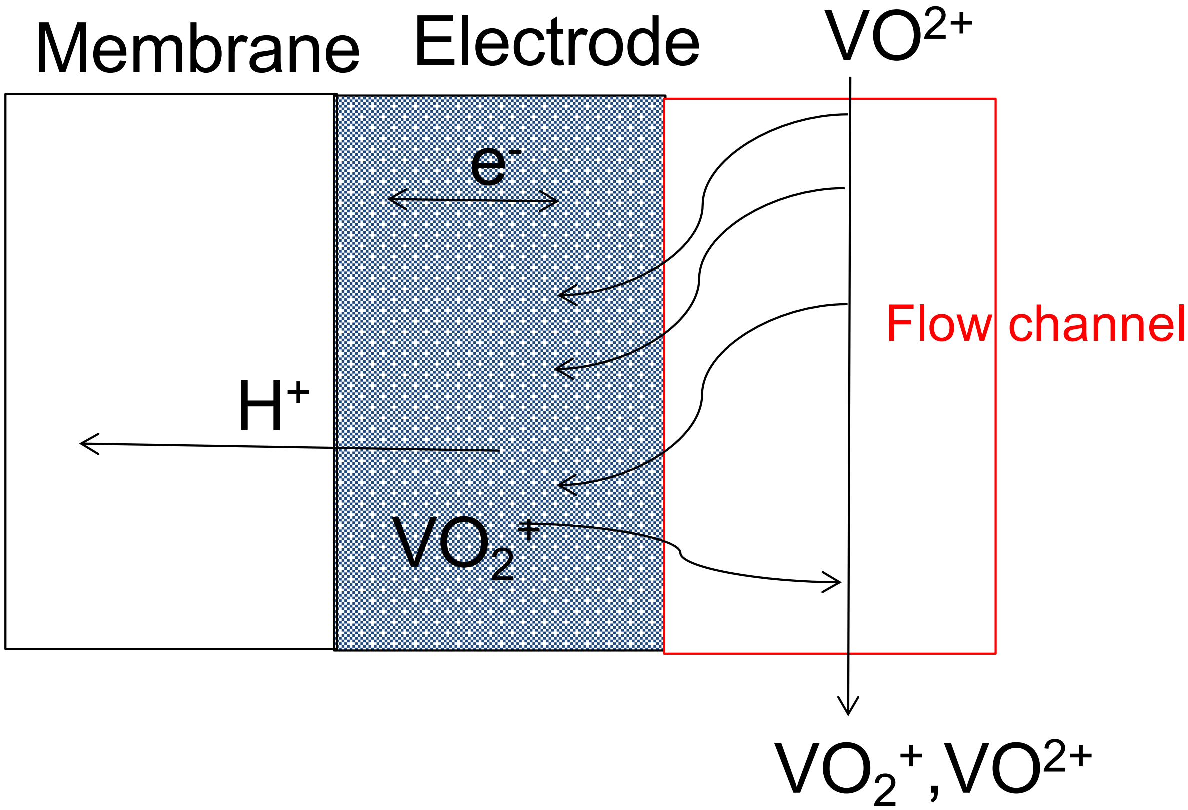
For Grid Scale Systems

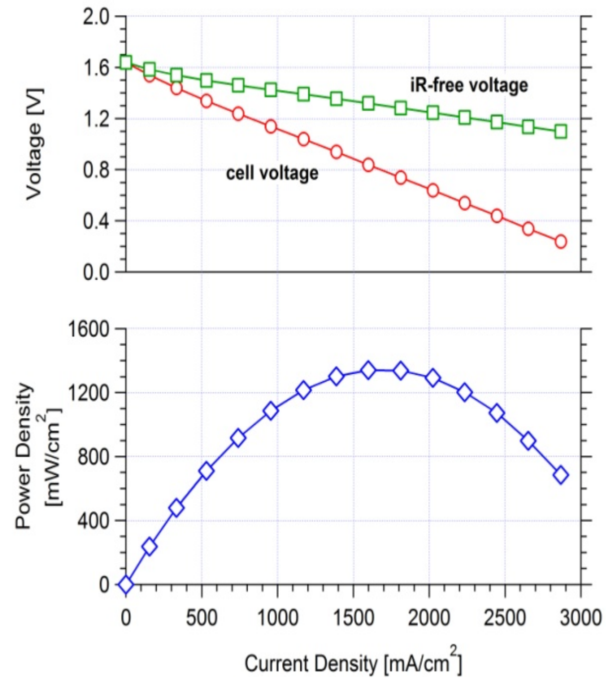
- Performance: power density high, energy density high (less critical)
- High efficiency operation (~90% RT)
- Cost: stack cost plus chemicals
  - $100/kW installed (may be a red herring)
- Safety: flammability, toxicity, intrinsic instability at high energy density

VRB Results : Basis for Analysis
We have reached an ohmic limit



Electrode is Mixed Conductor





Ionic processes deliver reagents into electronically shorted electrode

This leads us to ask the question…

Can Non-aqueous Flow Batteries ever Meet these Requirements?

Part 1:
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

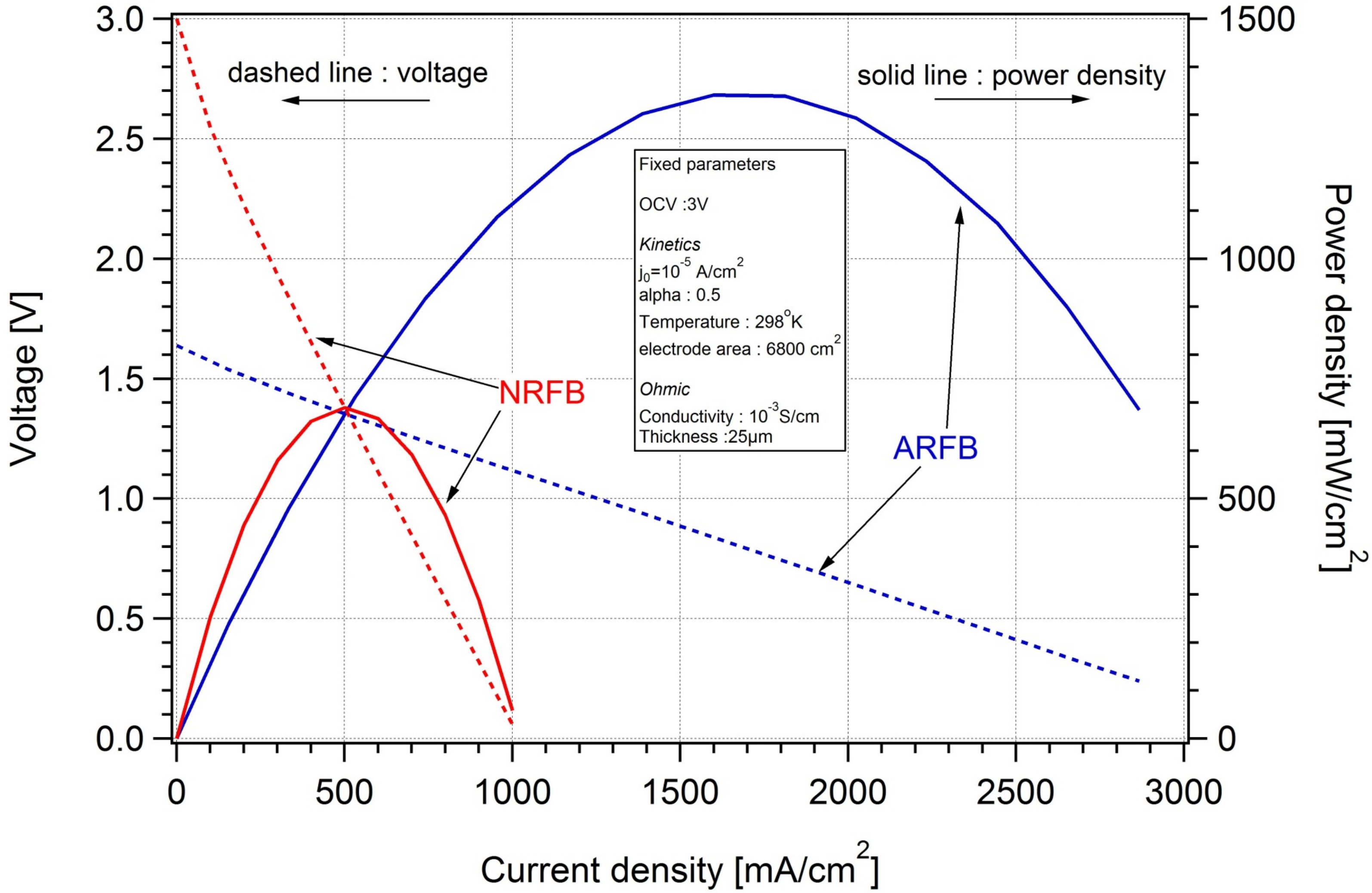
IN SHORT: THIS IS THE BEST ONE CAN DO!!!!

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

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

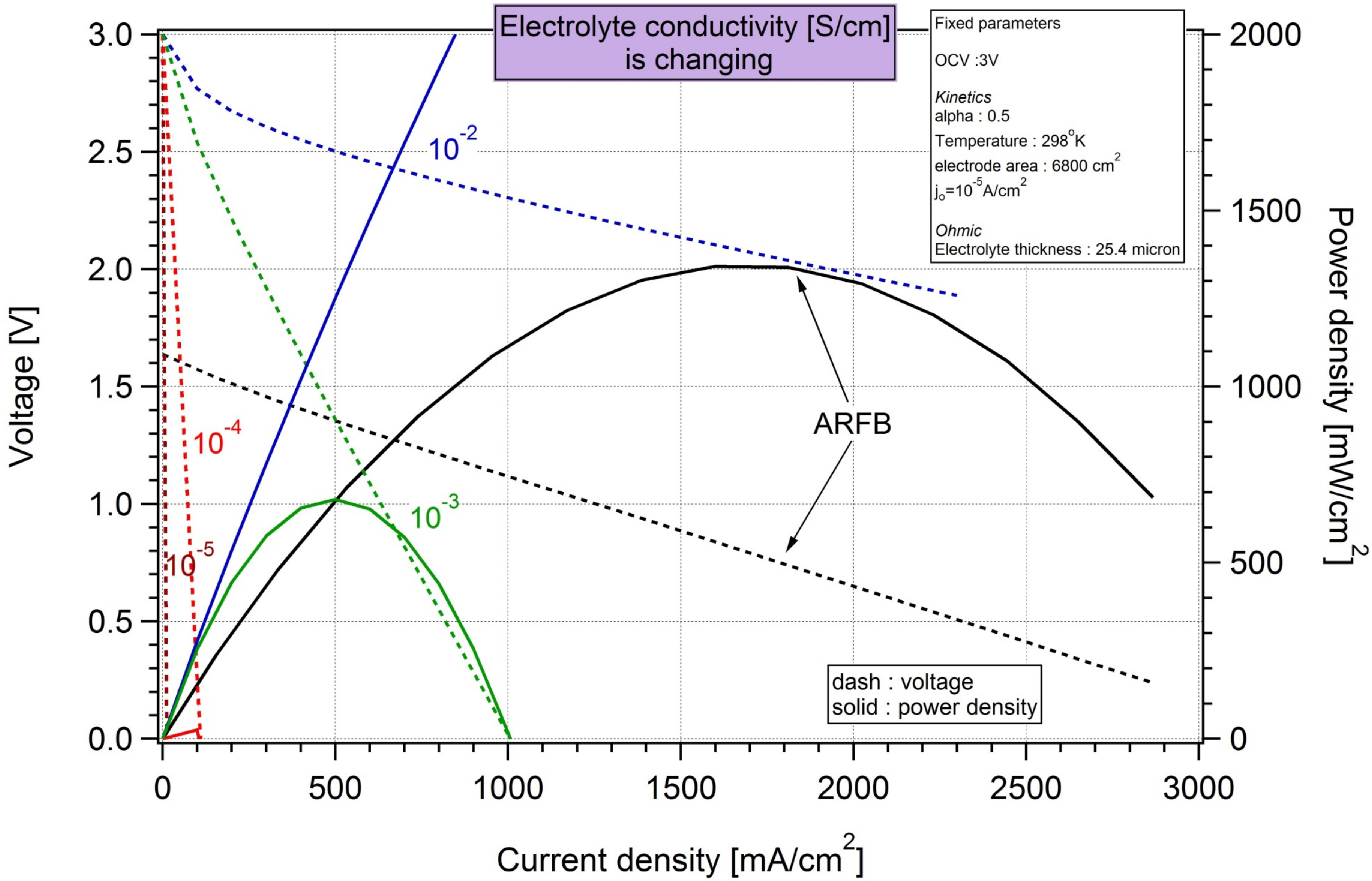
Base Case:

Ohmic limited, electrolyte only, typical lit value of conductivity



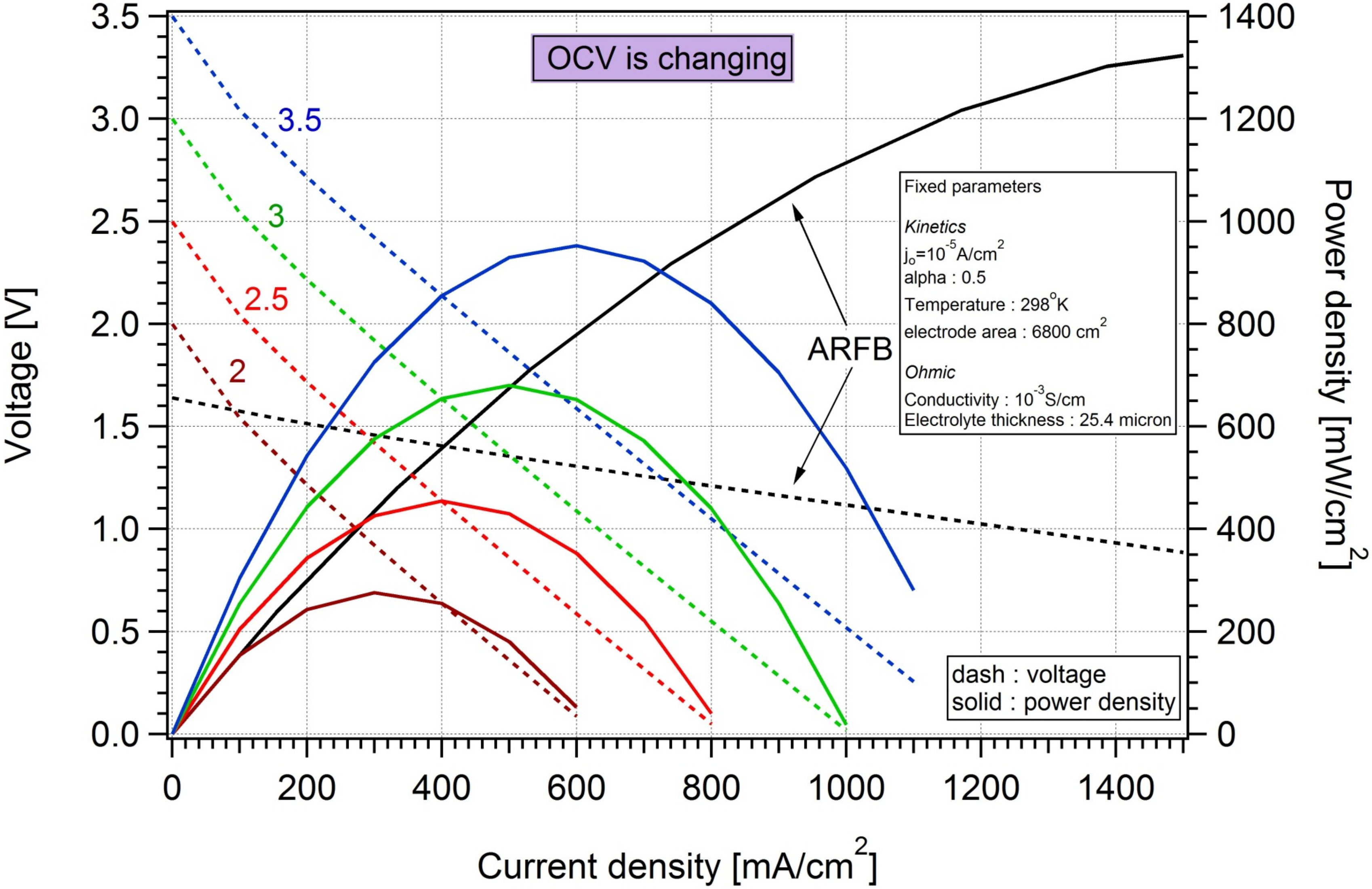
Effect of Changing Electrolyte Conductivity

Ohmic limited, **electrolyte only**, typical conductivity values

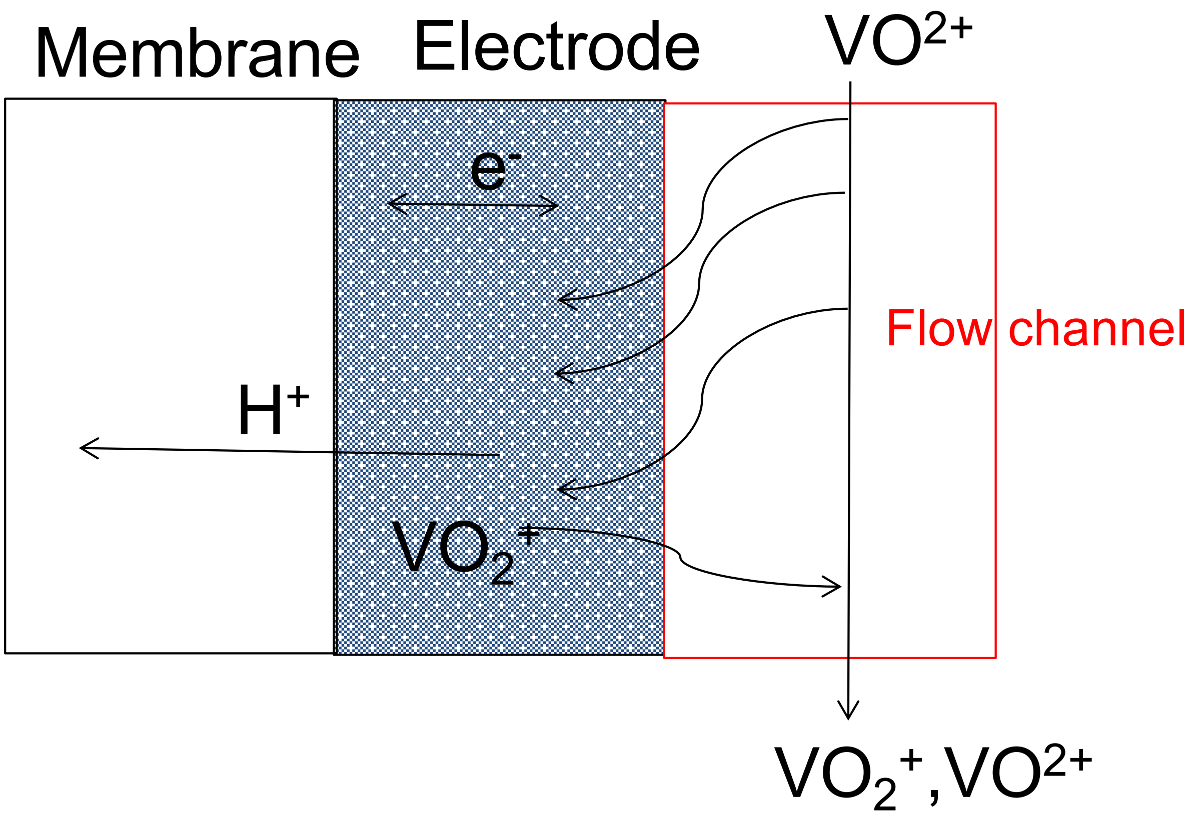


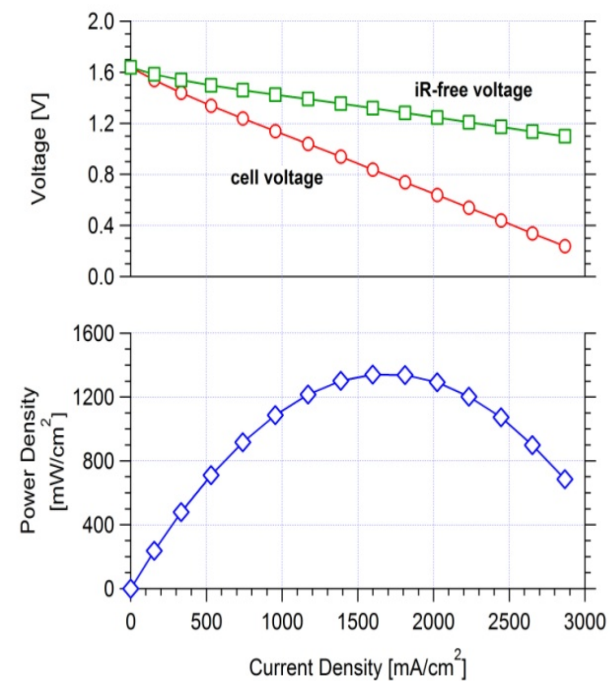
Effect of changing OCV from Base Case

Ohmic limited, electrolyte only, typical lit value of conductivity



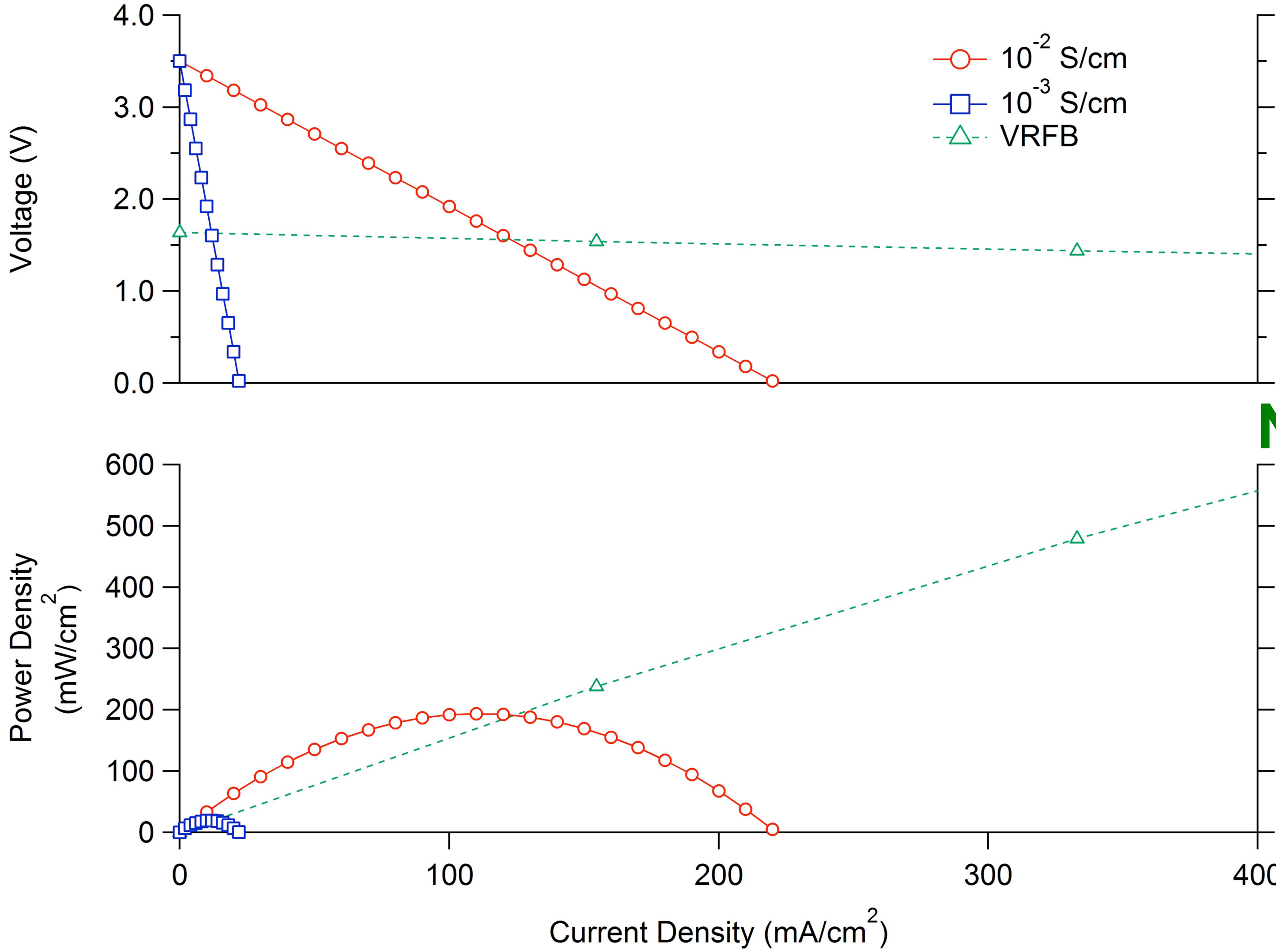
Electrode is Mixed Conductor





Ionic processes deliver reagents into electronically shorted electrode

Adding in Ohmic Loss in Electrodes



Note the scale

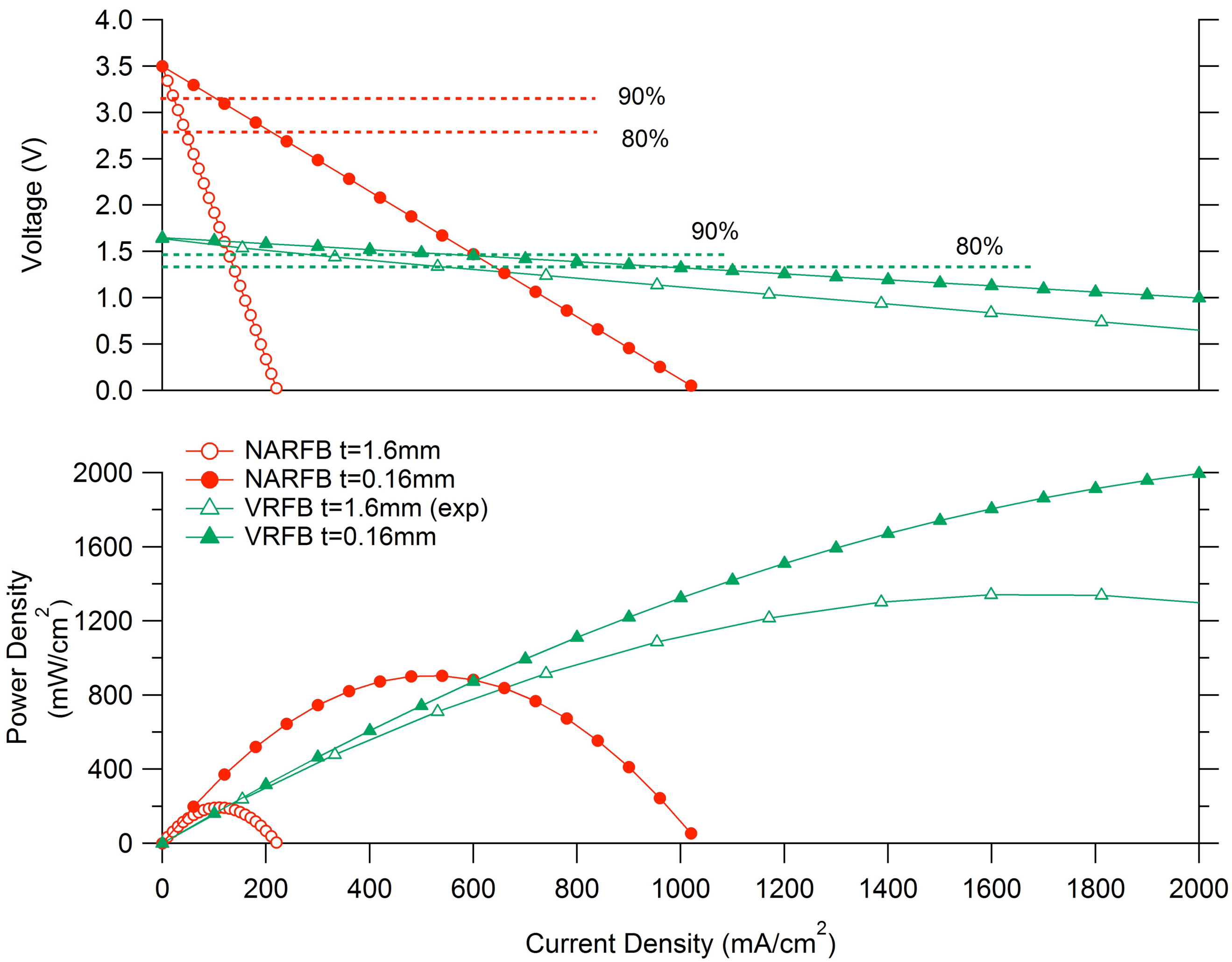
Room for Some Optimism

Recent Electrolyte Work in my Group

Kun Lou: based on understanding of molecular interactions between solvent, cations and membrane fixed sites….

Acetonitrile + membranes + certain cations give adequate conductivity and greatly reduced cross-over.

Design Possibility: What if we make the electrode 1/10th the thickness?



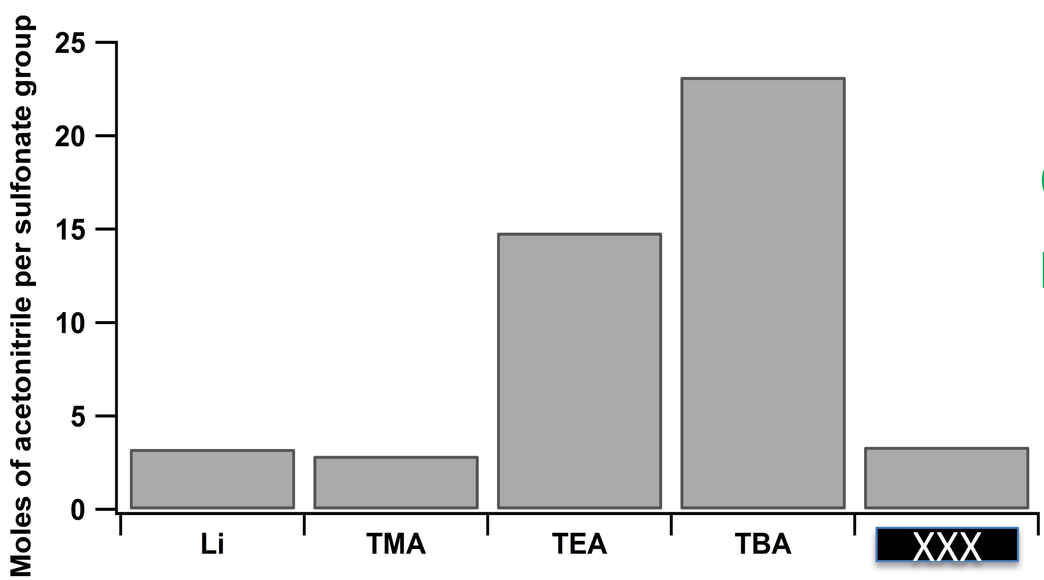
Design Possibility: What if we make the electrode 1/10th the thickness?

		VRFB		NARFB	
Electrode thickness (mm)	Operating efficiency	Current density (mA/cm^2)	Power density (mW/cm^2)	Current density (mA/cm^2)	Power density (mW/cm^2)
1.6	90%	332	495	22	69
	80%	688	908	44	123
0.16	90%	490	730	103	324
	80%	1010	1334	240	645

And remember:
the VRFB numbers are ~ half our current SOTA

Conductivity, Solvent Uptake of Different Membranes

Cation	Solvent	Ionic Conductivity (S/cm)
H	H2O	1.06x10-1
Li	Acetonitrile	1.10x10-3
TMA	Acetonitrile	2.43x10-3
XXX	Acetonitrile	7.83x10-3
TEA	Acetonitrile	1.14x10-2
TBA	Acetonitrile	1.81x10-2

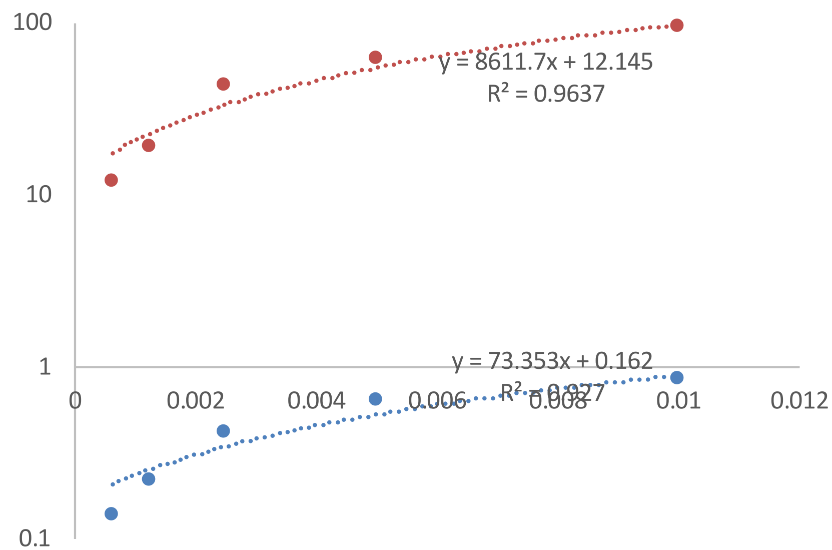


Good conductivity w/ minimal solvent uptake

Crossover measurement

Compare crossover of various membrane forms…

Modest cross-over during the course of a week!



Vacac calibration curve (UV-vis)

Part 2:

Some Economic Considerations

Basis

- DAYS LCOS calculation
- Include stacks, tanks, peripherals—assumed equivalent for aqueous, non-aqueous
- Stacks are essentially PEM stack-like with cheaper catalysts (none!) and membranes
- Pumping costs included
- Cost of money included (10% discount rate)
- Lifetime variable

- Very complicated pile of parameters: some ratios presented here based on cost, operational parameters

Operating Voltage Effects

- Assumed that NARFB operates at 2 V discharge, 3 volts charge per cell
  - For base case stack with aq: $LCOS_{aq}$
  - For base case stack with non-aq: $LCOS_{n}$
- $LCOS_{aq}$ = 0.22 $/kWhr (1 hr)
- $LCOS_{n}$= 0.08 $/kWhr (1 hr)

- **Advantage non-aqueous**

Operating Current Density Effect

- Assumed that NARFB operates at 2 V discharge, 3 volts charge per cell
- Assume the aq. RFB operates at 2x current density

- $LCOS_{aq}$ = 0.152 \$/kWhr (1 hr)
- $LCOS_{n}$ = 0.08 \$/kWhr (1 hr)

- **Advantage non-aqueous**

Including Cost of Electrolyte (Solvent)

- Assumed that NARFB operates at 2 V discharge, 3 volts charge per cell
- Assume the aq. RFB operates at 2x current density

- $LCOS_{aq}$ = 0.22 $/kWhr (1 hr)
- $LCOS_{n}$= 0.10 $/kWhr (1 hr) 1M V(acac)
- Advantage **non-aqueous**

Including Cost of Electrolyte (Complex)

- Assumed that NARFB operates at 2 V discharge, 3 volts charge per cell
- Assume the aq. RFB operates at 2x current density
- $LCOS_{aq}$ = 0.22 $/kWhr (1 hr)
- $LCOS_{n}$= 0.21 $/kWhr (1 hr) for 4x V(acac)/V
- 1M V(acac)
- Advantage **wash (no solvent cost)**

Scenarios

- $LCOS_{aq}$ = 0.22 $/kWhr (1 hr)
- **Scenario: double current density--** 0.11 $/kWhr (1 hr) for NA
- **Scenario: dilute complex, 0.1 M---** 0.385 $/kWhr (1 hr) for NA

Some Calculation Details

- Solvent: aqueous acid is free; non-aqueous solvent is not
- Solute: looked up typical multiples between metal complex (e.g. $VOSO_4$) and OM equivalent (e.g $V(acac)_3$) for several metals.
  - Assumed vanadium costs ~same as stack for a typical VRB; complex costs ~(OM/aq)*$Vstack
  - Also played with solubility limits; this affects mostly tank costs in calculation but probably affects performance as well.

Conclusions from LCOS Estimates

- If we look at stack costs, non-aqueous systems look pretty good.
- When we include the cost of solvents and solutes (based on today's prices), NA can be pricey
  - Scenario of boosting performance shows that this can be overcome with performance increase even with significant extra cost of solute.
  - High solubility is critical

Acknowledgments

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Key People
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