Redox Flow Batteries
New Active Species & Electrolytes

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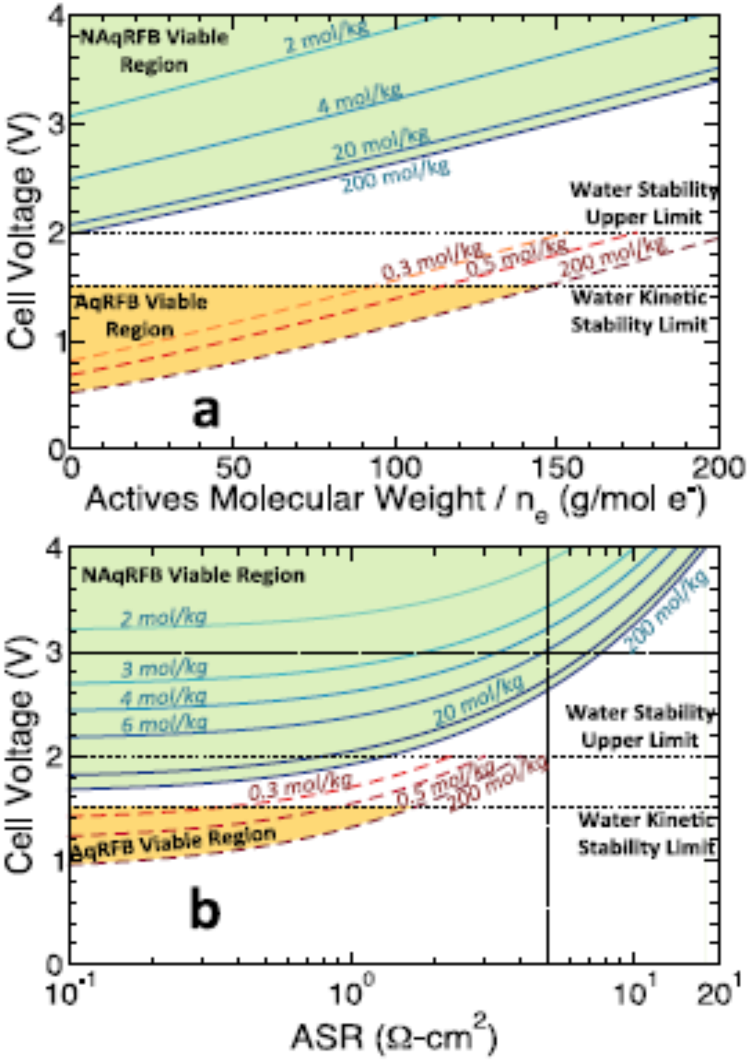
JCSER techno-economic analysis on RFB electrolytes

This work expanded upon JCSER's 2014 TEA modeling of RFBs

- **Electrolyte-centric approach** is used to develop ***explicit Design Maps*** for both NAqRFB and AqRFB that show paths to RFB System cost of < $100/kWh

Key viable parameters for:

- ***NAqRFB chemistries:***
  - ***Much larger Design Space than Aq***
  - **OCV ≥ 3.0V (prefer ≈ 4.0V)**
  - **ASR ≤ 5 Ω-cm^2 (10X higher than Aq)**
  - Redox-active concentration 2-4 mol/kg
  - Active-molecule MW ≤100 g/mol
- ***AqRFB chemistries:***
  - **OCV ≥ 1.0V (prefer ≈ 1.5V)**
  - **ASR ≤ 0.5 Ω-cm^2**
  - Active species: < $5/kg
  - Active MW ≤ 100 g/mol



F. Brushett (**MIT**), K.C. Smith (**UIU-C**), *et.al.*
Journal Power Sources (2016)

Example of high performance NonAqueous RFB**

- **Symmetrical cell with “Fc1N112” redox**
  - N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium bis(trifluoromethane)sulfonimide ([Fc1N112$^+$][TFSI$^-$]) and its oxidized form ([Fc1N112^{2+}][TFSI$^-$]$_2$) in tetraethyl-ammonium bis(trifluromethane)sulfonamide (TEATFSI) and acetonitrile (MeCN)
- **At 50% SOC:**
  - **Total cell ASR ≈ 2 Ω-cm^2** (at < 0.3 V)
  - Done with 2.55- and 25-cm^2 cells

- Demonstrates that electrode losses can be low with NonAq RFBs
- However, key challenges:
  - Membrane
    - Porous Celguard is not selective
  - Positive Reactant
    - Needs to enable acceptable OCV (≥ 3.0V)

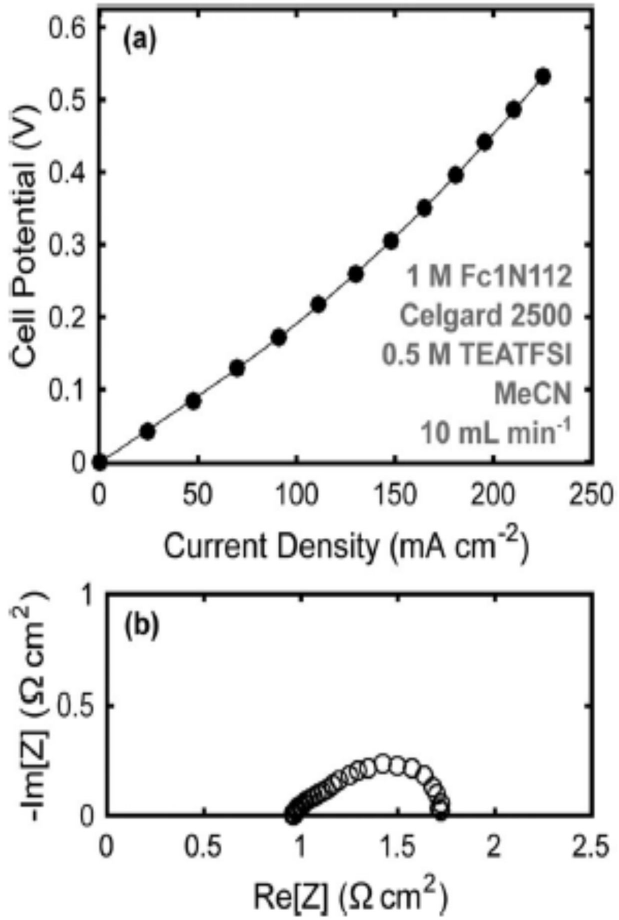


Figure 10. (a) Polarization and (b) Nyquist plot of the lowest ASR configuration tested in this work: 1 M Fc1N112$^{+/2+}$ (50% SOC), Celgard 2500, 2x SGL 25AA, 0.5 M TEATFSI / MeCN, 10 mL min^{-1}.

J. Milshtein, F. Brushett (**MIT**), R. M. Darling (**UTRC**), *et.al. JES, **164*** (2017) A2487

** *Results obtained as part of JCESR*

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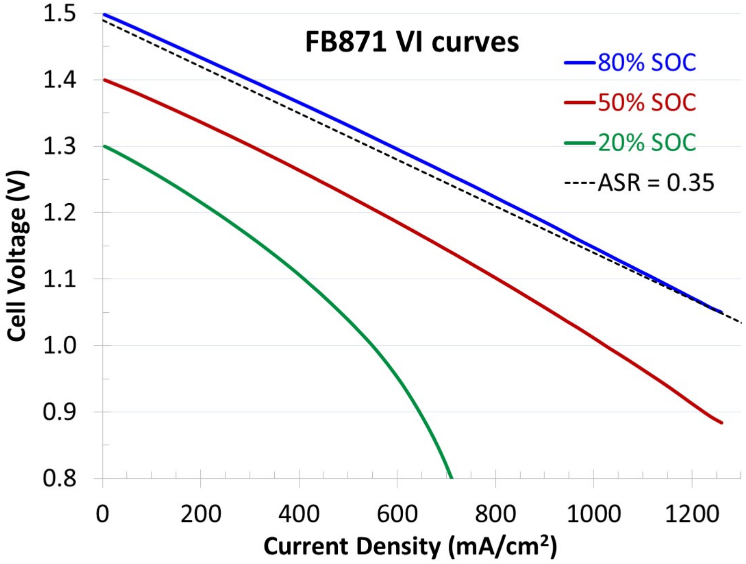
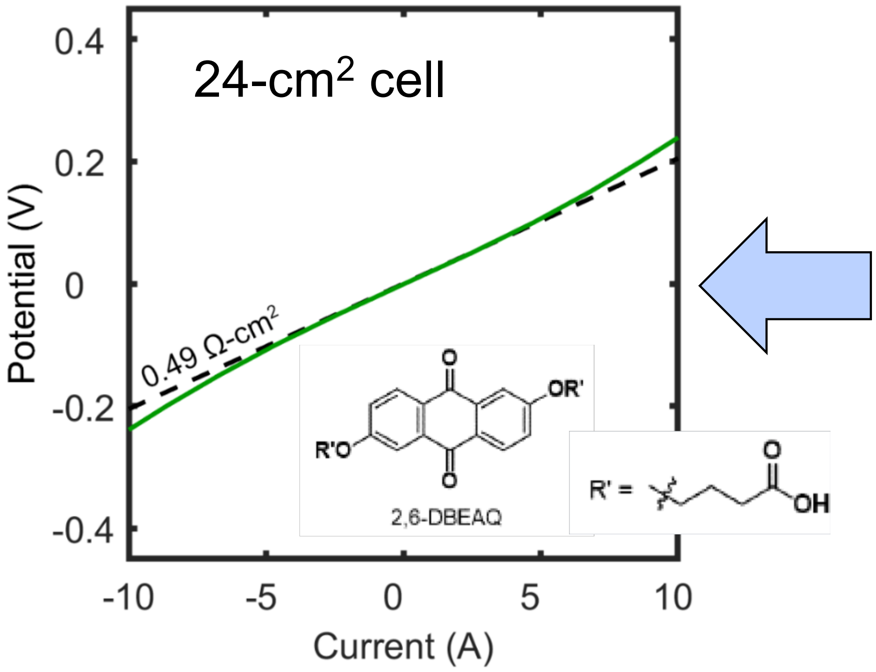
*Examples of high performance Aqueous RFBs***

With hydrocarbon membranes (not ion-exchange membranes)

- *These **electrolyte-imbibed membranes** may potentially be good for NonAq*

- **Complete VRFB cell**
- **At 80% SOC:**
  - **ASR ≈ 0.35 Ω-cm^2**





- **Symmetrical DBEAQ cell**
  - **0.5 M DBEAQ, 1M KCl, *pH* 12**
- **At 50% SOC:**
  - **ASR ≈ 0.49 Ω-cm^2**

** *Results obtained as part of UTRC's ARPA-E "IONICS" project*

High OCV is critical

Should fully exploit electrolyte stability window with Engineered RFB Actives

- *Energy Density*
  E (kWh/L) α V_{cell}
- *Power Density*
  P (W/m^2) α $(V_{cell})^2$

- Stability Window is significantly larger than thermodynamic limits
- ***Most successful aqueous batteries have cell voltages that are > 1.23 V***
  - Pb-acid batteries have nominal OCV of 2.15V; charge up to 2.7 V
  - VRFBs have an OCV of > 1.5 V; charge up to 1.55 to 1.6 V per cell
- ***One should determine the stability window for the intended electrolyte***

Neutral-*pH* Aqueous RFB example:

CV indicates Potential Window ≈ **2.7 V**

OCV ≈ 0.82 V (30%)

Figure from:

T. Leo Liu, *et.al.* “Unprecedented Storage Capacity and Cycling Stability of Ammonium Ferrocyanide Catholyte Material in pH Neutral Aqueous Redox Flow Batteries,” *Joule* (2018).

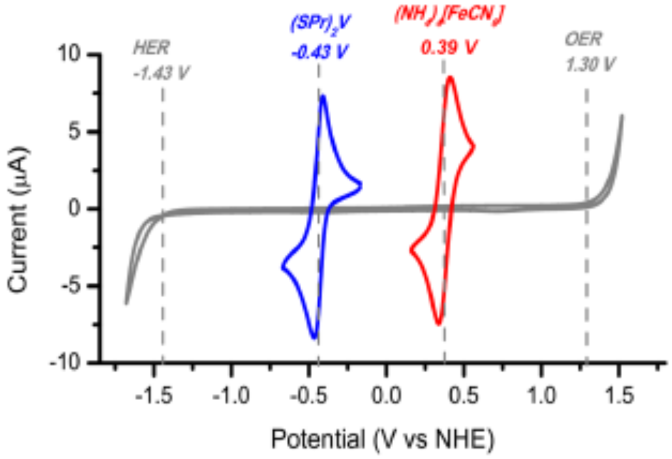
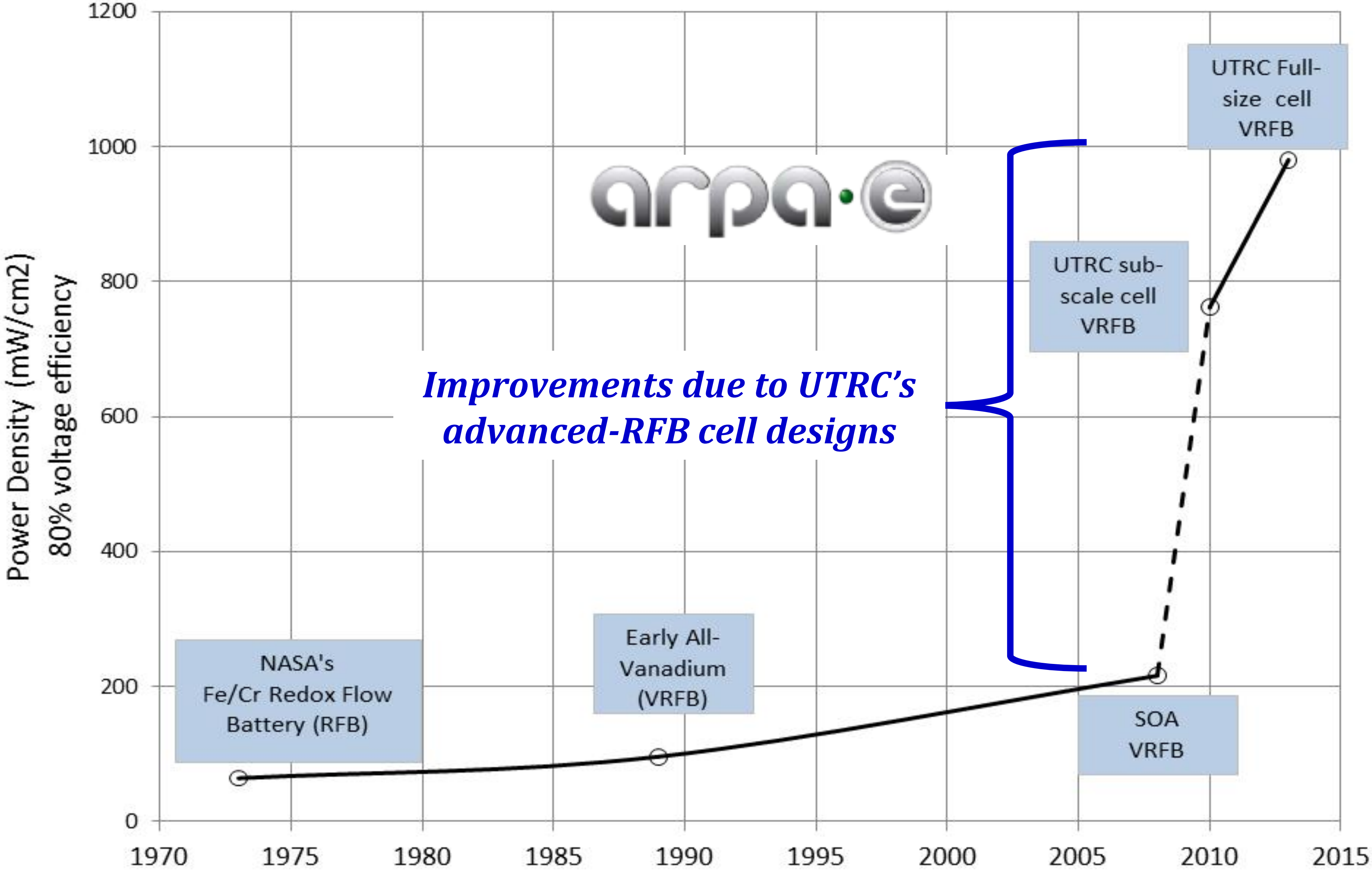


Figure S13. CV curves of **$(NH_4)_4[Fe(CN)_6]$** (red trace) and $(SPr)_2V$ (blue trace). Gray curve is the CV curve of 0.5 M NH_4Cl, labeled with the onset potentials for hydrogen evolution reaction (HER, −1.43 V) and oxygen evolution reaction (OER, 1.30 V).

APPENDIX

*“Breakthrough Flow-Battery Stack” developed by UTRC **

UTRC’s VRFB cells use same material set as other VRFB cells



*** ARPA-E’s title for UTRC’s *GRIDS* Project**

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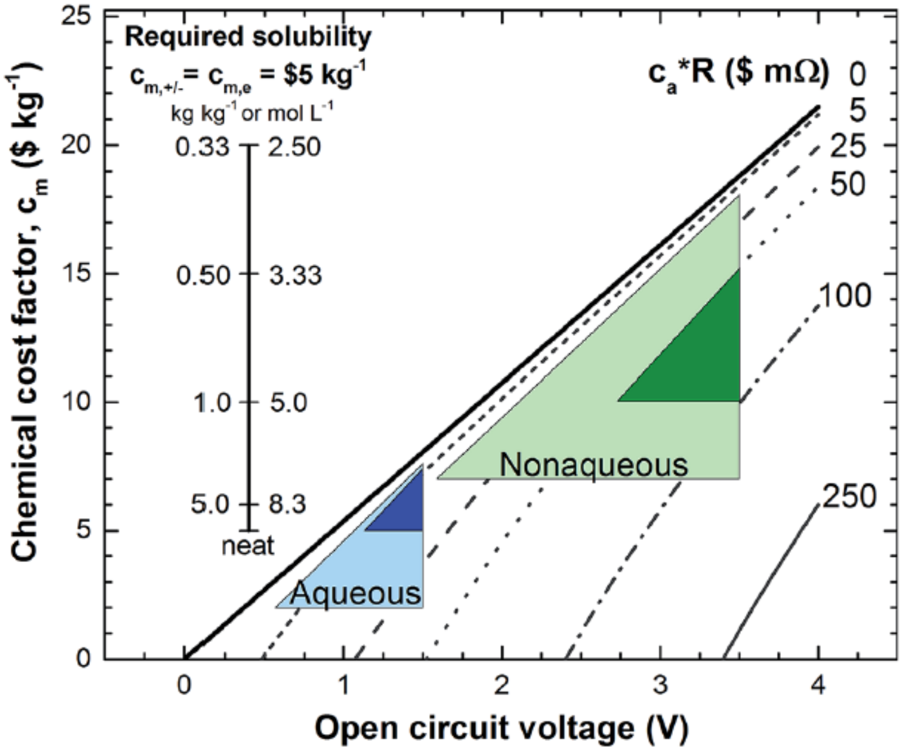
Approved for Public Release

Techno-Economic Modeling of EES Options

DOE’s Battery Hub analysis on *High Energy EES*

- Recent analysis provides insights into paths to low-cost, high energy batteries
  - *Modeled **5-hr discharge capacity***
- Key results:
  - Dashed lines yield **RFB System cost of $120/kWh** (with 5-h system)
  - Aqueous Systems
    - Solvent cost, σ, OCV
  - Non-Aqueous Systems
    - OCV, Solvent cost, σ



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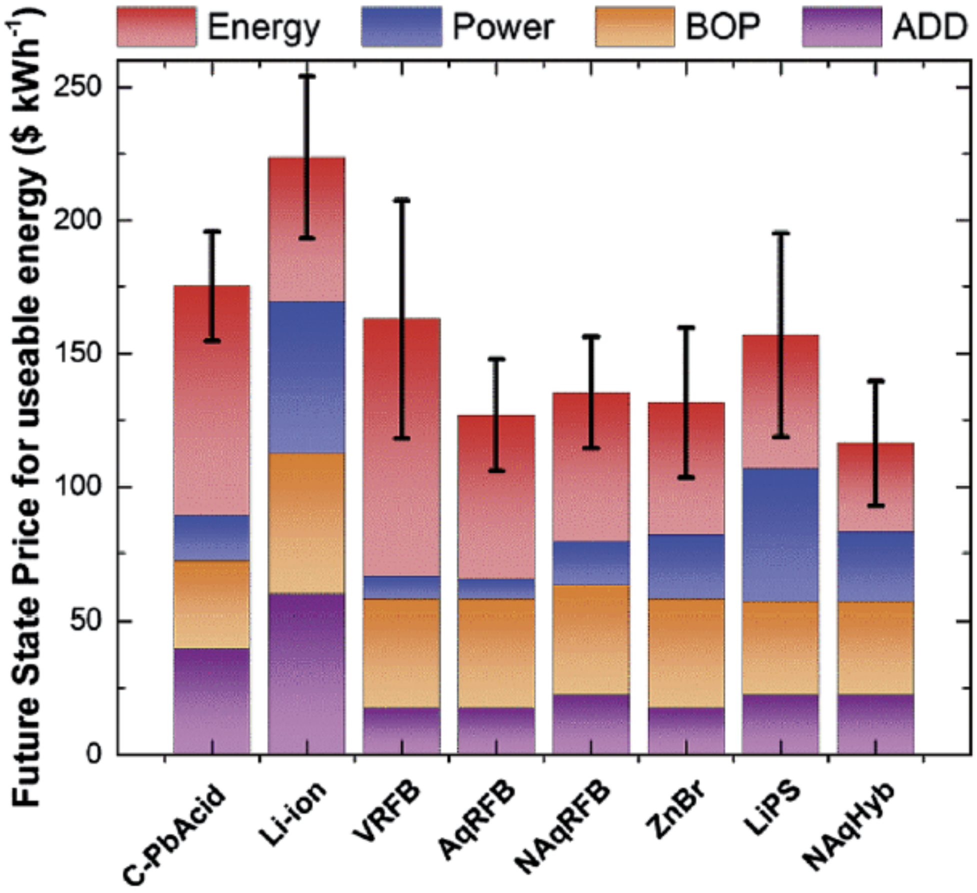
Analysis Authors:
Robert M. Darling (UTRC)
J. A. Kowlaski and F. R. Brushett (MIT)
K. G. Gallagher and S. Ha (ANL)

“Pathways to low-cost electrochemical energy storage: a comparison of aqueous and non-aqueous flow batteries” ***Energy & Environmental Science*** (2014)

Techno-economic Results on High Energy EES

Advanced RFBs are best path to long-discharge applications (5-hr)

- Study assumes ***10-GWh*** production facilities
- "**ADD**" cost = factory depreciation, overhead, labor, margin, *etc*.
- Flow Batteries show lower manufacturing contributions to system price
- **BOP** costs are fairly similar for all battery types
- Aqueous RFBs have lowest **Power** sub-system costs
- **Energy** costs vary widely; depends on more than just the active material cost ($/kg)



R. M. Darling, *et.al*., ***Energy & Environ. Science*** (2014)

Lifetime and ***learning-curve path*** will discriminate going forward

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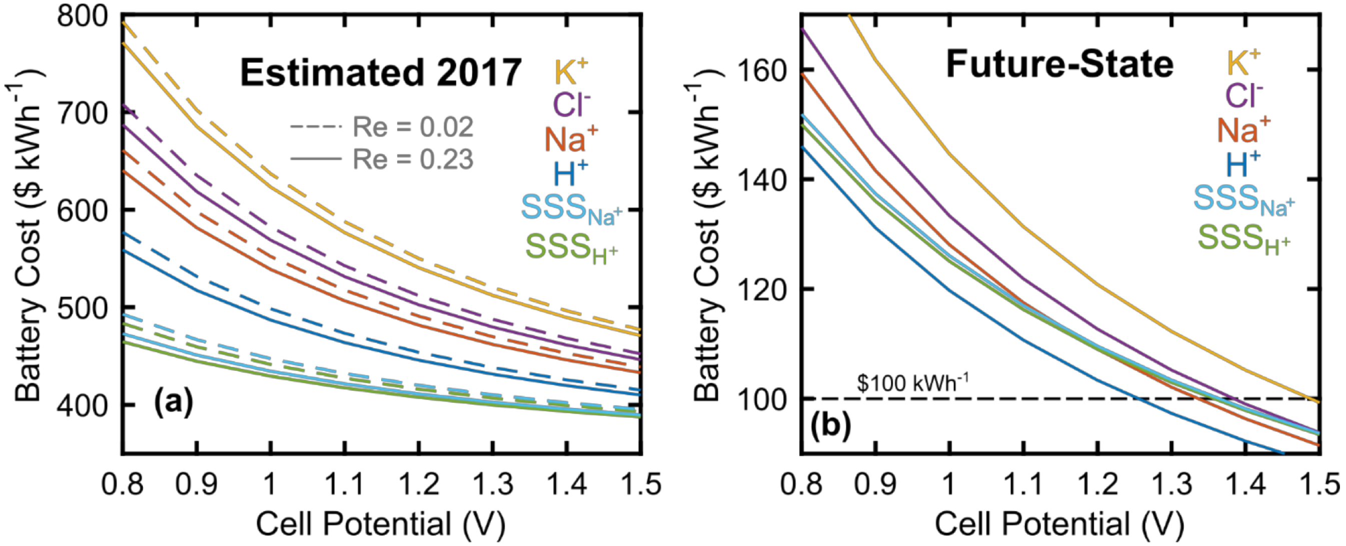
Path to Low Cost with Separators & RFB Reactants

Impact of charge carrier on Aqueous-RFB System costs

- TEA modeling shows that charge carrier does have a significant impact
  - Due to higher ionic conductivities → higher performance stacks
- Size-Selective Separators (SSS), *i.e.*, *not* ion-exchange membranes (IEMs), enable lower costs, *especially at low production volumes*
- **In the near-term: SSS and charge carrier are key enablers to low cost**
- **Longer-term: OCV is key differentiator**



"The Critical Role of Supporting Electrolyte Selection on Flow Battery Cost"
J. D. Milshtein, *R. M. Darling*, Javit Drake, M. L. Perry, & F. R. Brushett; *J. of the Electrochemical Society*, **V164**, A3883 (2017).

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Battery cost as a function of cell potential with **(a)** present-day and **(b)** future-state costs, for various working ion / membrane types and two extreme values of Re. This analysis assumes 5 h discharge time.

VNX 1000 SERIES

1,000 kW / 6-10 Hours

Modular Architecture

Independent scaling of power and energy

- Optimal system sizing for each application
- Flexibility to add power or energy as project needs change over time

Shown: 1 MW / 8 MWh DC System

Simplicity

Maximizes power density & minimizes footprint to reduce material and site costs

- Reduces container spacing & pipe runs
- Reduces wetted electrolyte surfaces, minimal propensity for leaks
- Minimizes moving components via centralization of all pumps, controls, etc. in stack container
- Electrolyte containers have no moving parts

Durable, Quality Components

Maximize system life and minimize operational expense

- Materials meet chemical industry standards
- Containers are marine grade for maximum climate resistance
- Electrolyte 100% double walled/contained

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Grid-Scale Validation

✓

Military & Microgrids

(Ft. Devens, MA)

Operational (3+ yr)

160kW / 640 kWh System

- ✓ Micro-Grid Control Compatibility
- ✓ Time-of-Use Rate Reduction
- ✓ Demand Charge Reduction

U.S. ARMY ENGINEER RESEARCH AND DEVELOPMENT CENTER
ERDC

✓

Wind Integration**

(Worcester, MA)

Operational (1+ yr)

500kW / 3,000 kWh System

- ✓ Wind Integration (600kW Wind)
- ✓ Time-of-Use Rate Reduction
- ✓ Demand Charge Reduction

nationalgrid

Q1
2019

Solar Integration**

(Everett, MA)

Installation

500kW / 3,000 kWh System

- ✓ PV Integration (605kW Solar)
- ✓ Voltage Support
- ✓ Load Following

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** *These two demonstrations supported by DOE's OE Program*

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VIONX™ ENERGY