Connecting system targets with material properties:

Application-informed fundamental science of redox flow batteries

Fikile R. Brushett

Department of Chemical Engineering
Massachusetts Institute of Technology

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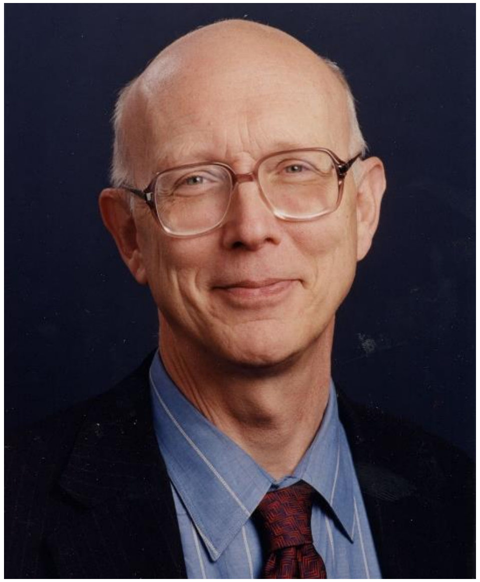
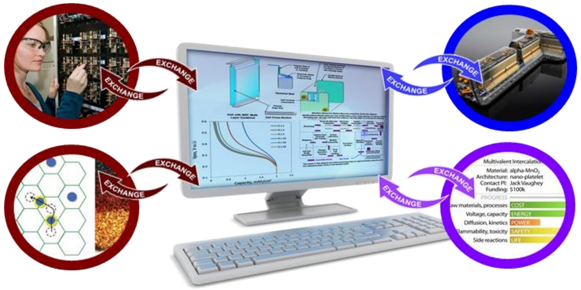
On the importance of models in science

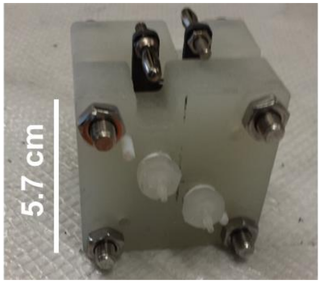
The importance of models in science is often underestimated. Models represent more complex classes of related systems and contribute to the study of those classes by focusing research on particular, tractable problems. The development of useful, widely accepted models is a critical function of scientific research: many of the techniques (both experimental and analytical) and concepts of science are developed in terms of models; they are thoroughly engrained in our system of research and analysis.

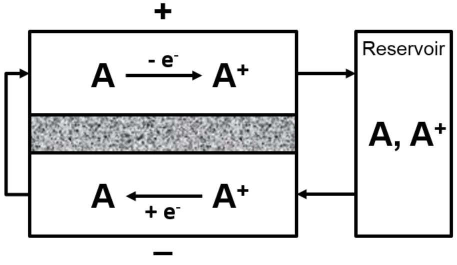
- George M. Whitesides, Harvard Univ.

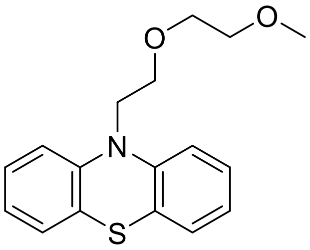


Models should be viewed in the broadest sense:



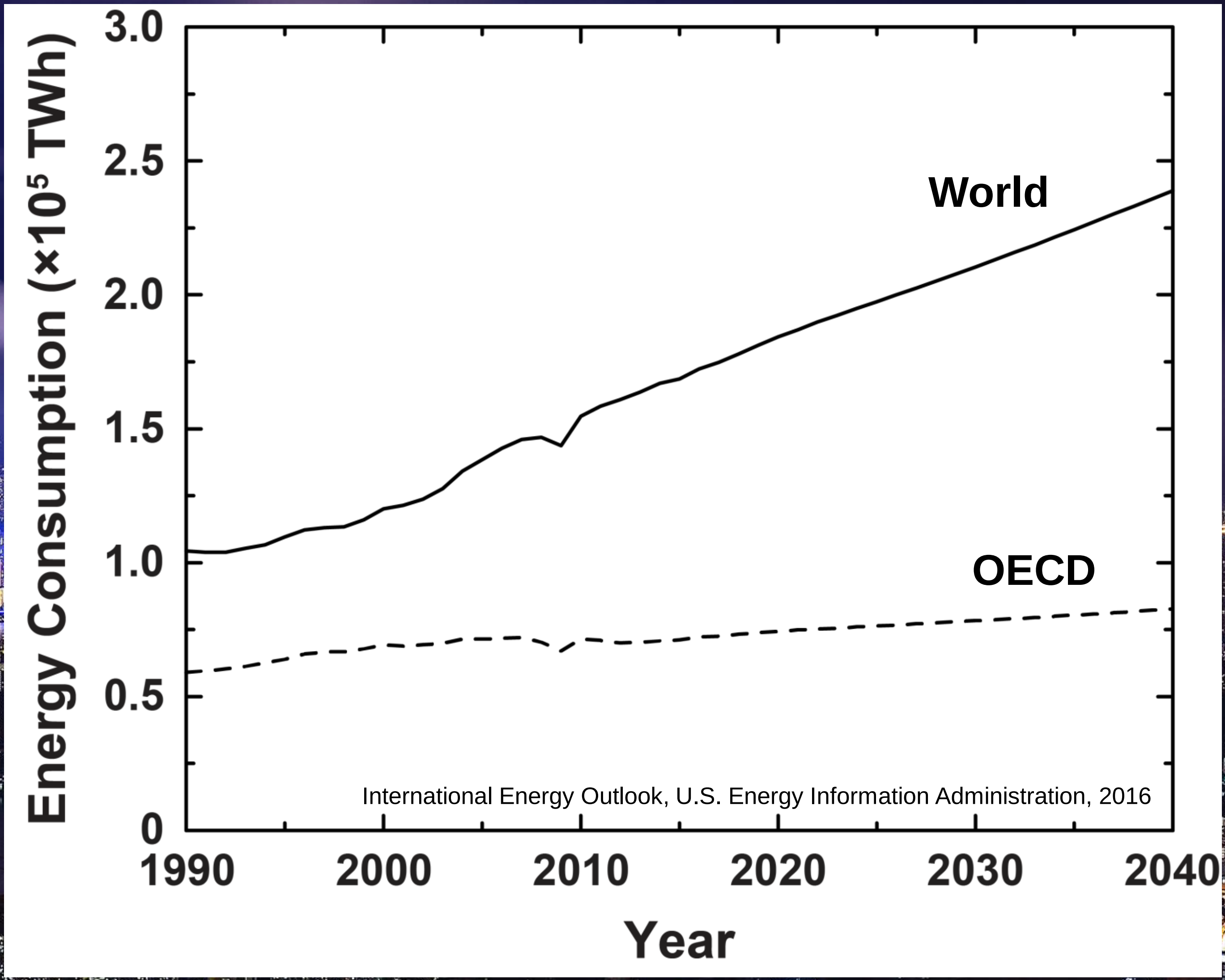






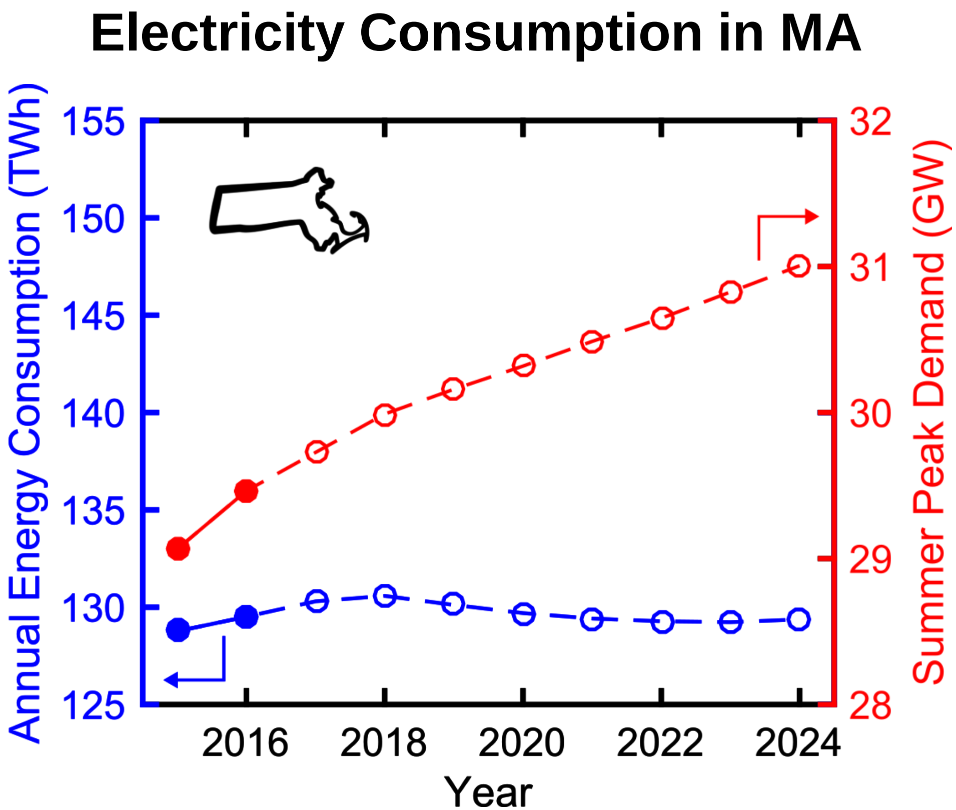
V.M. Krishnamurthy et al., *Chem. Rev.*, 2008, 108, 946

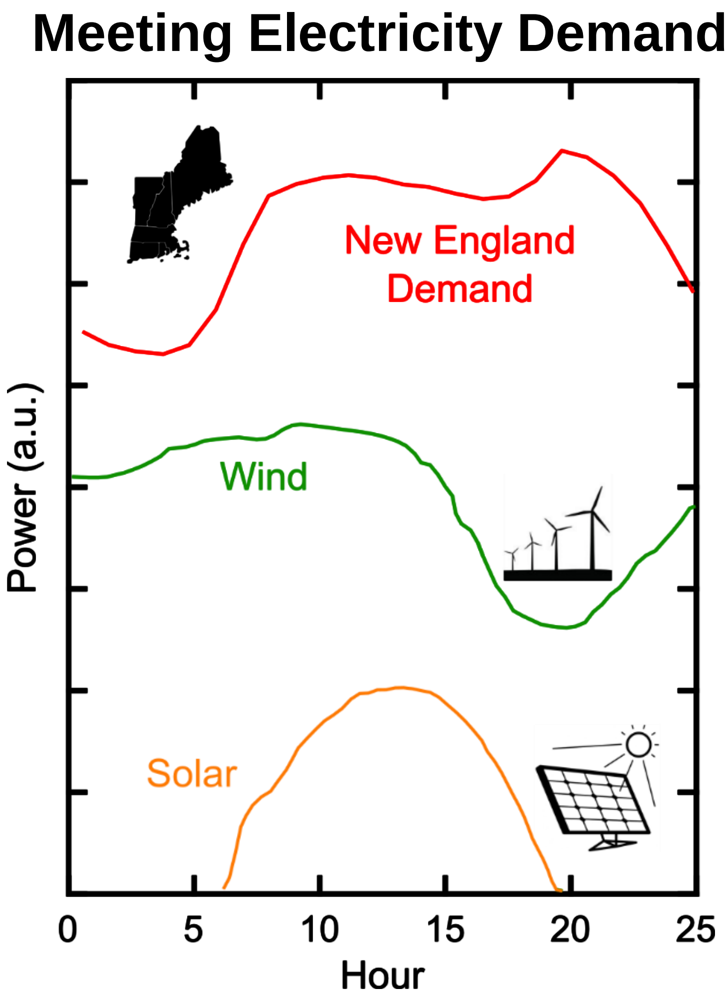
A grand challenge of the 21st century



Hong Kong City after raining; interfacelift website

Power generation challenges



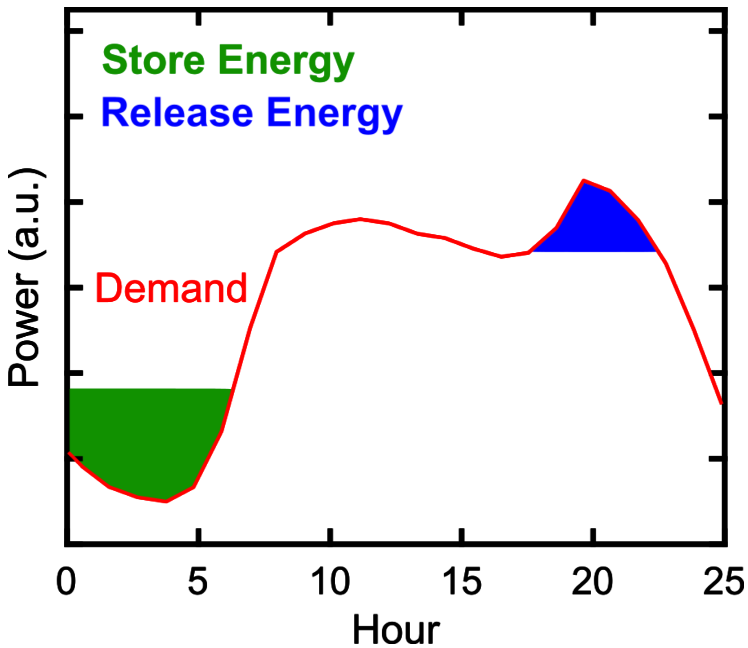


Alleviating peak demand and integrating renewables are major challenges impeding improved *sustainability*, increased *efficiency*, and decreased *cost*

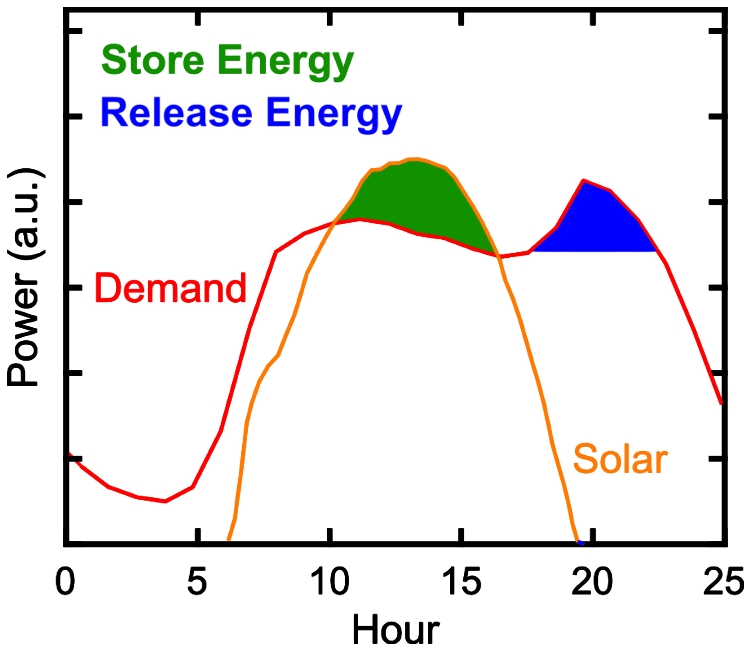
MA DOER, *State of Charge: Massachusetts Energy Storage* Initiative, 2016
US EIA, *Demand for Electricity Changes Through the Day*, 2011

How can energy storage help?

Load-Leveling, Arbitrage, or Peak Shift



Alleviate Intermittency of Renewables

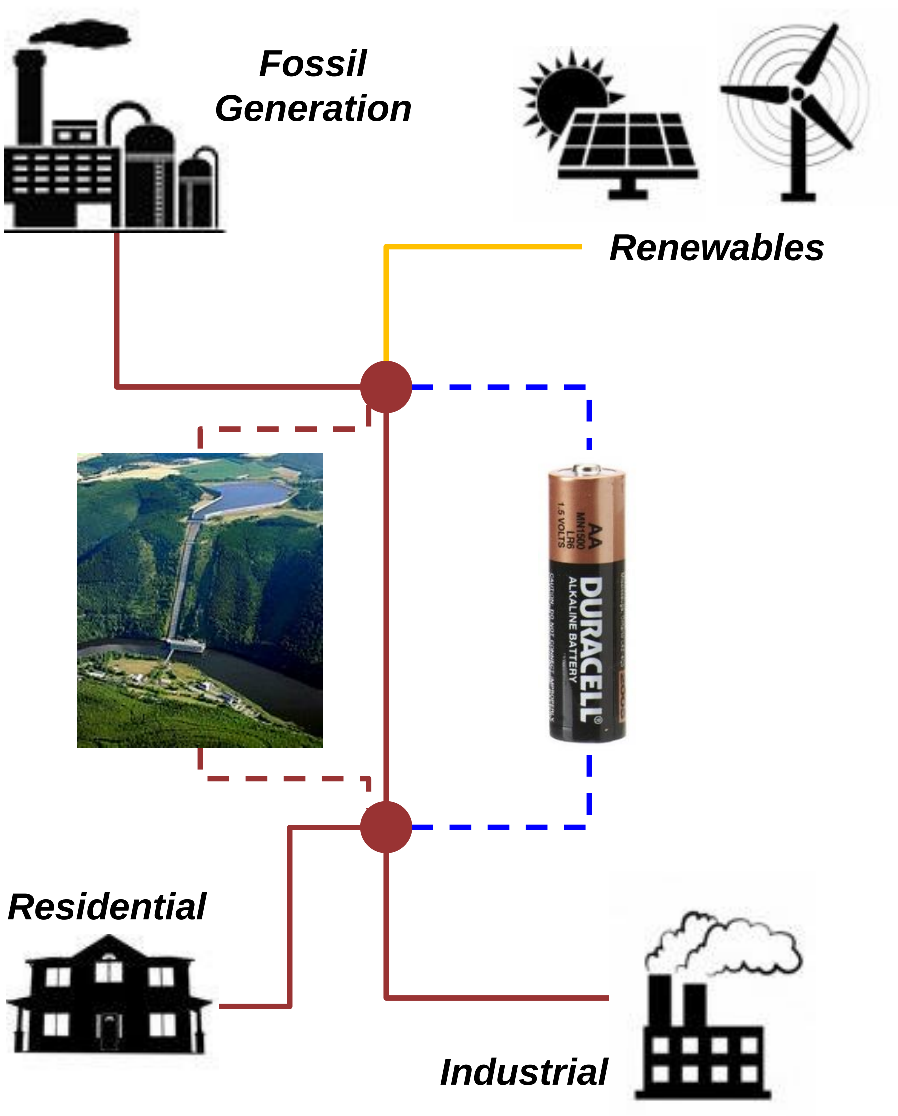


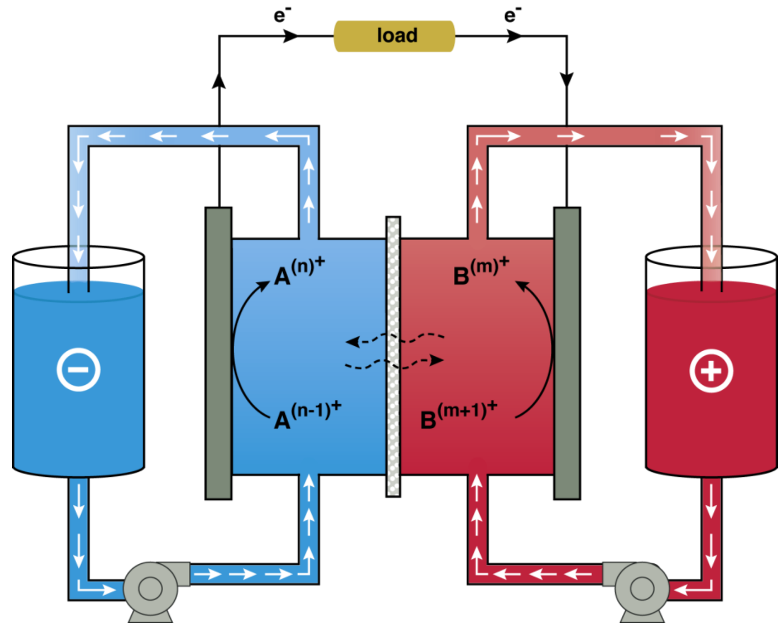
Other services: regulation, frequency response, voltage support, reserves, black start, deferral of infrastructure upgrades, damping

Energy storage can provide a number of key services to improve infrastructure associated with the power sector

DOE/EPRI 2013 Electricity Storage Handbook in Collaboration with NRECA, SAND2013-5131 (2013)

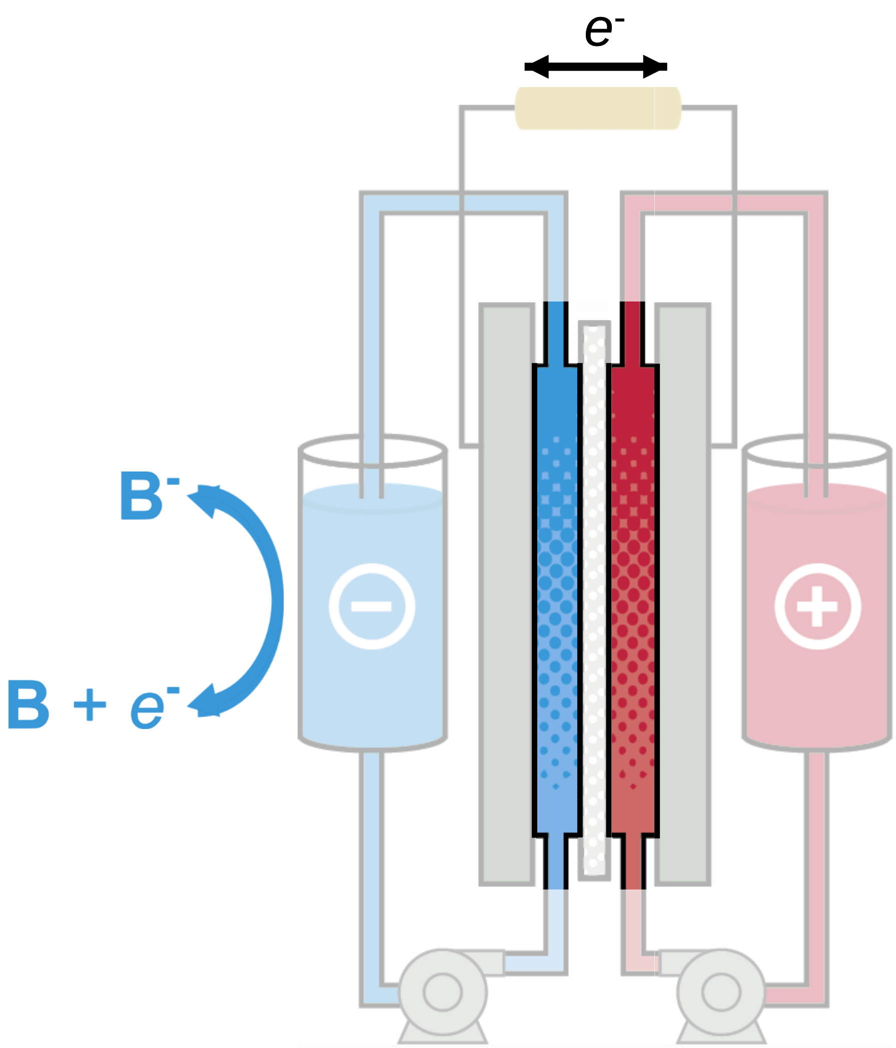
Grid Storage: From pumped-hydro to batteries

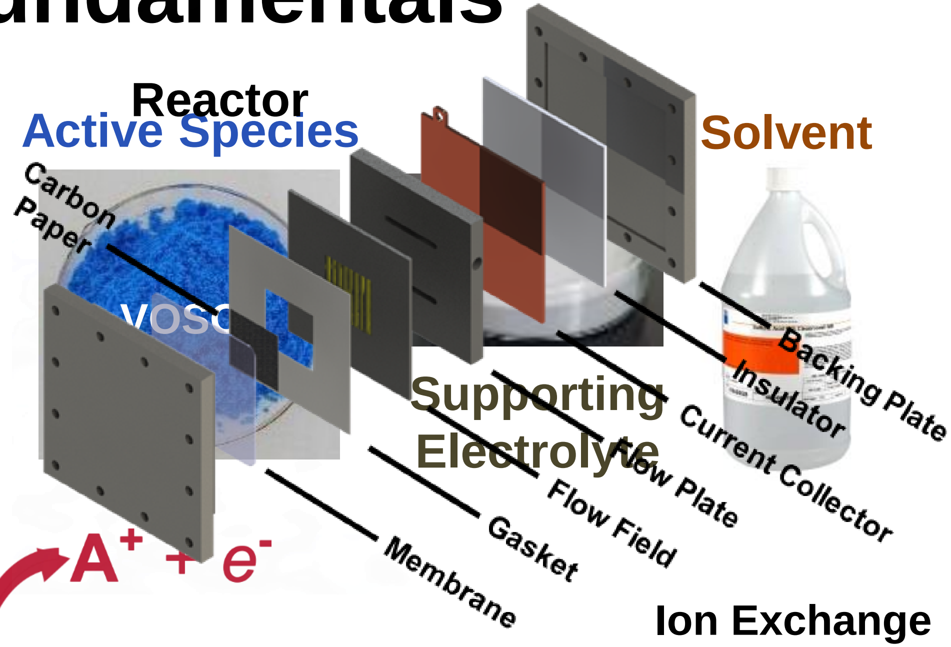




DOE Global Energy Storage Database (2017). *www.instructables.com*. Bosch Energy Storage Solutions, *Researchers at Fraunhofer Institute Report Progress in Redox-Flow Batteries* (2013). Roach, *Big Batteries are Starting to Boost the Electric Grid*, NBC News (2014)

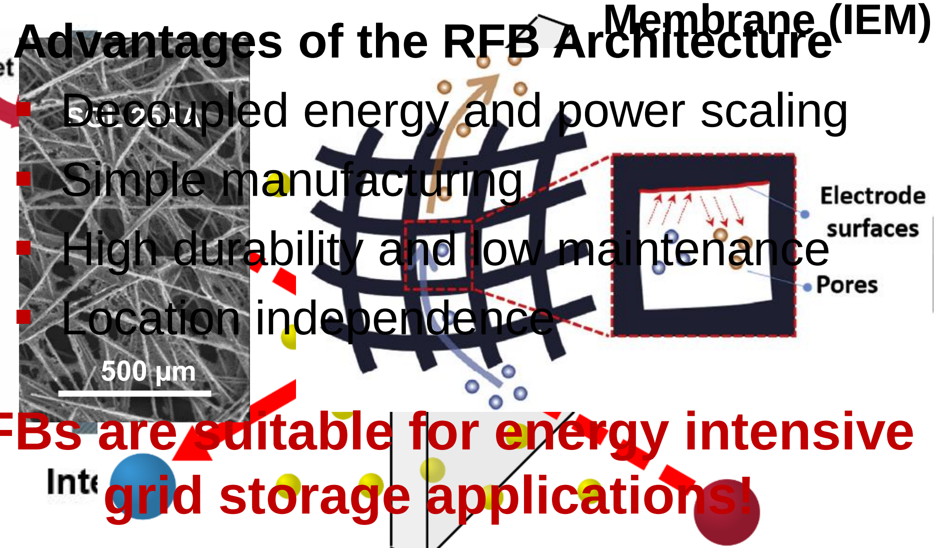
Redox flow battery fundamentals





Advantages of the RFB Architecture

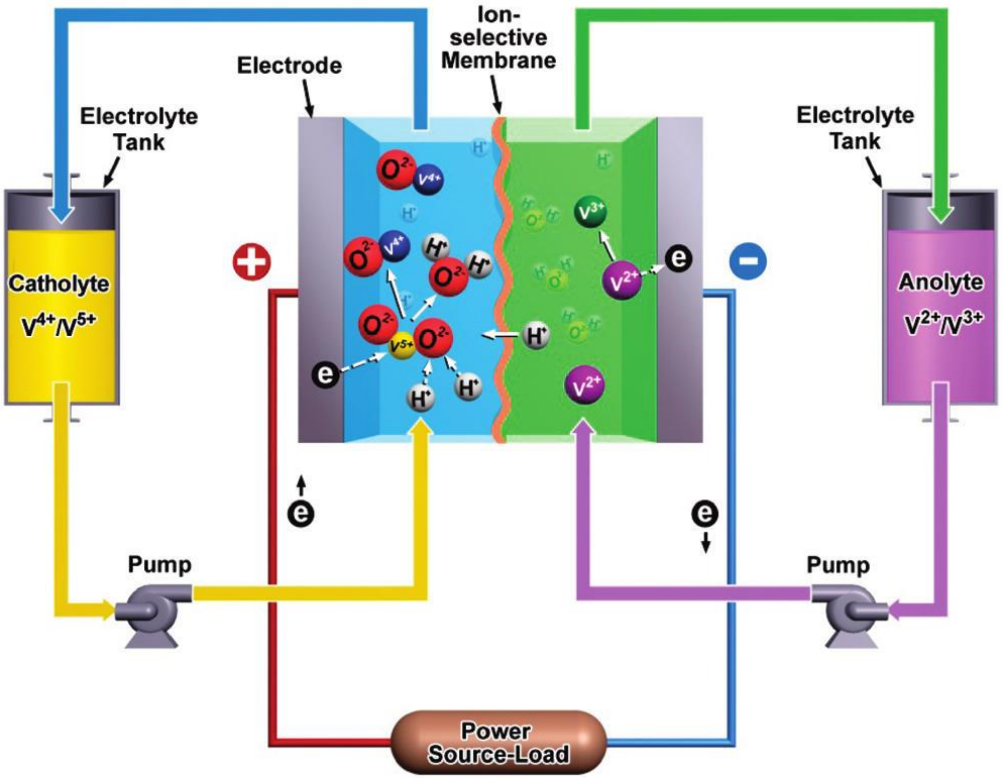
- Decoupled energy and power scaling
- Simple manufacturing
- High durability and low maintenance
- Location independence

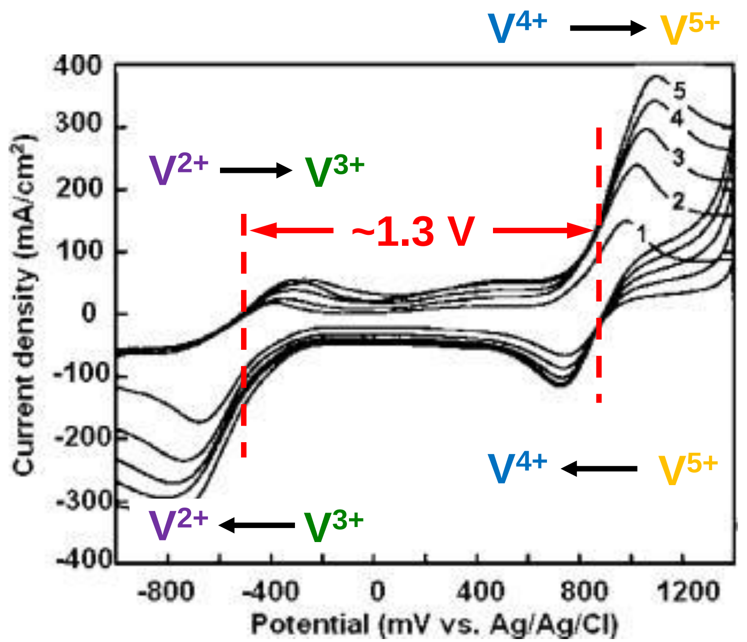


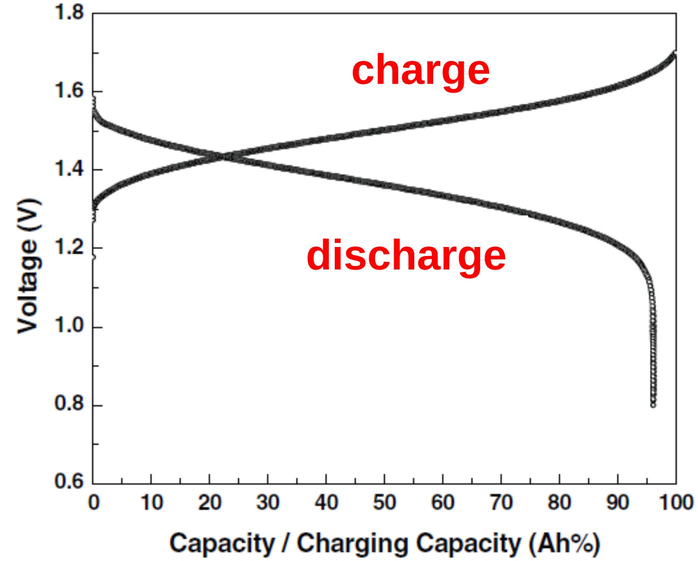
RFBs are suitable for energy intensive grid storage applications!

Su et al., in *Rechargeable Batteries*, Springer, (2015) 673. Zhou et al., *J. Power Sources*., 339 (2017); Rashpov et al., *J. Electrochem. Soc*., 162 (2015) F603. Gyuk, US DOE Program Planning Document (2011). Darling et al., *Energy Environ. Sci*., 7 (2014) 3459

All vanadium flow battery







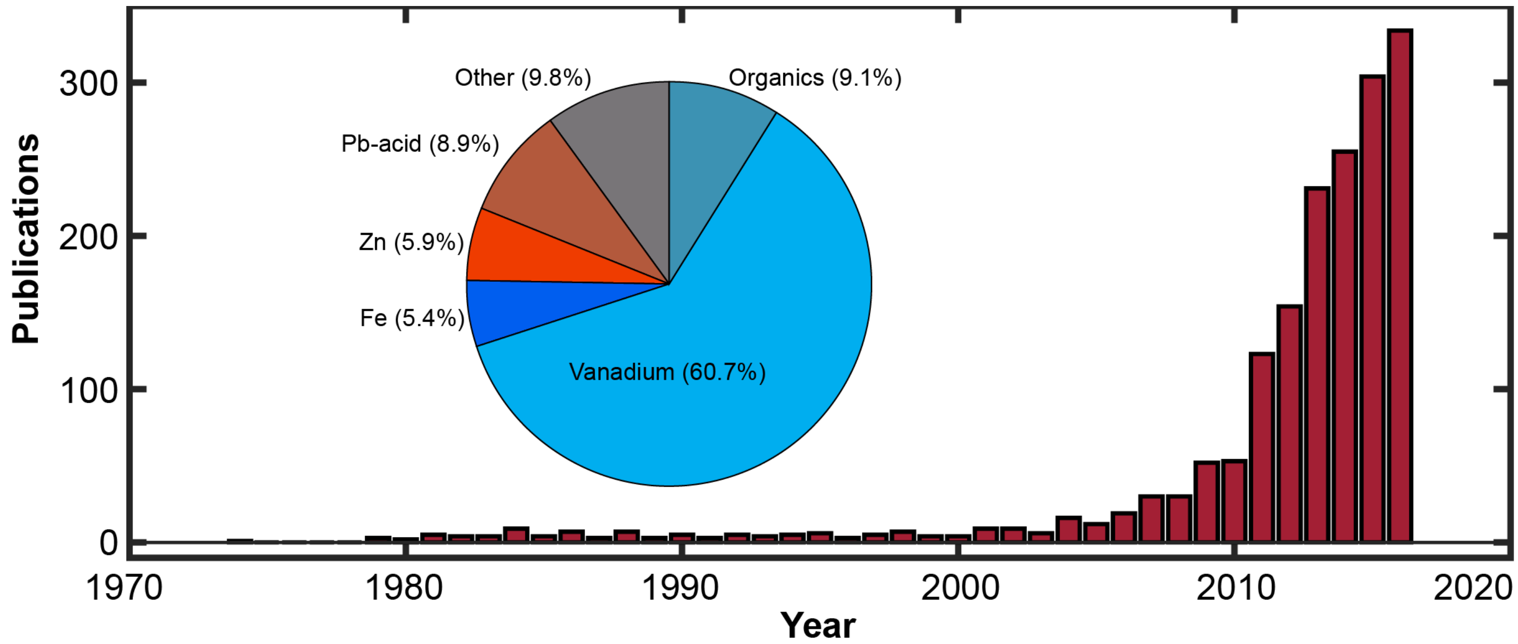
catholyte: $VO^{2+} + H_2O \leftrightarrow VO_2^{+} + 2H^{+} + e^{-}$

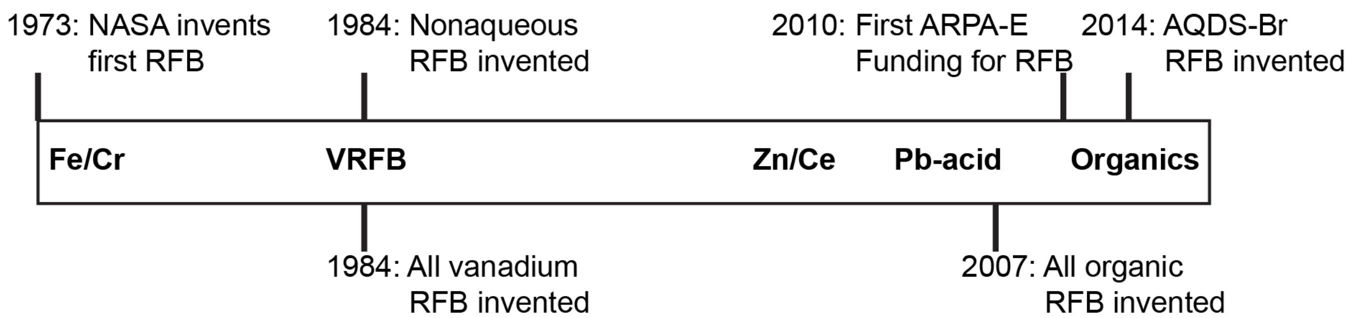
anolyte: $V^{3+} + e^{-} \leftrightarrow V^{2+}$

overall: $VO^{2+} + H_2O + V^{3+} \leftrightarrow VO_2^{+} + 2H^{+} + V^{2+}$

Z. Yang et al., *Chem. Rev.*, 2011, 111, 3577

Flow batteries are a nascent technology





Opportunities for transformational technology advancement through the development of new redox chemistries and reactor designs.

Publication data determined by a keyword search using Scopus to quantify the number of publications for each topic

Established system level targets for grid EES

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

$150 kWh^{-1}

4 h discharge

5000 cycles

> 80% system eff.

arpa·e

$100 kWh^{-1}

≥ 1 h discharge

5000 cycles

iea

$90 / MWh / Cycle

↓

$100 - 500 kWh^{-1}

1000 - 5000 cycles

~90% system eff.

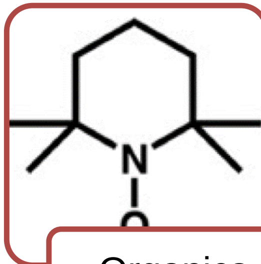
Currently, flow batteries cost <u>$400-500 kWh^{-1}</u>

I. Gyuk et al., *Grid Energy Storage*, US DOE, Washington DC (2013); US DOE – HQ Advanced Research Projects Agency – Energy (ARPA-E), *GRIDS FOA* (2010); International Energy Agency, *Technology Roadmap: Energy Storage* (2014)

Pathways for next-gen flow batteries

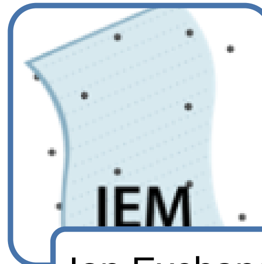
Active Materials

Transition
Metal salts

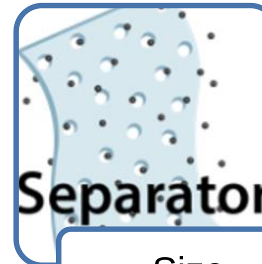


Organics,
Polymers

Membranes



Ion Exchange
Membrane



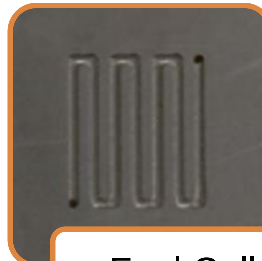
Size
Selective

Supporting Electrolytes

Acidic
Aqueous

Nonaqueous,
Neutral pH

Cell Design



Fuel Cell
Flow Fields

RFB-Specific
Flow Fields

What does success look like?

Kowalski et al., *Curr. Opin. Chem. Eng.*, 2016, 13, 45; Perry & Weber, *J. Electrochem. Soc.*, 2016, 163, A5064;
Doris et al., *Angew. Chem. Int. Ed.*, 2016, 55, 1595; Zhou et al., *J. Power Sources*, 2017, 339, 1

Assessing design space via techno-economics

- Materials properties
- Cost parameters
- Component performance

↔

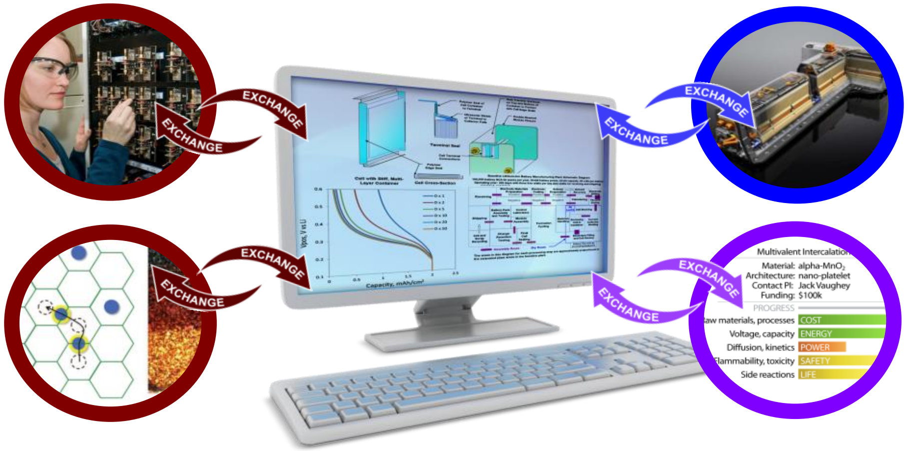
↔

Desired system price and performance

Can we connect materials properties to system targets?

V. Viswanathan et al., *J. Power Sources*, 2014, 247, 1040; S. Ha et al., *J. Power Sources*, 2015, 296, 122; A. Crawford et al., *Int. J. Energy Research*, 2016, 40, 1611; R. Darling & K. Gallagher et al., *J. Electrochem. Soc.*, 2016, 163, A5029; R. Darling & K. Gallagher et al., *Energy Environ. Sci.*, 2014, 7, 3459; R. Dmello & J. Milshtein et al., *J. Power Sources*, 2016, 330, 261

Our approach to techno-economic modeling



- Consider “future state” with high-volume production in competitive market
- Hybrid bottom-up / top-down approach for less well-known systems
- Strong collaboration with academic, national laboratory, and industry partners

- 5 h storage
- $100/kWh*
  *w/o inverter & installation
- 7000 cycles
- 20 year life

Price = area + materials + overhead + system

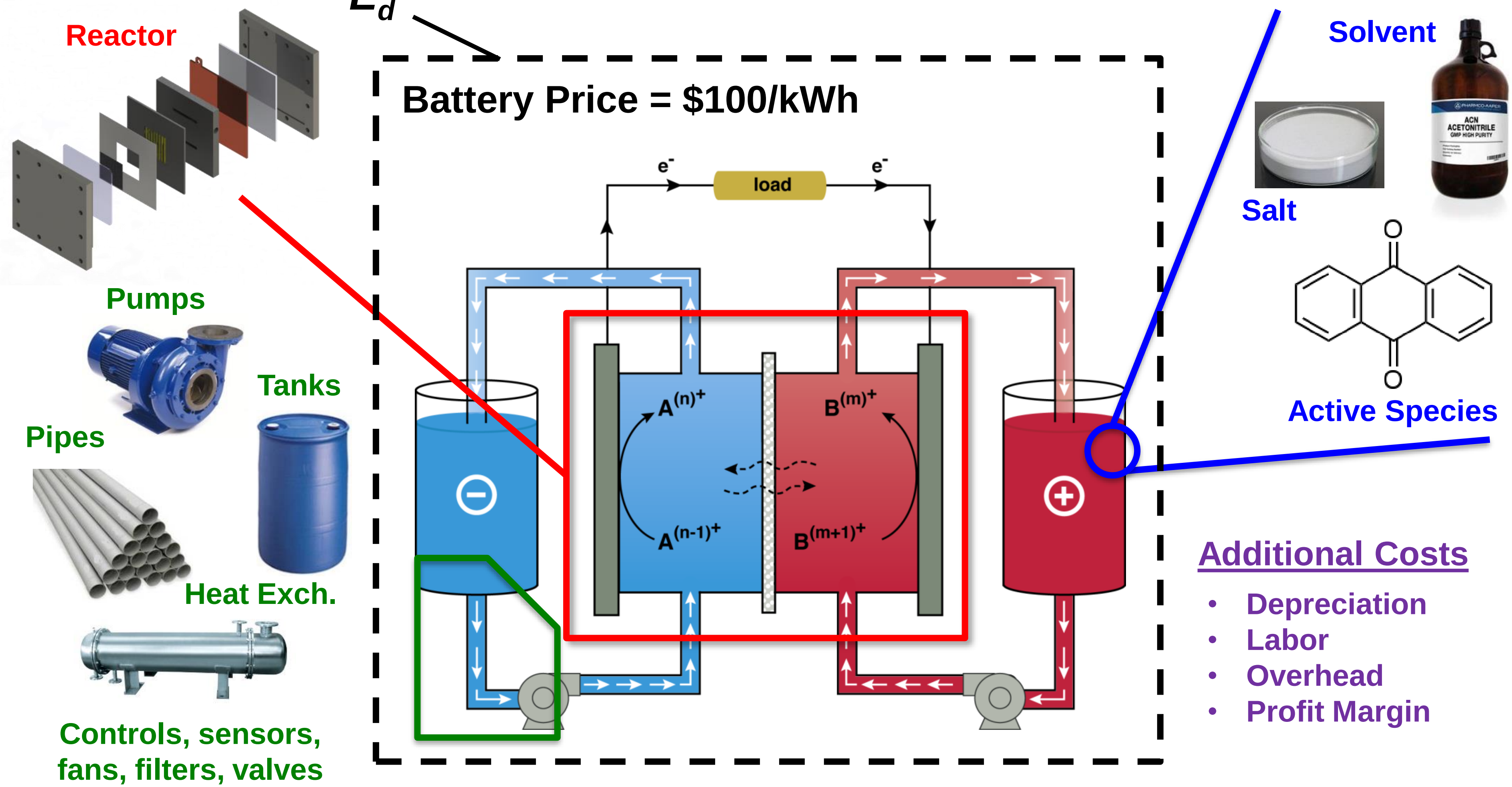
$$P = c_a A + \sum_i c_{m,i} m_i + \left(c_{add} + c_{bop}\right) E_d t_d^{-1}$$

Assume $20/kWh for inverter and $30/kWh installation

R. Darling & K. Gallagher et al., *Energy Environ. Sci.*, 2014, 7, 3459; R. Dmello & J. Milshtein et al., *J. Power Sources*, 2016, 330, 261

Redox flow battery cost contributions

$$\frac{P}{E_d} = C_{Reactor} + C_{Electrolyte} + C_{BOP} + C_{Additional}$$

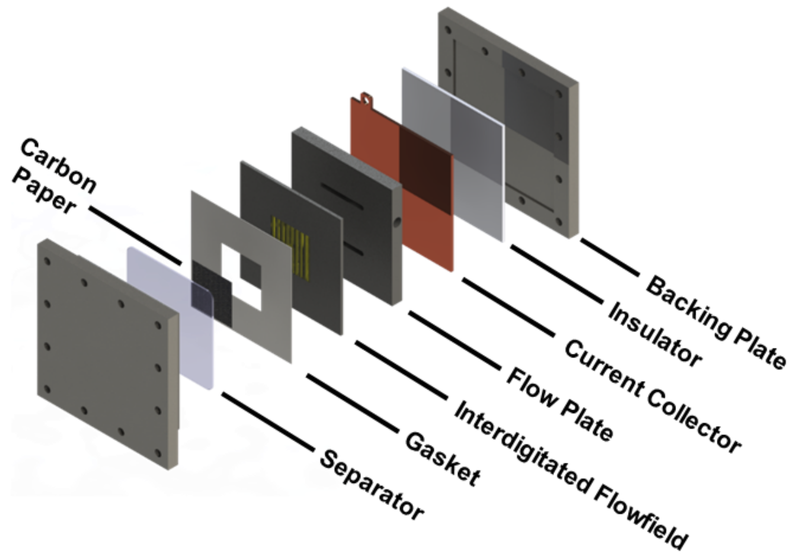


R. Darling & K. Gallagher et al., *Energy Environ. Sci.*, 2014, 7, 3459; R. Dmello & J. Milshtein et al., *J. Power Sources*, 2016, 330, 261

Electrochemical reactor cost ($C_{reactor}$)

$$C_{reactor} = \frac{c_a R}{\varepsilon_{sys} U^2 \varepsilon_v (1-\varepsilon_v) t_d}$$

- cost ($\$\ m^{-2}$) — c_a
- resistance ($\Omega\ m^2$) — R
- efficiency (-) — ε_{sys}
- potential (V) — U
- discharge time (h) — t_d



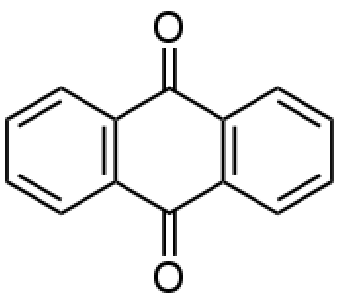
Component	Year 2014 Cost, $\$/m^2$	Future Cost, $\$/m^2$
Graphite flow field plate	55	25-35
Stainless-steel flow field plate	40	10-20
Carbon fiber felt / paper electrode	70	10-30
Fluorinated ion-exchange membrane	500	25-75
Frames, seals, and manifolds	6	1-3

V. Viswanathan et al., *J. Power Sources*, 2014; B.D. James & A.B. Spisak, Report from Strategic Analysis Inc., October 2012; M. Mathias et al., *The Electrochemical Society Interface*, Fall 2005

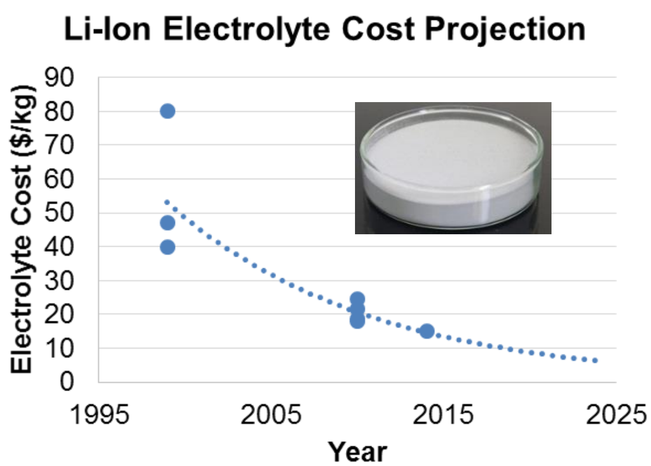
Electrolyte cost contributions ($C_{electrolyte}$)

$$C_{electrolyte} = \frac{1}{\varepsilon_{sys}\varepsilon_q F \varepsilon_v U}\left(\frac{s_+ M_+}{\chi_+ n_{e+}} c_{m,+} + \frac{s_- M_-}{\chi_- n_{e-}} c_{m,-} + 2 r_{avg} M_{salt} c_{salt} + \frac{2}{m_{avg}} c_{sol}\right)$$

Discharge Energy — **Active Material** — **Salt** — **Solvent**



~$4.40/kg (2014)



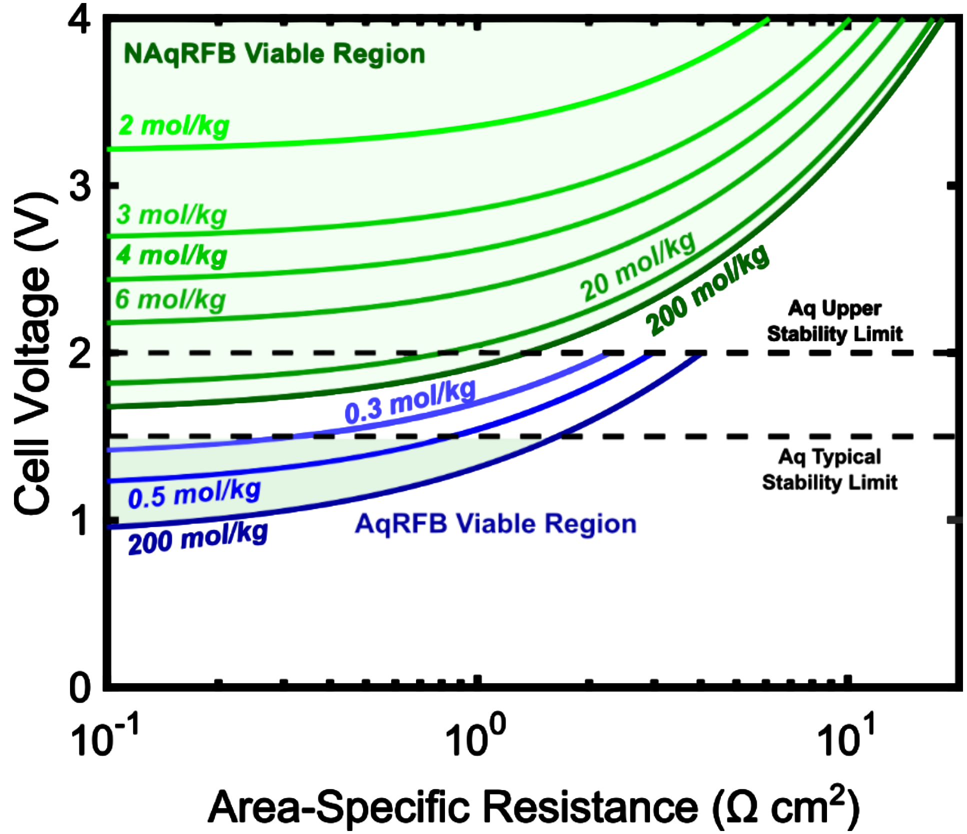
~$1.50/kg (2006)

~$0.095/kg (2006)

ICIS Indicative Chemical Prices A-Z, 2006. B. Huskinson et al., *Nature*, 2014, 505, 195. P.A. Nelson et al., ANL-12/55, 2012. L. Gaines & R. Cuenca, ANL/ESD-42, 2000, vol. 036. R. Darling & K. Gallagher et al., *Energy Environ. Sci.*, 2016, 7, 3459

Utilizing explicit design maps to identify key challenges and performance needs

\$100 kWh^{-1} Design Map



Key challenges

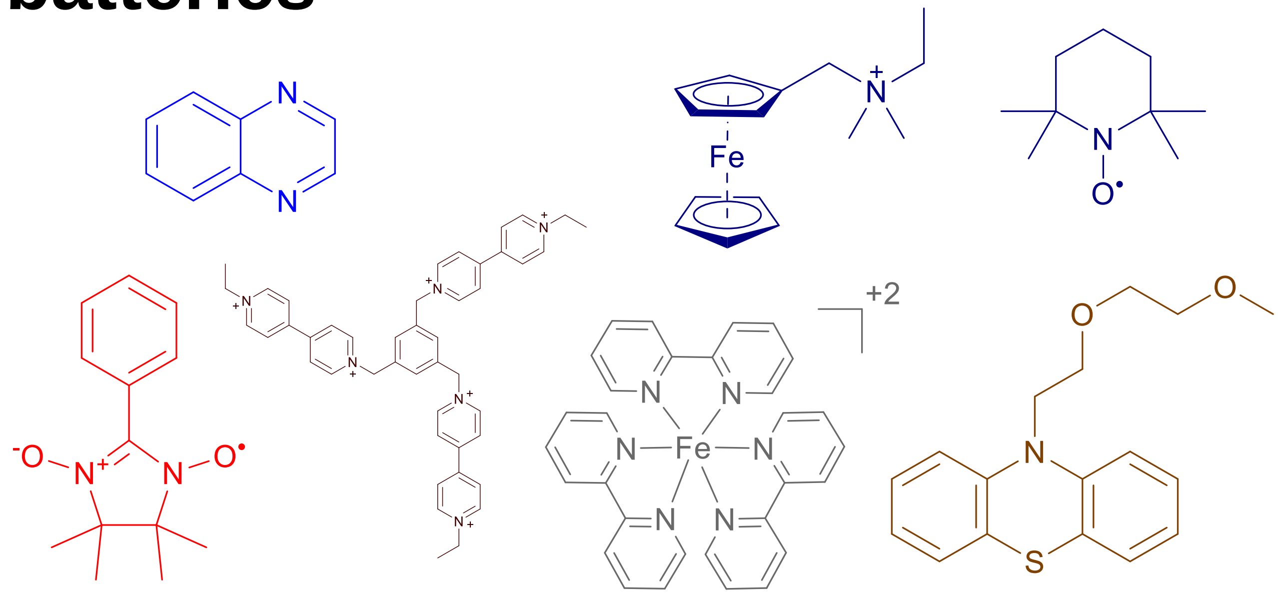
- All RFBs:
  - Active species cost < \$7 kg^{-1}
  - Molecular weight < 200 g mol_e^{-1}
- Aq RFBs:
  - Cell Voltage ≥ 1.4 V
  - ASR < 1.5 Ω cm^2
- NAq RFBs:
  - Actives conc: 2 – 4 mol kg^{-1}
  - Cell Voltage ≥ 2.8 V
  - ASR < 5 Ω cm^2
  - Salt Cost Factor < \$0.5 mol^{-1}

NAqRFBs have a broader range of potentially-viable options but significantly more technological risks than AqRFBs

Dmello & Milshtein et al., *J. Power Sources*, 330 (2016) 261

Discovery & development of new active species for redox flow batteries

- Low equivalent weight
- Symmetric NAqRFBs
- Large (low crossover)
- Model behavior
- Multi-electron transfer
- Highly soluble (liquid)



Apply systematic experimental pipeline

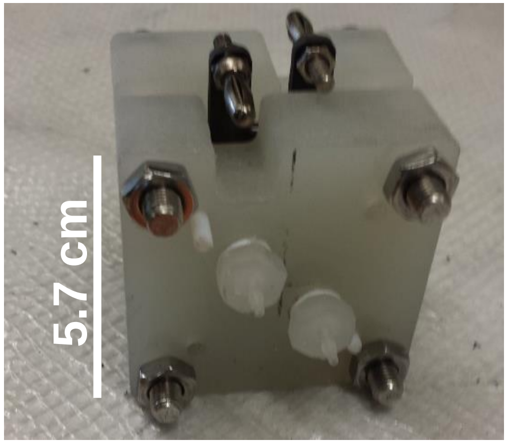
Dilute Species Decay	Cyclic Voltammetry	Bulk Electrolysis	Solubility	Flow Cell
• Charged stability?	• Redox Active?	• Holds charge?	• Energy density?	• Prototype demo

Identify and employ active species as <u>learning platforms</u> or as <u>performance materials</u> (for \$100 kWh^{-1})

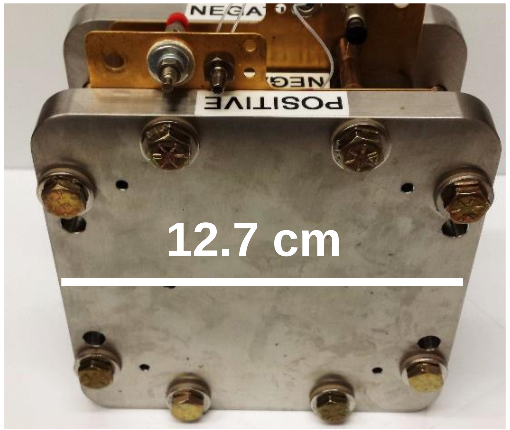
Milshtein et al., *Electrochim. Acta.* 2015, 180, 695; Laramie & Milshtein et al., *J. Power Sources*, 2016, 327, 681; Milshtein & Kaur et al., *Energy Environ. Sci.*, 2016, 9, 3531. Milshtein et al., *J. Power Sources*, 2016, 327, 151; Duan et al., *J. Mater. Chem. A.* 2016, 4, 3531

Scaling redox flow batteries

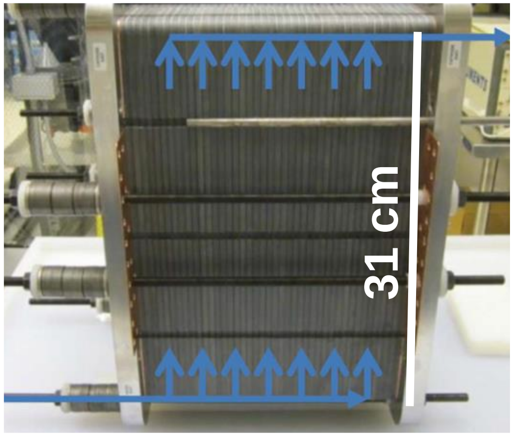
Additional challenges: reaction environment, materials needs, safety



Research Cell



Sub-Scale



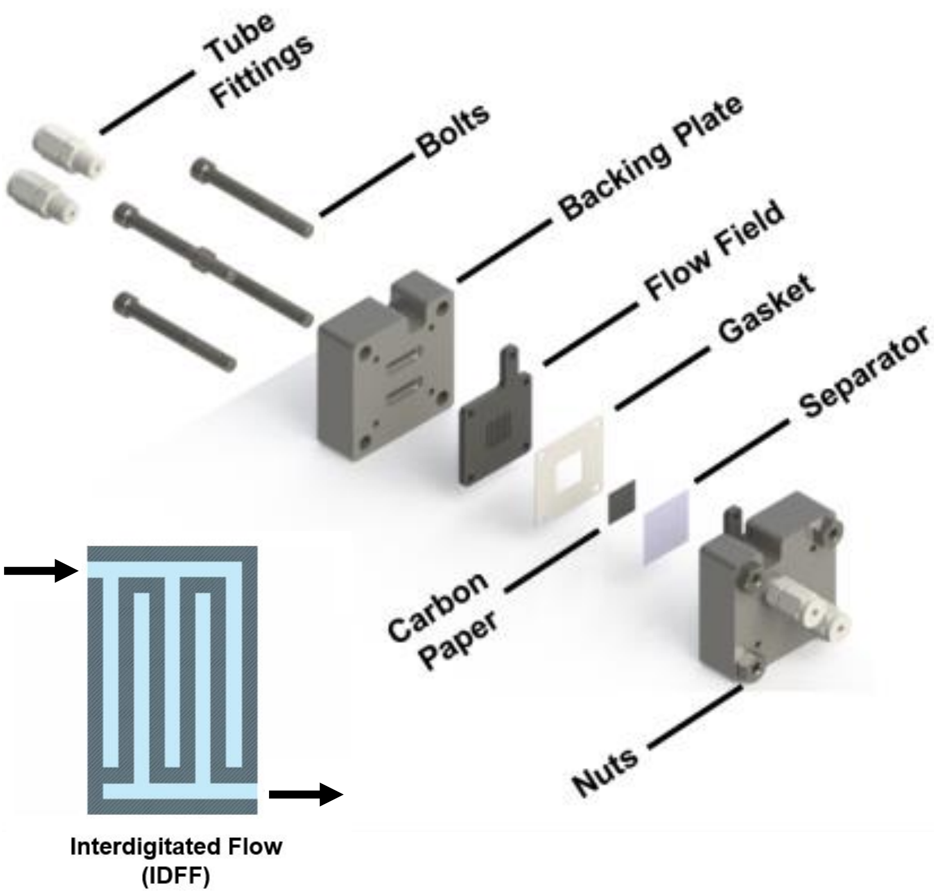
Full Stack

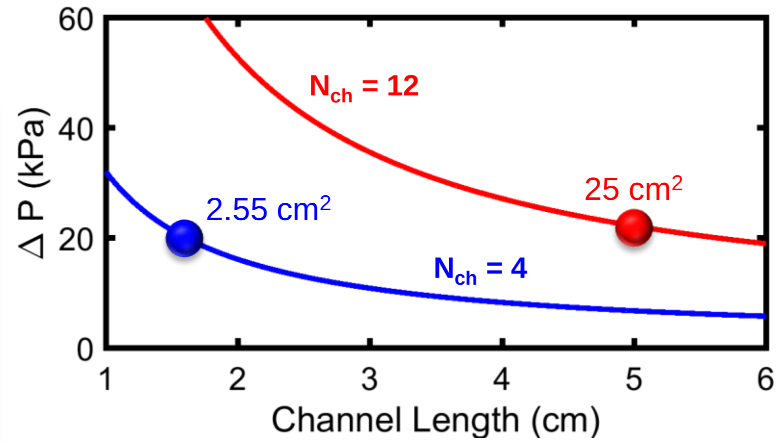
Improved control of electrolyte flow environment

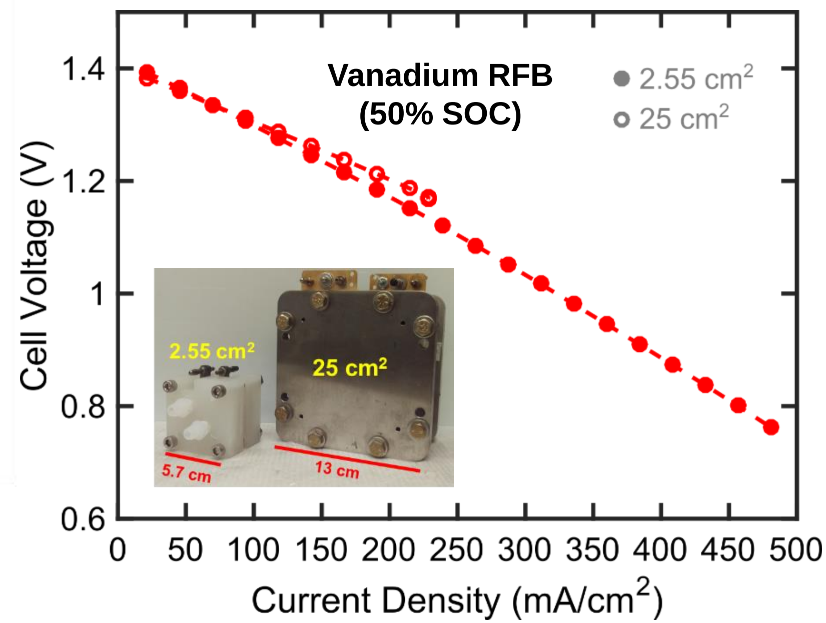
Darling et al., *J. Electrochem Soc.*, 2017, 164, E3081

Flexible platform for materials characterization

Need to enable controlled and scalable experiments within a small cell

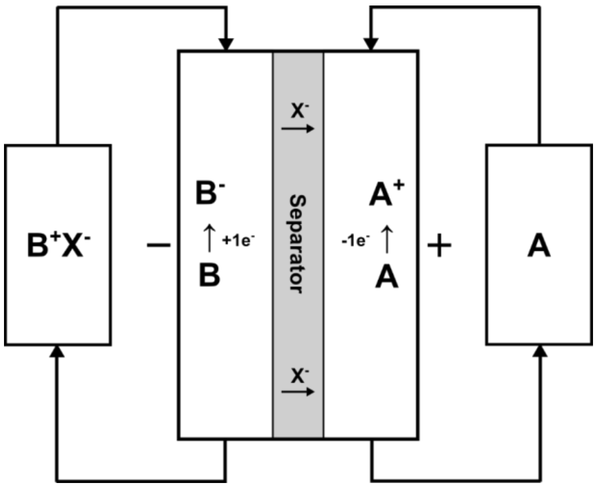






Milshtein & Kaur et al., *Energy Environ. Sci*. 2016, 9, 3531; Milshtein et al., *J. Power Sources*, 2016, 327, 151;
Milshtein & Fisher et al., *ChemSusChem*., 2017, 10, 2080; Milshtein & Barton et al., *in preparation,* 2017

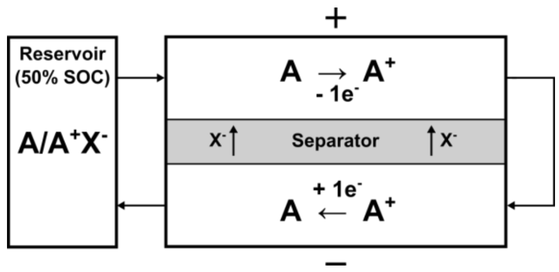
Leveraging flow cells as analytical platforms



Full Cell Testing

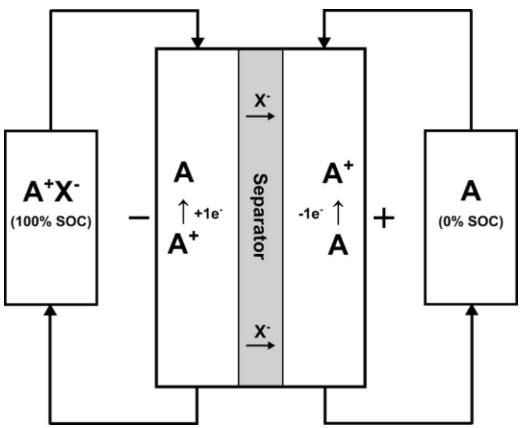
- Operation are practical conditions (polarization, cycling, capacity decay)
- Requires two redox couples & a membrane / separator
- Data analysis convoluted by interdependent factors

Single Electrolyte Cell



- Steady cell polarization, at constant SOC, over a wide range of conditions
- Impedance analysis can enable deconvolution of resistive losses
- Requires a stable well-defined redox couple

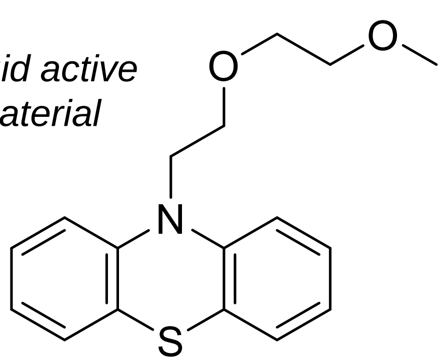
Symmetric Cell

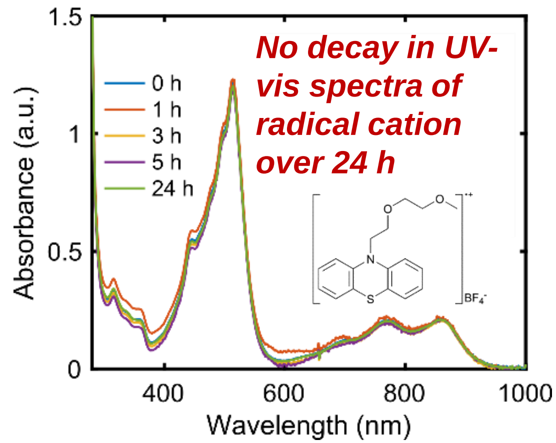


- Charge / discharge cycling with a single electrolyte under practical conditions
- Enables performance and decay analysis of a single redox couple
- Requires a stable well-defined redox couple

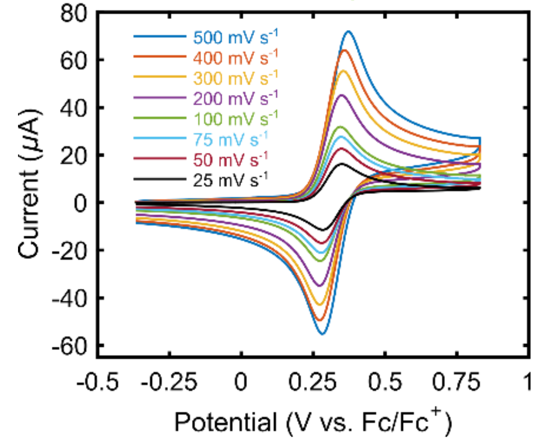
Towards soluble & stable organic active species

Liquid active material

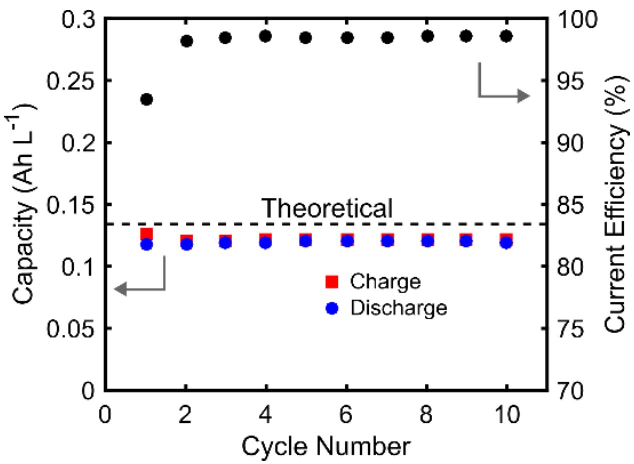




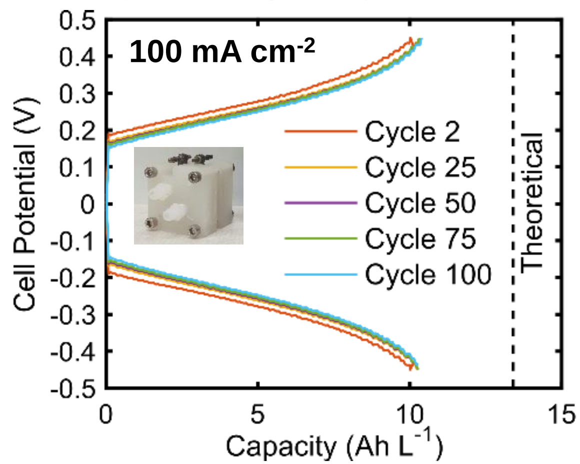
Electrochemically reversible



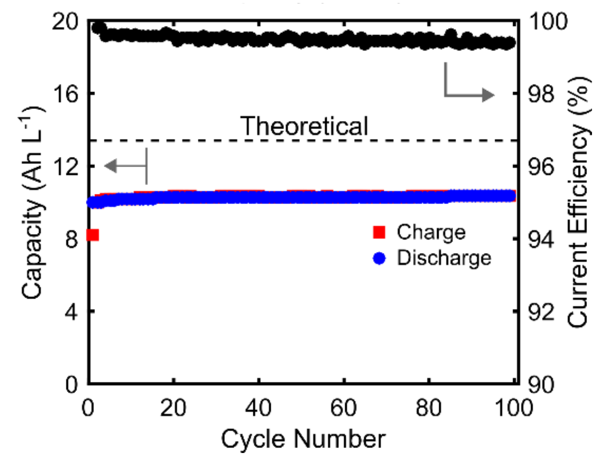
Stores charge at dilute concentrations



High rate capability in a flow cell



Negligible capacity fade at high conc.



Validated new, liquid-phase positive electrolyte material, from molecular discovery to flow cell implementation

Milshtein & Kaur et al., *Energy Environ. Sci.*, 2016, 9, 3531

Area specific resistance impacts cost

$$C_{reactor} = \frac{c_a R}{\varepsilon_{sys} U^2 \varepsilon_v (1-\varepsilon_v) t_d}$$

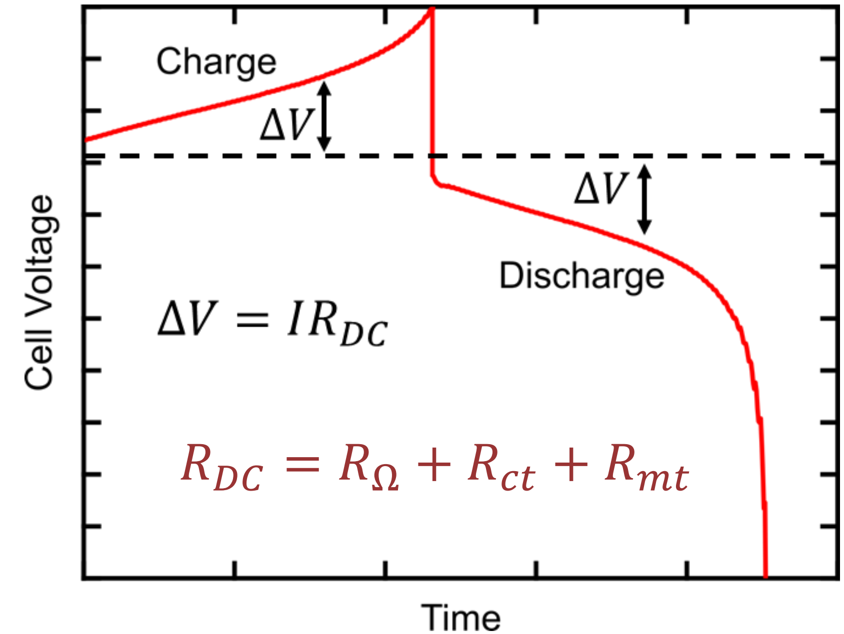
cost ($ m^{-2})

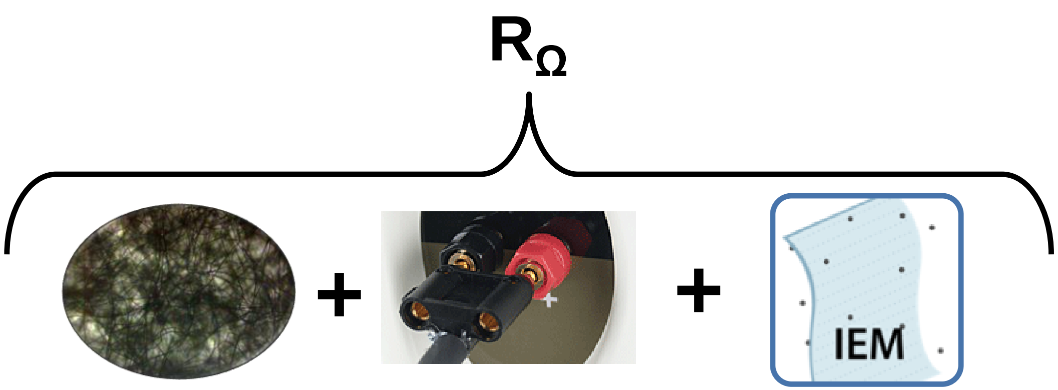
resistance (Ω m^2)

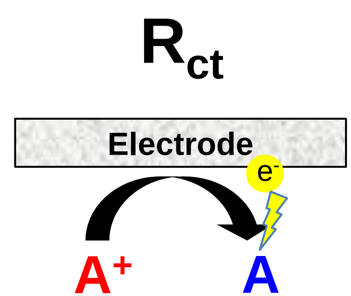
efficiency (-)

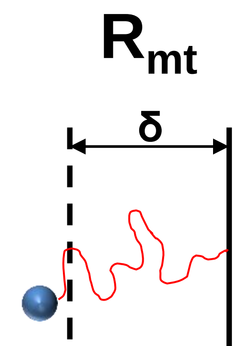
potential (V)

discharge time (h)







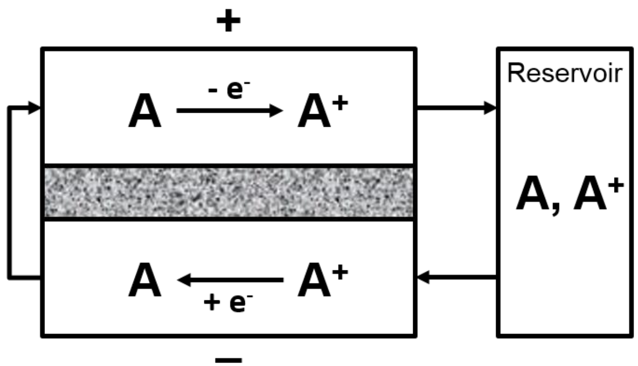


Minimizing ASR is a powerful & chemistry-agnostic strategy for reducing reactor cost contributions to the total battery cost

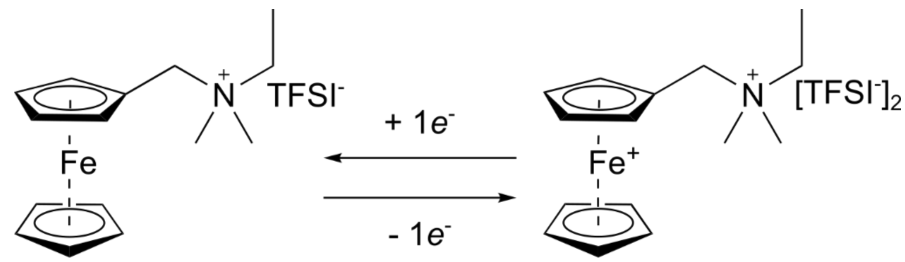
Darling & Gallagher et al., *Energy Environ. Sci.*, 7 (2014) 3459. Dmello & Milshtein et al., *J. Power Sources*, 330 (2016) 261

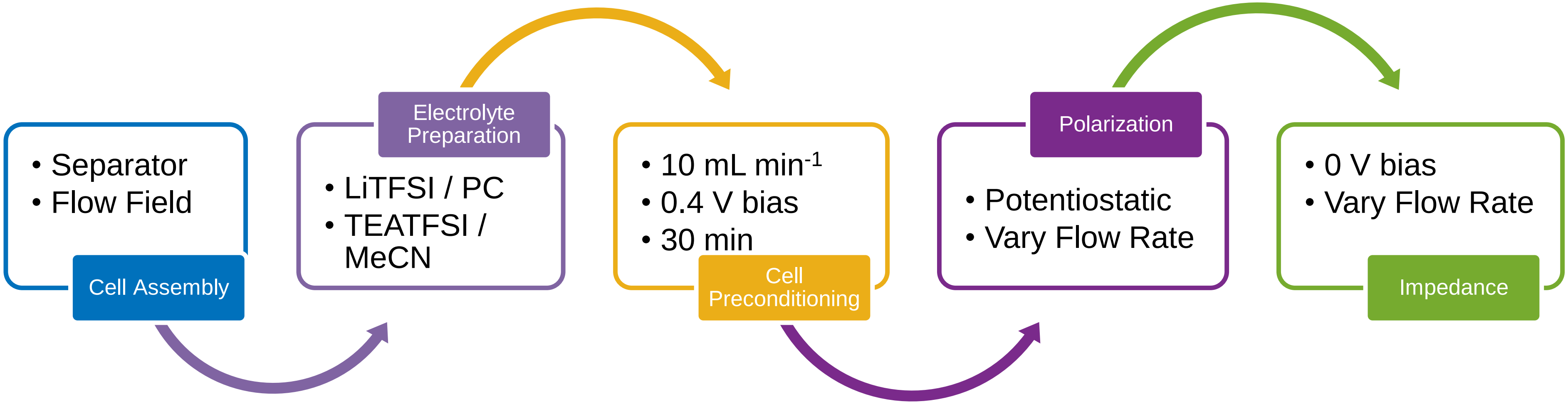
Minimizing cell ASR in nonaqueous RFBs

ASR Target: $< 5\ \Omega\ cm^2$



E° = 3.5 V vs Li/Li^+

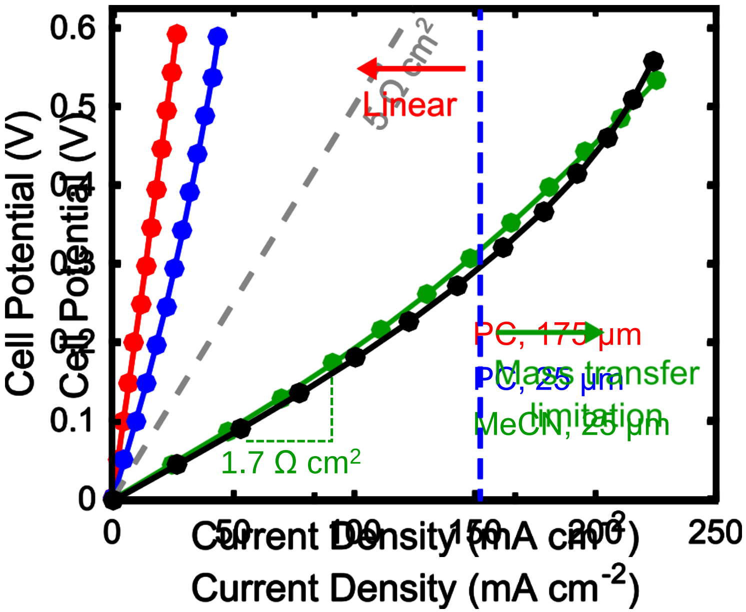




Systematically vary electrolyte properties, component properties, and cell operating conditions to identify and mitigate resistive contributions

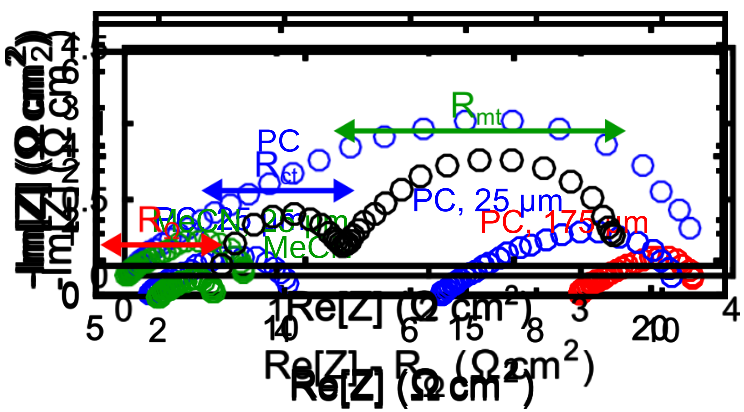
Dmello & Milshtein et al., *J. Power Sources*, 2016, 330 261; Wei et al., *Adv. Energy Mater.*, 2015, 5 1400678; Milshtein et al., *J. Electrochem. Soc.*, 2017, 164, A2487-A2499

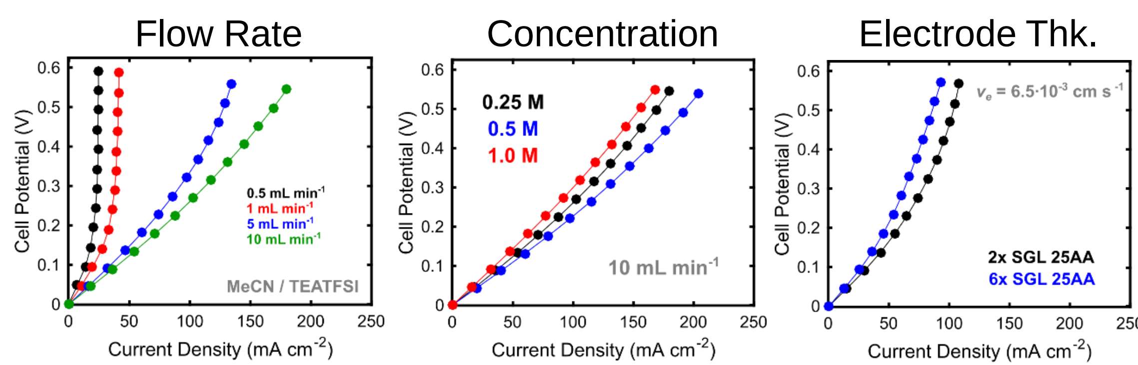
Systematic approach to reducing cell ASR



- Ohmic losses are largest concern
- Mass transfer is 2nd largest contributor
- Kinetic losses are negligible

	κ (mS cm^{-1})	μ (mPa·s)
LiTFSI / PC		
TEATFSI / MeCN		





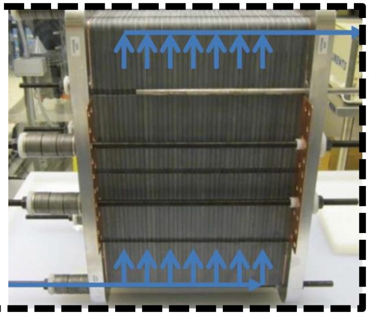
Demonstrated lowest ASR to date, with a new emphasis on understanding mass transfer

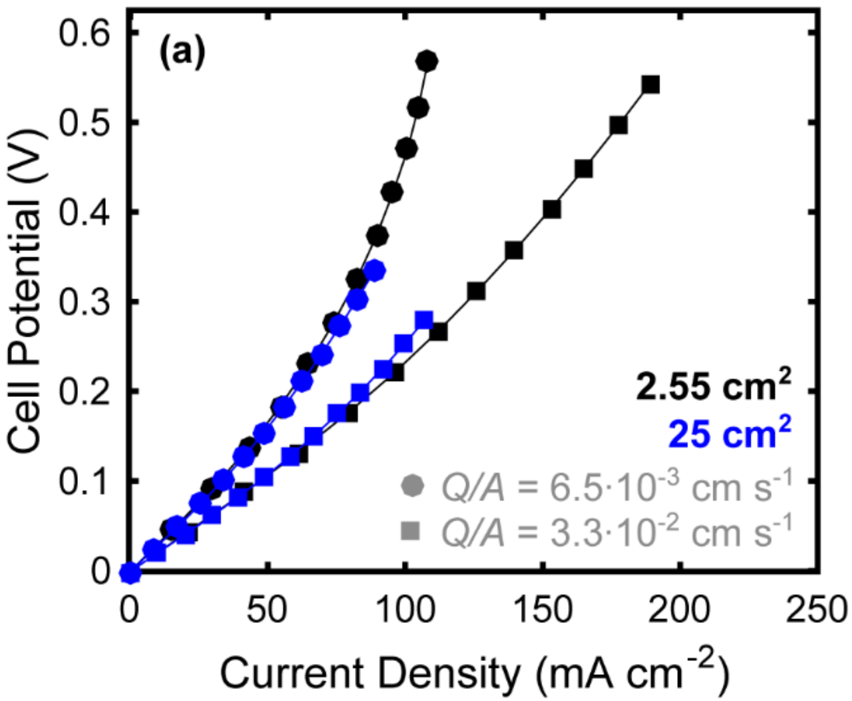
Milshtein et al., *J. Electrochem. Soc.*, 2017, 164, A2487-A2499

Scalable results obtained in the small flow cell

10x

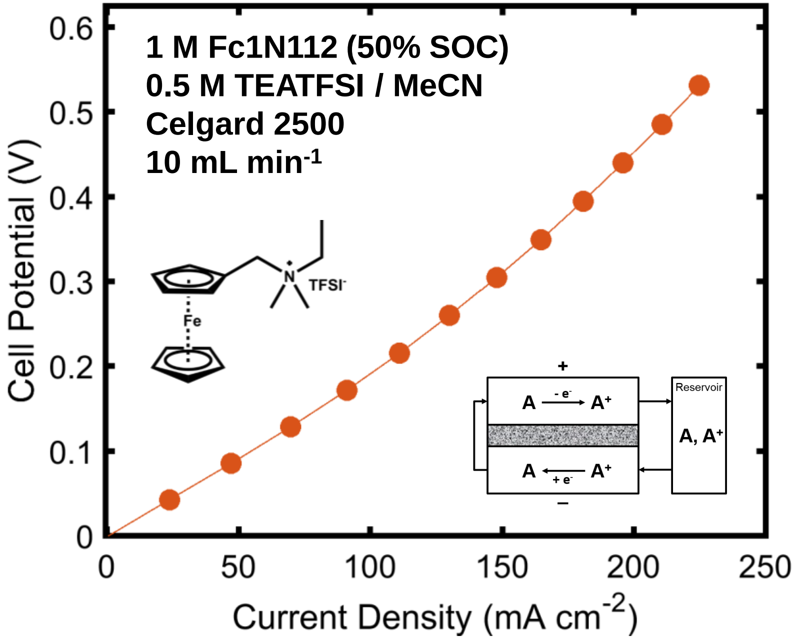
Future?

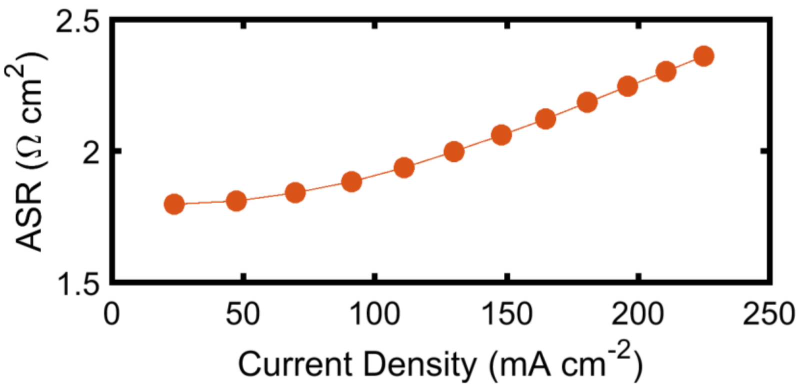


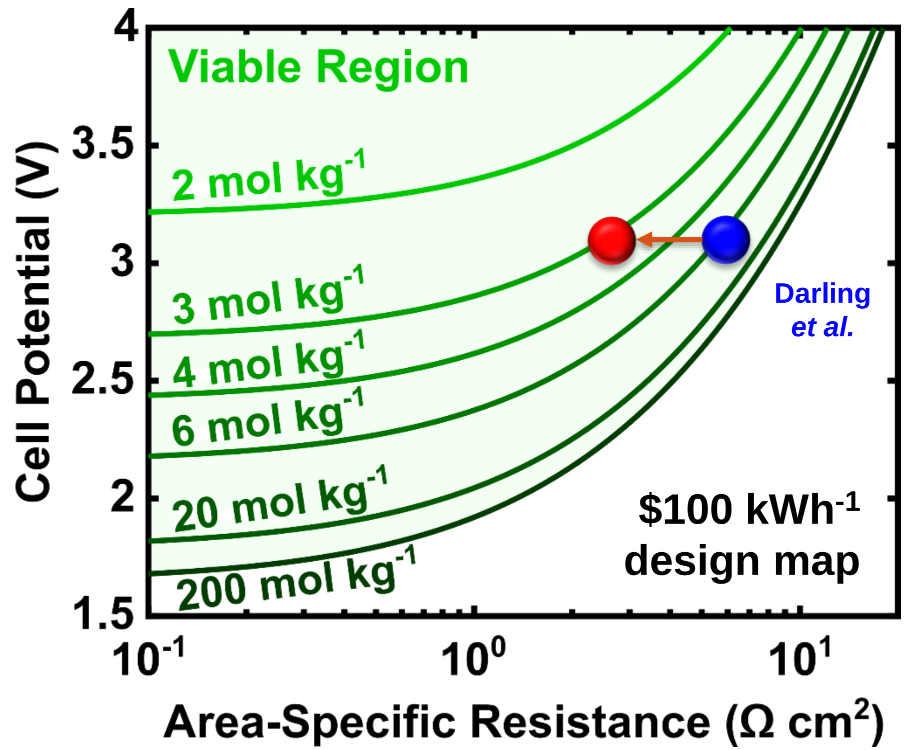


Milshtein et al., *J. Electrochem. Soc.*, 2017, 164, A2487-A2499

More power, more design space…







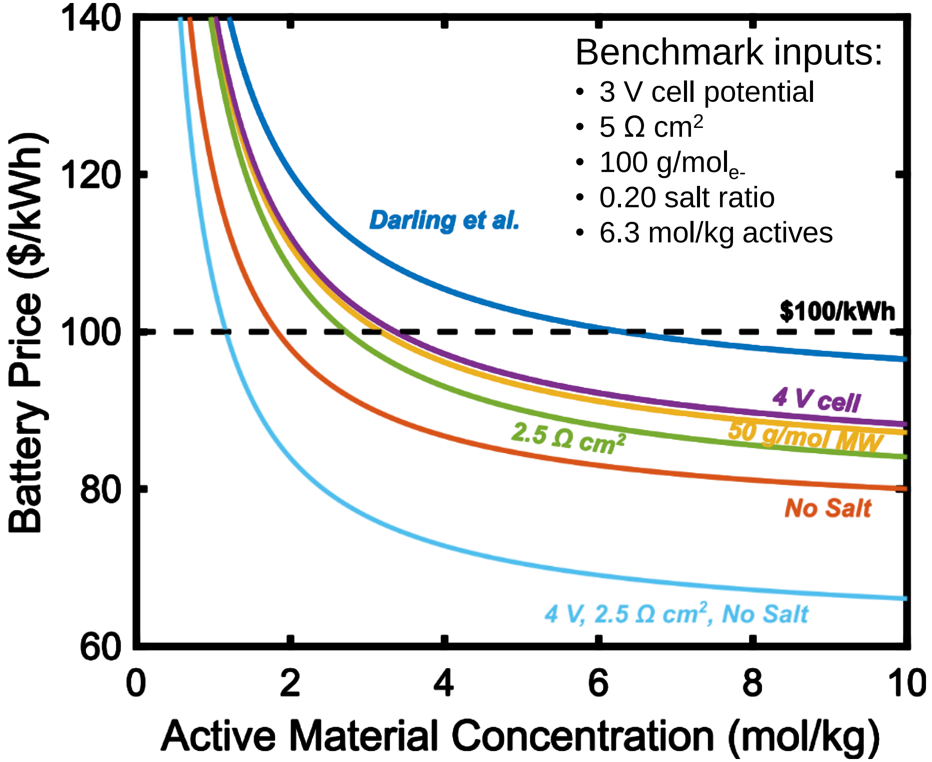
Achieving molality targets:

- Moles of active species per kg solvent
  - 1 M Fc1N112 = 3.1 mol kg^{-1}
- Low density solvents are ideal
- Need high partial molar volume of actives

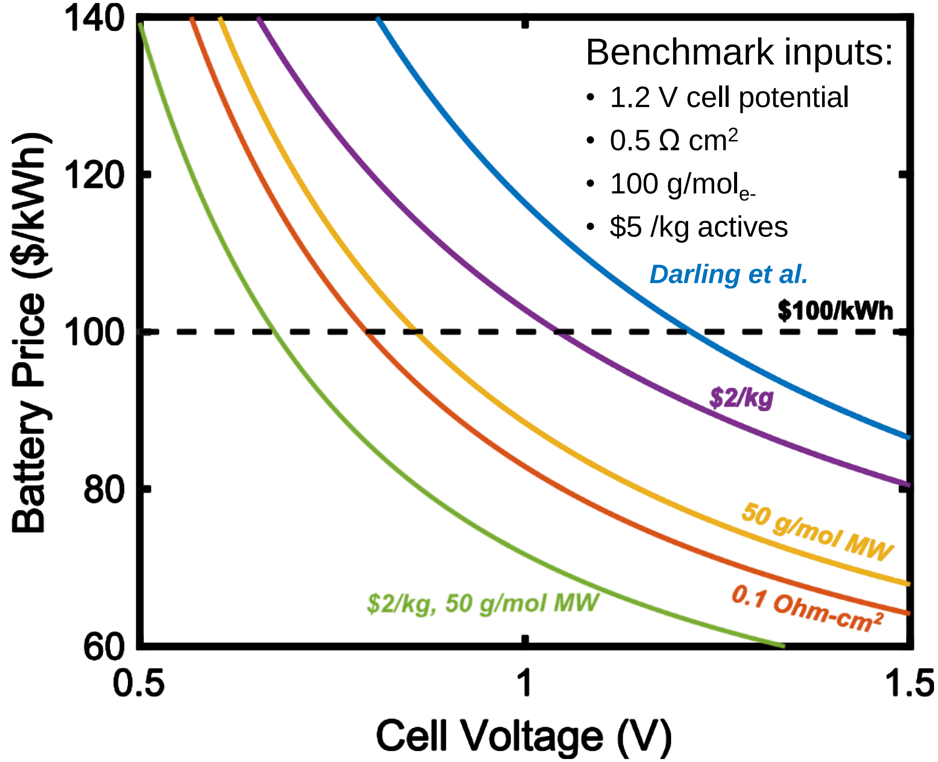
Dmello & Milshtein et al., *J. Power Sources*, 2016, 330, 261; Milshtein et al., *J. Electrochem. Soc.*, 2017, 164, A2487

Design options for decreasing RFB price

Nonaqueous



Aqueous



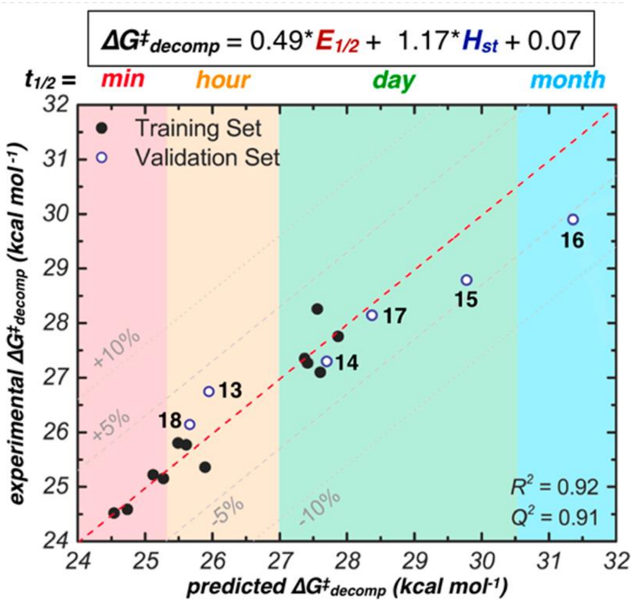
While both approaches have credible pathways to low prices, each has <u>different fundamental scientific needs necessitating different research approaches</u> to tackle unique technical roadblocks.

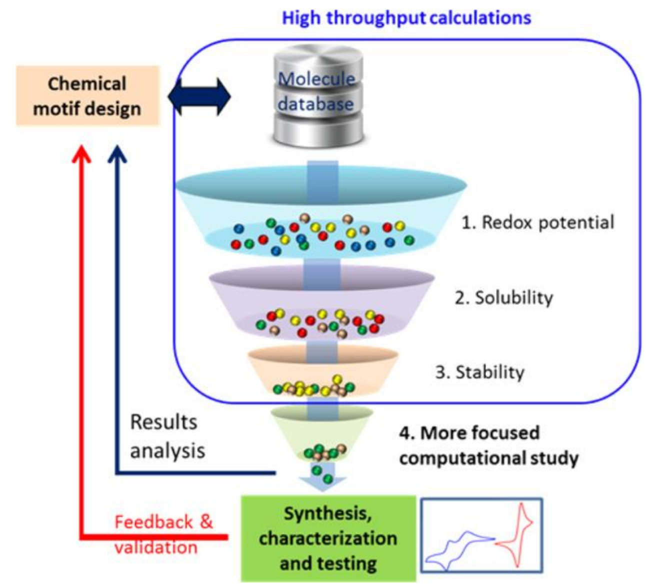
Darling & Gallagher et al., *Energy Environ. Sci.*, 2014, 7, 3459; Dmello & Milshtein et al., *J. Power Sources*, 2016, 330, 261

Grand Challenge:

Guided synthesis of matter with precise properties

How can we accelerate the invention, discovery, and synthesis of molecules, materials, and interfaces with targeted property sets?





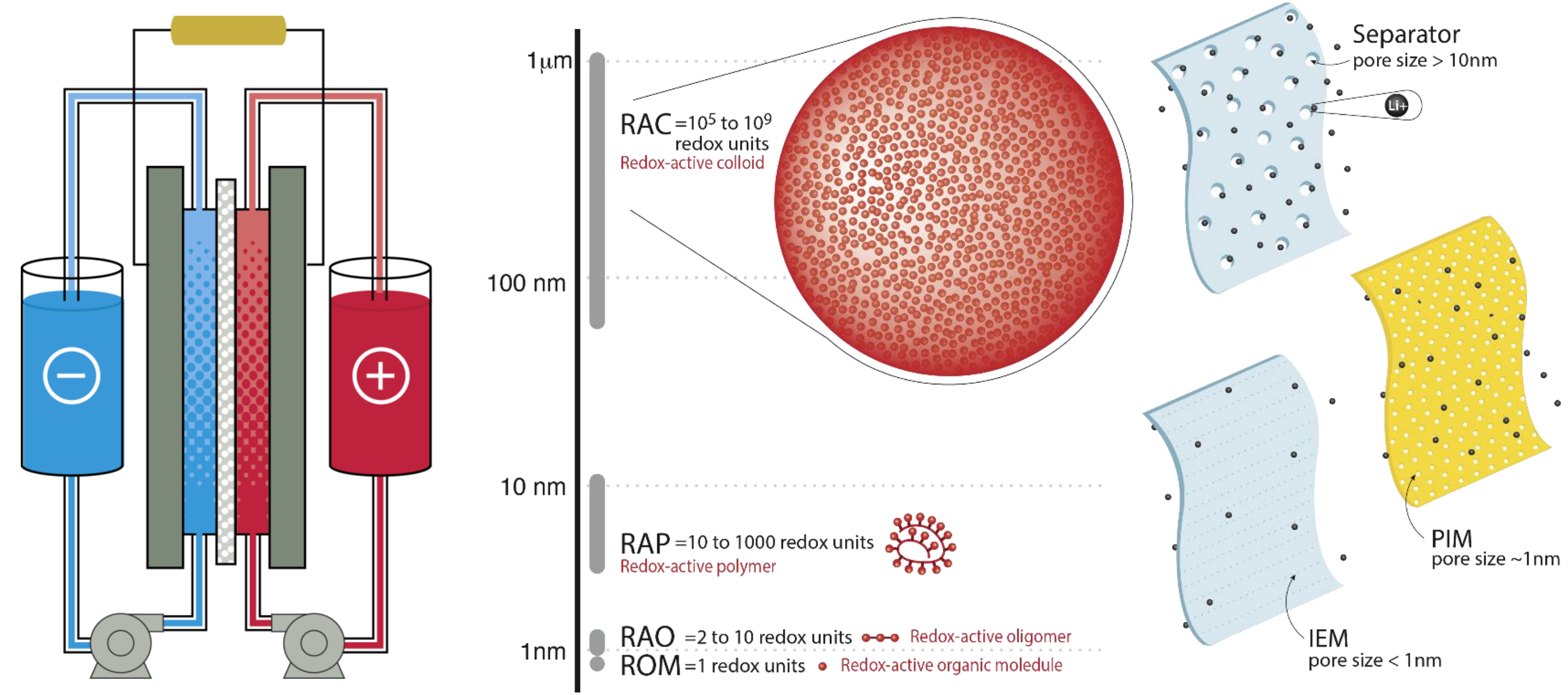
QSPR = Quantitative Structure-Property Relationships

Are outcomes of these models universally applicable of dependent on “local” factors?

Sevov et al., *J. Amer. Chem. Soc.*, 2017, 139, 2924; Cheng et al., *J. Phys. Chem. Lett.*, 2015, 6, 283; J. De Yoreo et al., Report of the Basic Energy Sciences Workshop on Synthesis Science for Energy Relevant Technology, DOE BES, 2017

Grand Challenge:

Coordinated design of molecules & membranes

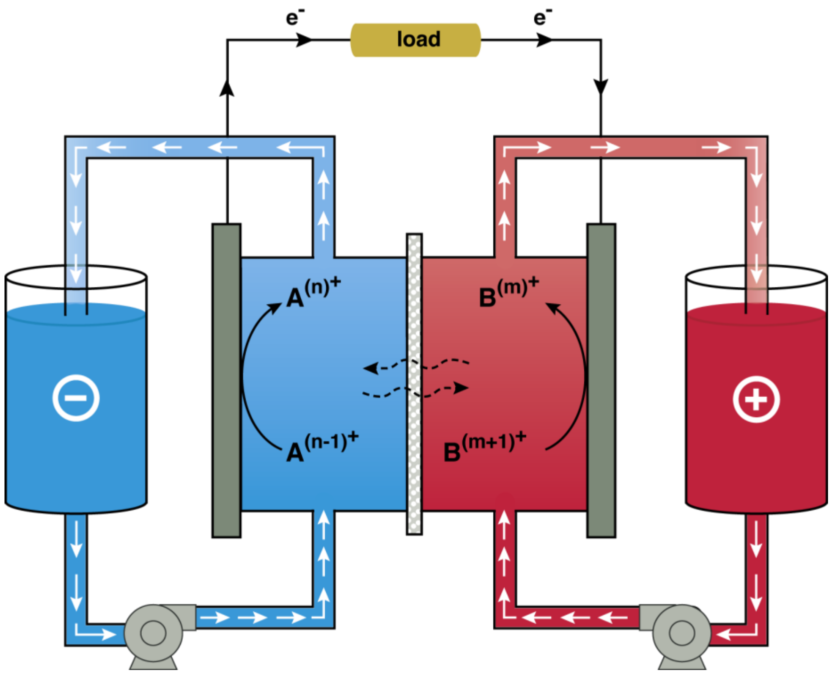


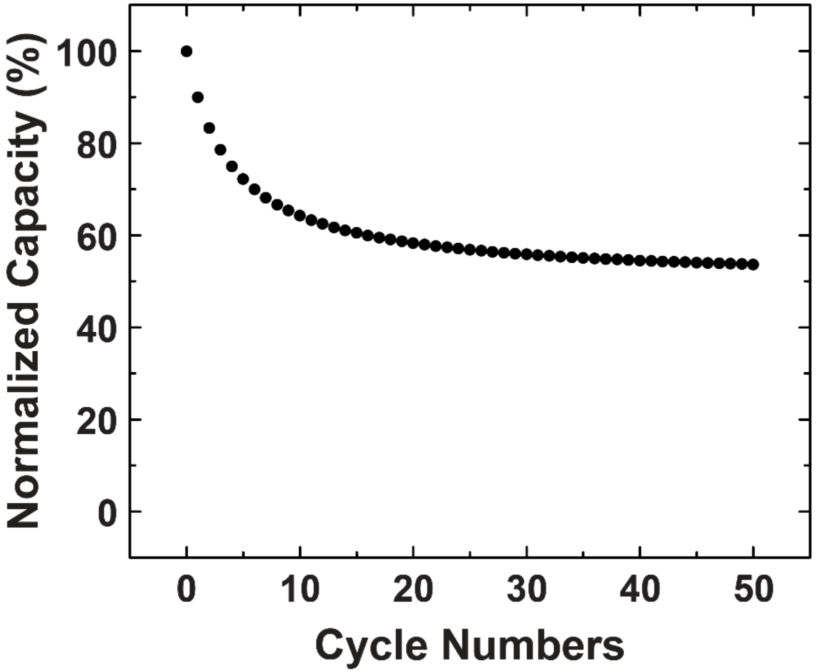
Is there a sweet spot where transport, redox kinetics, solubility and cost can be balanced as to enable advanced RFBs?

Nagarjuna et al., *J. Am. Chem. Soc.*, 2014, 136, 16309; Montoto et al., *J. Am. Chem. Soc*,, 2016, 138, 13230; Burgess et al., *Acc. Chem. Res.*, 2016, 49, 2649; Doris et al., *Angew. Chem.*, 2017, 56, 1595; Kowalski & Braten, in preparation

Grand Challenge:

Quantifying and mitigating decay mechanisms

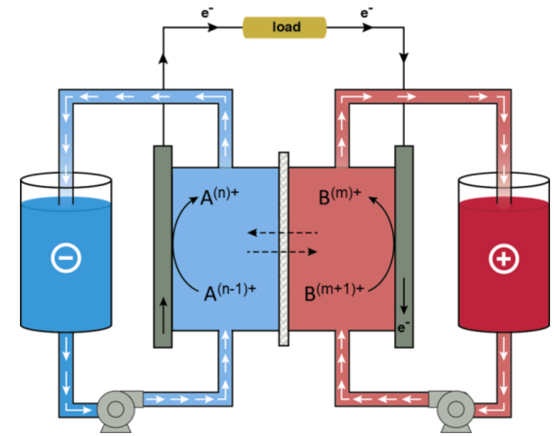


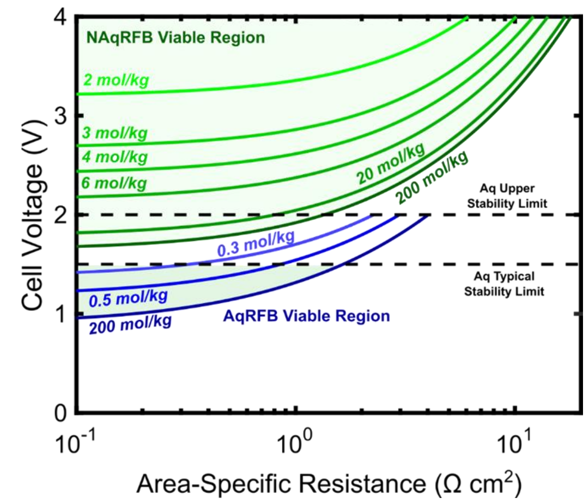


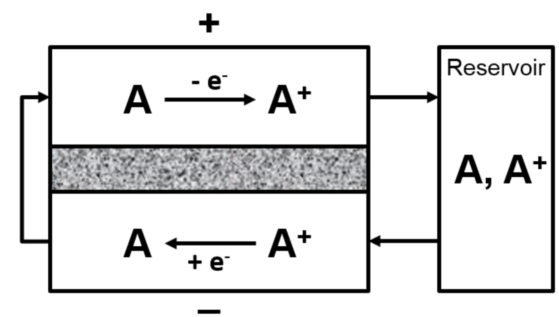
What are the modes of performance degradation in flow batteries and how can we predict lifetime without having to operate for that lifetime?

Concluding remarks

- RFBs are a nascent, yet promising, technology with several pathways to the low prices needed for broad deployment.
- Aqueous and nonaqueous RFBs follow different cost reduction pathways based on their fundamentally different materials characteristics.
- Early-stage integration of techno-economic analysis can highlight challenges which require advances in basic energy sciences.
- Models are of importance for systematic scientific investigation and should be viewed in the broadest sense, so as to capture different approaches and techniques.







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Brushett Group Members

Jeffrey Kowalski
John Barton
Steven Brown
Michael Orella
Thomas Carney
McLain Leonard
Katherine Greco
AJ Fenton

Antoni Forner-Cuenca (PD)
Sujat Sen (PD)

Susan Odom (VS)
Javit Drake (VS)
Matteo Gigli (VS)

Alumni

Jarrod Milshtein (Giner)
Liang Su (MIT DMSE)
Emily Carino (ANL)
Apurba Sakti (MITEI)
Kyler Carroll (Wildcat Tech.)
Chaerin Kim

Brushett Group Collaborators

Yet-Ming Chiang (MIT)
Audun Botterud (MIT)
Martin Bazant (MIT)

Jeffrey Moore (Univ. of Illinois)
Joaquin Rodriguez-Lopez (Univ. of Illinois)
Kyle Smith (Univ. of Illinois)

Brett Helms (Lawrence Berkeley NL)

Robert Darling (UTRC)
Mike Perry (UTRC)

Levi Thompson (Univ. of Michigan)

Susan Odom (Univ. of Kentucky)
John Anthony (Univ. of Kentucky)
James Landon (Univ. of Kentucky)

Kevin Gallagher (Argonne NL)
Lu Zhang (Argonne NL)
Rajeev Assary (Argonne NL)
Larry Curtiss (Argonne NL)
Lynn Trahey (Argonne NL)

Xiaoliang Wei (Pacific Northwest NL)
Wei Wang (Pacific Northwest NL)

Nigel Brandon (Imperial CL)
Vladimir Yufit (Imperial CL)