Flow Battery Capacity Fade and Power Density with Aqueous-Soluble Organics

Research supported by U.S. DOE award DE-AC05-76RL01830 through PNNL subcontract 428977

PI: Michael J. Aziz, Harvard School of Engineering and Applied Sciences

- **Context from prior research: Decomposition, capacity fade rate and how to measure it**
- **Extremely stable anionic viologen active species enabling CEM**
- **Record-breaking low fade rate from quinones informed by mechanistic understanding**
- **Enhanced power density through engineering electrode design & operating parameters**
- **Review of ASO capacity fade rates from all published studies**

Harvard Milestones, 9/10/2019—9/9/2020

(1) Reduce capacity fade rate of full cell to < 0.02%/day

→ achieved 0.0018%/day (<1%/yr)

(2) Utilize understanding of electrode science & engineering to raise peak galvanic power density from 0.24 to 0.35 W/cm^2.

→ achieved 0.40 W/cm^2

Publications

[1] M. Wu, Y. Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" *Chem* **6**, 1432 (2020); https://doi.org/10.1016/j.chempr.2020.03.021

[2] A.A. Wong and M.J. Aziz, "Method for Comparing Porous Carbon Electrode Performance in Redox Flow Batteries", *J. Electrochem. Soc.* **167**, 110542 (2020); https://dx.doi.org/10.1149/1945-7111/aba54d

[3] L. Tong, M.-A. Goulet, D.P. Tabor, E.F. Kerr, D. DePorcellinis, E.M. Fell, A. Aspuru-Guzik, R.G. Gordon, and M.J. Aziz, "Molecular engineering of an alkaline naphthoquinone flow battery" *ACS Energy Letters* **4**, 1880 (2019); https://pubs.acs.org/doi/abs/10.1021/acsenergylett.9b01321

[4] G. Sedenho, D. De Porcellinis, Y. Jing, E.F. Kerr, L.M. Mejia-Mendoza, A. Aspuru-Guzik, R.G. Gordon, F.N. Crespilho, and M.J. Aziz, "Effect of molecular structure of quinones and carbon electrode surfaces on the interfacial electron transfer process", *ACS Appl. Energy Mater.* **3**, 1933 (2020); https://doi.org/10.1021/acsaem.9b02357

[5] F.R. Brushett, M.J. Aziz and K.E. Rodby, "On lifetime and cost of redox-active organics for aqueous flow batteries" Invited Viewpoint article for *ACS Energy Letters*. **5**, 879 (2020); https://doi.org/10.1021/acsenergylett.0c00140

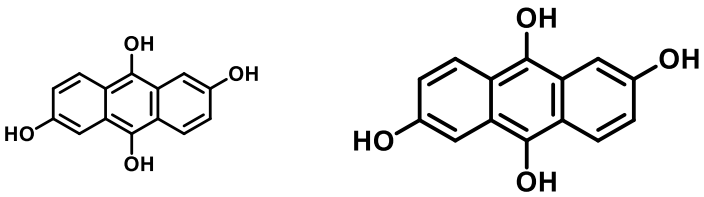
[6] D.G. Kwabi, Y.L. Ji and M.J. Aziz, "Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review" *Chem. Rev.* **120**, (2020); https://doi.org/10.1021/acs.chemrev.9b00599

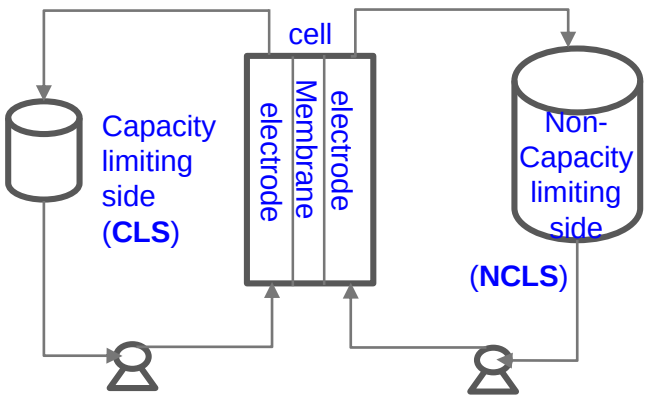
[7] S. Jin, E.M. Fell, L. Vina-Lopez, Y. Jing, P.W. Michalak, R.G. Gordon, and M.J. Aziz, "Near Neutral pH Redox Flow Battery with Low Permeability and Long-Lifetime Phosphonated Viologen Active Species" *Advanced Energy Materials* **10**, 2000100 (2020); https://doi.org/10.1002/aenm.202000100

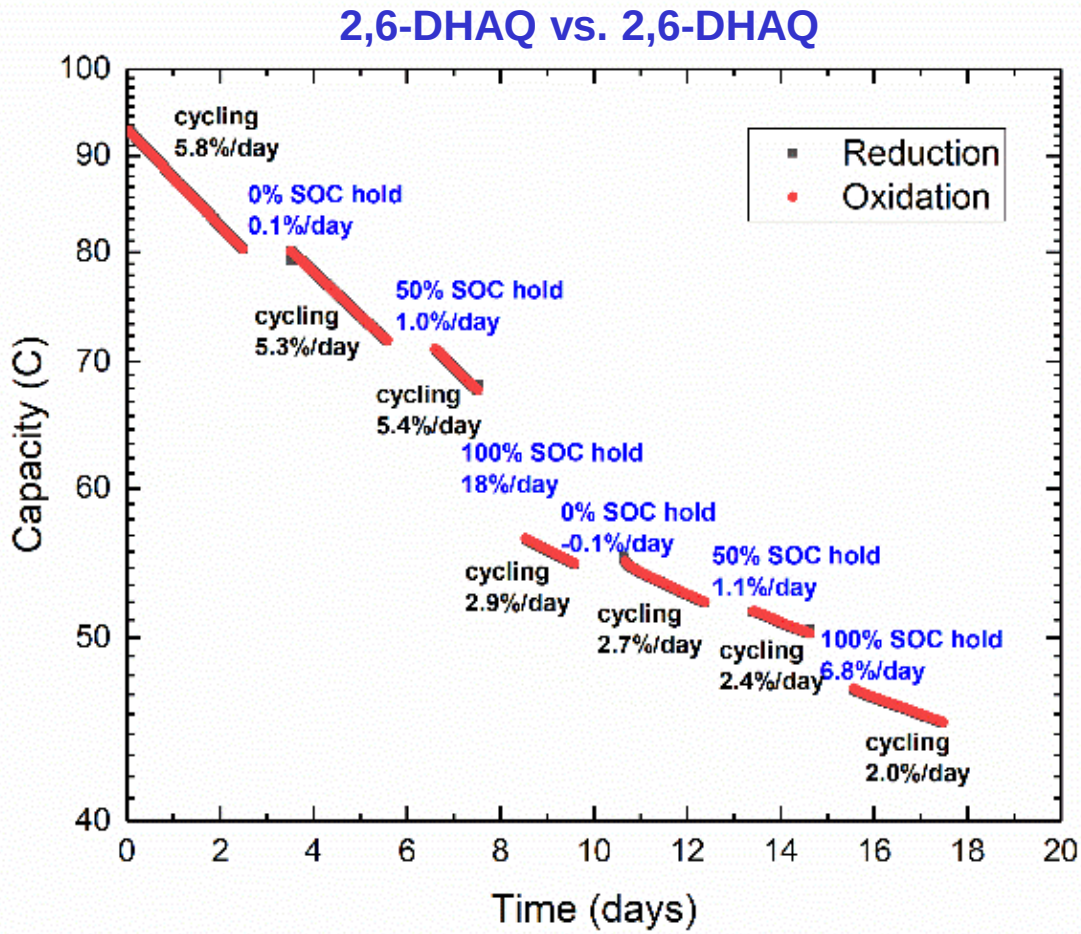
[8] Y. Jing, M. Wu, A.A. Wong, E.M. Fell, S. Jin, D.A. Pollack, E.F. Kerr, R.G. Gordon and M.J. Aziz, "In situ Electrosynthesis of Anthraquinone Electrolytes in Aqueous Flow Batteries", *Green Chemistry*, in press (2020).

Context from our Prior Research: Capacity Fade Rate Depends Mainly on SOC, *not* Cycle Rate

Unbalanced compositionally-symmetric cell cycling experiment
Both sides 2,6-DHAQ, 50% SOC,
0.1 M in 1 M KOH, glove box (**OCV = 0**)



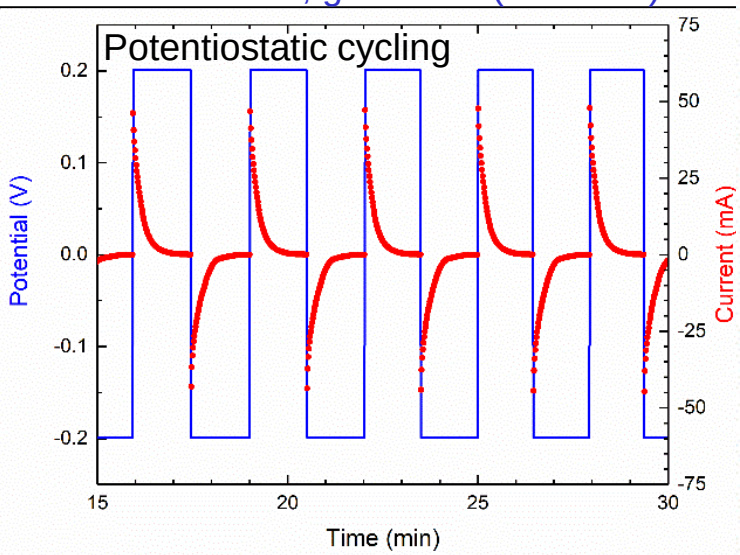




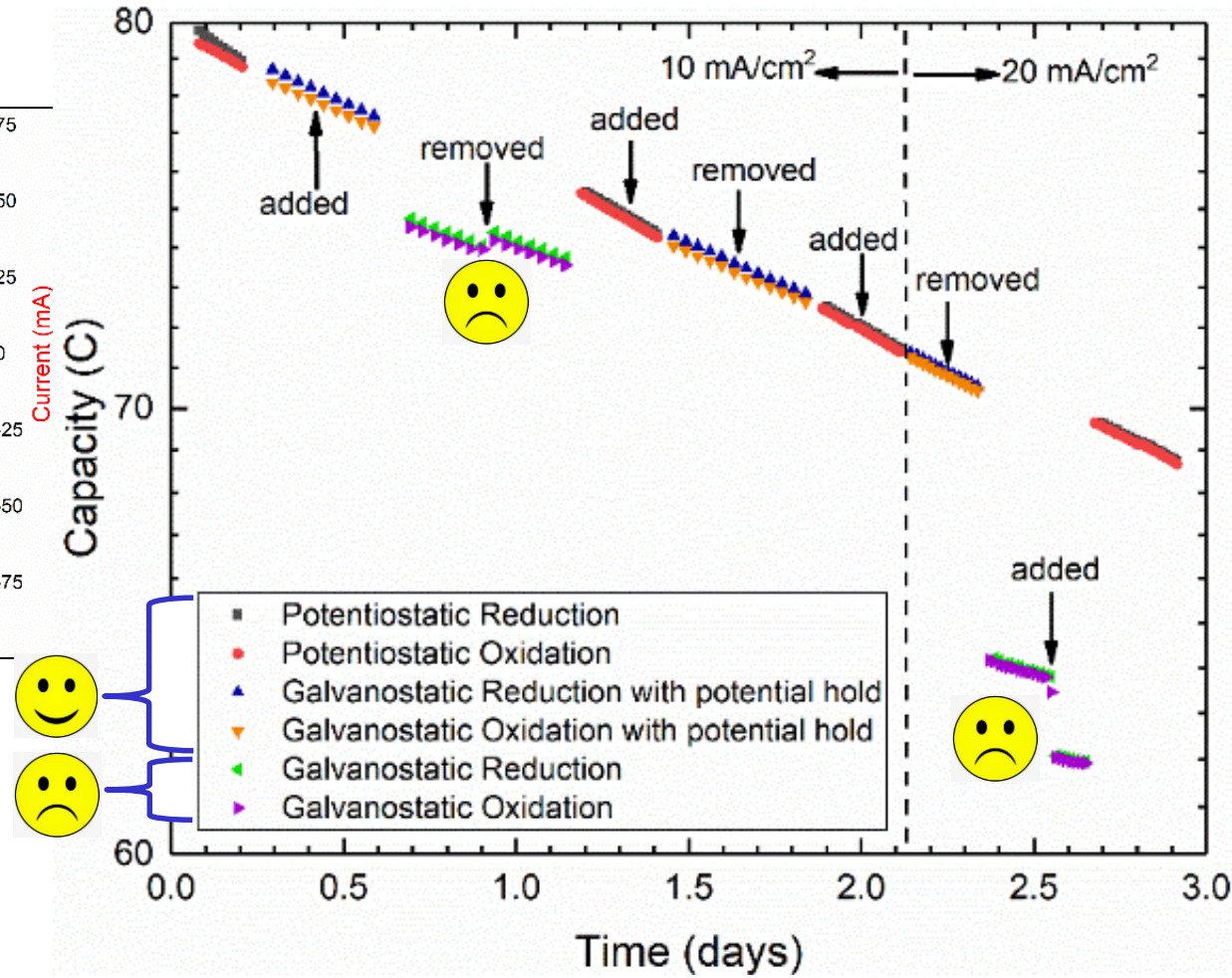
Marc-Antoni Goulet & M.J. Aziz, "Flow Battery Molecular Reactant Stability Determined by Symmetric Cell Cycling Methods", *JES* **165**, A1466 (2018)

Context from our Prior Research: Potentiostatic Cycling Eliminates Capacity Fade Artifact from ASR Drift

Unbalanced compositionally-symmetric cell cycling experiment
Both sides 2,6-DHAQ, 50% SOC,
0.1 M in 1 M KOH, glove box (**OCV = 0**)



0.13 Ω added/removed in series*



Marc-Antoni Goulet & M.J. Aziz, "Flow Battery Molecular Reactant Stability Determined by Symmetric Cell Cycling Methods", *JES* **165**, A1466 (2018)

*represents 25% increase in membrane ASR

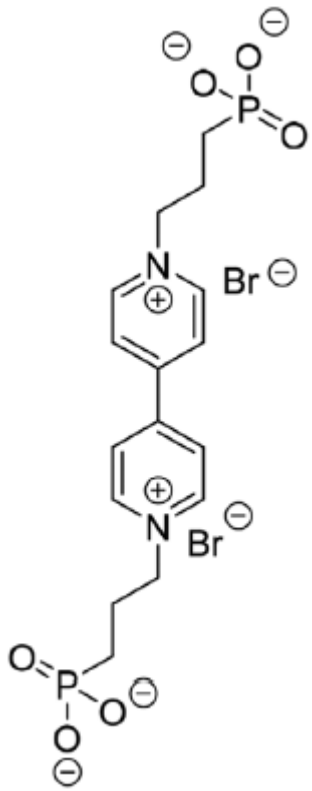
A pH 9 Aqueous Flow Battery with Anionic Viologen Species Enabling Cation Exchange Membrane

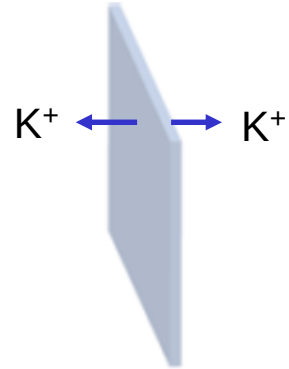
Negative couple: BPP-Viologen

1.0 M (27 Ah/L); 6.2 mL; pH 9

solubility: 1.23 M (34 Ah/L)

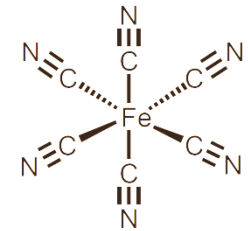
capacity-limiting side



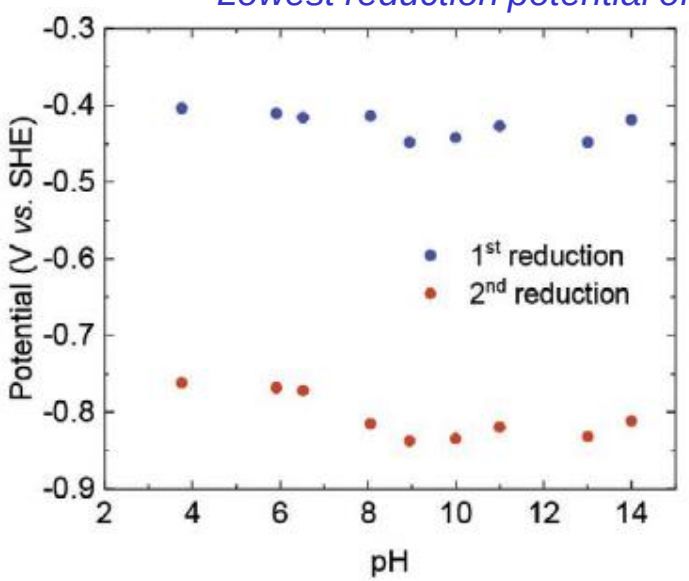


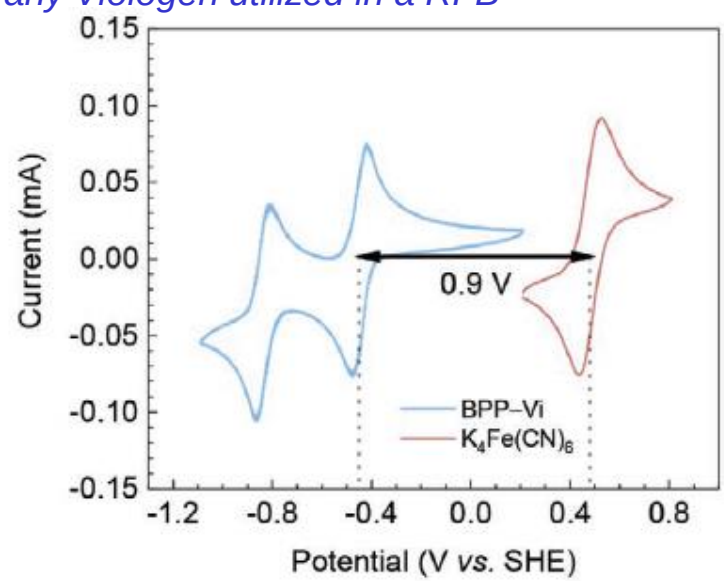
non-fluorinated cation exchange membrane

Positive couple:
$Fe(CN)_6^{3-/4-}$



Lowest reduction potential of any Viologen utilized in a RFB





S. Jin, E.M. Fell, L. Vina-Lopez, Y. Jing, P.W. Michalak, R.G. Gordon, and M.J. Aziz, "Near Neutral pH RFB with Low Permeability and Long-Lifetime Phosphonated Viologen Active Species" *Adv. Energy Mater.*, **10**, 2000100 (2020)

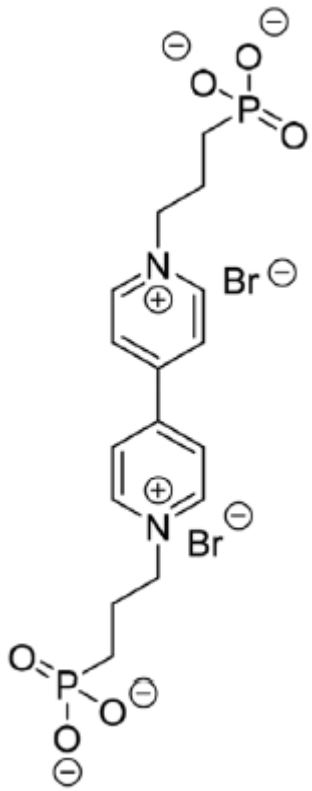
Extremely Low Fade Rate of Anionic Viologen

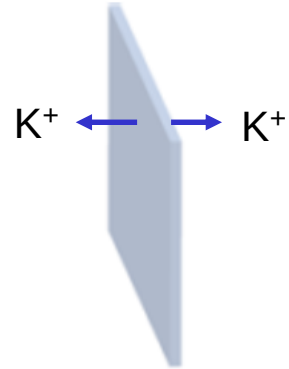
Negative couple: BPP-Viologen

1.0 M (27 Ah/L); 6.2 mL; pH 9

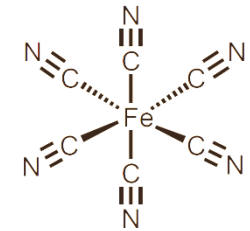
solubility: 1.23 M (34 Ah/L)

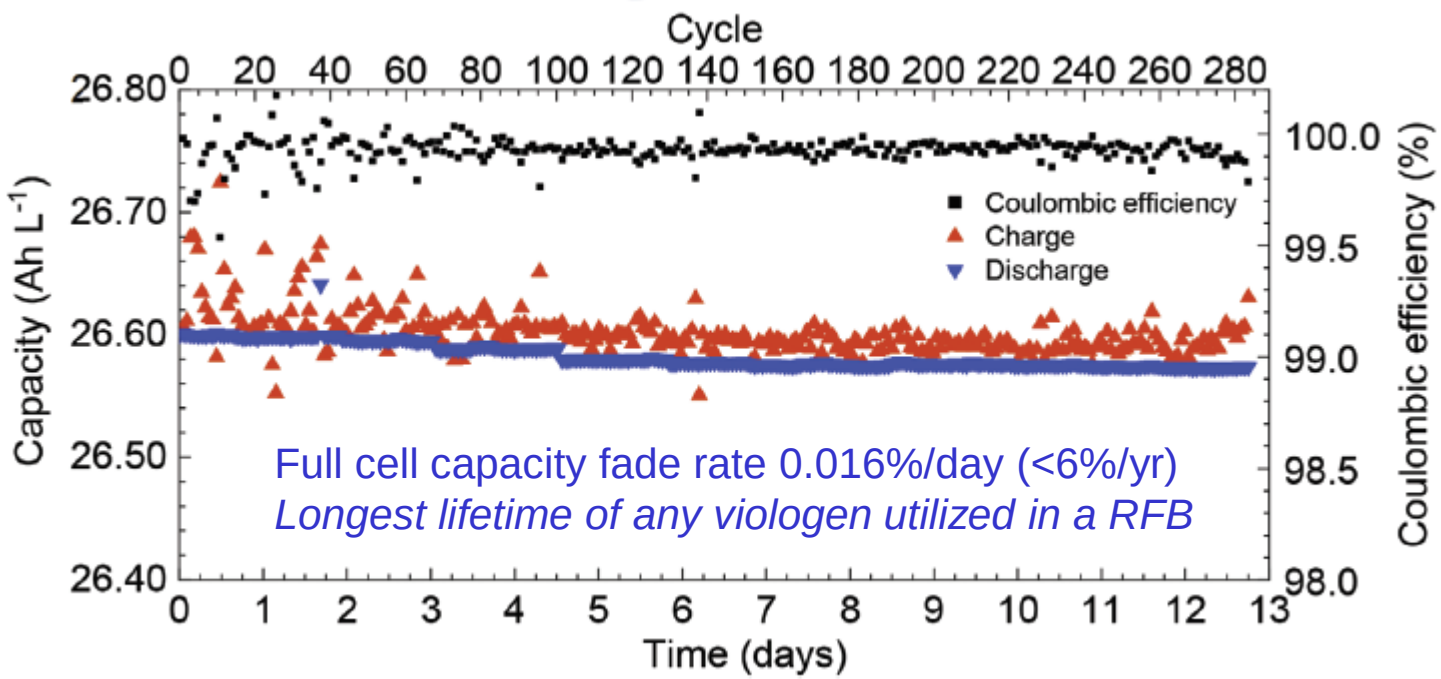
capacity-limiting side





Positive couple:
$Fe(CN)_6^{3-/4-}$

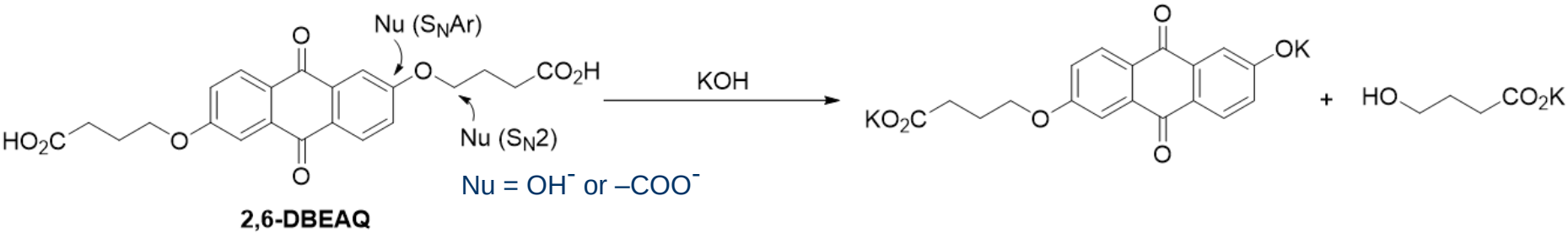




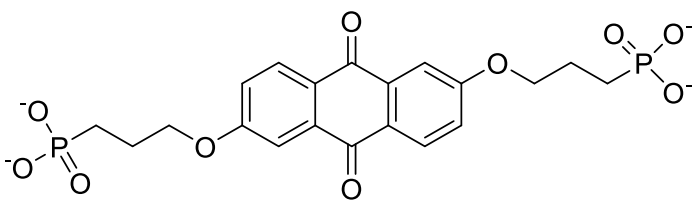
S. Jin, E.M. Fell, L. Vina-Lopez, Y. Jing, P.W. Michalak, R.G. Gordon, and M.J. Aziz, "Near Neutral pH RFB with Low Permeability and Long-Lifetime Phosphonated Viologen Active Species" *Adv. Energy Mater.*, **10**, 2000100 (2020)

Setting New Records for Low Capacity Fade Rates

Methuselah I: 2,6-di-butanoate ether anthraquinone (DBEAQ): Capacity fade rate 0.04%/day



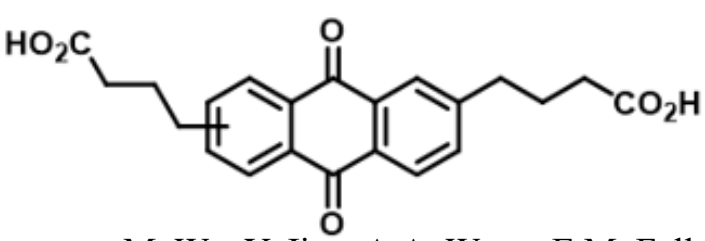
Methuselah II: 2,6-di-propyl-phosphonate ether anthraquinone (DPPEAQ): Fade rate 0.014%/day



Reasons for enhanced stability of DPPEAQ:

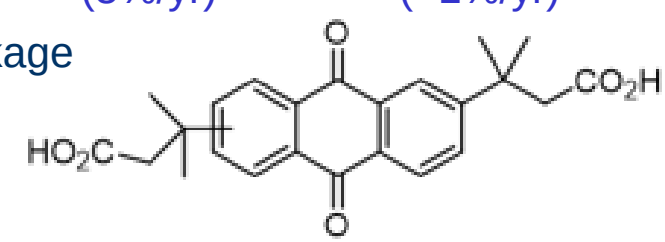
- Solubility ≥ 1.5 M e^- @ pH 9, cuts [OH^-]
- Phosphonate is a weaker nucleophile than carboxylate

Di-butanoate anthraquinone (DBAQ):
0.0084%/day
(3%/yr)



Ultra-Stable:
No –O– linkage

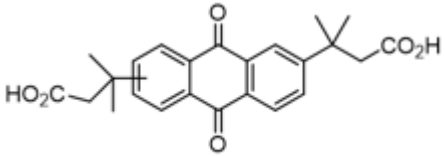
Di-pivolic acid anthraquinone (DPivOHAQ):
0.014%/day – 0.0018%/day
(5%/yr) (<1%/yr)



M. Wu, Y. Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" **Chem** *6*, 1432 (2020)

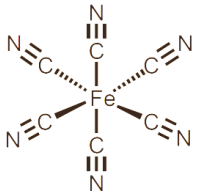
Performance of Slowest-Fading Molecule: DPivOHAQ

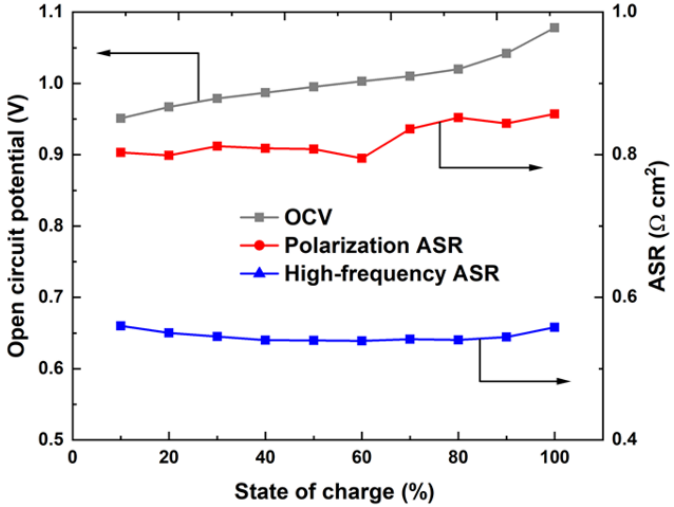
Negative Species: di-pivolic acid anthraquinone (DPivOHAQ)

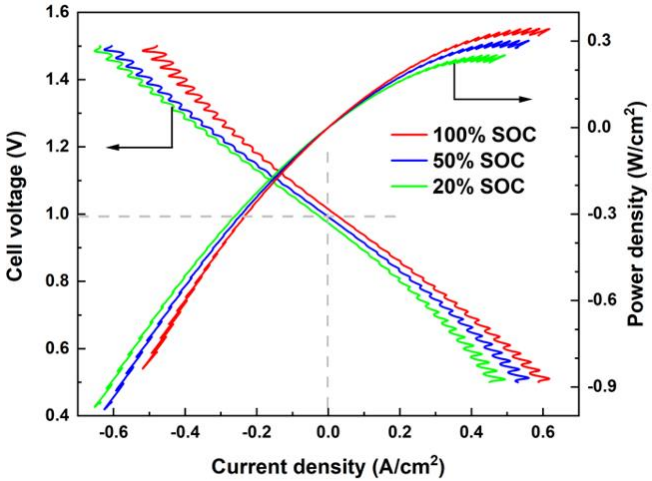


DPivOHAQ

Positive Species: ferro/ferricyanide







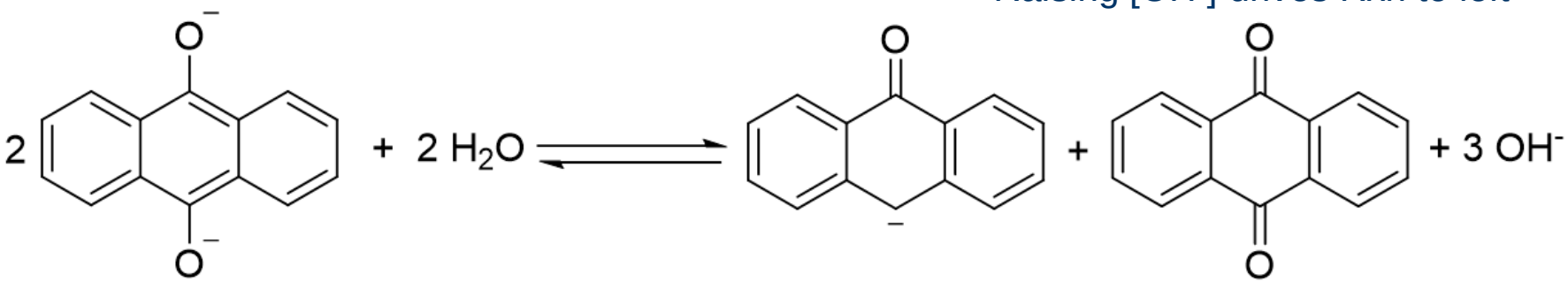
- *Negolyte:*
  0.5M DPivOHAQ, pH 12 KOH (5 mL)
  Solubility: 1.48 M e^- (39.7 Ah/L)
- Fumasep® E-620K; AvCarb cloth

- *Posolyte:*
  0.3M $K_4Fe(CN)_6$ + 0.1M $K_3Fe(CN)_6$,
  pH 12 KOH (80 mL)
  Solubility: 1.2 M e^- (32.2 Ah/L)

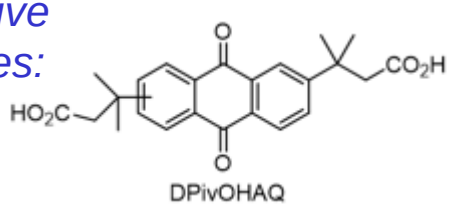
M. Wu, Y. Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" **Chem** *6*, 1432 (2020)

Mechanism-Informed Electrolyte Design

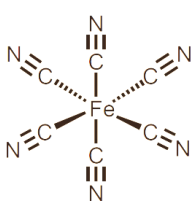
Le Chatelier's Principle:
Raising [OH^-] drives Rxn to left

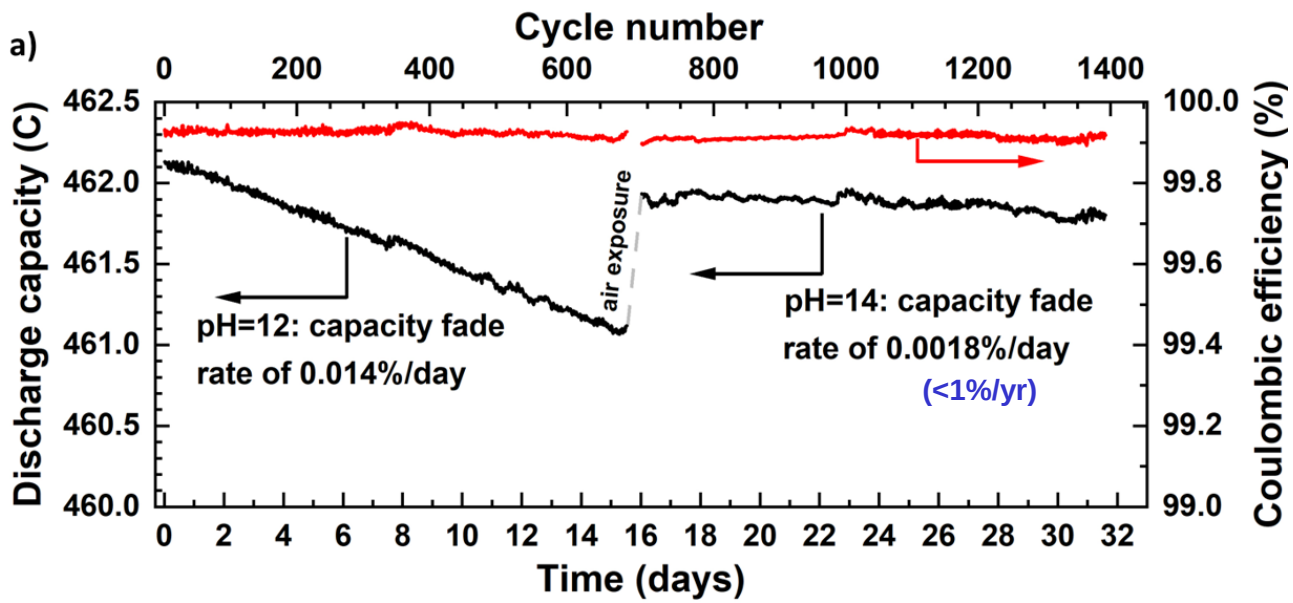


Negative Species:



Positive Species:

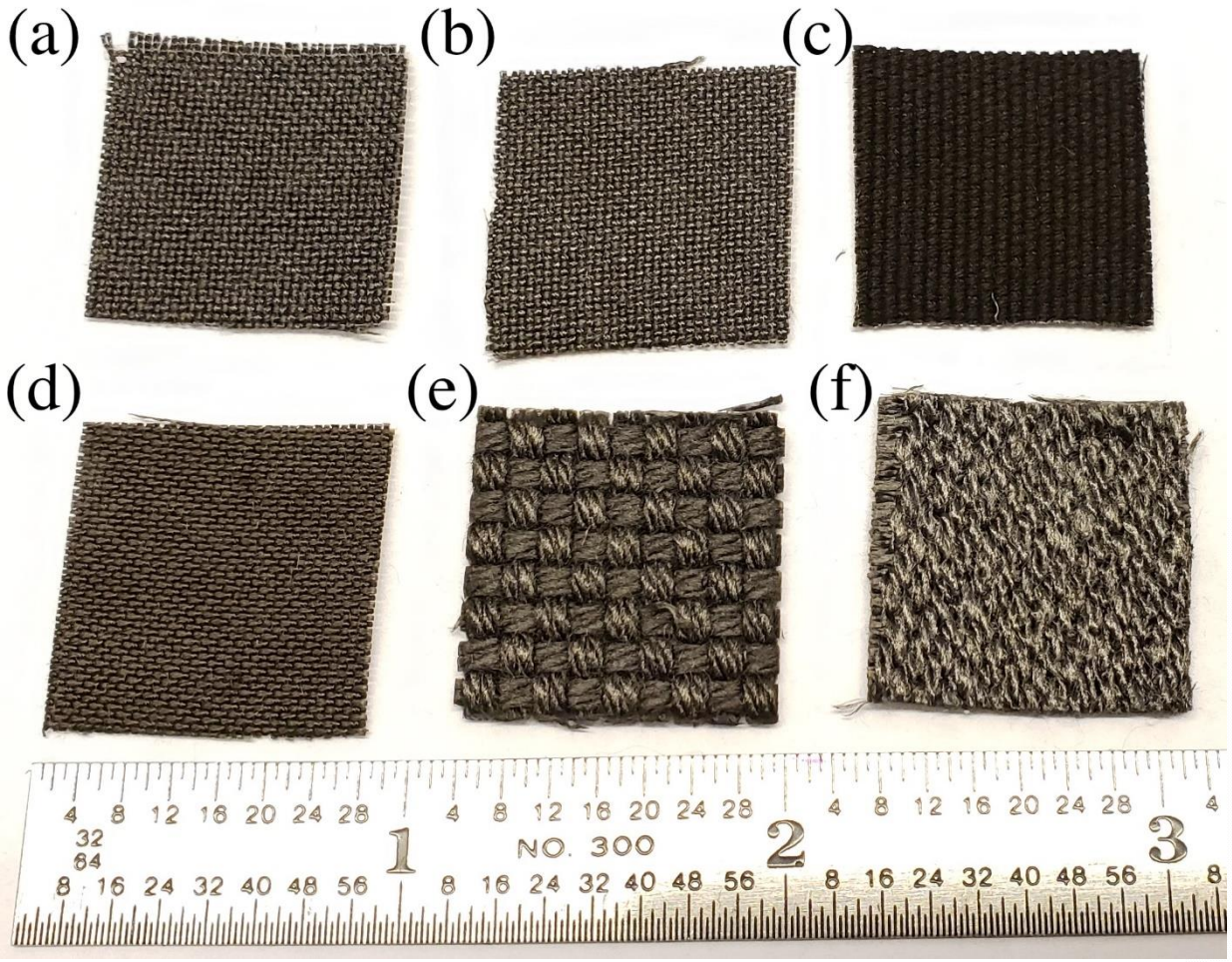




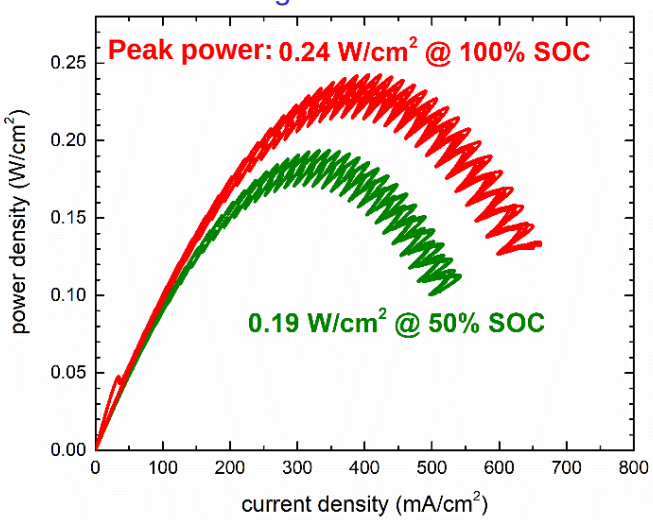
M. Wu, Y. Jing, A.A. Wong, E.M. Fell, S. Jin, Z. Tang, R.G. Gordon and M.J. Aziz, "Extremely Stable Anthraquinone Negolytes Synthesized from Common Precursors" **Chem** *6*, 1432 (2020)

Enhancing Power Density

Investigation of numerous electrode materials



2,6-DBEAQ "Methuselah I": Original Performance

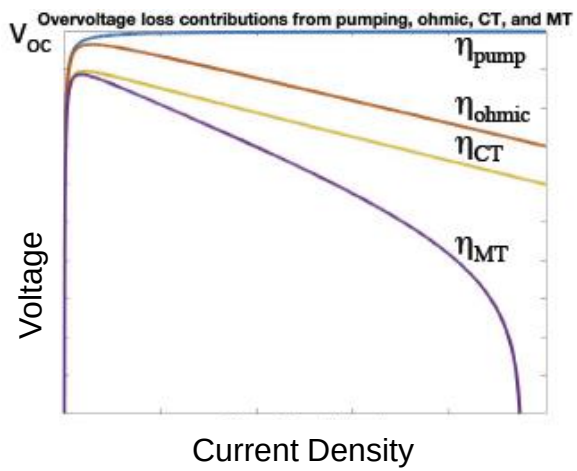


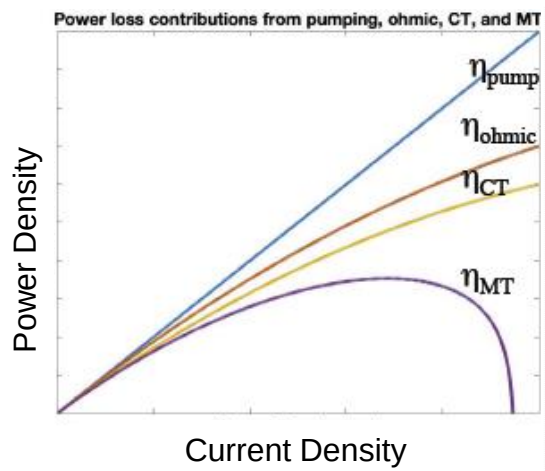
A.A. Wong and M.J. Aziz, "Method for Comparing Porous Carbon Electrode Performance in Redox Flow Batteries", *J. Electrochem. Soc.* **167**, 110542 (2020)

Steps to Enable Enhanced Power Density

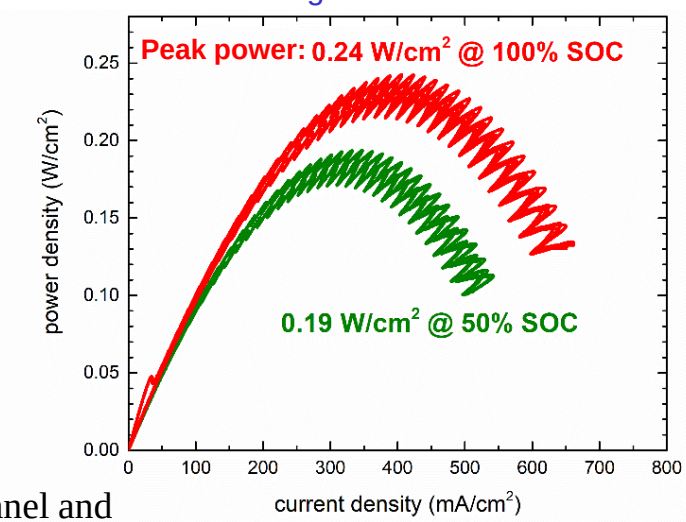
- Selection of six electrode materials
- Measurement of surface area
- Measurement of voltage lost to pumping, η_{pump}, vs. strain (percentage compression)
- Measurement of voltage lost to electron (electrode) and ion (membrane) conduction, η_{Ohmic}
- Measurement of voltage lost to Charge Transfer, η_{CT}, to/from molecules
- Determination of voltage lost to molecular diffusion (Mass Transport), η_{MT}
- Gerhardt's Model* for losses vs. engineering parameters and operating parameters

$$V_{Discharge} = V_{OC} - \eta_{pump} - \eta_{ohmic} - \eta_{CT} - \eta_{MT}$$





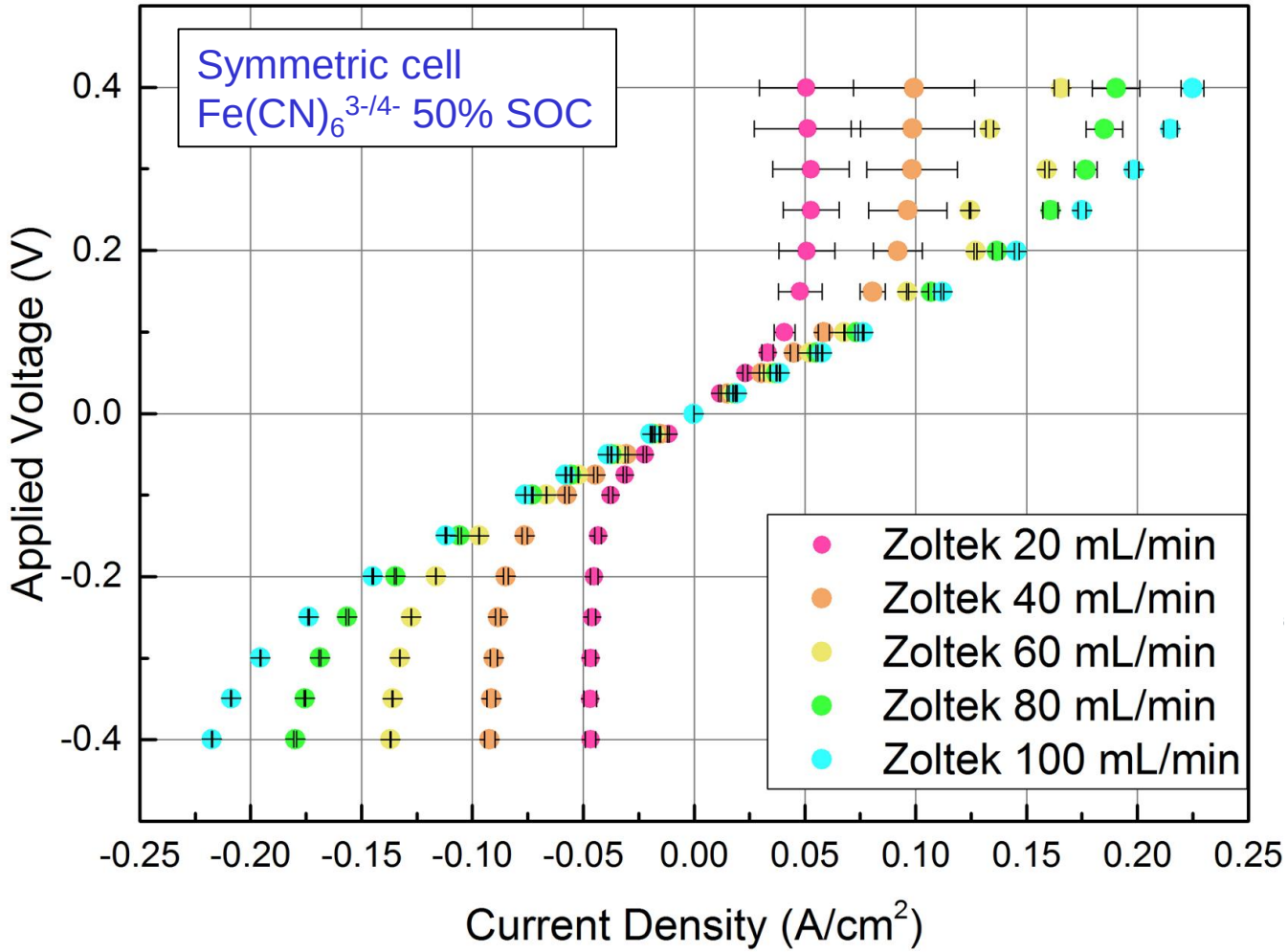
2,6-DBEAQ "Methuselah I": Original Performance



*M.R. Gerhardt, A.A. Wong, and M.J. Aziz, "The Effect of Interdigitated Channel and Land Dimensions on Flow Cell Performance" *J. Electrochem. Soc.* **165**, A2625 (2018)

Mass Transport Overpotential

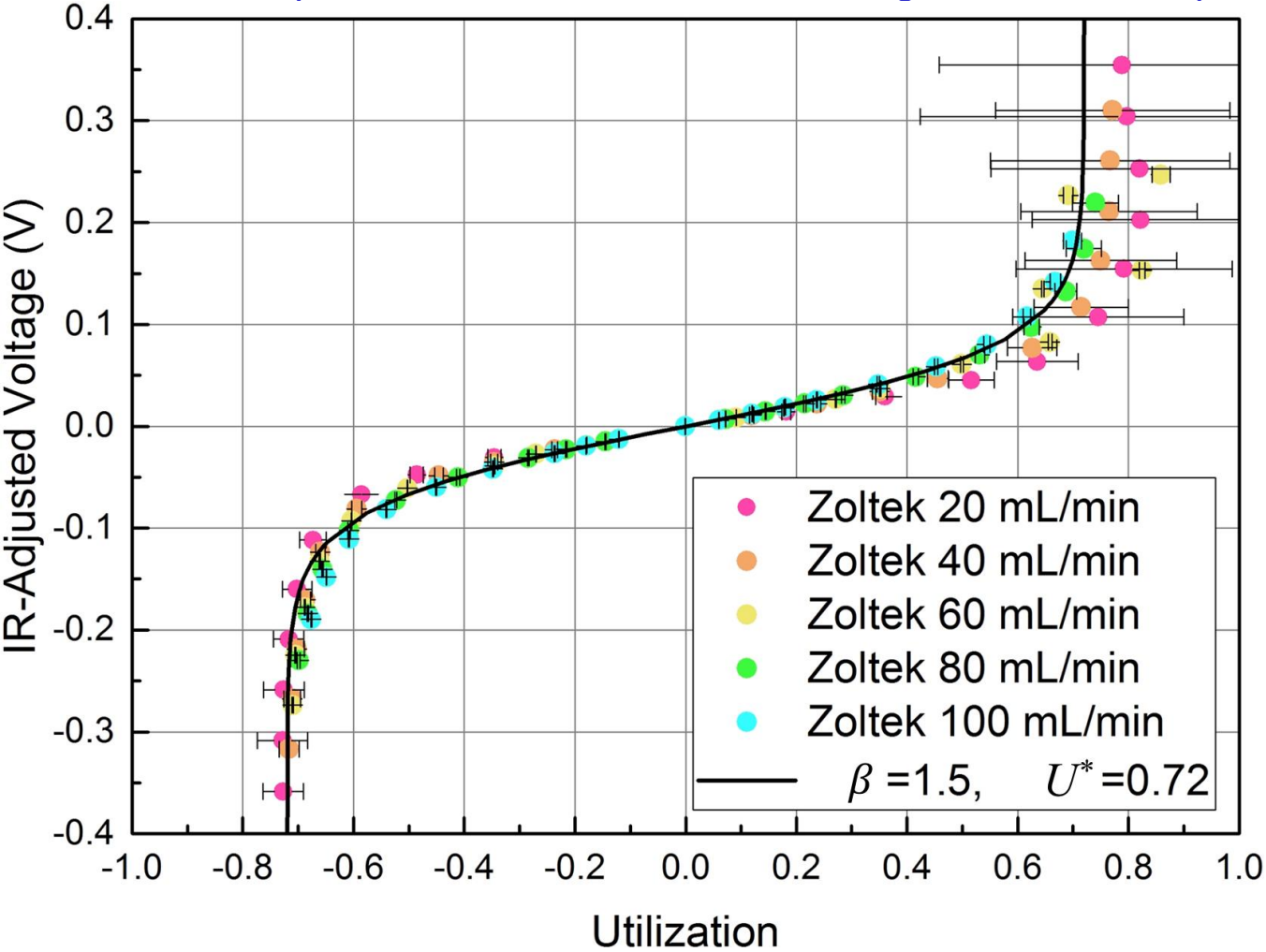
- Determination of voltage lost to molecular diffusion (Mass Transport), η_{MT}



A.A. Wong and M.J. Aziz, "Method for Comparing Porous Carbon Electrode Performance in Redox Flow Batteries", *J. Electrochem. Soc.* **167**, 110542 (2020)

Data collapse for Utilization

- Data collapse function for IR-corrected voltage vs. utilization (∝ current / flow rate)



Nernst equation:

$$E = E^{0'} + \frac{RT}{nF} \ln\left(\frac{[R] + \Delta c}{[O] - \Delta c}\right)$$

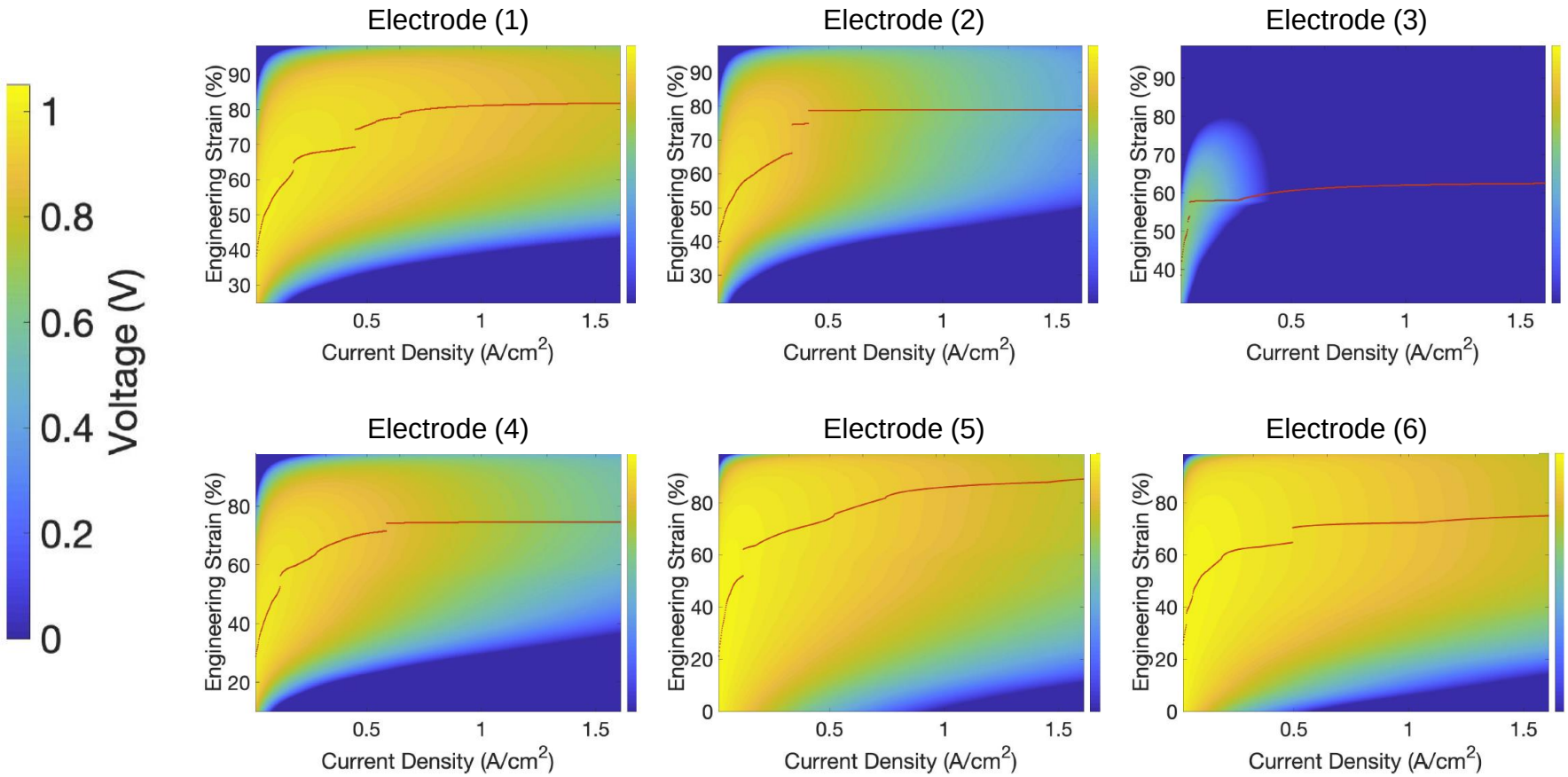
Hypothesized data collapse functional form:

$$\eta_{MT} = \beta \frac{RT}{nF} \ln\left(\frac{1 + U/U^*}{1 - U/U^*}\right)$$

A.A. Wong and M.J. Aziz, "Method for Comparing Porous Carbon Electrode Performance in Redox Flow Batteries", *J. Electrochem. Soc.* **167**, 110542 (2020)

Calibrated Model Predicts Sweet Spot for Each Electrode

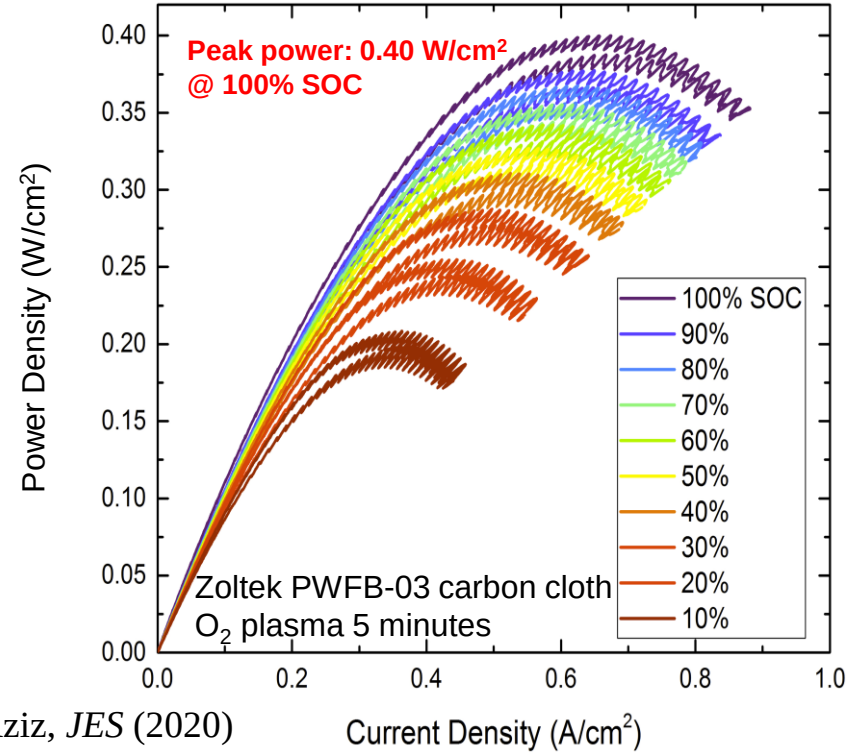
- Model for losses vs. engineering parameters and operating parameters
- Identify “sweet spot” in " " " " "



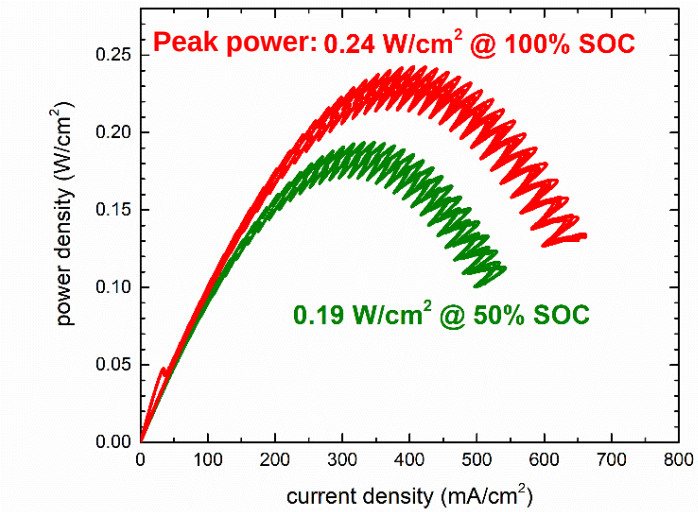
A.A. Wong and M.J. Aziz, “Method for Comparing Porous Carbon Electrode Performance in Redox Flow Batteries”, *J. Electrochem. Soc.* **167**, 110542 (2020)

Result: Power Density Enhanced by 65%

- Selection of numerous electrode materials
- Measurement of surface area
- Measurement of voltage lost to pumping, η_{pump}, vs. strain (percentage compression)
- Measurement of voltage lost to electron (electrode) and ion (membrane) conduction, η_{Ohmic}
- Measurement of voltage lost to Charge Transfer, η_{CT}, to/from molecules
- Determination of voltage lost to molecular diffusion (Mass Transport), η_{MT}
- Model for losses vs. engineering parameters and operating parameters
- Identify "sweet spot" in " " " " "



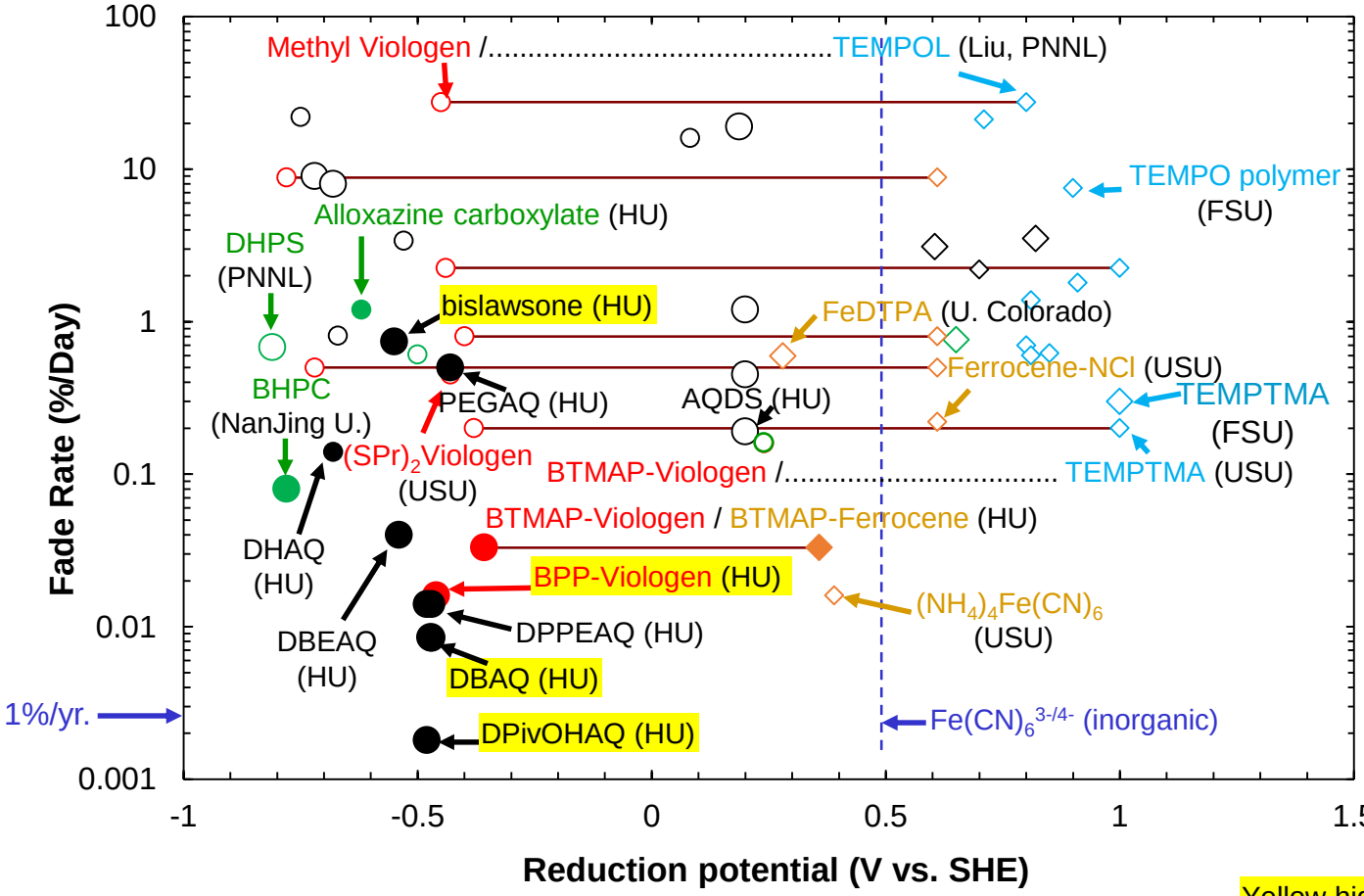
2,6-DBEAQ "Methuselah I":
Original Performance



A.A. Wong and M.J. Aziz, *JES* (2020)

Capacity Fade Rates: All Organic/Organometallic Aqueous Flow Battery Chemistries

Quinones **Viologens** **Aza-Aromatics** **Fe Coordination Complexes** **Nitroxide Radicals**



Diamonds: posolyte-limited
Circles: negolyte-limited
Tie Lines: capacity-balanced posolyte & negolyte

Filled: established fade
Open: apparent fade

Large: ≥ 1 M electrons
Small: < 1 M electrons

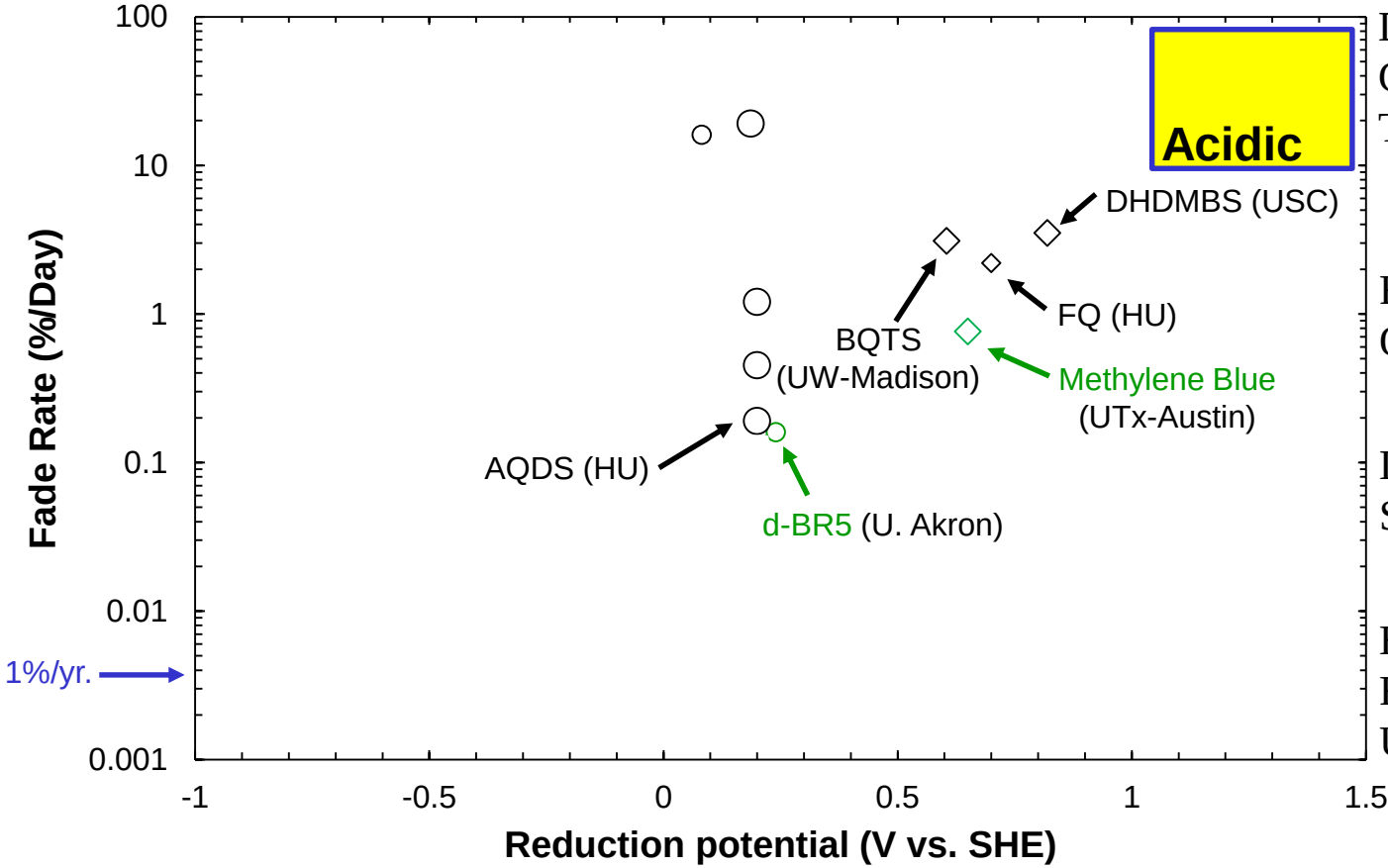
HU: Harvard U.
FSU: Friedrich Schiller U.
USU: Utah State U.

Yellow highlights: Harvard additions this year

Adapted from: D.G. Kwabi, Y.L. Ji and M.J. Aziz, "Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review" *Chem. Rev.* **120**, 6467 (2020)

Capacity Fade Rates: All Organic/Organometallic Aqueous Flow Battery Chemistries

Quinones **Viologens** **Aza-Aromatics** **Fe Coordination Complexes** **Nitroxide Radicals**



Diamonds: posolyte-limited
Circles: negolyte-limited
Tie Lines: capacity-balanced posolyte & negolyte

Filled: established fade
Open: apparent fade

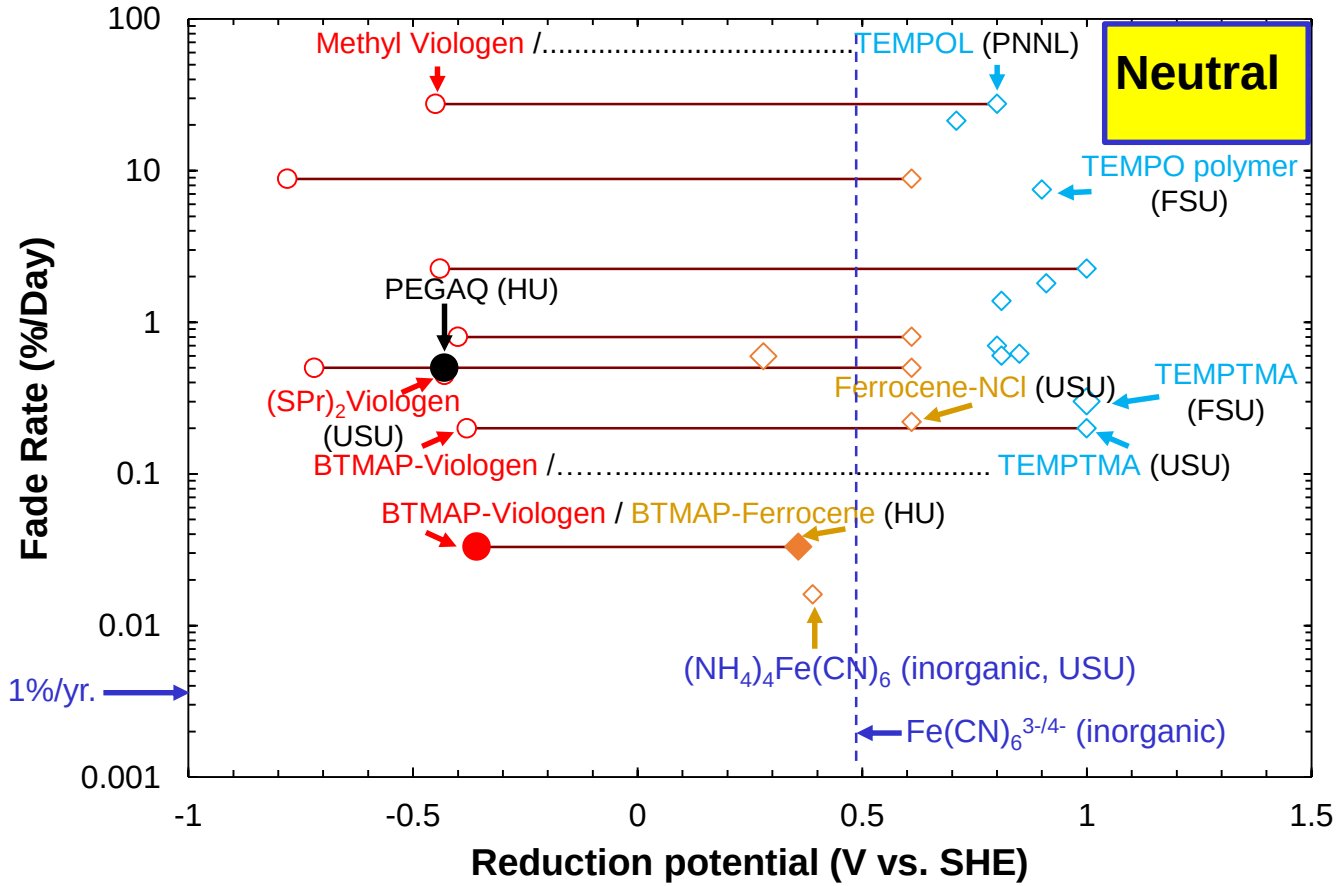
Large: ≥ 1 M electrons
Small: < 1 M electrons

HU: Harvard U.
FSU: Friedrich Schiller U.
USU: Utah State U.

Adapted from: D.G. Kwabi, Y.L. Ji and M.J. Aziz, "Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review" *Chem. Rev.* **120**, 6467 (2020)

Capacity Fade Rates: All Organic/Organometallic Aqueous Flow Battery Chemistries

Quinones **Viologens** **Aza-Aromatics** **Fe Coordination Complexes** **Nitroxide Radicals**



Diamonds: posolyte-limited
Circles: negolyte-limited
Tie Lines: capacity-balanced posolyte & negolyte

Filled: established fade
Open: apparent fade

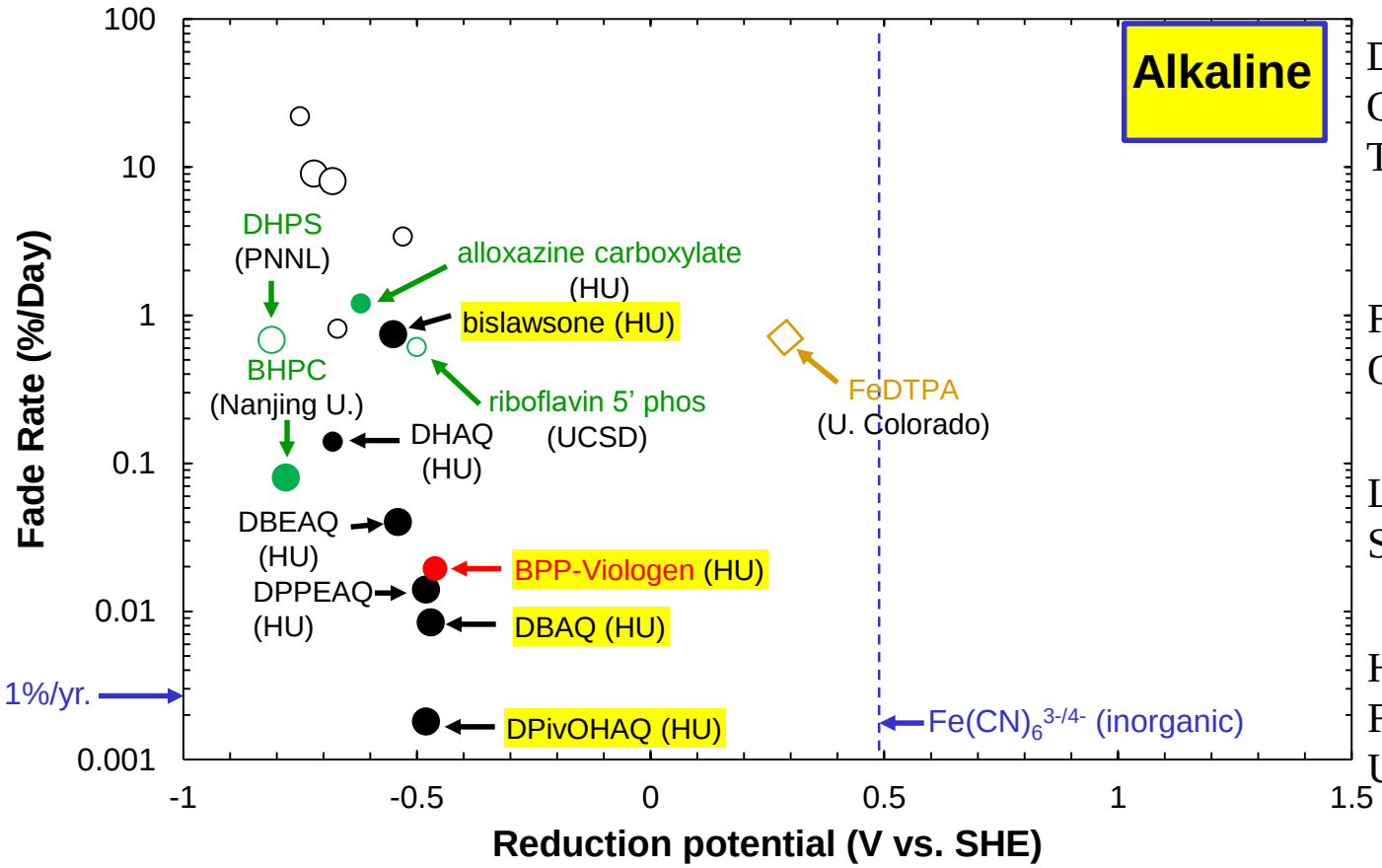
Large: ≥ 1 M electrons
Small: < 1 M electrons

HU: Harvard U.
FSU: Friedrich Schiller U.
USU: Utah State U.

Adapted from: D.G. Kwabi, Y.L. Ji and M.J. Aziz, "Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review" *Chem. Rev.* **120**, 6467 (2020)

Capacity Fade Rates: All Organic/Organometallic Aqueous Flow Battery Chemistries

Quinones **Viologens** **Aza-Aromatics** **Fe Coordination Complexes** **Nitroxide Radicals**



Diamonds: posolyte-limited
Circles: negolyte-limited
Tie Lines: capacity-balanced posolyte & negolyte

Filled: established fade
Open: apparent fade

Large: ≥ 1 M electrons
Small: < 1 M electrons

HU: Harvard U.
FSU: Friedrich Schiller U.
USU: Utah State U.

Yellow highlights: Harvard additions this year

Adapted from: D.G. Kwabi, Y.L. Ji and M.J. Aziz, "Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review" *Chem. Rev.* **120**, 6467 (2020)