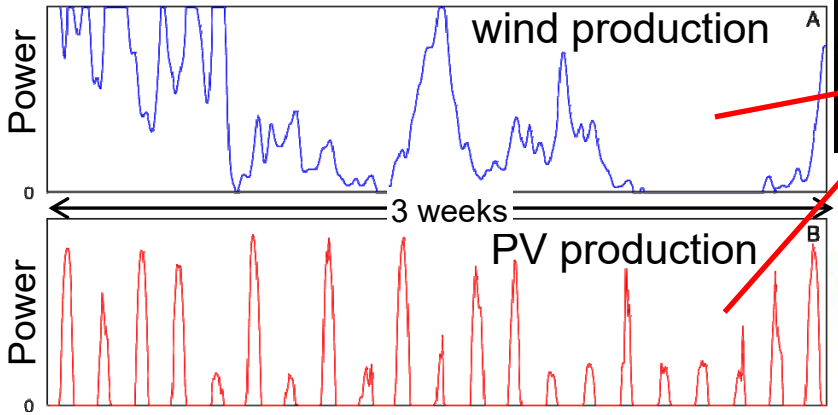
Aqueous-Soluble Organic Flow Battery Chemistry with Long Lifetime in Weak Alkaline Electrolyte

PI: Michael J. Aziz
Harvard School of Engineering & Applied Sciences
Cambridge MA



Research supported in part by OE award DE-AC05-76RL01830 through PNNL subcontracts 304500 (7/1/2016-5/31/2017 with extensions through 4/30/18) and 428977 (9/10/2018-9/9/2020)

Alkaline Benzoquinone Flow Battery

DHBQ

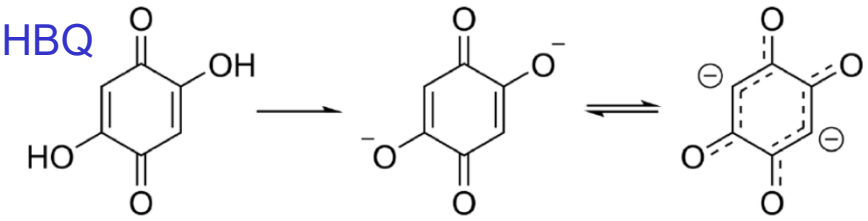
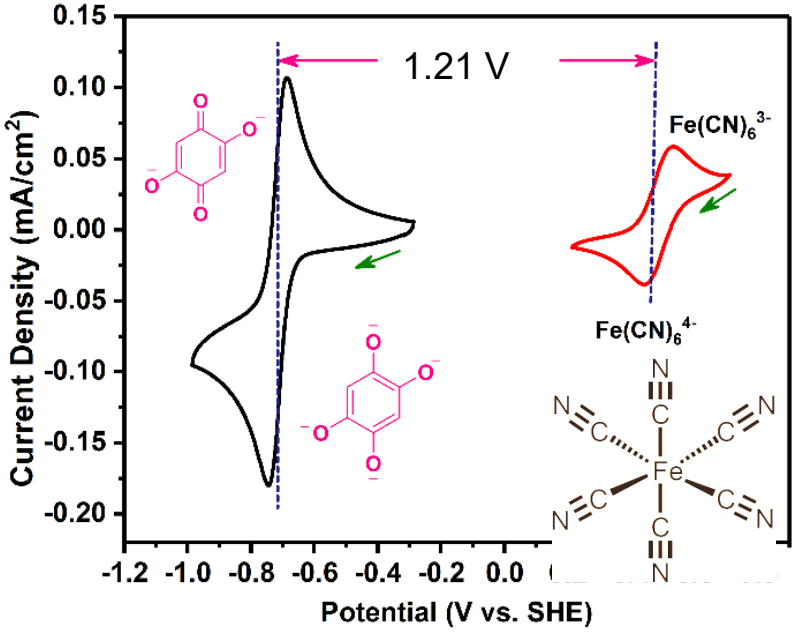
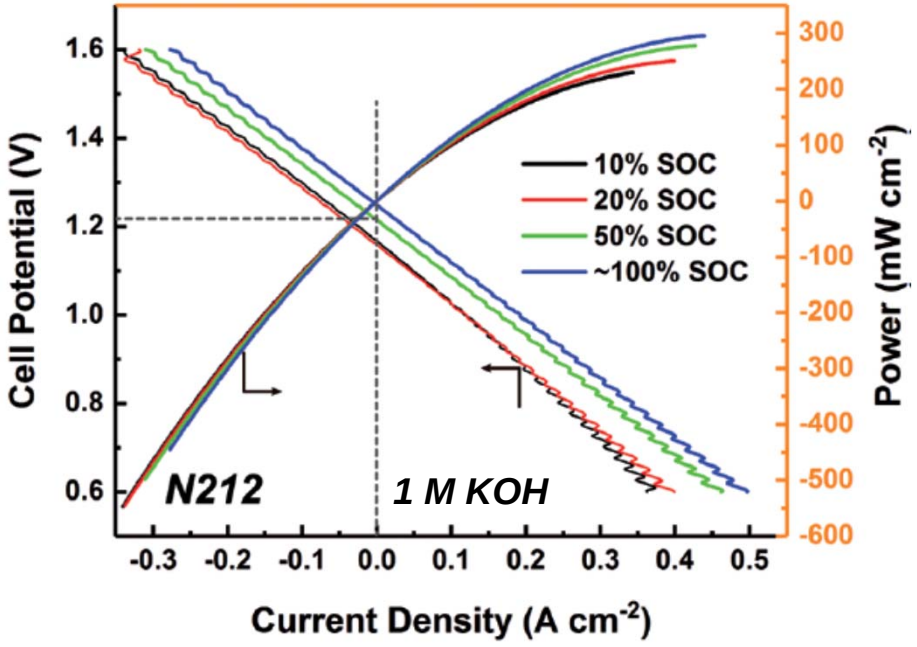


Figure 2. DHBQ and its resonance-stabilized dianions.

- Lowest cost
- Lowest Lifetime

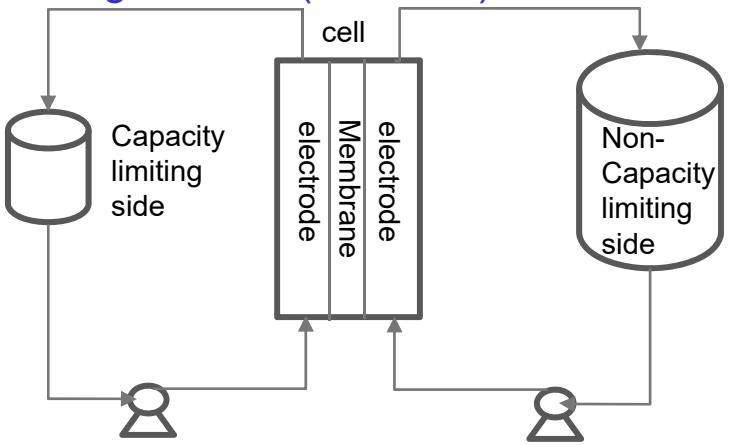




Zhengjin Yang, L. Tong, D.P. Tabor, E.S. Beh, M.-A. Goulet, D. De Porcellinis, A. Aspuru-Guzik, R.G. Gordon, and M.J. Aziz, "Alkaline benzoquinone aqueous flow battery for large-scale storage of electrical energy" *Advanced Energy Materials* **2017**, 1702056 (2017)

Capacity fade in aqueous-soluble organics is time-denominated, not cycle-denominated

Unbalanced compositionally-symmetric cell
cycling experiment
Both sides MV, 50% State of Charge,
0.1 M, 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)

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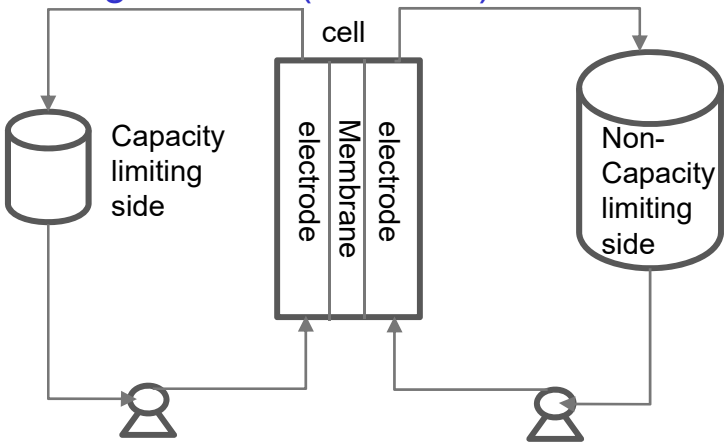
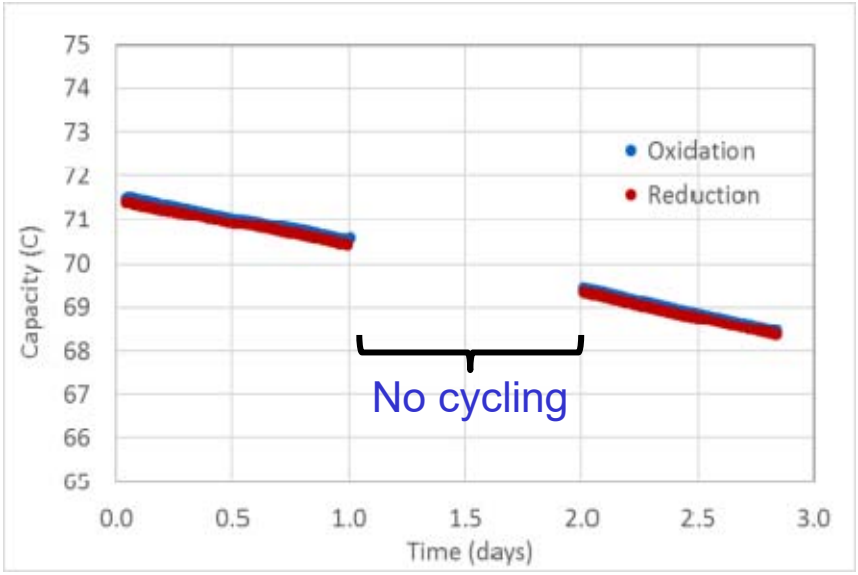
Both sides MV, 50% State of Charge, 0.1 M, glove box (**OCV = 0**)





Capacity fade rate: 0.002%/cycle
Extrapolates to 20% loss after 1000 cycles

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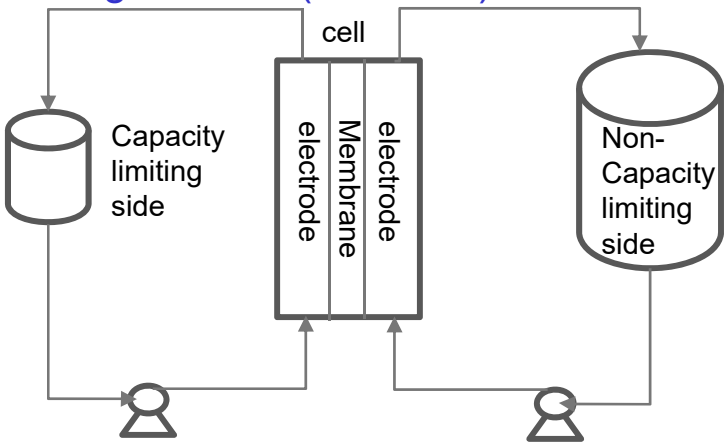
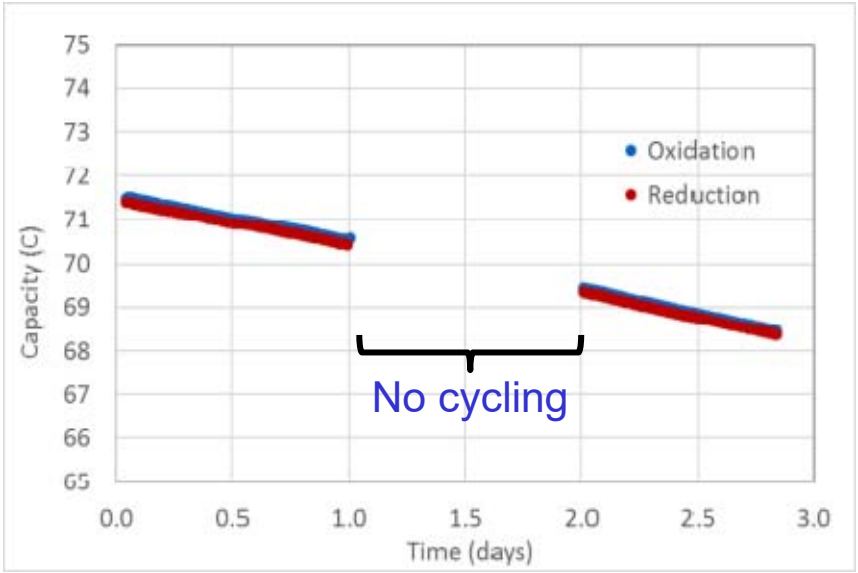


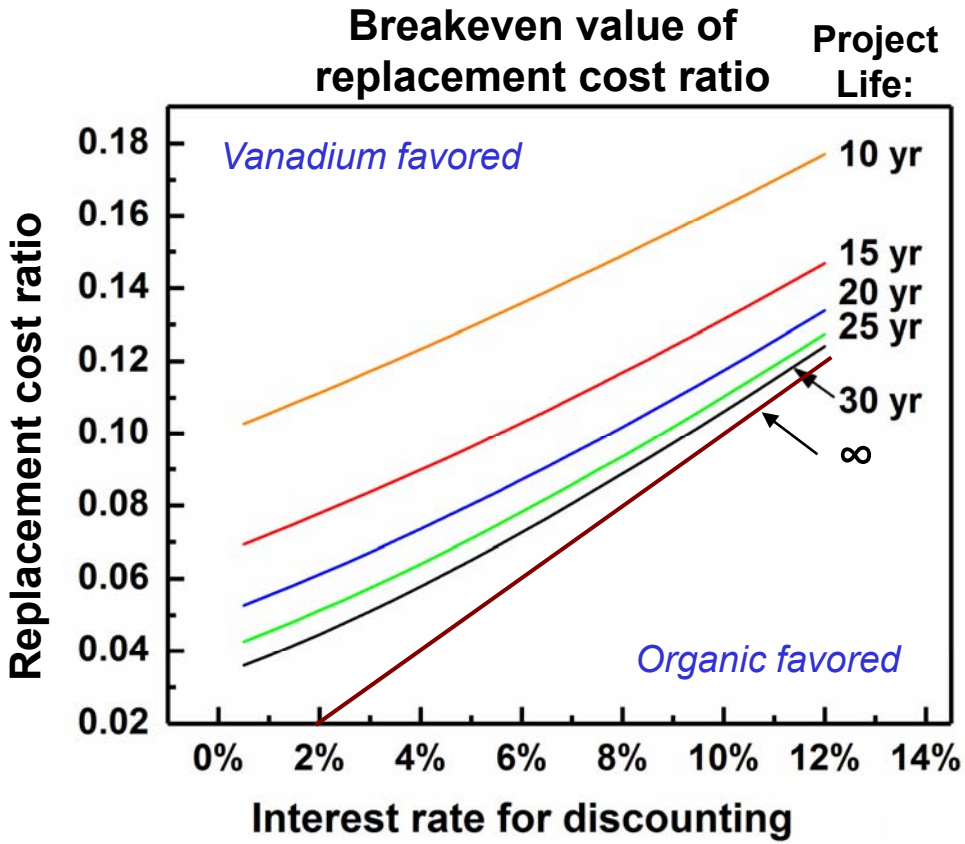


Capacity fade rate: 0.002%/cycle
Extrapolates to 20% loss after 1000 cycles
Capacity fade rate: 1.5%/day
Extrapolates to 20% loss after 13 days

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

Finite lifetime electrolyte vs. Vanadium

$$Replacement\ Cost\ Ratio \equiv \frac{replacement\ cost\ per\ year}{vanadium\ capital\ cost\ - organic\ capital\ cost}$$



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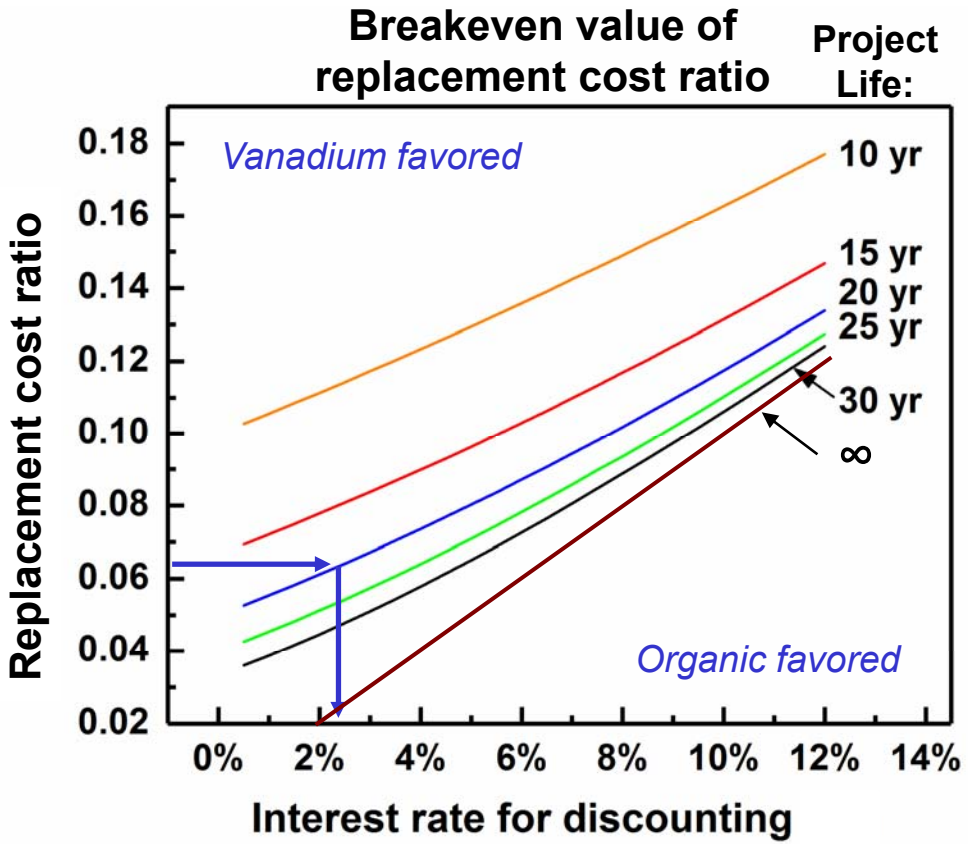
Finite lifetime electrolyte vs. Vanadium

$$Replacement\ Cost\ Ratio \equiv \frac{replacement\ cost\ per\ year}{vanadium\ capital\ cost\ - organic\ capital\ cost}$$

e.g.:
Vanadium cost = 100
Organic cost = 30,
but loses 15% capacity per year.
Ratio = 15%*30/(100-30)
= 0.064

➔20 year project breaks even at 2.3% discount rate (if no additional costs)



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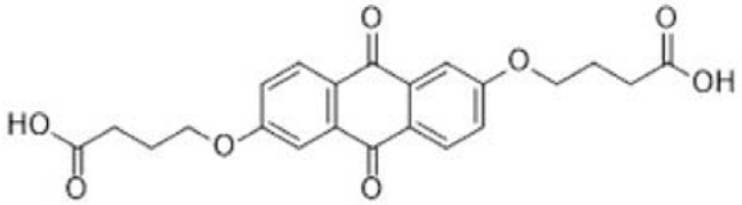
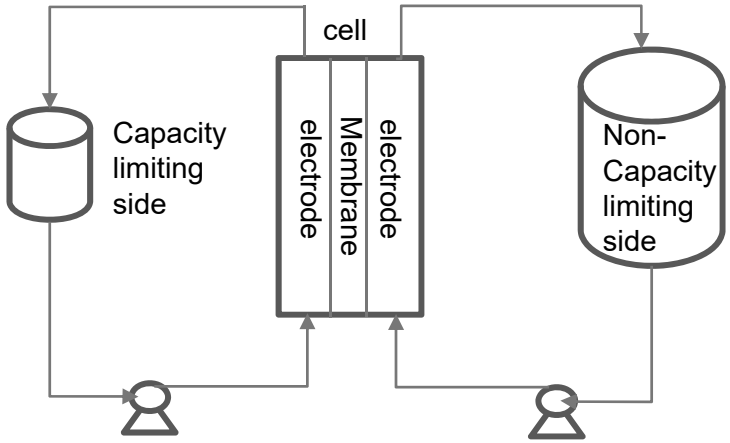
“Methuselah” Quinone: Symmetric Cell Cycling

Unbalanced compositionally-symmetric cell cycling experiment:

Both sides 2,6-DBEAQ
(2,6-di-butanoate ether anthraquinone)
50% SOC (**OCV: 0**), glove box





David Kwabi, Kaixiang Lin, Yunlong Ji, Emily Kerr, Marc-Antoni Goulet, Diana DePorcellinis, Daniel Tabor, Daniel Pollack, A. Aspuru-Guzik, R.G. Gordon, and M.J. Aziz, “Alkaline Quinone Flow Battery with Long Lifetime at pH 12”, *Joule* **2**, 1907 (2018); doi.org/10.1016/j.joule.2018.07.005

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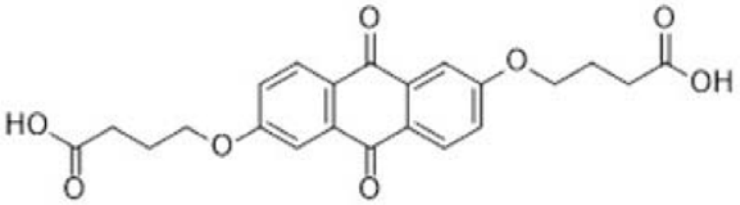
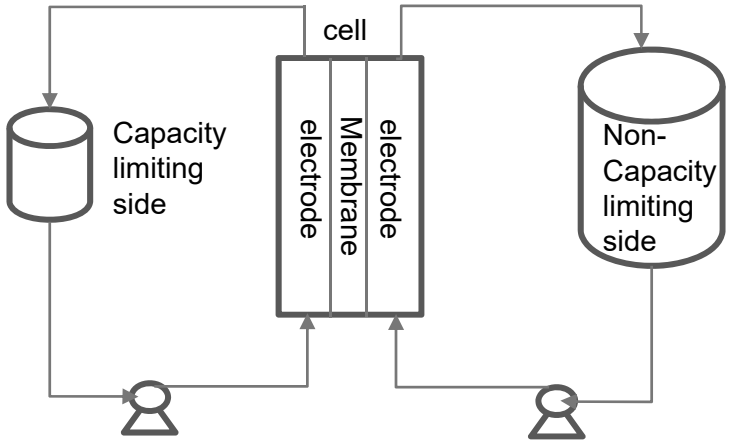
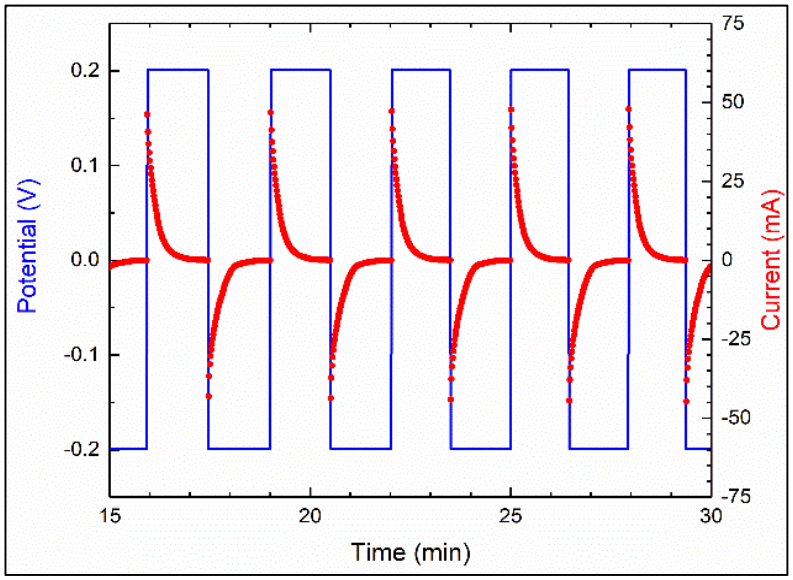




Potential holds eliminate artifacts e.g. drift in Area-Specific Resistance



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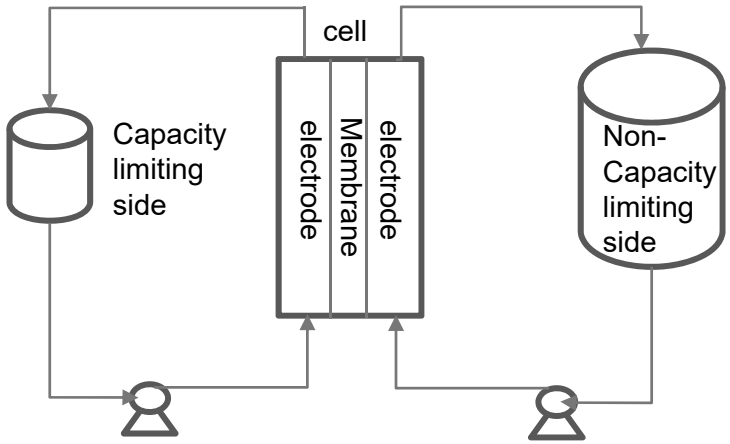
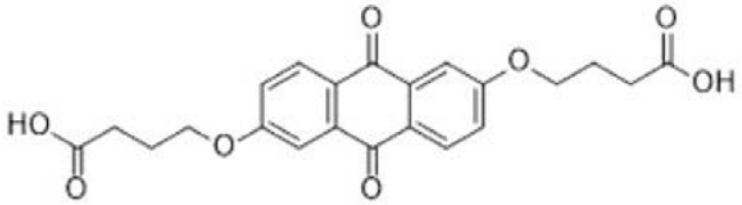
Methuselah Quinone: Symmetric Cell Cycling, pH 12

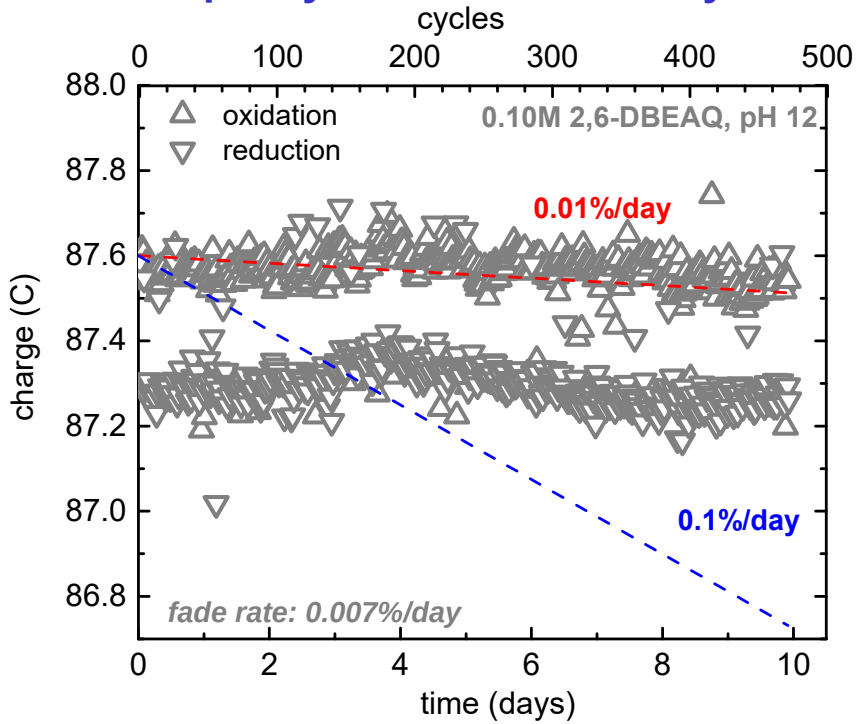
Unbalanced compositionally-symmetric cell cycling experiment:

Both sides 2,6-DBEAQ
(2,6-di-butanoate ether anthraquinone)
50% SOC (**OCV: 0**), glove box
0.1 M, pH 12 KOH





Potentiostatic cycling, ±0.2 V
Capacity Fade Rate: < 3% / year



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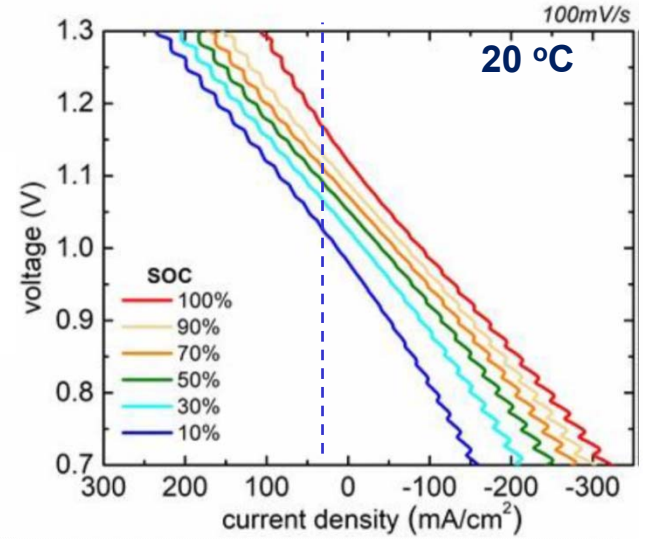
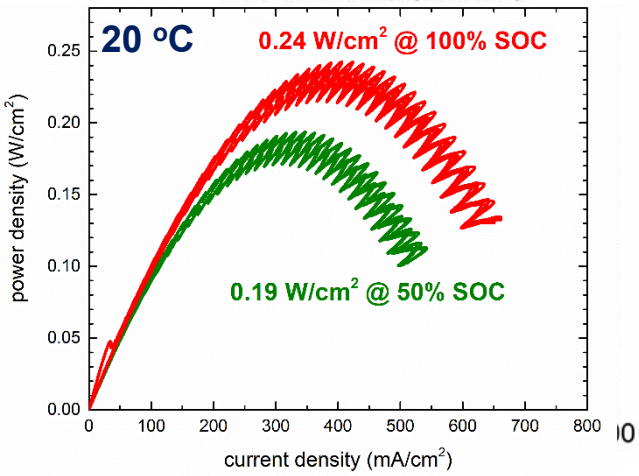
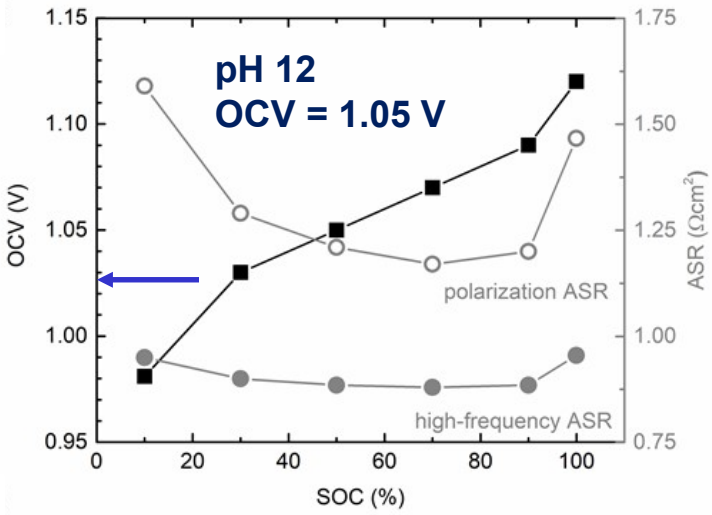
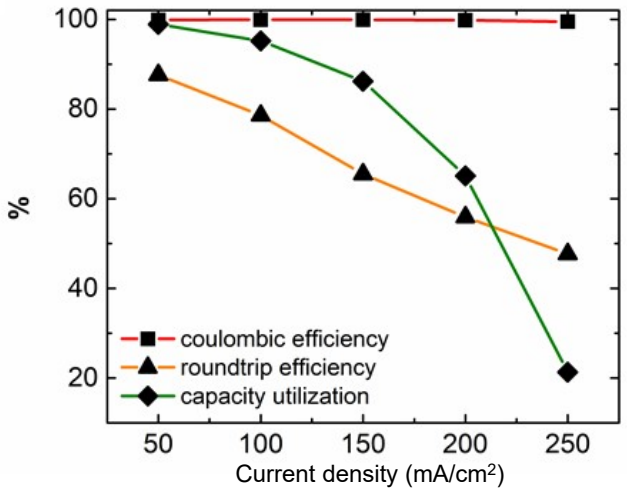
Methuselah – $Fe(CN)_6$ full cell performance









- Fumasep® E-620K (20 um sulfonated polyaryletherketone), < $25/m^2 at scale

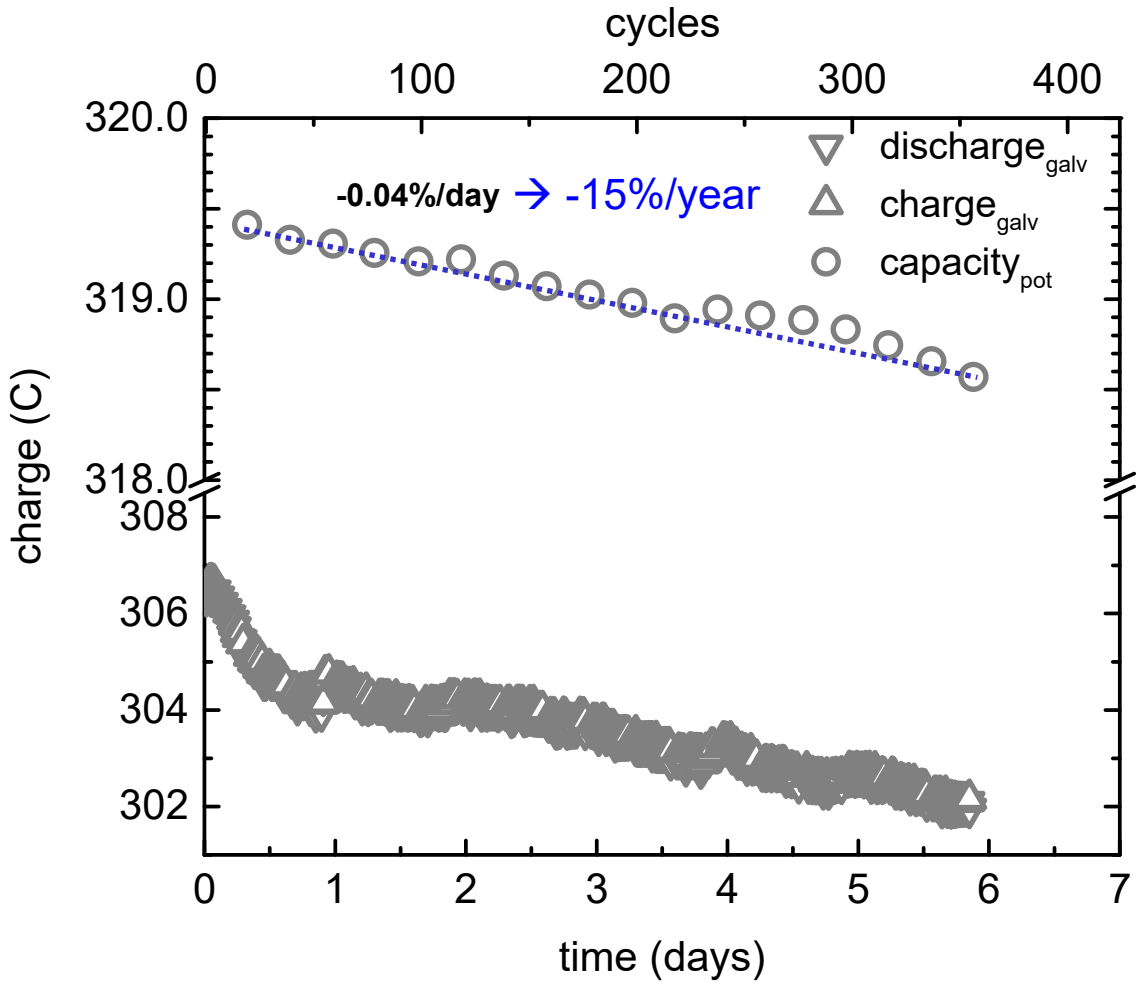
*DBEAQ permeability: 5.3×10^{-13} cm^2/s, 50% crossover in 3000 yr.

*Ferricyanide permeab'y: 4.4×10^{-12} cm^2/s, 50% crossover in 200 yr.

- Four SGL39AA electrodes per side
- Viton gasket

Negolyte: 5 ml of 0.5 M 2,6-DBEAQ at pH 12 (10 mM KOH); solubility 0.6 M (32 Ah/L)
Posolyte: 38 ml of 0.3 M potassium ferrocyanide, 0.1 M potassium ferricyanide at pH 12; solubility 1.25 M (34 Ah/L)
Theoretical energy density: 17 Wh/L

Methuselah – $Fe(CN)_6$ full cell cycling



- *Negolyte:*
  0.5M 2,6-DBEAQ, pH 12 (5 ml)
  Solubility: 0.6 M (32 Ah/L)
- *Posolyte:*
  0.3M ferro, 0.1M ferri, pH 12 (38 ml)
  Solubility: 1.25 M (34 Ah/L)
- Theoretical E/V: 17 Wh/L
- Fumasep® E-620K (20 um sulfonated polyaryletherketone, IEC 1.7 meq/g)
- 4 SGL39AA electrodes per side
- Viton gasket

Galvanostatic cycling @ 100 mA/cm^2 between 1.4 and 0.6 V with **potential holds every 20 cycles** until current < 2 mA/cm^2

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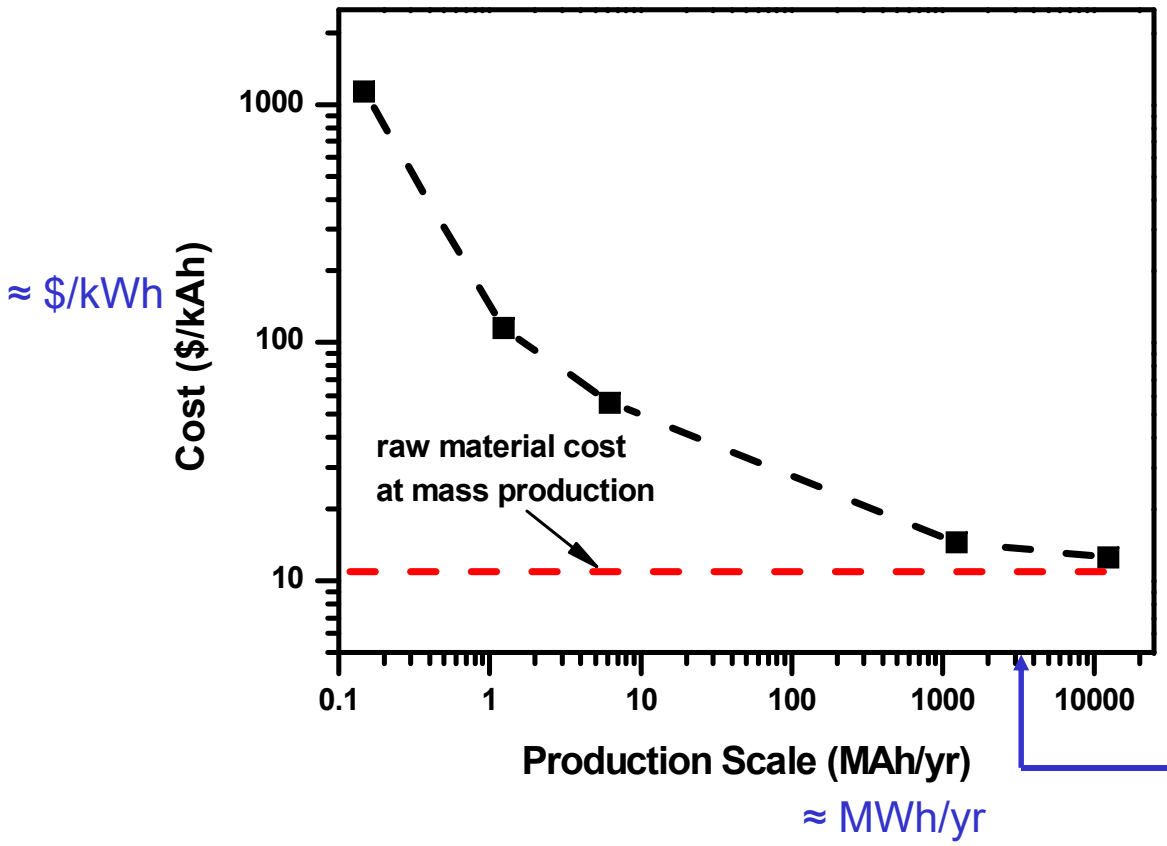
Cost of Anthraquinones vs. Scale

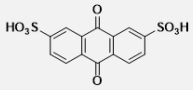
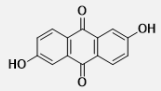
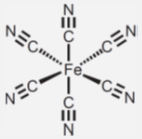
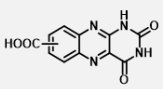
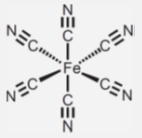
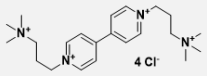
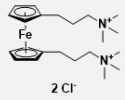
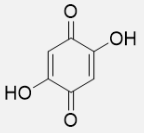
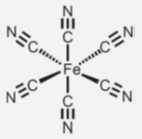
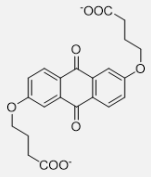
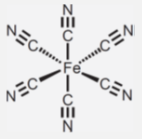
Estimate of anthraquinone (DHAQ and AQDS) mass production cost vs. production scale



Source: Borealis Technology Solutions LLC

Z. Yang, L. Tong, D.P. Tabor, E.S. Beh, M.-A. Goulet, D. De Porcellinis, A. Aspuru-Guzik, R.G. Gordon, and M.J. Aziz, "Alkaline benzoquinone aqueous flow battery for large-scale storage of electrical energy" *Advanced Energy Materials* **2017**, 1702056 (2017)

Summary: Harvard's RFBs utilizing Aqueous-Soluble Organics

Negative Electrolyte *Red text: capacity-limiting side*	Positive Electrolyte	Capacity loss (%/day)	Energy Density (Realized / Theoretical, in Wh L^{-1})		Volt-age (V)	Year	Merits	Limitations
 2,7-AQDS	Br_2 / hydrobromic acid	1.9	23	35	0.86	2014	Low cost; Highest power density	Inadequate lifetime; Toxic bromine
 2,6-DHAQ	 ferro/ferricyanide	4.6	6.8	9.2	1.2	2015	Low cost; Non-toxic, less corrosive (pH 14)	Inadequate lifetime; Reduced ion conductivity w.r.t. proton; Modest $[Fe(CN)_6]^{3-/4-}$ solubility
 alloxazine carboxylic acid	 ferro/ferricyanide	1.2	7.1	11	1.13	2016	High CE; High ACA capacity	Inadequate lifetime; Reduced ion conductivity w.r.t. proton; Modest $[Fe(CN)_6]^{3-/4-}$ solubility
 BTMAP-Vi	 BTMAP-Fc	0.03	13	20	0.75	2017	Neutral pH; Record calendar life; Low crossover	Low voltage; High resistance AEM
 1,4-DHBQ	 ferro/ferricyanide	10	9.2	12.4	1.21	2017	Lowest cost; High DHBQ capacity	Inadequate lifetime; Reduced ion conductivity w.r.t. proton; Modest $[Fe(CN)_6]^{3-/4-}$ solubility
 2,6-DBEAQ	 ferro/ferricyanide	0.01 (symm) 0.04 (full)	6.5	17.2	1.05	2018	Long calendar life; Low crossover; pH 12 operation	Modest $[Fe(CN)_6]^{3-/4-}$ solubility; Unknown mass-production cost; Full-cell vs. symmetric cell fade rate mystery

Harvard Department of Chemistry & Chemical Biology

HARVARD John A. Paulson School of Engineering and Applied Sciences

Acknowledgments

Back to front, left to right:

- Michael Marshak, Brian Huskinson, Prof. Shmuel Rubinstein, Zhengjin Yang, David Kwabi, Danny Tabor
- Rafa Gómez-Bombarelli, Andrew Wong, Sungjin "James" Kim, Michael Gerhardt, Joel Veak
- Eugene Beh, Kaixiang Lin, Lauren Hartle, Marc-Antoni Goulet, Prof. Sergio Granados-Focil
- Prof. Alán Aspuru-Guzik, Prof. Michael Aziz, Prof. Roy Gordon, Liuchuan Tong, Qing Chen, Diana De Porcellinis, Alvaro Valle

Not pictured: Dr. Yunlong Ji, Dr. Yan Jing, Daniel Pollack, Emily Kerr, Professor William Hogan, Professor Ted Betley, Saraf Nawar, Rebecca Gracia, Sidharth Chand, Tyler Van Valkenburg, Bilen Aküzüm, Ryan Duncan, Dr. Süleyman Er, Dr. Xudong Chen, Prof. Maurizio Salles, Dr. Changwon Suh, Louise Eisenach, Jennifer Wei

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