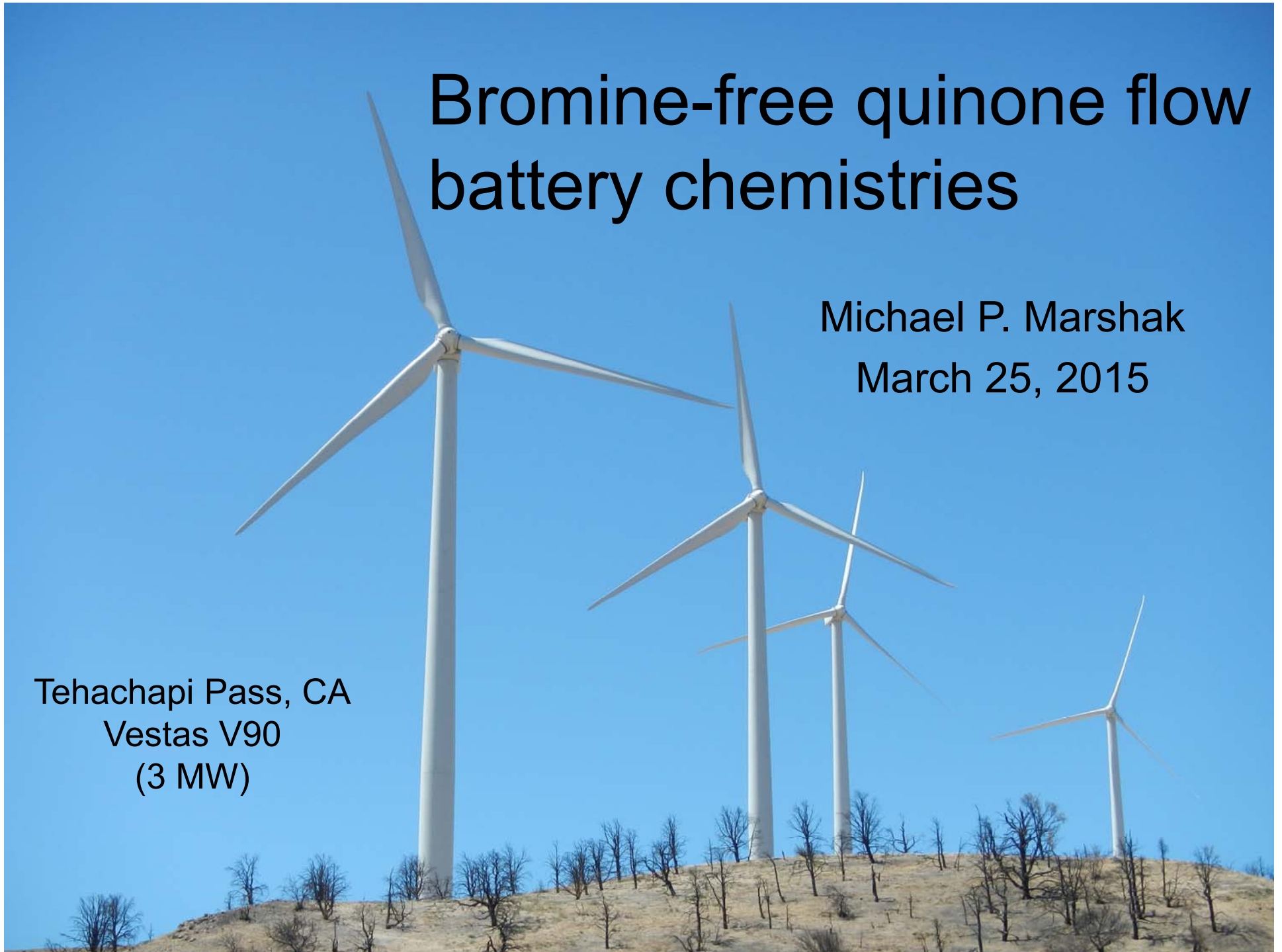


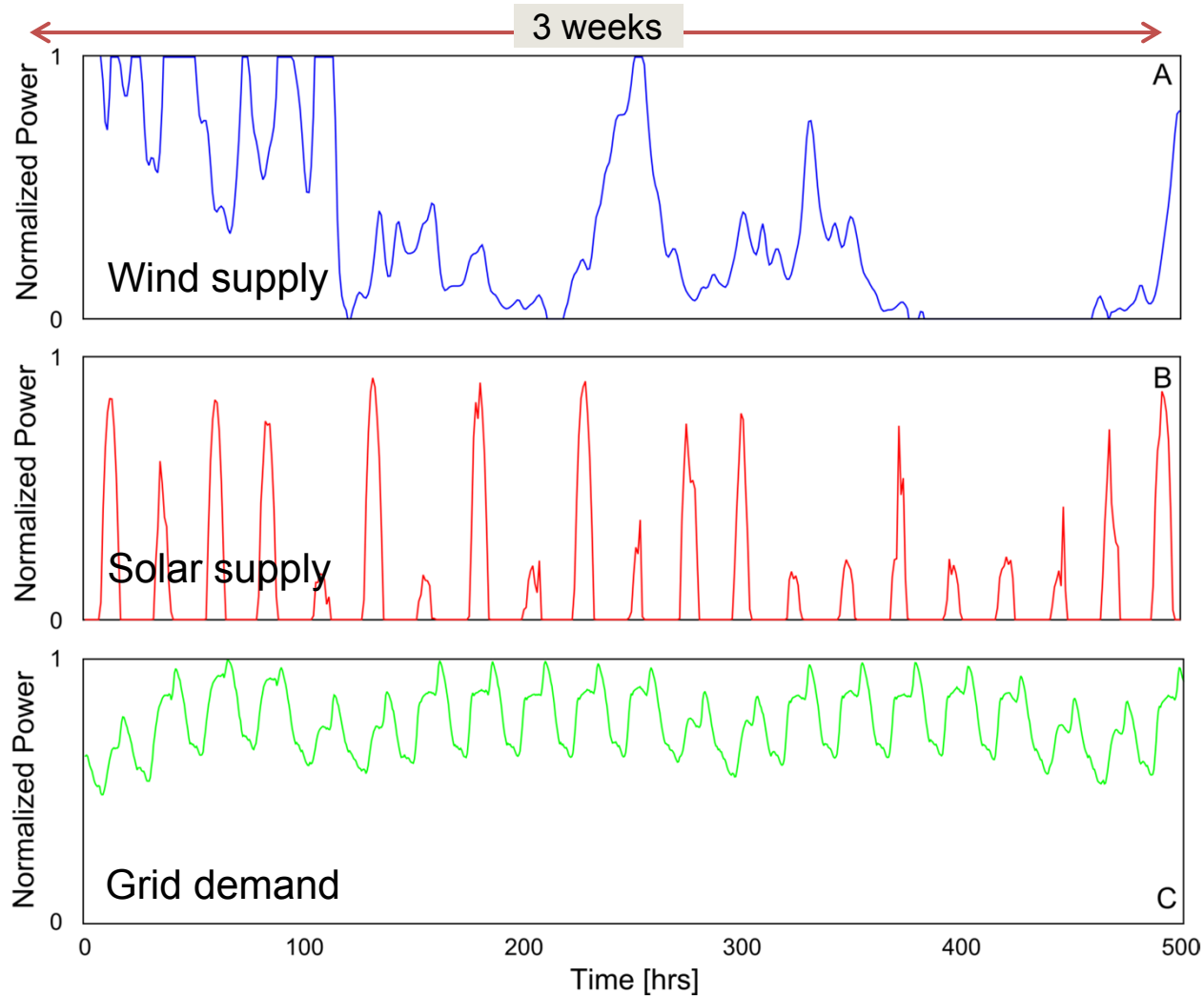
Bromine-free quinone flow battery chemistries

Michael P. Marshak
March 25, 2015

Tehachapi Pass, CA
Vestas V90
(3 MW)

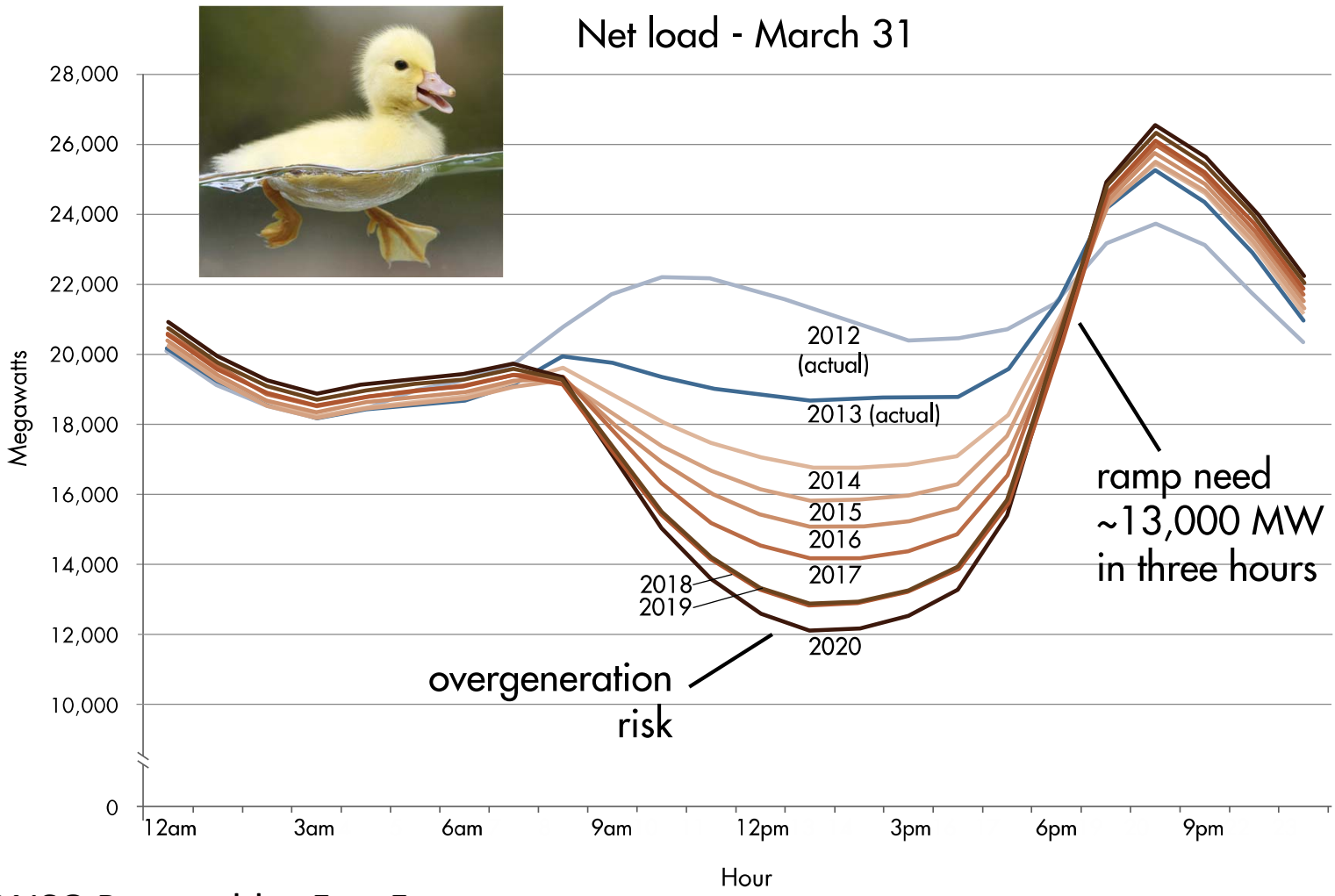


Renewable Energy is Intermittent

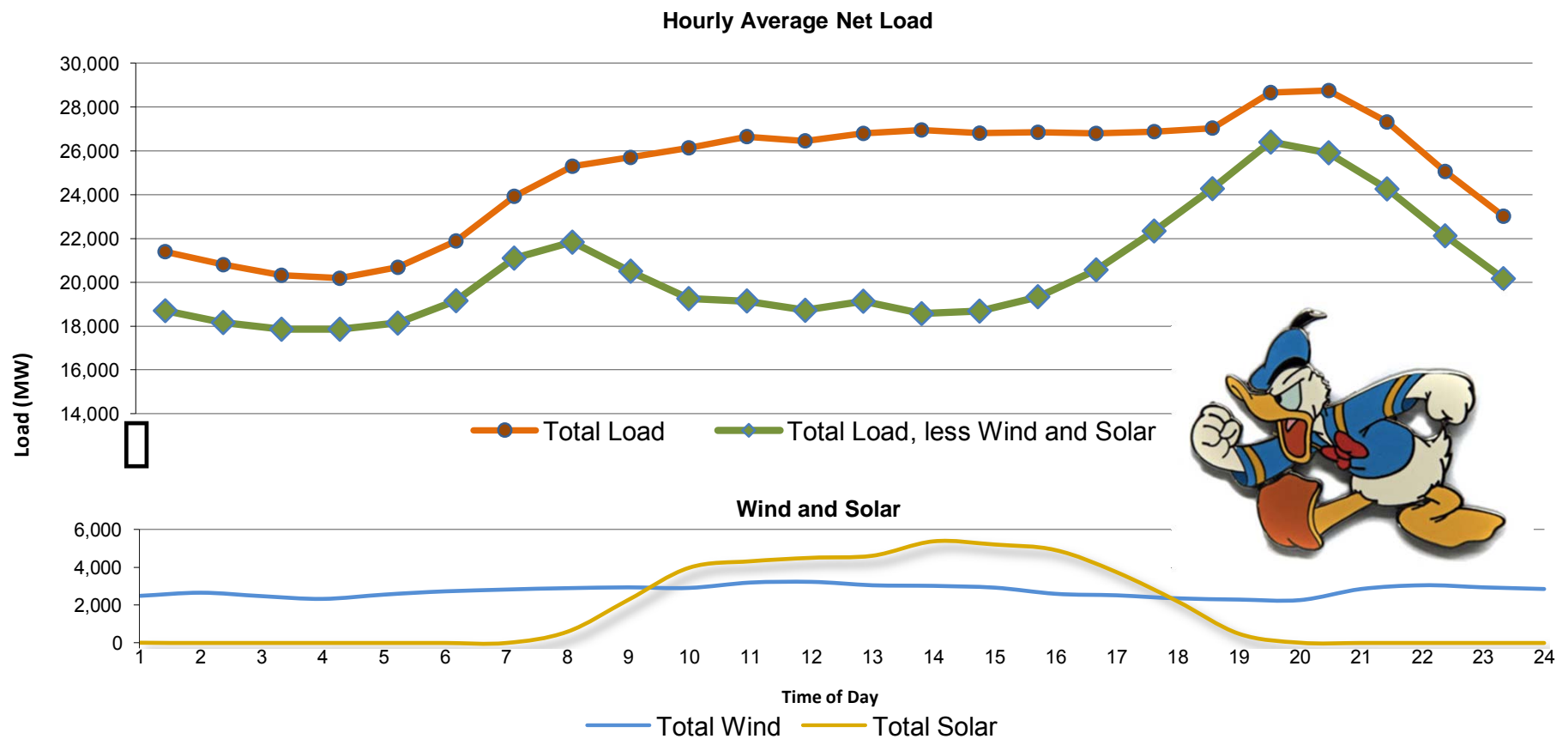


Rugolo, J. and Aziz, M. J. *Energy Environ. Sci.* 5, 7151 (2012)

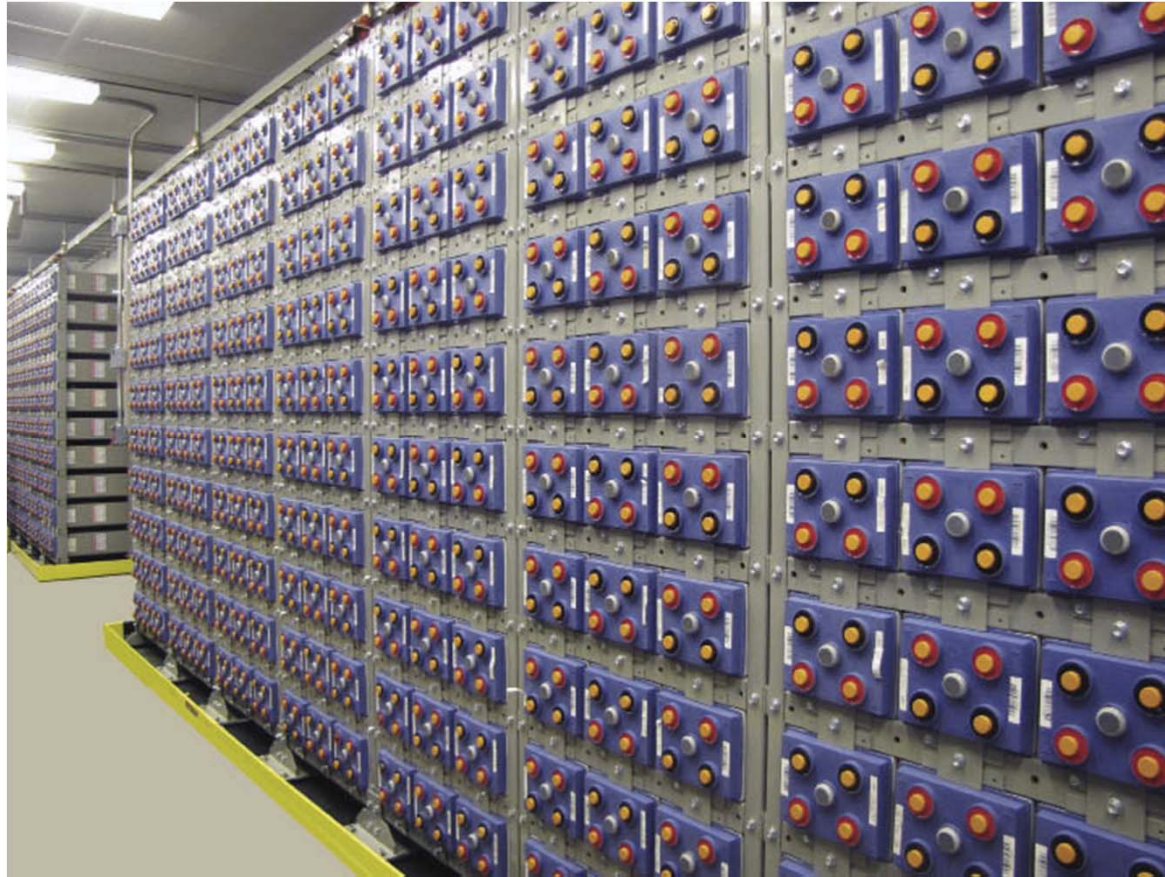
California's Supply-Demand "Duck Curve"



California Supply-Demand Mar 24, 2015

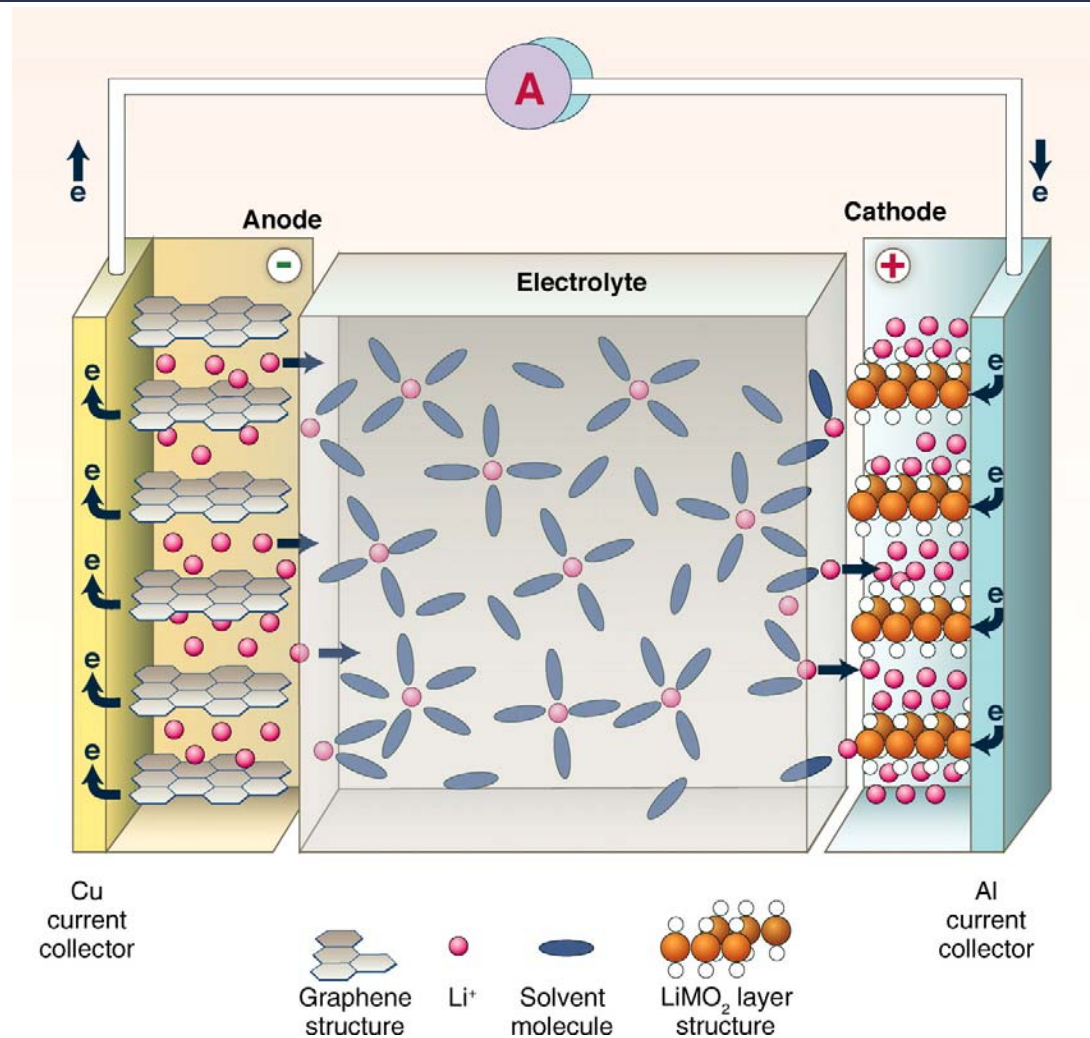


1 MWh Battery Bank

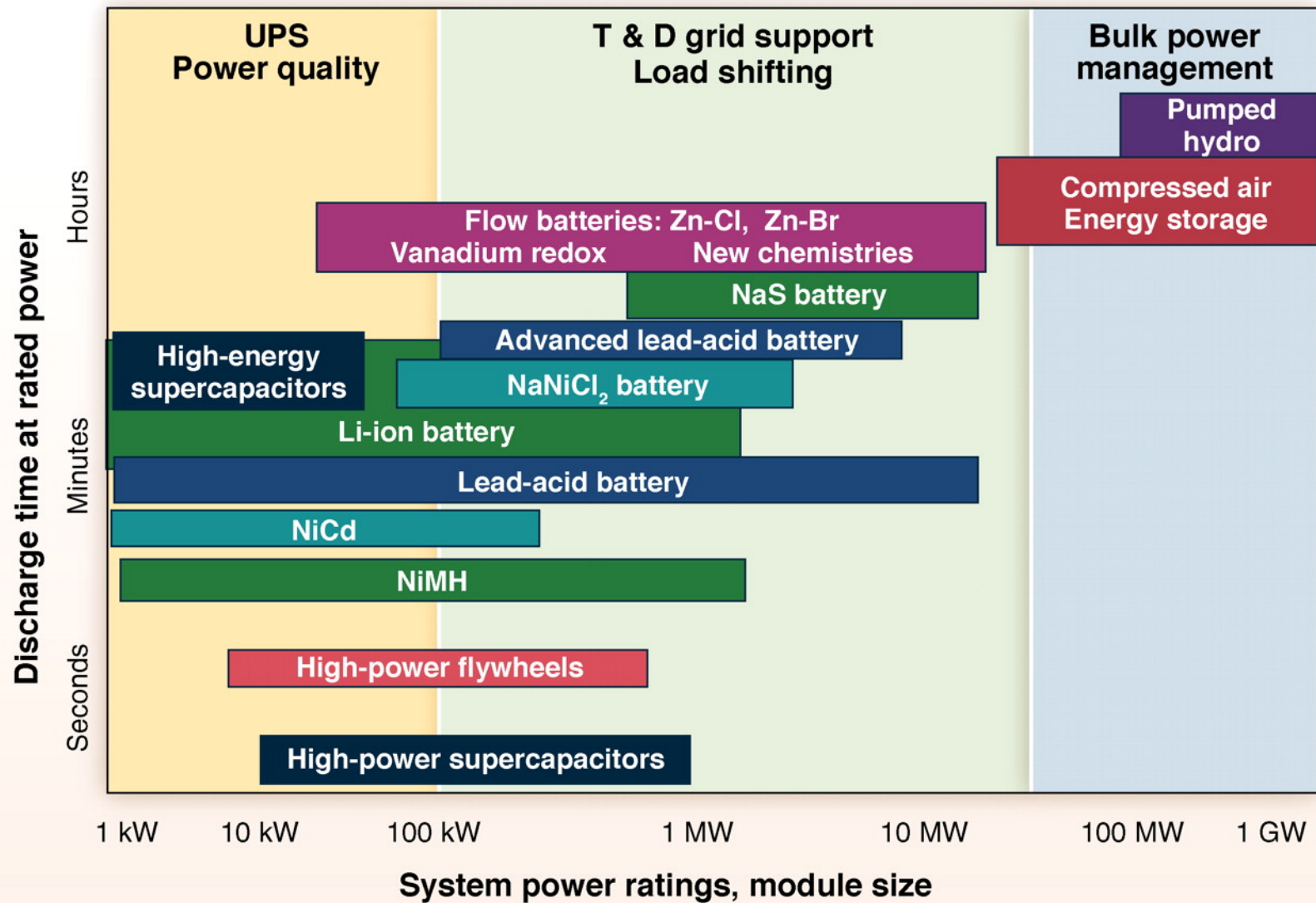


Lead Acid + NiCd
EnerSys, South Burlington, Vermont

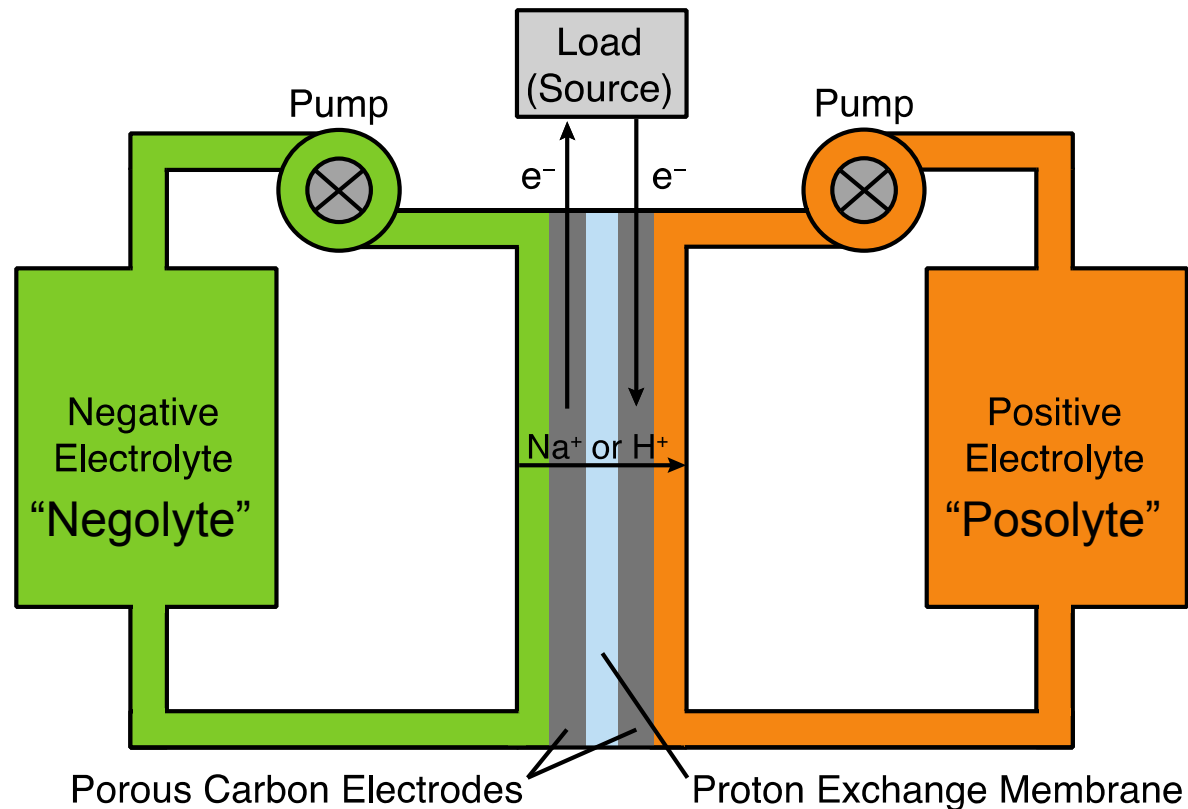
The Power:Energy Ratio is Fixed for Solid Electrode Batteries



B Dunn et al. *Science* **2011**, 334, 928-935.



Redox Flow Batteries

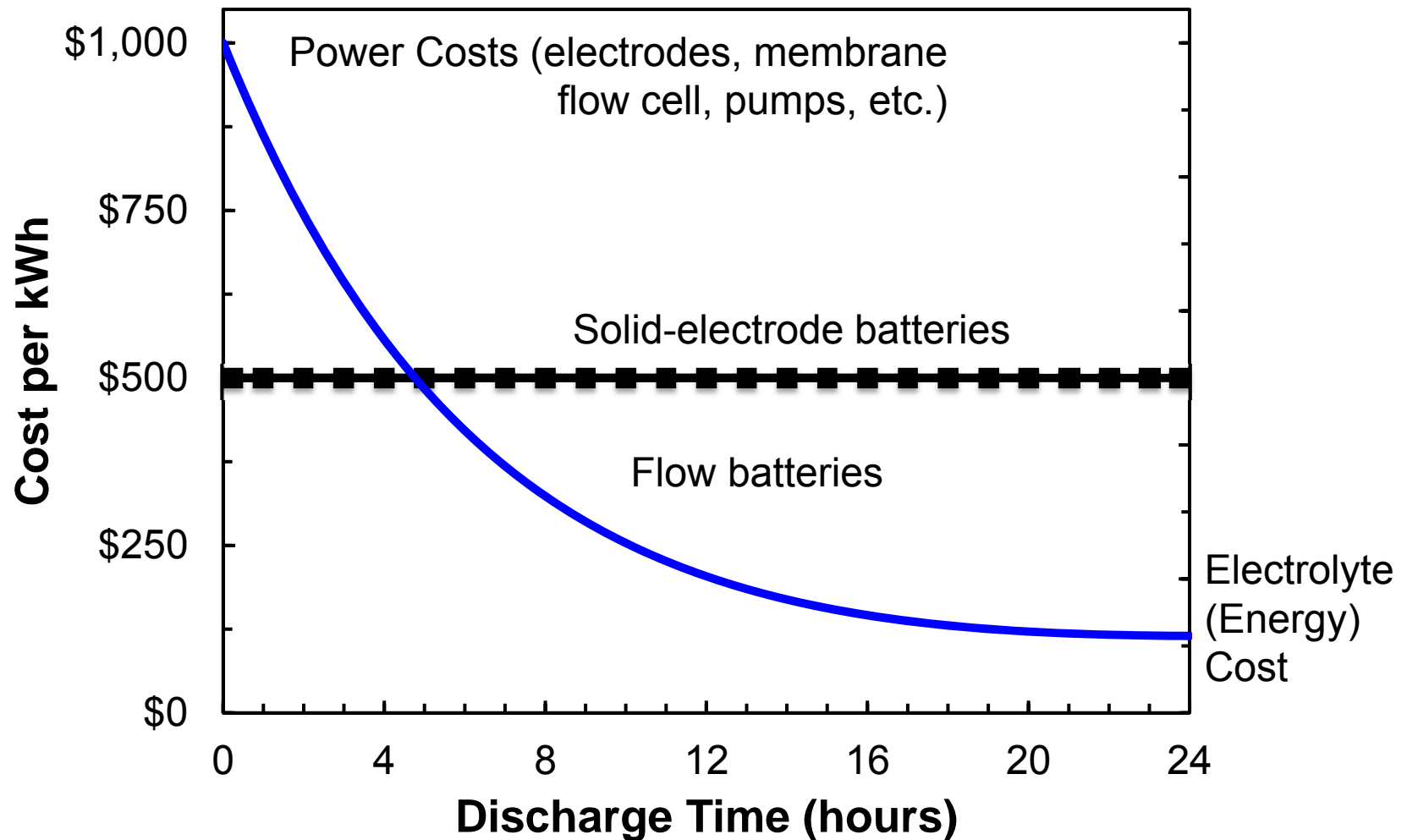


- Operates like a regenerative fuel cell
- All-liquid electrolyte
- Can independently scale power (electrode area) and energy (electrolyte volume)

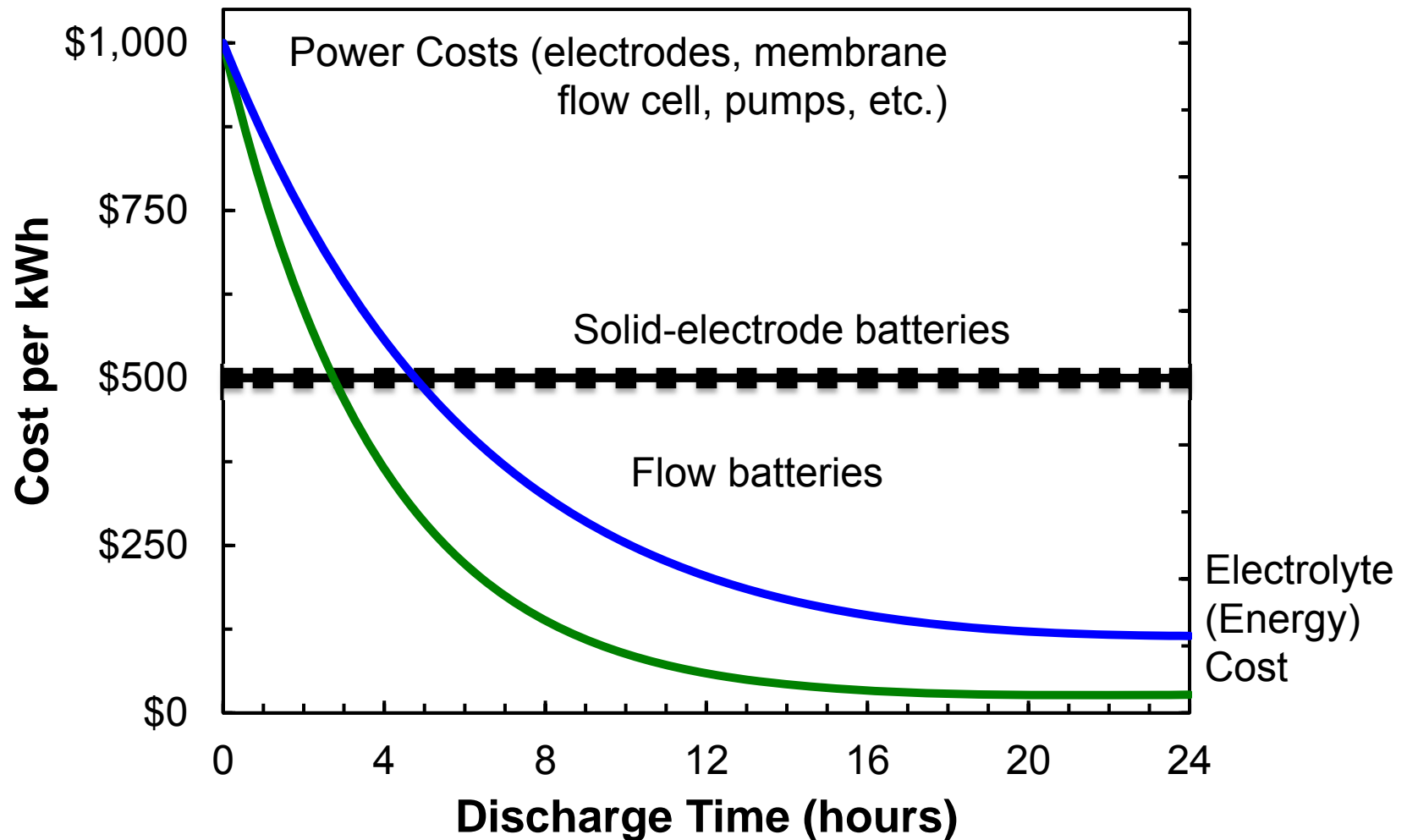
1 MWh FeCr EnerVault, Turlock, California



Flow Batteries Decrease Cost at Scale



Flow Batteries Decrease Cost at Scale



Common Flow Battery Chemistries

System	Cell Pot.	Challenges
All-Vanadium	1.4 V	Cost of Vanadium
Vanadium-Bromine	1.3 V	Membrane Crossover
Bromine-Polysulfide	1.5 V	Sulfate Precipitation
Iron-Chromium	1.2 V	Hydrogen Generation
Hydrogen-Bromine	1.1 V	Bromine poisons H ₂ catalysts Hydrogen Storage

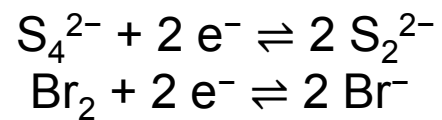
Nguyen, T.; Savinell, R. F. *Electrochem. Soc. Interface* **2010**, *19*, 54–56.

Bromine-Polysulfide Battery



Regenesys 12 MW, Little Barford, UK

Bromine-Polysulfide



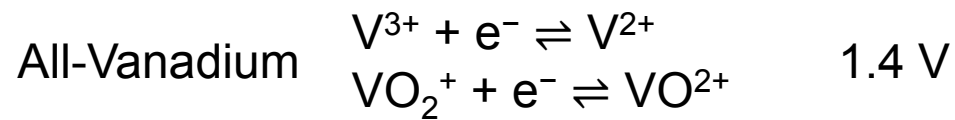
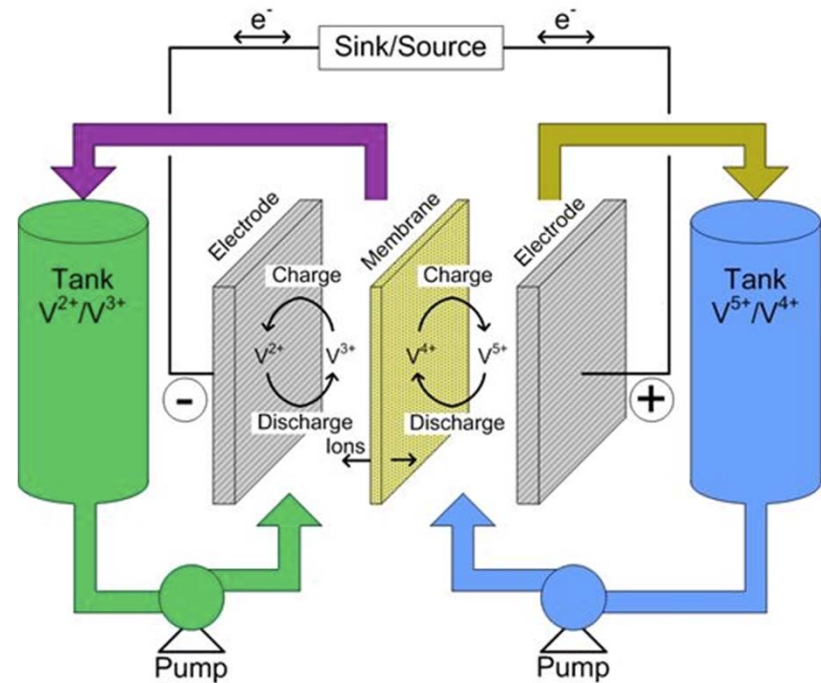
-0.4 V
1.09 V

1.5 V

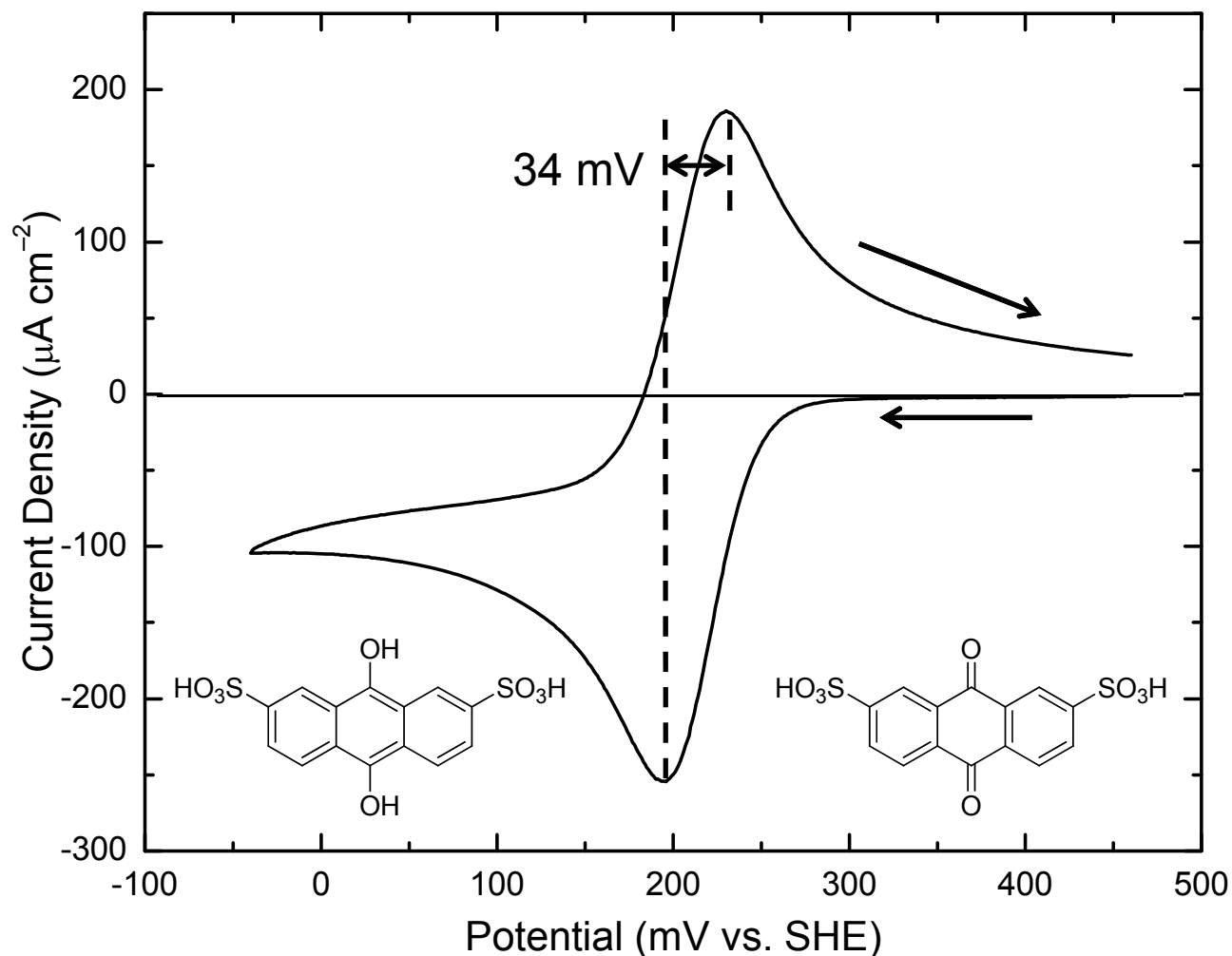
All-Vanadium Flow Battery



Source: Prudent Energy Corporation



Anthraquinone-2,7-Disulfonic Acid



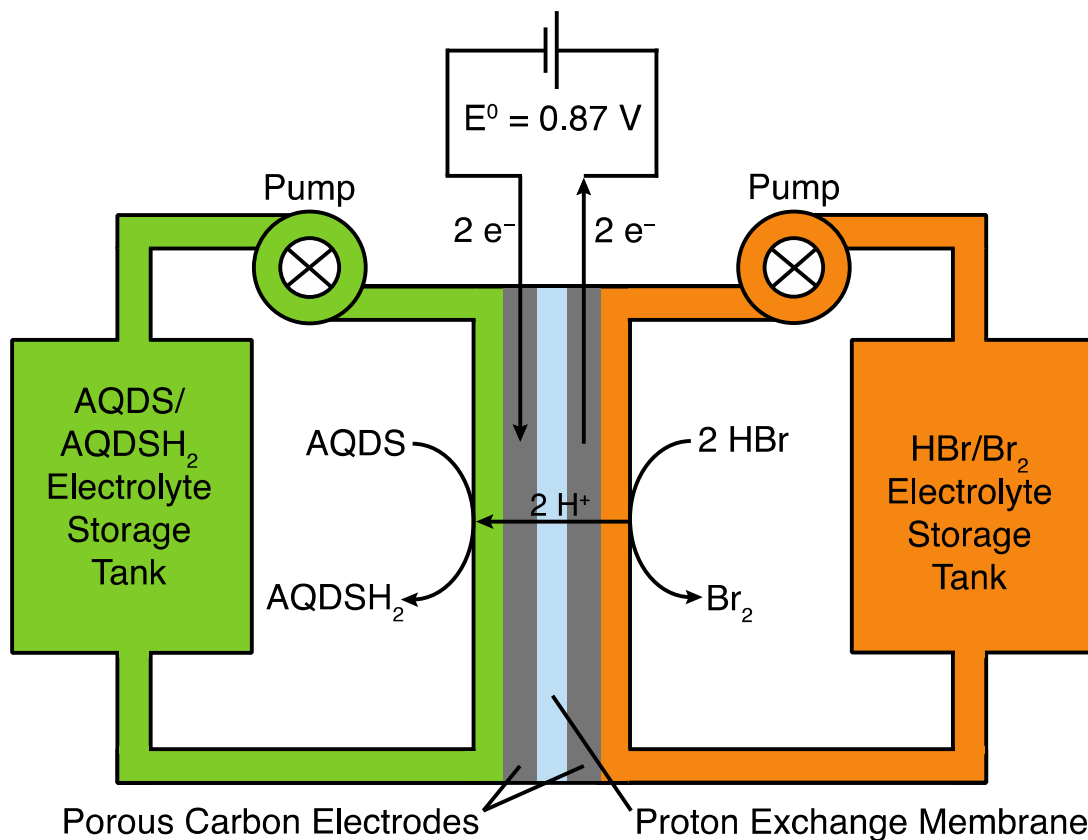
The E^0 for this process is 0.213 V vs. SHE

1 mM AQDS in 1 M H₂SO₄
Carbon Working Electrode

The Quinone-Bromine Flow Battery



Brian Huskinson

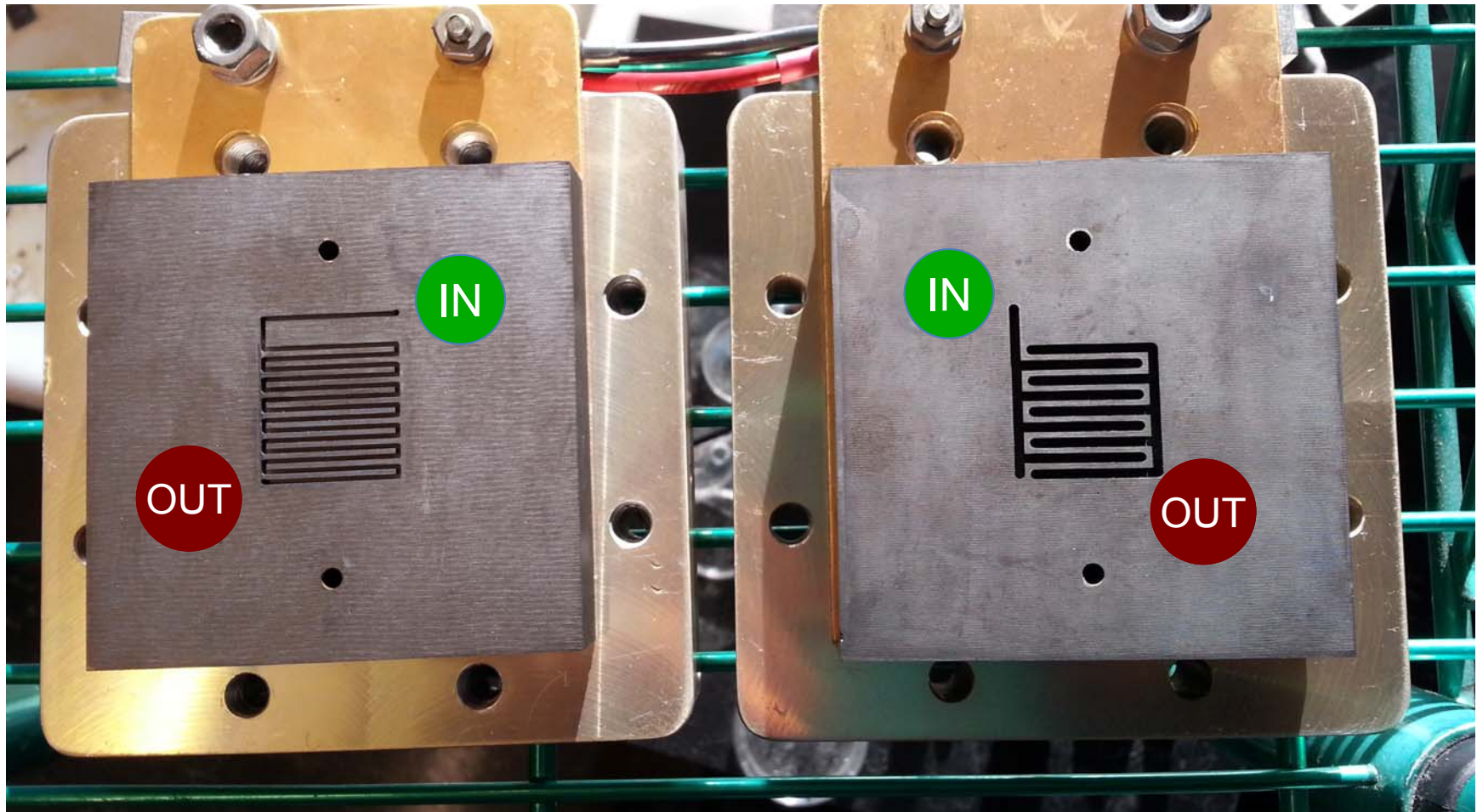


Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. *Nature*. **2014**, *505*, 195–198.

Flow Field Design

Serpentine

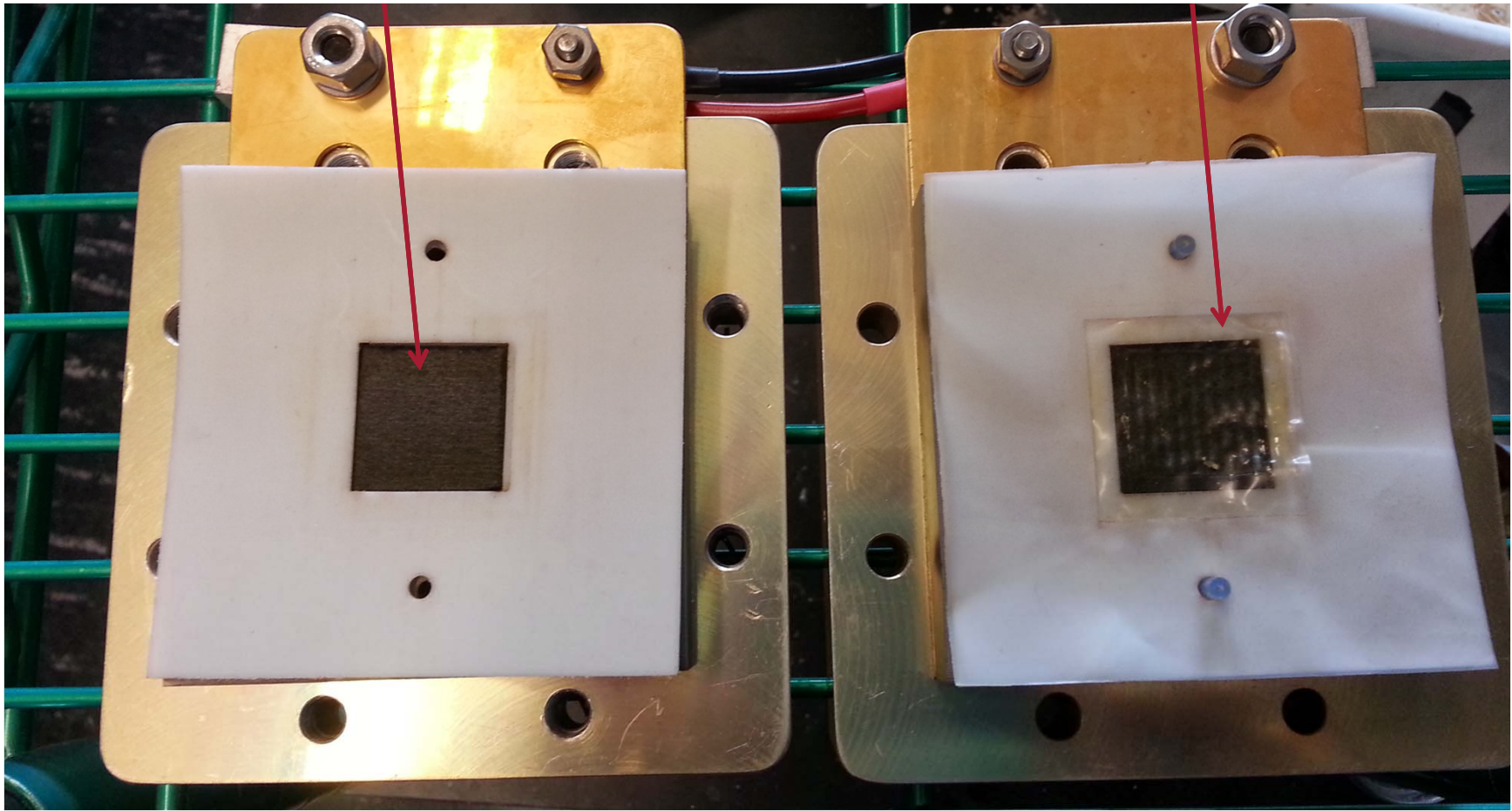
Interdigitated



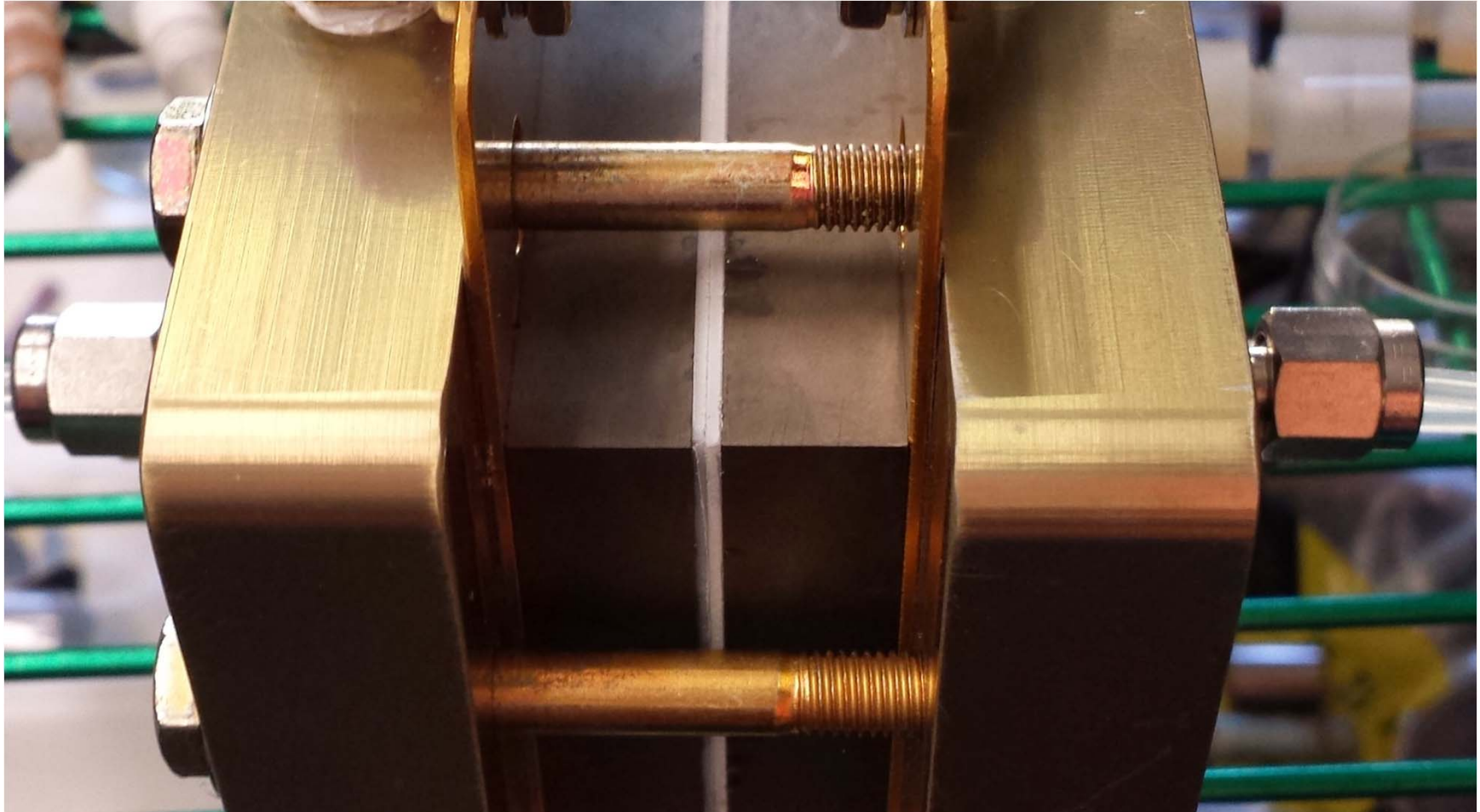
Membrane Electrode Assembly (MEA)

Carbon Paper

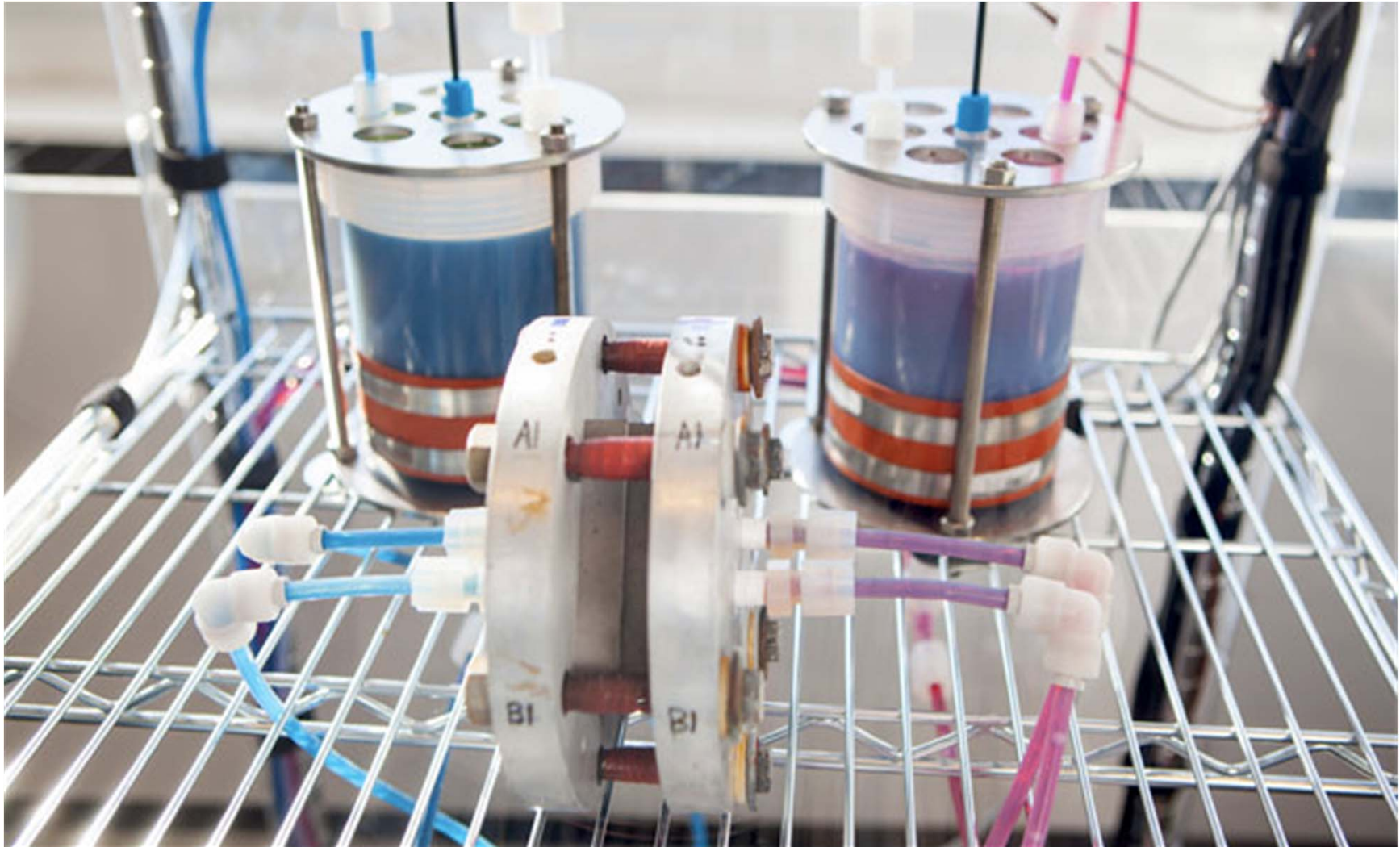
Nafion Membrane



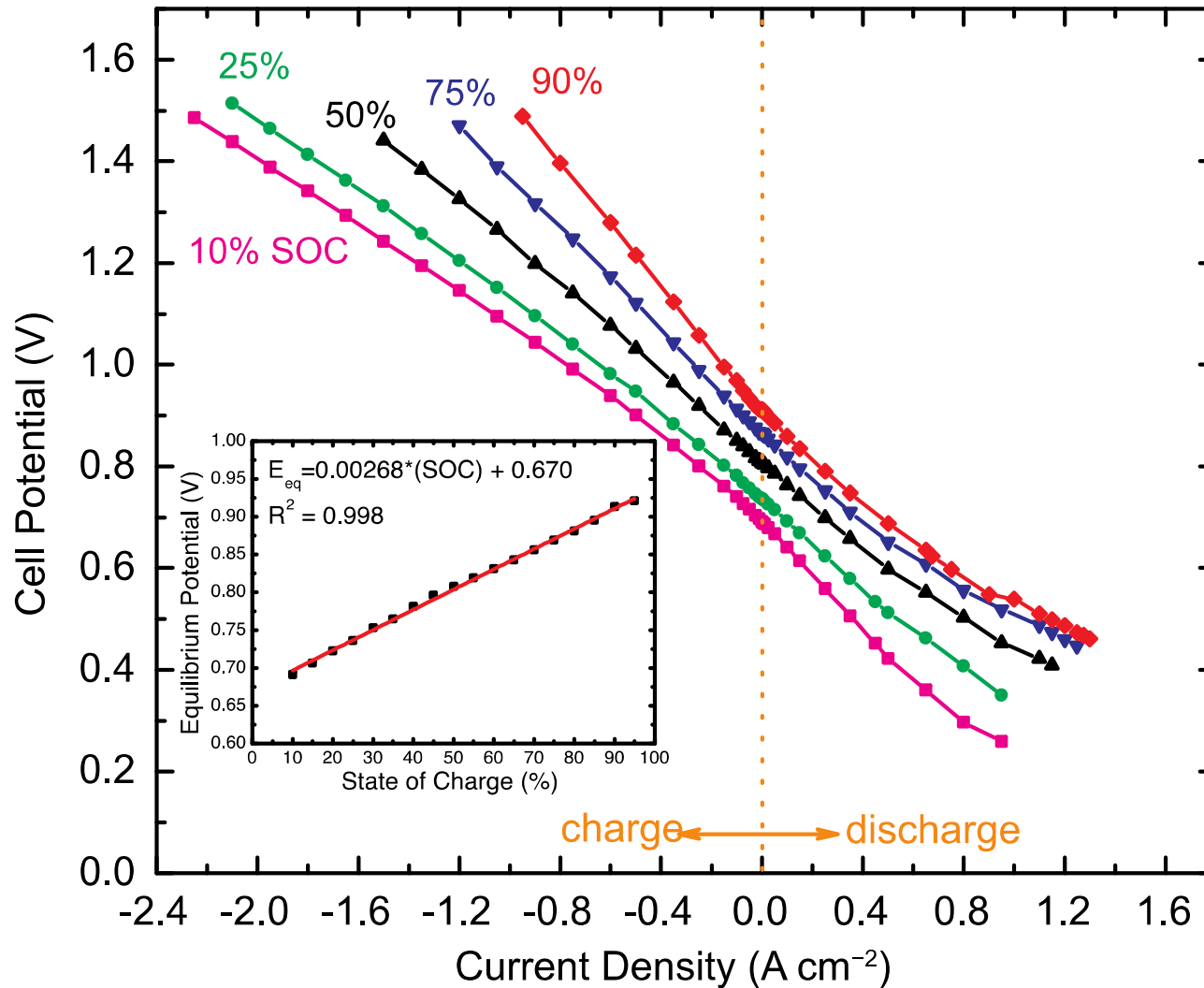
Assembled Cell



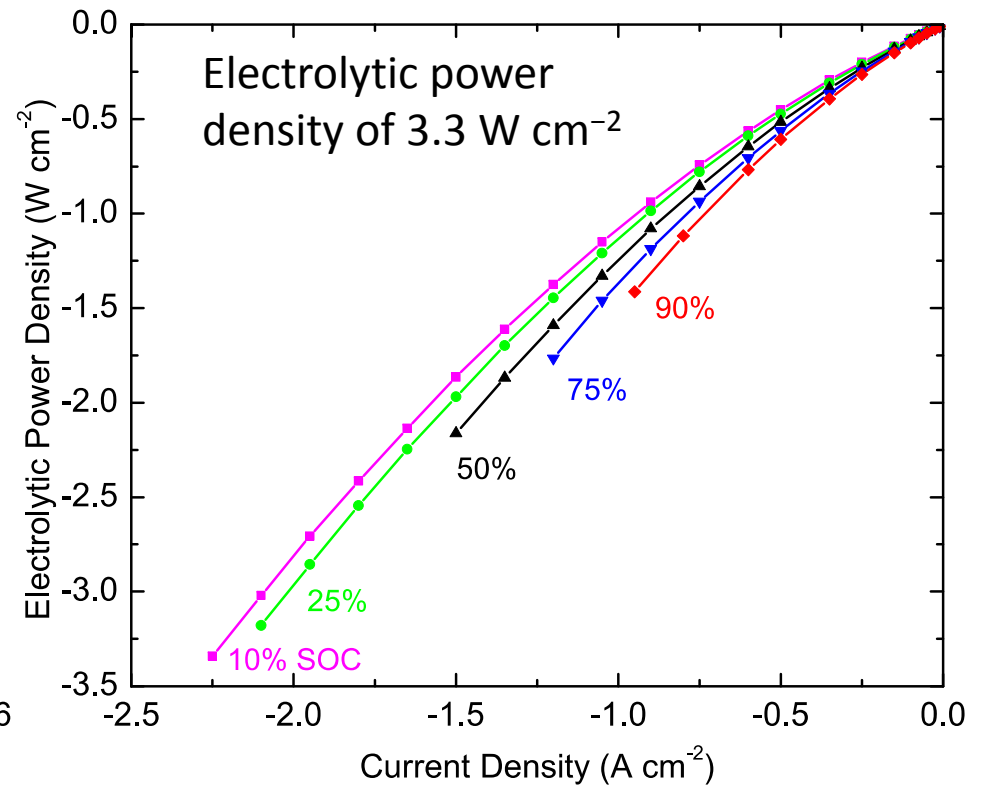
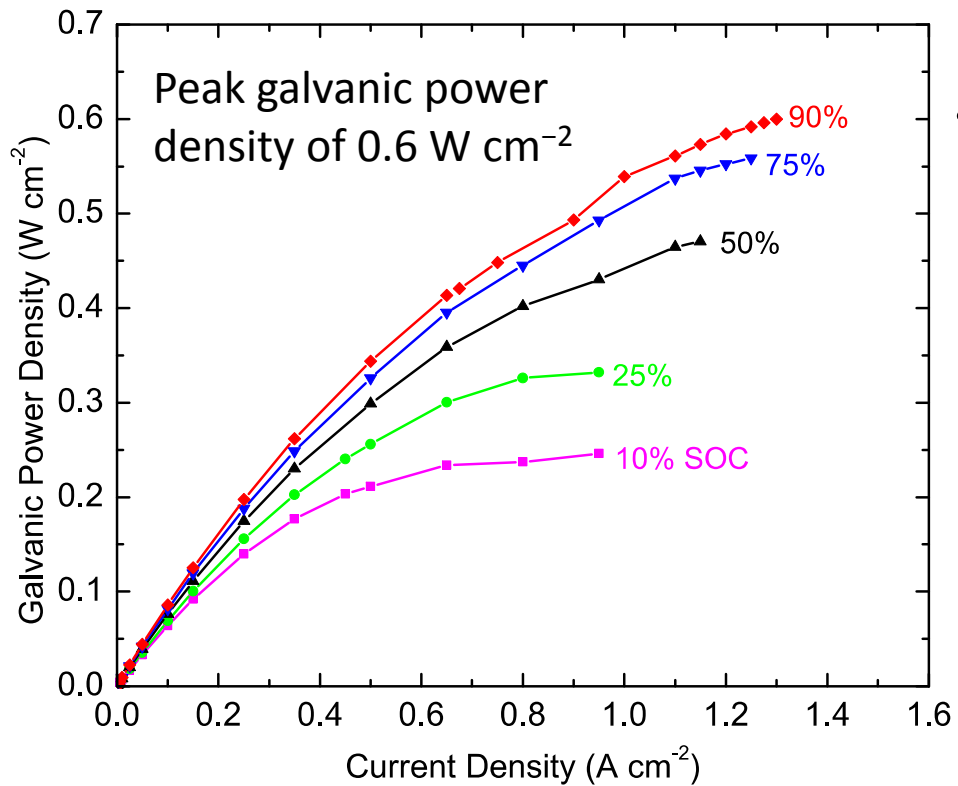
Flow Cell In Operation



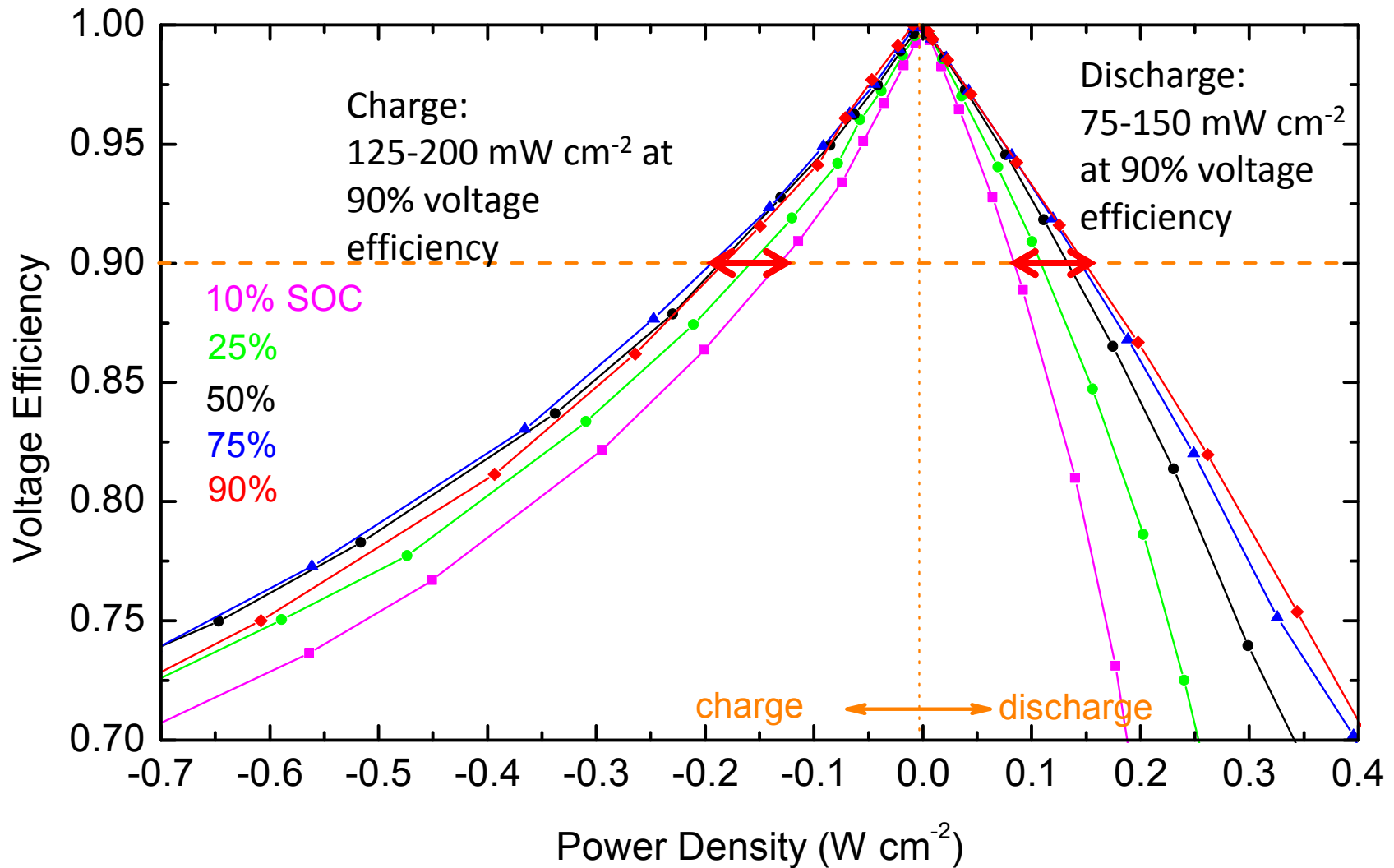
Cell Performance



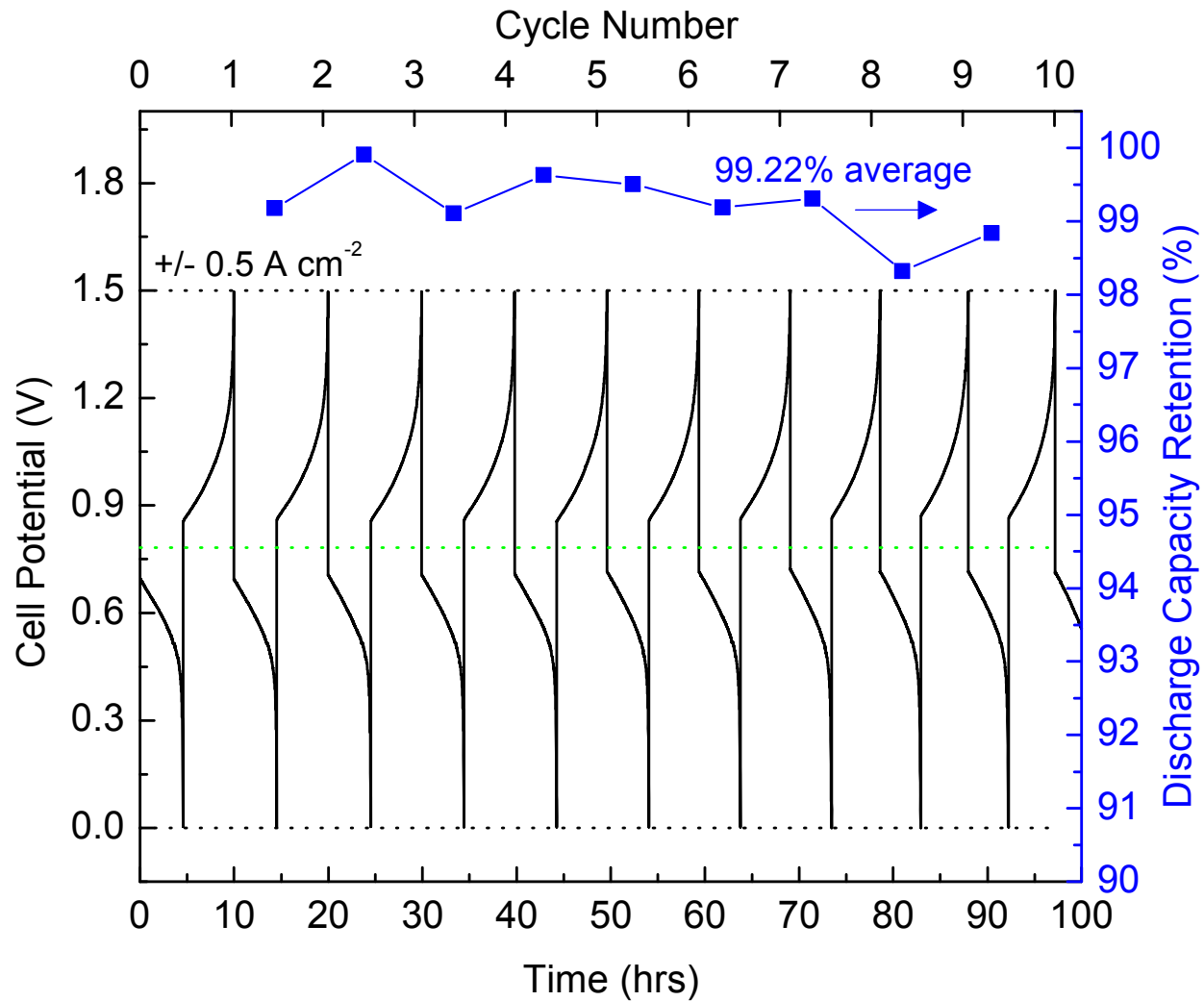
Cell Performance



Cell Performance

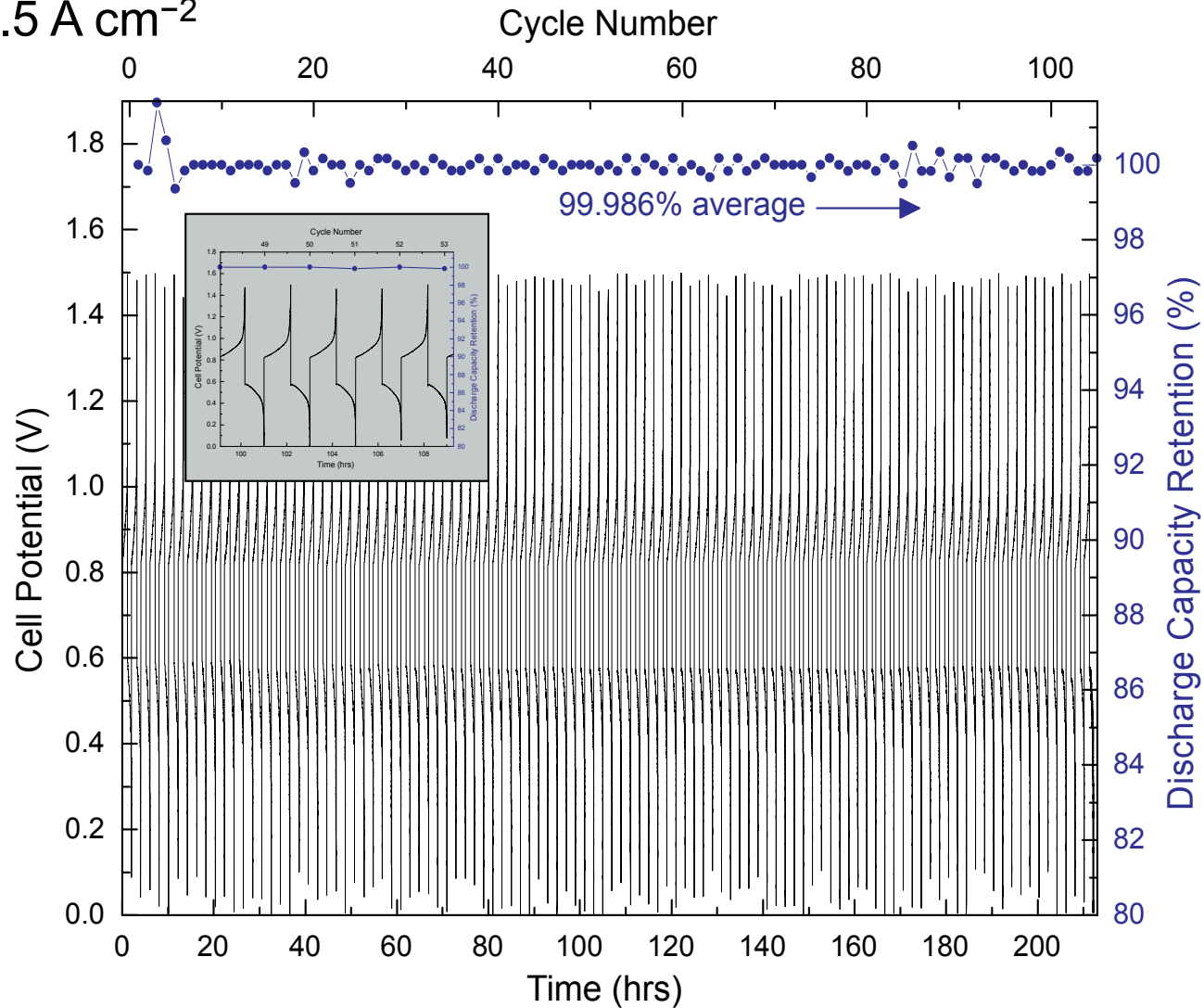


Battery Cycling



Extended Cycling

Cycling at 0.5 A cm^{-2}

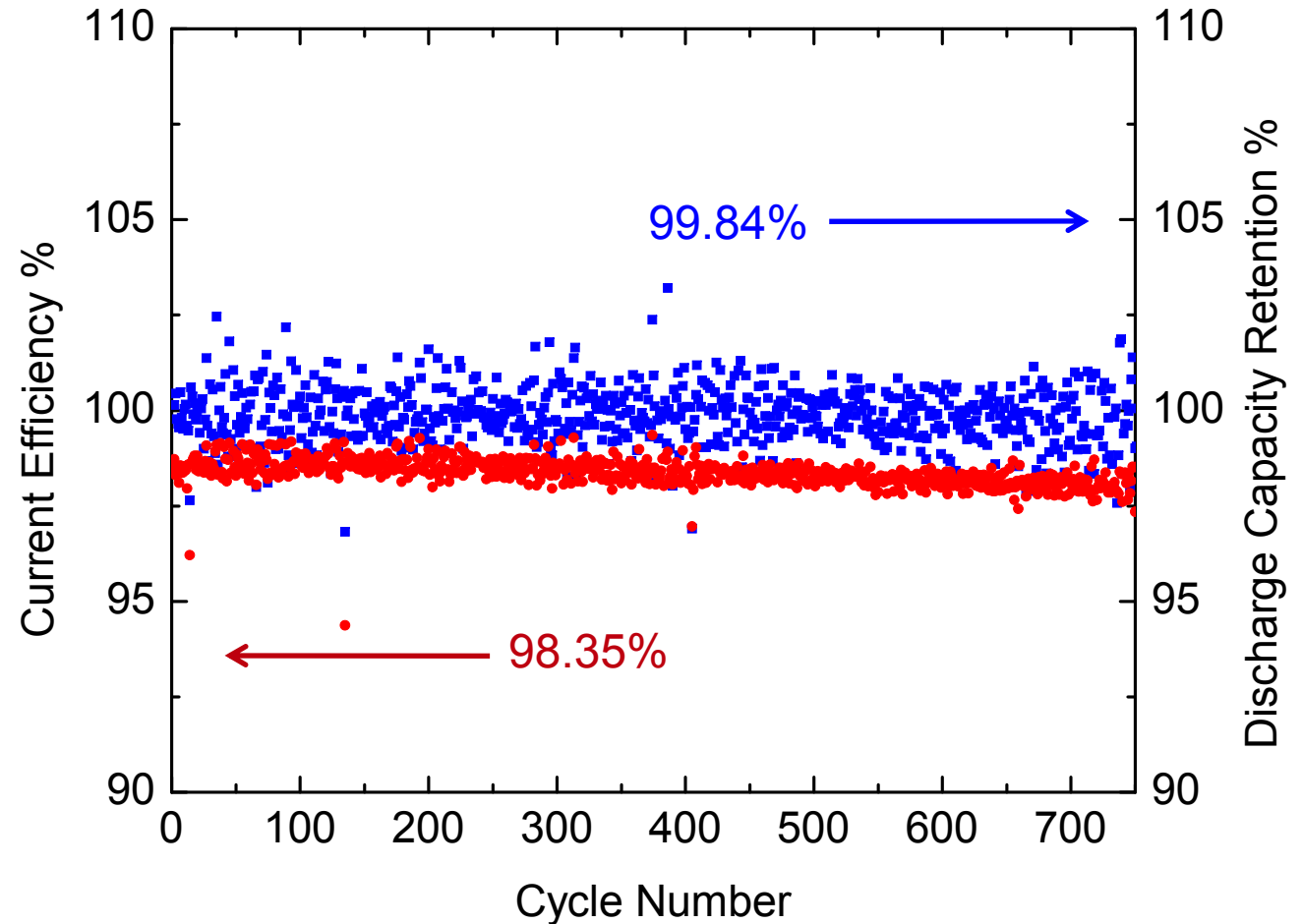


More Extended Cycling

Over 750 cycles at
 0.75 A cm^{-2}

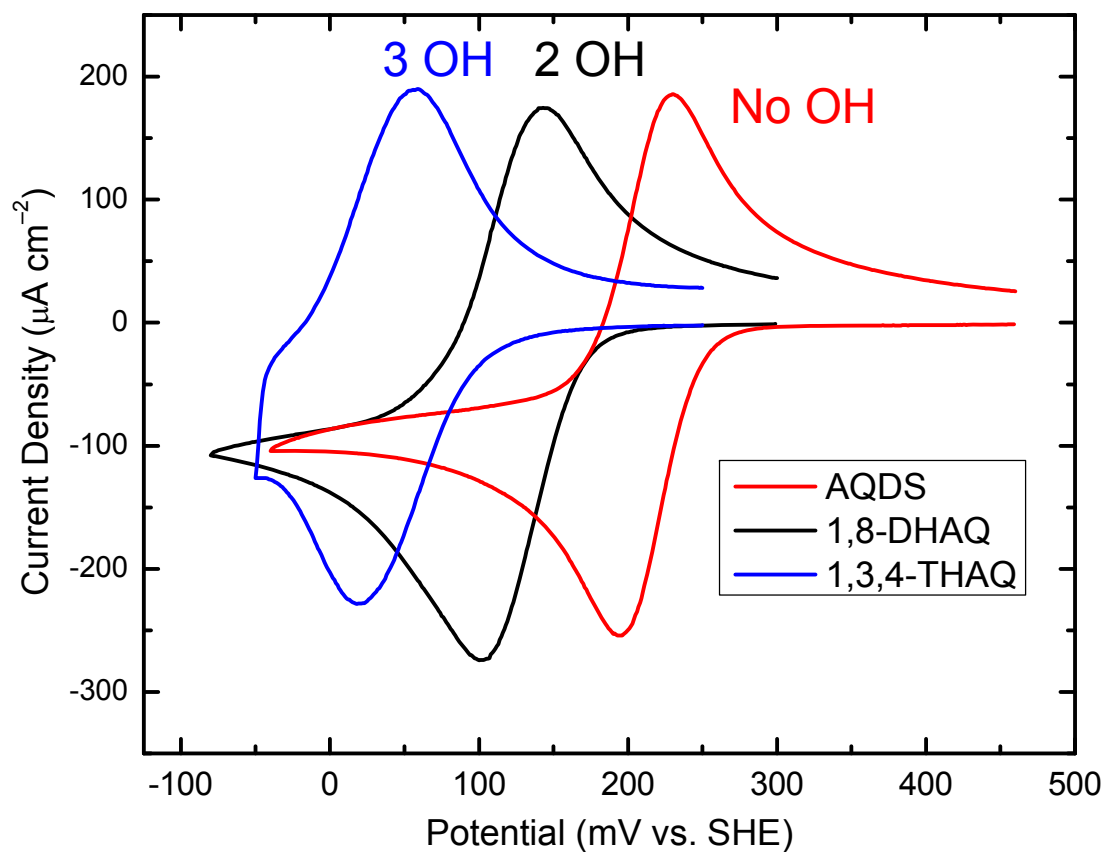
>98% Current
efficiency

>99% Charge capacity
retention

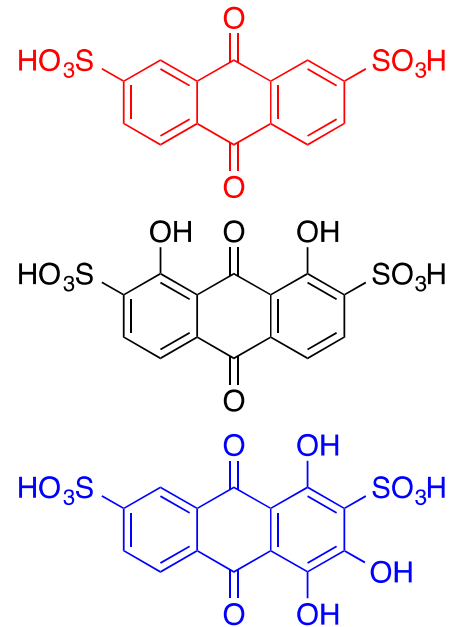


Huskinson, B., Marshak, M. P., Gerhardt, M. R. & Aziz, M. J.
ECS Trans. 61, 27–30 (2014).

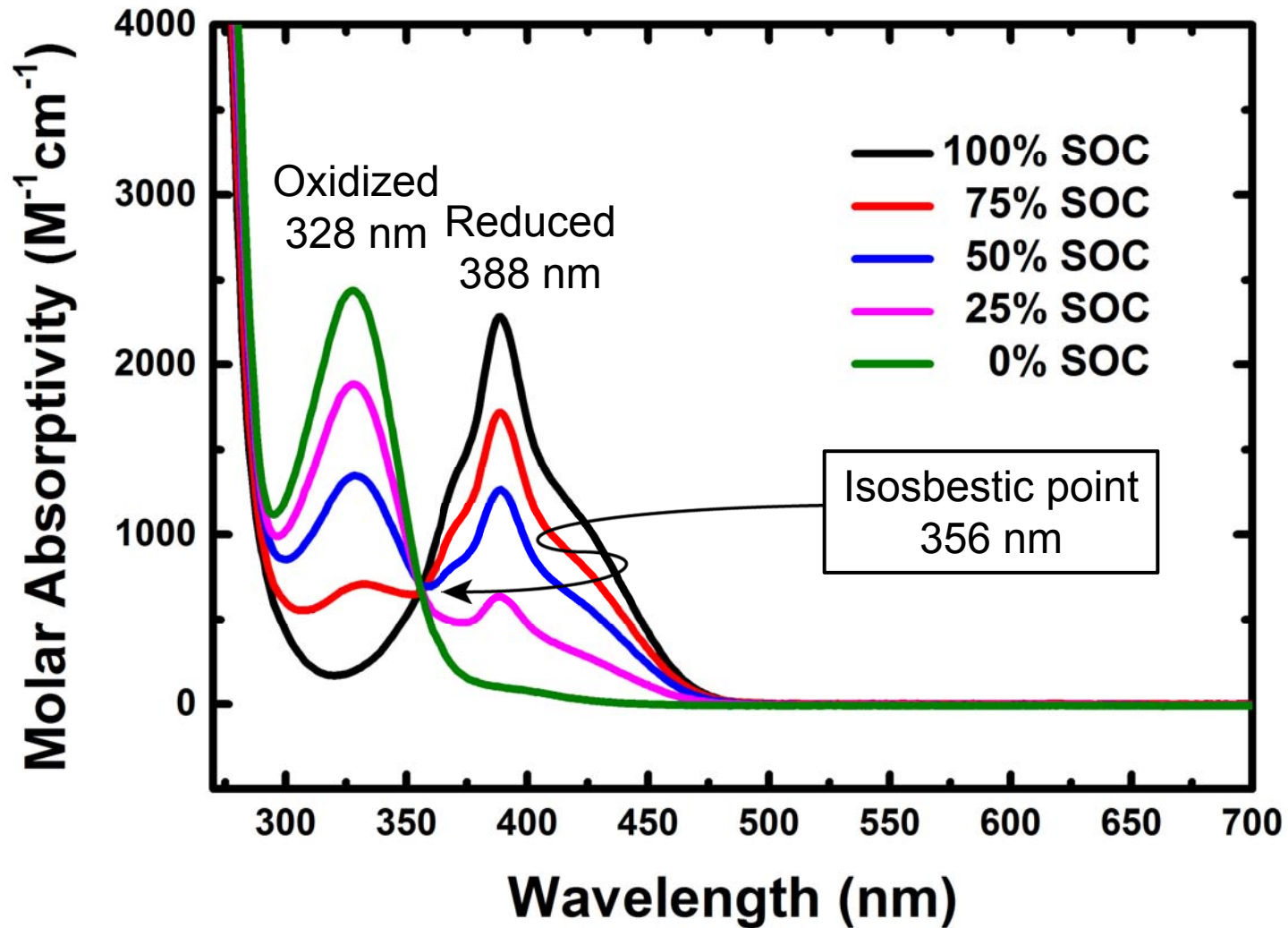
Towards 0.0 V and Beyond



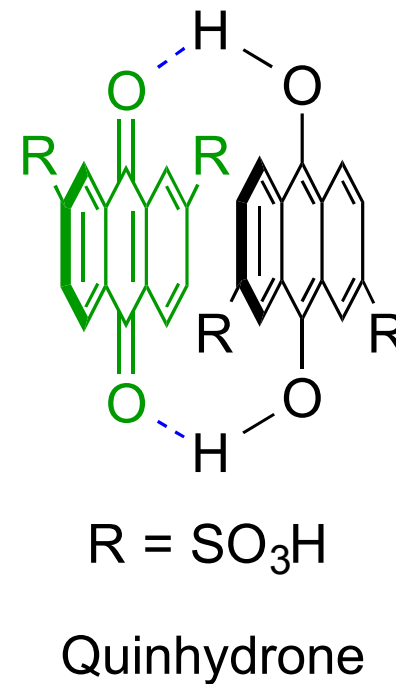
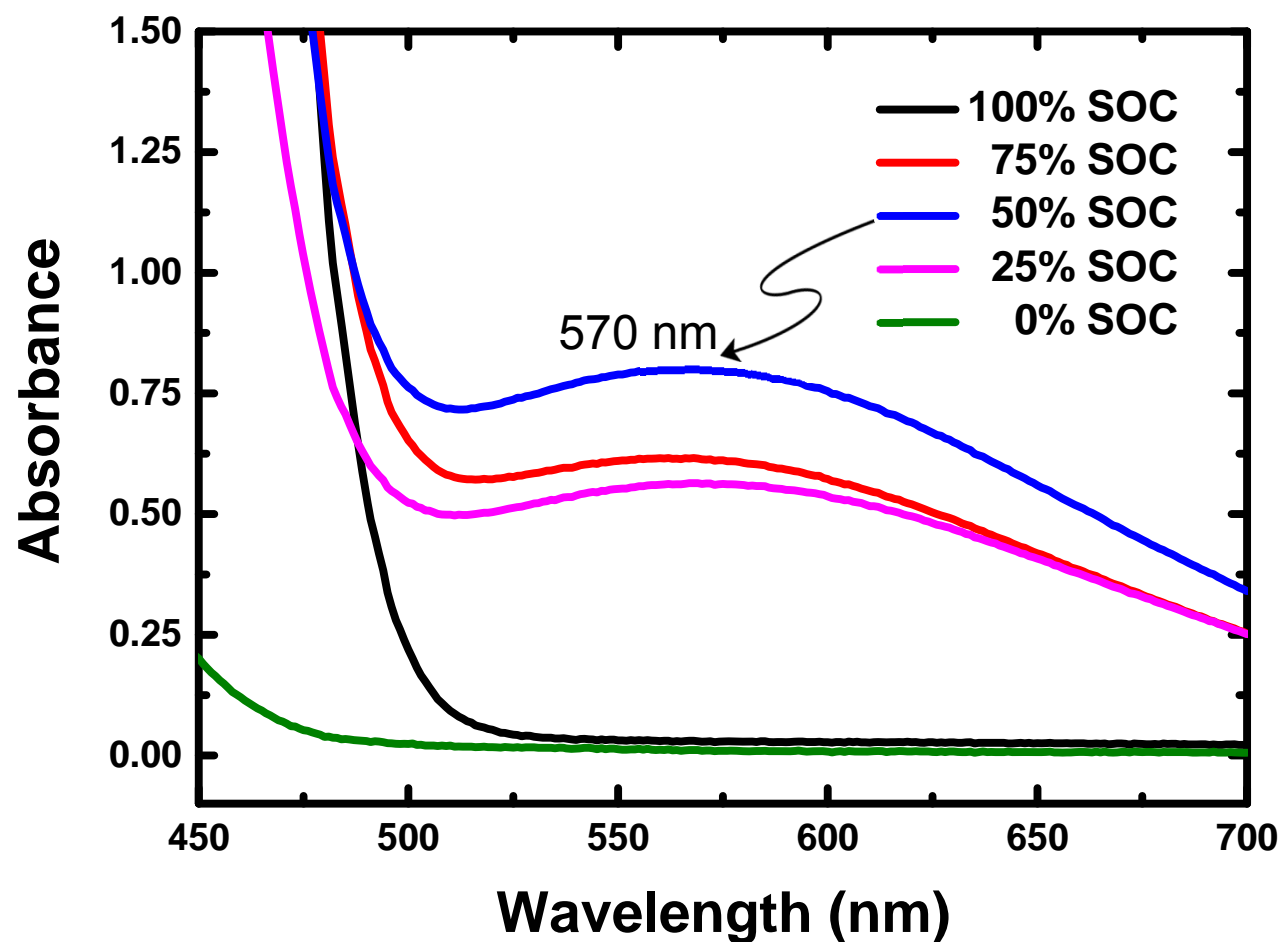
Reversible $2 e^- / 2 H^+$ reduction of quinone at 0 V is hydrogen storage with no catalyst required.



UV/Vis Spectra of Quinones

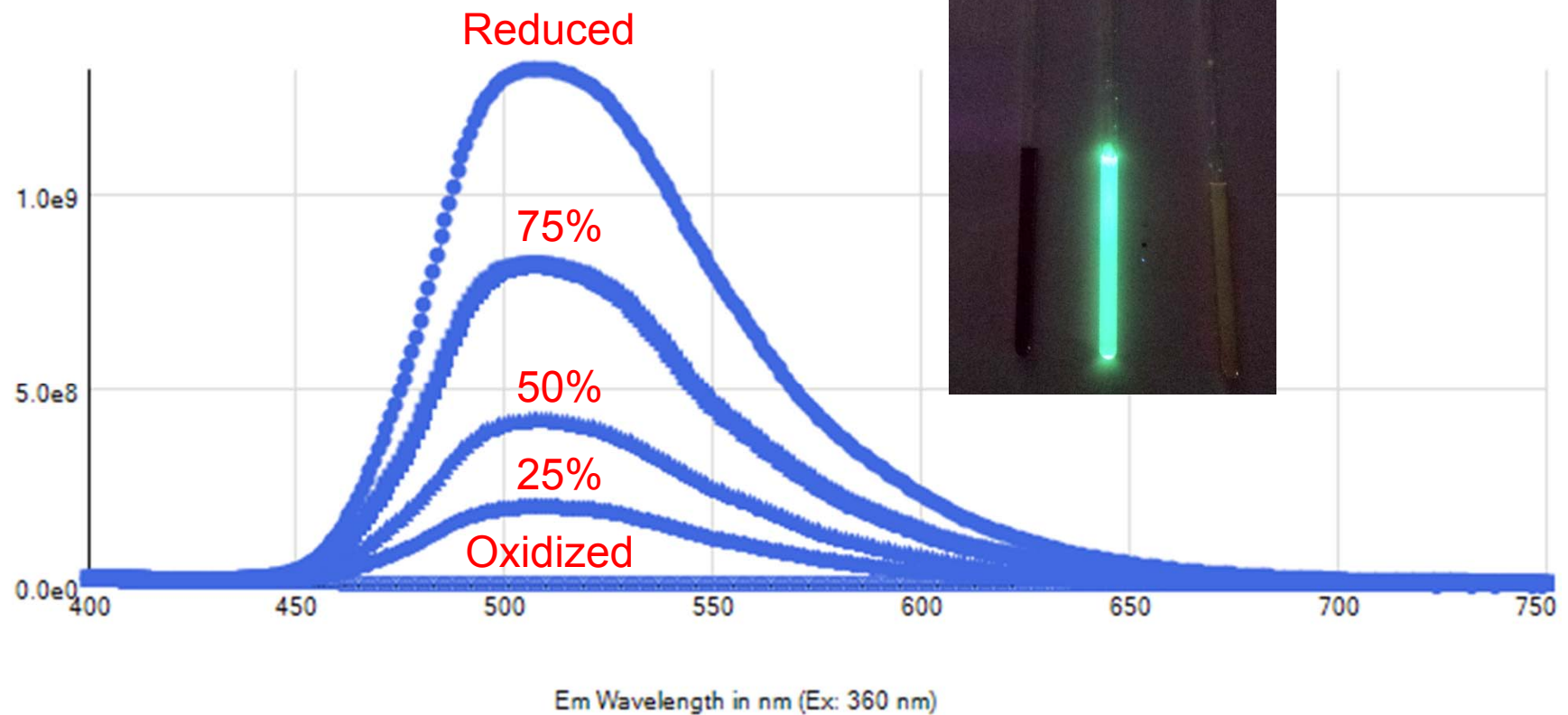


Evidence of Quinhydrone Formation



Anthraquinone Fluorescence

Excitation @ 360 nm

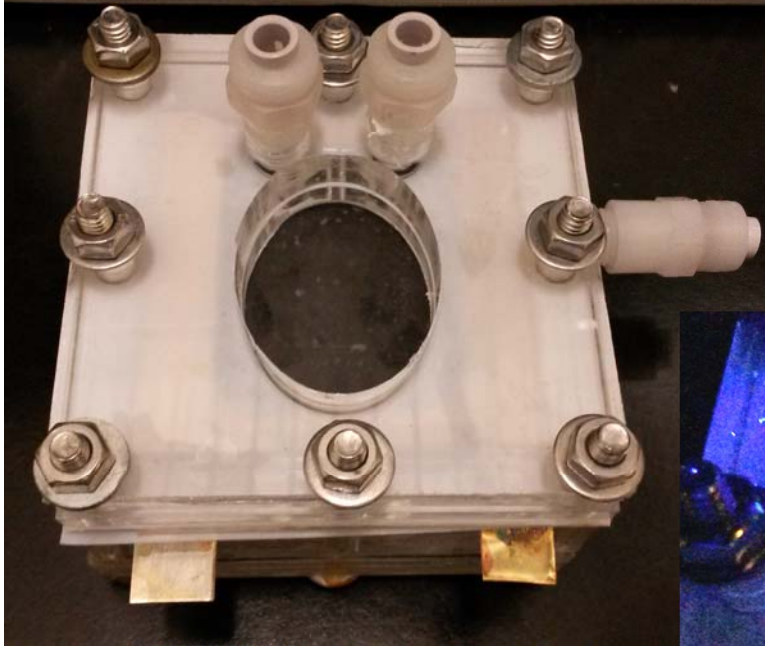


In-situ Flow Field Monitoring

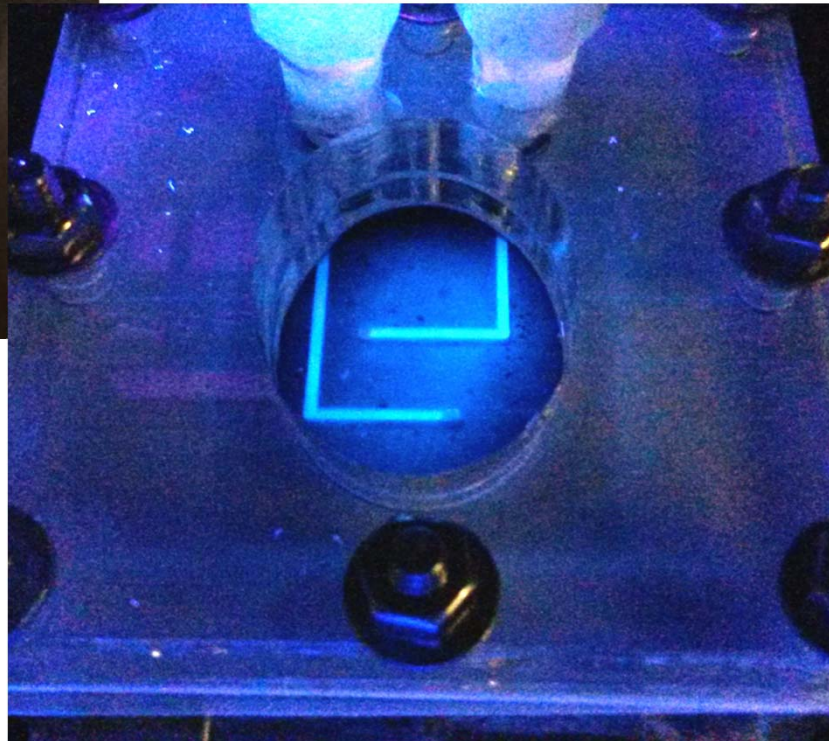
Fluorescence under
UV Lamp!



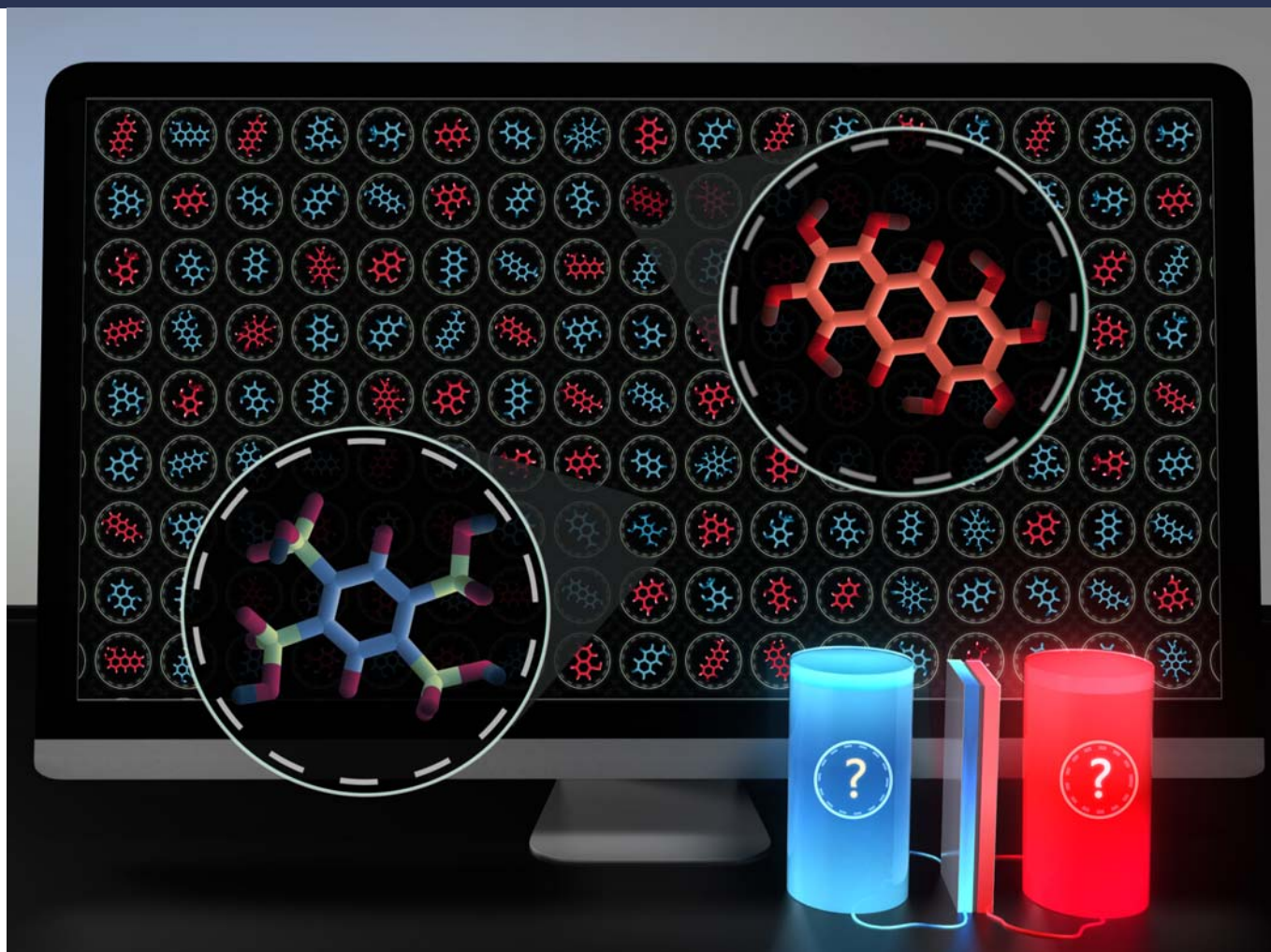
Andrew Wong



Electrochemical flow
cell with a transparent
conducting flow field

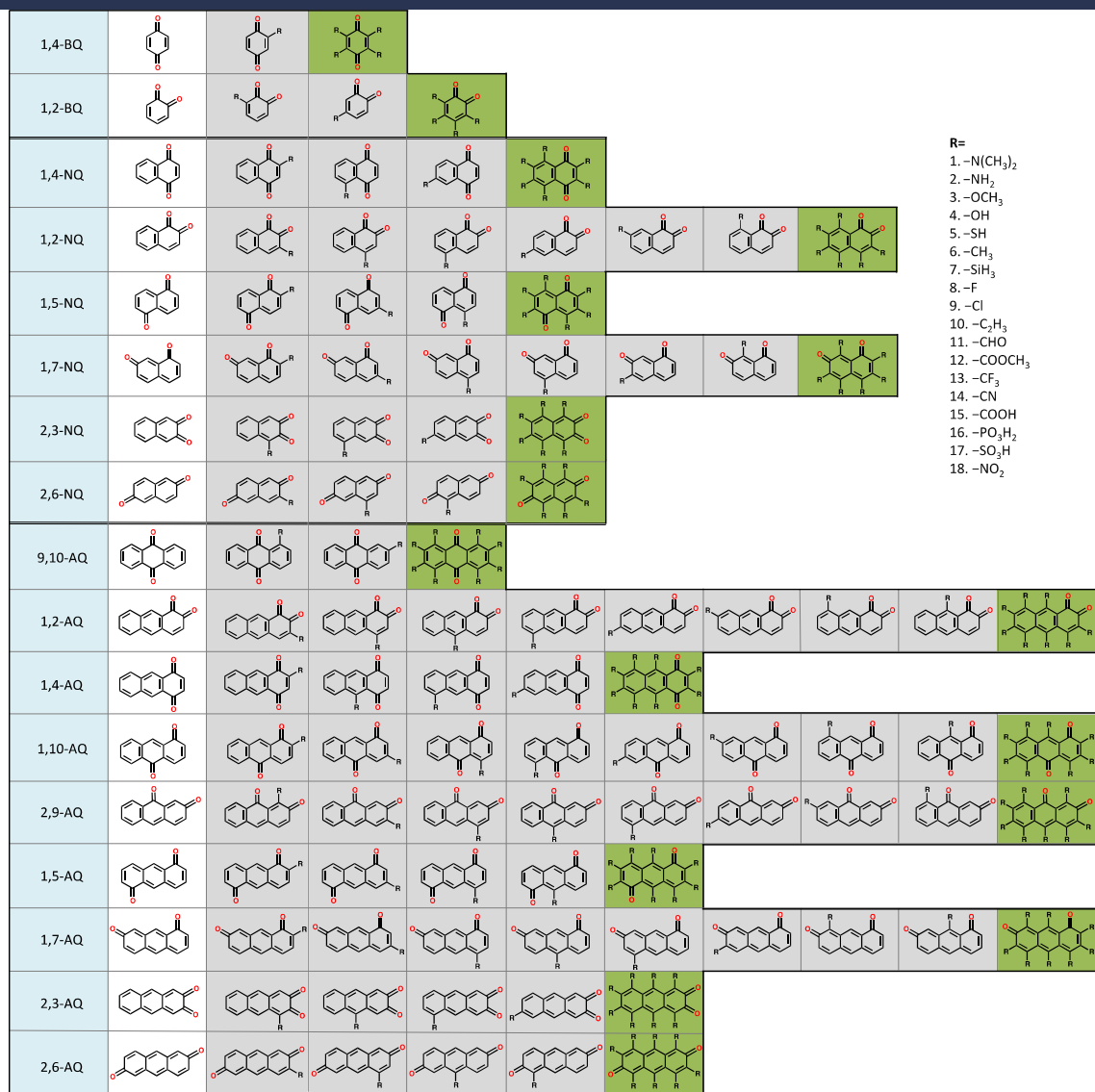


High-Throughput Computational Screening



Computational design of molecules for an all-quinone redox flow battery.
Er, S., Suh, C., Marshak, M. P. & Aspuru-Guzik, A. *Chem. Sci.* **2015**, Advance Article.

Virtual Library of Quinones



- R=
1. $-\text{N}(\text{CH}_3)_2$
 2. $-\text{NH}_2$
 3. $-\text{OCH}_3$
 4. $-\text{OH}$
 5. $-\text{SH}$
 6. $-\text{CH}_3$
 7. $-\text{SiH}_3$
 8. $-\text{F}$
 9. $-\text{Cl}$
 10. $-\text{C}_2\text{H}_5$
 11. $-\text{CHO}$
 12. $-\text{COOCH}_3$
 13. $-\text{CF}_3$
 14. $-\text{CN}$
 15. $-\text{COOH}$
 16. $-\text{PO}_3\text{H}_2$
 17. $-\text{SO}_3\text{H}$
 18. $-\text{NO}_2$



Changwon Suh



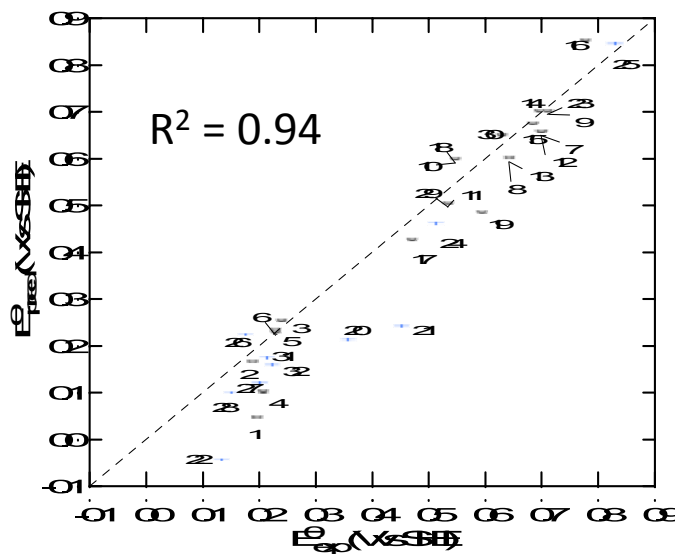
Süleyman Er



Prof. Alán Aspuru-Guzik

- unsubstituted
- single substitution
- full substitution

Screening Results

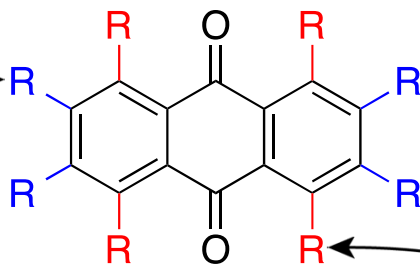


Electron-donating groups decrease E^0
NH₂, OH, NMe₂, OCH₃, SH, CH₃

Electron-withdrawing groups increase E^0
NO₂, CO₂Me, CO₂H, CN, CHO,
CF₃, SO₃H, PO₃H₂

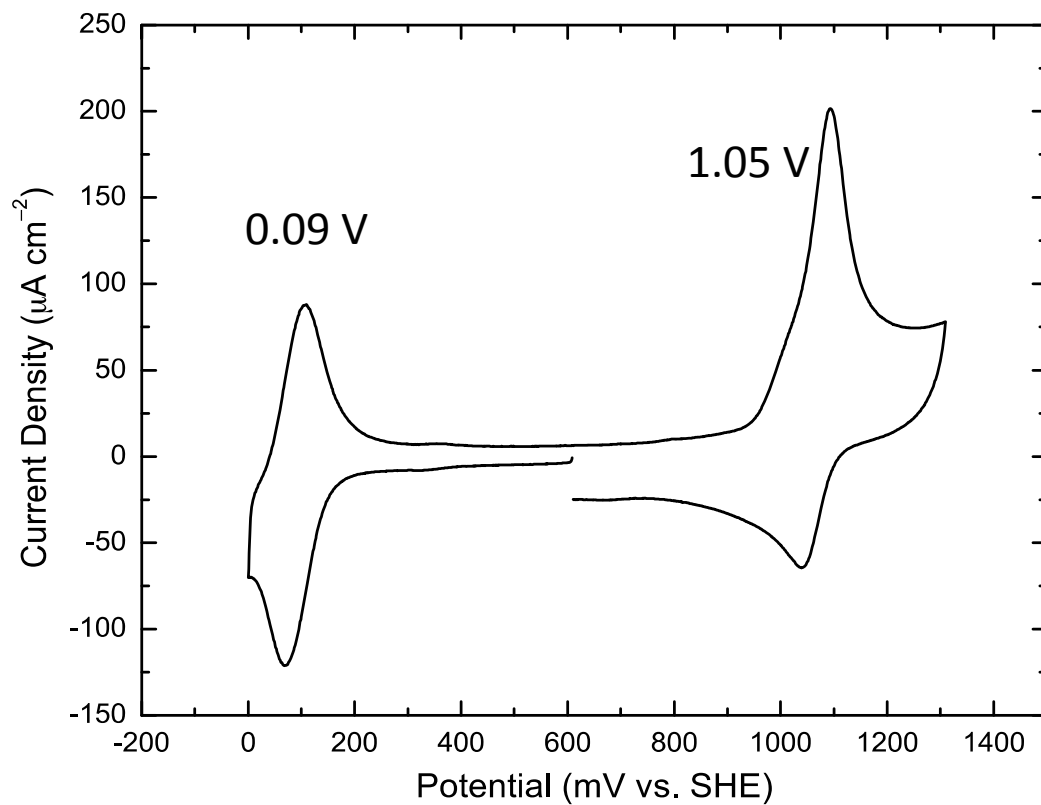
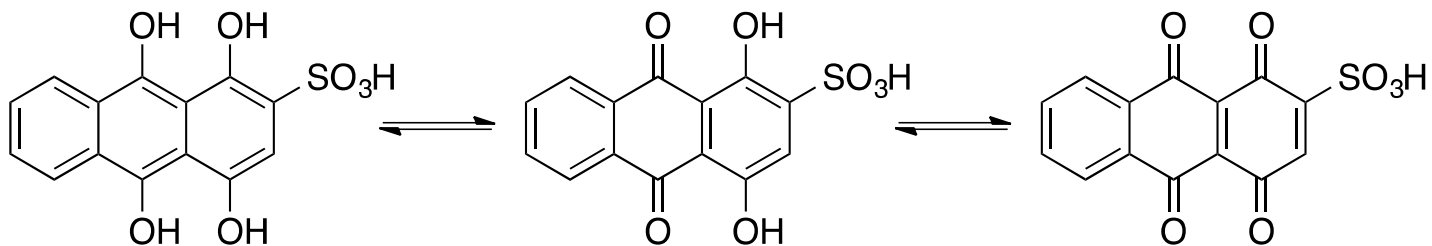
Some have surprisingly little impact:
F, Cl, SiH₃, C₂H₅

Biggest effect
on solubility

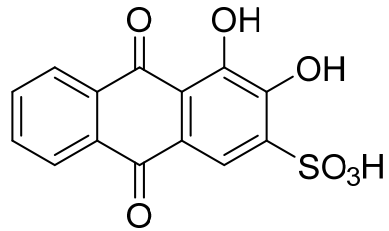


Biggest effect
on E^0

New Cell Chemistry #1: Fused Quinones



Quinone-Quinone Cell



0.1 M Quinone in H₂O

OCP = 1.03 V

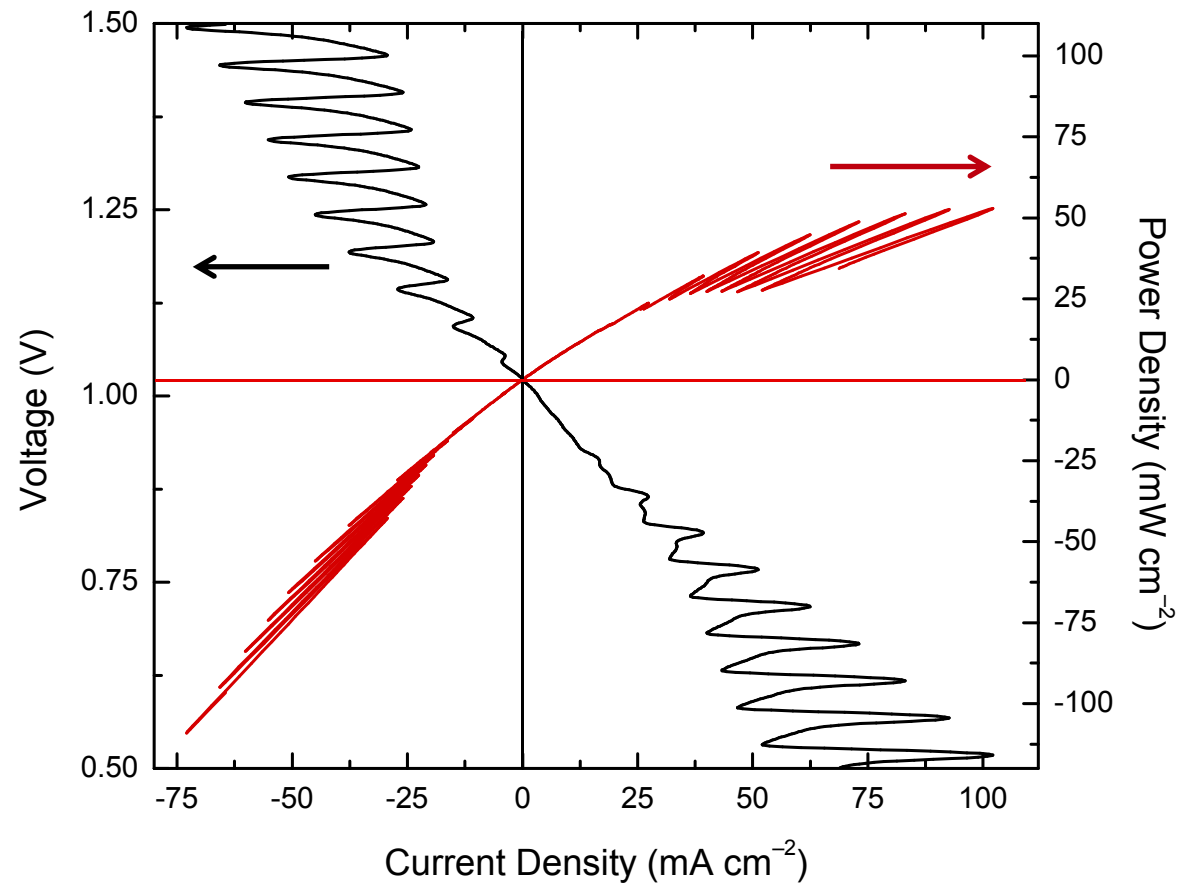
Peak Power = 50 mA cm⁻²

>99% Coulombic Efficiency

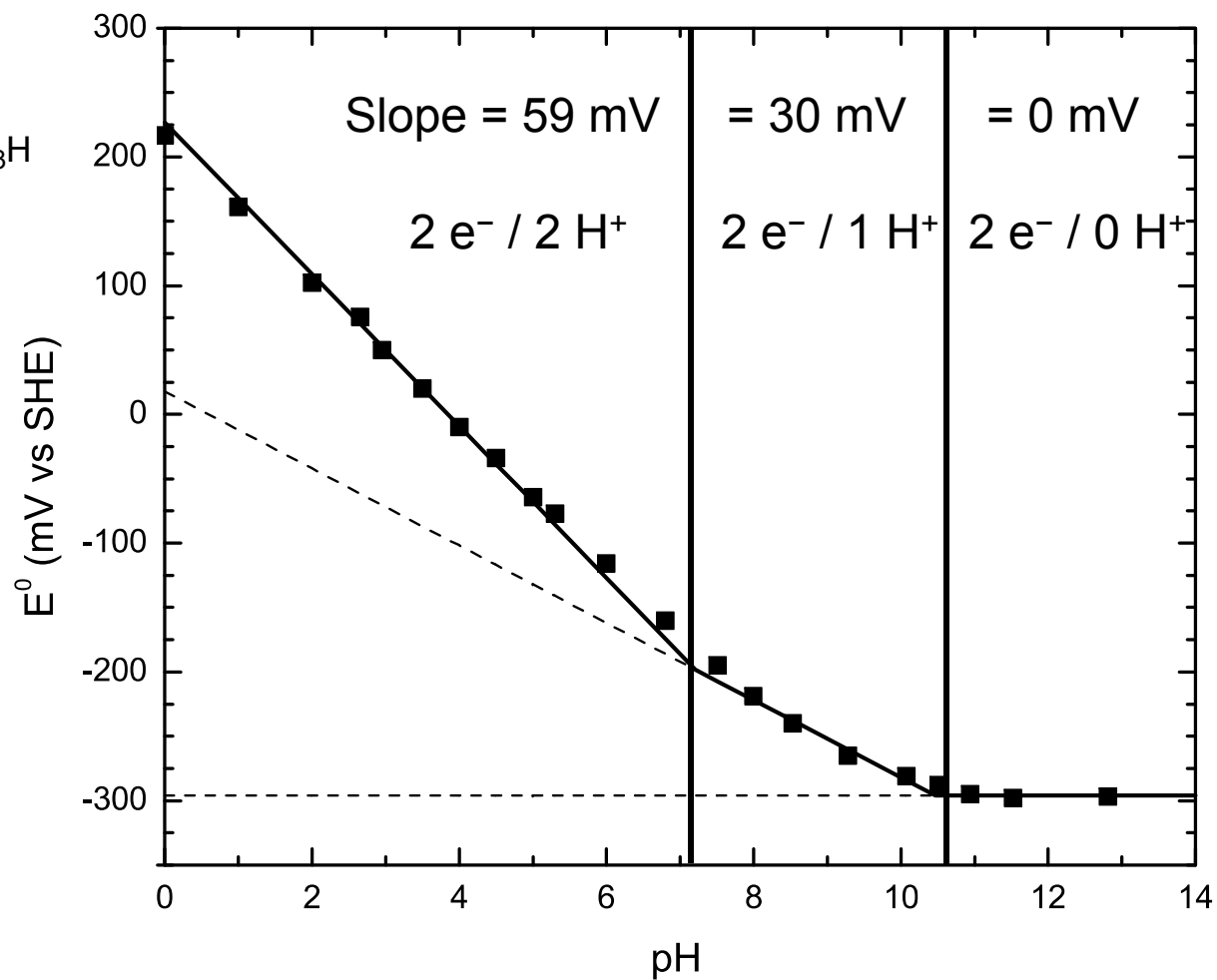
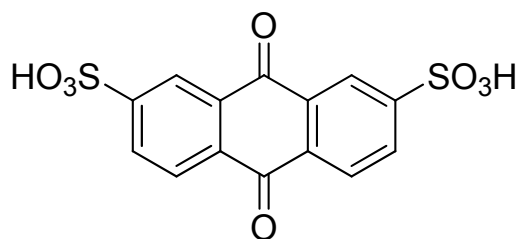
High cell resistance
due to low ion conc.



With Liuchuan Tong



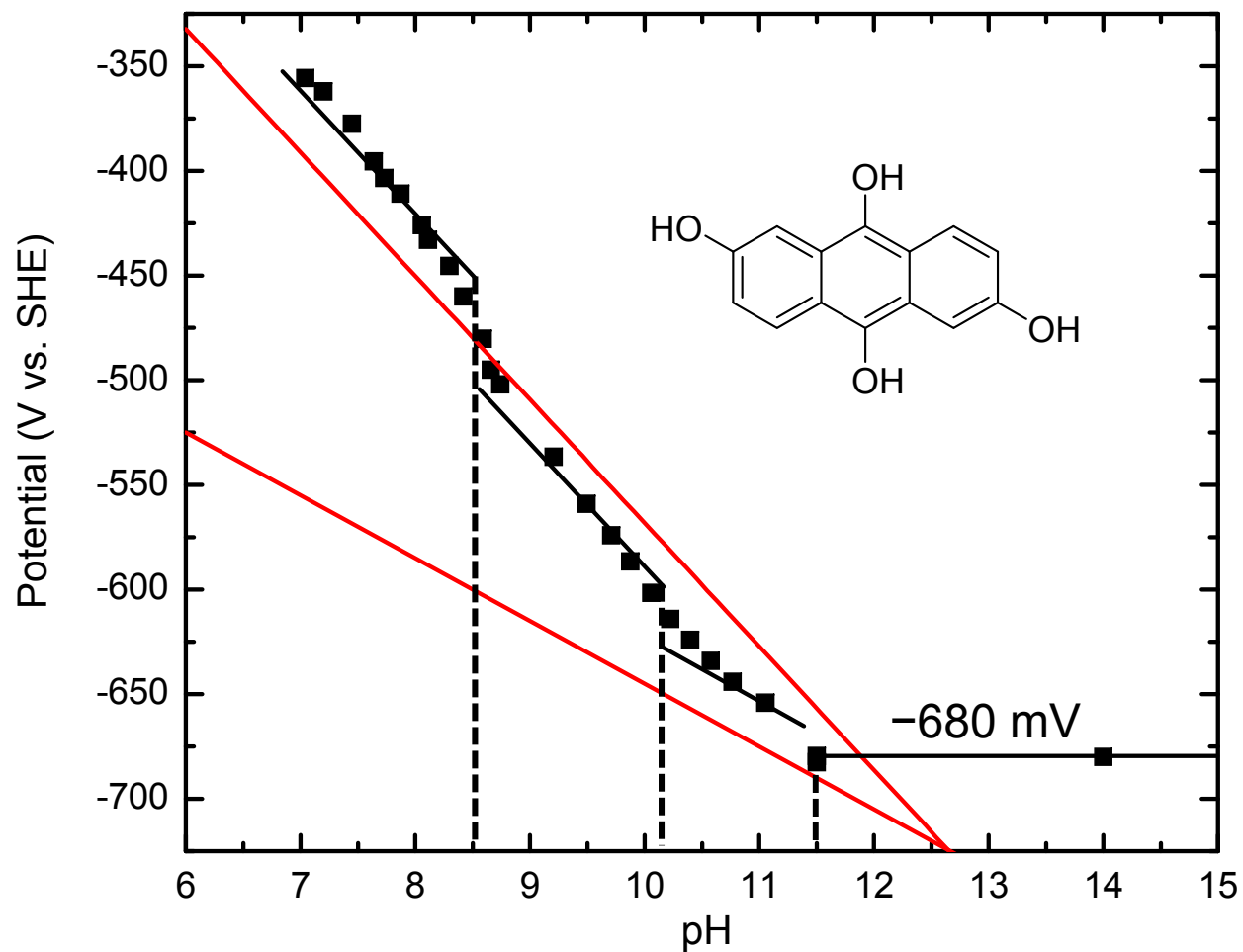
New Cell Chemistry #2: Quinones In Base



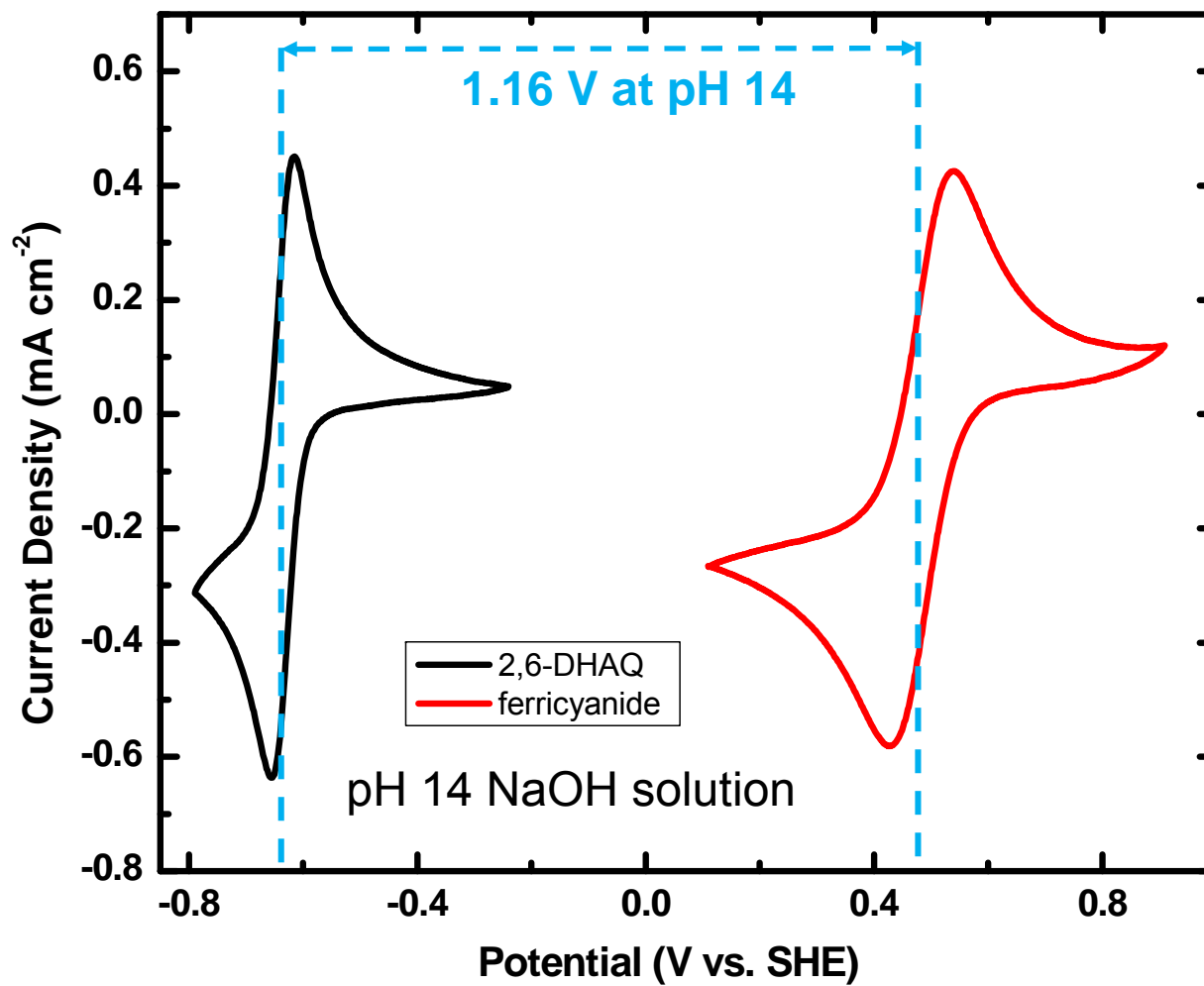
Quinones In Base



Kaixiang Lin

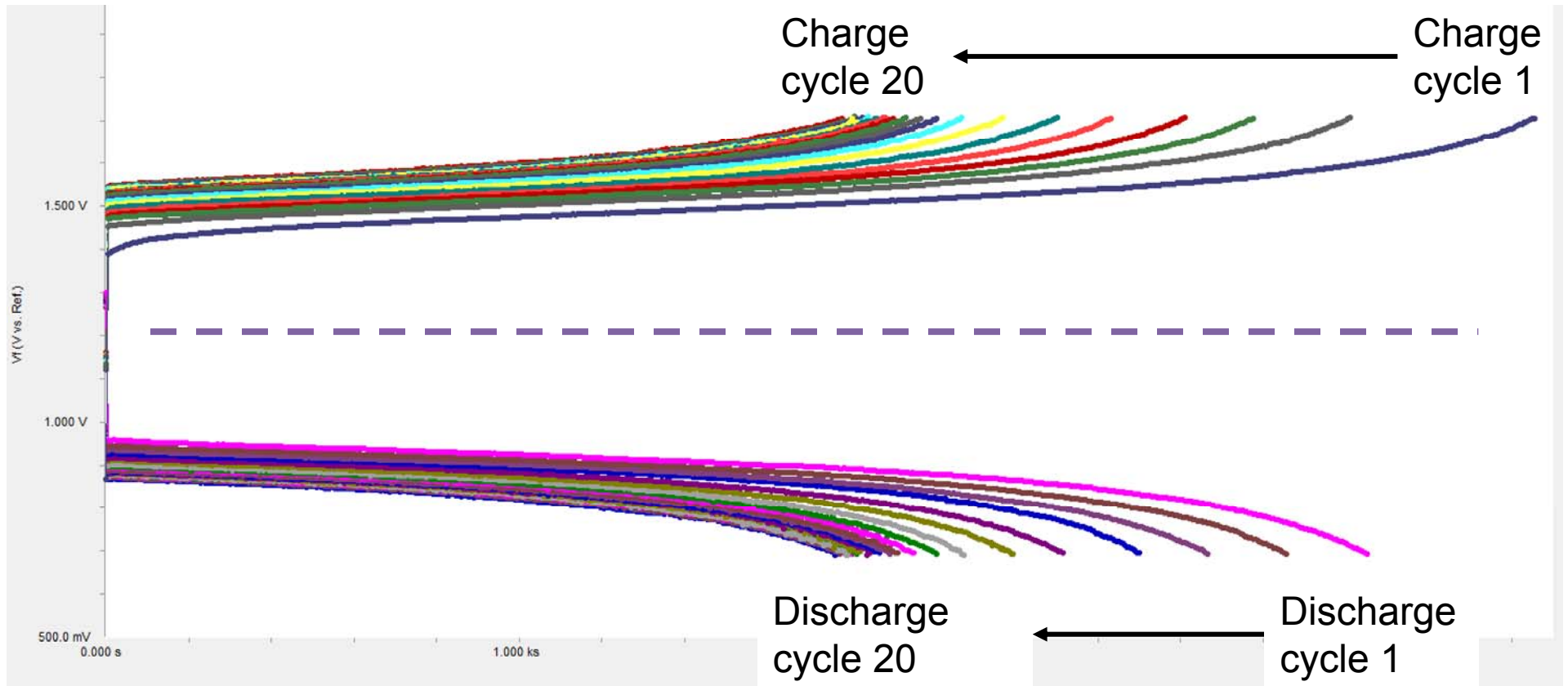


$\text{Fe}(\text{CN})_6^{4-/3-}$ For Posolyte

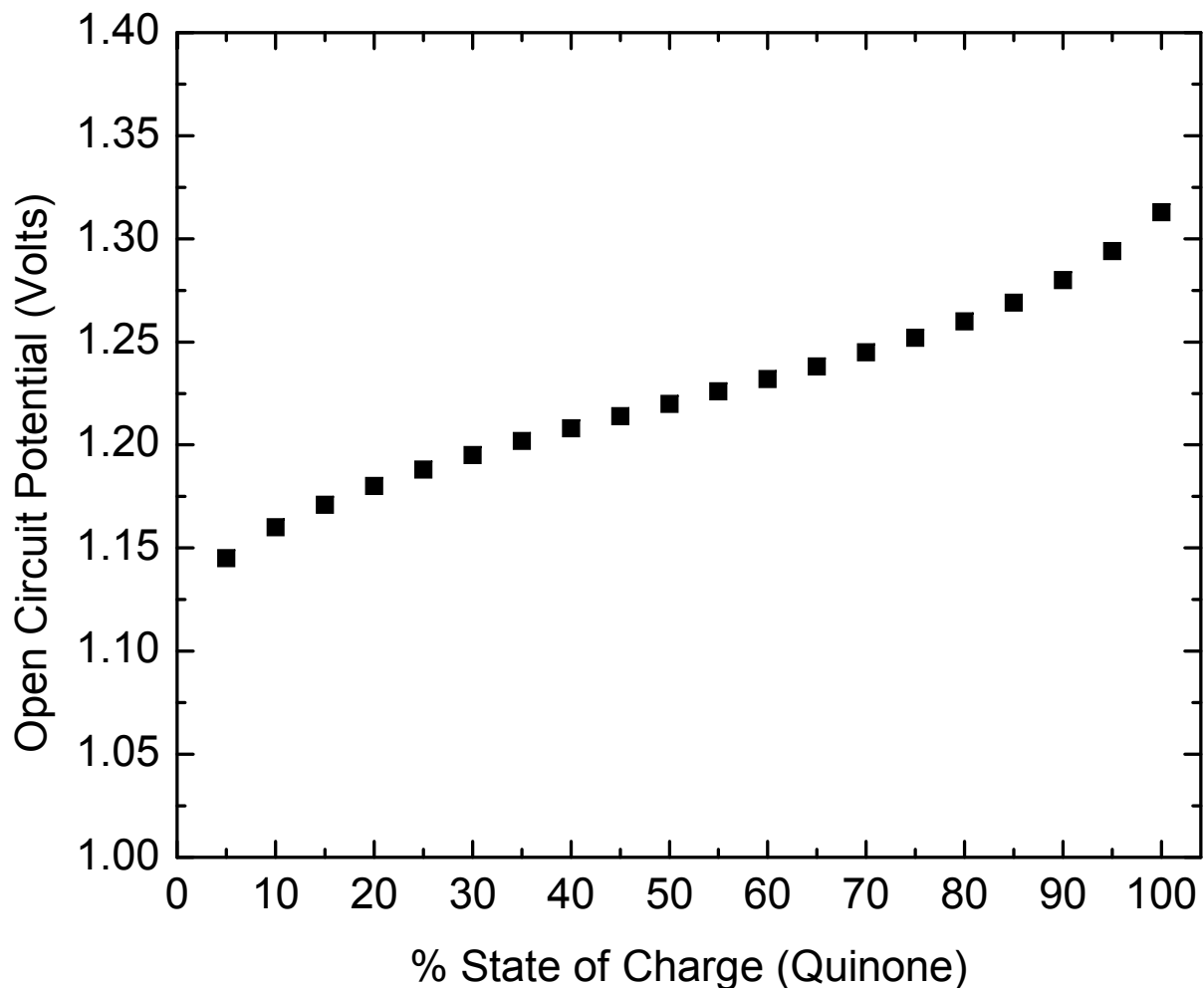


Quinone-Ferrocyanide Battery Cycling

Cycle	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Current efficiency	88.5	95.1	96.3	96.0	95.4	95.6	95.8	97.3	97.5	97.4	98.2	98.3	98.4	98.0	99.2	98.6	98.9	98.6	98.3	99.4
Capacity retention		93.6	93.4	93.8	92.5	94.9	94.5	96.8	97.3	98.0	99.0	98.7	98.9	98.7	98.3	101.1	99.4	98.8	99.4	99.5



Cell voltage can be increased by adding extra $\text{Fe}(\text{CN})_6^{3-}$

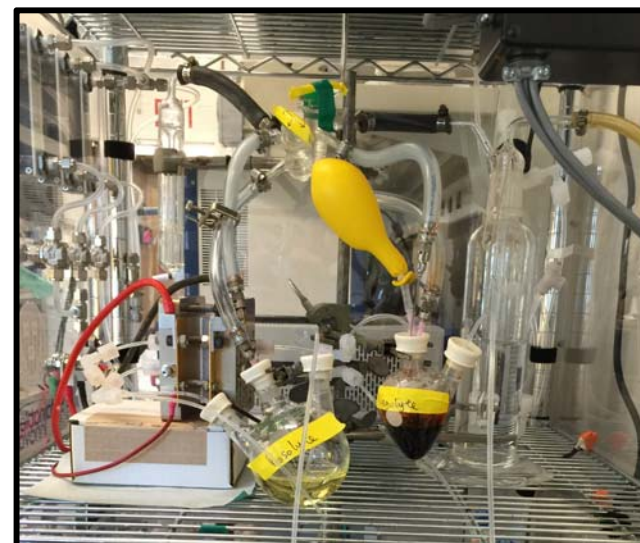


Negolyte:

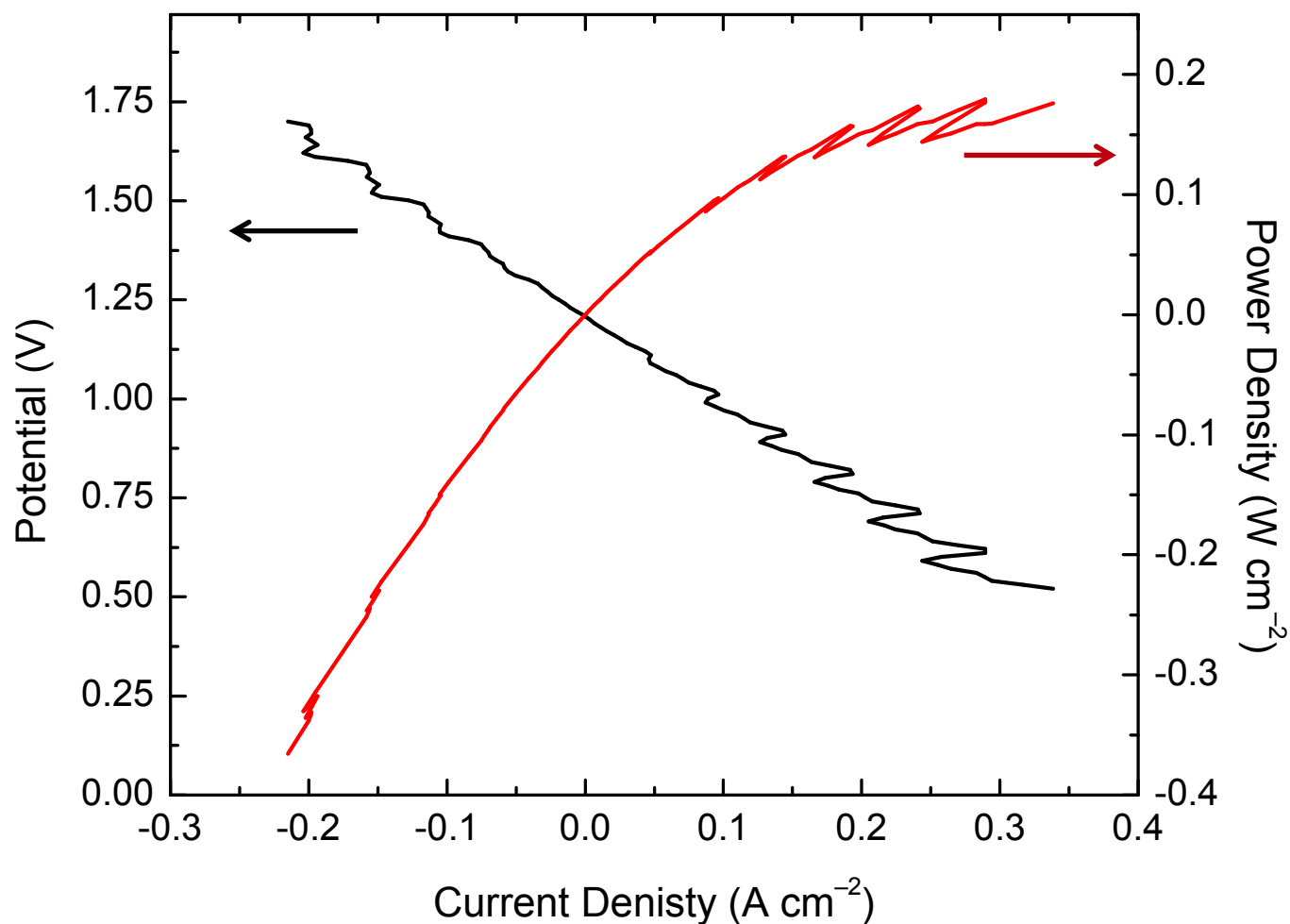
0.5 M 2,6-dihydroxy-AQ
in 3 M KOH

Posolyte (2.4x volume):

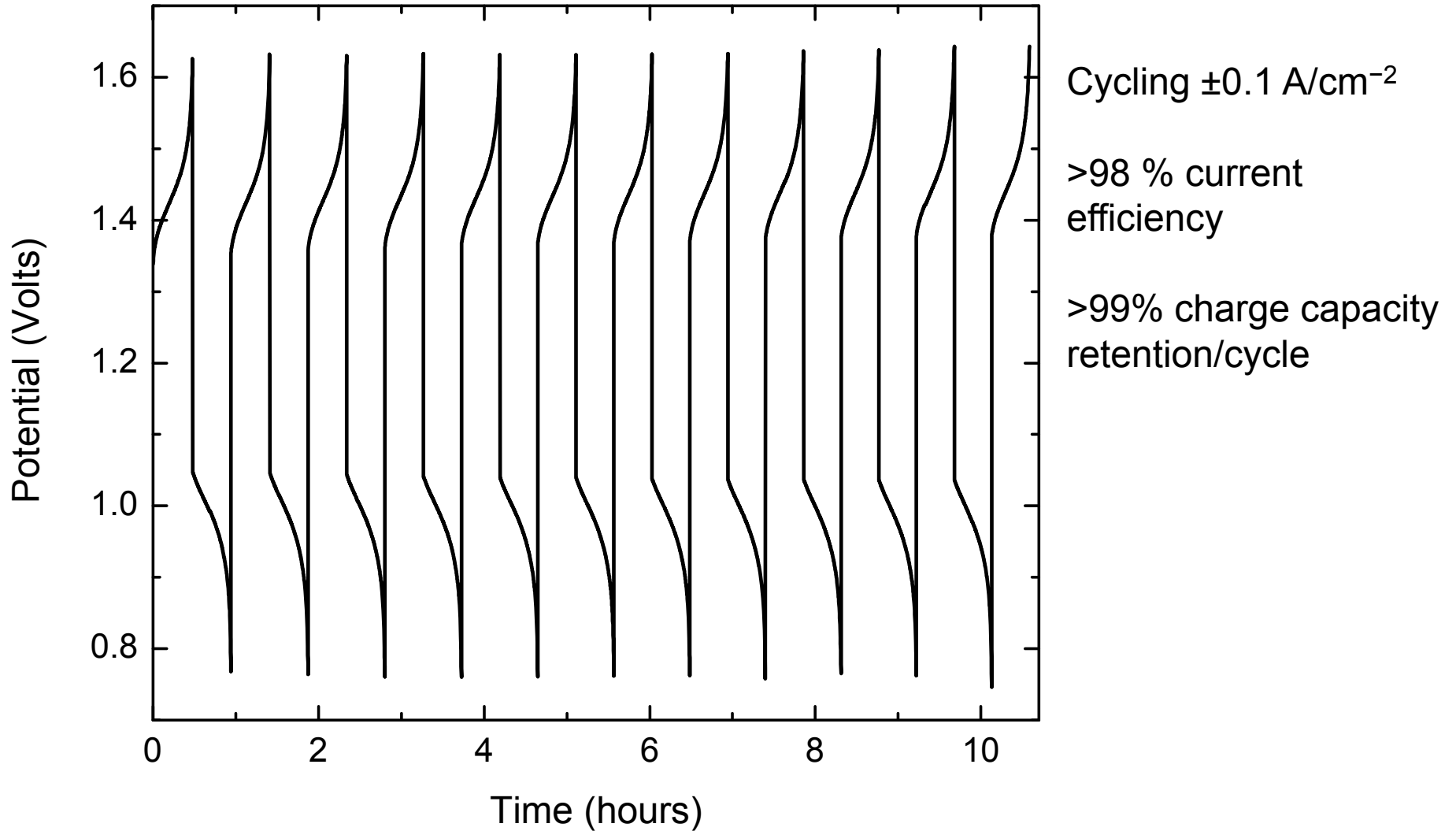
0.4 M $\text{K}_4\text{Fe}(\text{CN})_6$
0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$
in 1 M KOH



200 mW cm⁻² performance despite higher cell resistance



Stable to repeated cycling



Summary

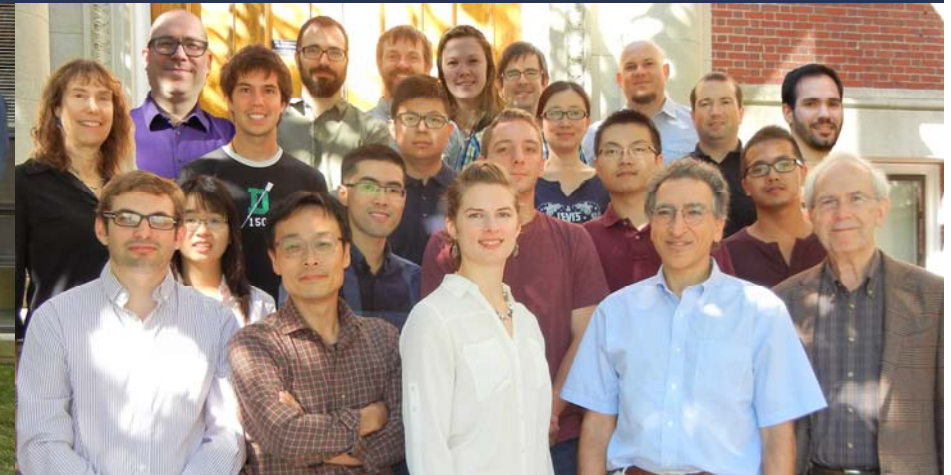
Three Quinone Battery Chemistries

1. Quinone-Bromine Cell (0.95 V, 1 W cm⁻²)
2. All-Quinone Cell (1.03 V, 0.05 W cm⁻²)
3. Quinone-Ferrocyanide Cell (1.22 V, 0.2 W cm⁻²)

- ✧ High-Throughput Computational Screening
- ✧ State of Charge Monitoring by Spectroscopy
- ✧ Flow Field Optimization with Fluorescence
- ✧ New Quinone Materials



Acknowledgements



Michael Aziz:

Brian Huskinson, Michael Gerhardt, Qing Chen, Andrew Wong
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Xudong Chen, Lauren Hartle, Liuchuan Tong, Kaixiang Lin, David Hardee
Ryan Duncan, Rachel Burton, Cooper Galvin, Sidharth Chand

Alán Aspuru-Guzik:

Changwon Suh, Süleyman Er, Edward Pyzer Knapp, Rafael Bombarelli,
Jennifer Wei, Tyler Van Valkenburg

William Hogan (HKS)

Sustainable Innovations: Trent Molter, Phil Baker

