Bromine-free quinone flow battery chemistries

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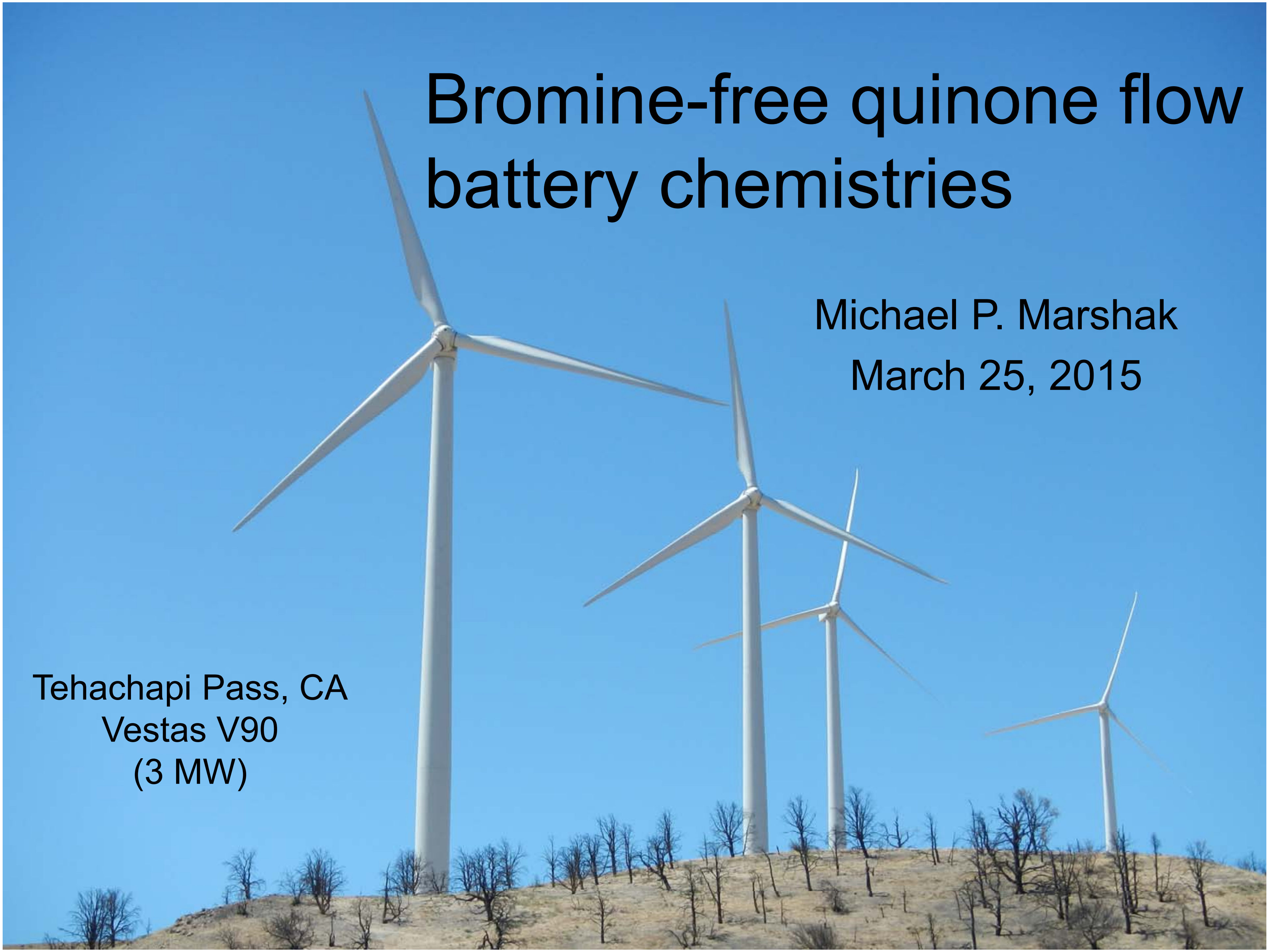
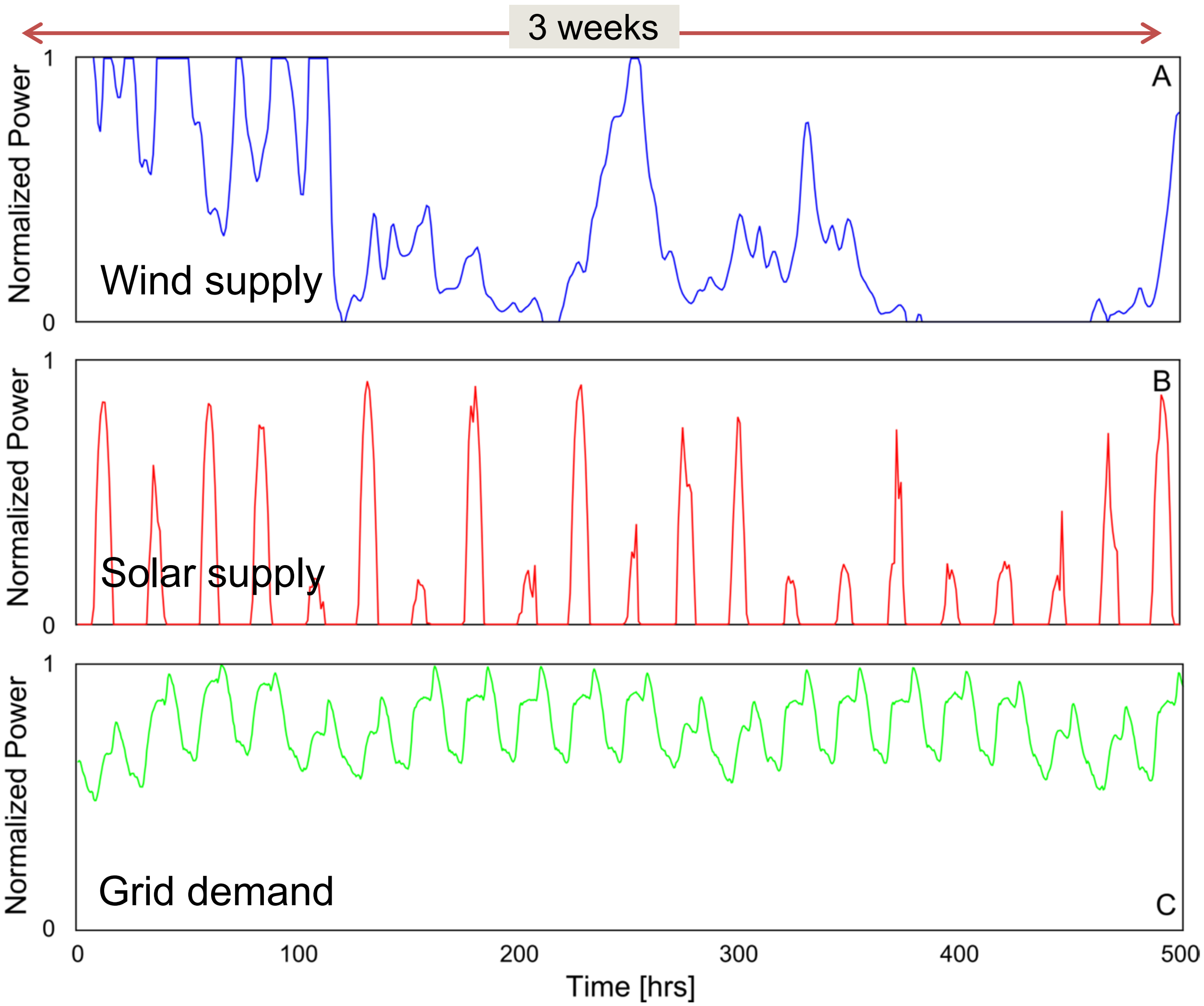
Michael P. Marshak

March 25, 2015



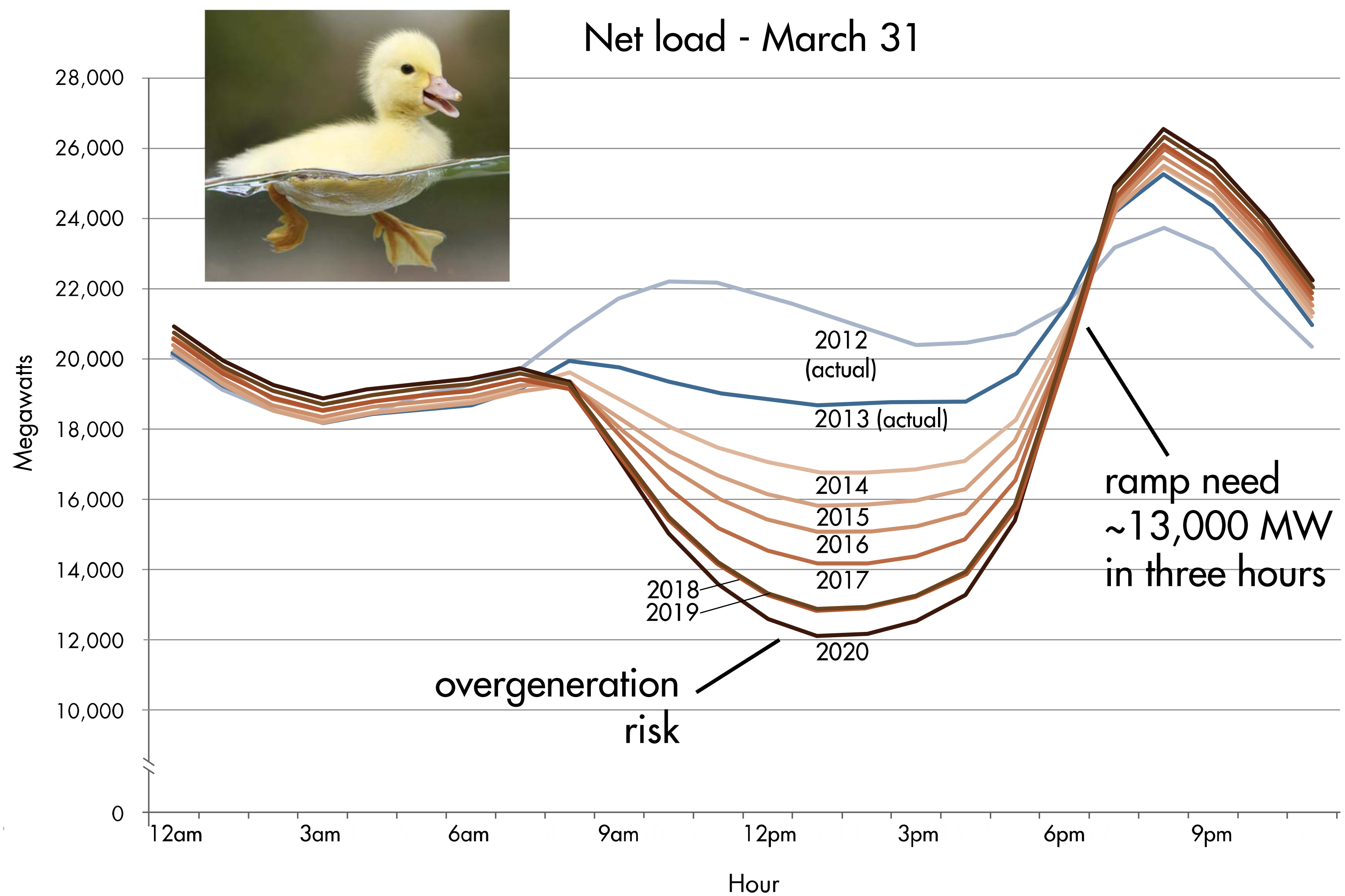
Tehachapi Pass, CA
Vestas V90
(3 MW)

Renewable Energy is Intermittent



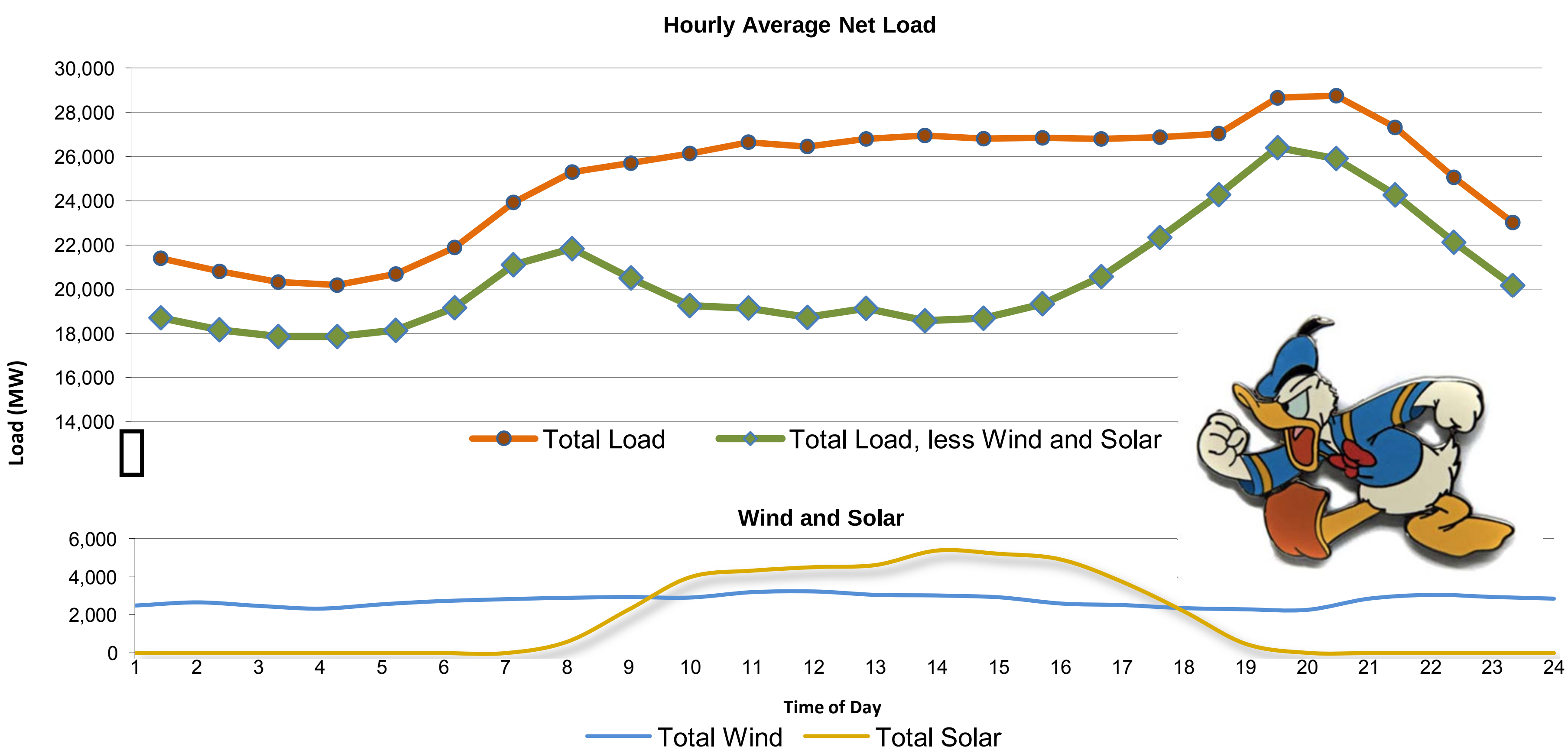
Rugolo, J. and Aziz, M. J. *Energy Environ. Sci.* 5, 7151 (2012)

California's Supply-Demand "Duck Curve"



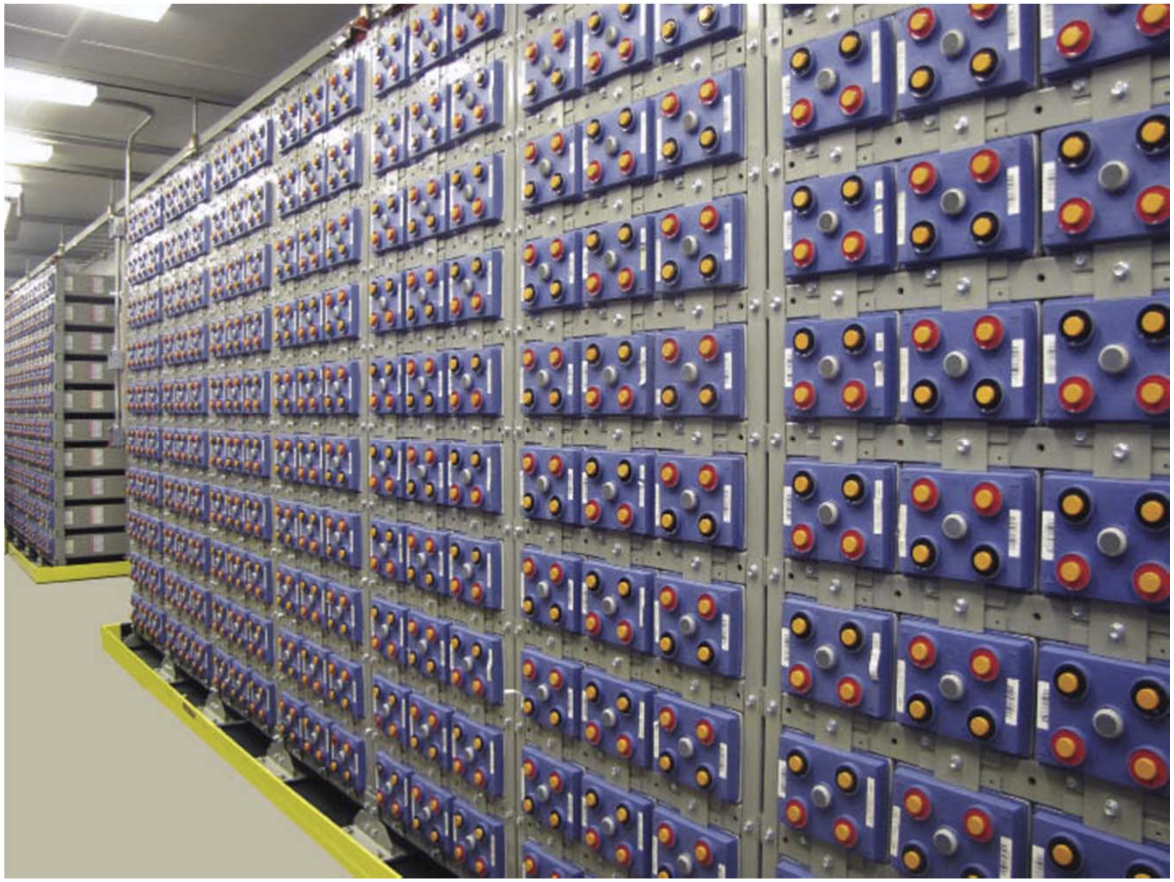
CAISO Renewables Fast Facts

California Supply-Demand Mar 24, 2015



CAISO Daily Renewables Watch www.caiso.com/green/renewableswatch.html

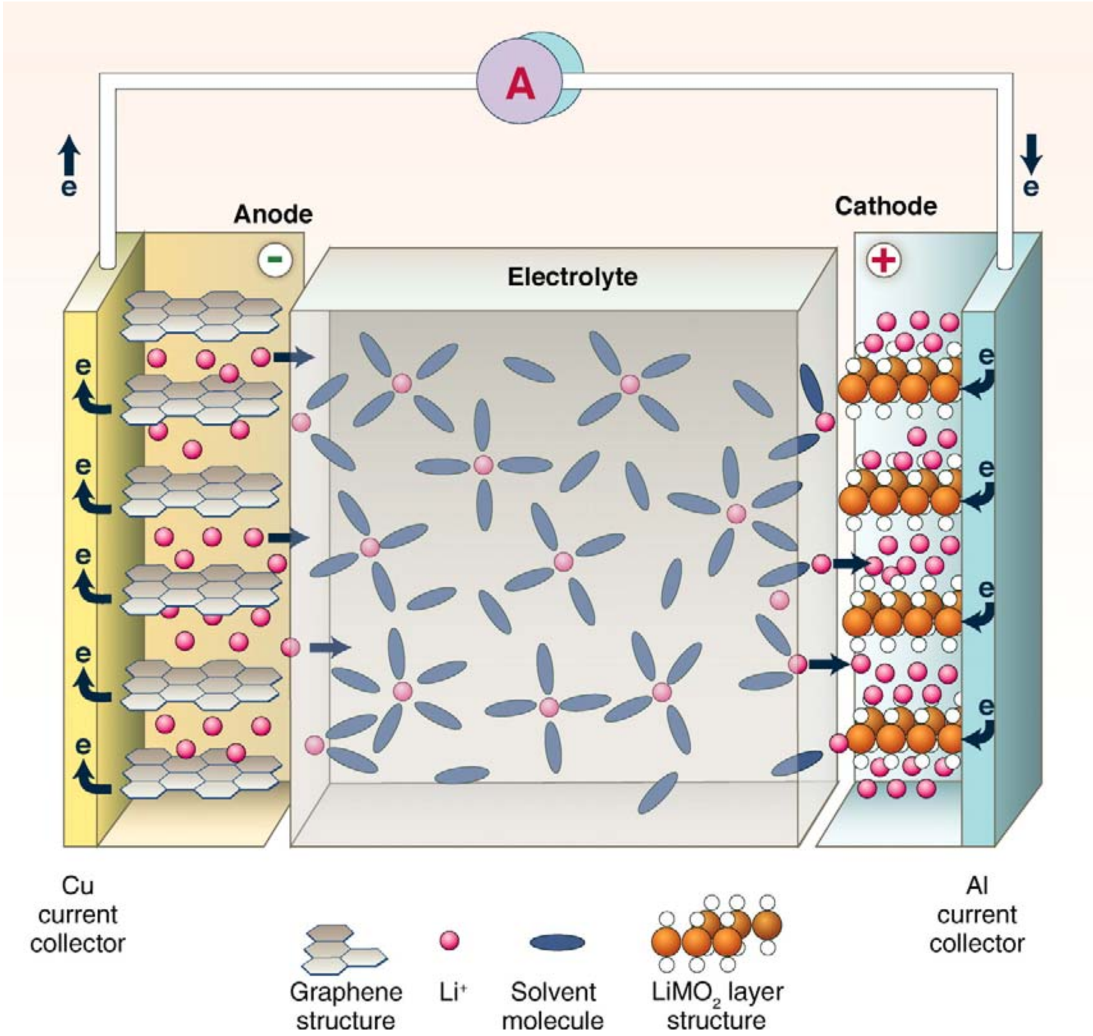
1 MWh Battery Bank



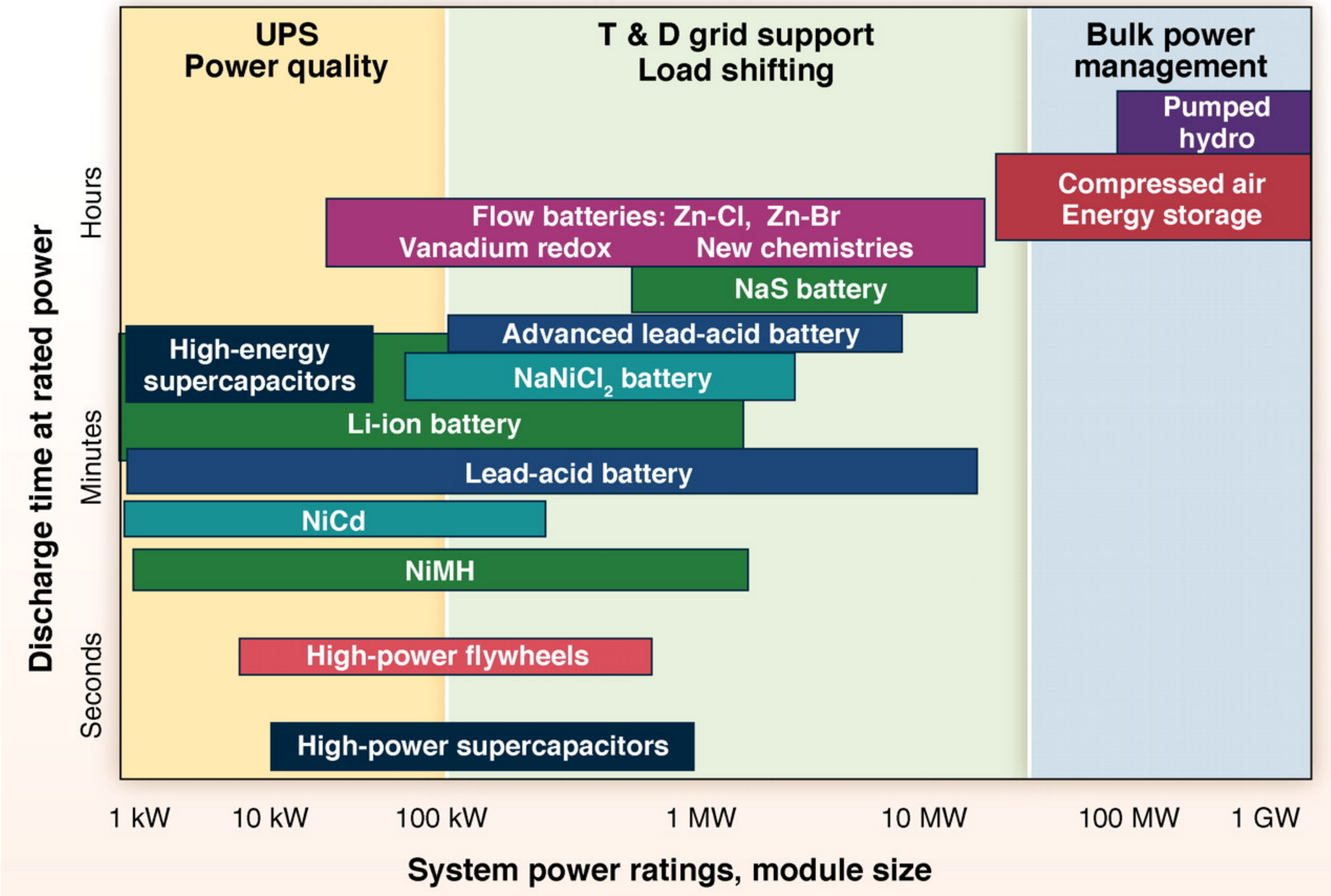
Lead Acid + NiCd

EnerSys, South Burlington, Vermont

The Power:Energy Ratio is Fixed for Solid Electrode Batteries

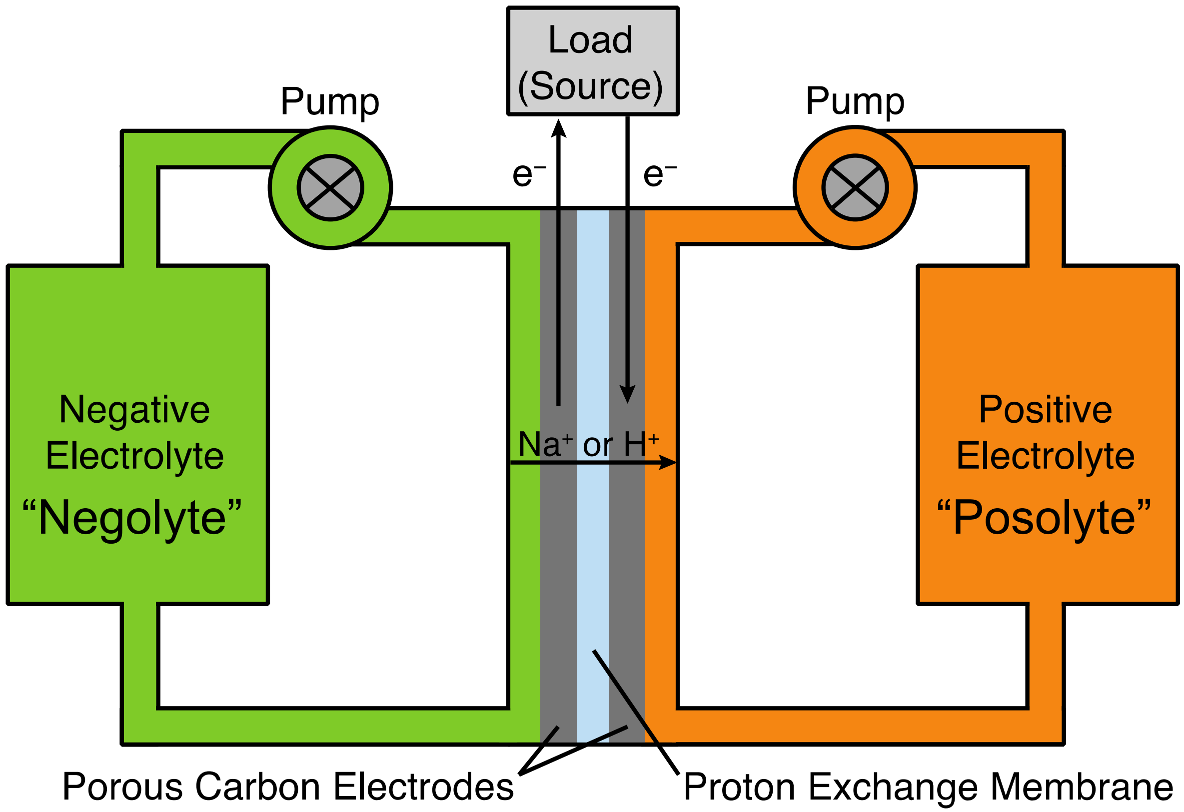


B Dunn et al. *Science* **2011**, *334*, 928-935.



UPS
Power quality
T & D grid support
Load shifting
Bulk power
management
Pumped
hydro
Compressed air
Energy storage
Flow batteries: Zn-Cl, Zn-Br
Vanadium redox
New chemistries
NaS battery
Advanced lead-acid battery
High-energy
supercapacitors
NaNiCl2 battery
Li-ion battery
Lead-acid battery
NiCd
NiMH
High-power flywheels
High-power supercapacitors
Discharge time at rated power
Seconds
Minutes
Hours
1 kW
10 kW
100 kW
1 MW
10 MW
100 MW
1 GW
System power ratings, module size

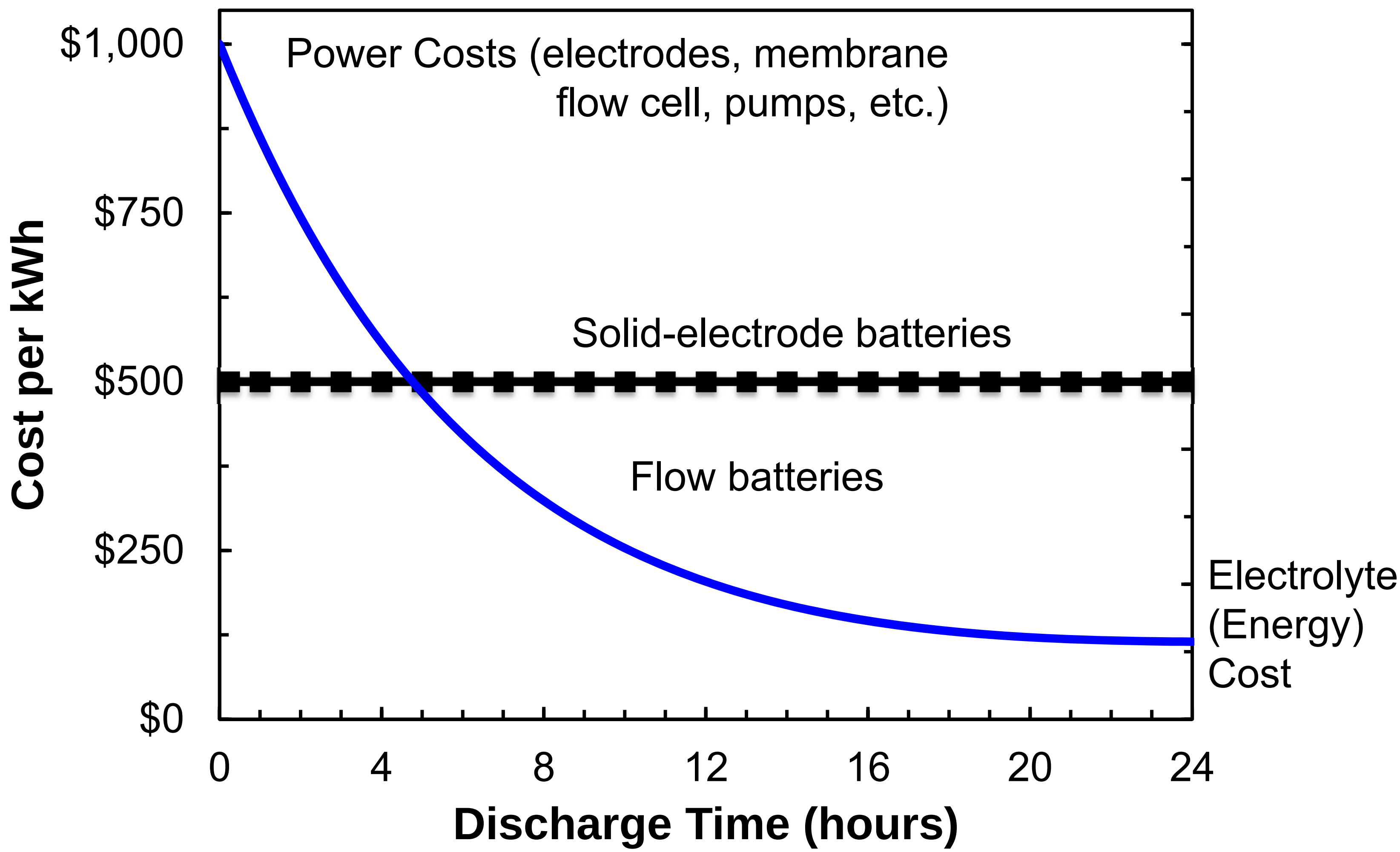
Redox Flow Batteries



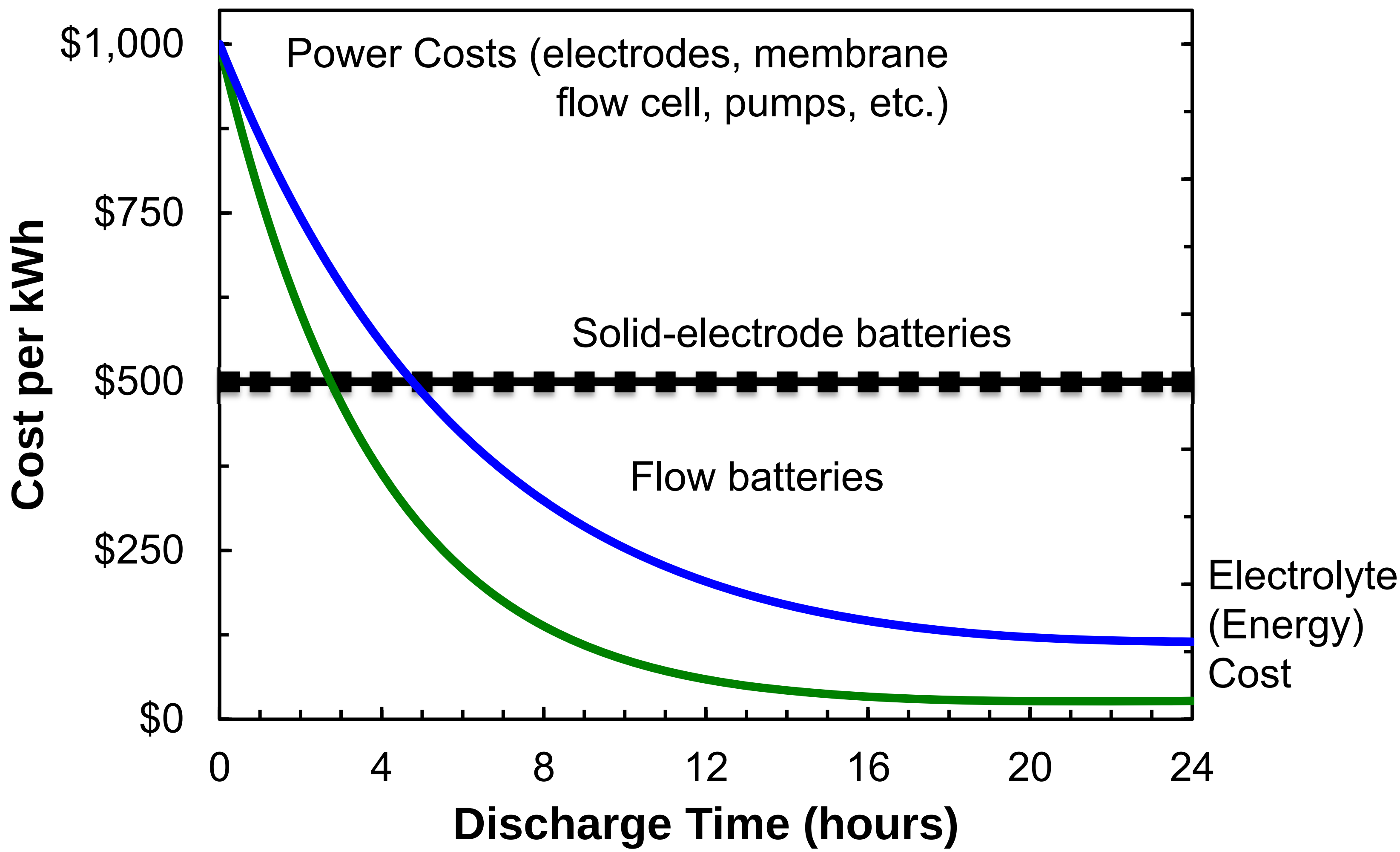
- Operates like a regenerative fuel cell
- All-liquid electrolyte
- Can independently scale power (electrode area) and energy (electrolyte volume)

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.

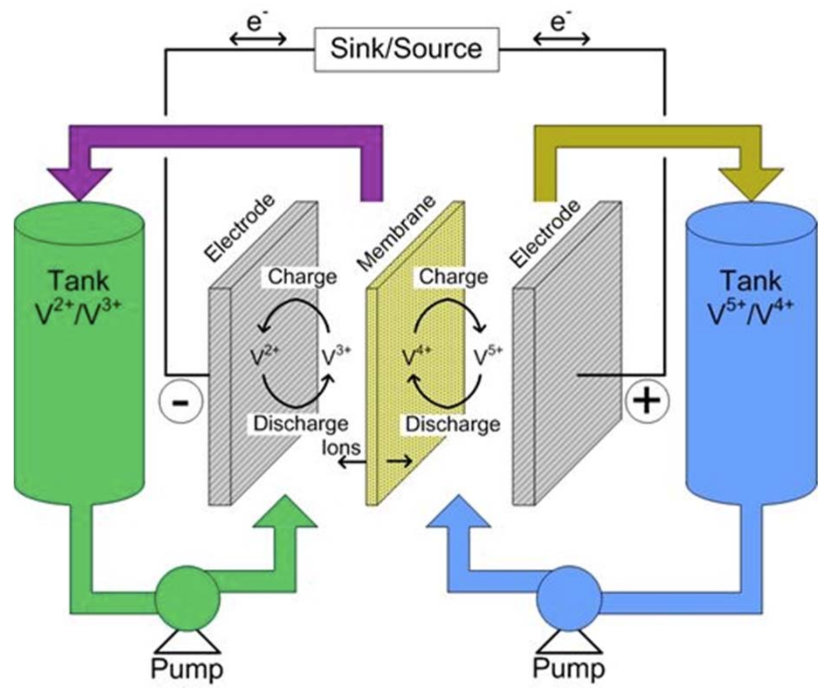
Bromine-Polysulfide Battery

Regenesys 12 MW, Little Barford, UK

Bromine-Polysulfide	$S_4^{2-} + 2\,e^- \rightleftharpoons 2\,S_2^{2-}$ $Br_2 + 2\,e^- \rightleftharpoons 2\,Br^-$	−0.4 V 1.09 V	1.5 V

All-Vanadium Flow Battery

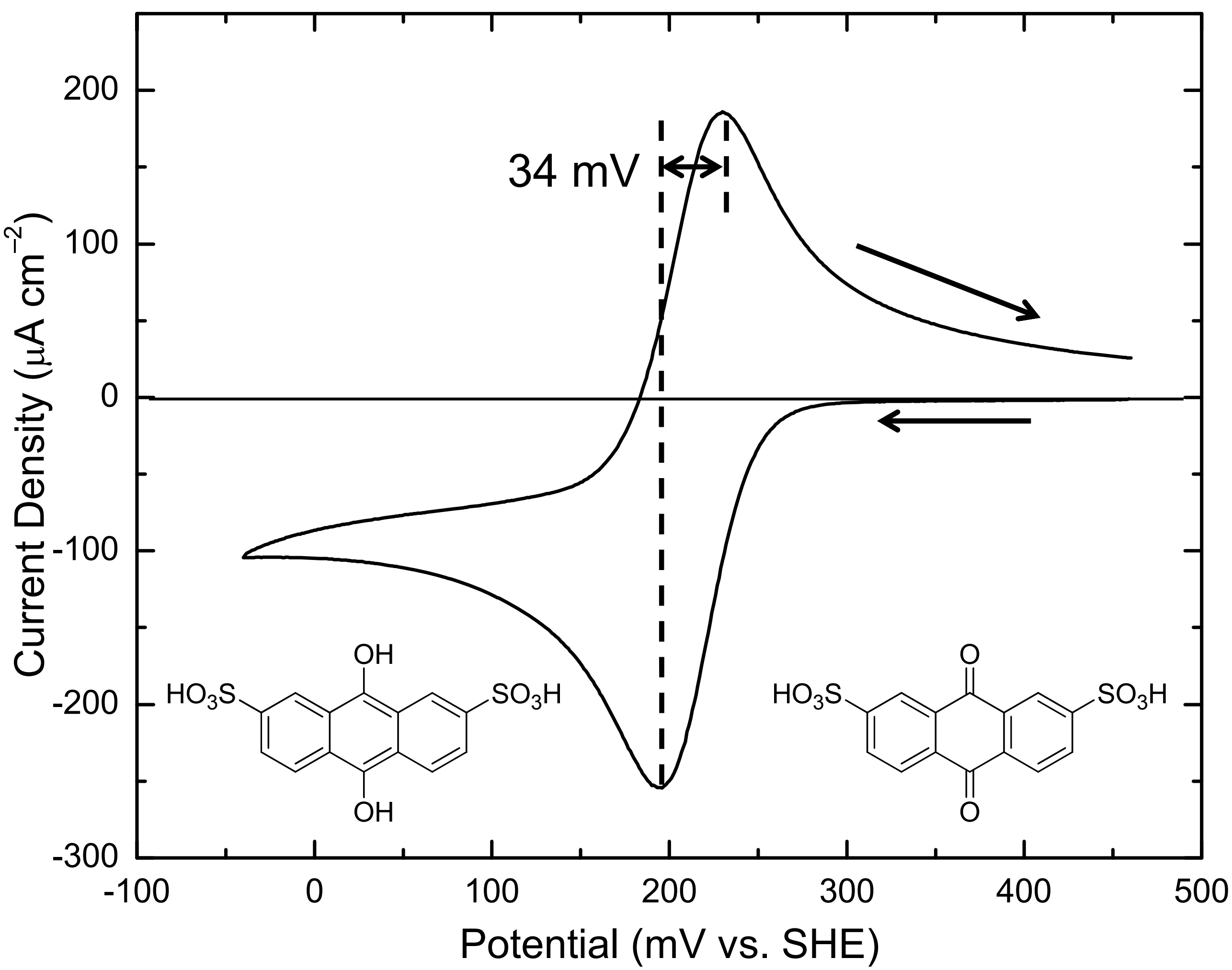
Source: Prudent Energy Corporation



All-Vanadium	$V^{3+} + e^- \rightleftharpoons V^{2+}$ $VO_2^+ + e^- \rightleftharpoons VO^{2+}$	1.4 V

Anthraquinone-2,7-Disulfonic Acid

$AQDSH_2 \rightleftharpoons AQDS + 2\,H^+ + 2\,e^-$

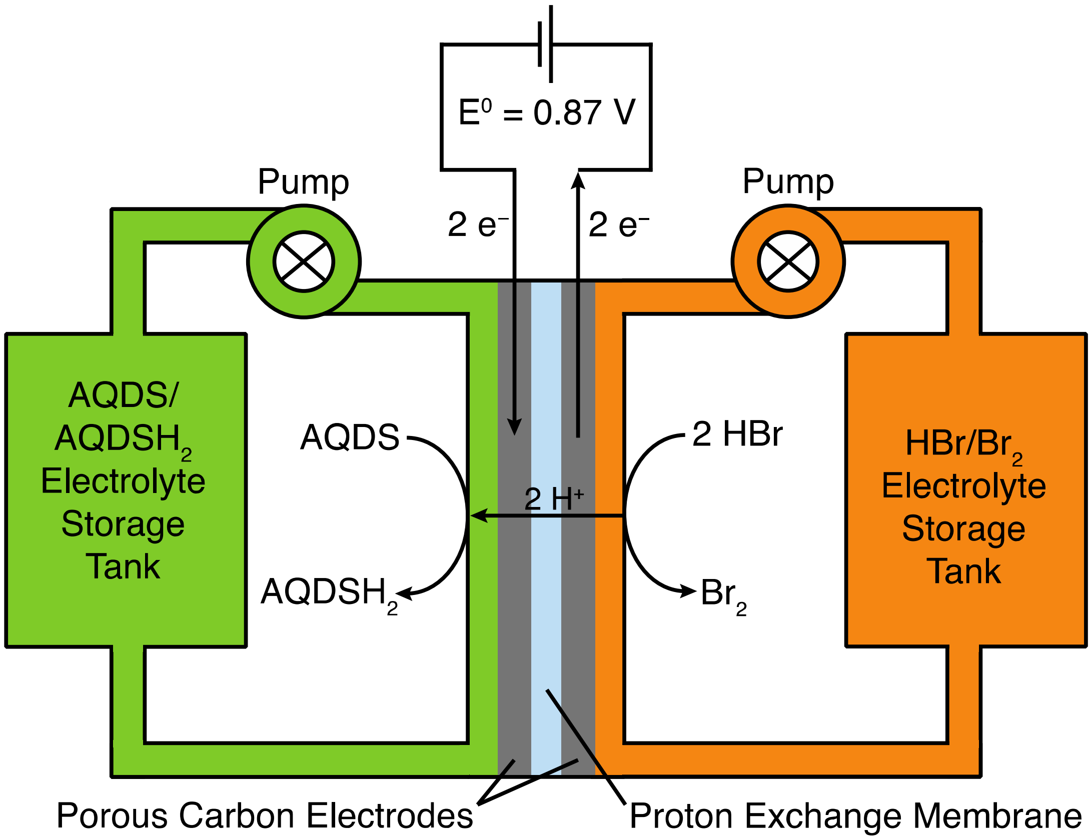


The E^0 for this process is 0.213 V vs. SHE

1 mM AQDS in 1 M H_2SO_4
Carbon Working Electrode

The Quinone-Bromine Flow Battery

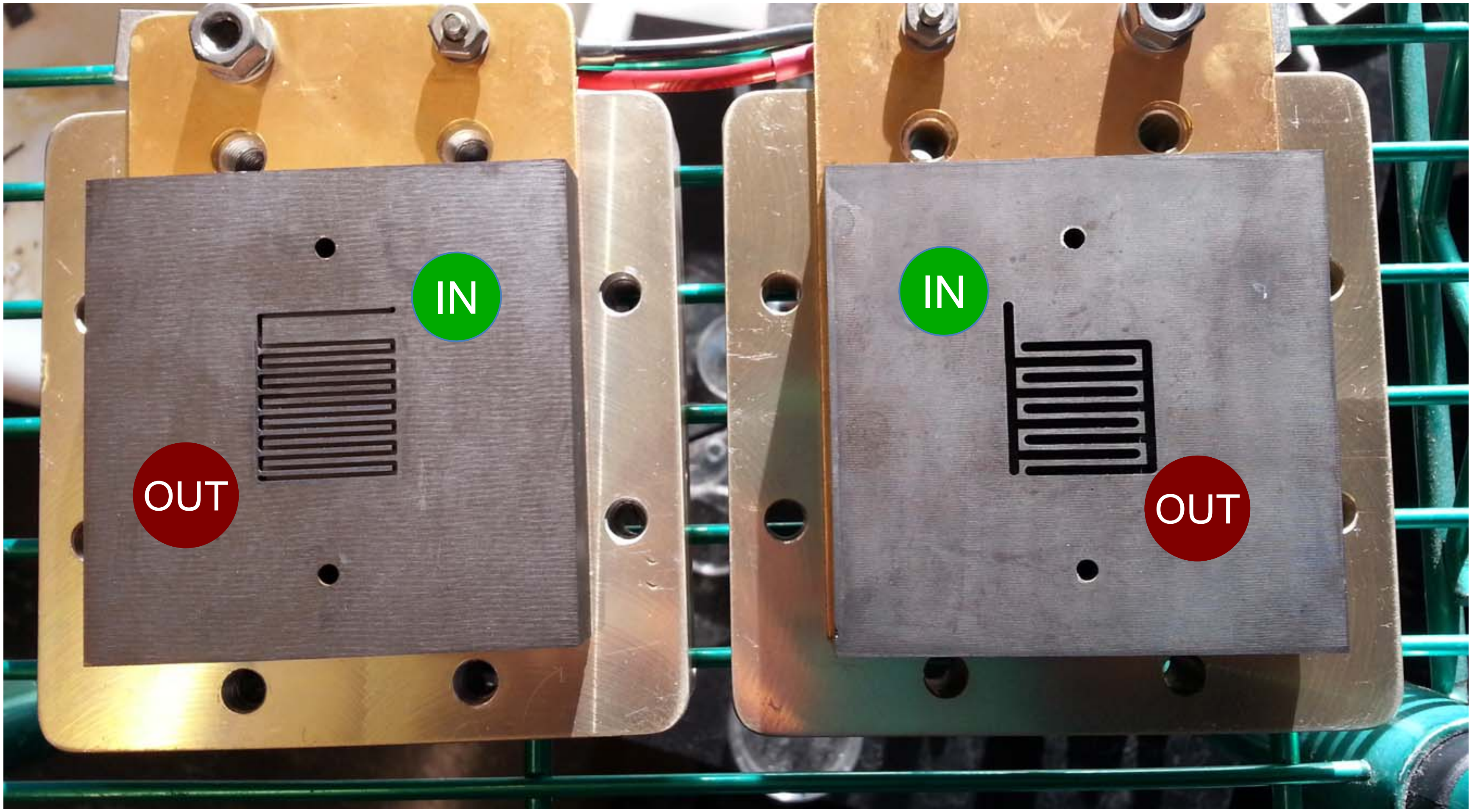
Brian Huskinson



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.

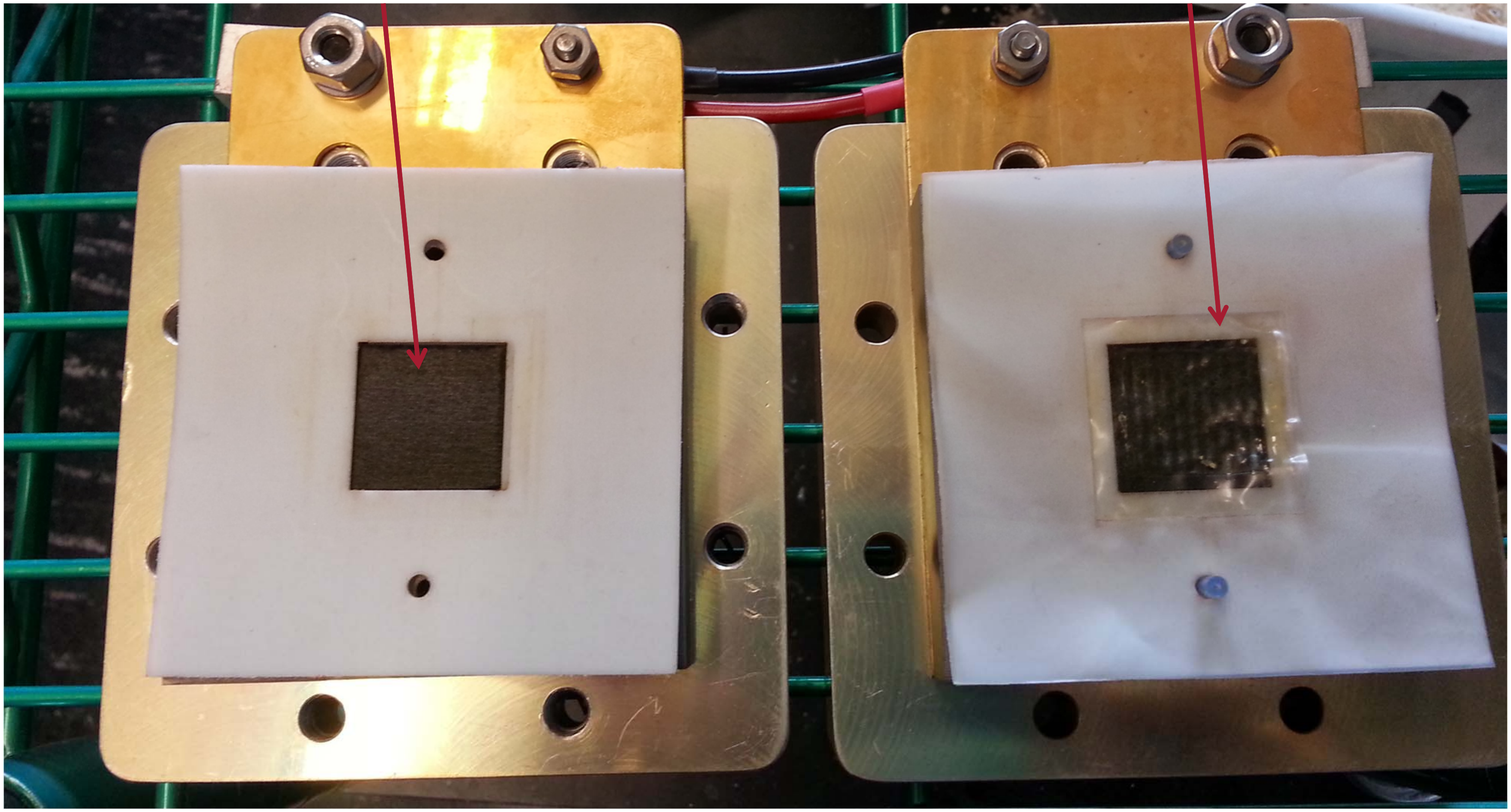
Flow Field Design

Serpentine Interdigitated

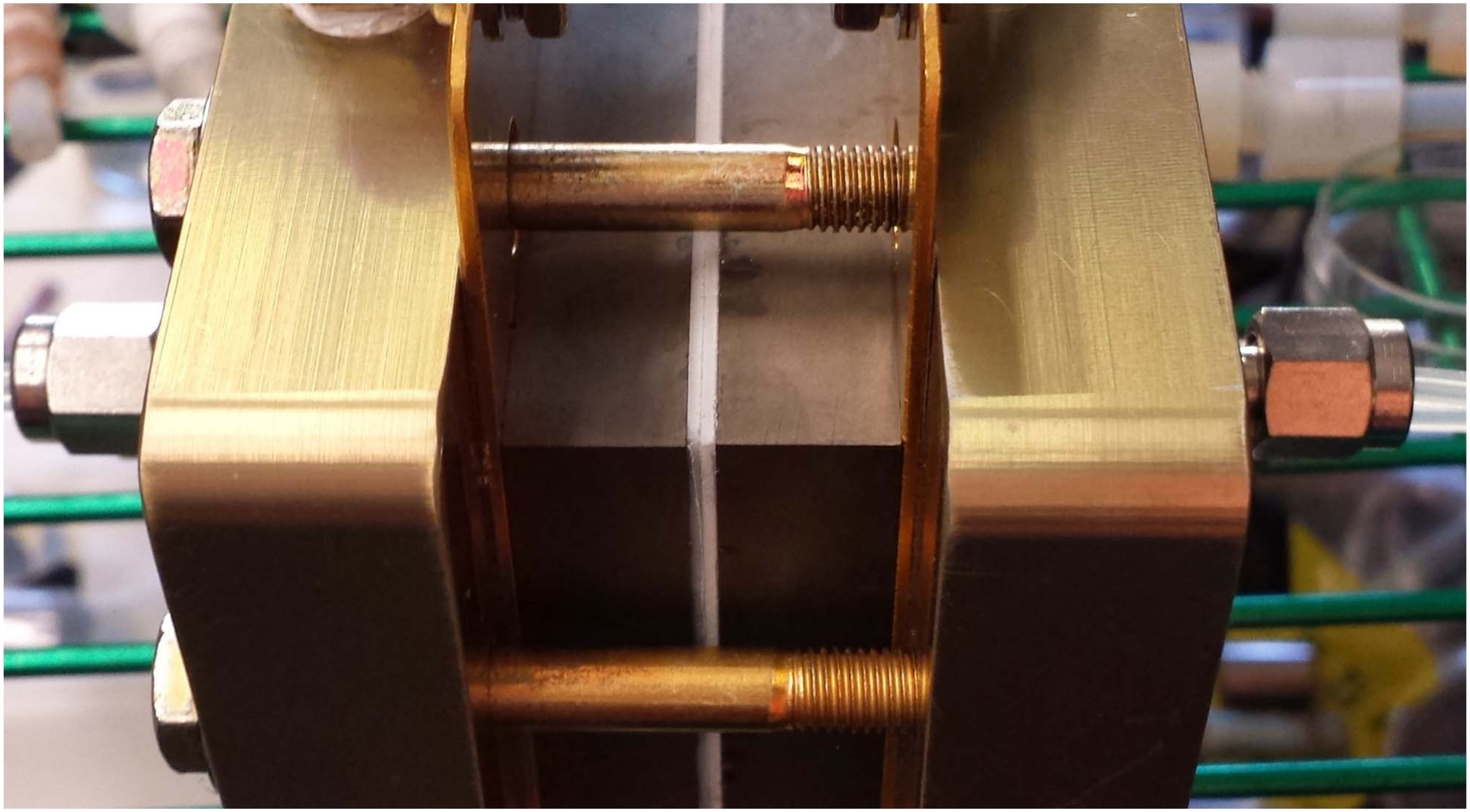


Membrane Electrode Assembly (MEA)

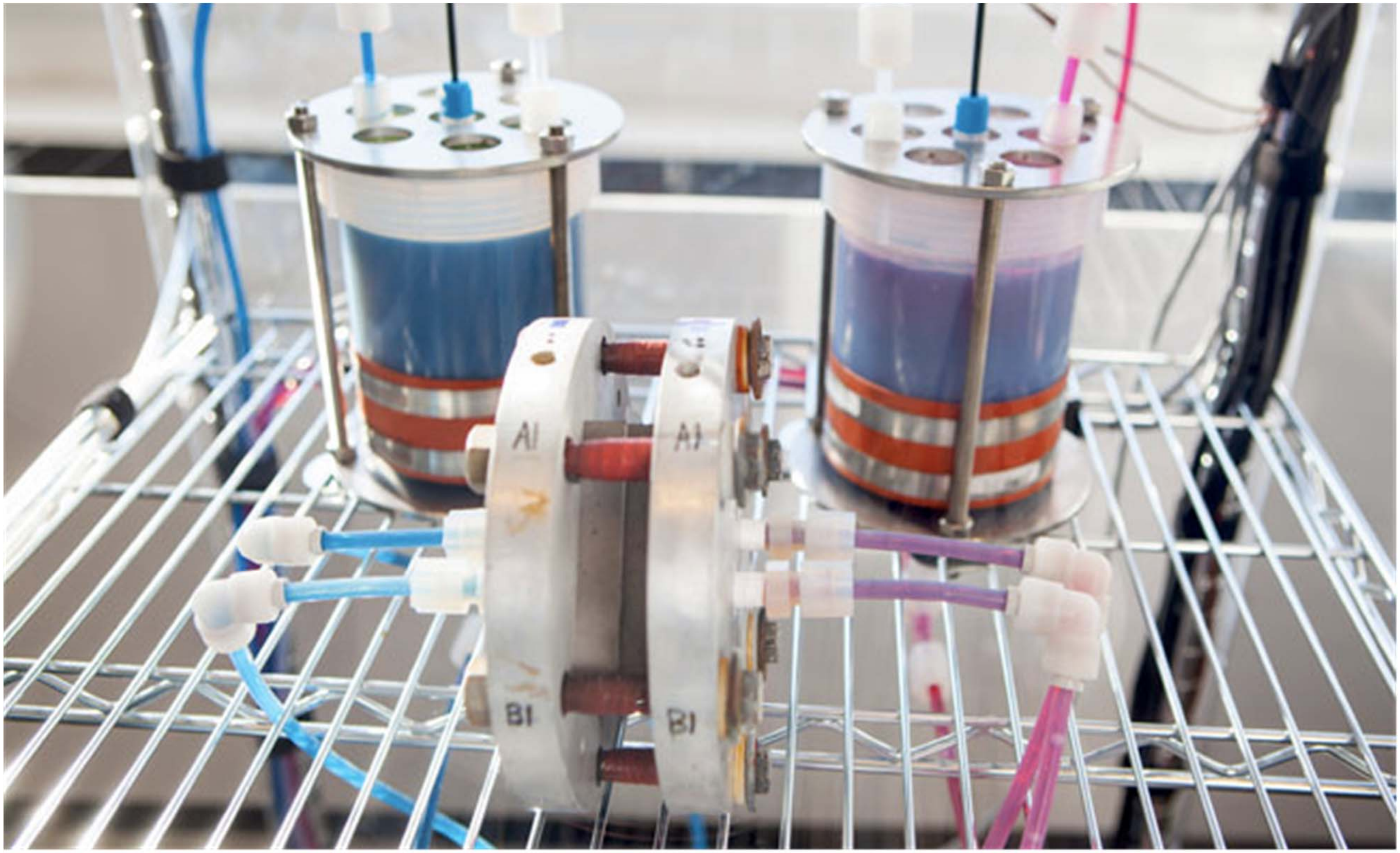
Carbon Paper Nafion Membrane



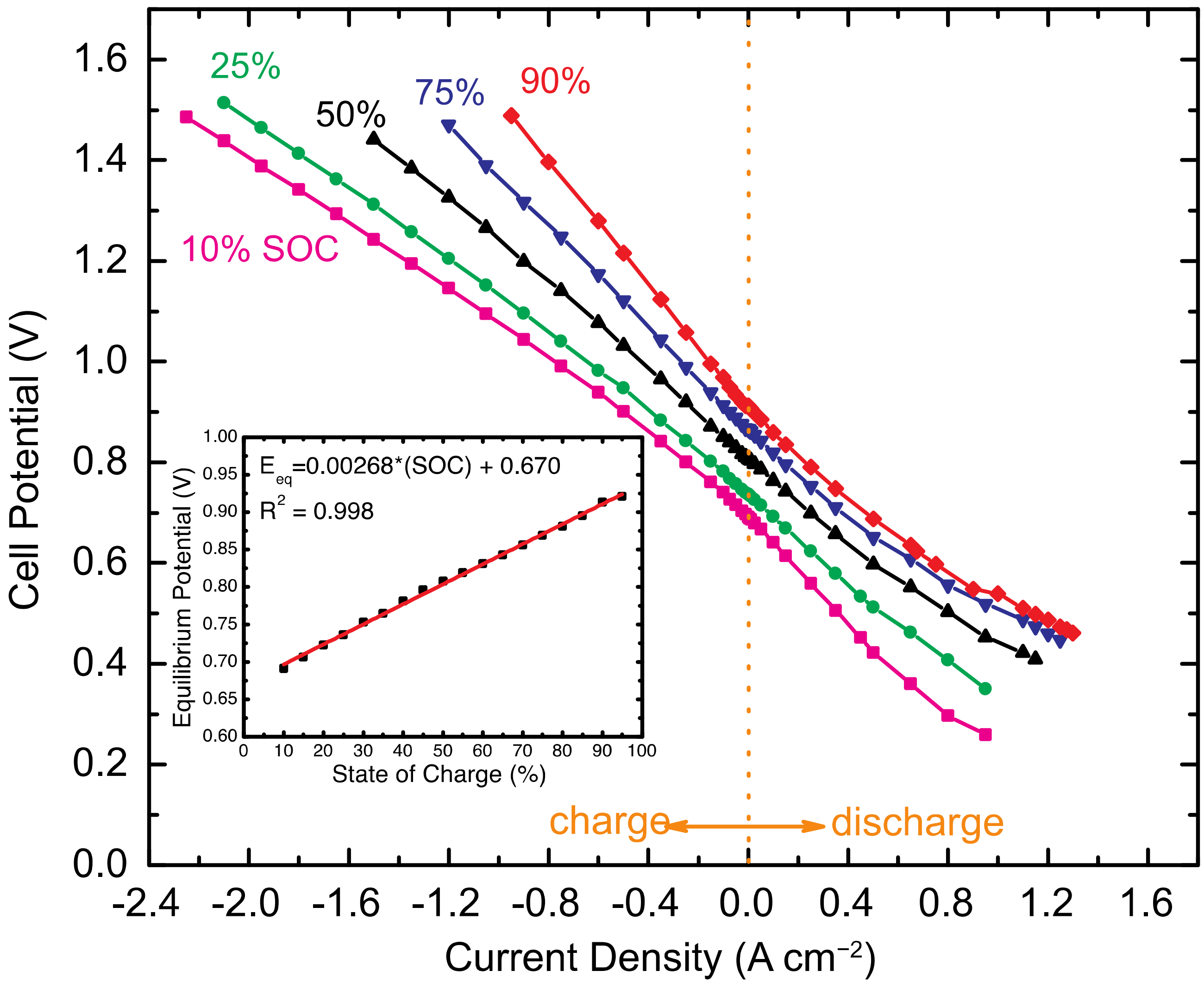
Assembled Cell



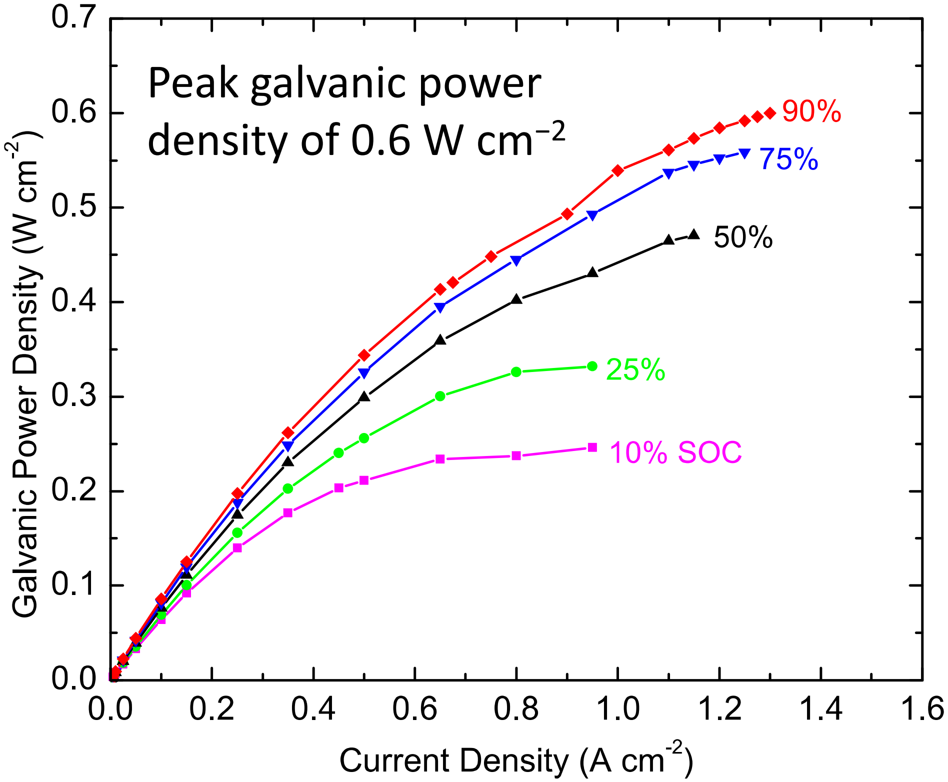
Flow Cell In Operation

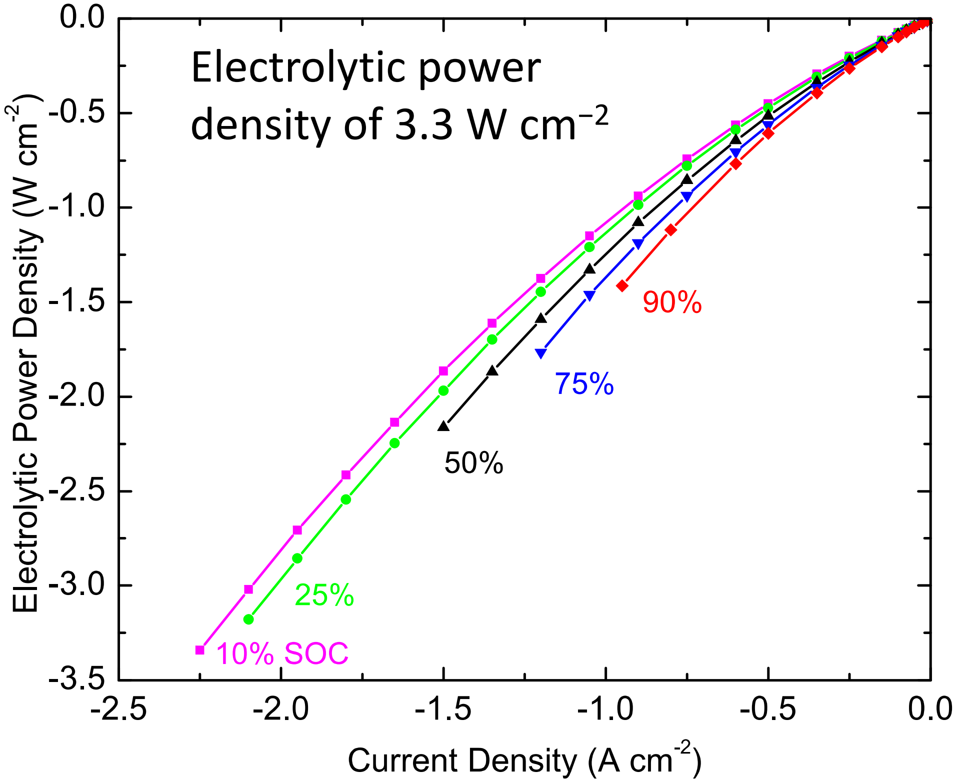


Cell Performance

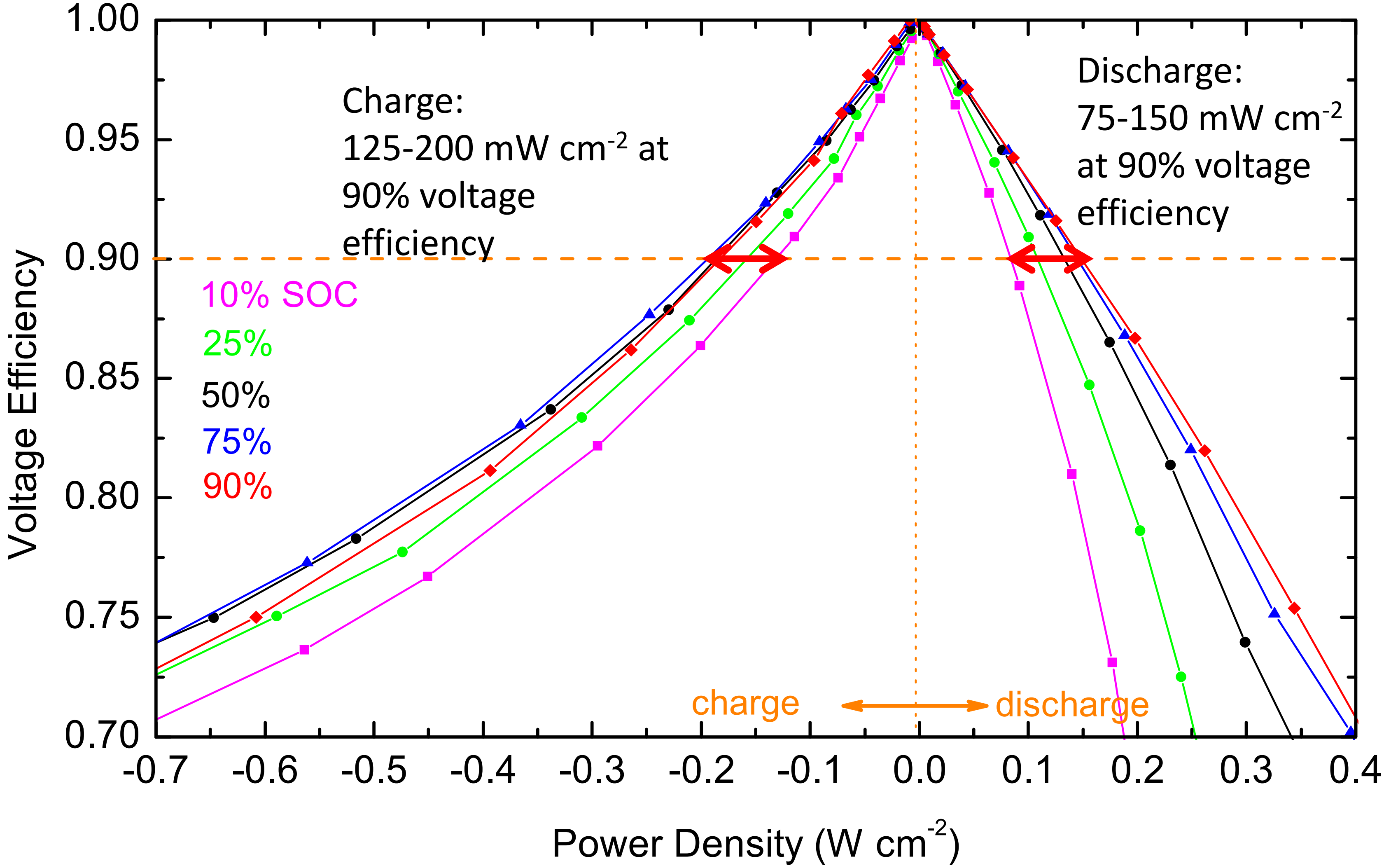


Cell Performance

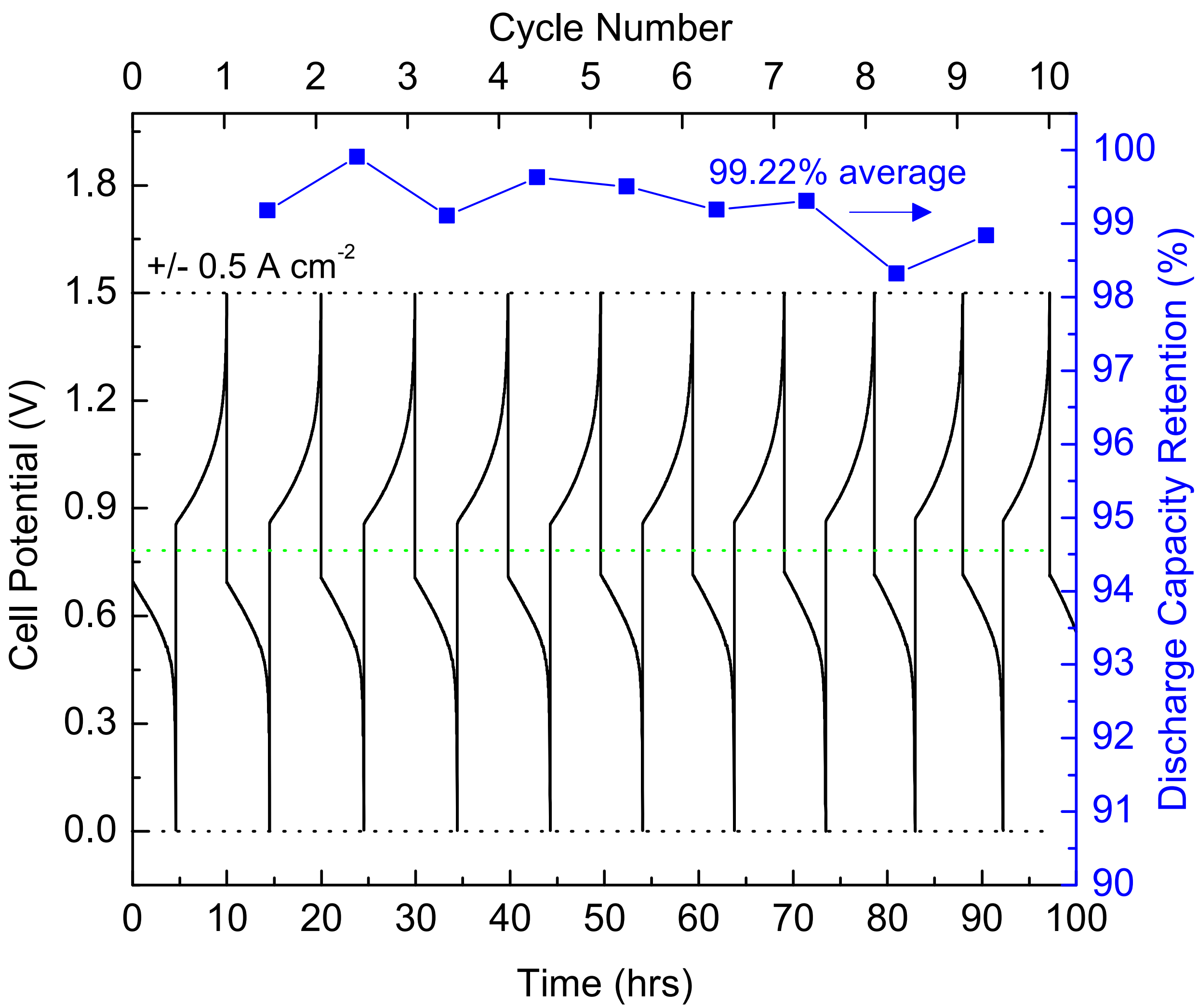




Cell Performance

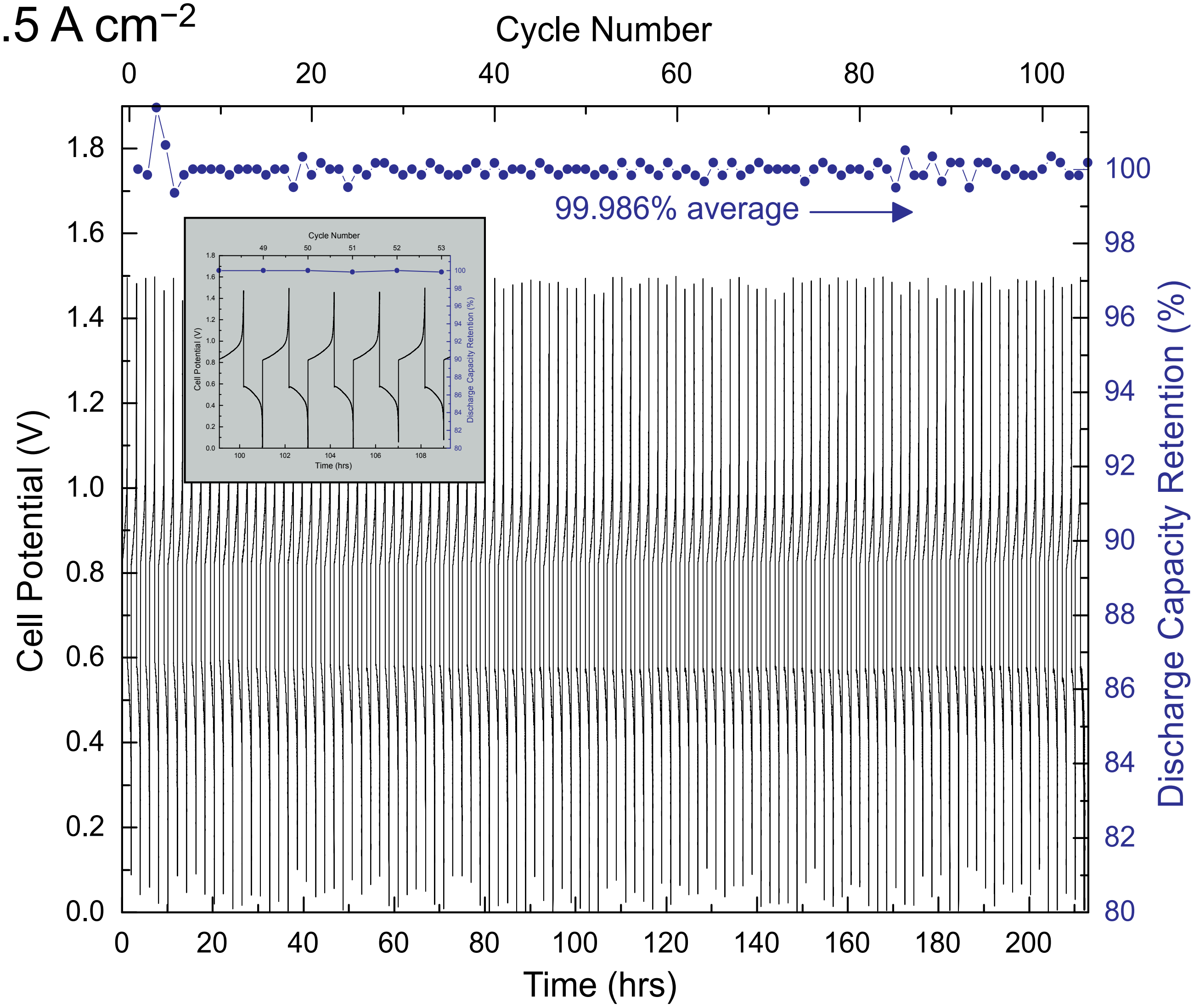


Battery Cycling



Extended Cycling

Cycling at 0.5 A cm^{-2}

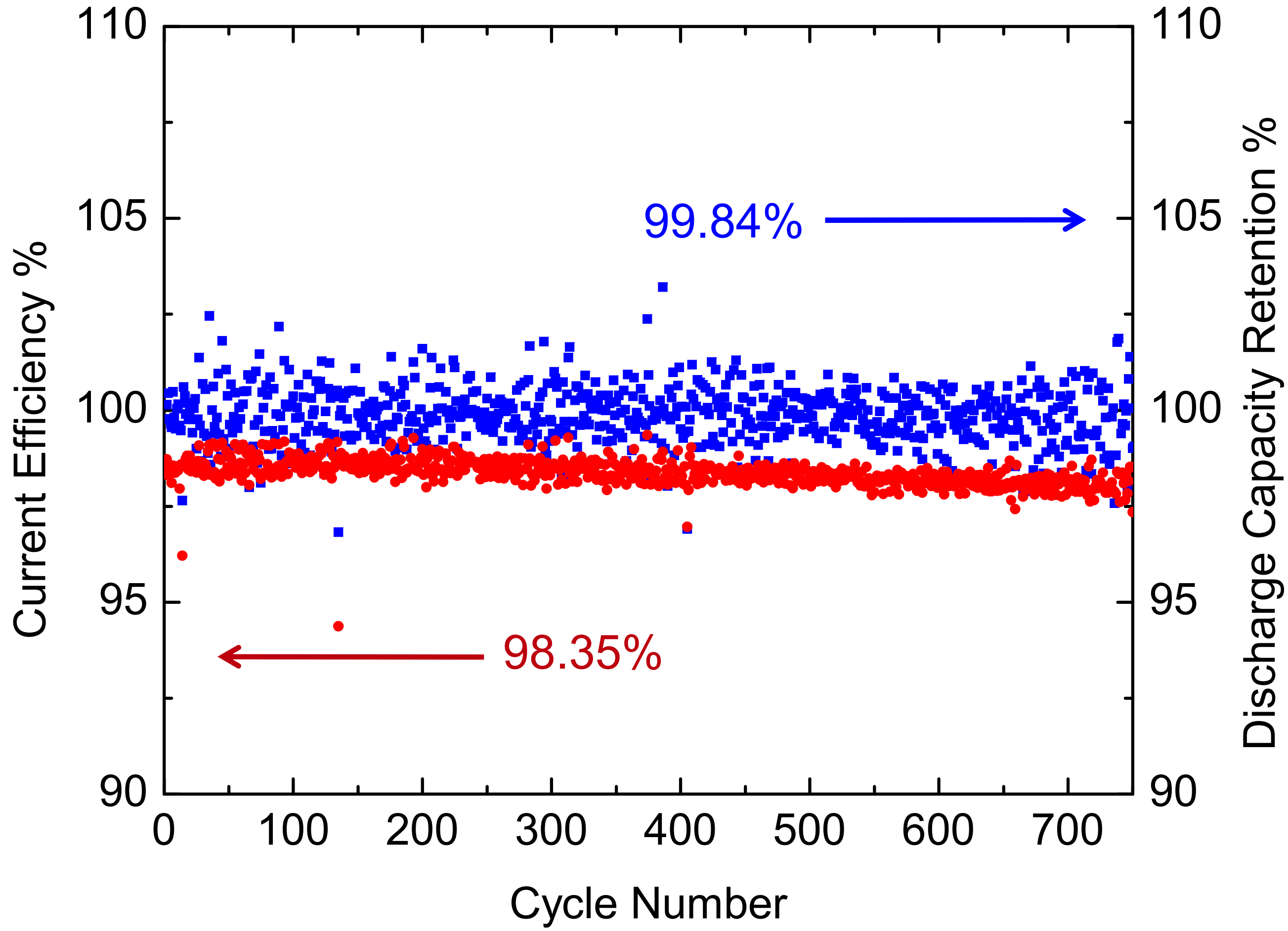


More Extended Cycling

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

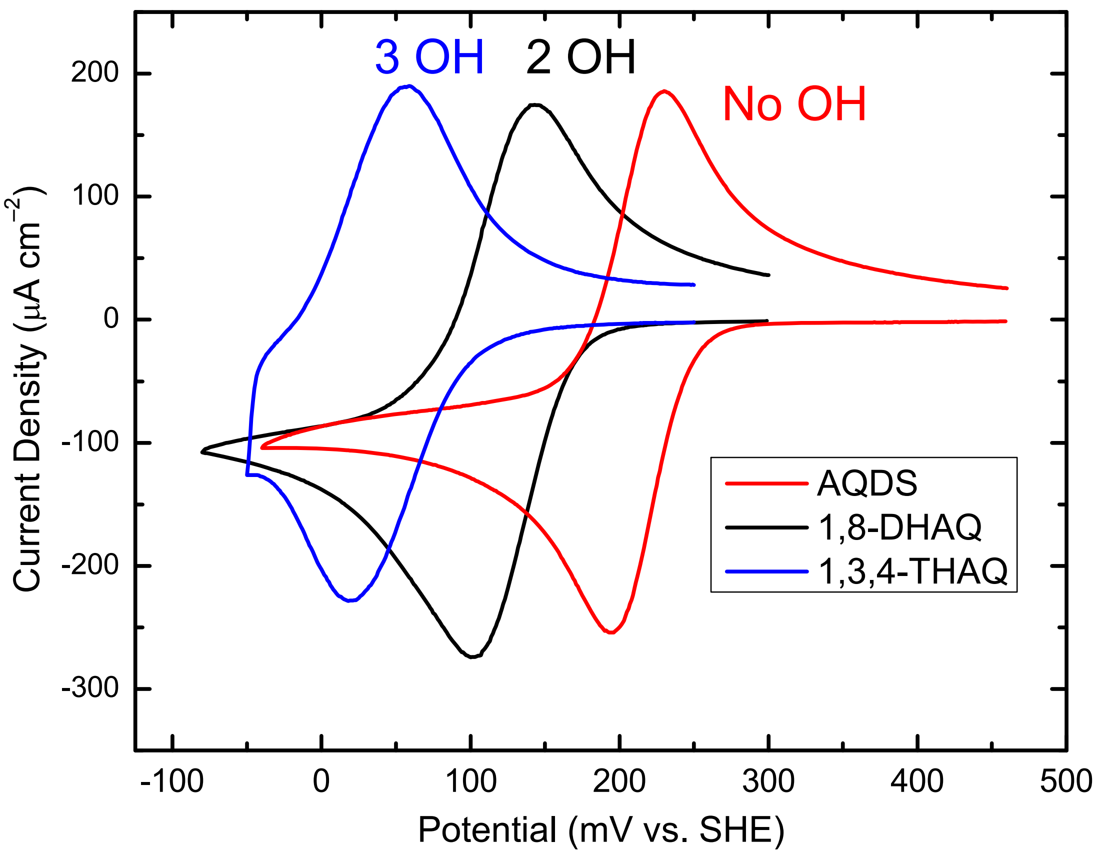
>98% Current efficiency

>99% Charge capacity retention

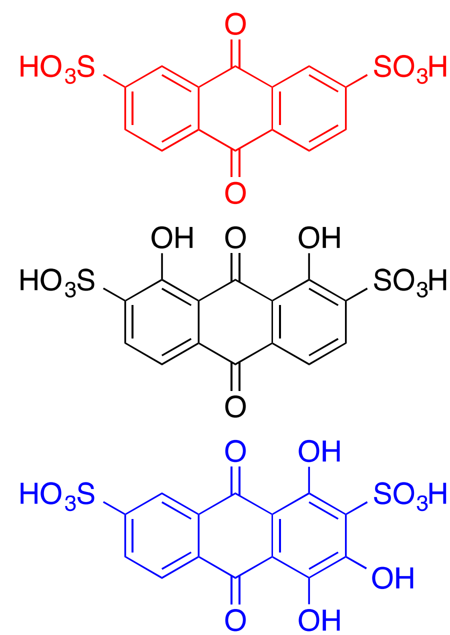


Huskinson, B., Marshak, M. P., Gerhardt, M. R. & Aziz, M. J.
ECS Trans. 61, 27–30 (2014).

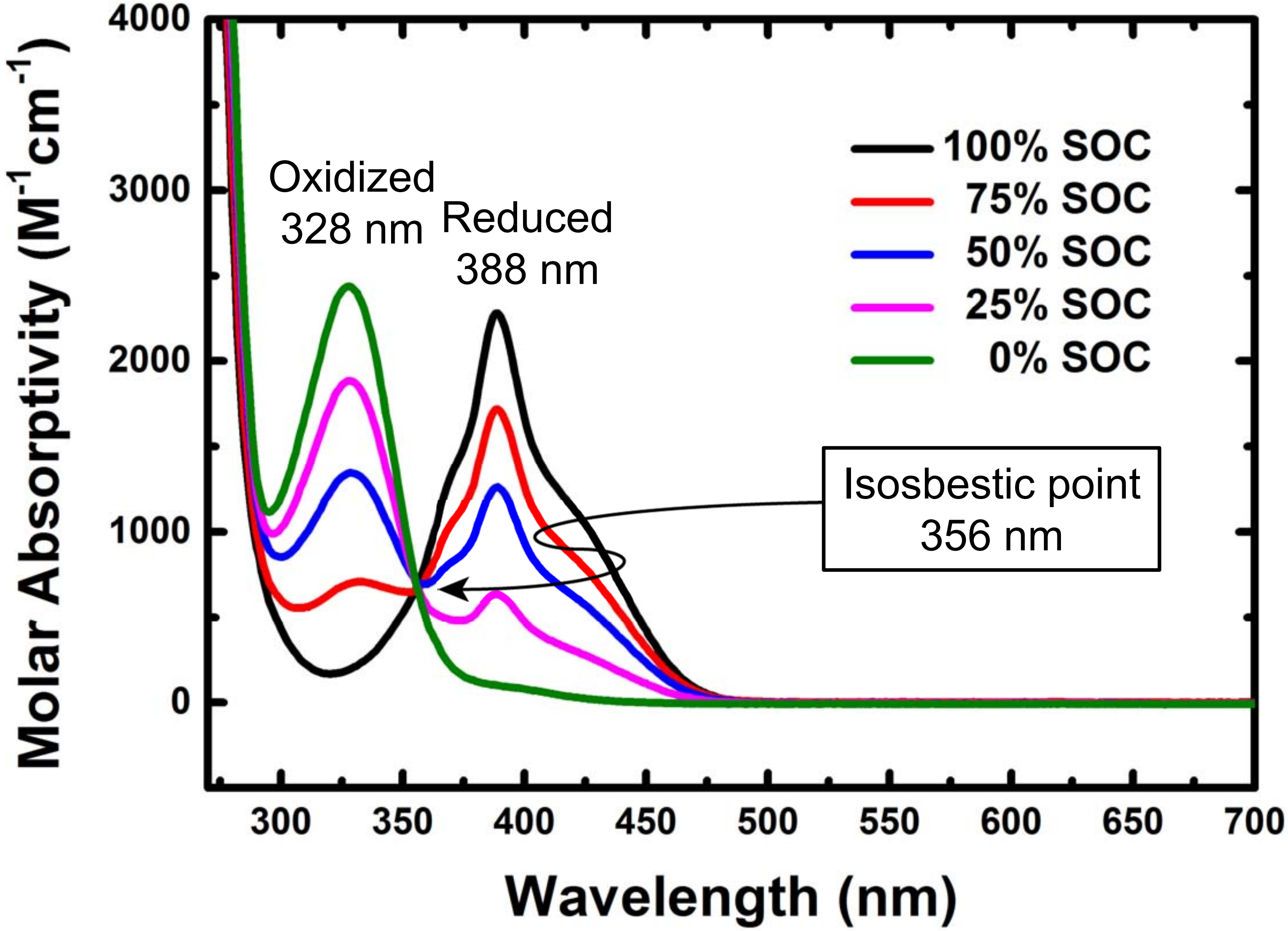
Towards 0.0 V and Beyond



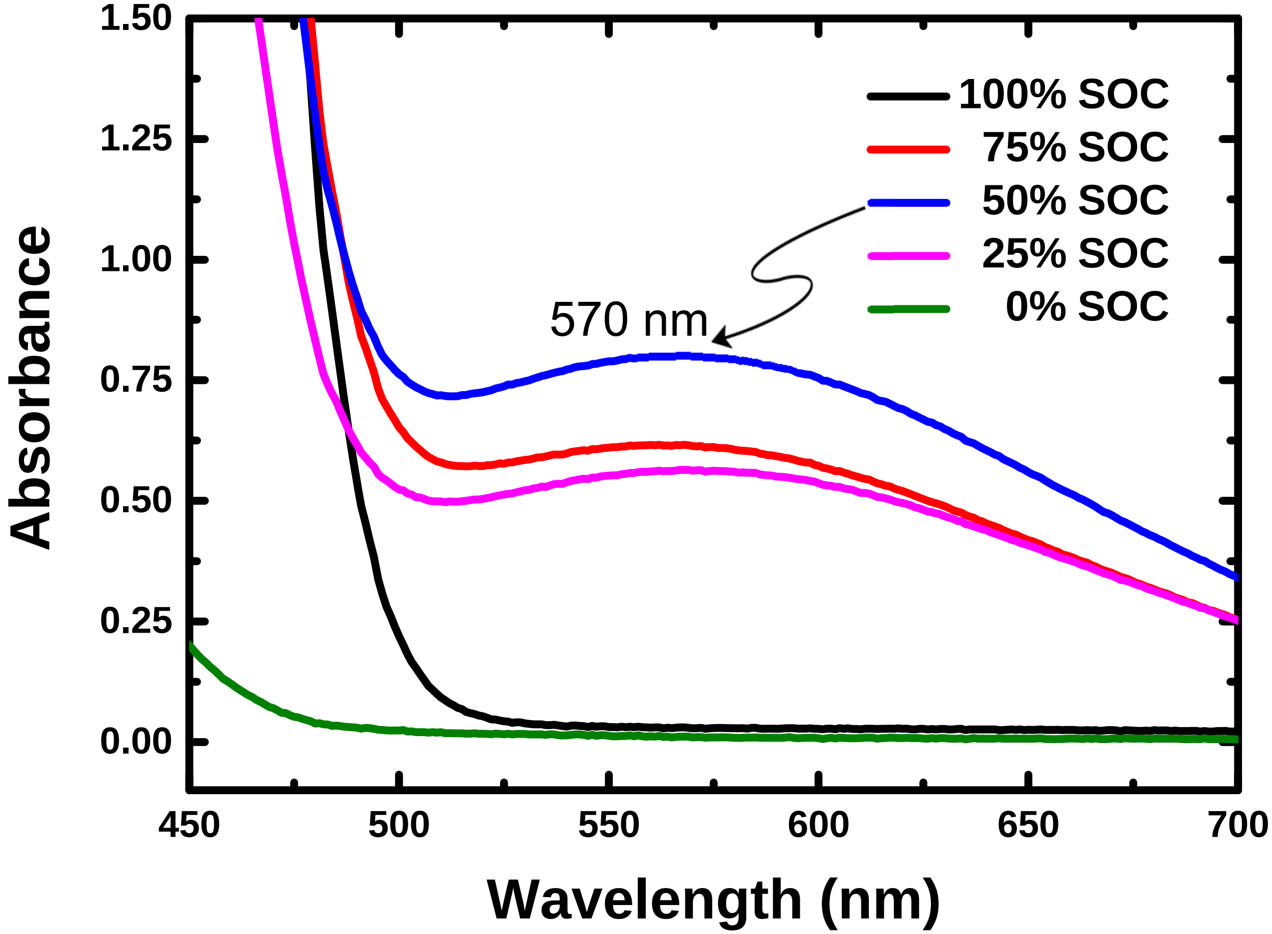
Reversible 2 e^- / 2 H^+ reduction of quinone at 0 V is hydrogen storage with no catalyst required.

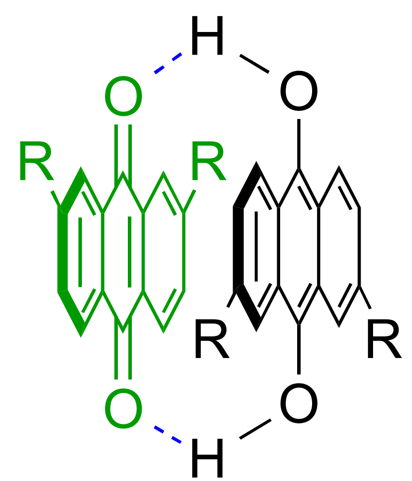


UV/Vis Spectra of Quinones



Evidence of Quinhydrone Formation



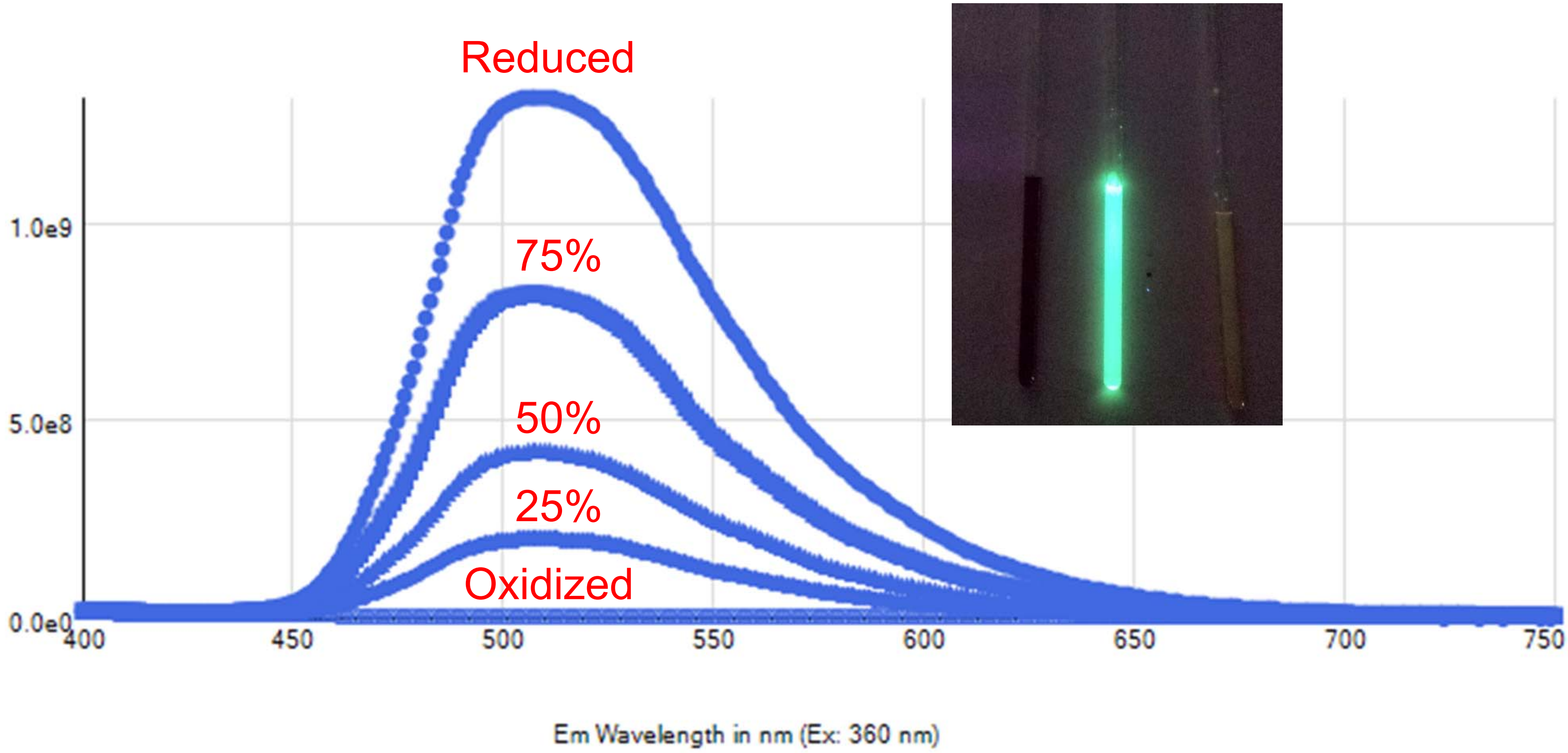


R = SO_3H

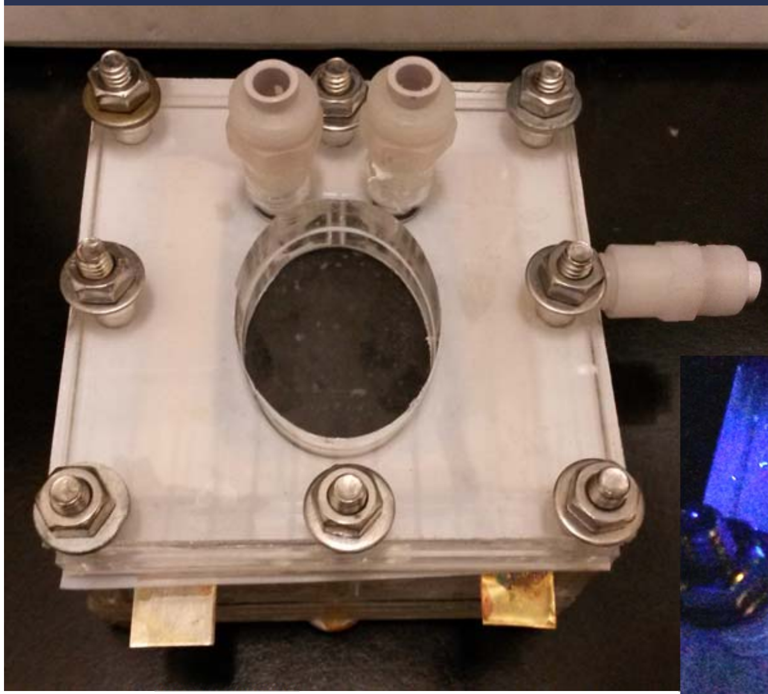
Quinhydrone

Anthraquinone Fluorescence

Excitation @ 360 nm

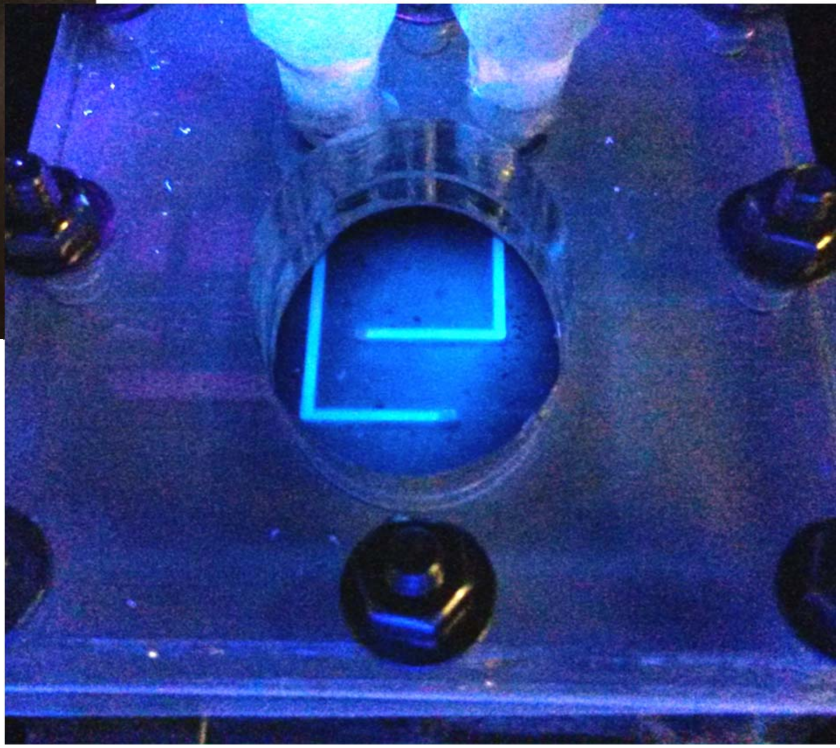


In-situ Flow Field Monitoring



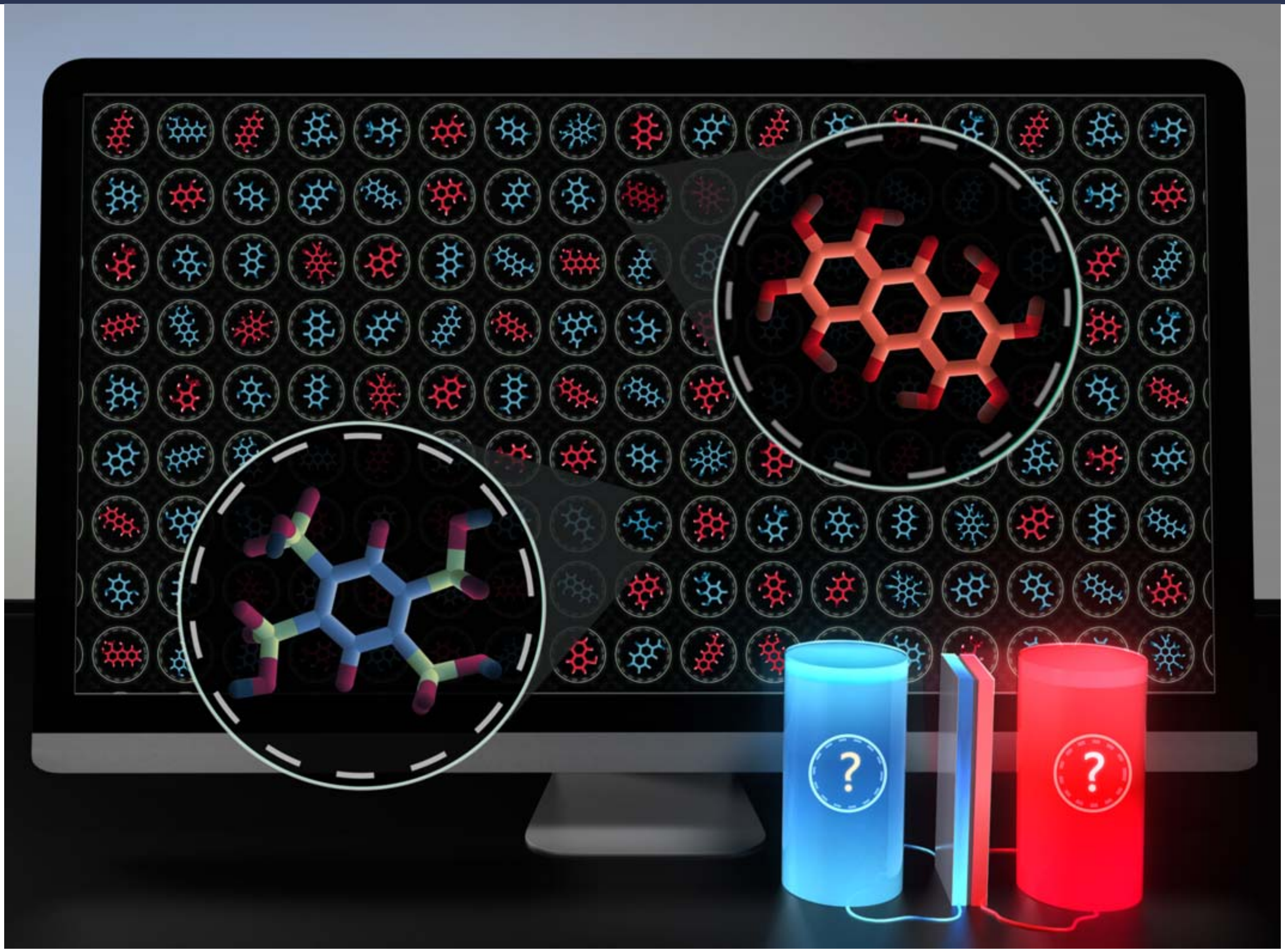
Electrochemical flow cell with a transparent conducting flow field

Fluorescence under UV Lamp!



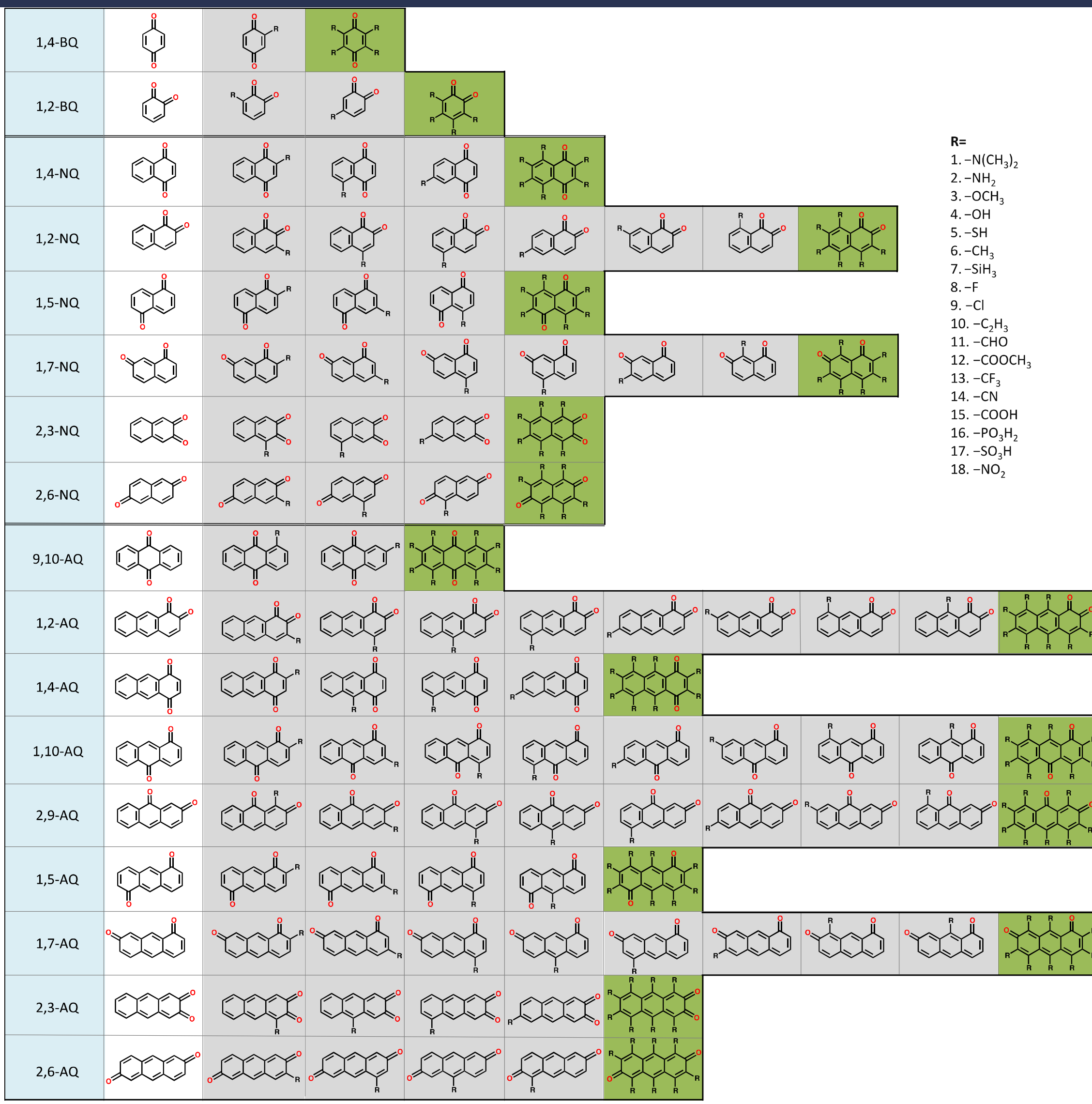
Andrew Wong

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. $-N(CH_3)_2$
2. $-NH_2$
3. $-OCH_3$
4. $-OH$
5. $-SH$
6. $-CH_3$
7. $-SiH_3$
8. $-F$
9. $-Cl$
10. $-C_2H_3$
11. $-CHO$
12. $-COOCH_3$
13. $-CF_3$
14. $-CN$
15. $-COOH$
16. $-PO_3H_2$
17. $-SO_3H$
18. $-NO_2$

Changwon Suh

Süleyman Er

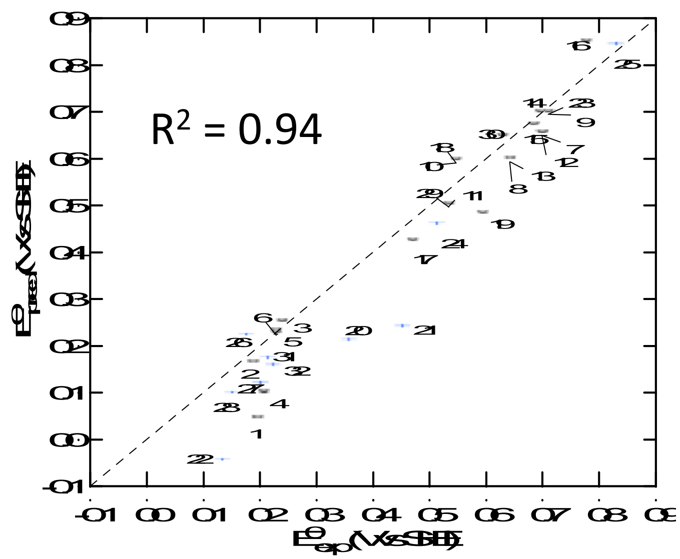
Prof. Alán Aspuru-Guzik

unsubstituted

single substitution

full substitution

Screening Results

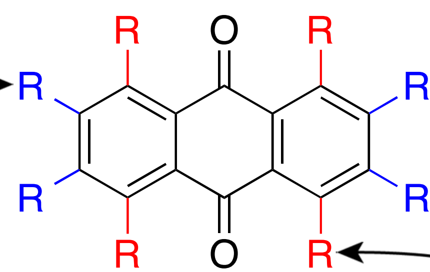


Electron-donating groups decrease E^0
NH_2, OH, NMe_2, OCH_3, SH, CH_3

Electron-withdrawing groups increase E^0
NO_2, CO_2Me, CO_2H, CN, CHO,
CF_3, SO_3H, PO_3H_2

Some have suprisingly little impact:
F, Cl, SiH_3, C_2H_3

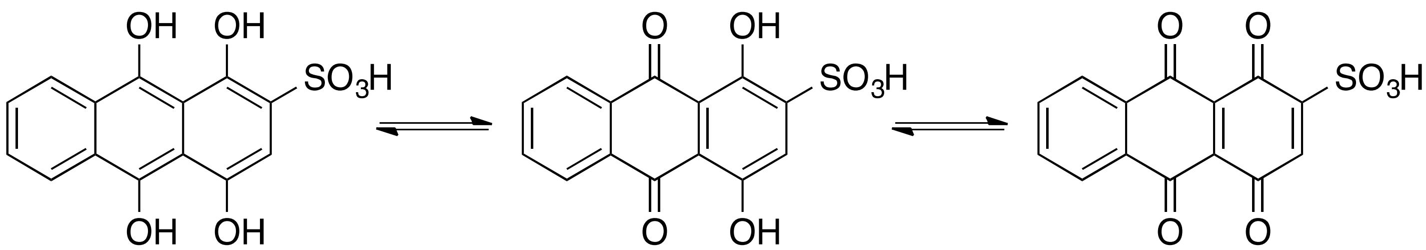
Biggest effect on solubility

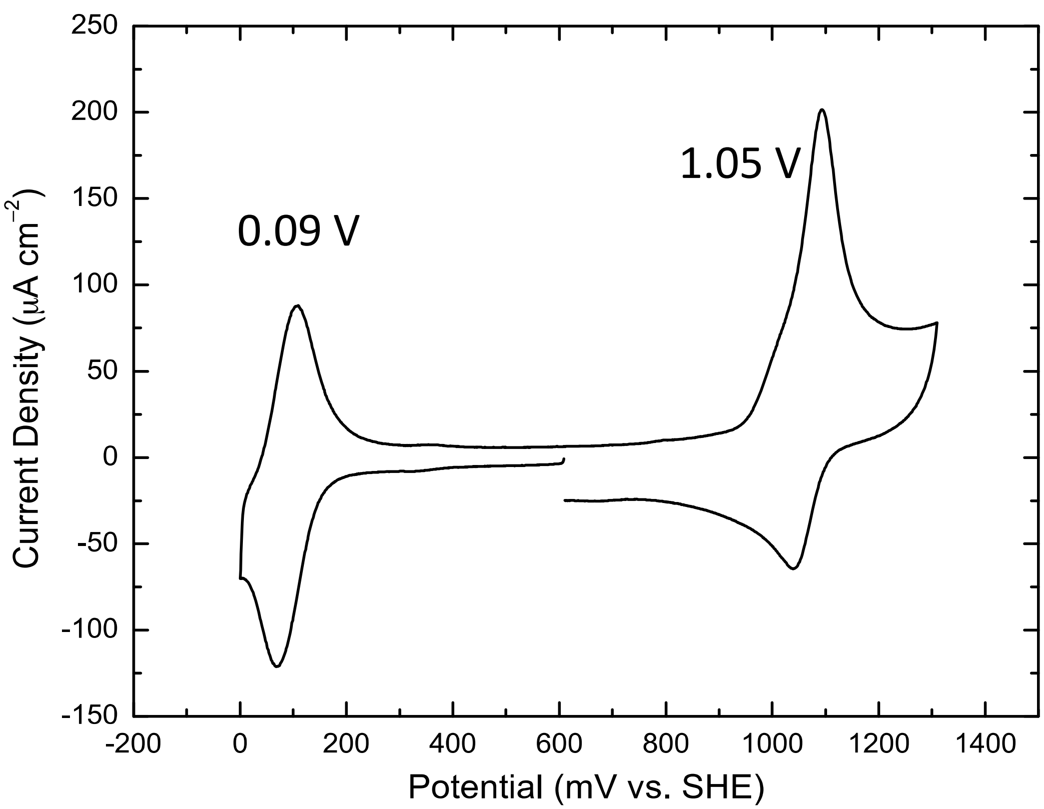


Biggest effect on E^0

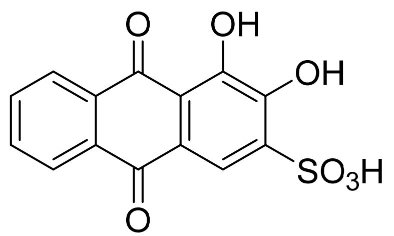
Er, S., Suh, C., Marshak, M. P. & Aspuru-Guzik, A. *Chem*. *Sci*. **2015**, Advance Article.

New Cell Chemistry #1: Fused Quinones



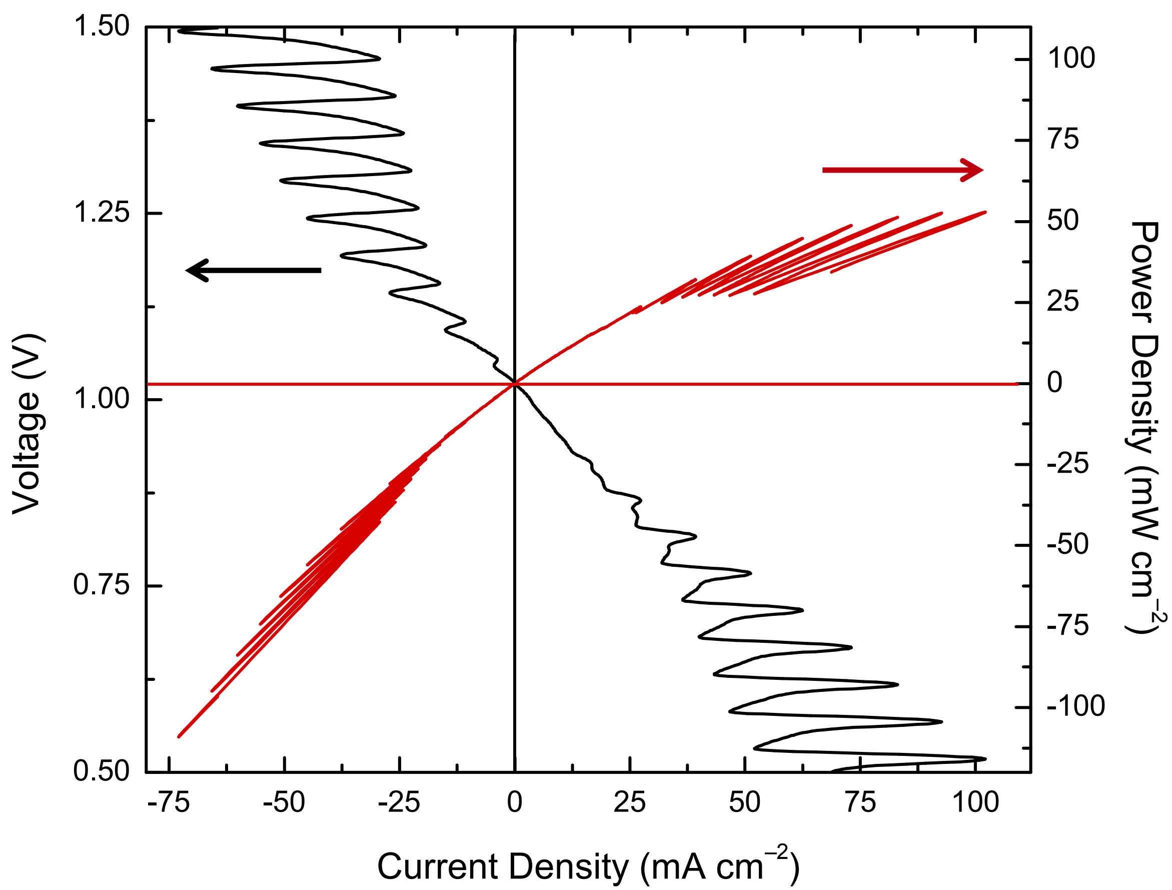


Quinone-Quinone Cell



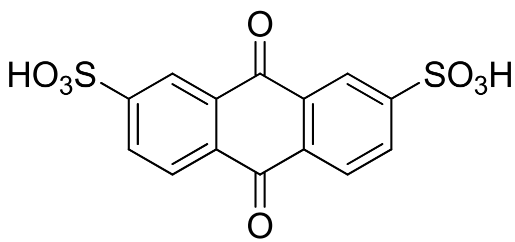
0.1 M Quinone in H_2O
OCP = 1.03 V
Peak Power = 50 mA cm^{-2}
>99% Coulombic Efficiency

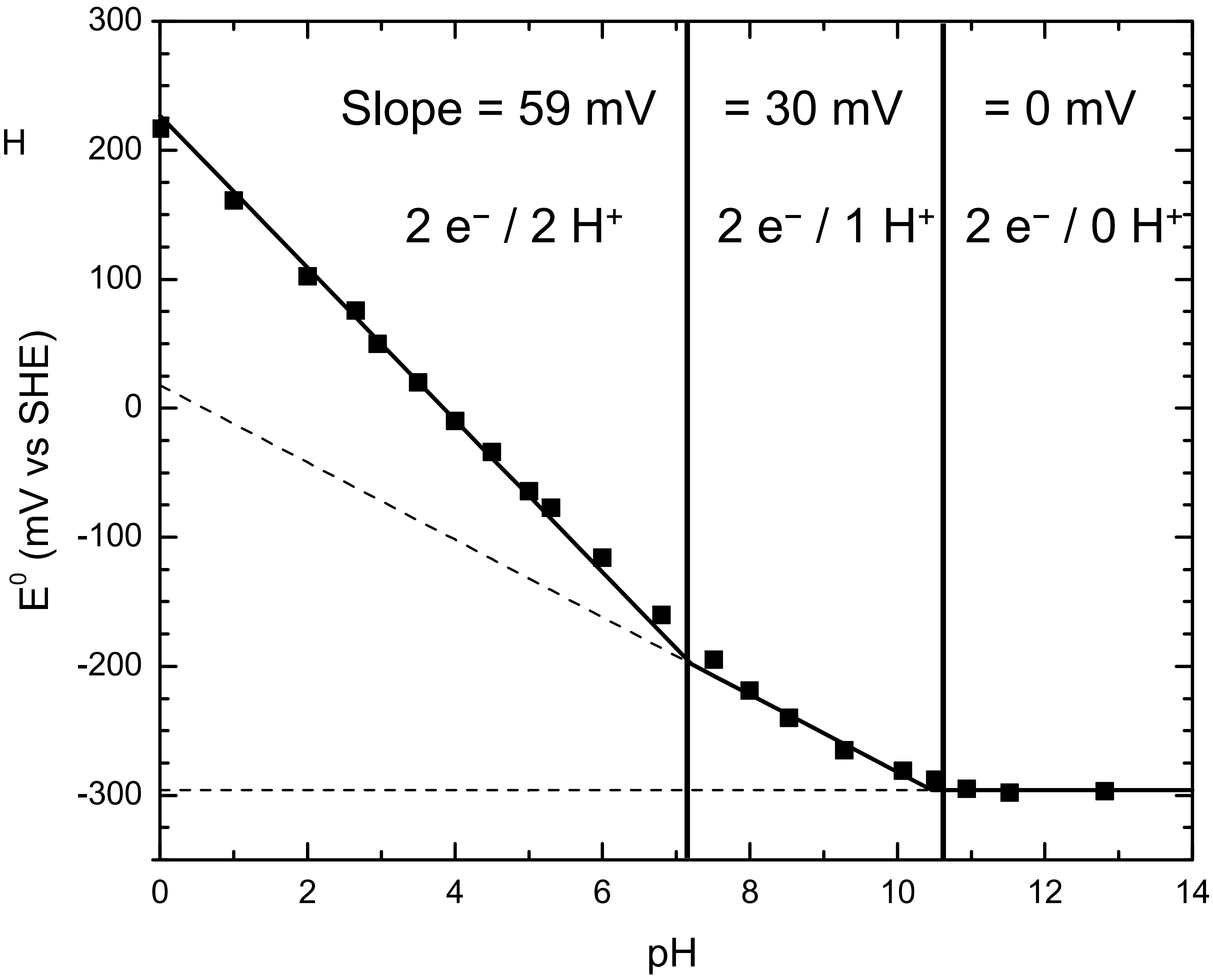
High cell resistance
due to low ion conc.



With Liuchuan Tong

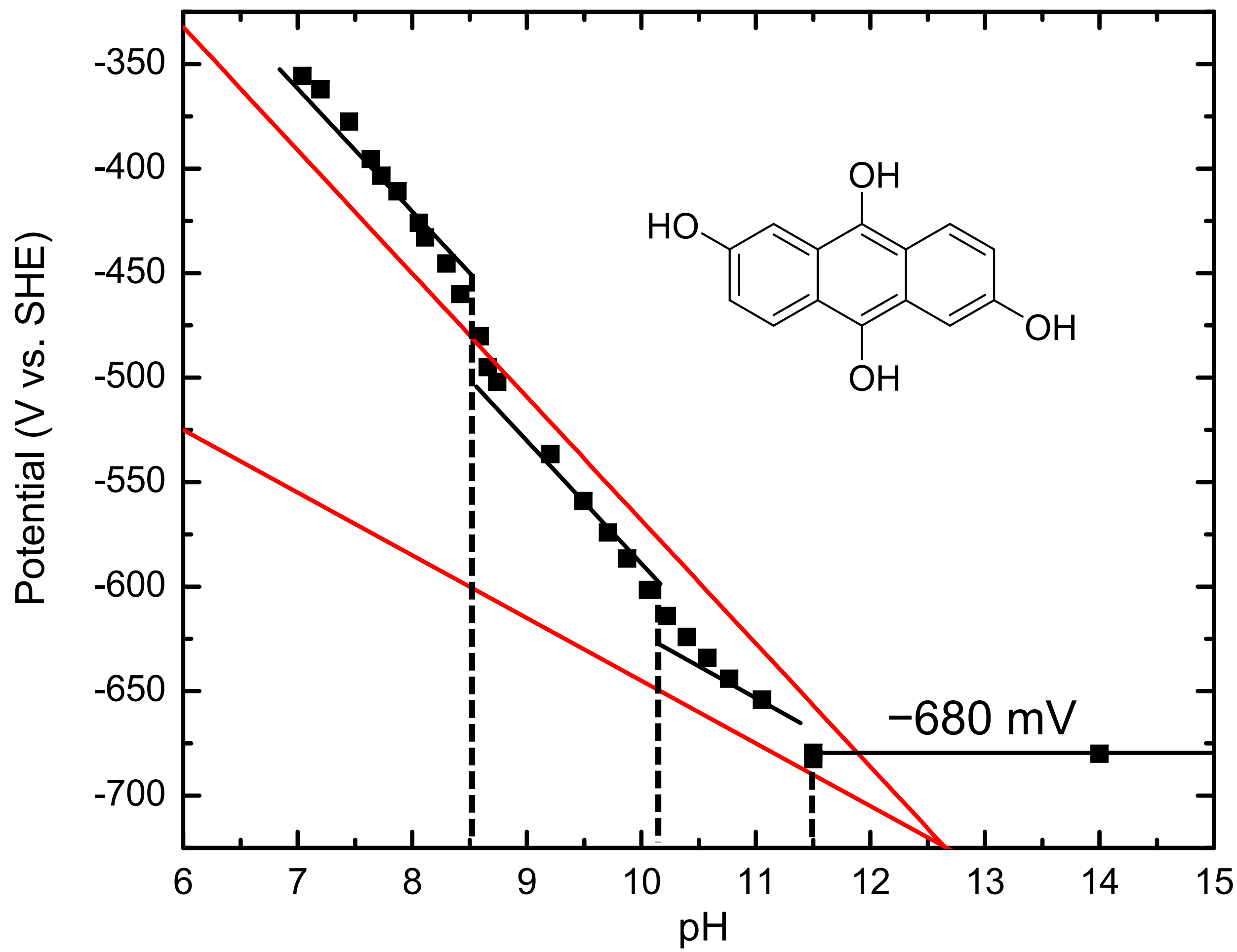
New Cell Chemistry #2: Quinones In Base



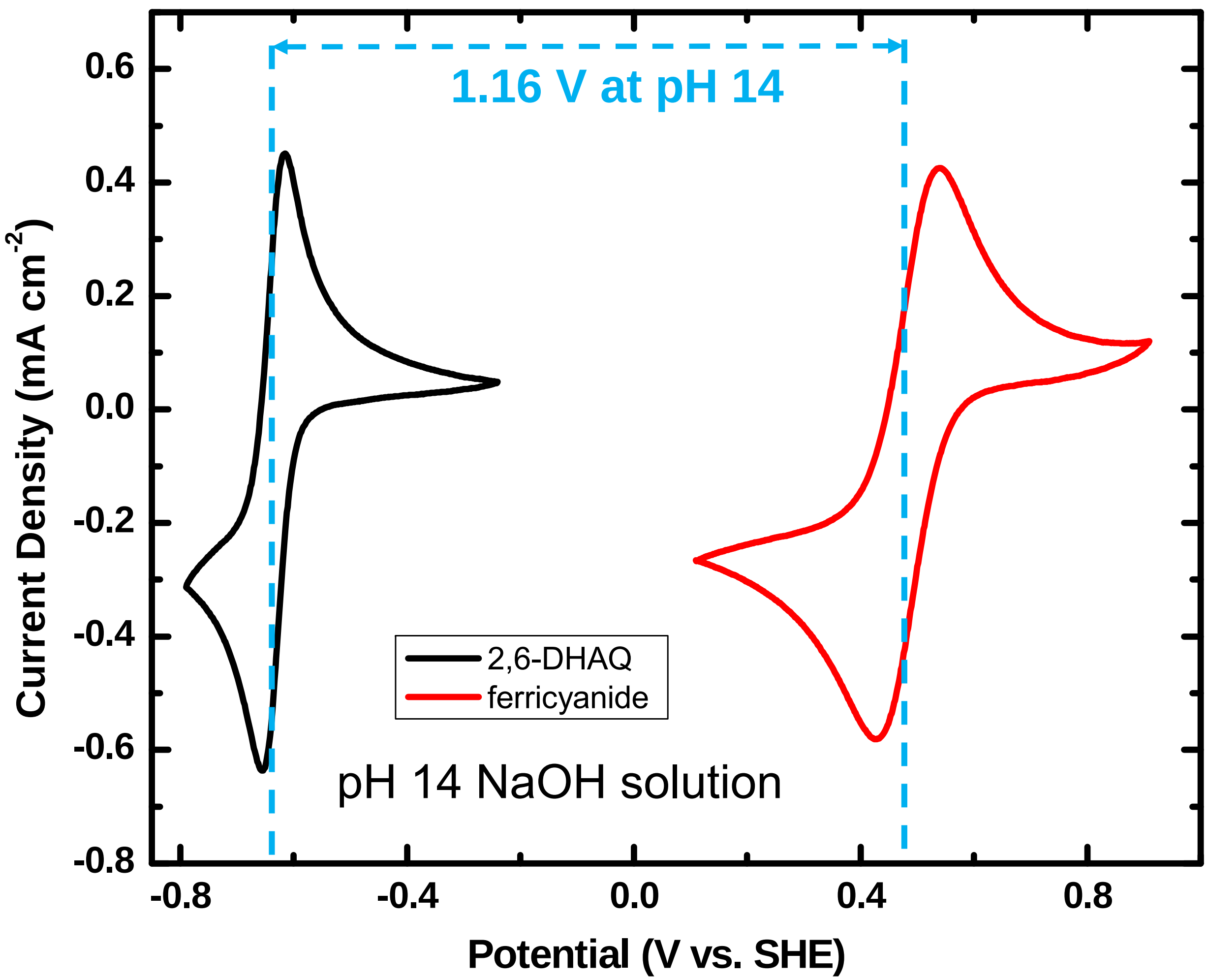


Quinones In Base

Kaixiang Lin

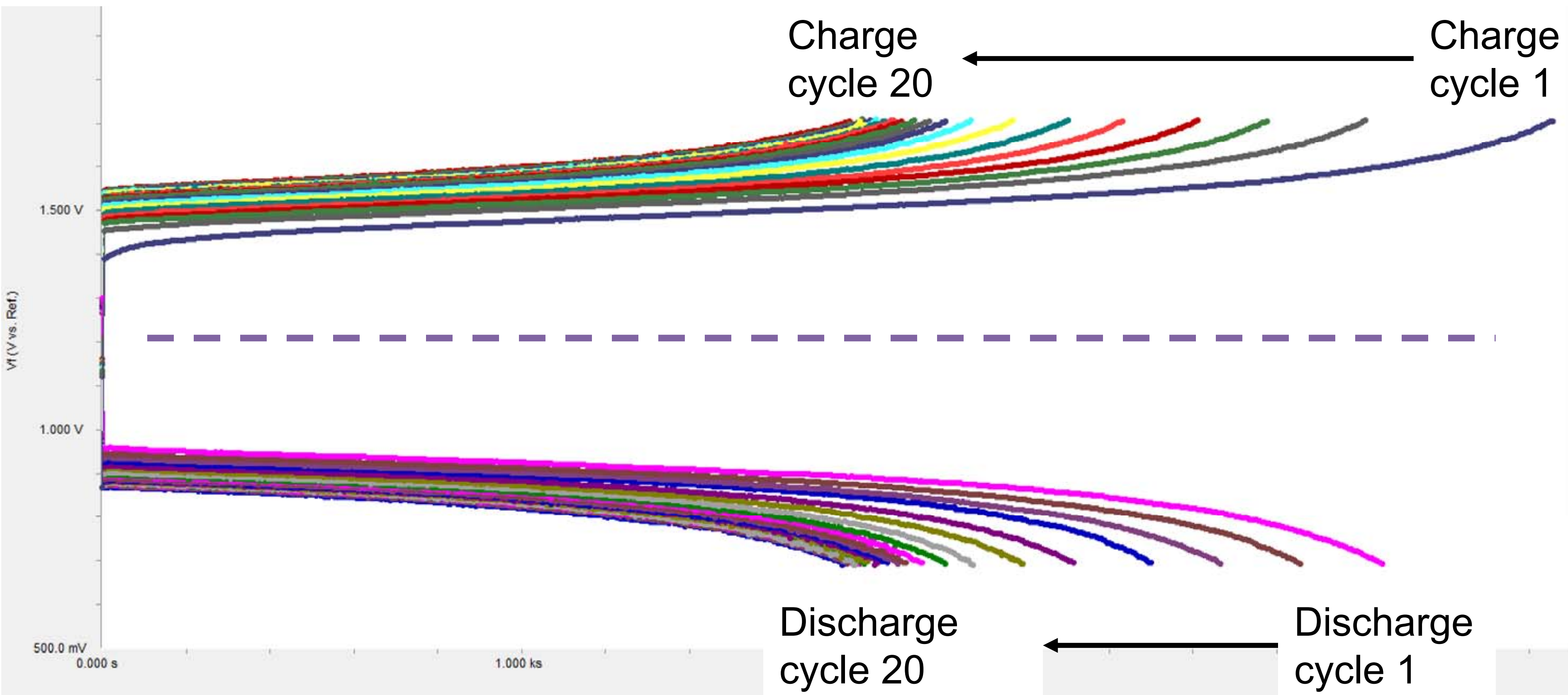


$Fe(CN)_6^{4-/3-}$ For Posolyte

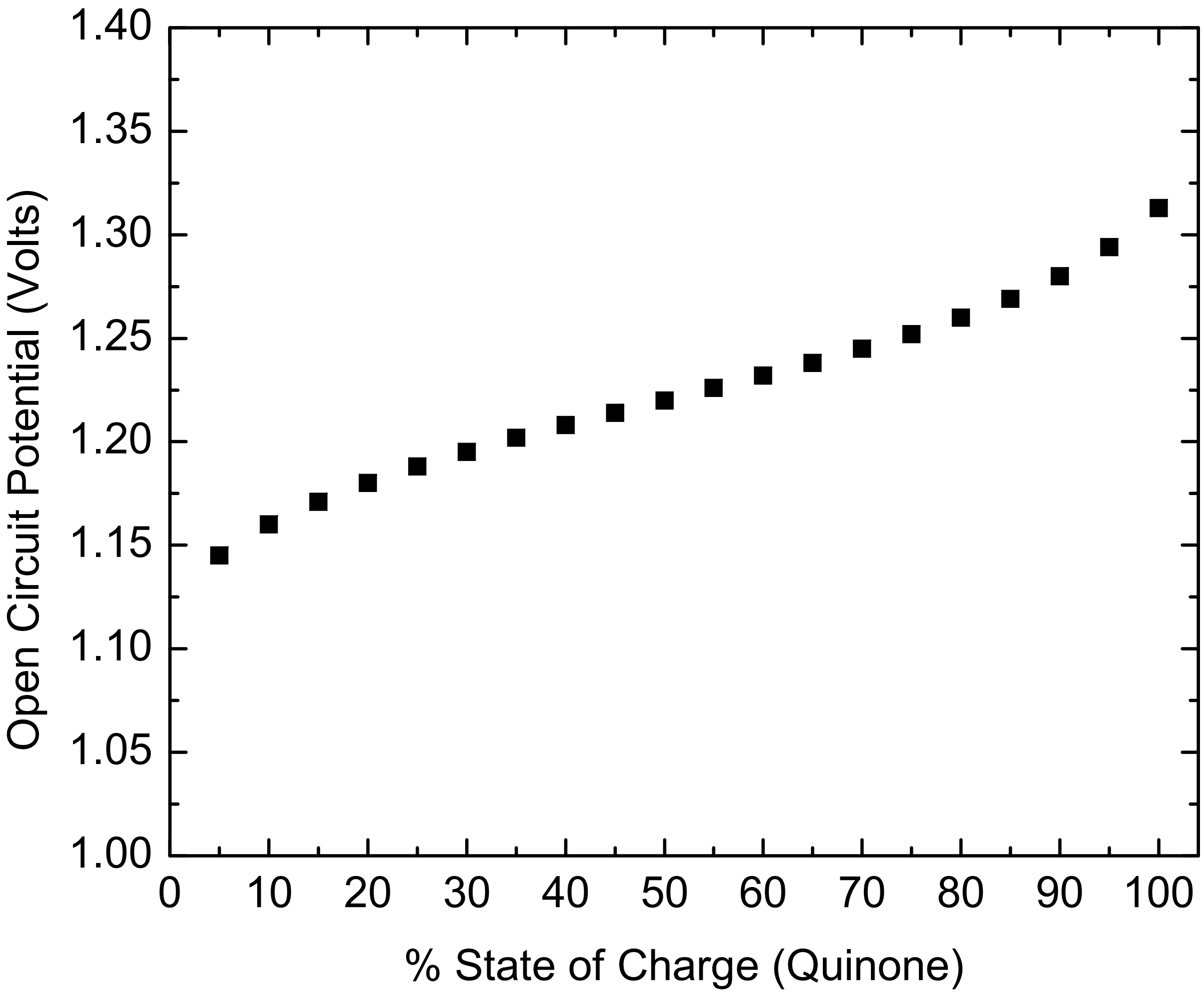


Quinone-Ferrocyanide Battery Cycling

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



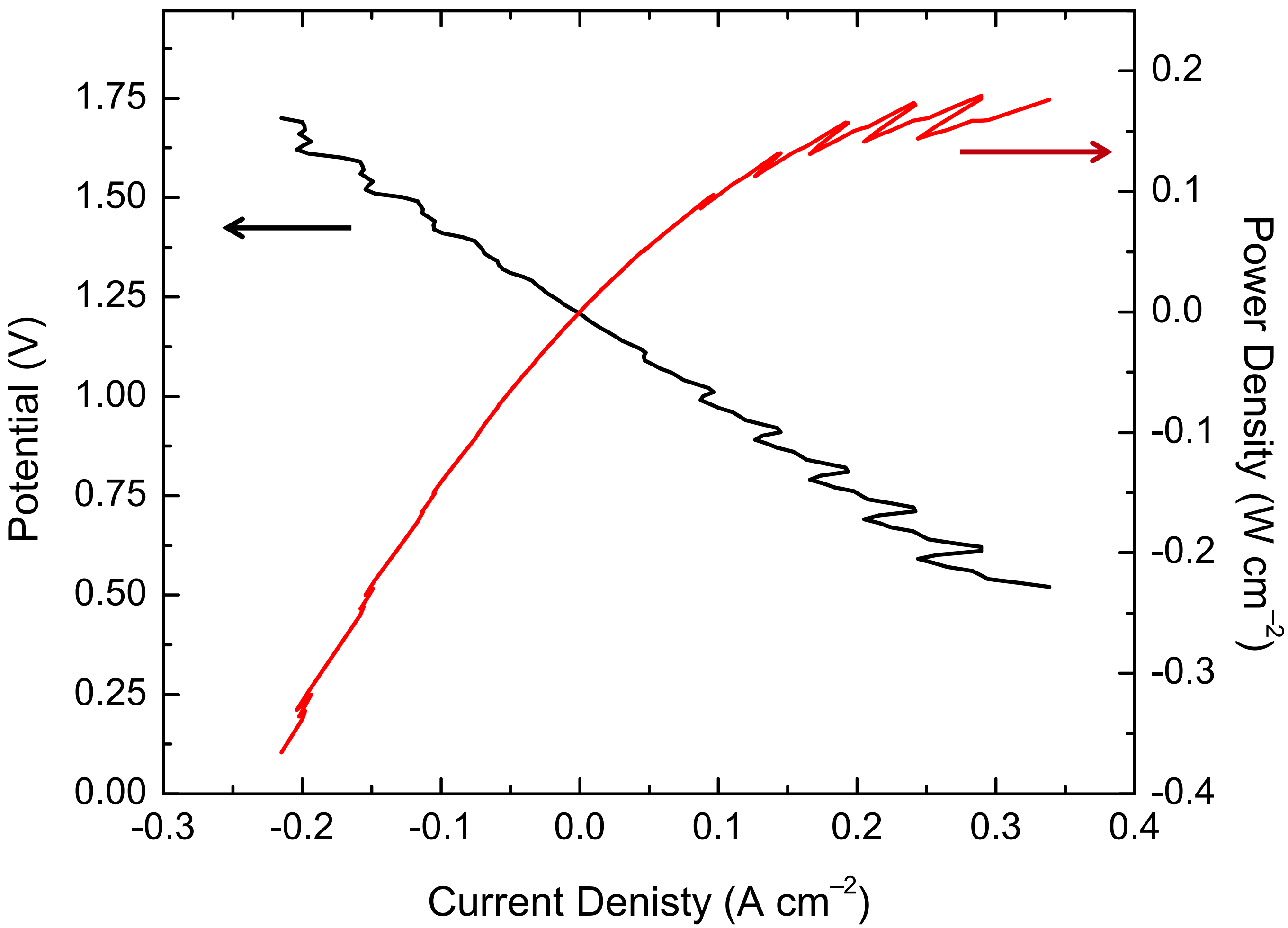
Cell voltage can be increased by adding extra $Fe(CN)_6^{3-}$



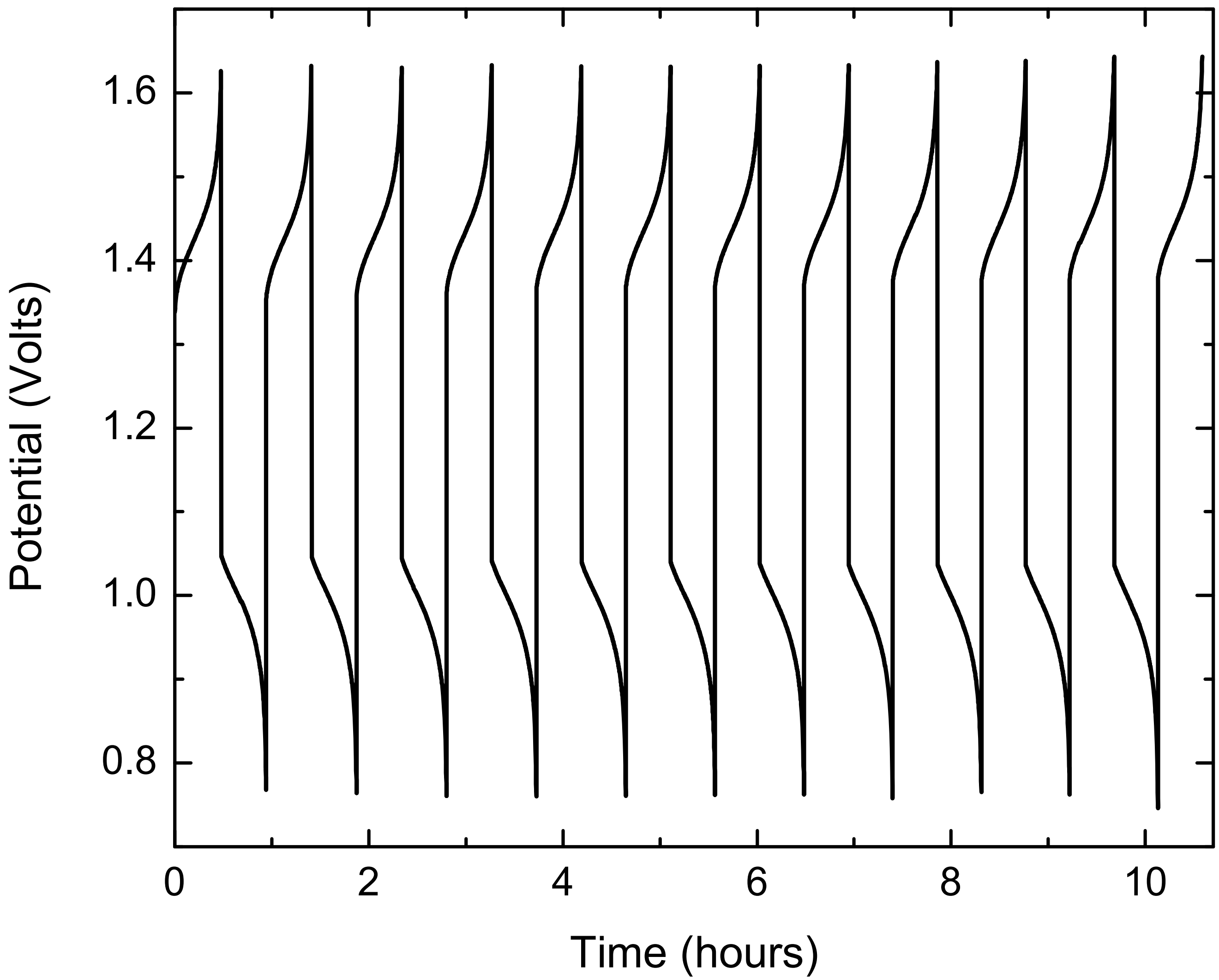
Negolyte:
0.5 M 2,6-dihydroxy-AQ
in 3 M KOH

Posolyte (2.4x volume):
0.4 M $K_4Fe(CN)_6$
0.1 M $K_3Fe(CN)_6$
in 1 M KOH

200 mW cm^{-2} performance despite higher cell resistance



Stable to repeated cycling



Cycling ±0.1 A/cm^{-2}

>98 % current efficiency

>99% charge capacity retention/cycle

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})

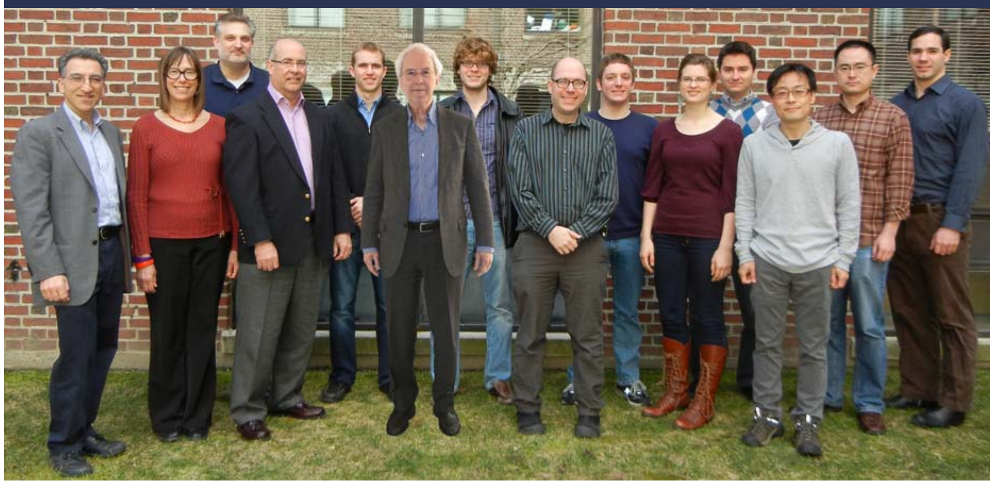
✧ High-Throughput Computational Screening

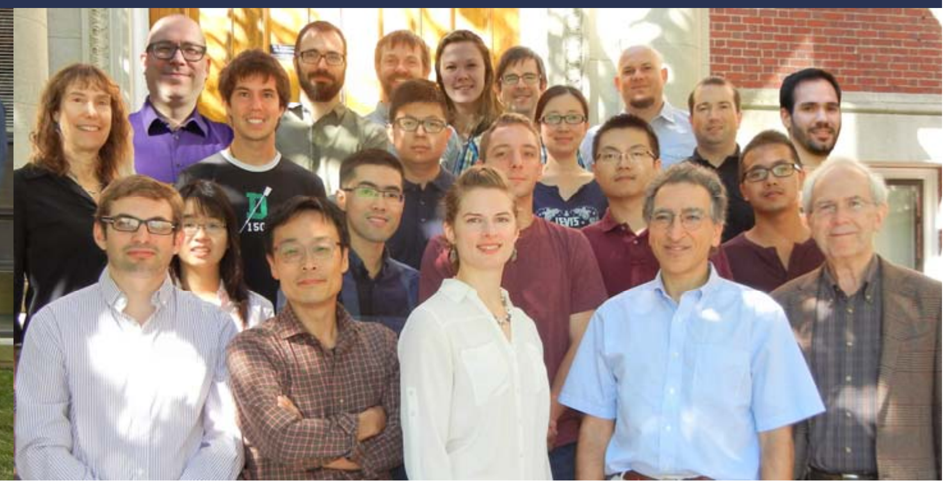
✧ State of Charge Monitoring by Spectroscopy

✧ Flow Field Optimization with Fluorescence

✧ New Quinone Materials

Acknowledgements





Michael Aziz: Brian Huskinson, Michael Gerhardt, Qing Chen, Andrew Wong
Xin Li, Xinyou Ke, Saraf Nawar

Roy Gordon: 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

arpa-e
Award # DE-AR0000348

Sustainable Innovations
3 kW Quinone-Bromine
Prototype in production