Redox Flow Batteries Based on Aqueous Soluble Organics

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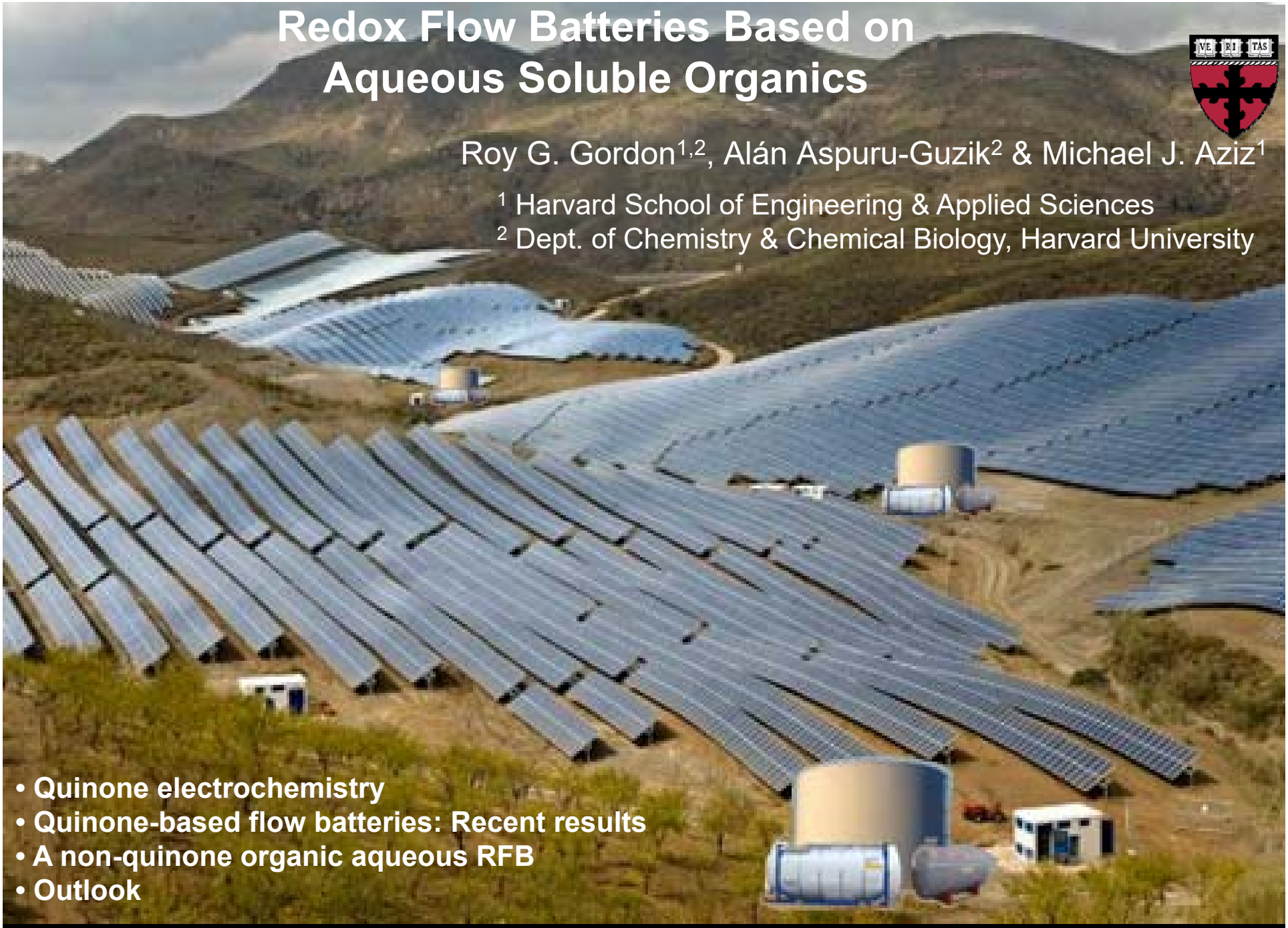
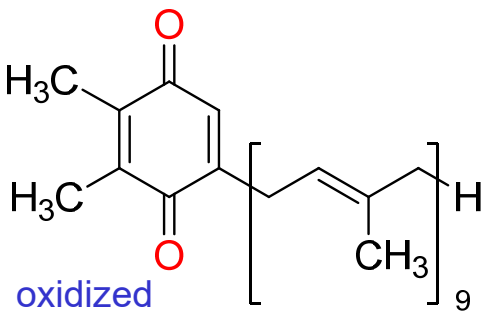


- **Quinone electrochemistry**
- **Quinone-based flow batteries: Recent results**
- **A non-quinone organic aqueous RFB**
- **Outlook**

Beyond Lithium Ion IX, PNNL, 5/26/2016

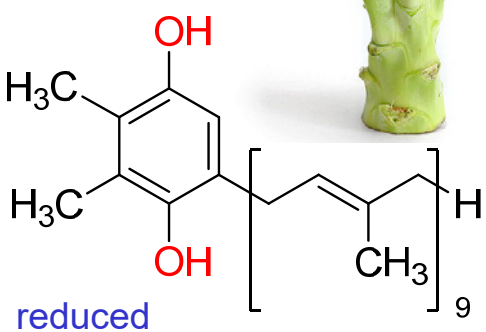
Quinones for Battery Storage

Plastoquinone
in photosynthesis



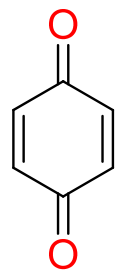
oxidized

$+2\ H^+,$
$+2\ e^-$

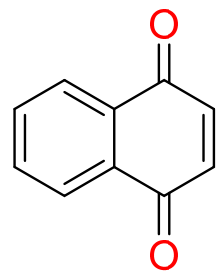


reduced

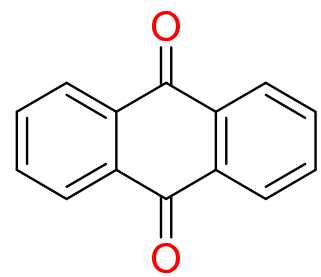
simplest
quinone



Benzoquinone



Naphthoquinone

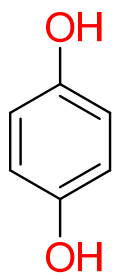


Anthraquinone

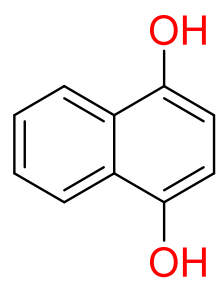
$+2\ H^+,$
$+2\ e^-$

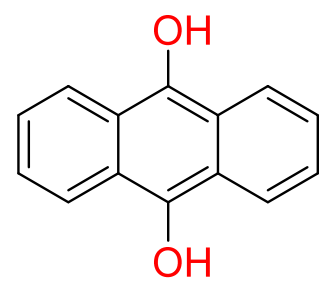
$+2\ H^+,$
$+2\ e^-$

$+2\ H^+,$
$+2\ e^-$

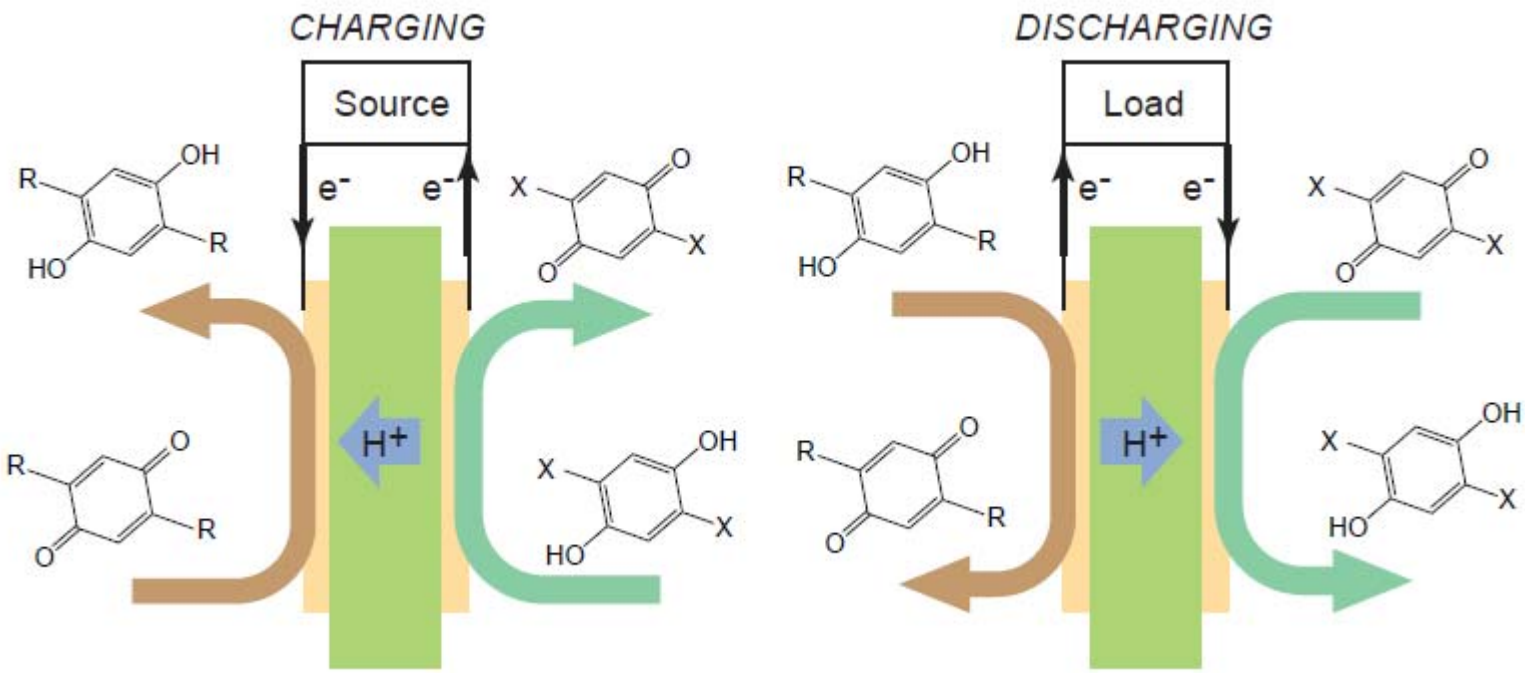


Hydroquinone





The Vision: Quinone-Based Aqueous Flow Batteries

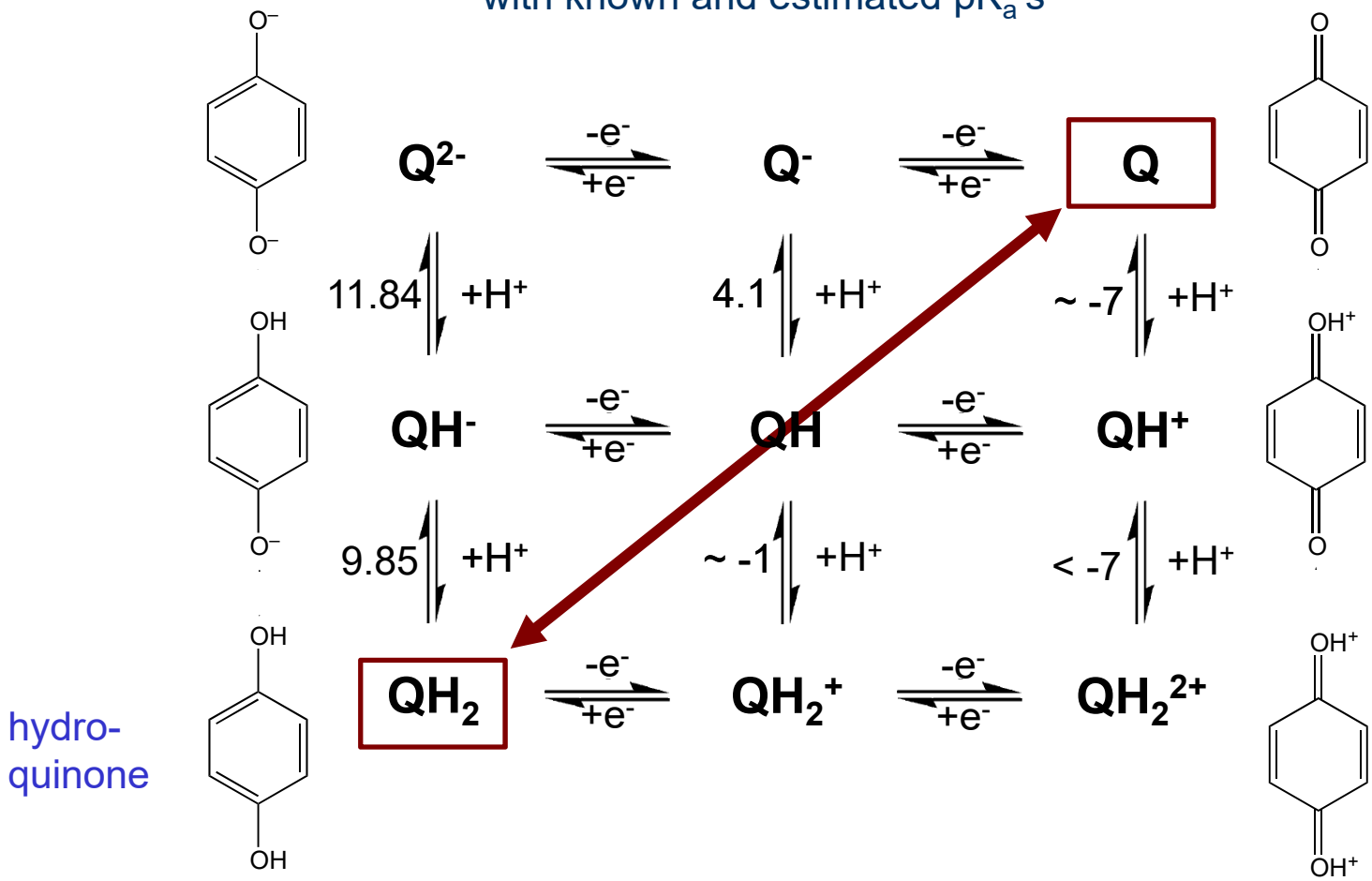


Primary requirements:

- Reduction potential
- Aqueous Solubility
- Redox kinetics
- Stability
- Cost

Quinones/Hydroquinones: Reversible

proton and electron addition reactions
with known and estimated pK_a's



"pBQ"

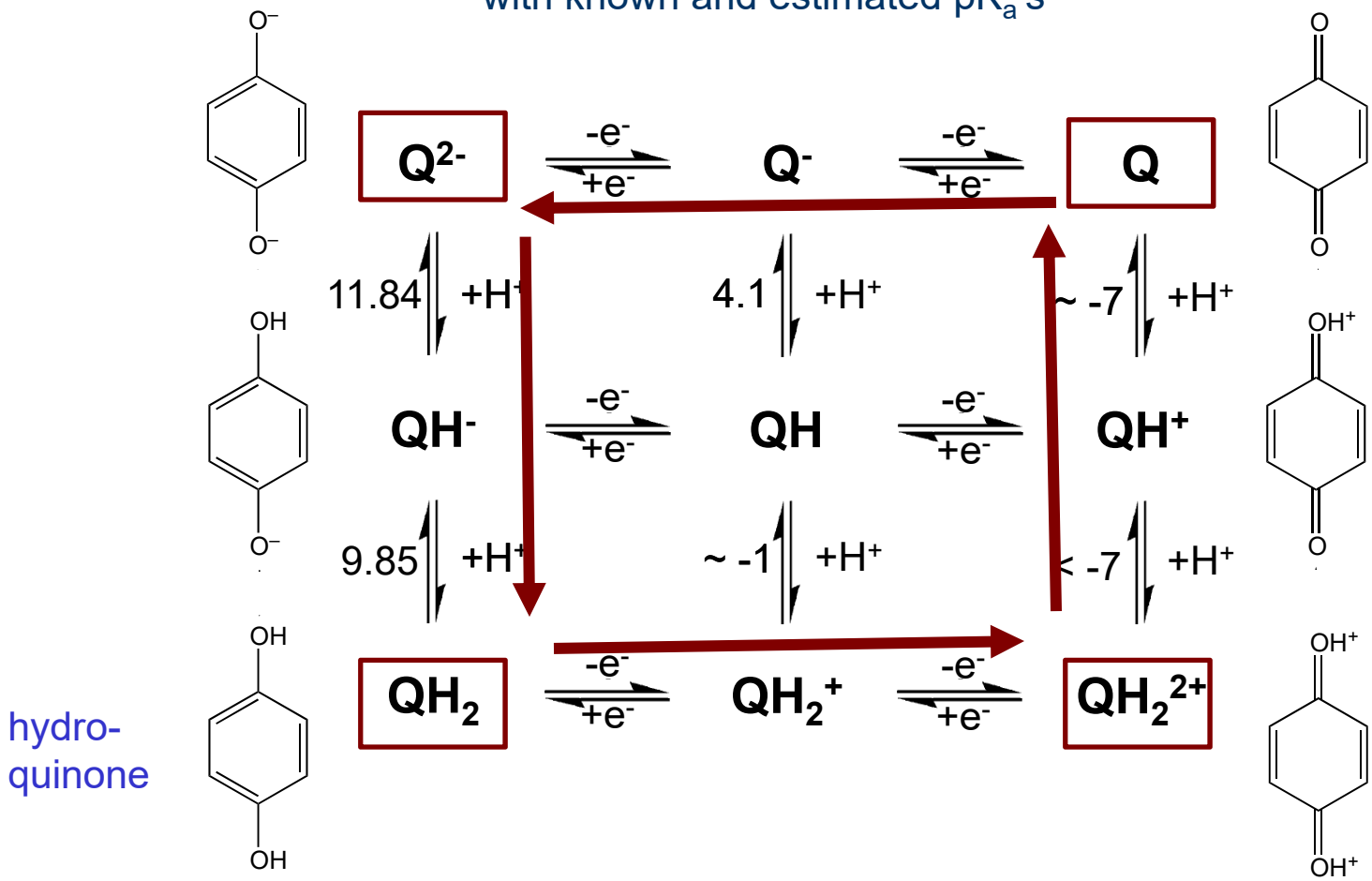
para-
benzo-
quinone

hydro-
quinone

Quan, Sanchez, Wasylkiw, Smith, "Voltammetry of Quinones in Unbuffered Aqueous Solution...", *JACS* **129**, 12847 (2007)

Quinones/Hydroquinones: Reversible or Irreversible

proton and electron addition reactions
with known and estimated pK_a's



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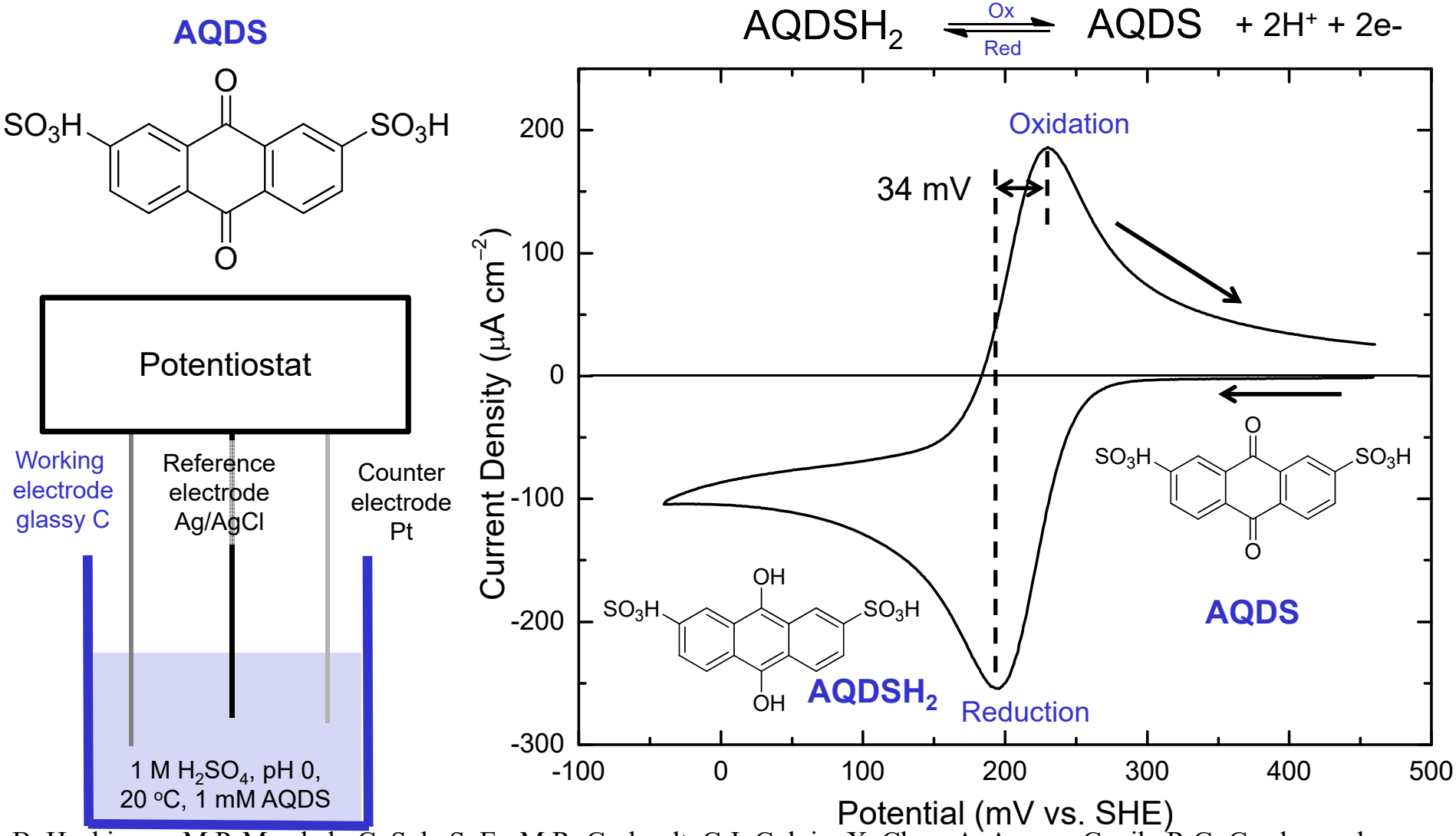
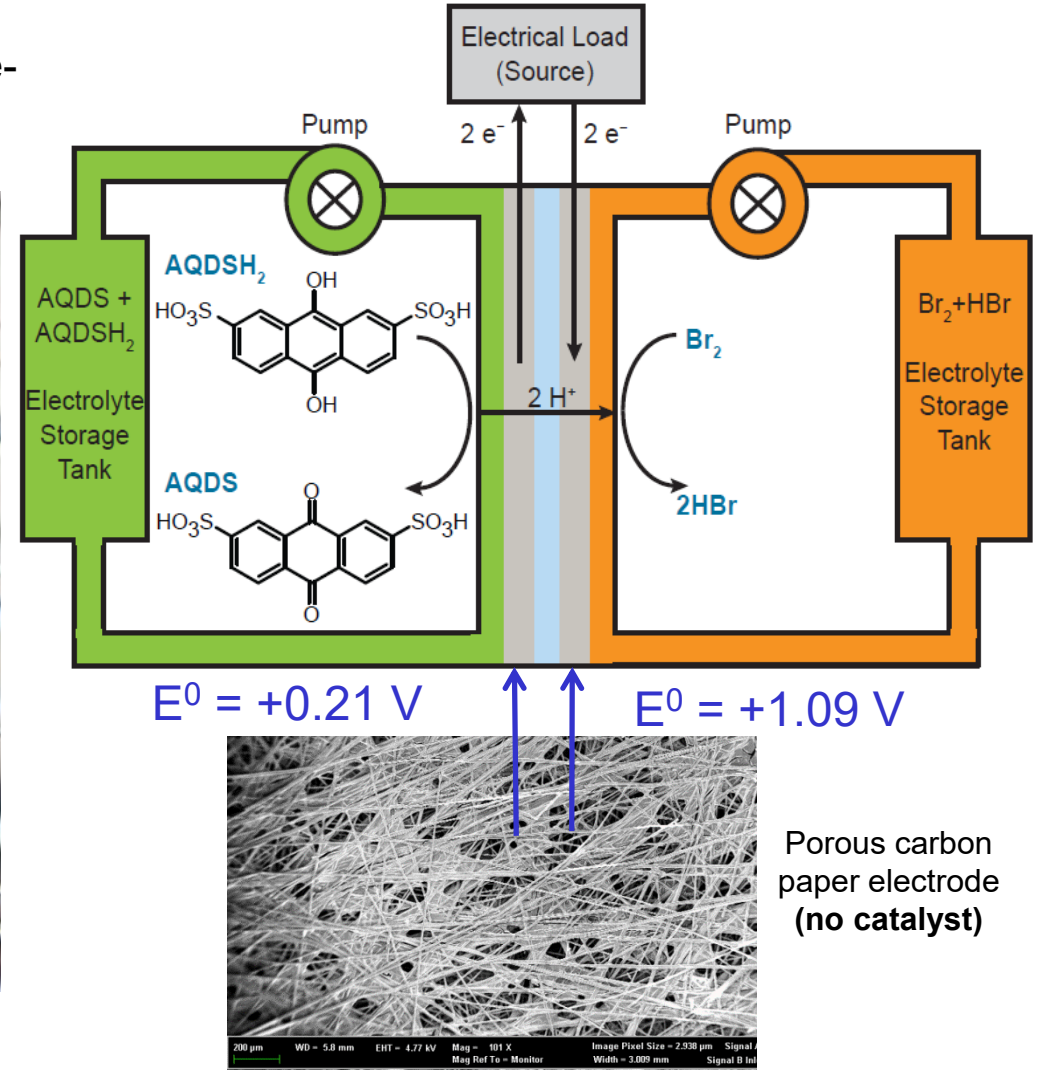
Anthraquinone Di-sulfonate (AQDS)



B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

Quinone-Bromide Flow Battery

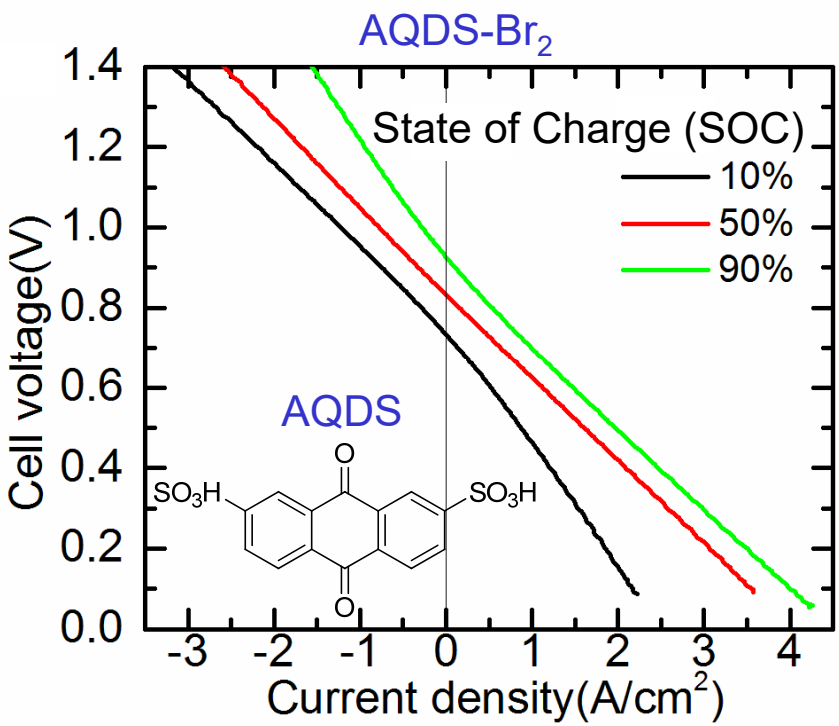
$$AQDSH_2 \underset{Red}{\overset{Ox}{\rightleftharpoons}} AQDS + 2H^+ + 2e^-$$

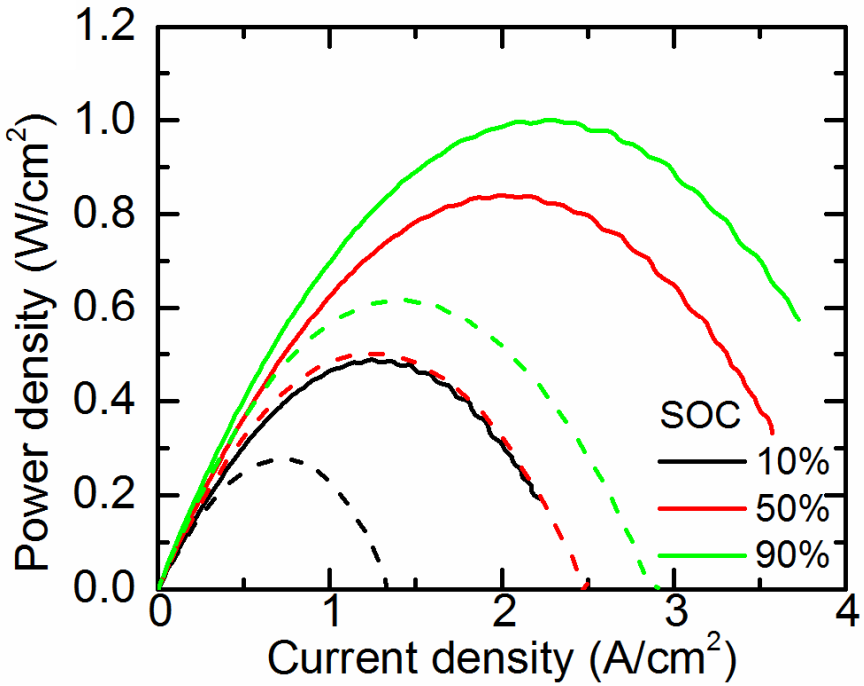


Porous carbon paper electrode **(no catalyst)**

B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

Recent AQDS-Bromide Cell Performance



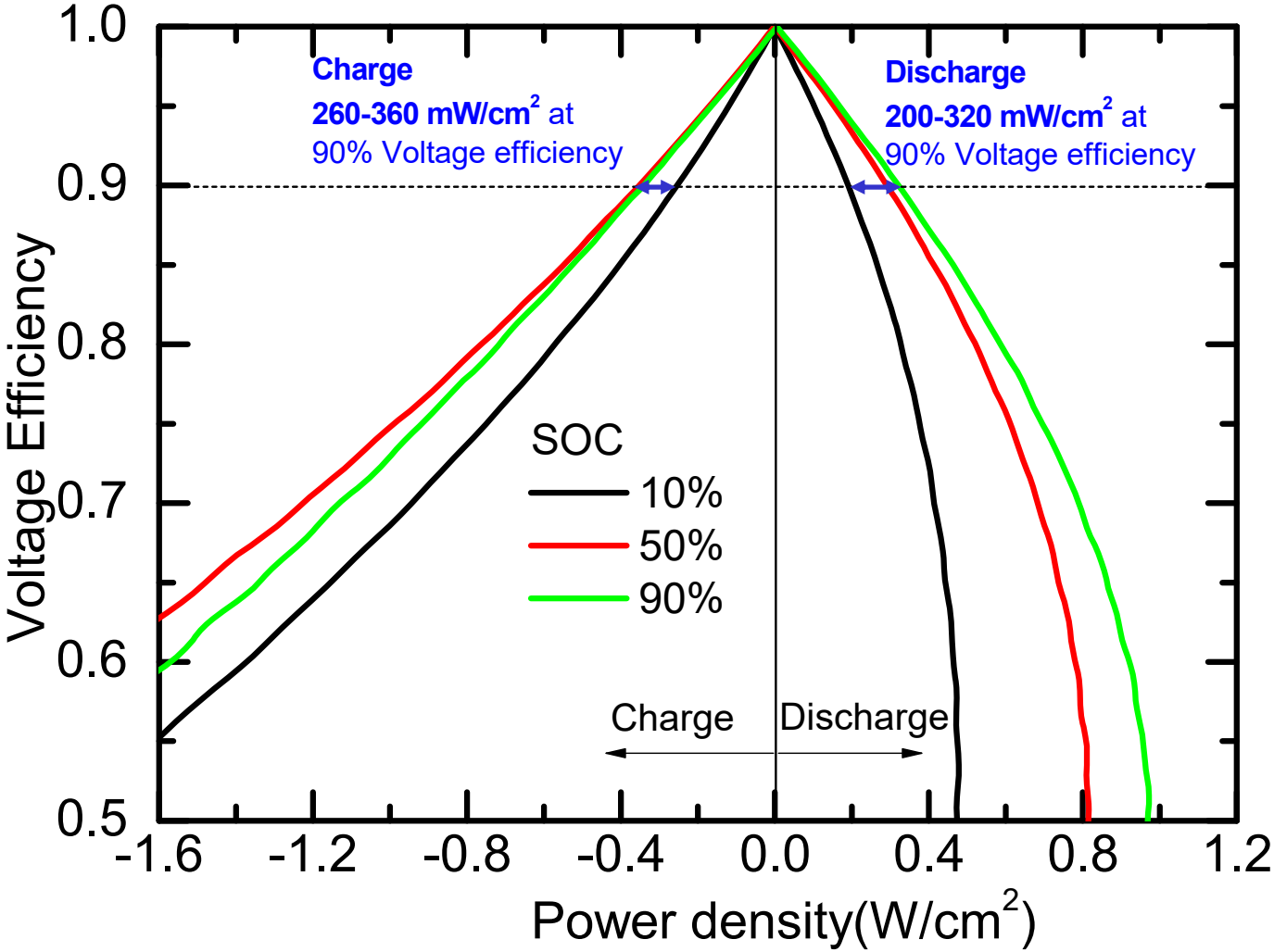


Temperature: 40 °C Flow Field: Interdigitated Posolyte: 3M HBr + 2M Br_2, 24 ml Flow rate: 200mL/min (poso)	Negolyte: 1 M AQDS + 1 M H_2SO_4, 20 ml Flow rate: 400mL/min (neg) Electrode: 2 cm^2, Baked SGL 10AA x 3 Membrane: Nafion 212, pre-treated

→spans decades of VRB development in 2 years

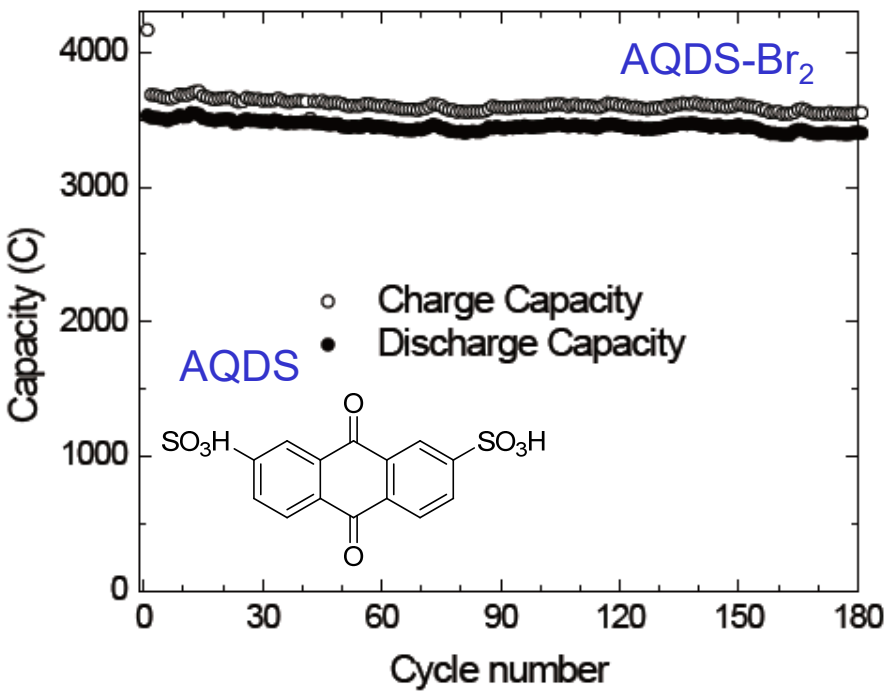
Q. Chen, M.R. Gerhardt, L. Hartle, and M.J. Aziz, "A quinone-bromide battery with 1 W/cm^2 power density", *J. Electrochem. Soc.* **163**, A5010 (2016), doi: 10.1149/2.0021601jes

Voltage Efficiency

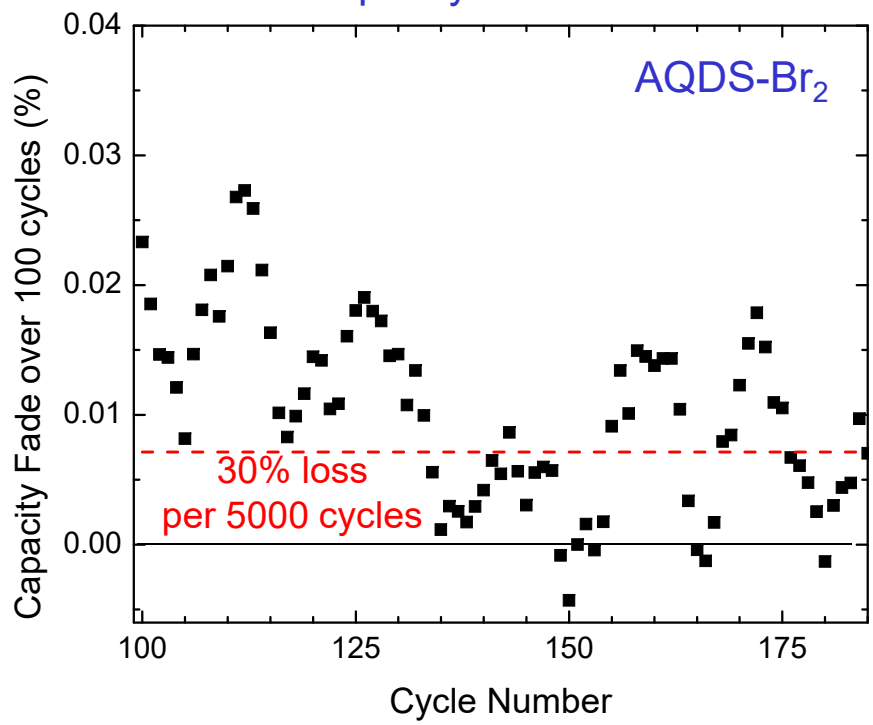


Recent AQDS-Bromine Cycling Performance

Charge and Discharge Capacity



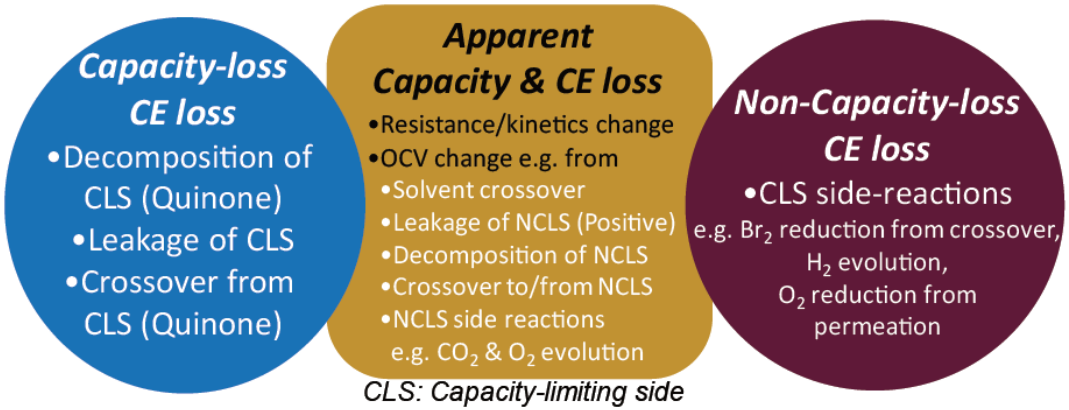
Capacity Fade Rate



Current Efficiency = (Coulombs of discharge) / (coulombs of charge)

Capacity Retention = (Coulombs of discharge) / (immediately preceding coulombs of discharge)

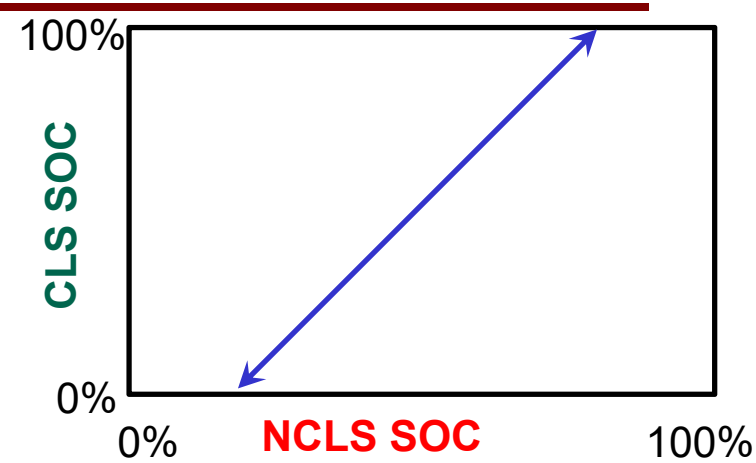
Capacity and Current Efficiency Loss Mechanisms

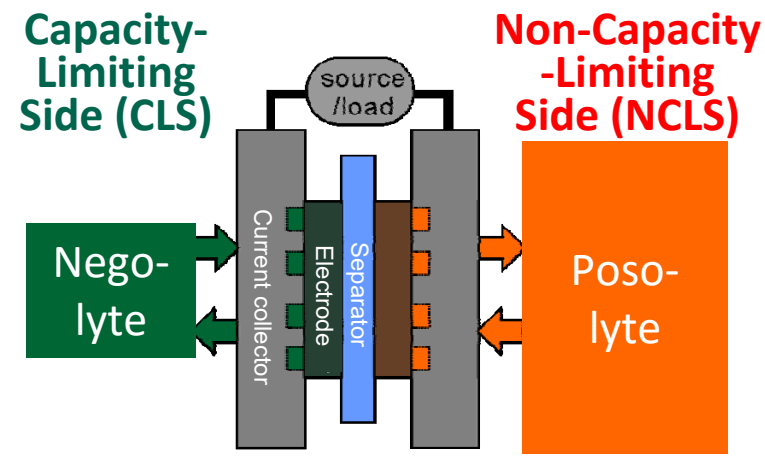


CLS: Capacity-limiting side
NCLS: Non-capacity-limiting side

	Mechanism	Equivalent current density (mA/cm^2)
1	Quinone decomposition	≤0.01
2	Quinone crossover	1.4×10^{-4}
3	Leakage (Dominates capacity loss)	0 – 0.12
4	Bromine crossover (Dominates CE loss)	1.2
5	Oxygen permeation	0.01
6	Hydrogen evolution	Negligible
	CAPACITY LOSS	0.01-0.12
	CURRENT EFFICIENCY LOSS	1.08

Q. Chen. L. Eisenach, and M.J. Aziz, "Cycling analysis of a quinone-bromide redox flow battery", *J. Electrochem. Soc.* **163**, A5057 (2016)





AQDS+2e$^-$+2H$^+$ → H_2AQDS
(1.0 M; 0.025 moles)
H_2SO_4 (1.0 M)

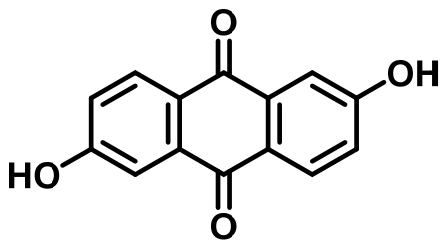
HBr → ½Br_2+e$^-$+H$^+$
(3.0 M; 0.36 moles)
Br_2
(0.5 M; 0.06 moles)

Halogen-Free Alkaline Flow Cell

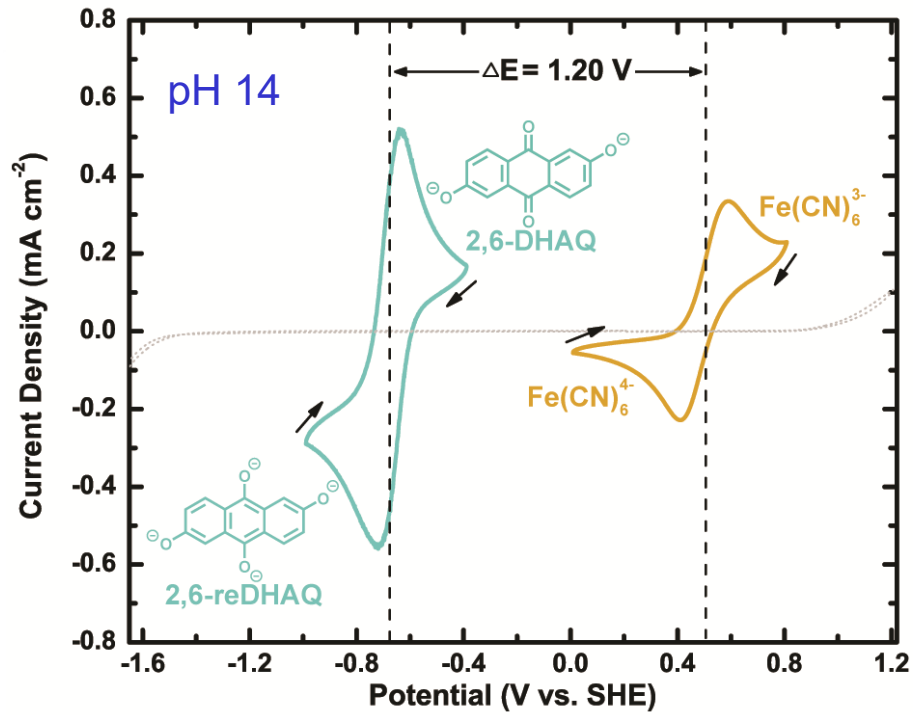
DHAQ-Fe(CN)$_6$

Recent results from new quinone negolyte 2,6-DHAQ
Against bromine-free "food additive"† posolyte Fe(CN)$_6$‡

DHAQ



2,6-dihydroxyanthraquinone



Kaixiang Lin, Q. Chen, M. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A. Valle, D. Hardee, R.G. Gordon, M.J. Aziz & M.P. Marshak, "Alkaline Quinone Flow Battery", *Science* **349**, 1529 (2015).

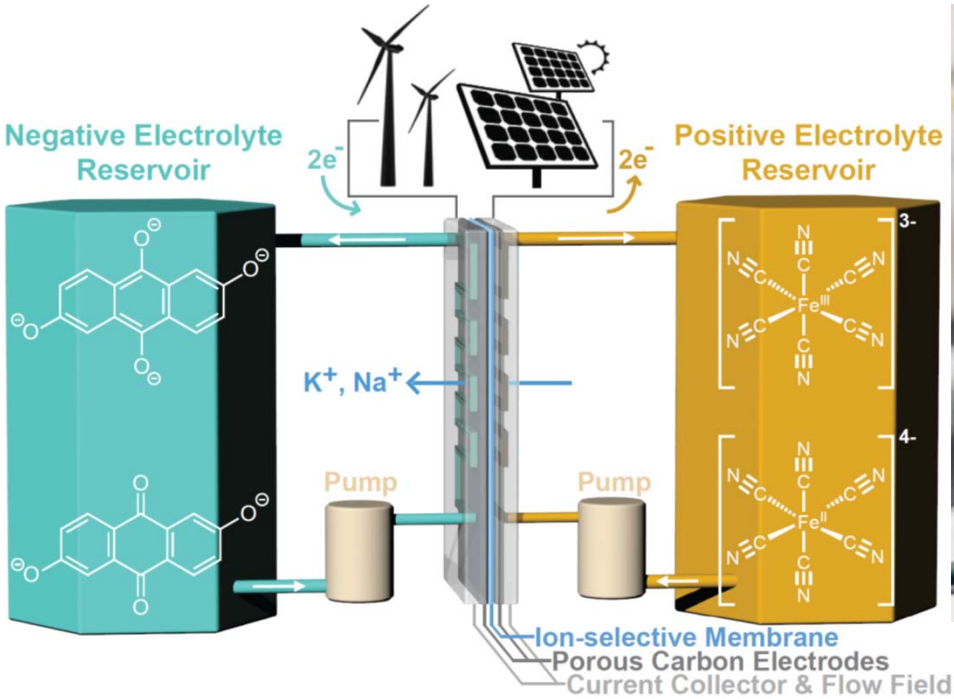
†Seventeenth Report of the Joint FAO/WHO Expert Committee on Food Additives. Report No. 539, *Wld Hlth Org. techn. Rep. Ser.* (539, World Health Organization, 1974).

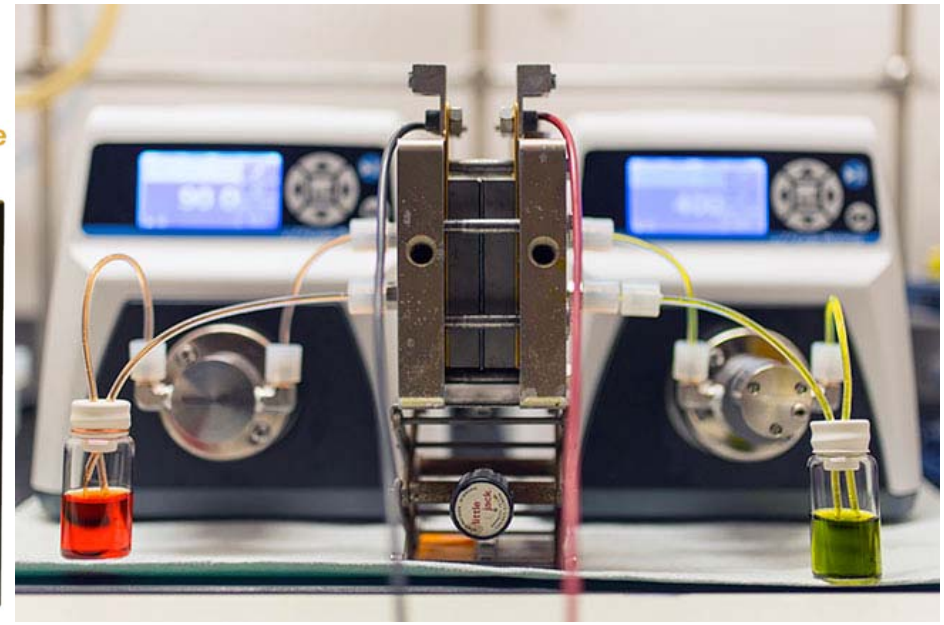
‡R.P. Hollandsworth, J . Zegarski and J .R. Selman, Zinc/ferricyanide battery development. Phase IV, SAND85-7195, Sandia National Laboratories, May 1985.

Halogen-Free Alkaline Flow Cell

DHAQ-$Fe(CN)_6$

Recent results from new quinone negolyte 2,6-DHAQ
Against bromine-free "food additive"† posolyte $Fe(CN)_6$‡





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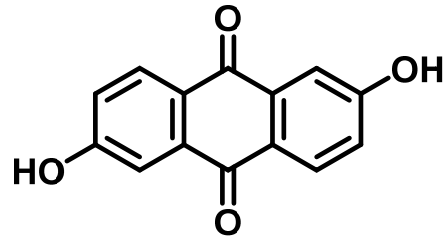
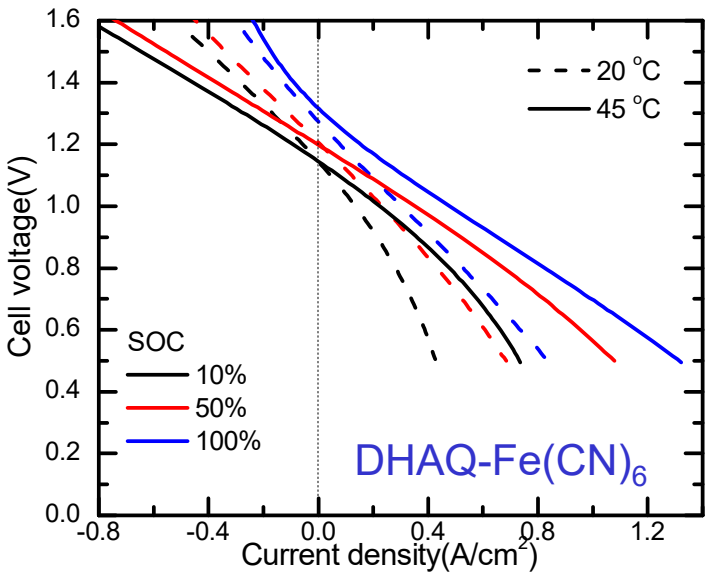
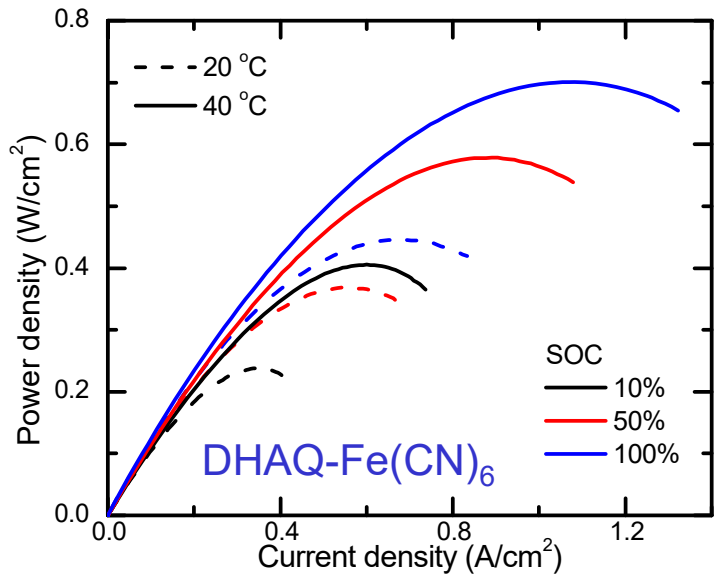
Alkaline Quinone Flow Battery

DHAQ



2,6-dihydroxyanthraquinone





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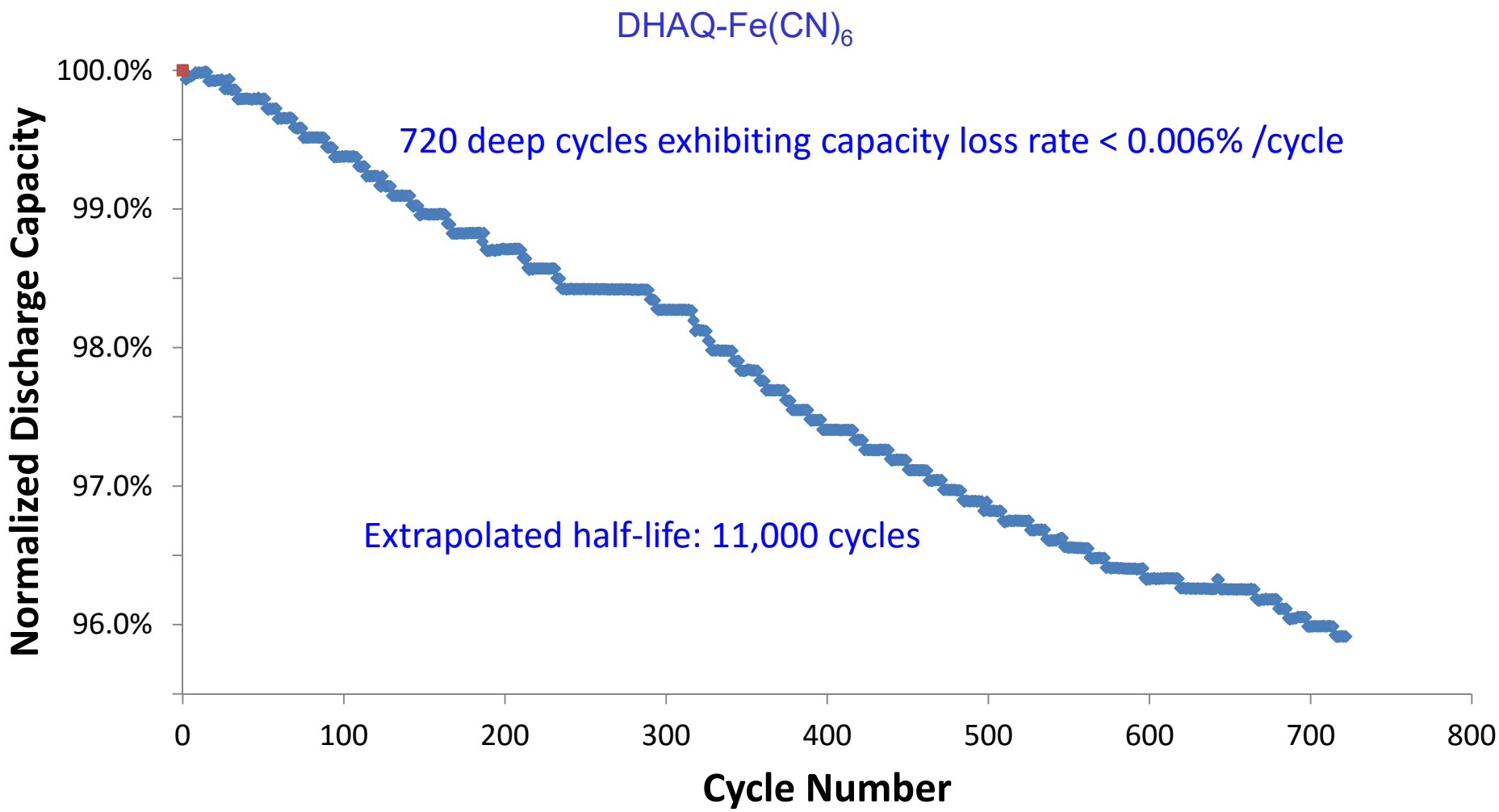
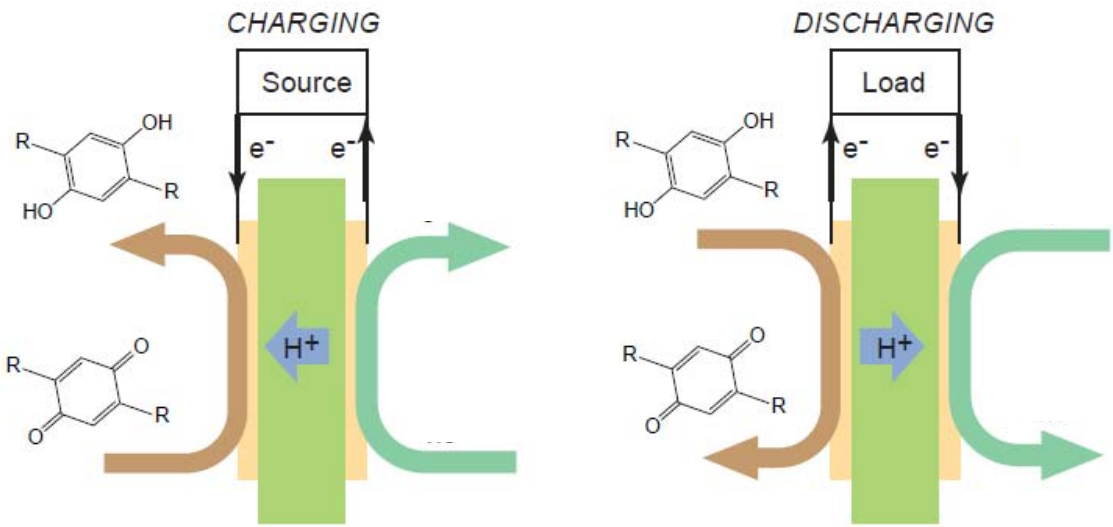
Robust Molecules



Andrew Wong

Quinones for Energy Storage

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low area/kW → low cost/kW
All-liquid storage:	Enables inexpensive BOS and high cycle life
Aqueous electrolyte:	Enables fireproof operation
Non-toxic:	Ideal for commercial, residential markets
Scalability:	Enables rapid chemistry scaleup
Tunability:	Enables performance improvements
Small organic molecules:	Enable inexpensive separator → low cost/kW



Quinones for Energy Storage

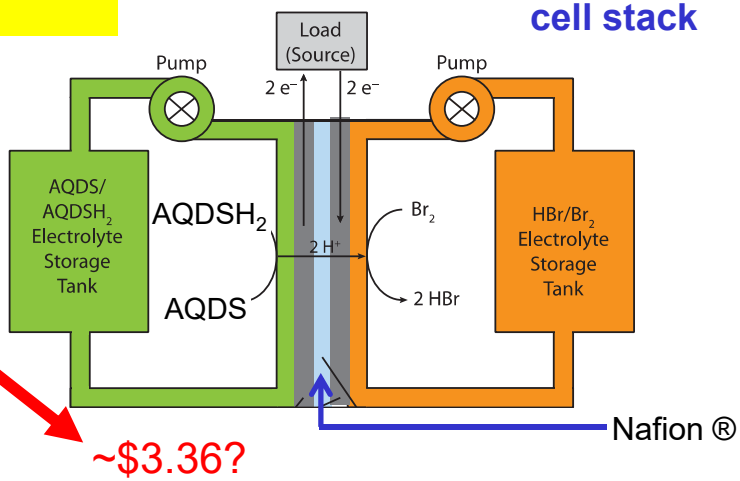
Low chemicals cost: Enables low cost/kWh

Cost of Chemicals Sets Floor on System Cost / kWh

Low chemicals cost: Enables low cost/kWh

$$\begin{bmatrix}\text{system}\\ \text{cost}\end{bmatrix} = \underbrace{\begin{bmatrix}\text{cost}\\ \text{per kWh}\end{bmatrix}}_{\text{energy storage chemicals and solvent}}\begin{bmatrix}\text{energy}\\ \text{capacity}\end{bmatrix} + \underbrace{\begin{bmatrix}\dfrac{\text{cost/area}}{\text{power/area}}\end{bmatrix}\begin{bmatrix}\text{power}\\ \text{capacity}\end{bmatrix}}_{\text{electrochemical cell stack}} + \begin{bmatrix}\text{BOS}\\ \text{cost}\end{bmatrix}$$

Compound	$/kg
Vanadium pentoxide (V_2O_5)	fluctu-ates
Anthraquinone	<4.74
Bromine	1.76



~$3.36?

Full Cell: Electrolytes	$/kWh
Anthraquinone with Bromine	~21

Quinones for Energy Storage

Low chemicals cost: Enables low cost/kWh

Rapid redox kinetics: Enable low area/kW → low cost/kW

Redox couple	k_0 [cm/s] (electrode material)
AQDS/$AQDSH_2$	7.2×10^{-3} (carbon)
Br_2/Br^-	5.8×10^{-4} (carbon)
Fe^{3+}/Fe^{2+}	2.2×10^{-5} (gold)
Cr^{3+}/Cr^{2+}	2×10^{-4} (mercury)
VO_2^+/VO^{2+}	3×10^{-6} (carbon)
V^{3+}/V^{2+}	4×10^{-3} (mercury)

Quinone kinetics on glassy carbon exceed those of most other battery redox couples

Quinones for Energy Storage

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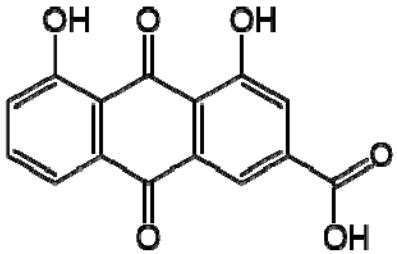

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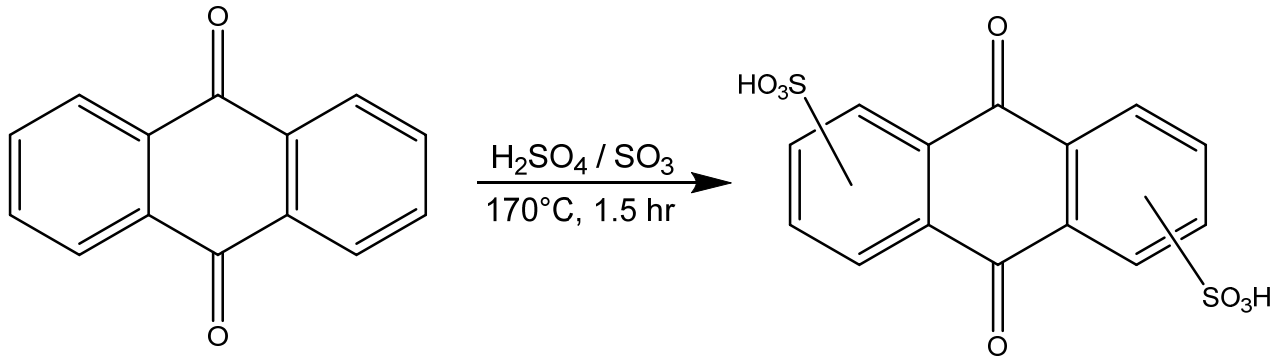
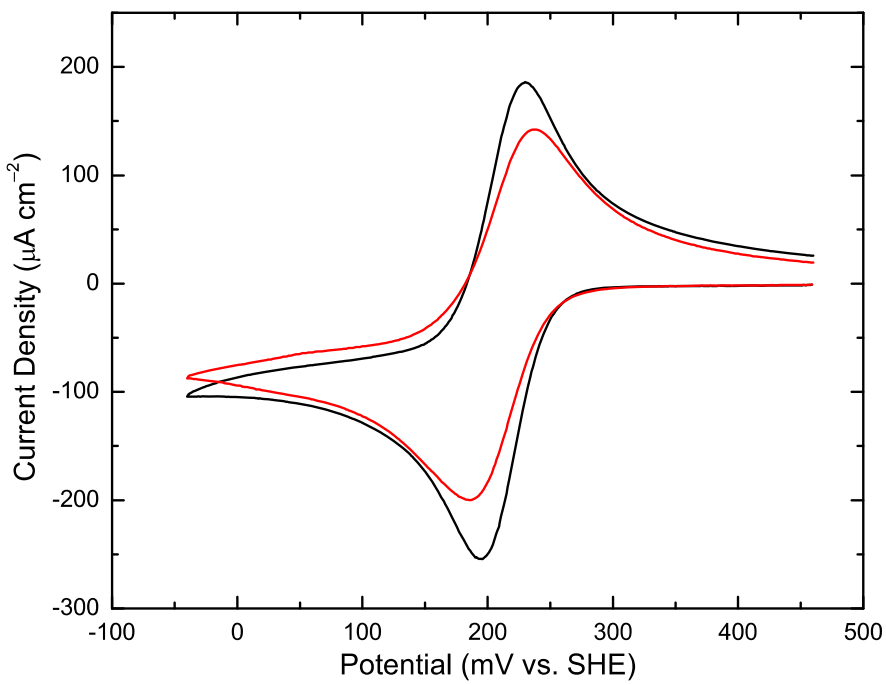
Scalability





Bulk synthesis of AQDS mixtures without purification leads to nearly identical cell performance.

Quinones for Energy Storage

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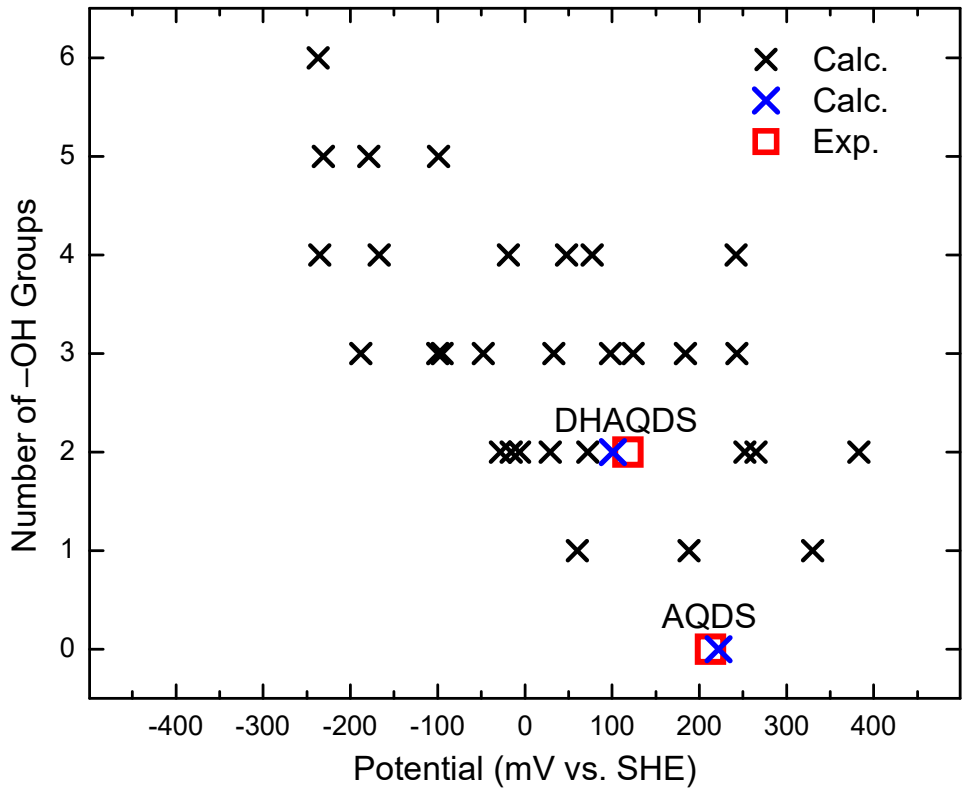
Tunability:	Enables performance improvements

Computational Screening

Electron-donating –OH groups lower the reduction potential.



Changwon Suh, Süleyman Er, Michael Marshak, Alán Aspuru-Guzik, "Computational design of molecules for an all-quinone redox flow battery", *Chem. Sci.* **6**, 885 (2015)

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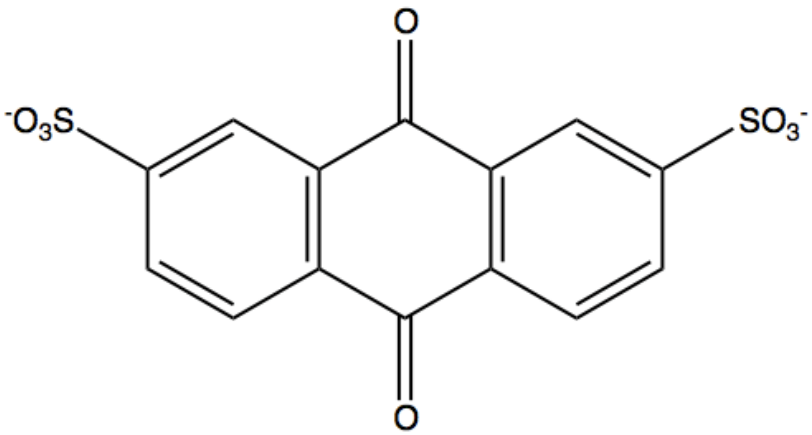
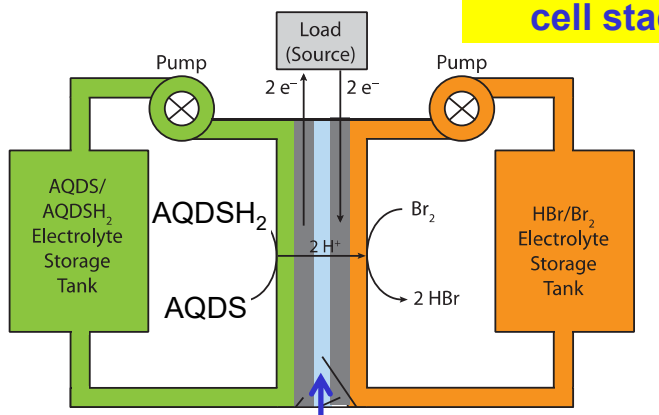
10 Angstroms



Cost of Nafion® Dominates System Cost / kW

$$\begin{bmatrix}\text{system}\\ \text{cost}\end{bmatrix} = \underbrace{\begin{bmatrix}\text{cost}\\ \text{per kWh}\end{bmatrix}}_{\text{energy storage chemicals and solvent}}\begin{bmatrix}\text{energy}\\ \text{capacity}\end{bmatrix} + \underbrace{\begin{bmatrix}\text{cost/area}\\ \text{power/area}\end{bmatrix}\begin{bmatrix}\text{power}\\ \text{capacity}\end{bmatrix}}_{\text{electrochemical cell stack}} + \begin{bmatrix}\text{BOS}\\ \text{cost}\end{bmatrix}$$



Nafion ® ~3/4 of the power stack cost

Table 1 Component cost factors for flow batteries

Material	Year 2014 cost, $ m^{-2}	Reference
Graphite flow field plate	55	51
Stainless-steel flow field plate	40	58 and 59
Carbon-fiber felt/paper electrodes	70	51
Fluorinated ion-exchange membrane	500	51
Polyolefin nanoporous separator	10	51
Fames, seals, and manifolds total	6	Est.

R.M. Darling, K.G. Gallagher, J.A. Kowalski, S. Ha, and F. Brushett, "Pathways to low-cost electrochemical energy storage: A comparison of aqueous and nonaqueous flow batteries", *Energy & Enviro. Sci.* **7**, 3459 (2014)

Prospects for $120/kWh

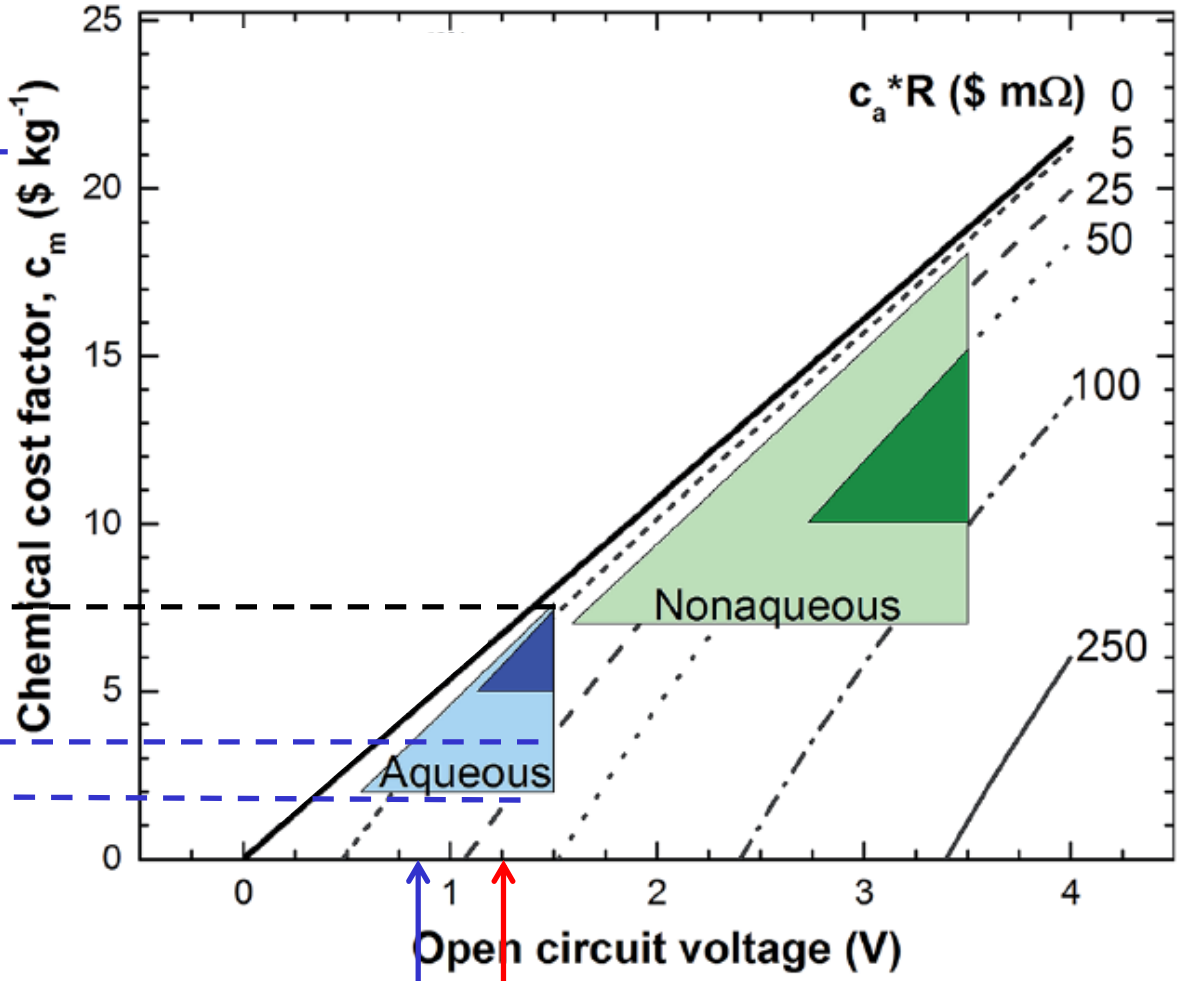
Assuming
100 g/(mol e-)

anthraquinone
2 e-/molecule;
104 g/(mol e-)

$7.50/kg

Current prices:
Anthraquinone: ~$3.36/kg$_{eff}$
Bromine: $1.76/kg

$Na_4Fe(CN)_6$; 1 e-/molecule;
304 g/(mol e-)
$1.20/kg; $3.64/kg$_{eff}$



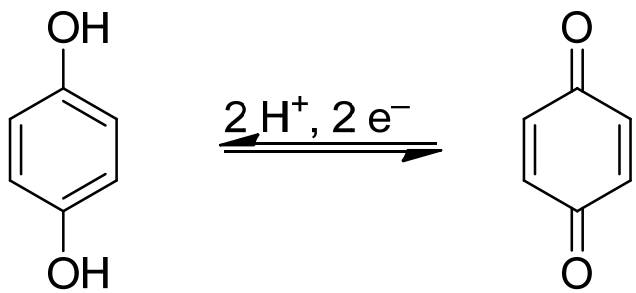
$18
$30

acid cell
alkaline cell

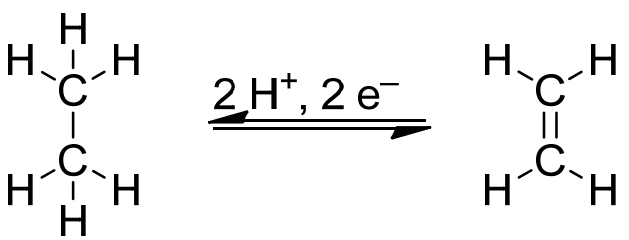
R.M. Darling, K.G. Gallagher, J.A. Kowalski, S. Ha, and F. Brushett, "Pathways to low-cost electrochemical energy storage: A comparison of aqueous and nonaqueous flow batteries", *Energy & Enviro. Sci.* **7**, 3459 (2014)

Are quinones special?

"[Quinones] seem to involve a different kind of process from such irreversible reductions as the hydrogenation of ethylene derivatives, or the reduction of aldehydes, ketones, and nitriles."



hydroquinone benzoquinone



ethane ethylene

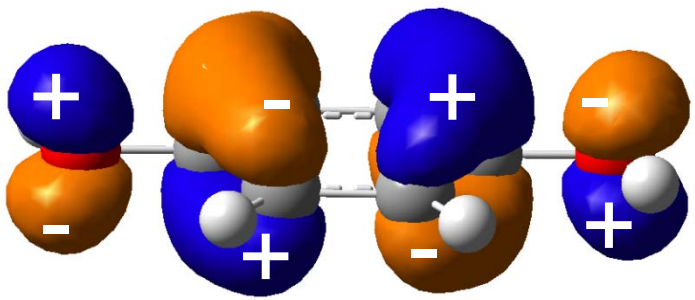
J. B. Conant

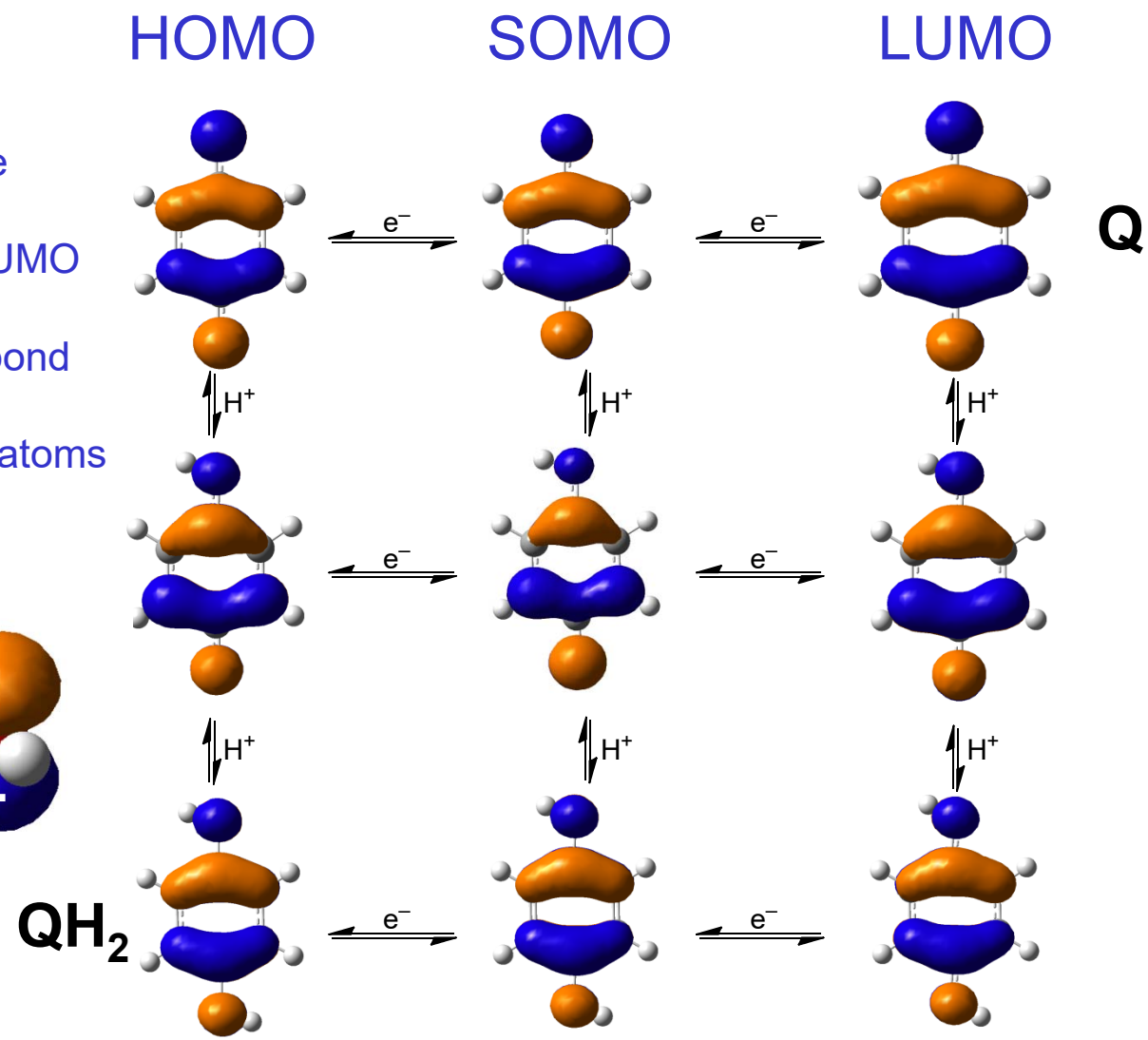
L. F. Fieser

J.B. Conant, H.M. Kahn, L.F. Fieser, S.S. Kurtz,, *J. Am. Chem. Soc.* **44**, 1382 (1922).

Redox-Active Orbital of Quinone

- Hydroquinone HOMO is π-type
- Virtually identical to quinone LUMO
- Zero electron density on O-H bond
- Near zero motion of any other atoms

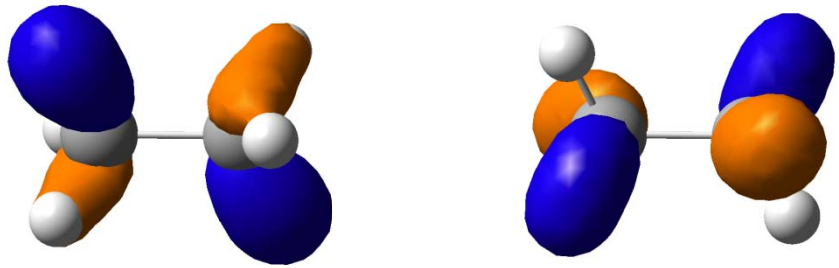




DFT Calculations using Gaussian03; B3LYP functional / TZVP basis set (Michael Marshak)

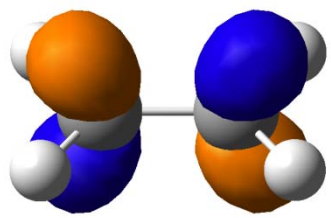
Ethane/Ethylene Orbitals

C_2H_6



Degenerate HOMO of Ethane consists of C−H σ bonds

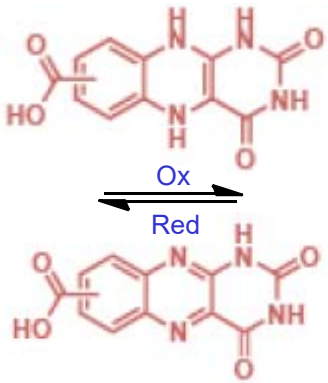
C_2H_4



LUMO of Ethylene is the π^* (anti-bond)

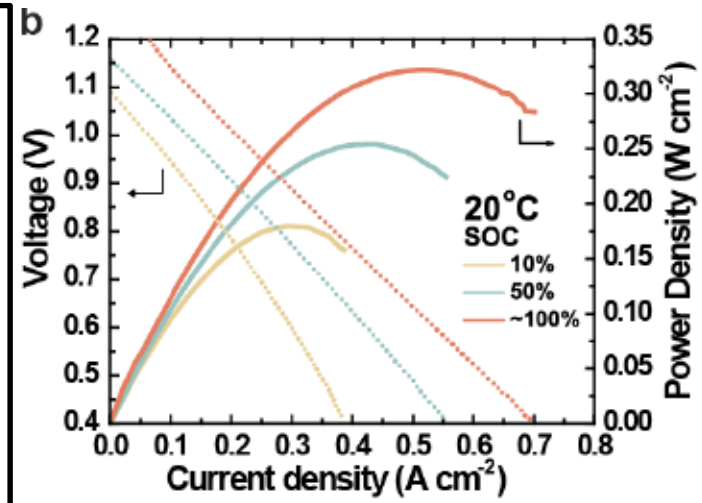
Beyond Quinones: Aza-aromatics for Flow Batteries

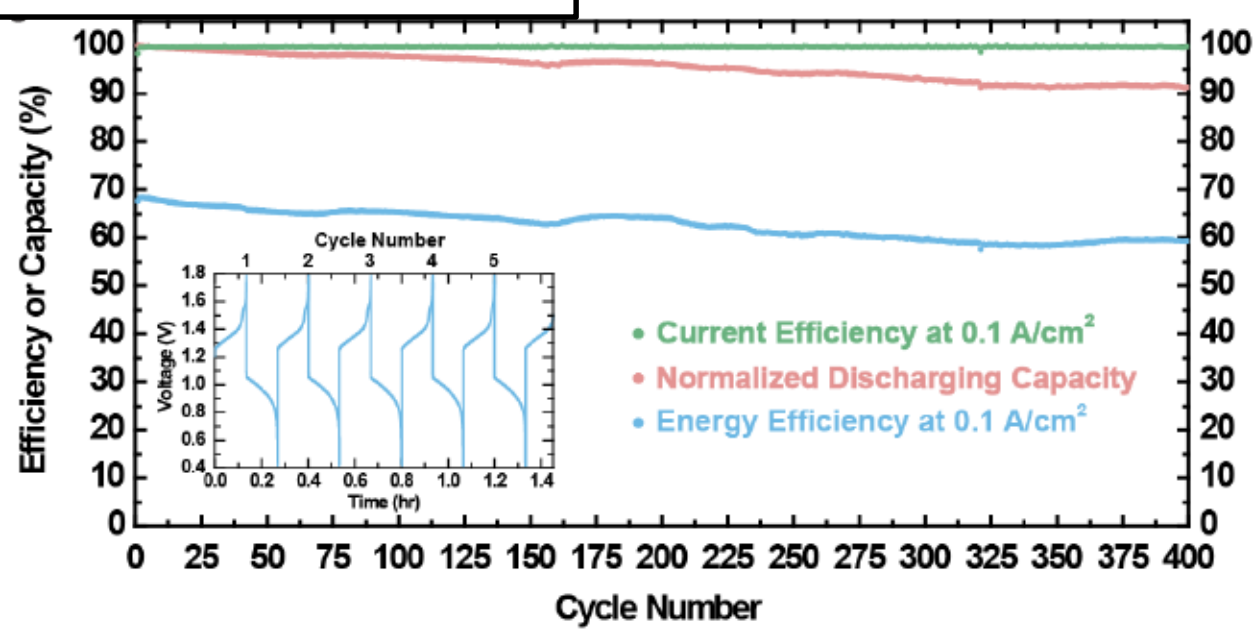
Negative couple:
Alloxazine 7/8-carboxylic acid (ACA)
Solubility: 4 mol e^-/L
= 107 Ah/L



Positive couple:
$Fe(CN)_6$

- Average current efficiency over **400 cycles** is > **99.7%** (negligible side reactions).
- Cell showed **5% capacity loss over 400 cycles** or ~ 0.013% capacity loss per cycle
- Peak power density at R.T. approaches **1/3 W cm^{-2}**





K. Lin, R. Gómez-Bombarelli, E. Beh, L. Tong, Q. Chen, A. Valle, A. Aspuru-Guzik, R.G. Gordon, M.J. Aziz, "Vitamin-Inspired Redox Flow Battery", *Nature Energy* (accepted)

Where Do We Stand?

1 Electrolyte Materials

- Decent voltage: >1 V
- High chemical stability
- Decent solubility: >2 M electrons
- Environmentally friendly and cheap chemistry with low corrosivity

3 Separator

- High mechanical & chemical stability
- Low resistance
- Low crossover
- Low cost

2 Electrochemistry

- Rapid redox kinetics
- Electrochemically stable
- Negligible side reactions (e.g. H_2 or O_2 evolution)

4 Engineering

- Optimized electrode architecture for high current density
- Optimized flow field for homogeneity, low pressure drop
- Inexpensive fabrication

What Do We Need?

1 Electrolyte Materials

- Decent voltage: >1 V
- High chemical stability
- Decent solubility: >2 M electrons
- Environmentally friendly and cheap chemistry with low corrosivity

2 Electrochemistry

- Rapid redox kinetics
- Electrochemically stable
- Negligible side reactions (e.g. H_2 or O_2 evolution)

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4 Engineering

- Optimized electrode architecture for high current density
- Optimized flow field for homogeneity, low pressure drop
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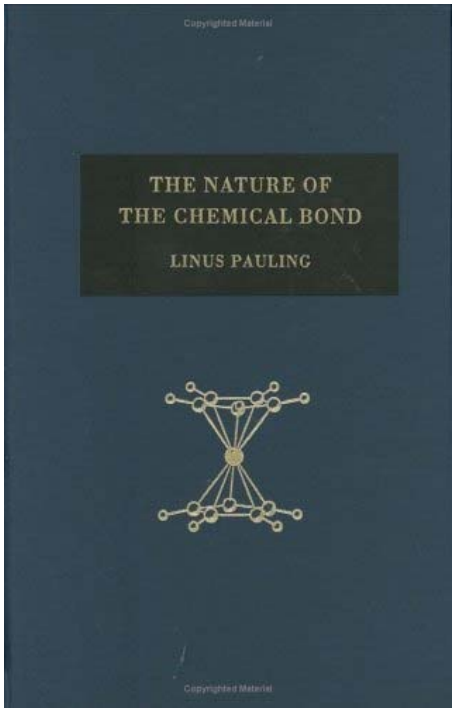
A HIGH-POTENTIAL MOLECULE WITH ALL THE ATTRIBUTES OF THE LOW-POTENTIAL MOLECULES

A HIGH-PERFORMANCE, LOW-COST SEPARATOR

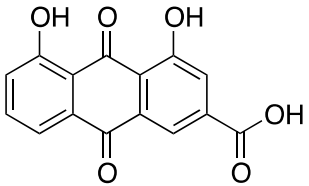
OPTIMIZED ELECTRODE...

Outlook

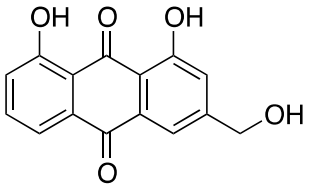


- Cost, tunability and stability of quinones make them competitive for stationary electrical energy storage
- High power density, low cost quinone-bromide Redox Flow Batt suitable for utility & industrial applications
- High voltage, low toxicity alkaline quinone-ferrocyanide RFB more suitable for residential, commercial use
- Drop-in replacement for more mature systems?
- There is still room for improvement

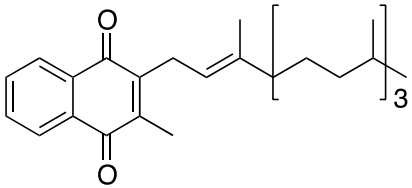
Quinones In Nature



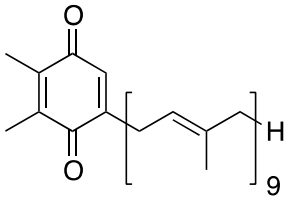
Rhein, found in Rhubarb



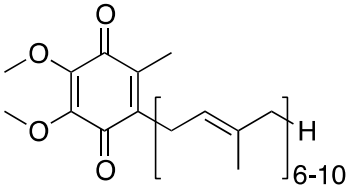
Emodin, found in Aloe Vera



Vitamin K_1, part of the electron transport chain in photosystem I



Plastoquinone, accepts electrons from chlorophyll in photosystem II



Coenzyme Q10, participates in the electron-transport chain in cellular respiration/reduction of O_2

Harvard Department of Chemistry & Chemical Biology

HARVARD John A. Paulson School of Engineering and Applied Sciences

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Top to bottom, left to right:
Andrew Wong, Prof. Mauricio Salles, Alvaro Valle, Dr. Junling Huang
Dhruv Pillai, Dr. Michael Marshak, Dr. Rafa Gómez-Bombarelli, Liuchuan Tong
Lauren Hartle, Dr. Sungjin "James" Kim, Dr. Changwon Suh,
Kaixiang Lin, Michael Gerhardt, Dr. Eugene Beh
Dr. Qing Chen, Louise Eisenach, Jennifer Wei
Prof. Michael Aziz, Prof. Roy Gordon, Prof. Alán Aspuru-Guzik
Inset: **Dr. Brian Huskinson**

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