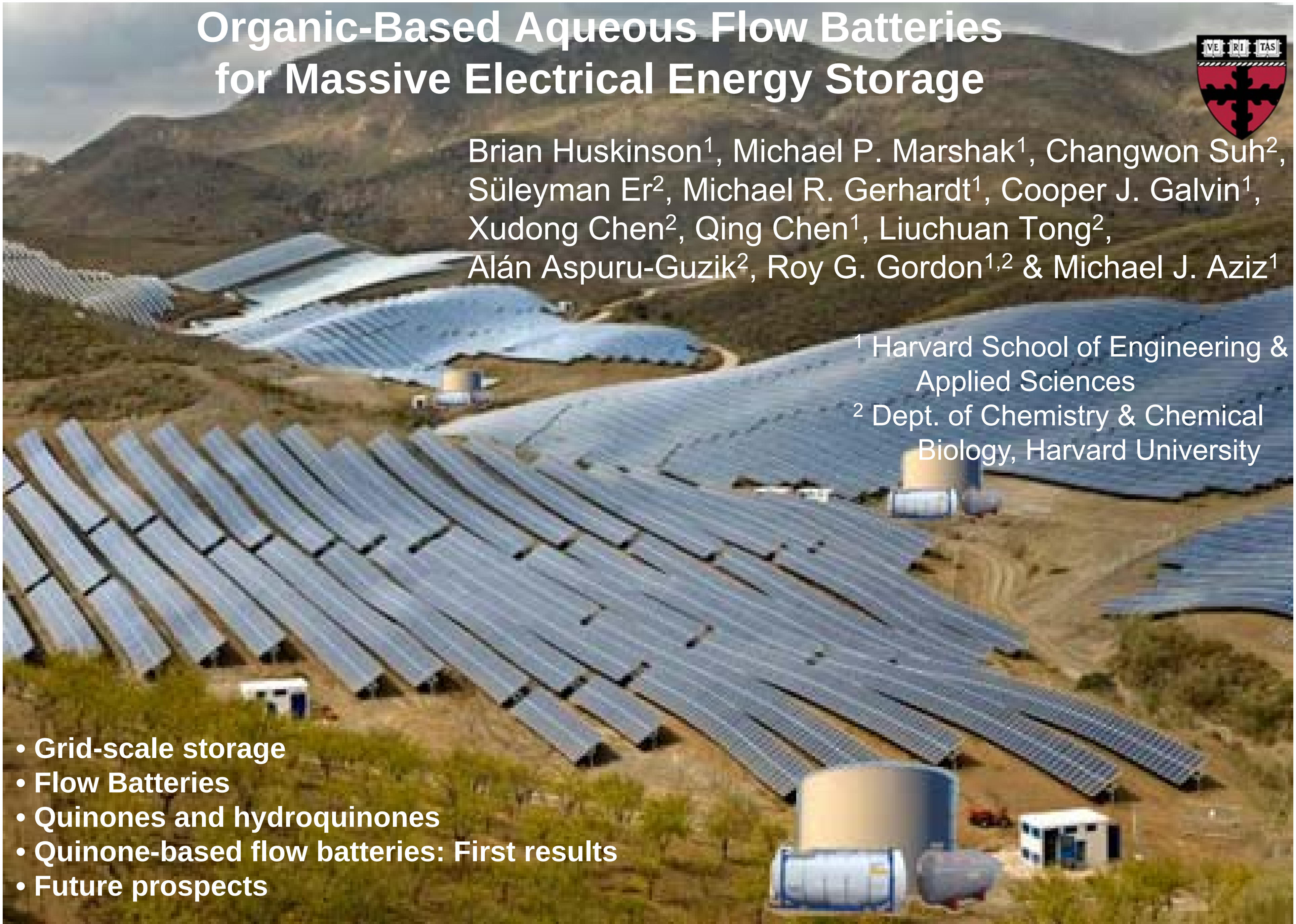
Organic-Based Aqueous Flow Batteries for Massive Electrical Energy Storage

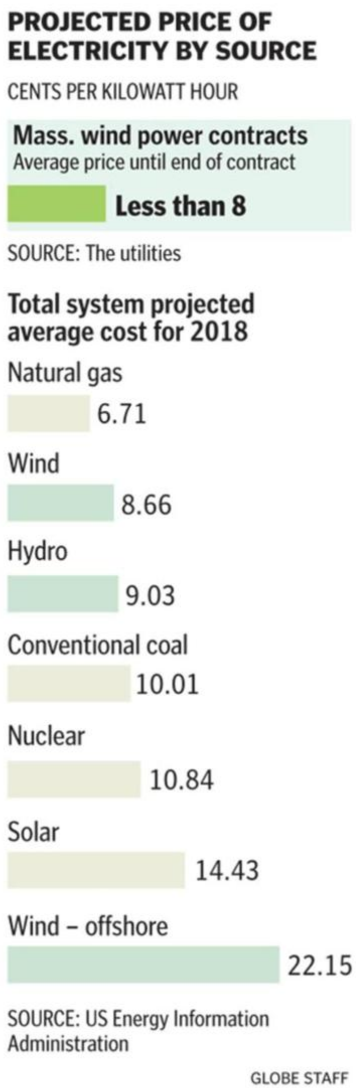


Brian Huskinson[1], Michael P. Marshak[1], Changwon Suh[2], Süleyman Er[2], Michael R. Gerhardt[1], Cooper J. Galvin[1], Xudong Chen[2], Qing Chen[1], Liuchuan Tong[2], Alán Aspuru-Guzik[2], Roy G. Gordon[1,2] & Michael J. Aziz[1]

[1] Harvard School of Engineering & Applied Sciences
[2] Dept. of Chemistry & Chemical Biology, Harvard University

- **Grid-scale storage**
- **Flow Batteries**
- **Quinones and hydroquinones**
- **Quinone-based flow batteries: First results**
- **Future prospects**

Wind Power Becomes Competitive



The Boston Globe **Business**

Wind power now competitive with conventional sources

Contracts would bring savings

By Erin Ailworth | GLOBE STAFF SEPTEMBER 23, 2013

The state's biggest utilities, in a milestone for New England's wind power industry, have signed long-term contracts to buy wind-generated electricity at prices below the costs of most conventional sources, such as coal and nuclear plants.

The contracts, filed jointly Friday with the Department of Public Utilities, represent the largest renewable energy purchase to be considered by state regulators at one time. If approved, the contracts would eventually save customers between 75 cents and $1 a month, utilities estimated.

"This proves that competitively priced renewable power exists and we can get it, and Massachusetts can benefit from it," said Robert Rio, a spokesman for Associated Industries of Massachusetts, a trade group that represents some of the state's biggest electricity users.

The utilities — National Grid, Northeast Utilities, and Unitil Corp. — would buy 565 megawatts of electricity from six wind farms in Maine and New Hampshire, enough to power an estimated 170,000 homes.

... initial reaction to the price — on average, less than 8 cents per kilowatt hour? "Wow." ...

Boston Globe 9/23/2013, http://www.bostonglobe.com/business/2013/09/22/suddenly-wind-competitive-with-conventional-power-sources/g3RBhfV440kJwC6UyVCjhI/story.html

Electricity Prices Go Negative (Europe)

10/12/2013

The Economist | World politics | Business & finance | Economics | Science & technology | Culture

European utilities

How to lose half a trillion euros

Europe's electricity providers face an existential threat

Oct 12th 2013 | From the print edition

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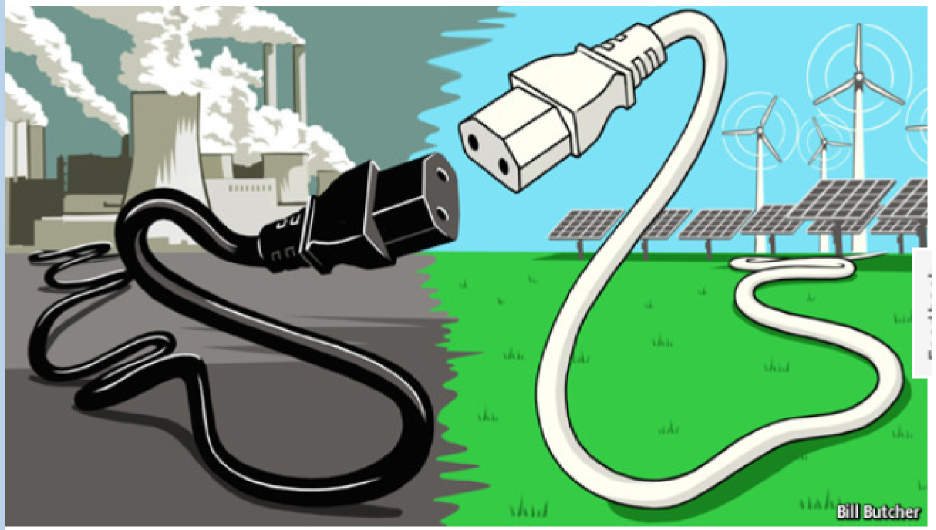
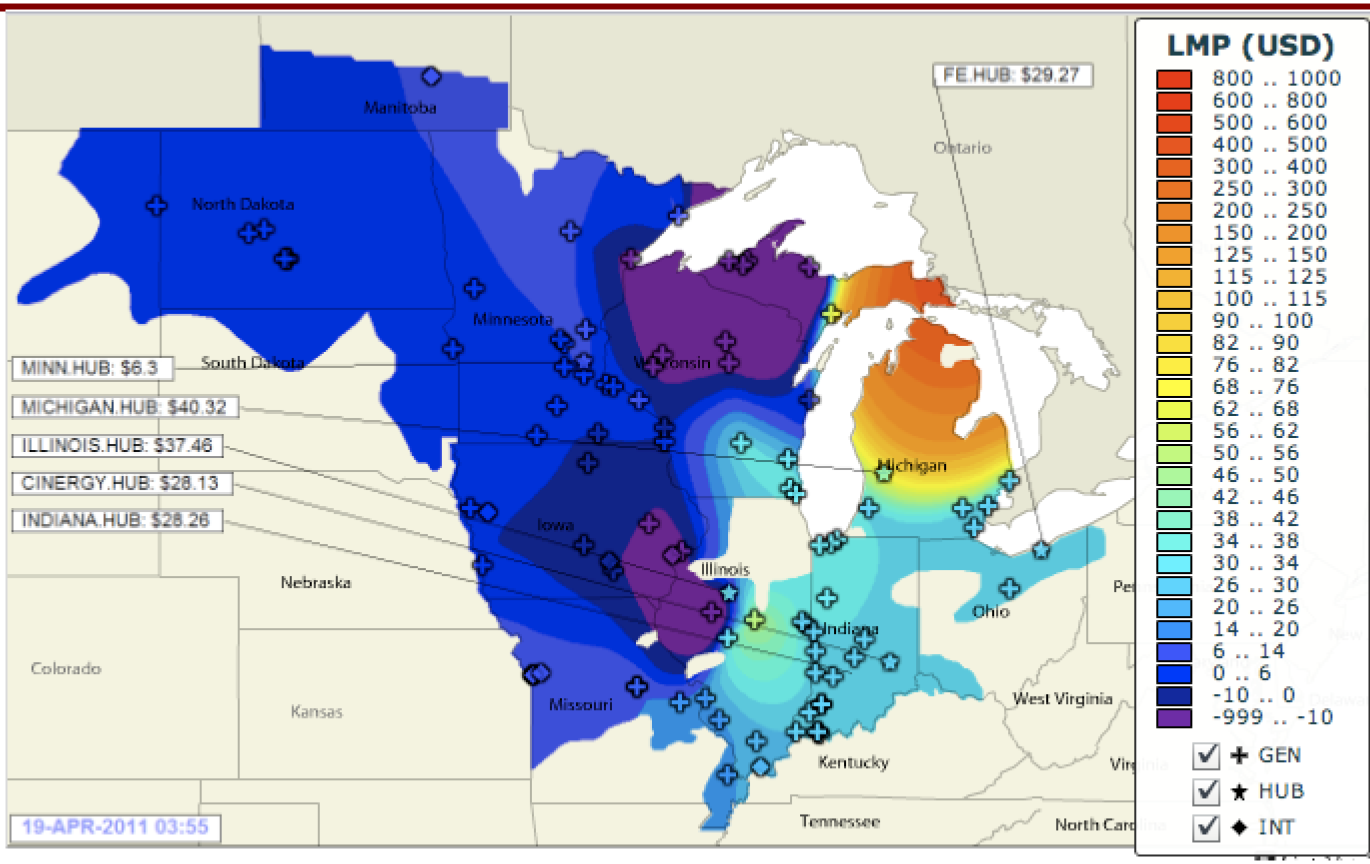


ON JUNE 16th something very peculiar happened in Germany's electricity market. The wholesale price of electricity fell to minus €100 per megawatt hour (MWh). That is, generating companies were having to pay the managers of the grid to take their electricity. It was a bright, breezy Sunday. Demand was low. Between 2pm and 3pm, solar and wind generators produced 28.9 gigawatts (GW) of power, more than half the total. The grid at that time could not cope with more than 45GW without becoming unstable. At the peak, total generation was over 51GW; so prices went negative to encourage cutbacks and protect the grid from overloading.

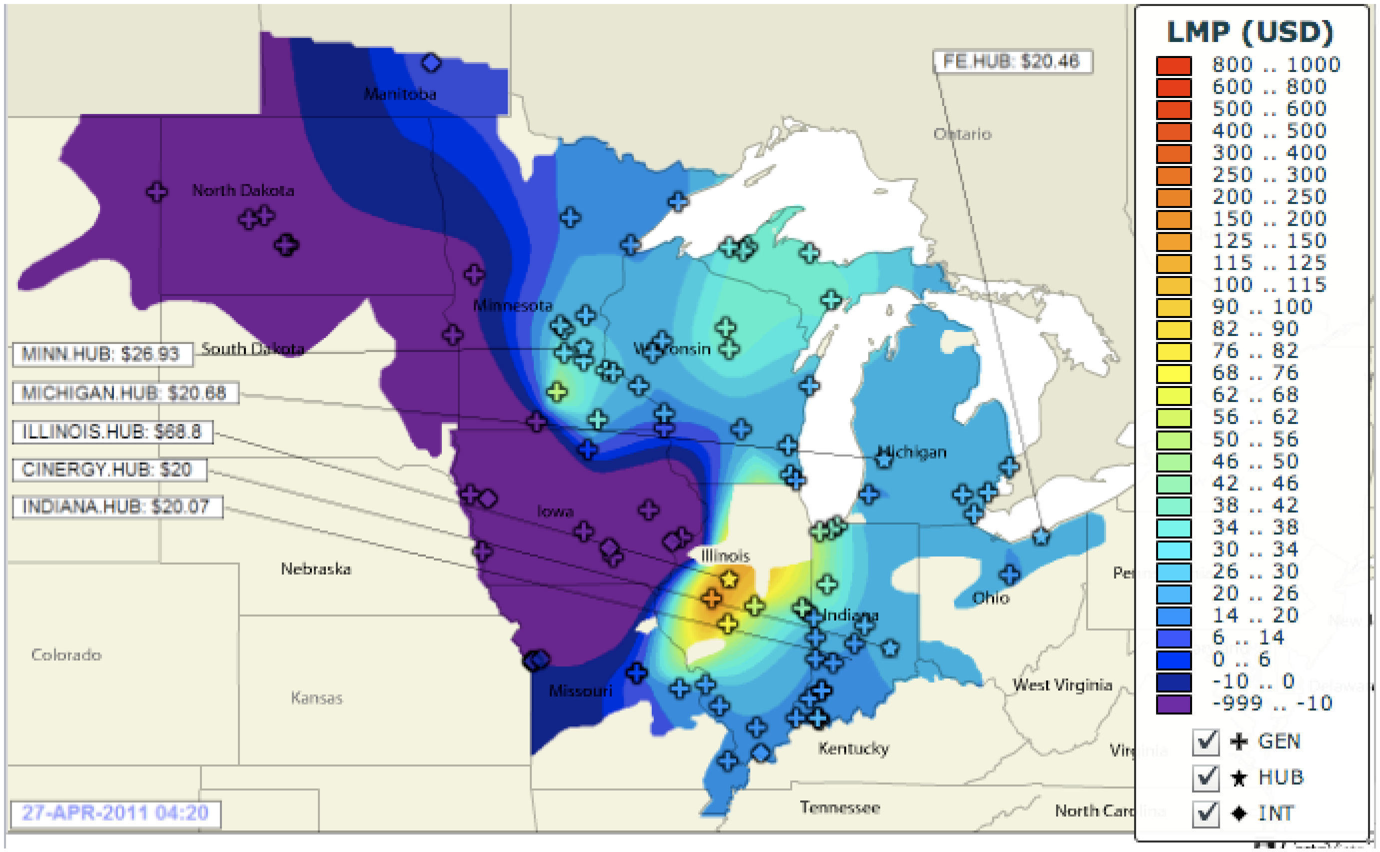
Electricity Prices Go Negative (US)



Slide courtesy of Prof. George Baker, HBS

https://www.misoenergy.org/LMPContourMap/MISO_MidWest.html

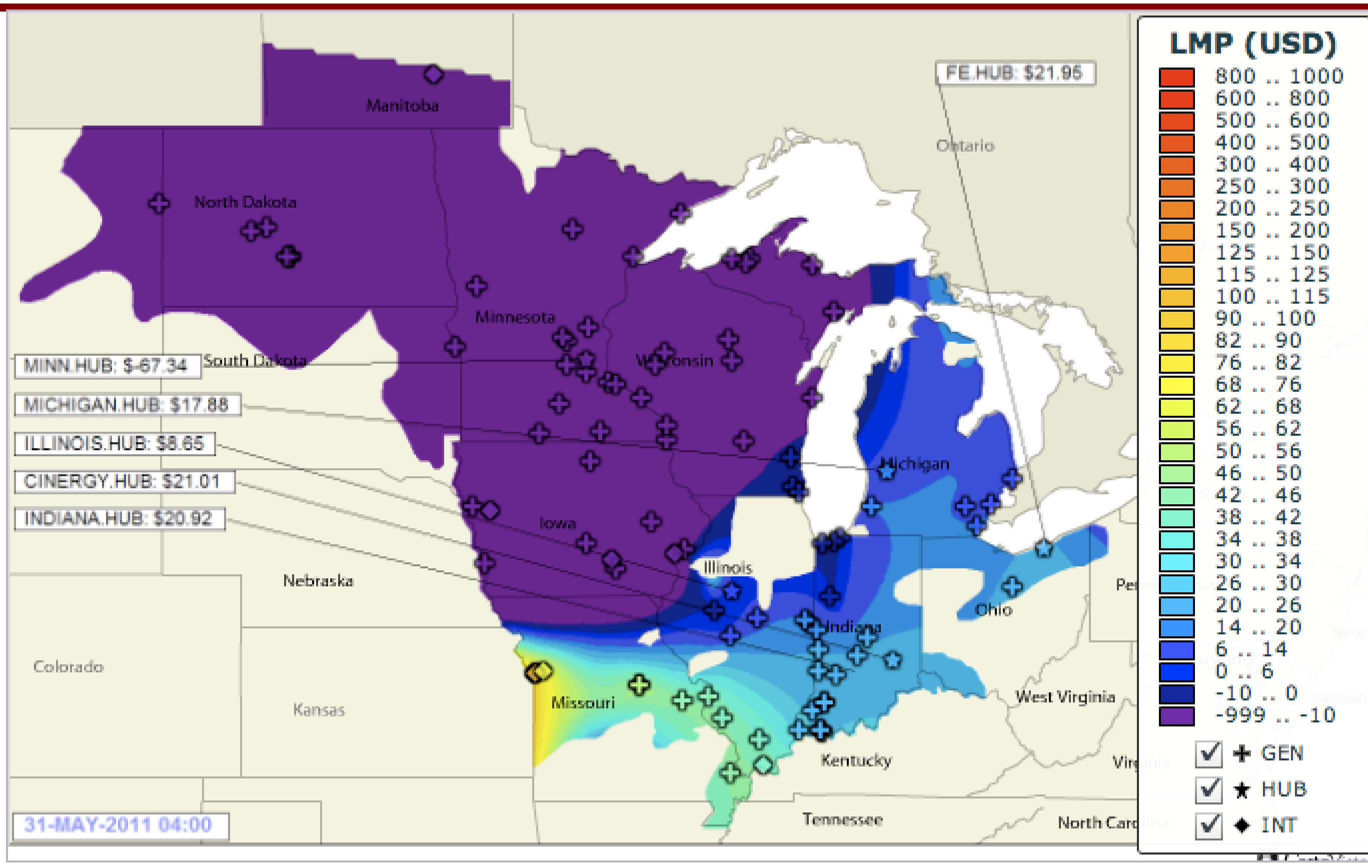
Electricity Prices Go Negative (US)



Slide courtesy of Prof. George Baker, HBS

https://www.misoenergy.org/LMPContourMap/MISO_MidWest.html

Electricity Prices Go Negative (US)



Slide courtesy of Prof. George Baker, HBS

https://www.misoenergy.org/LMPContourMap/MISO_MidWest.html

Intermittency Causes California to Require Storage

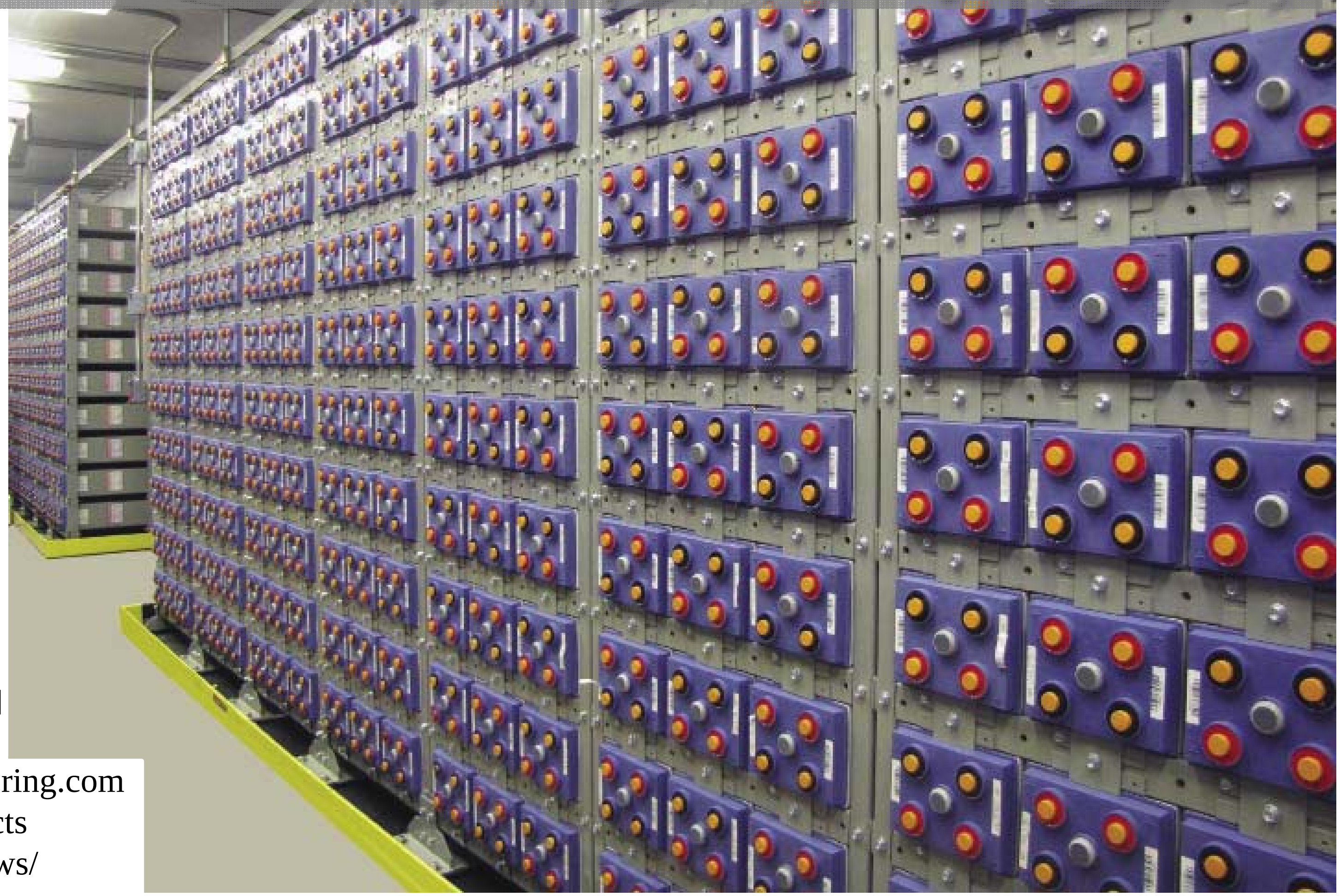
Greenwire The Leader in Energy and Environmental Policy News

START A TRIAL NOW. CLICK HERE!

10/17/2013

California adopts energy storage mandate for major utilities

California today became the first state in the country to require utilities to invest in energy storage, a move...



USA electric power
(Dec. 2013):

1100 GW_e gen. capacity

24.6 GW (2.3%) storage:
= 23.37 GW PHES,
+1.23 GW other storage

Enersys Nickel-Cadmium
+ Valve-regulated Lead-Acid
1 MWh, 1.5 MW
http://www.windpowerengineering.com
/featured/business-news-projects
/improving-grid-lots-stored-mws/

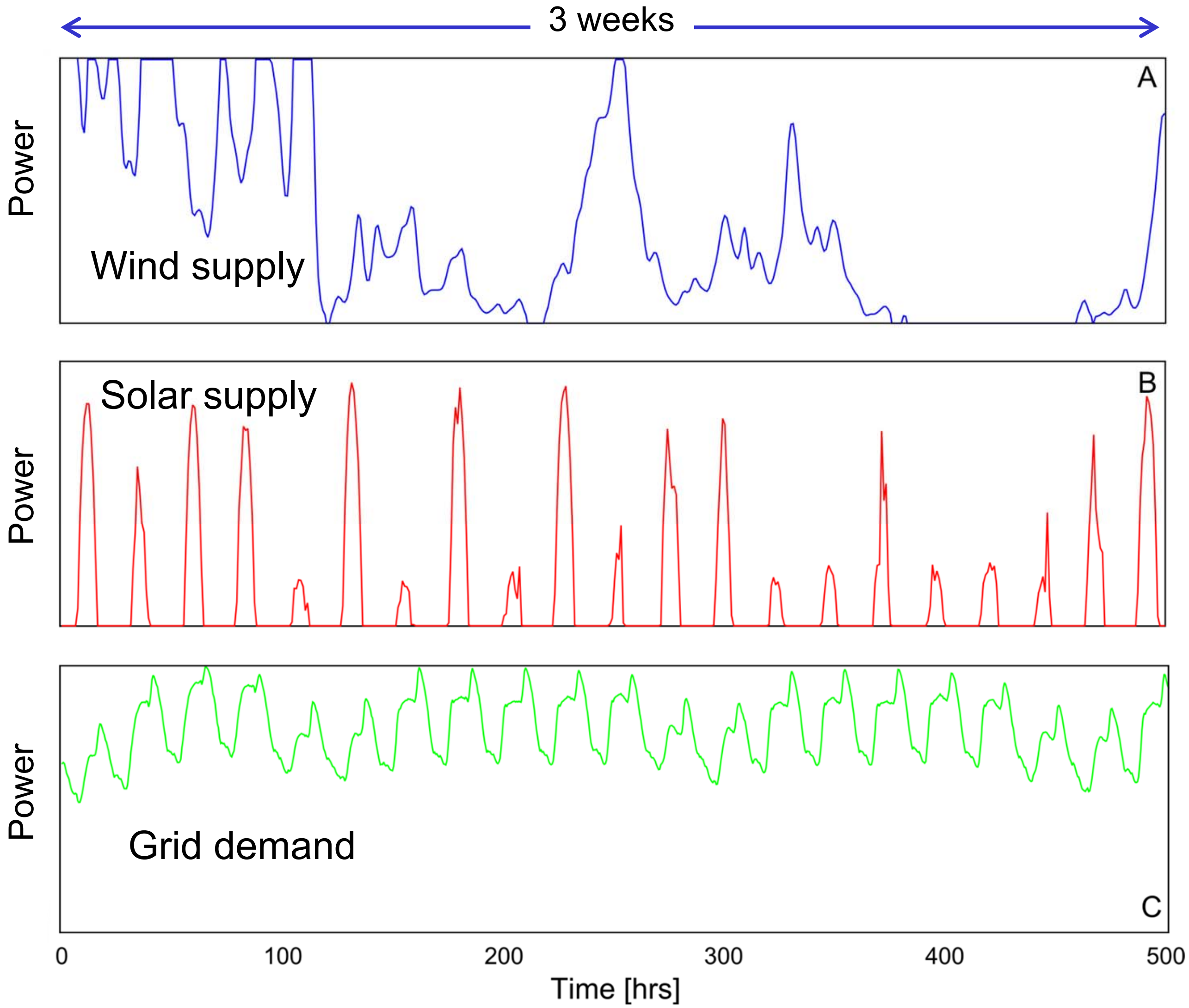
Large-Scale Deployment of Off-Grid Storage

No access to grid: 1.4 Billion people (incl. 550 million in Africa, 400 million in India)

Photo courtesy of Prof. Sri Narayan, University of Southern California

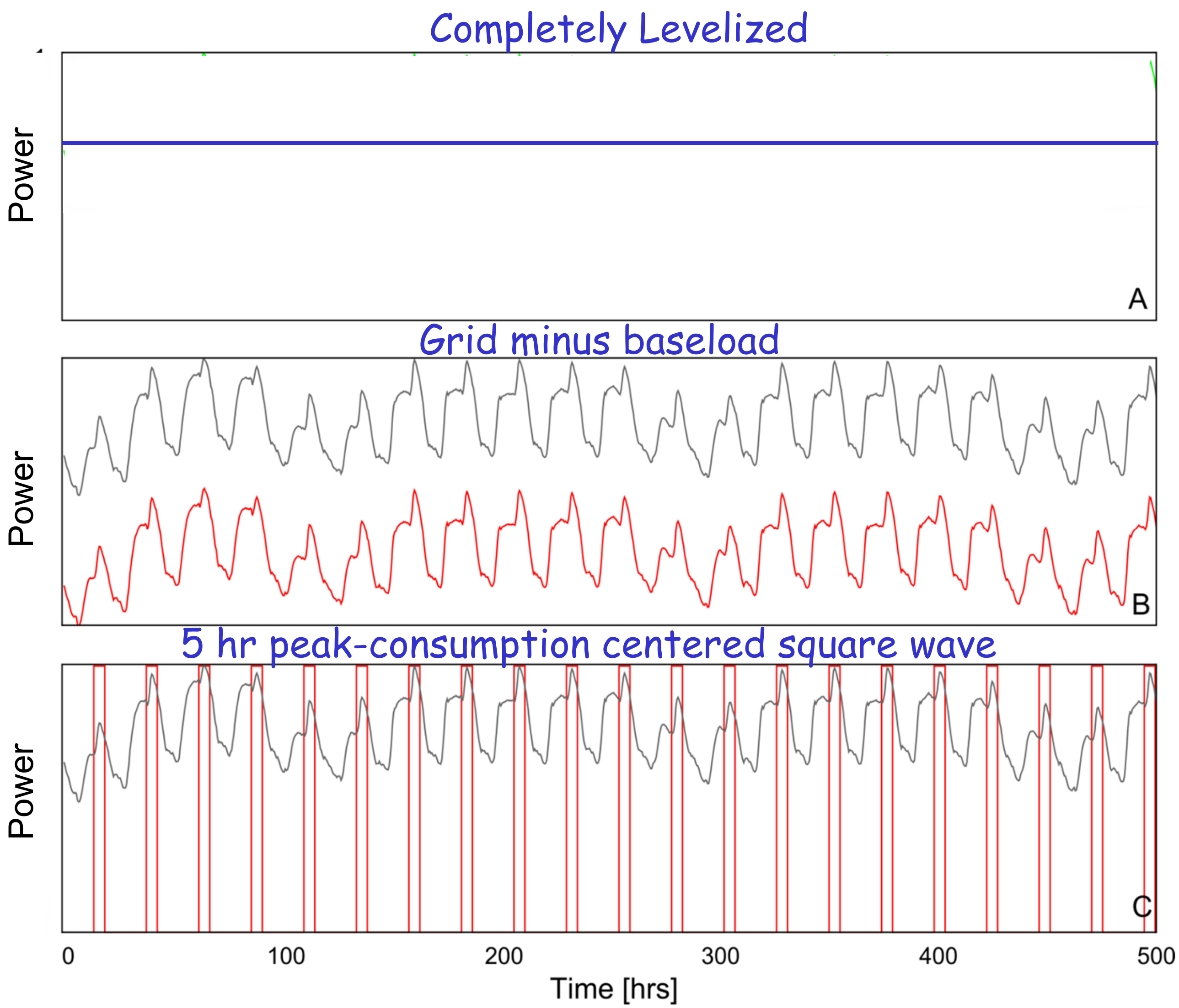
http://www.raisinahill.org/2013/02/indo-us-dispute-on-solar-panel.html
http://3.bp.blogspot.com/-beOrvaf2wzw/URT3ohD796I/AAAAAAAABkA/9xwL0o5qO6I/s1600/Home+Lighting+System+in+a+hut+in+Jaisalmer+District+of+Rajasthan..jpg

Storage Makes Intermittent Renewables Dispatchable



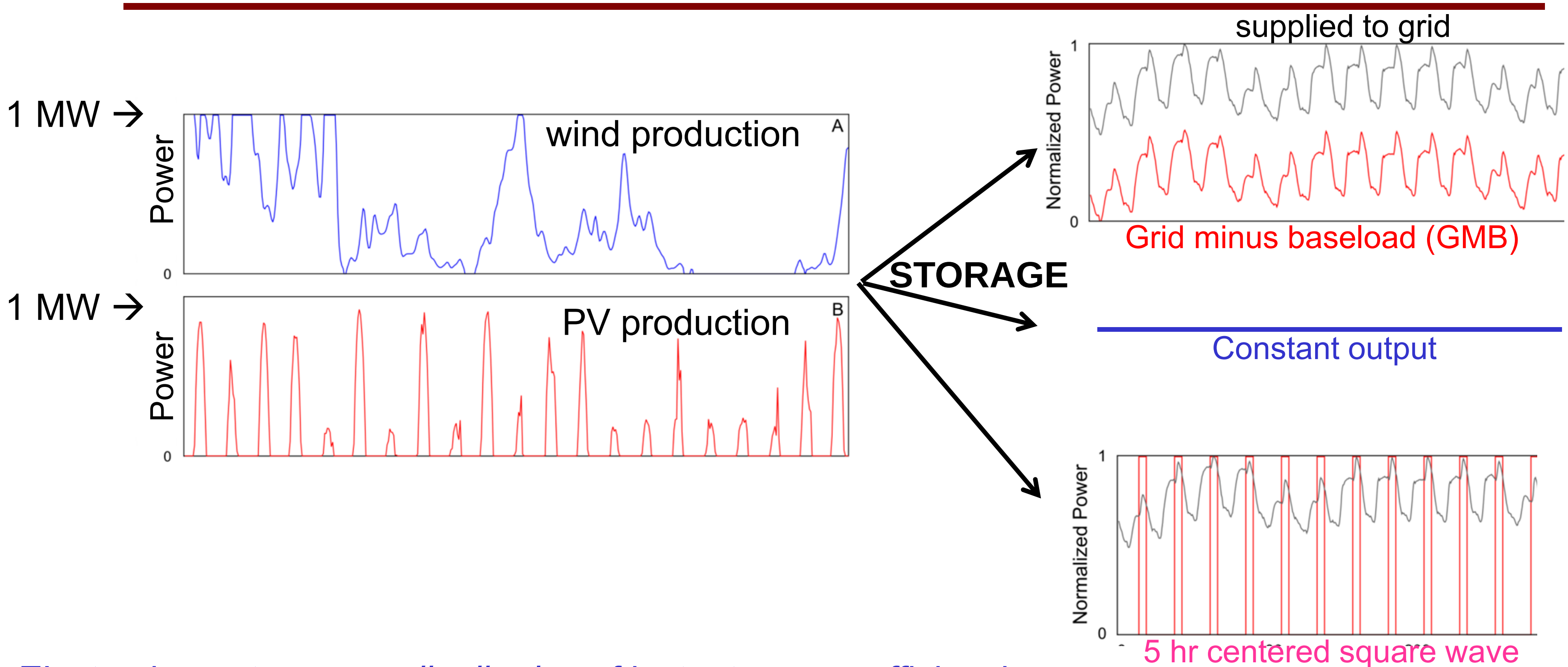
J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Some Grid Supply Scenarios Enabled by Storage



J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Three storage scenarios: Power and energy requirements, 1 MW nameplate production



Electrochem storage: a *distribution* of instantaneous efficiencies

Requirement: high system efficiency

➔ 1 MW nameplate PV requirement:

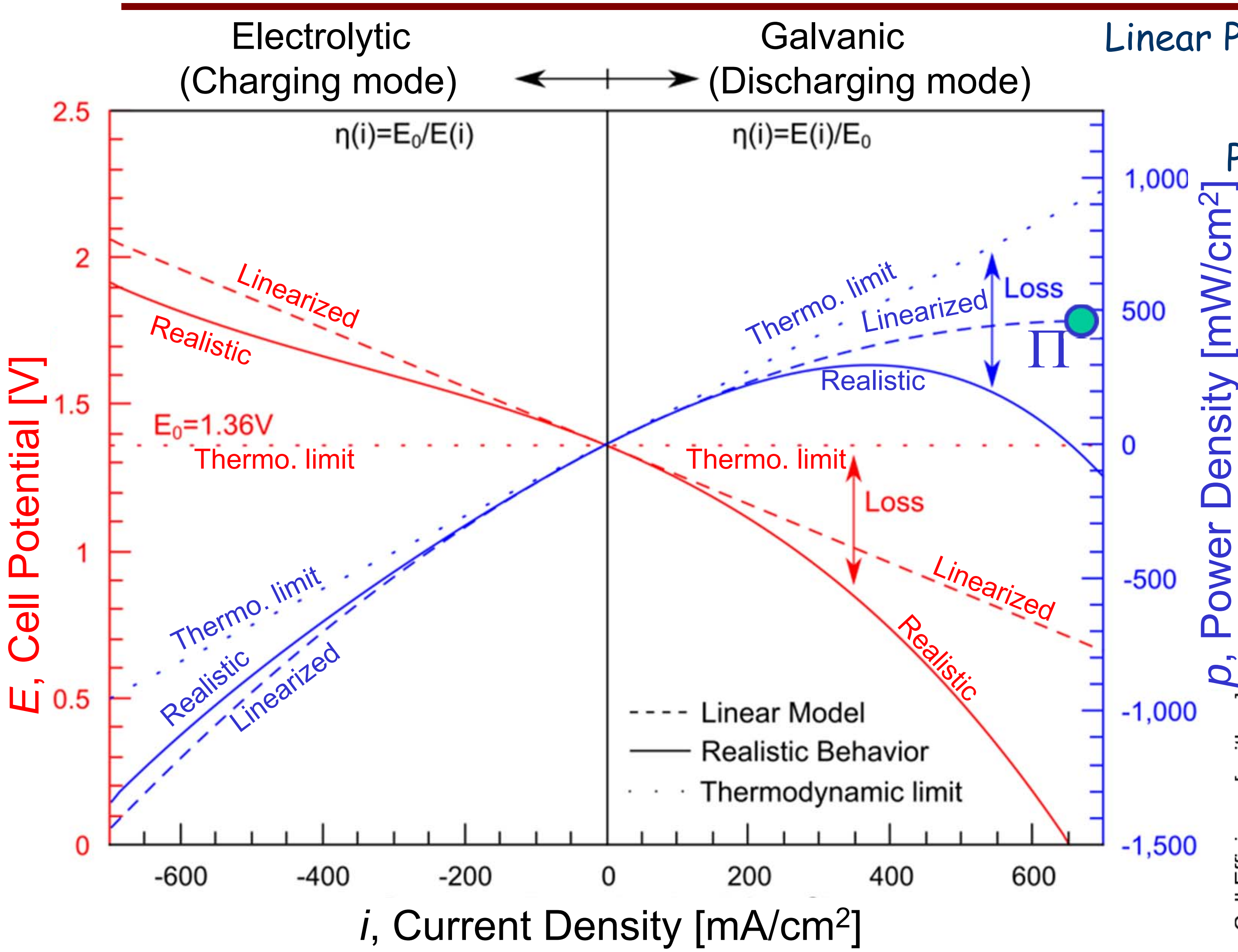
~?? MW peak power capacity; ?? MWh energy capacity (Energy/Power = ?? hr)

➔ 1 MW nameplate wind requirement:

~?? MW peak power capacity; ?? MWh energy capacity (Energy/Power = ?? hr)

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Storage: A *Distribution* of Efficiencies



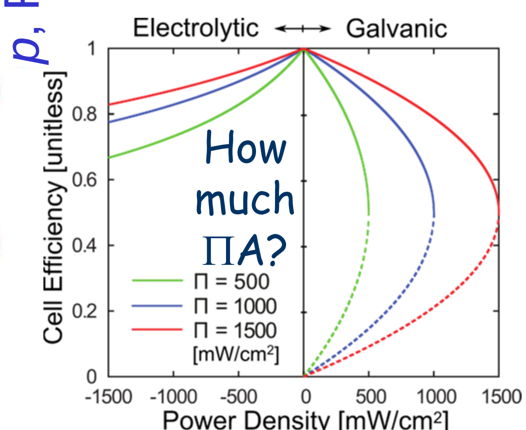
Linear Potential Approximation:

$$E(i) = E_{eq} - \rho i$$

Power dens'y: $p = E(i) \cdot i$

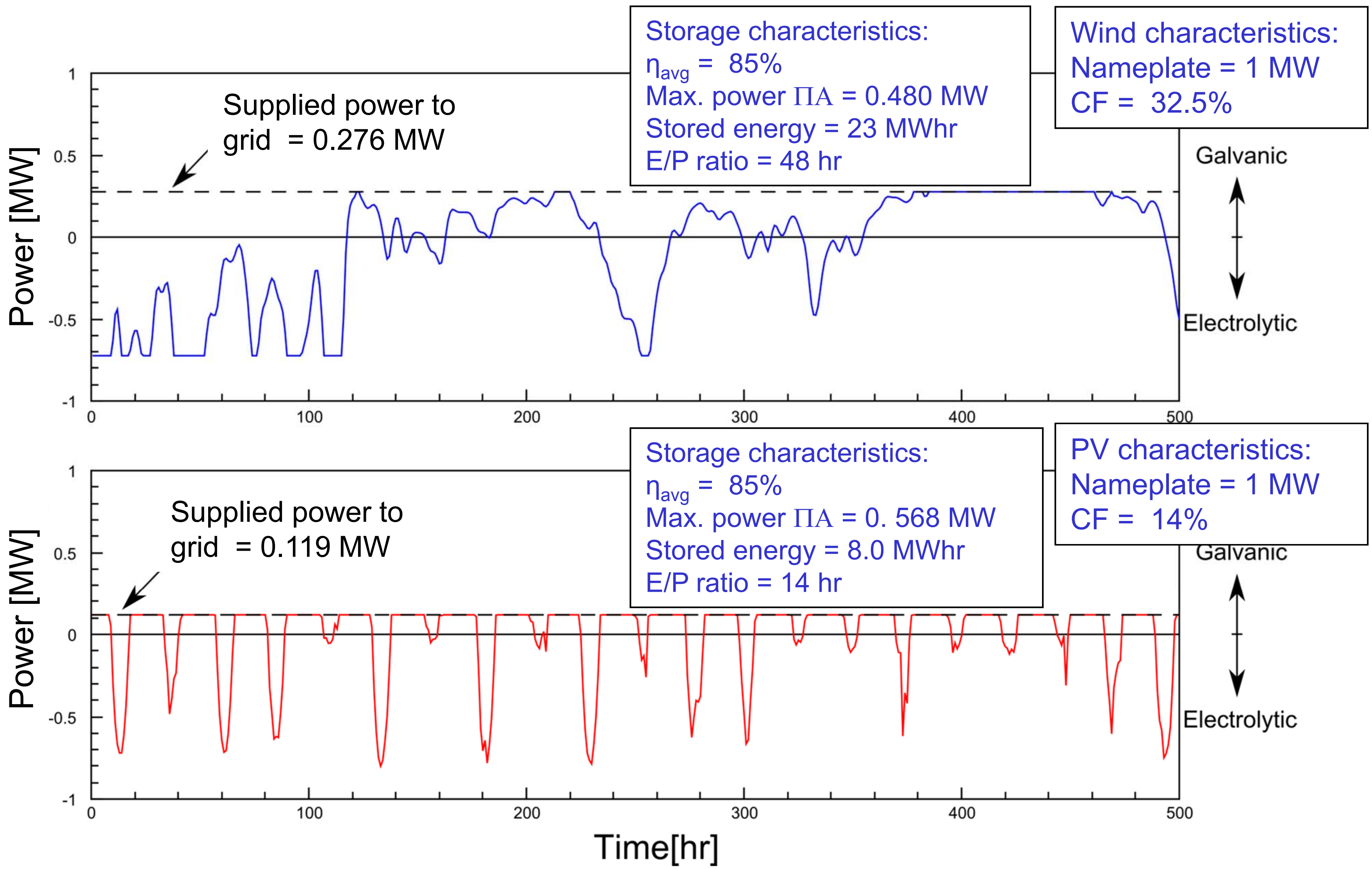
Peaks at: $\Pi \equiv \frac{E_{eq}^2}{4\rho}$

$$\eta(p) = \begin{cases} \frac{1+\sqrt{1-\frac{p}{\Pi}}}{2} & : p \geq 0 \\ \frac{2}{1+\sqrt{1-\frac{p}{\Pi}}} & : p < 0 \end{cases}$$



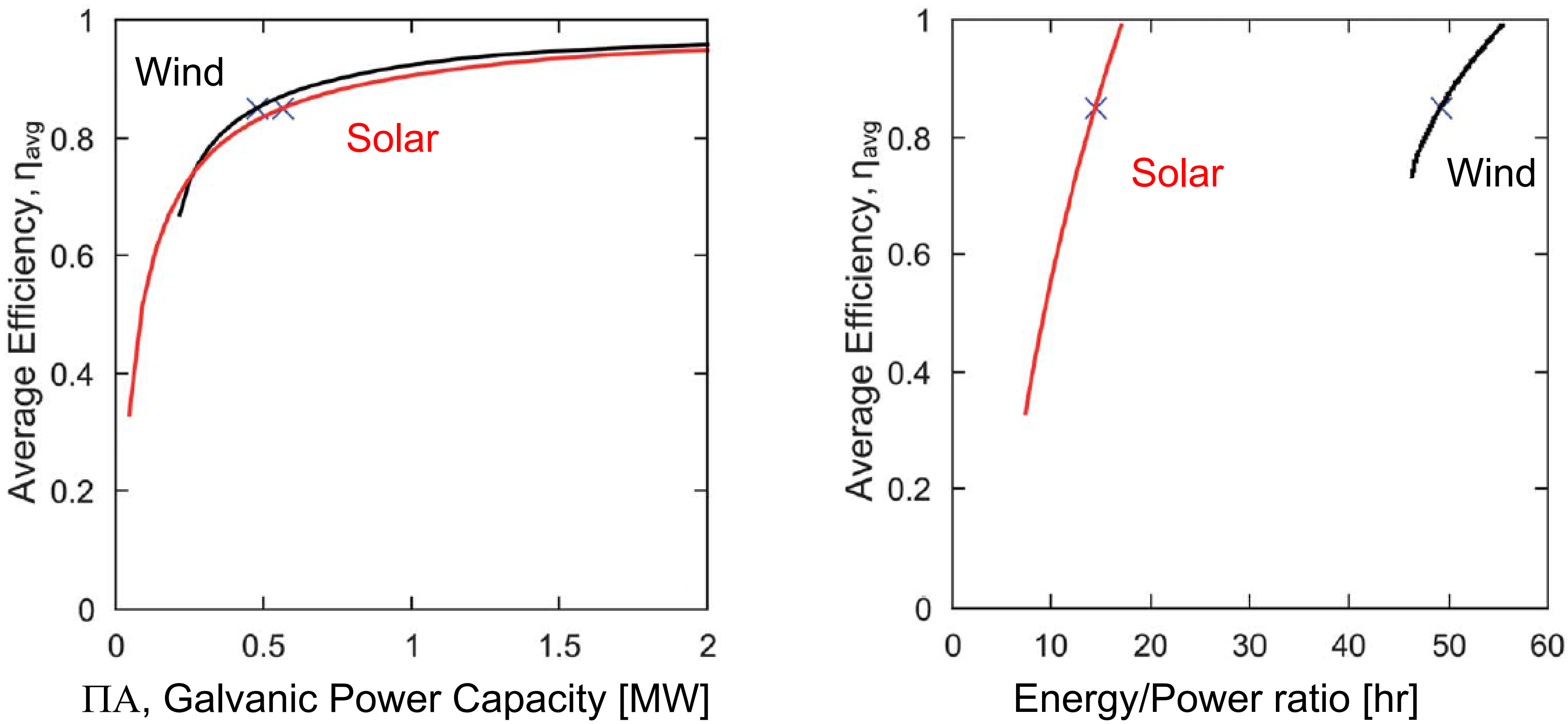
J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* 5, 7151 (2012)

Storage Requirements for 1 MW Nameplate Production Capacity



J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* 5, 7151 (2012)

Diminishing Returns on Buying Storage Power



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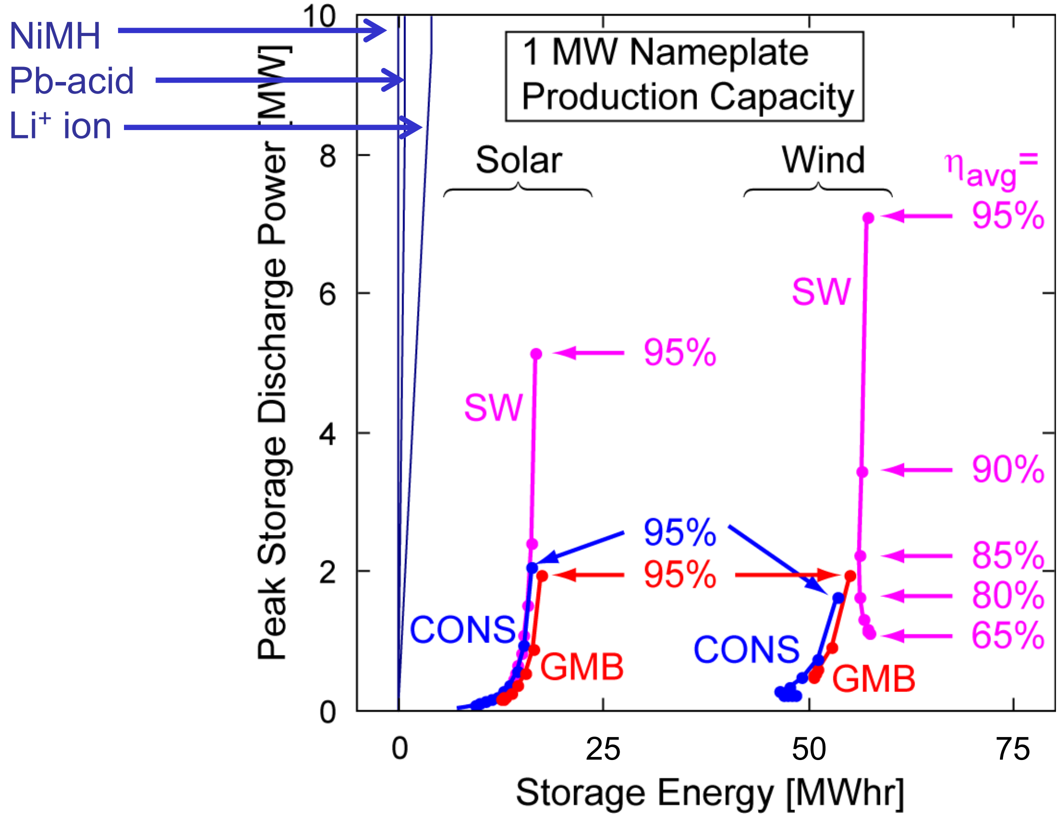
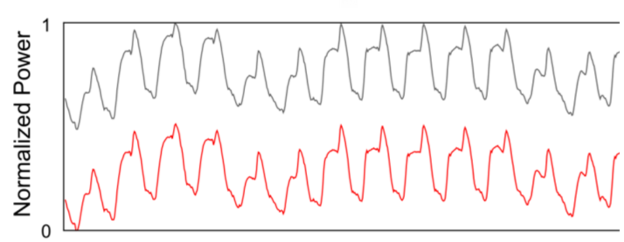
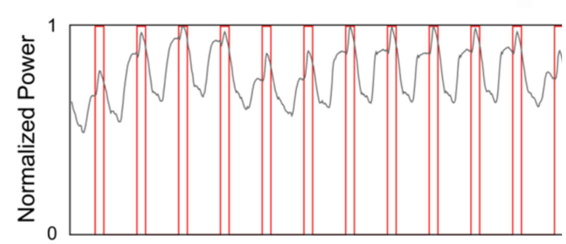






Constant output (CONS) in blue

Grid minus baseload (GMB) in red

5 hr centered (SW) in pink

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate		
	Solar	**Wind**
Power	1 MW	1 MW
Energy	16 MWhr	60 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr

J. Rugolo and M.J. Aziz, “Electricity Storage for Intermittent Renewable Sources”, *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	1 MW
Energy	16 MWhr	60 MWhr	0.2 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	2 MW
Energy	16 MWhr	60 MWhr	0.4 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			**Available**
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	3 MW
Energy	16 MWhr	60 MWhr	0.6 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, “Electricity Storage for Intermittent Renewable Sources”, *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	4 MW
Energy	16 MWhr	60 MWhr	0.8 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			**Available**
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	5 MW
Energy	16 MWhr	60 MWhr	1.0 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	10 MW
Energy	16 MWhr	60 MWhr	2.0 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, “Electricity Storage for Intermittent Renewable Sources”, *Energy Environ. Sci.* **5**, 7151 (2012)

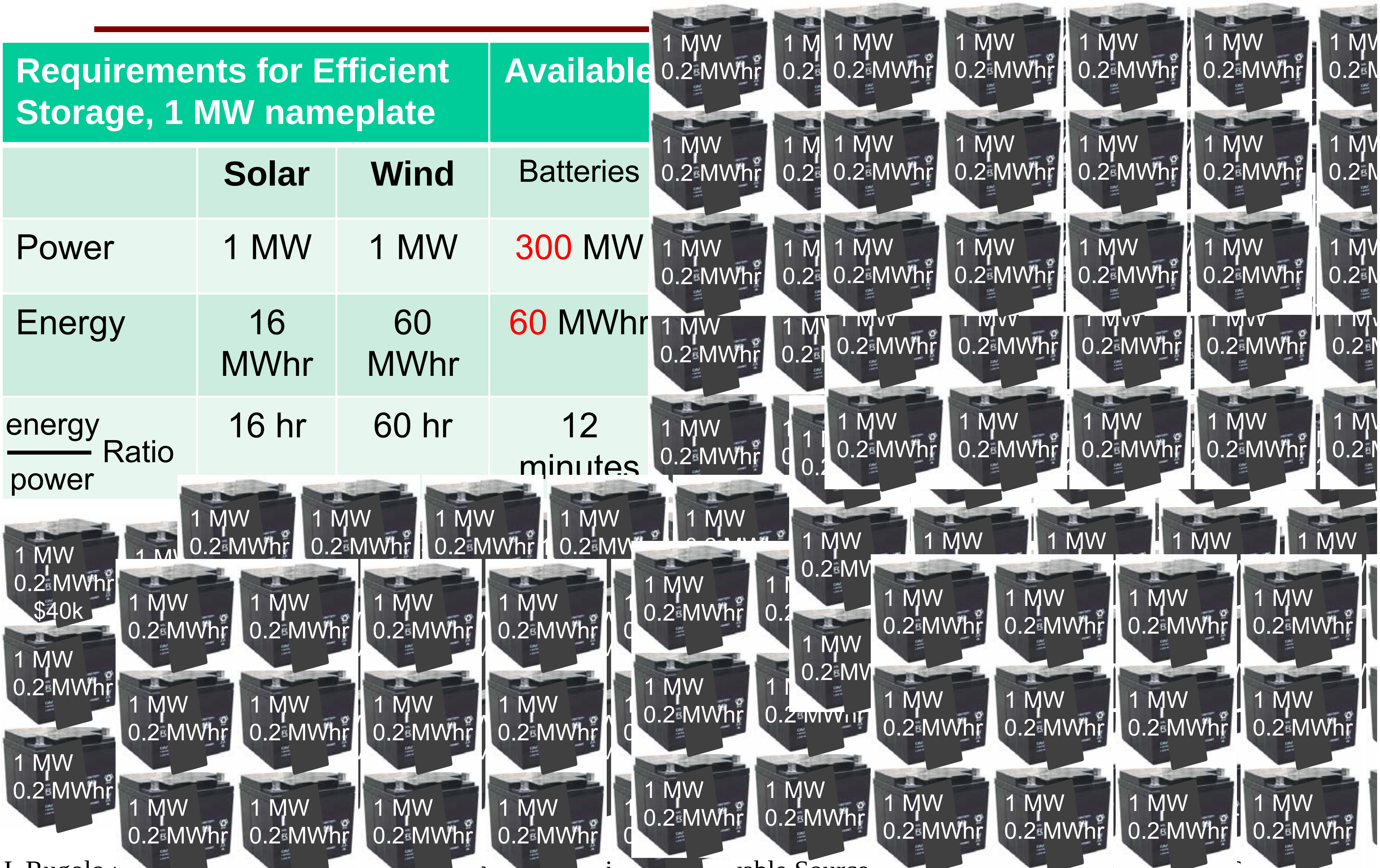
Batteries Have Only About 1% of the Required Energy for a Given Power

Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	15 MW
Energy	16 MWhr	60 MWhr	3.0 MWhr
energy / power Ratio	16 hr	60 hr	12 minutes

J. Rugolo and M.J. Aziz, “Electricity Storage for Intermittent Renewable Sources”, *Energy Environ. Sci.* **5**, 7151 (2012)

Batteries Have Only About 1% of the Required Energy for a Given Power

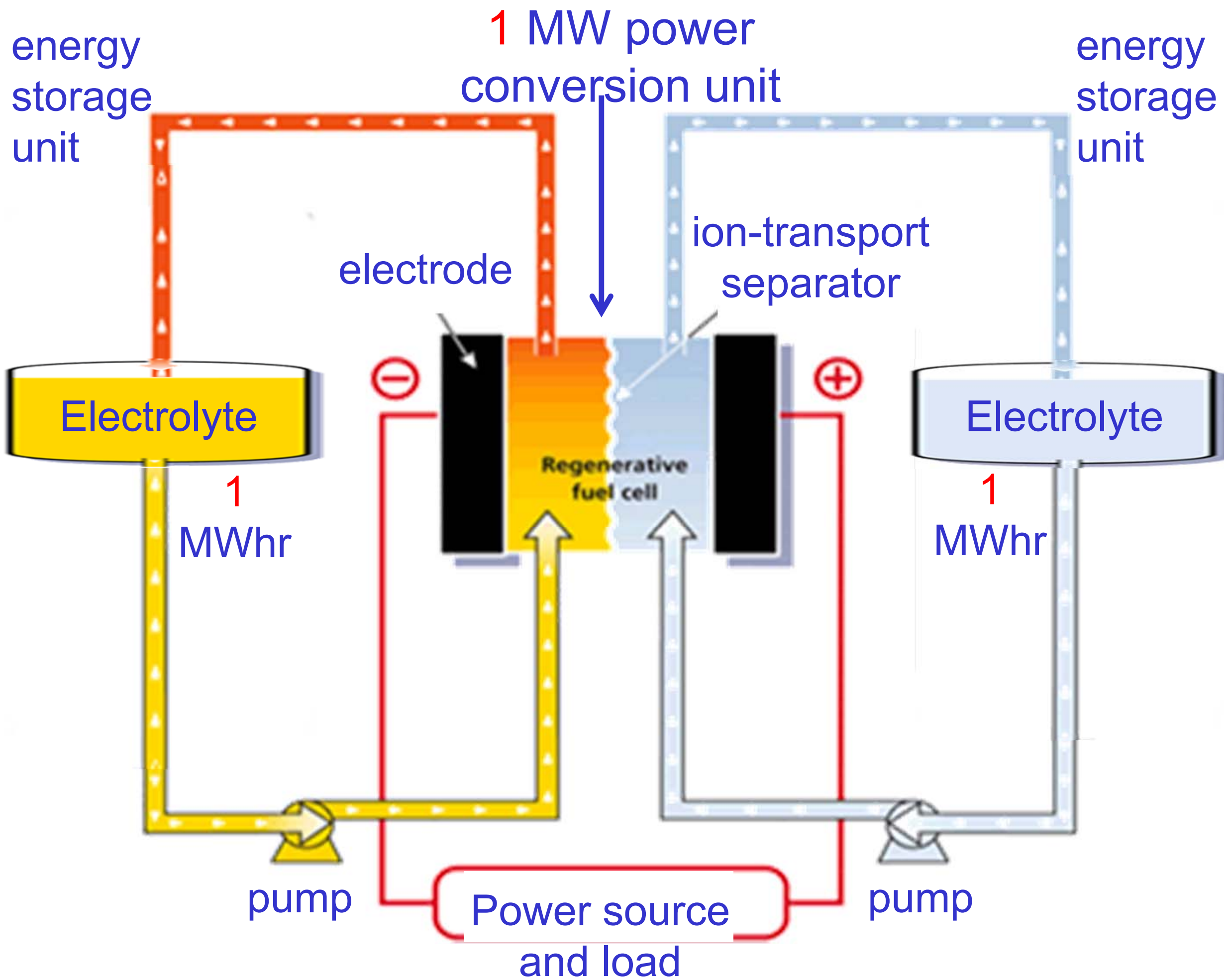
Requirements for Efficient Storage, 1 MW nameplate			Available
	Solar	**Wind**	Batteries
Power	1 MW	1 MW	300 MW
Energy	16 MWhr	60 MWhr	60 MWhr
energy / power Ratio	16 hr	60 hr	12 minutes



J. Rugolo a… …vable Sources", *Energy Environ. Sci.* 5, 7151 (2012)

Flow Batteries Independently Size Energy and Power

Requirements for Efficient Storage, 1 MW nameplate		
	Solar	**Wind**
Power	1 MW	1 MW
Energy	16 MWhr	60 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr

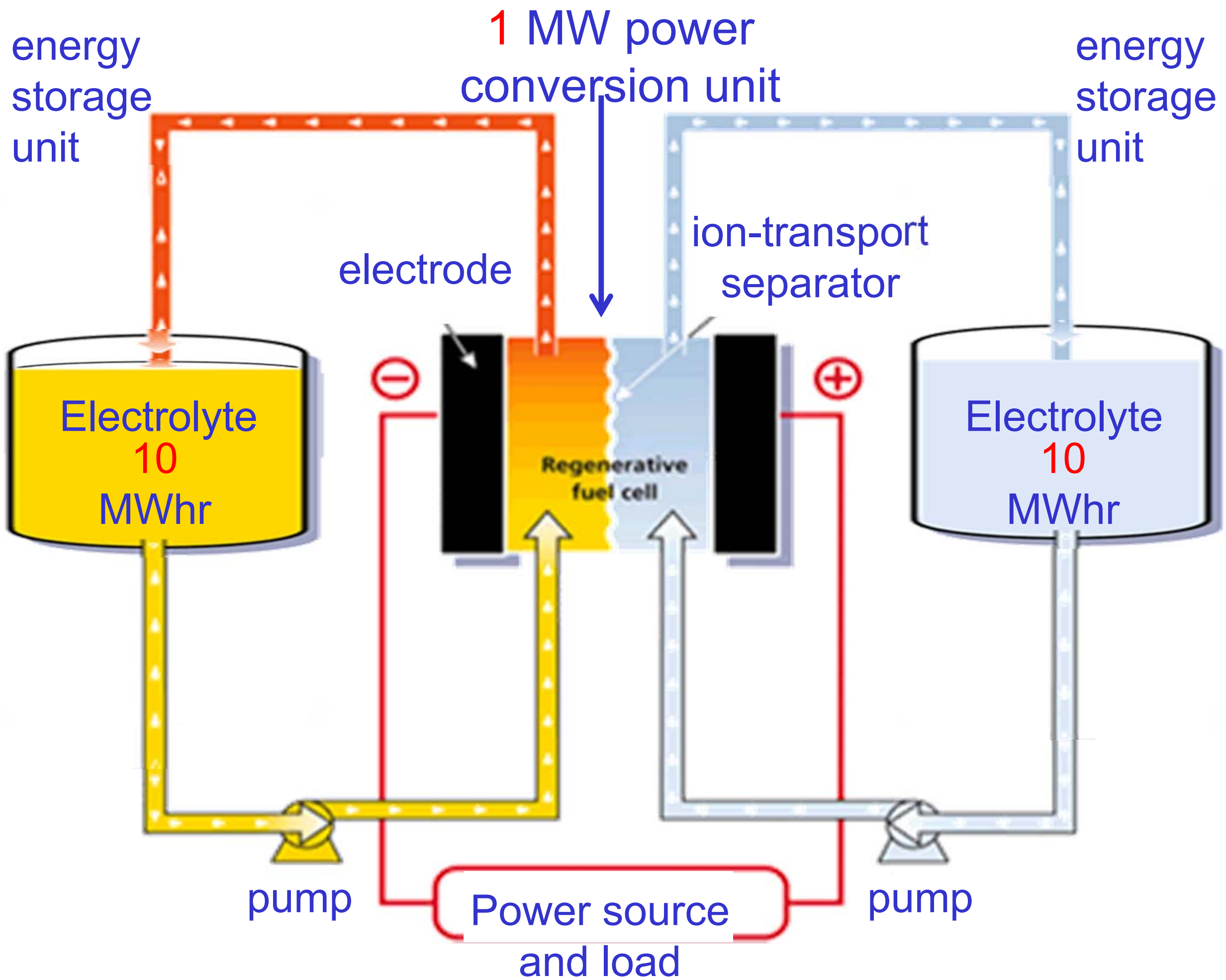


based on image from vrbpower.com

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Flow Batteries Independently Size Energy and Power

Requirements for Efficient Storage, 1 MW nameplate		
	Solar	**Wind**
Power	1 MW	1 MW
Energy	16 MWhr	60 MWhr
energy / power Ratio	16 hr	60 hr



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Flow Batteries Independently Size Energy and Power

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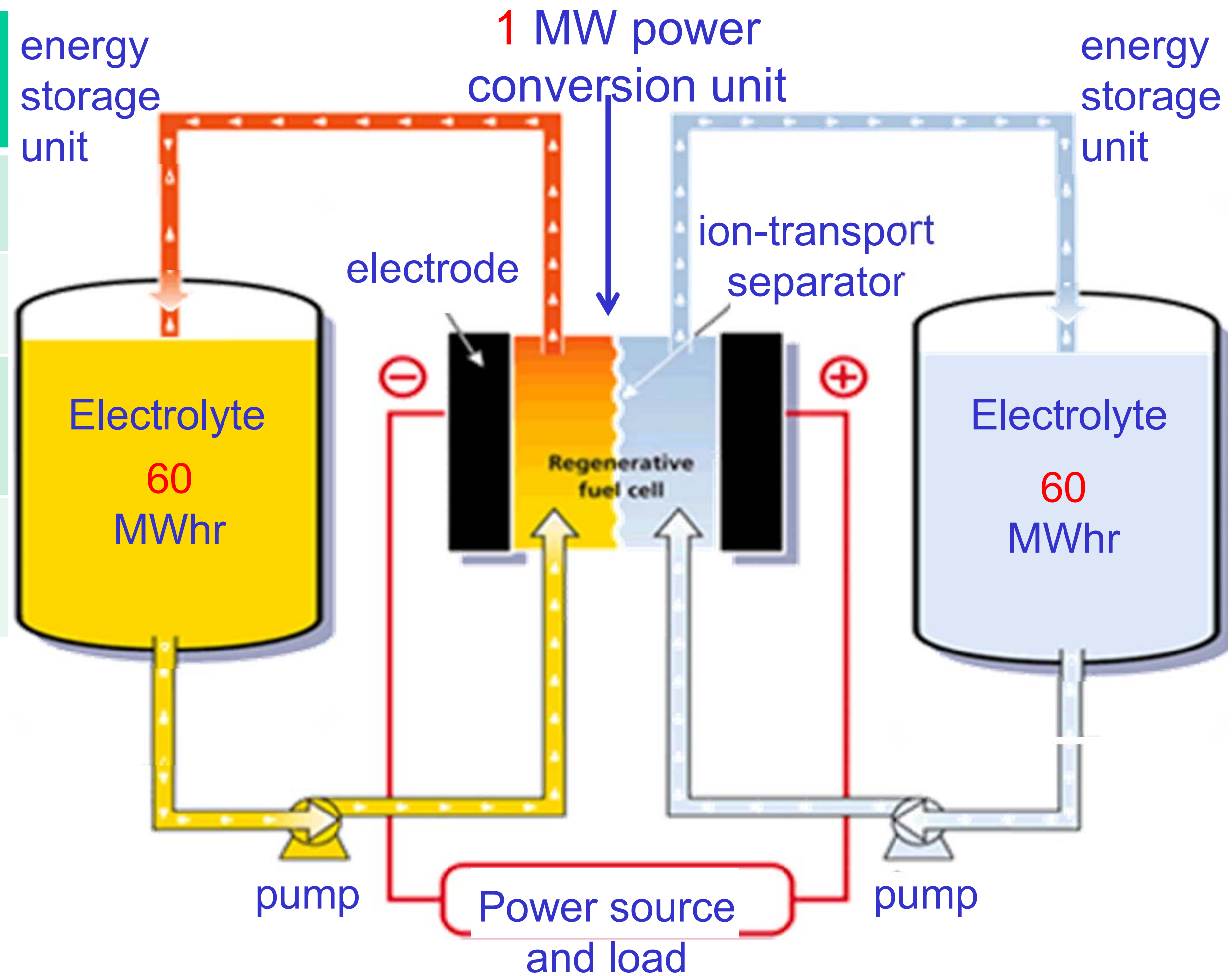

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Flow Batteries Independently Size Energy and Power

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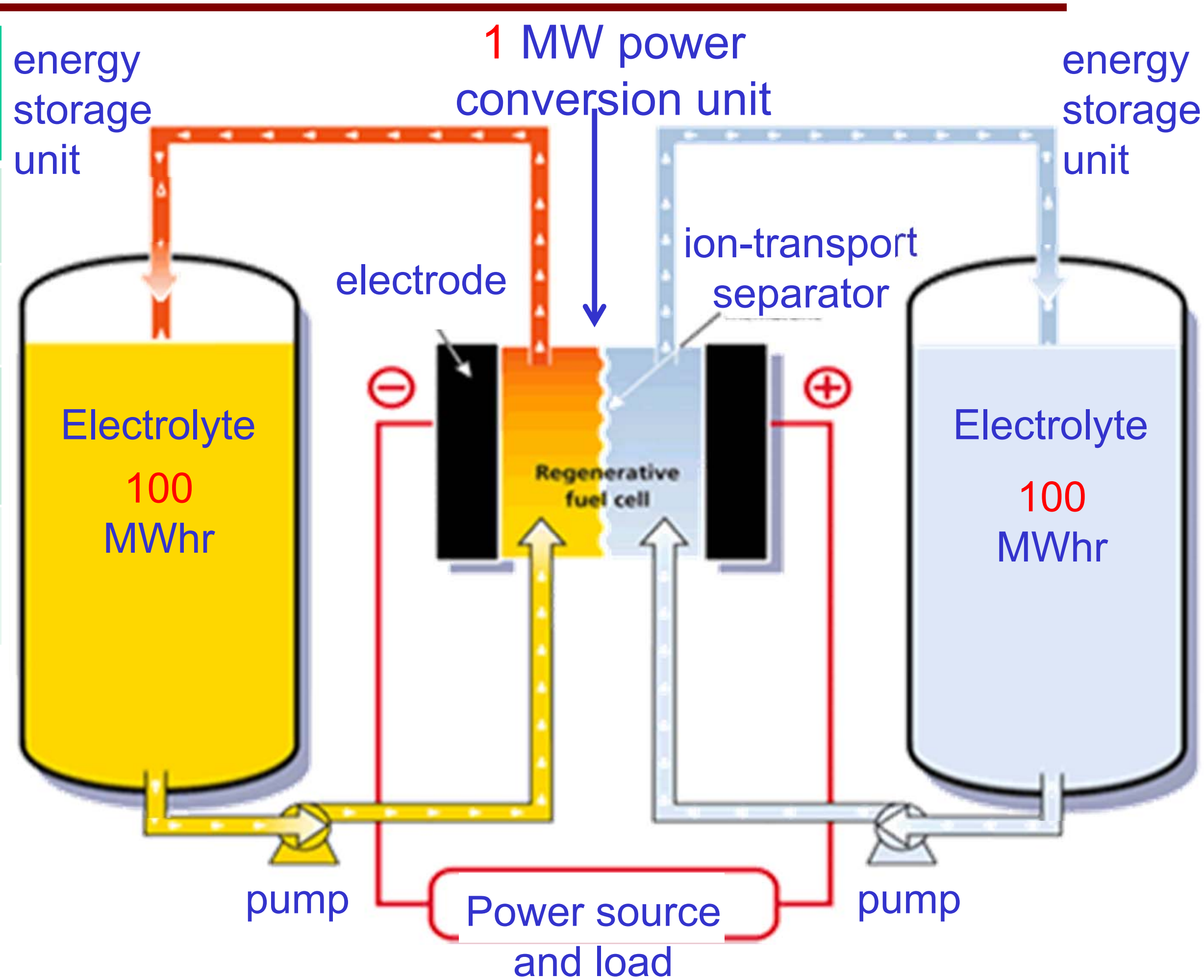
Power	1 MW	1 MW
Energy	16 MWhr	60 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr



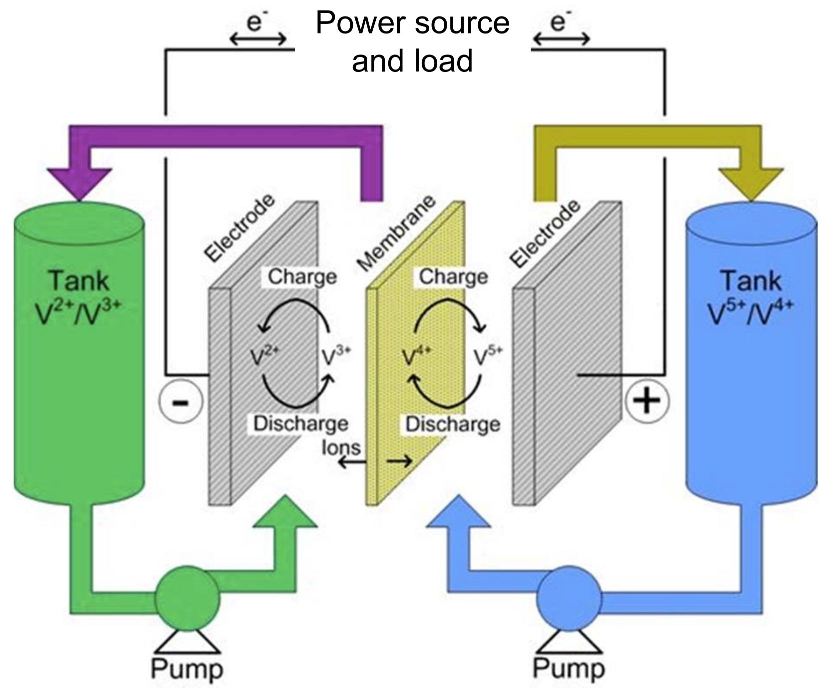
based on image from vrbpower.com

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

“Hope and Change” for Electrical Energy Storage

Vanadium Redox Flow Battery: the Most Commercialized RFB

Source: Prudent Energy Corporation

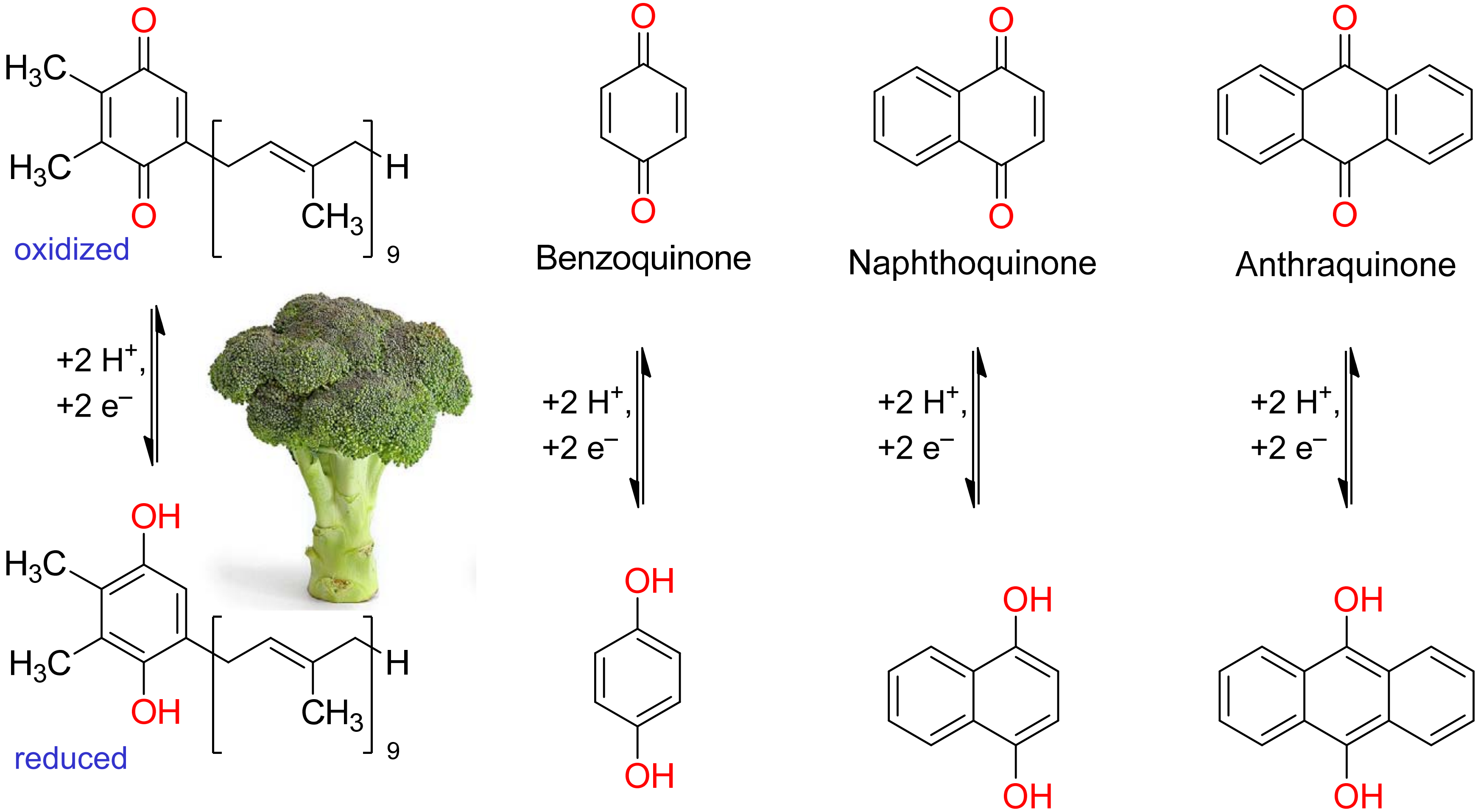


$$V^{3+} \underset{Ox}{\overset{Red}{\rightleftharpoons}} V^{2+} \qquad VO_2^{+} \underset{Ox}{\overset{Red}{\rightleftharpoons}} VO^{2+}$$

Quinones for Battery Storage

Plastoquinone
in photosynthesis

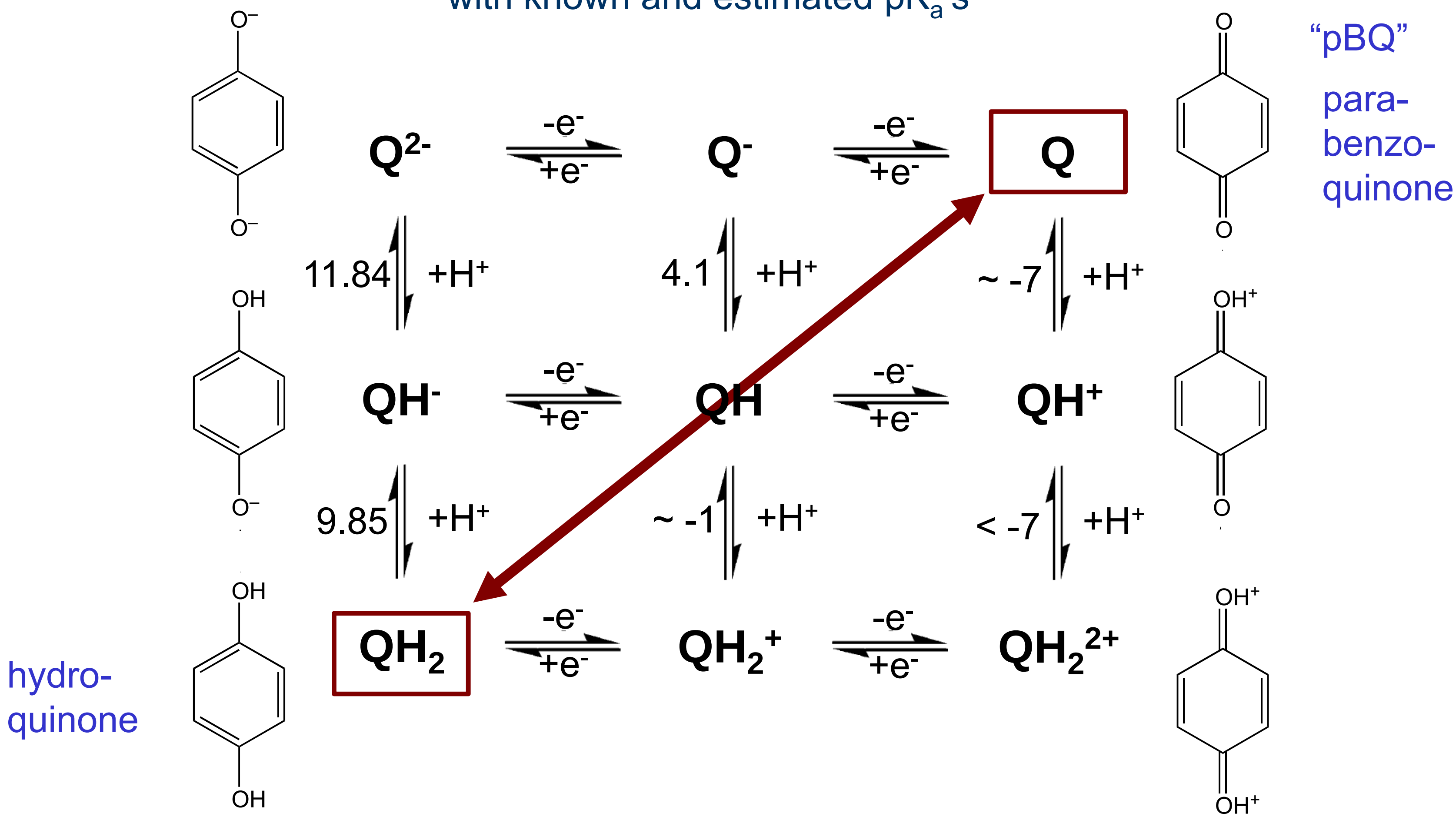
simplest
quinone



Hydroquinone

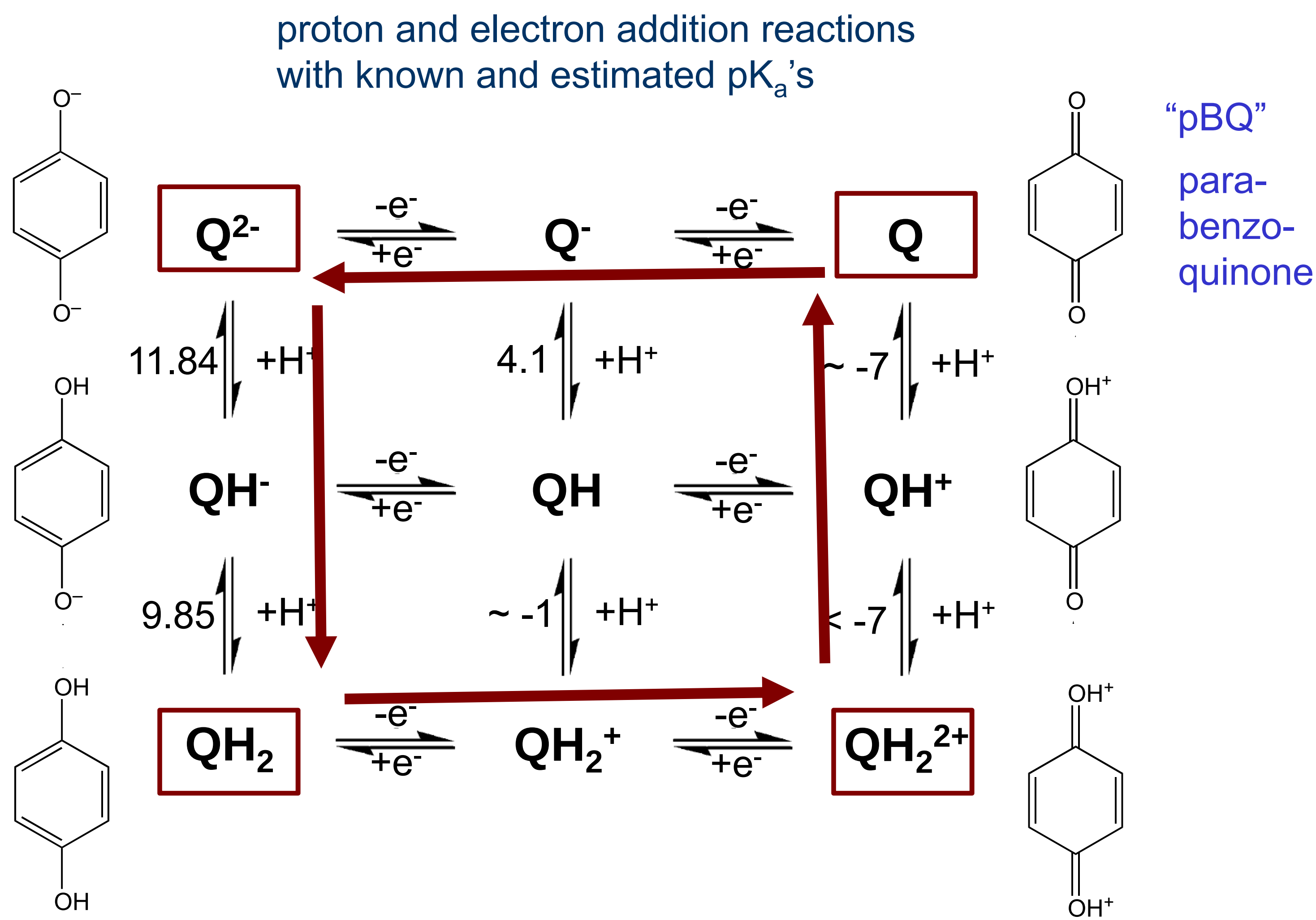
Quinones/Hydroquinones: Reversible

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



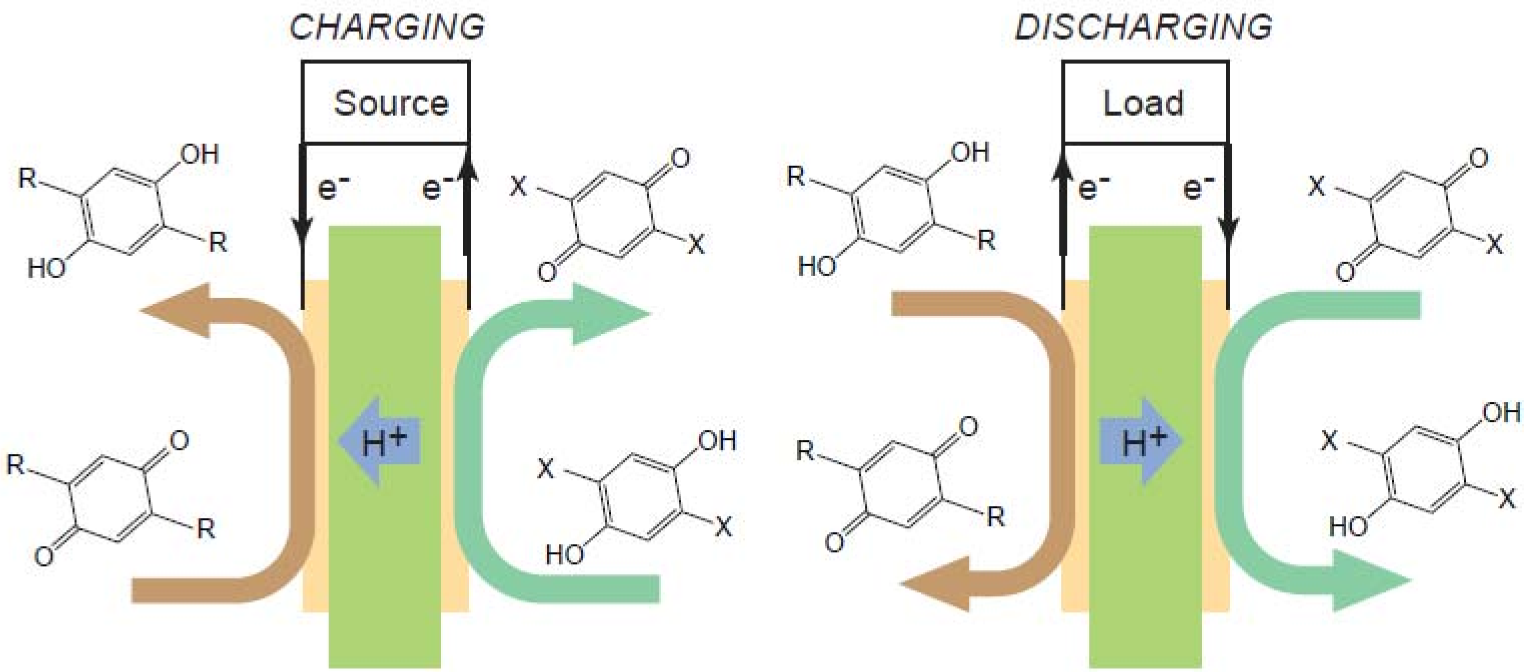
Quan, Sanchez, Wasylkiw, Smith, "Voltammetry of Quinones in Unbuffered Aqueous Solution...", *JACS* **129**, 12847 (2007)

Quinones/Hydroquinones: Reversible or Irreversible



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

Quinone-Based Flow Batteries



Primary requirements:

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

Cost of Chemicals Sets Floor on System Cost / kWh

Compound	$/kg	Source	$/kAh per side	$/kWh per side
Vanadium pentoxide (V_2O_5)	14.37	USGS (2011)	48.77	40.64
Anthraquinone	<4.74	eBioChem	<18.41	<21.46
Benzoquinone	5.27	Shanghai Smart Chemicals Co.	10.63	10.63
Bromine	1.76	USGS (2006)	5.25	6.12

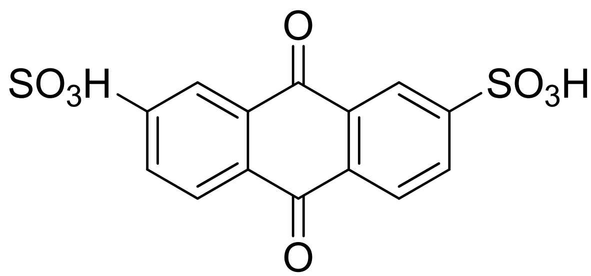
"I wish I could get that price!"

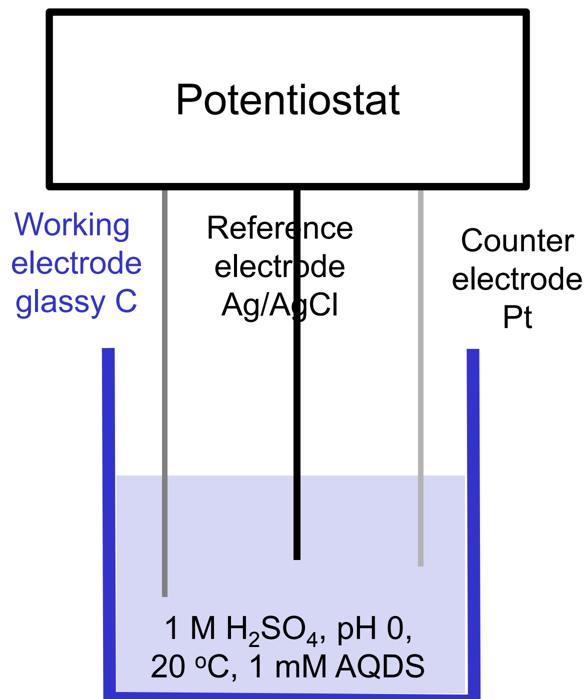
Full Cell	$/kAh	$/kWh
Anthraquinone with Bromine	<23.66	<27.58
Anthraquinone with Benzoquinone	<29.04	<32.09
Vanadium with Vanadium	97.54	81.28

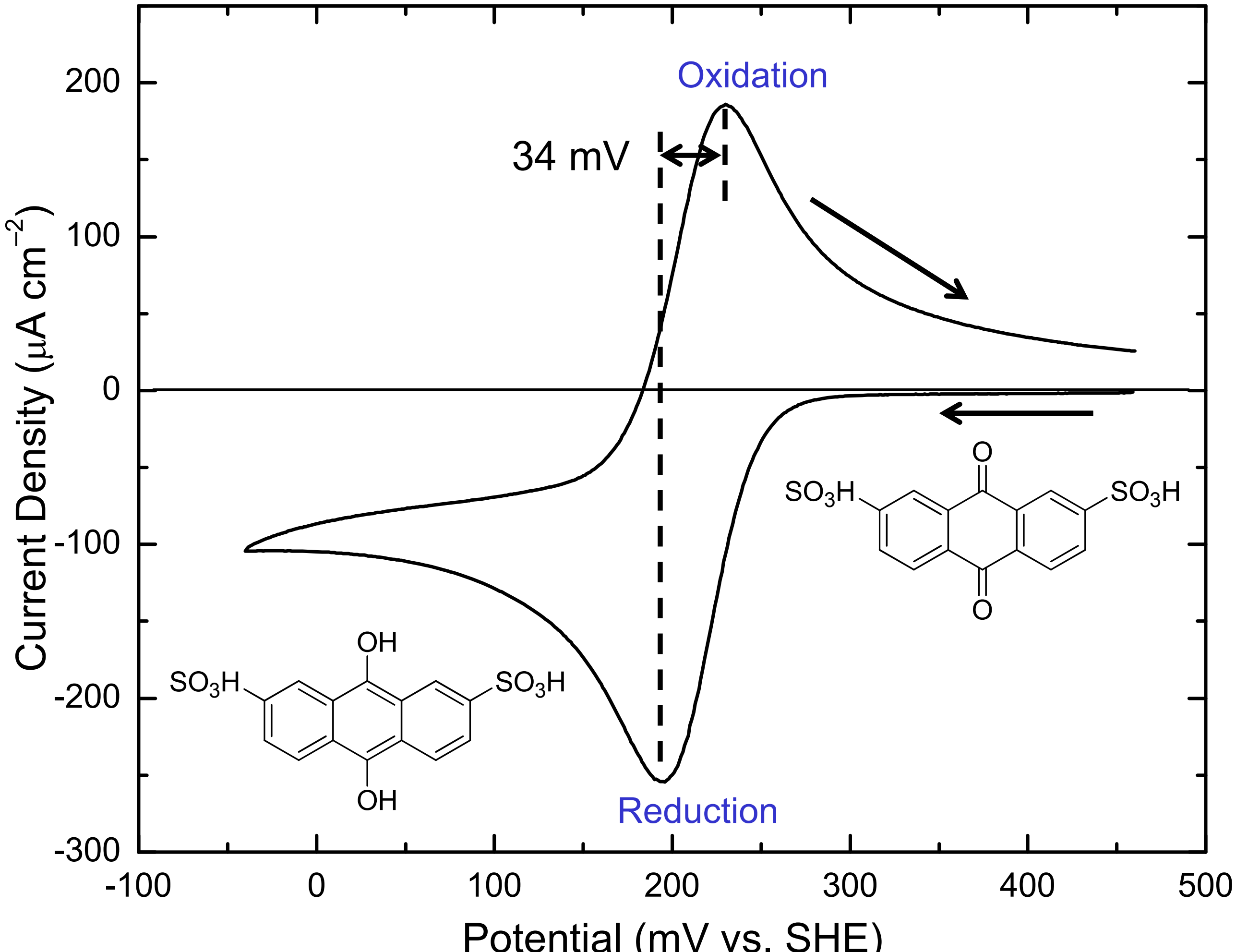
Anthraquinone Di-sulfonate (AQDS)

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

AQDS

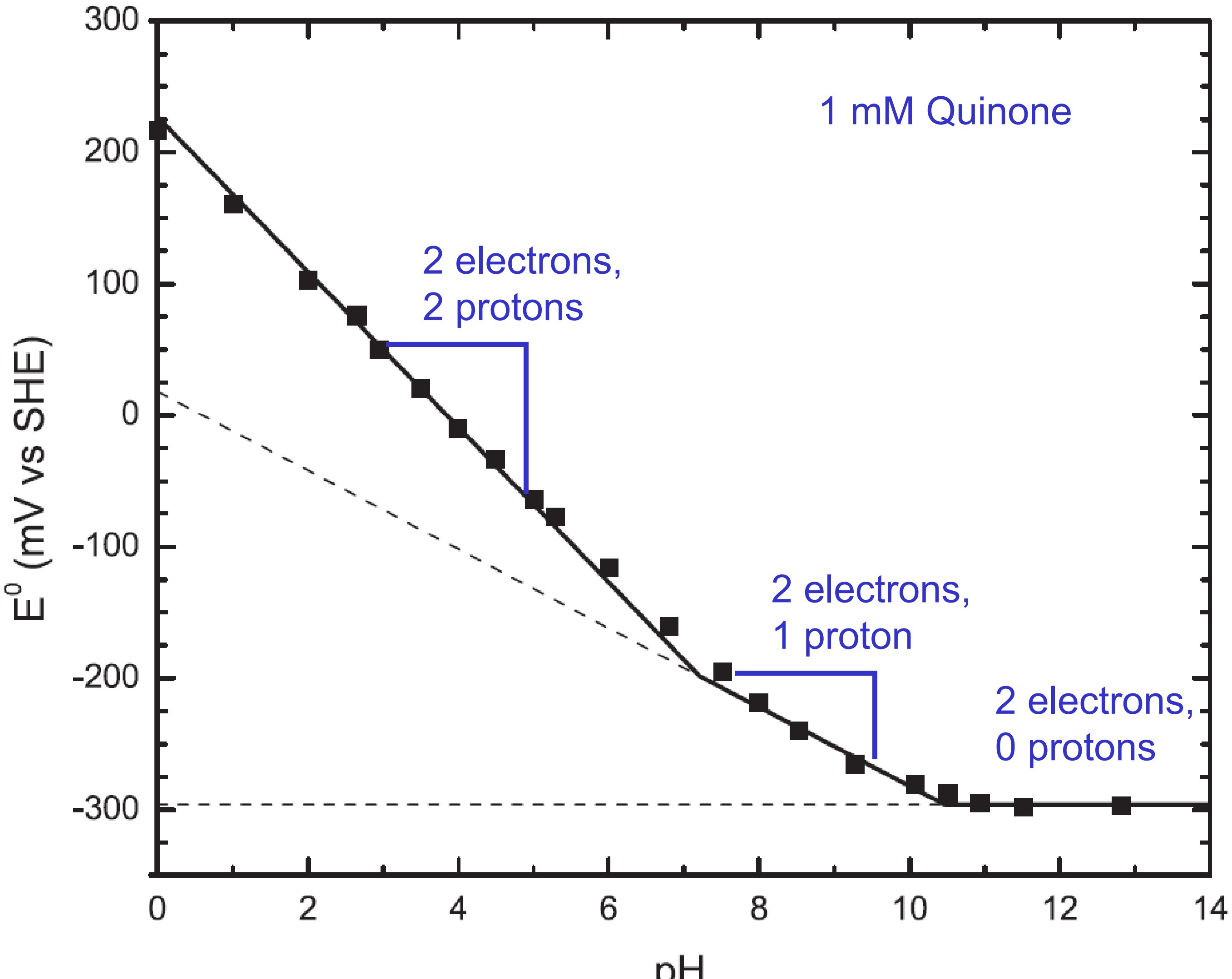






B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

AQDS Pourbaix Diagram



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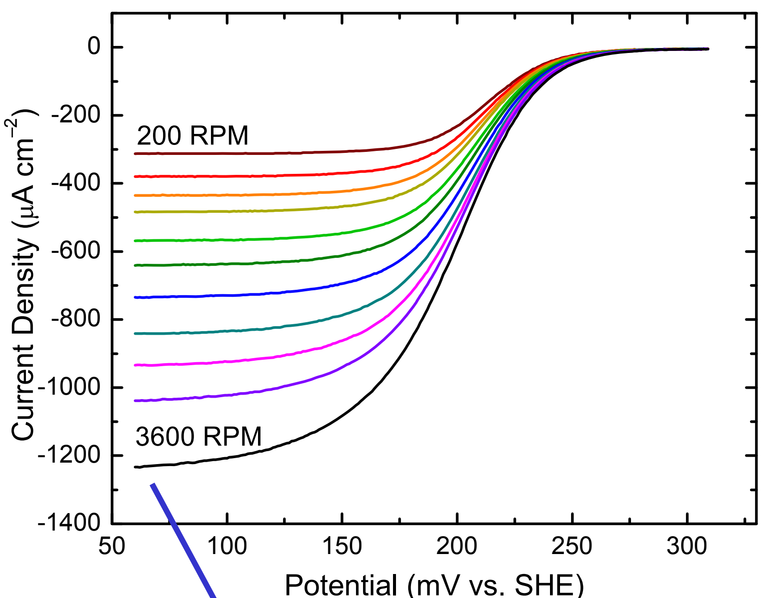
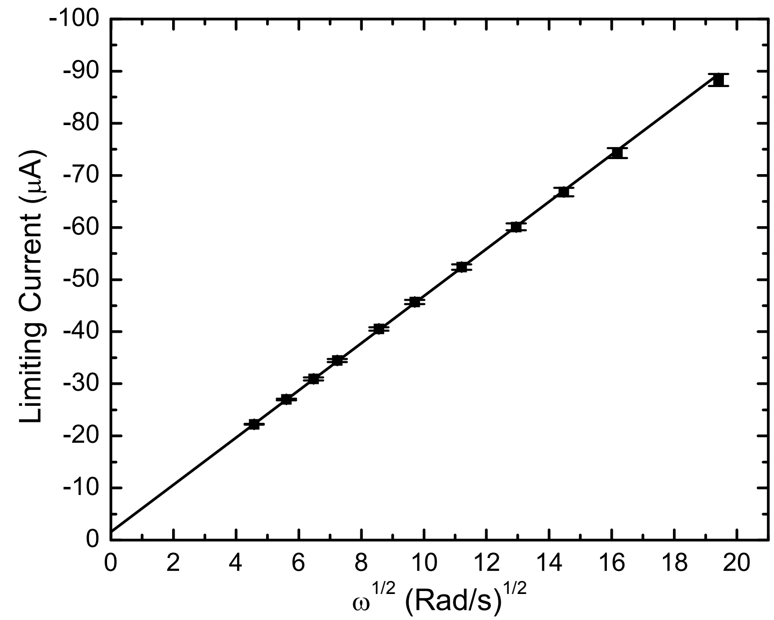
AQDS: Rotating Disk Electrode Response





i_L = Current limited by mass transport

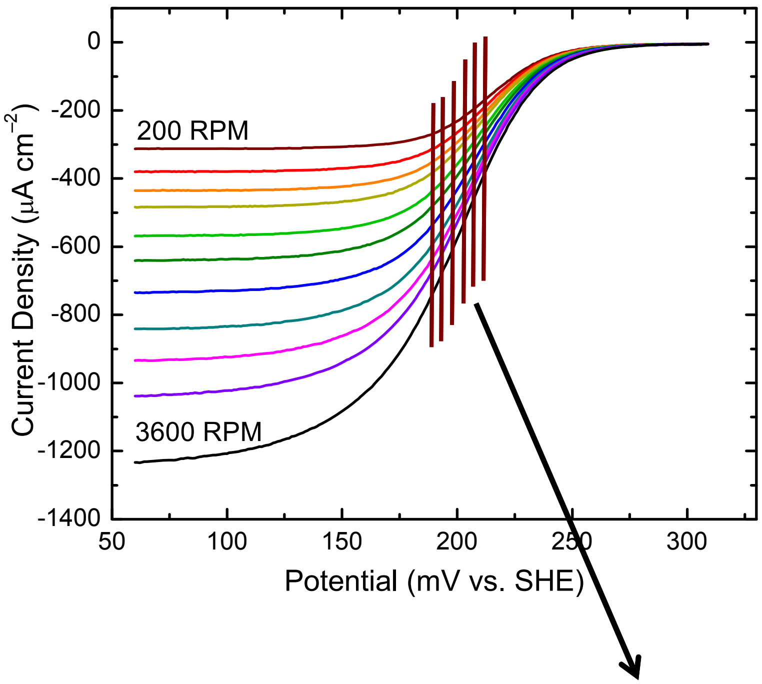
Levich Equation:

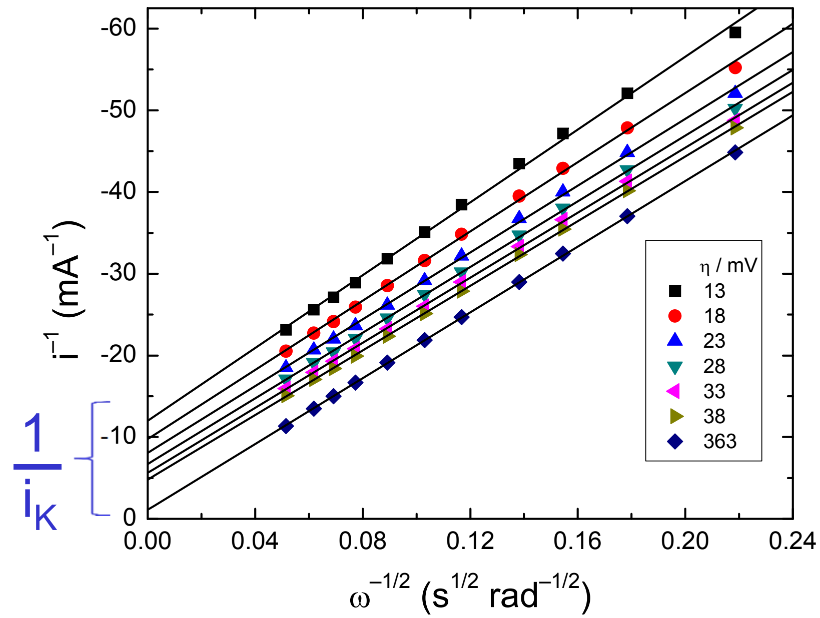
$i_L = 0.62n\ F\ A\ D^{2/3}\ \omega^{1/2}\ \nu^{1/6}\ C_O^*$

$D = 3.8 \times 10^{-6}\ cm^2/s$.

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)

AQDS: Rotating Disk Electrode Response





Current is limited
by mass transport
and electrode kinetics

Koutecký-Levich Plot:
Extrapolate to infinite rotation rate
Gives the kinetically-limited current, i_K

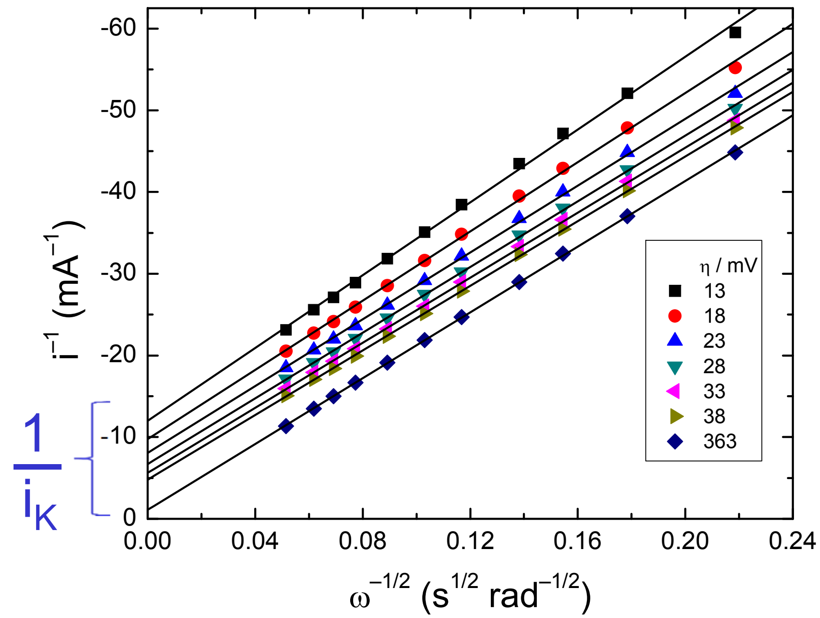
B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

AQDS: Rotating Disk Electrode Response

exchange current density i_{k0} →
rate const $k_0 = i_{k0}/(FAC) = 7.2 \times 10^{-3}$ cm/s

F = Faraday's constant
A = surface area
C = concentration

Redox couple	k_0 [cm/s] (electrode)
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)*

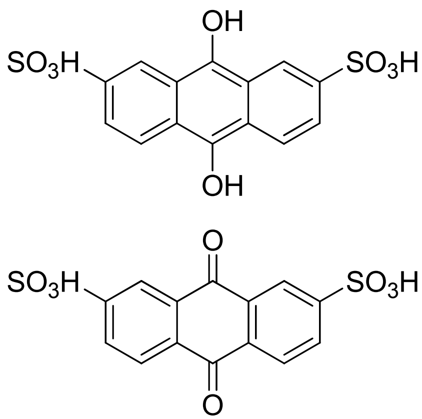


Koutecký-Levich Plot:
Extrapolate to infinite rotation rate
Gives the kinetically-limited current, i_K

*Weber, A. Z.; Mench, M. M.; Meyers, J. P.; Ross, P. N.; Gostick, J. T.; Liu, Q. *J. Appl. Electrochem.* 2011, *41*, 1137

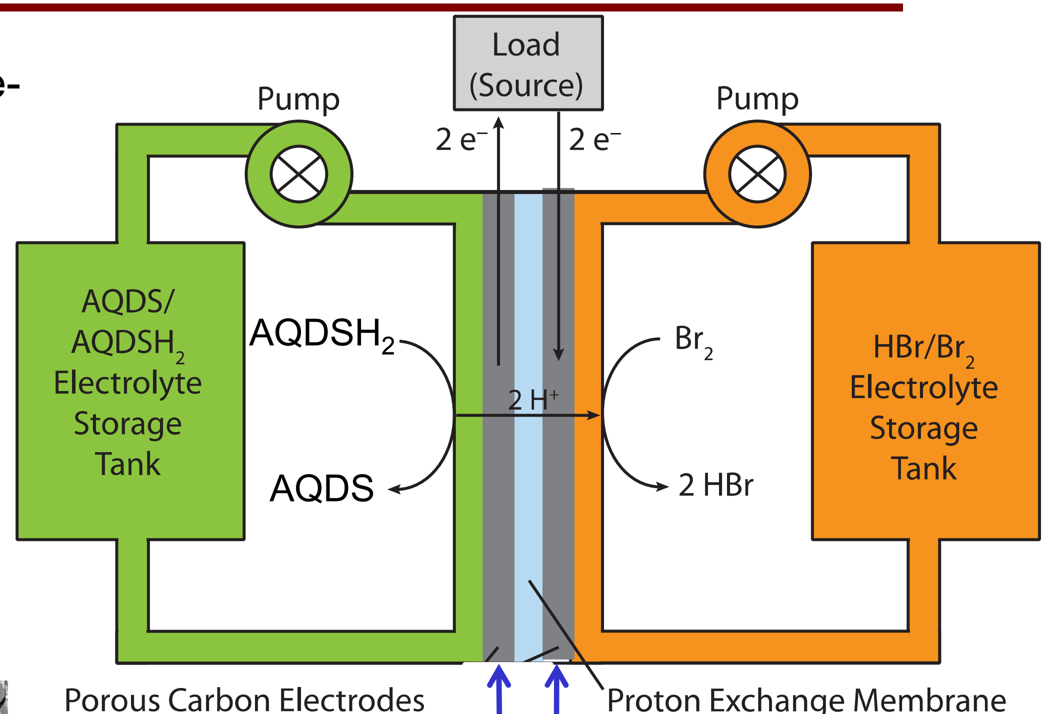
Quinone-Bromide Flow Battery

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

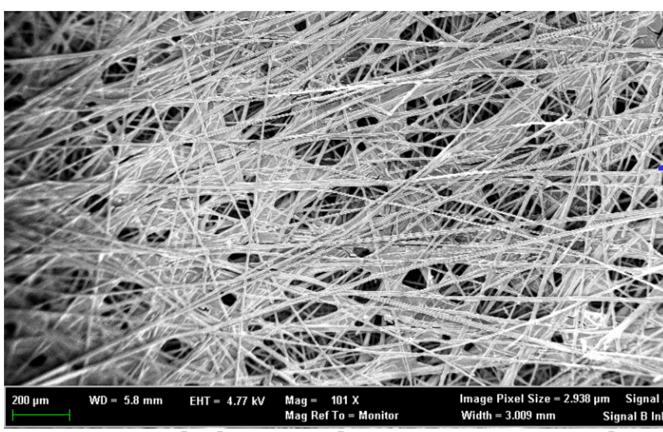


$AQDSH_2$

AQDS



E^0: +0.21 V   +1.09 V

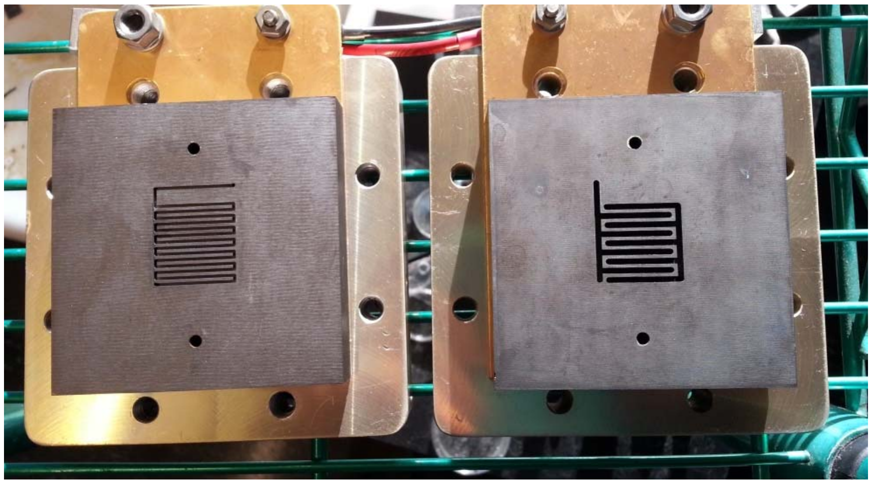


Porous carbon
paper electrode
(no catalyst)

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)

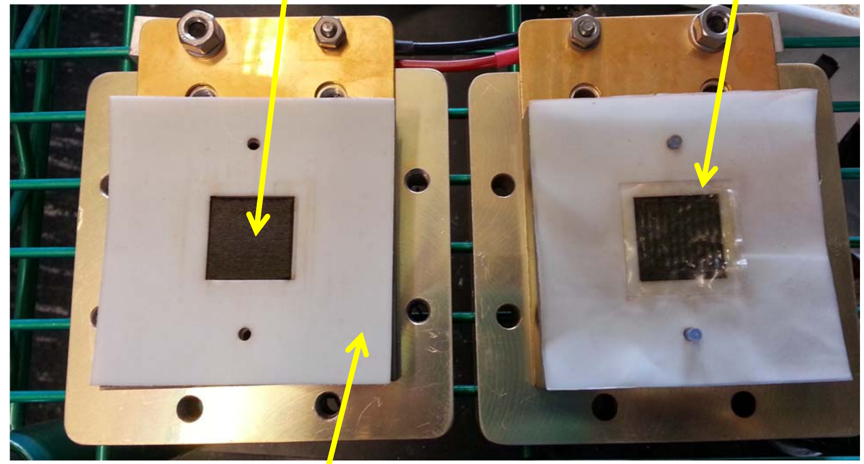
Cell Assembly

Serpentine flow field or Interdigitated flow field



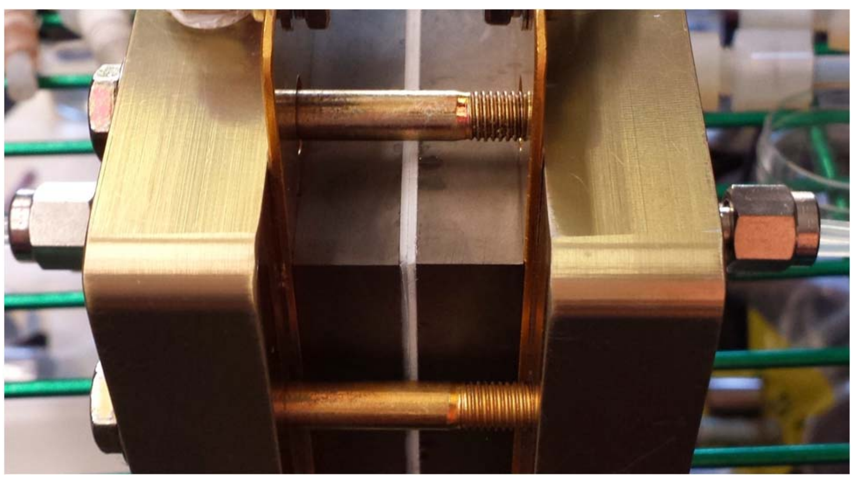
Carbon paper

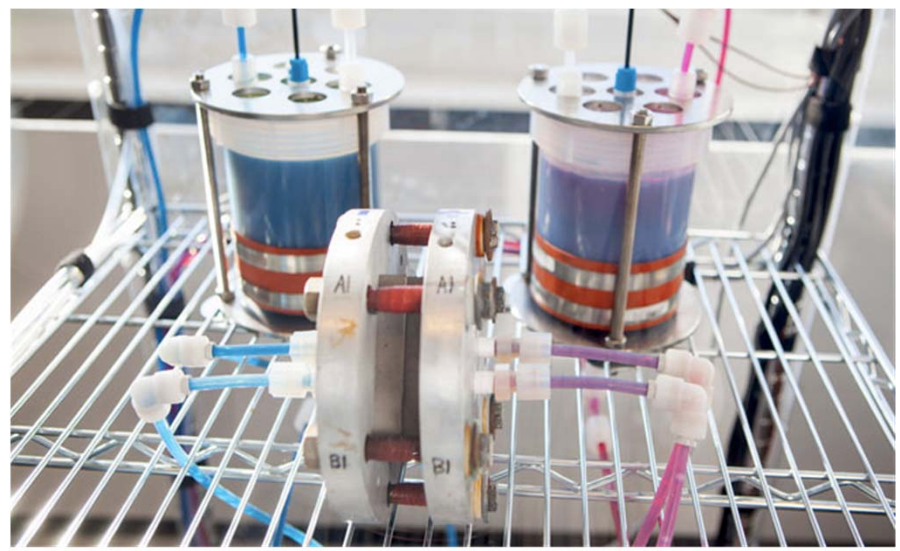
Nafion membrane



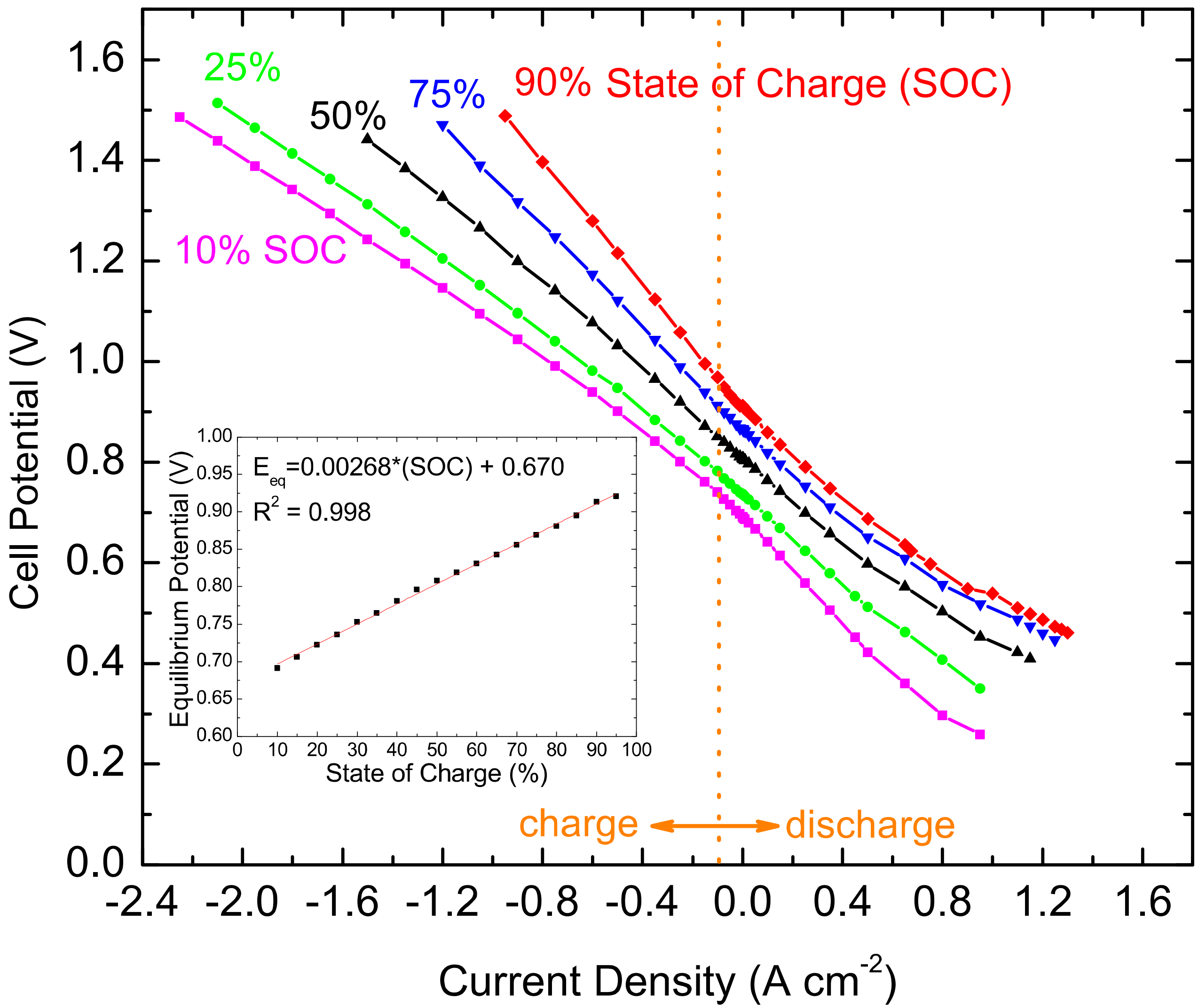
Teflon gasket

Assembled single-cell stack





Cell Performance



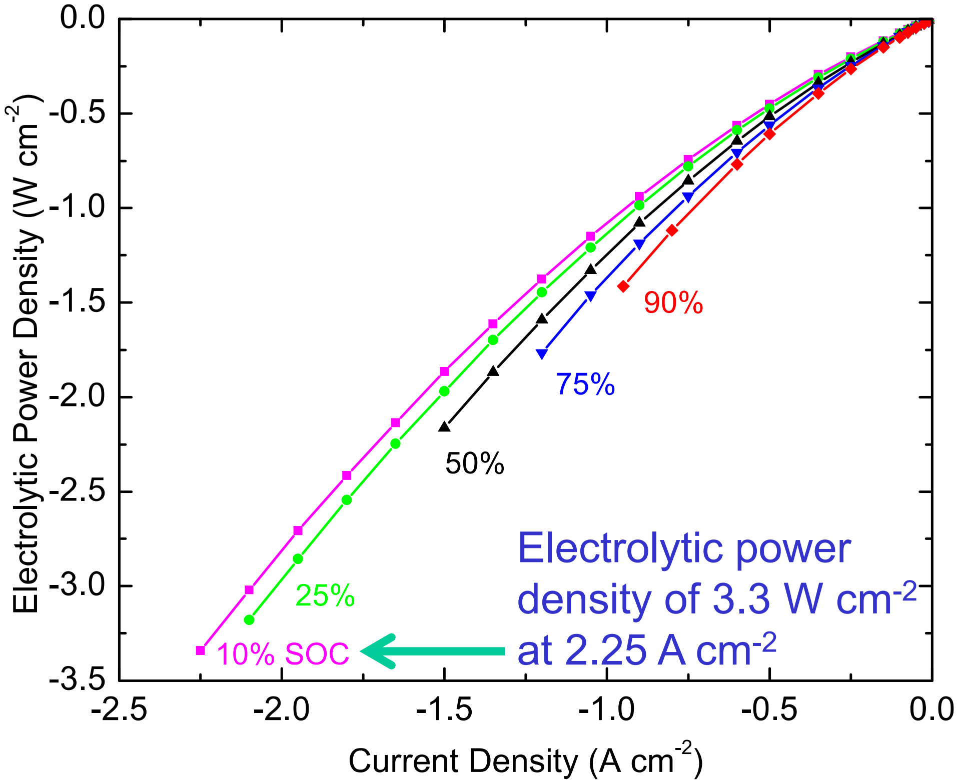
- Interdigitated flow fields
- Toray carbon paper electrodes (pretreated, 6 layers/side, **no added catalyst**)
- Nafion 212 (50 um), 40 °C
- posolyte: 3 M HBr + 0.5 M Br_2
- negolyte: 1 M 2,7-AQDS + 1 M H_2SO_4

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)

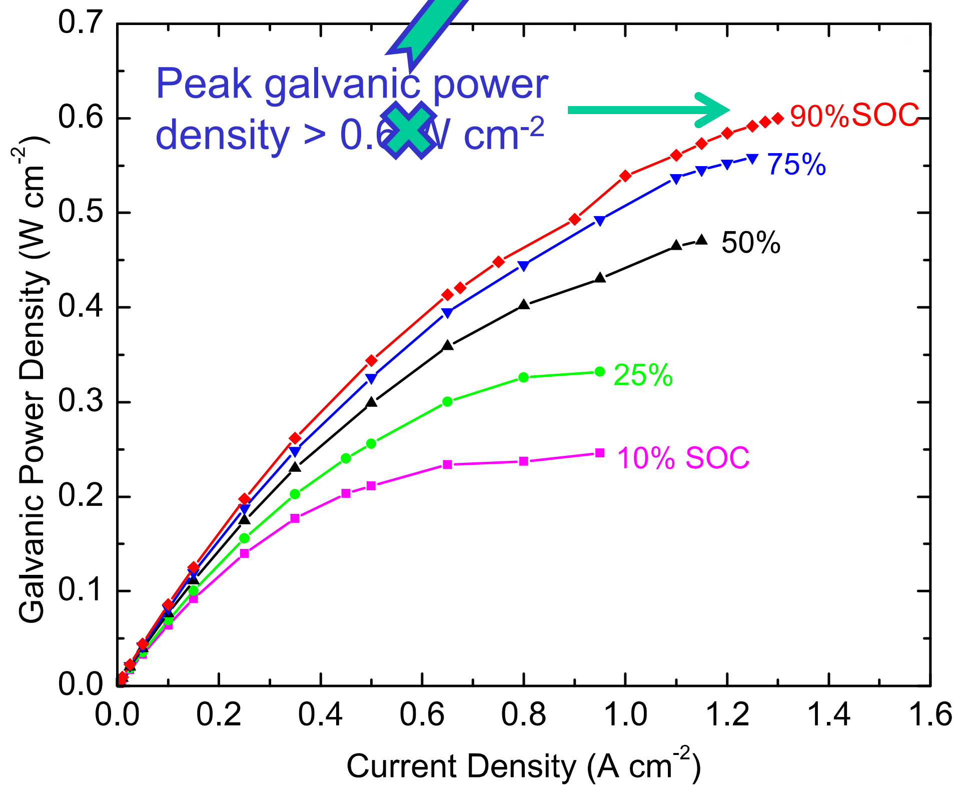
Cell Performance

now 1.0 W/cm^2

Electrolytic power density



Galvanic power density

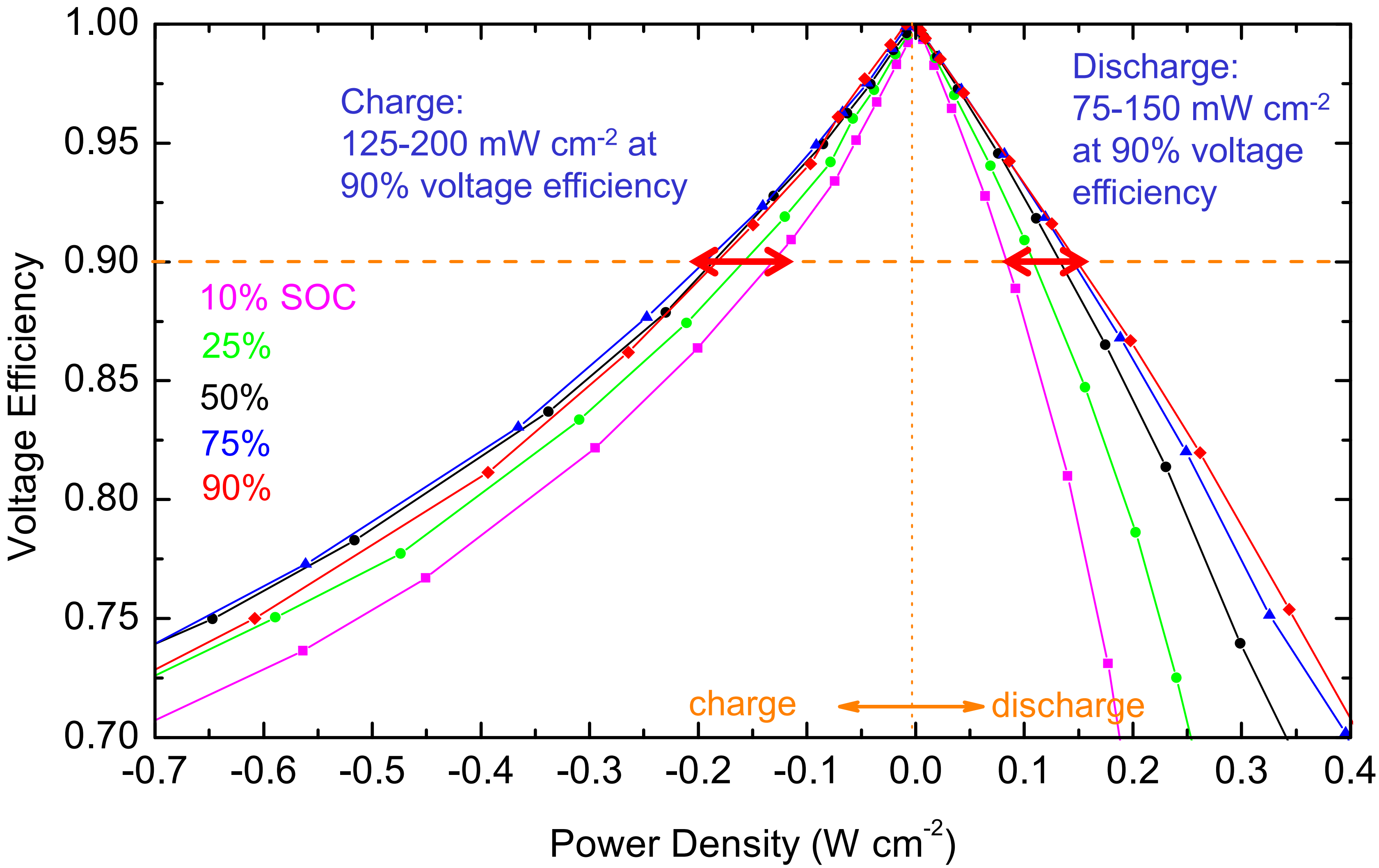


→spans decades of VRB development in 1 year

- 40 ^{o}C
- posolyte: 3 M HBr + 0.5 M Br_2
- negolyte: 1 M AQDS + 1 M H_2SO_4

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)

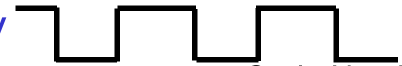
Voltage Efficiency

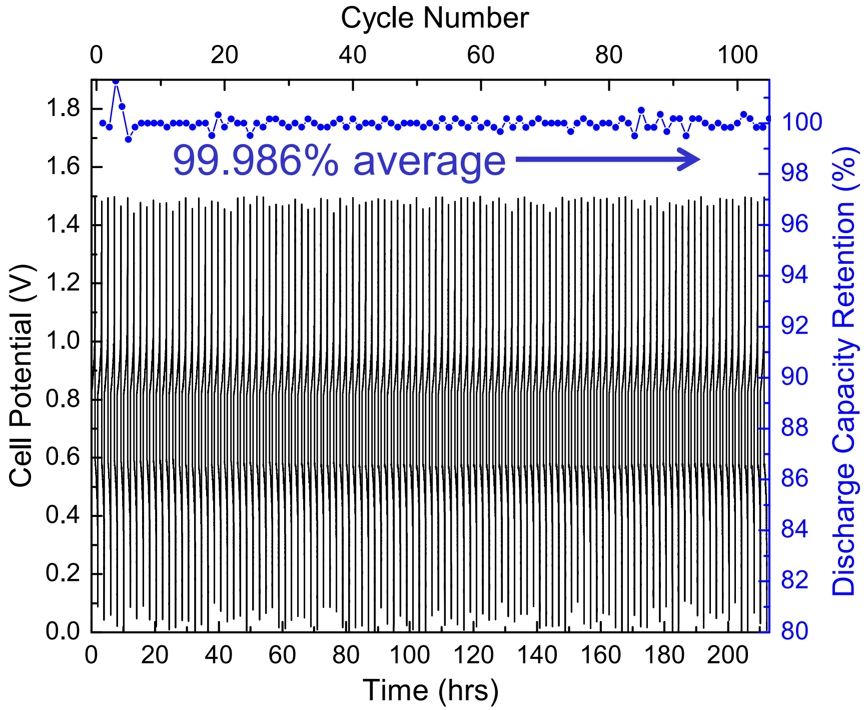


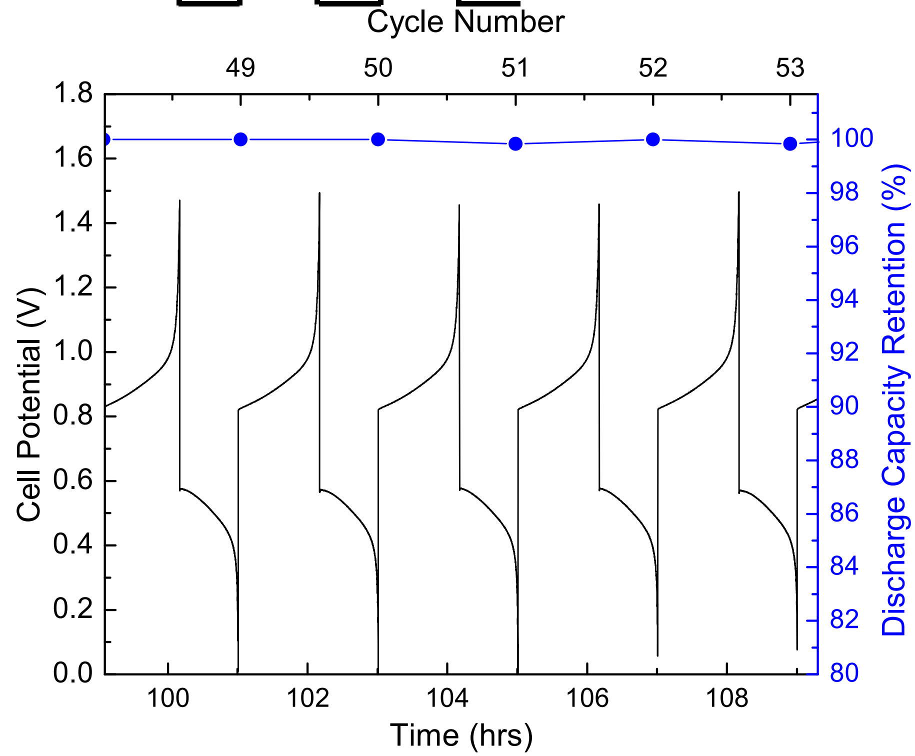
B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, “A metal-free organic-inorganic aqueous flow battery”, *Nature* **505**, 195 (2014)

Cycling to ~10^2

Impose ±0.25 A/cm^2 square wave, switched at 0, +1.5 V







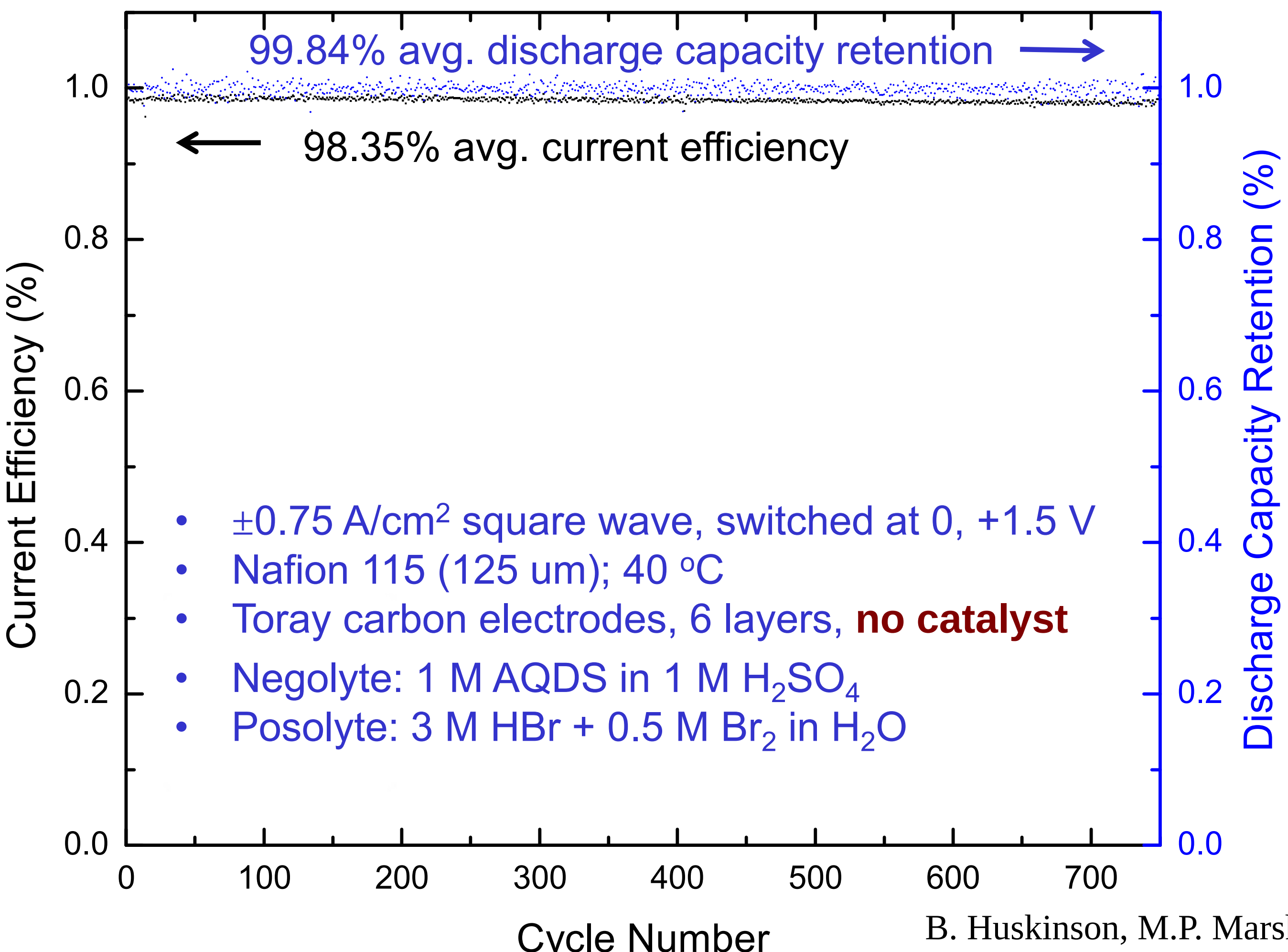
Capacity Retention = (Coulombs of discharge) / (immediately preceding coulombs of discharge)

- Nafion 115 (125 um); 30 °C
- Toray carbon electrodes 2 cm^2, 6 layers, **no catalyst**
- Negolyte: 1 M AQDS in 1 M H_2SO_4
- Posolyte: 3 M HBr + 0.5 M Br_2 in H_2O

B. Huskinson, M.P. Marshak, M.R. Gerhardt and M.J. Aziz, "Cycling of a quinone-bromide flow battery for large-scale electrochemical energy storage", *ECS Trans*. **61**, 27 (2014)

Cycling to ~10^3

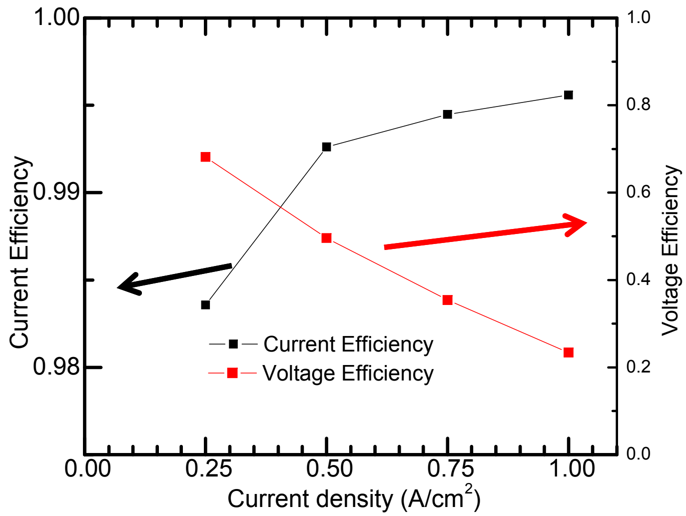
Capacity Retention = (Coulombs of discharge) / (immediately preceding coulombs of discharge)
Current Efficiency = (Coulombs of discharge) / (immediately preceding coulombs of charge)



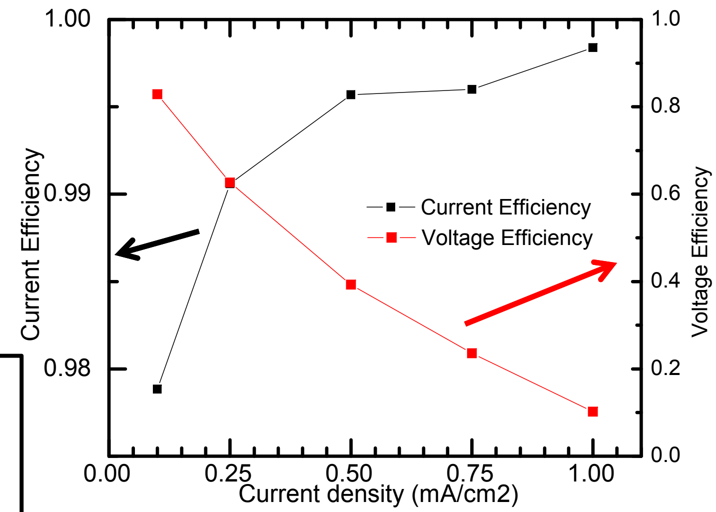
B. Huskinson, M.P. Marshak, M.R. Gerhardt and M.J. Aziz, "Cycling of a quinone-bromide flow battery for large-scale electrochemical energy storage", *ECS Trans.* **61**, 27 (2014)

Efficiency vs. Current Density

Nafion 212

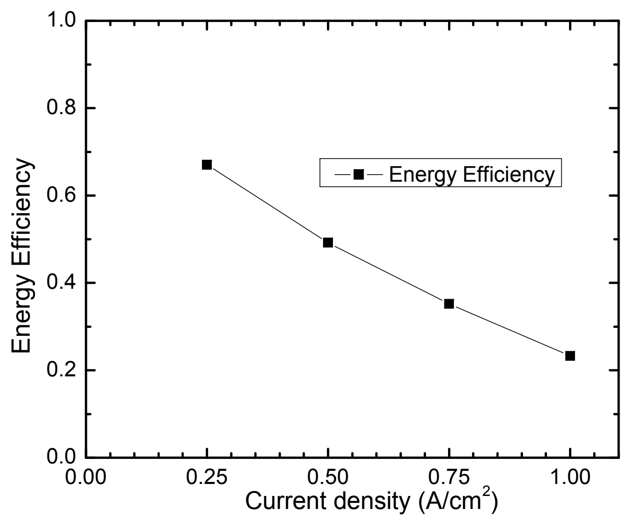


Nafion 115

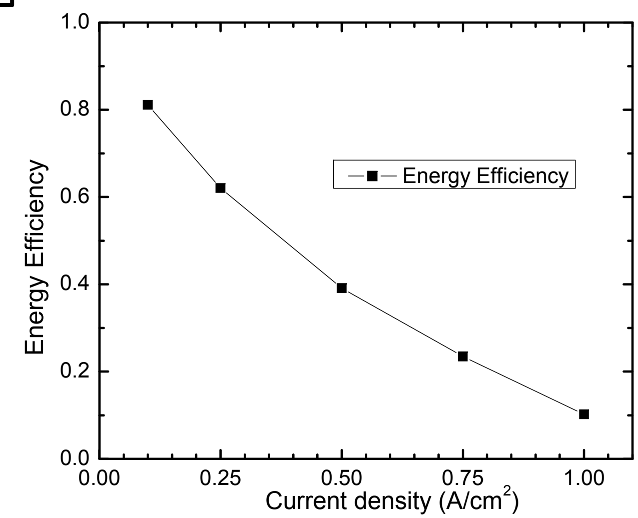


current efficiency loss:

- Br_2 crossover?
- O_2 permeation?
- H_2 evolution?



Negolyte: 20 mL
(1M AQDS + 1M H_2SO_4)
Posolyte: 125 mL
(**3.5M HBr** + 0.5M Br_2)
Electrode Area: 5 cm^2



Additional Advantages of Quinones for Energy Storage

Low chemicals cost: Enables low cost/kWh

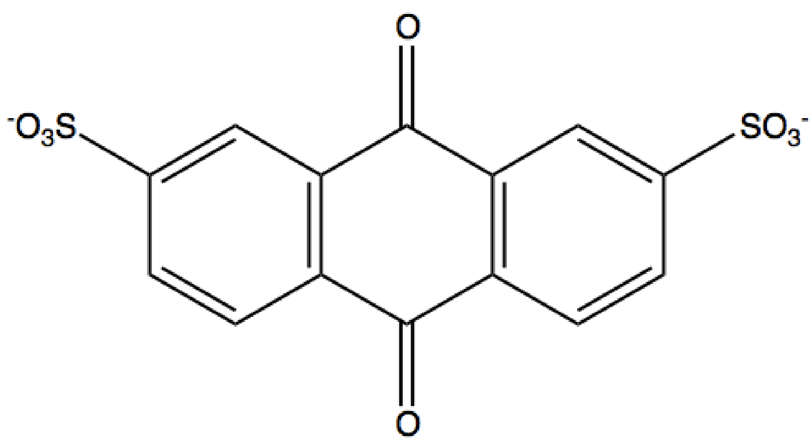
Rapid redox kinetics: Enable low cost/kW

Redox couple	k_0 [cm/s] (electrode material)
$AQDS/AQDSH_2$	7.2×10^{-3} (carbon)
Br_2/Br^-	$5.8 \text{ X } 10^{-4}$ (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

Additional Advantages of Quinones for Energy Storage

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator



- Dianions: reduced crossover through cation-exchange membranes
- Quinones on both sides would eliminate Br_2 exposure and Br_2 crossover
  → **hydrocarbon membranes**
- Bulky molecules may enable inexpensive separator
- Possibility of functionalizing with additional R groups for physical or chemical membrane exclusion

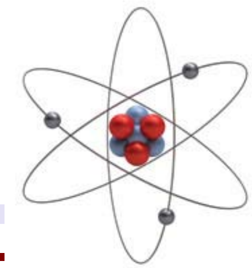
Quinones as an Energy Storage Medium

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator
All-liquid storage:	Enables inexpensive BOS and high cycle life

Quinones as an Energy Storage Medium

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator
All-liquid storage:	Enables inexpensive BOS and high cycle life
Aqueous electrolyte:	Enables fireproof operation

Li-ion batteries → ubiquitous
. . . but safety concerns are not going away



- Damaged/overheated Li-ion cells can ignite spontaneously & create fierce fires
- Li cells have been implicated in at least 24 combustion incidents on or around aircraft in 2010-2012, both in cargo and carry-on bags (*Wall Street Journal*, 12/30/2012)
- **Li-ion batteries containing more than 25 grams (0.88 oz) equivalent lithium content (ELC) are forbidden in air travel** (*safetravel.dot.gov*)

Company	Date of Recall	# recalled
Sony	2006	10,000,000
Dell	December 2006	22,000
Lenovo	March 2007	~205,000
Nokia	August 2007	46,000,000

9-Nov-2008—Li-ion fire destroys Pearl Harbor-docked Advanced SEAL Delivery System (ASDL); $237M in damage

May-2011—fire ignites in battery pack 3 weeks after crash test of Chevy Volt

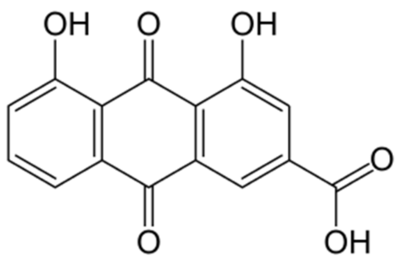
3-Sep-2010—Li battery fire ignites aboard UPS 747 departing Dubai; crash kills both pilots

7-Jan-2013—fire ignites in Li-ion battery pack (2× size of a car battery) of auxiliary power unit in 787 Dreamliner while on the ground in Boston

Slide courtesy of Dr. Debra Rolison, NRL

Quinones as an Energy Storage Medium

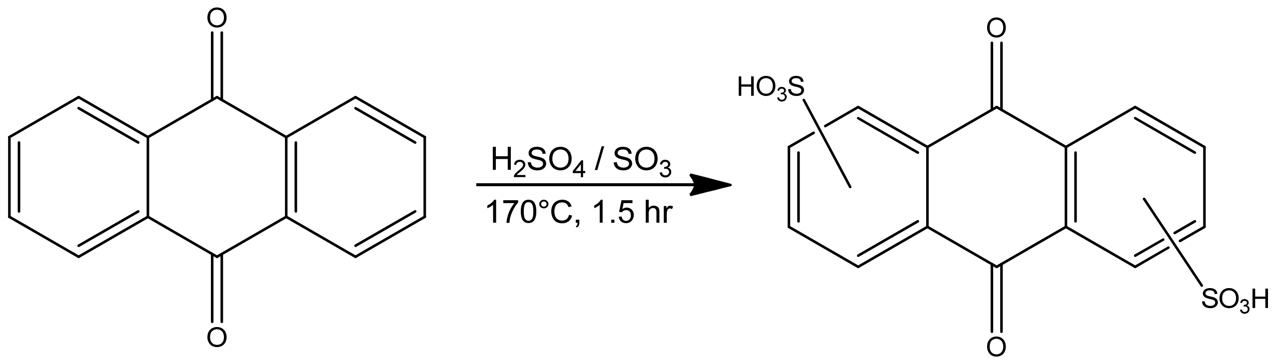
Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator
All-liquid storage:	Enables inexpensive BOS and high cycle life
Aqueous electrolyte:	Enables fireproof operation
Non-toxic:	Ideal for commercial, residential markets



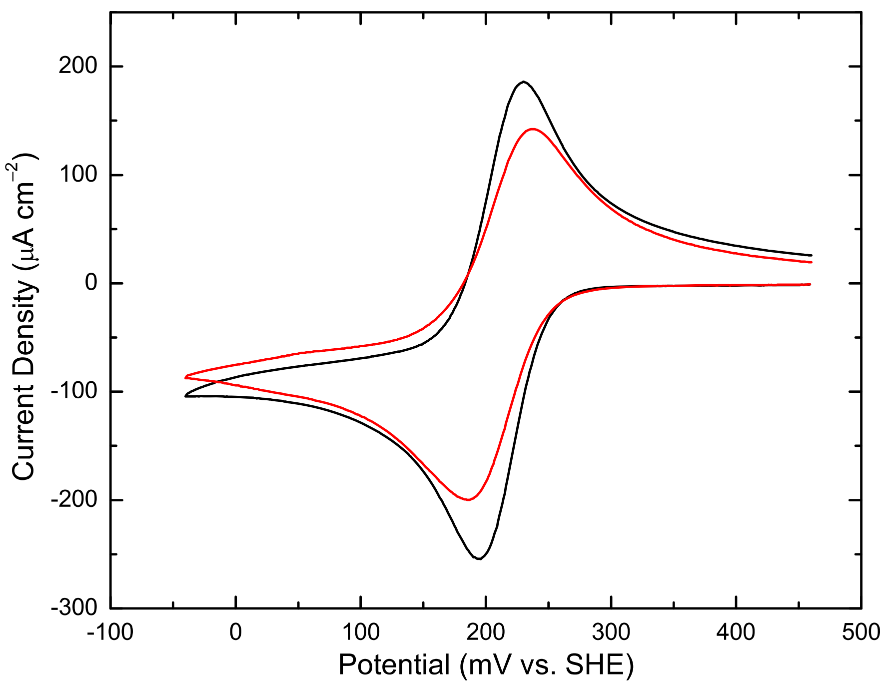
Quinones as an Energy Storage Medium

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator
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

Scalability



$ 4.74 / kg



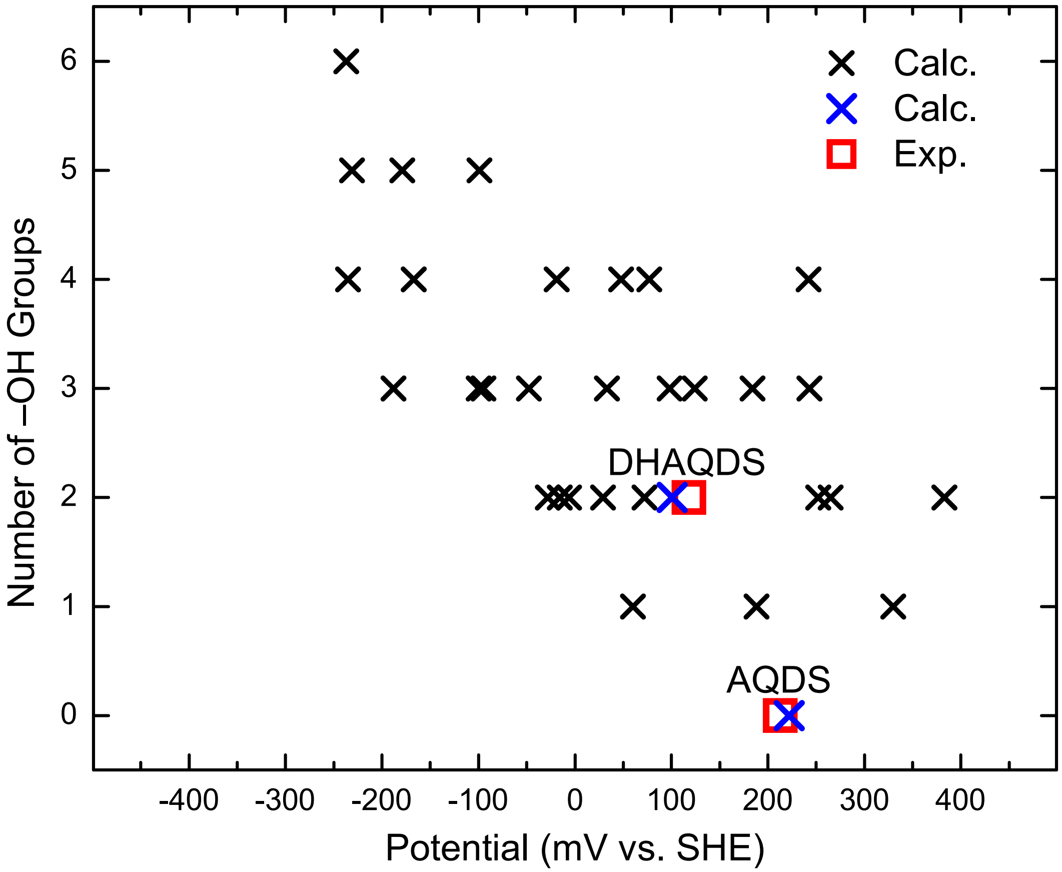
Bulk synthesis of AQDS mixtures without purification leads to nearly identical half-cell performance.

Estimated electrolyte cost of <$21/kWh for AQDS and $6 for Br Gives <$27/kWh cost of chemicals for QBFB.

Quinones as an Energy Storage Medium

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low cost/kW
Small organic molecules:	Enable inexpensive separator
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

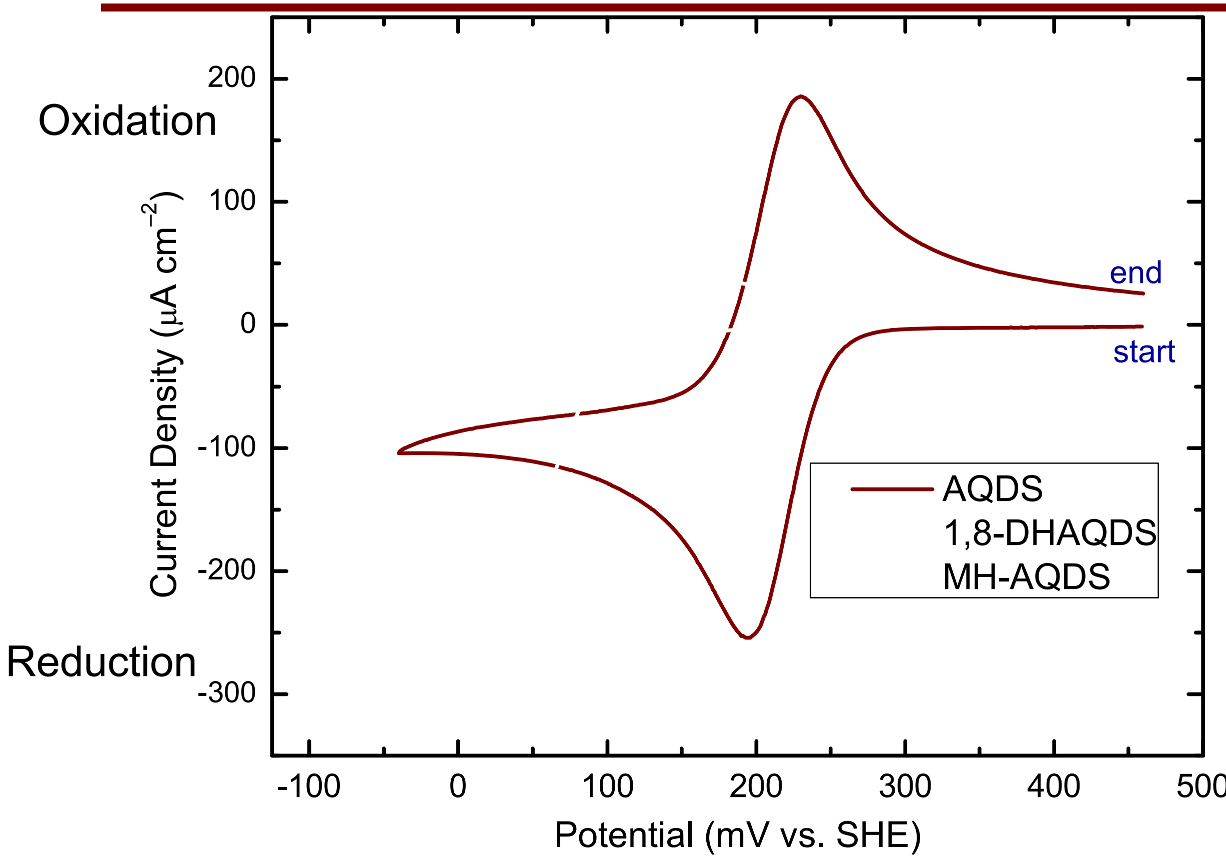
Computational Screening



Electron-donating –OH groups lower the reduction potential.

Changwon Suh, Süleyman Er, Michael Marshak, Alán Aspuru-Guzik

Tunability



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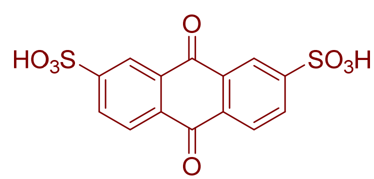
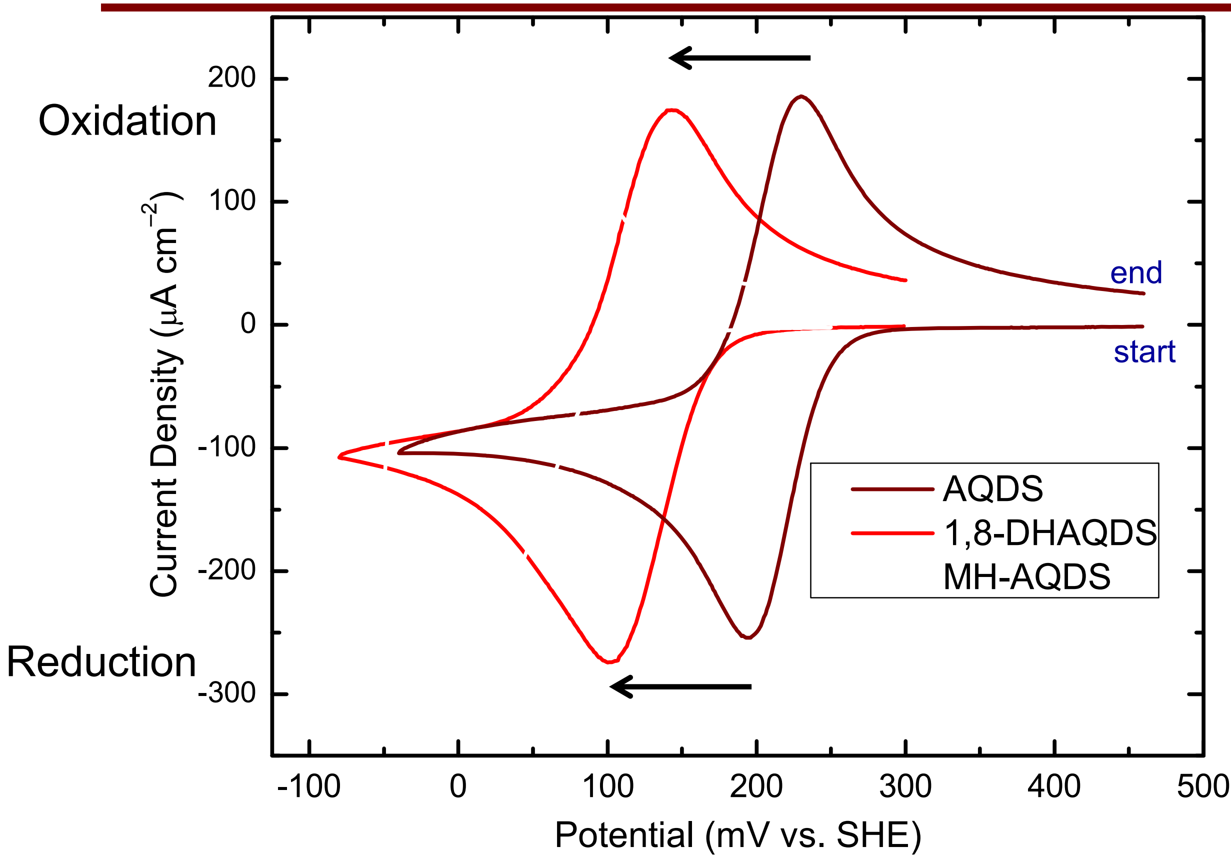
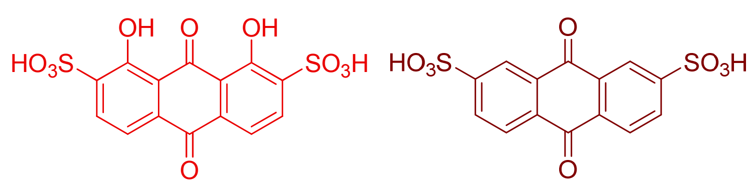


AQDS

$E^0 = 0.210$ V

Tunability



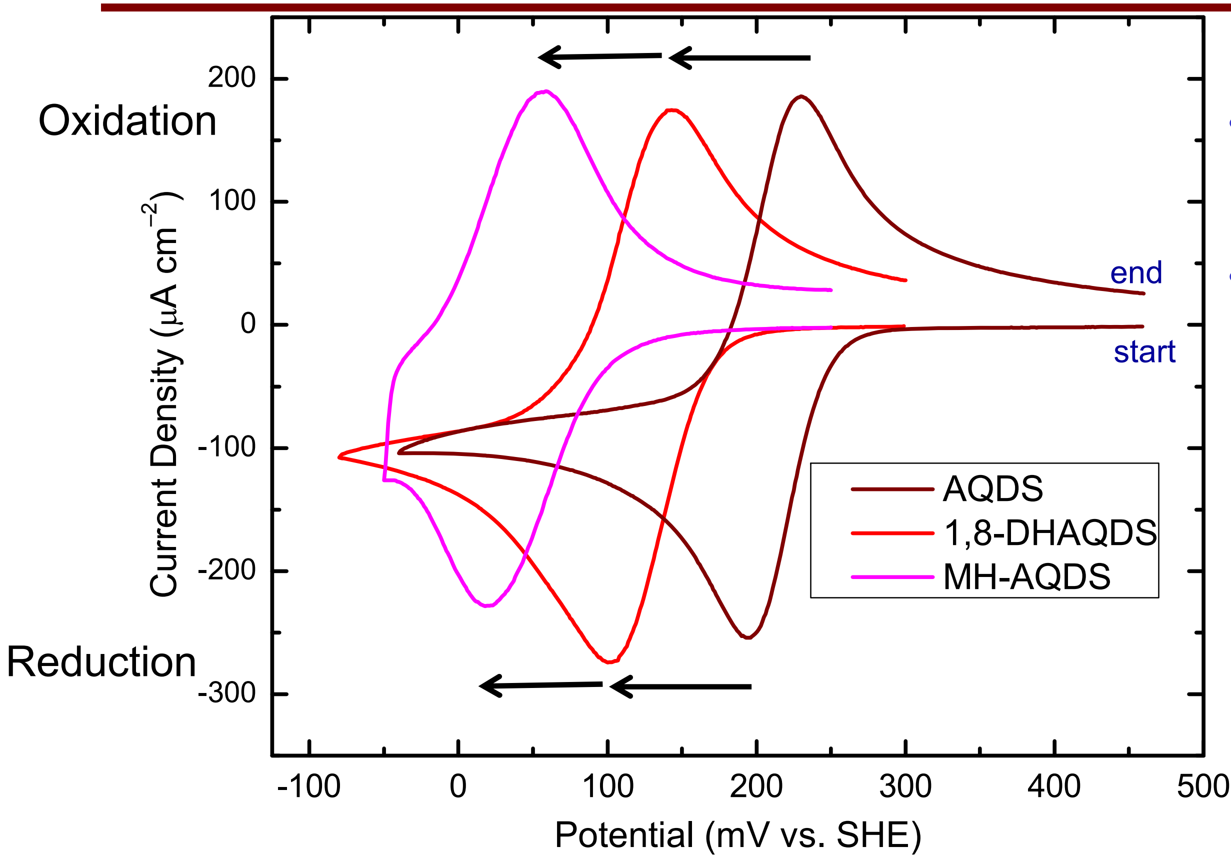


1,8-DHAQDS
E^0 = 0.118 V

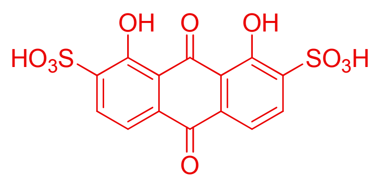
AQDS
E^0 = 0.210 V

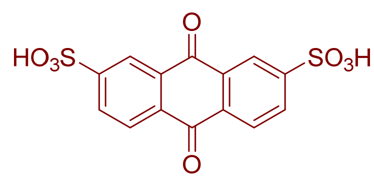
Cooper Galvin

Tunability



- Addition of OH groups lowers the reduction potential by ~170 mV
- Expect ~20% increase in OCV of Quinone-Bromide cell





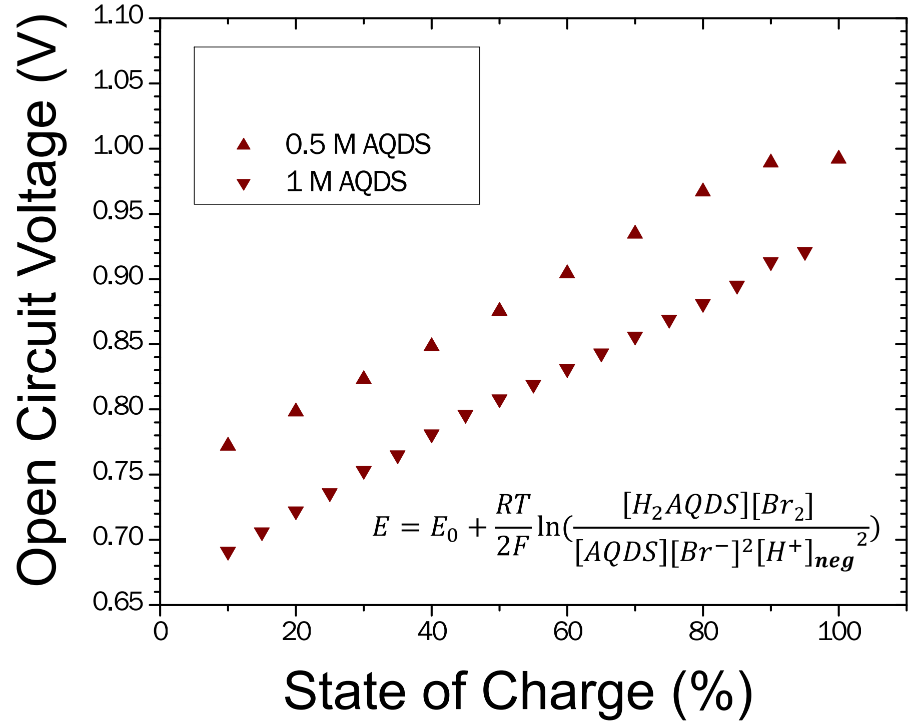
MH-AQDS
$E^0 = 0.039$ V

1,8-DHAQDS
$E^0 = 0.118$ V

AQDS
$E^0 = 0.210$ V

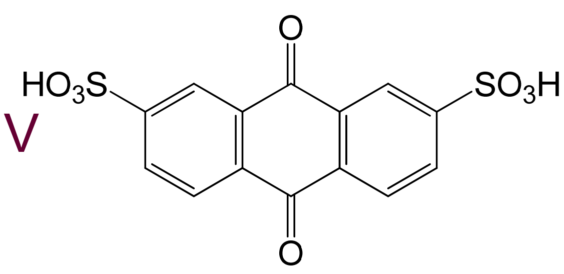
Cooper Galvin,
Michael Marshak

Tunability Demonstration in Quinone-Bromide Cell



Preliminary results from DHAQDS and AQS flow cells against HBr/Br_2 show open circuit voltage rising above 1.0 V at high state of charge.

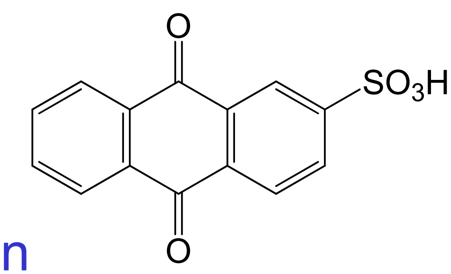
AQDS
$E^0 = 0.210$ V

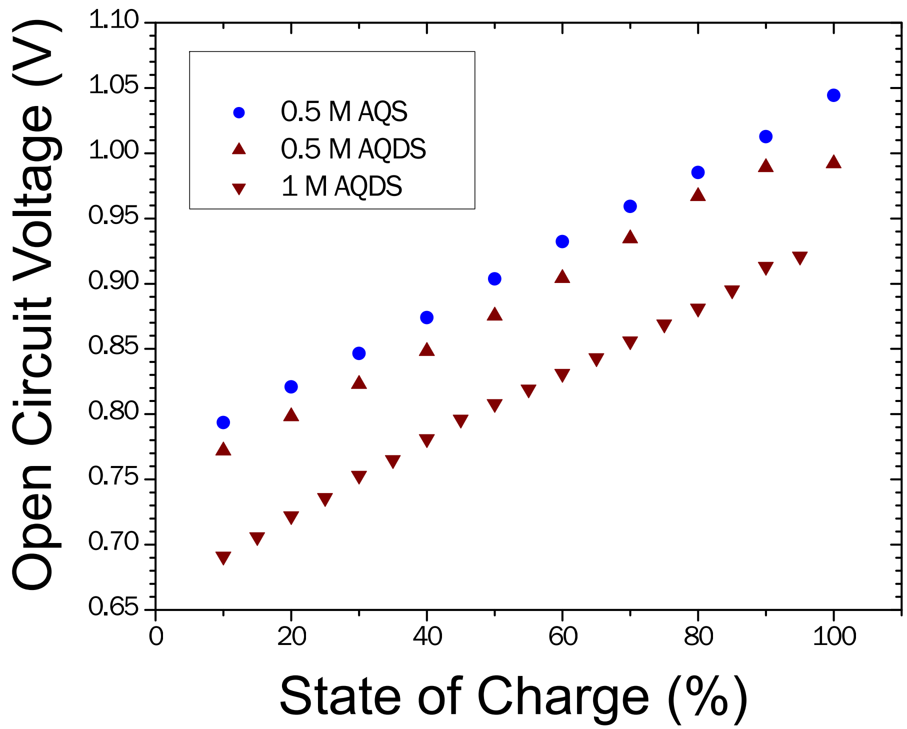


Michael Gerhardt (unpublished)

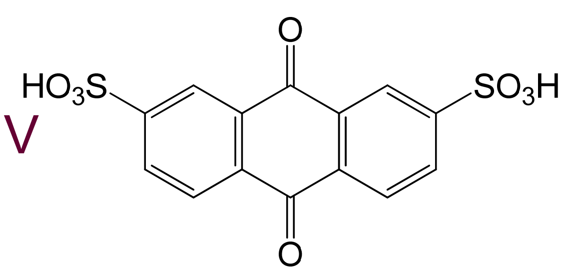
Tunability Demonstration in Quinone-Bromide Cell

AQS
$E^0 = 0.193$ V
17 mV OCV gain





AQDS
$E^0 = 0.210$ V

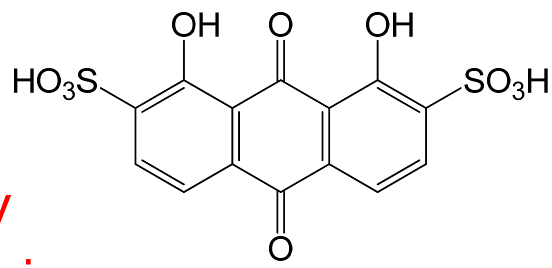


Preliminary results from DHAQDS and AQS flow cells against HBr/Br_2 show open circuit voltage rising above 1.0 V at high state of charge.

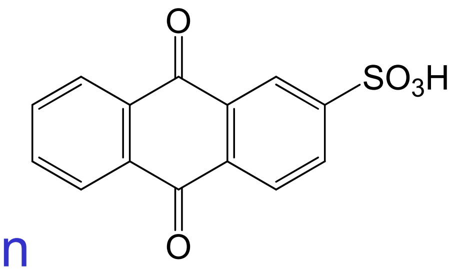
Michael Gerhardt (unpublished)

Tunability Demonstration in Quinone-Bromide Cell

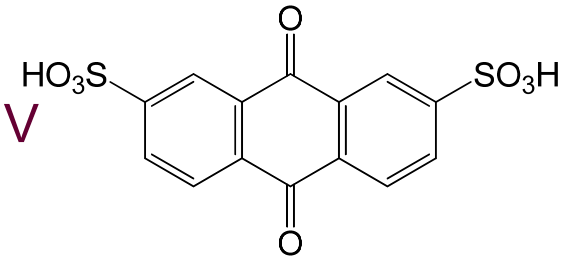
DHAQDS
$E^0 = 0.118$ V
92 mV OCV gain

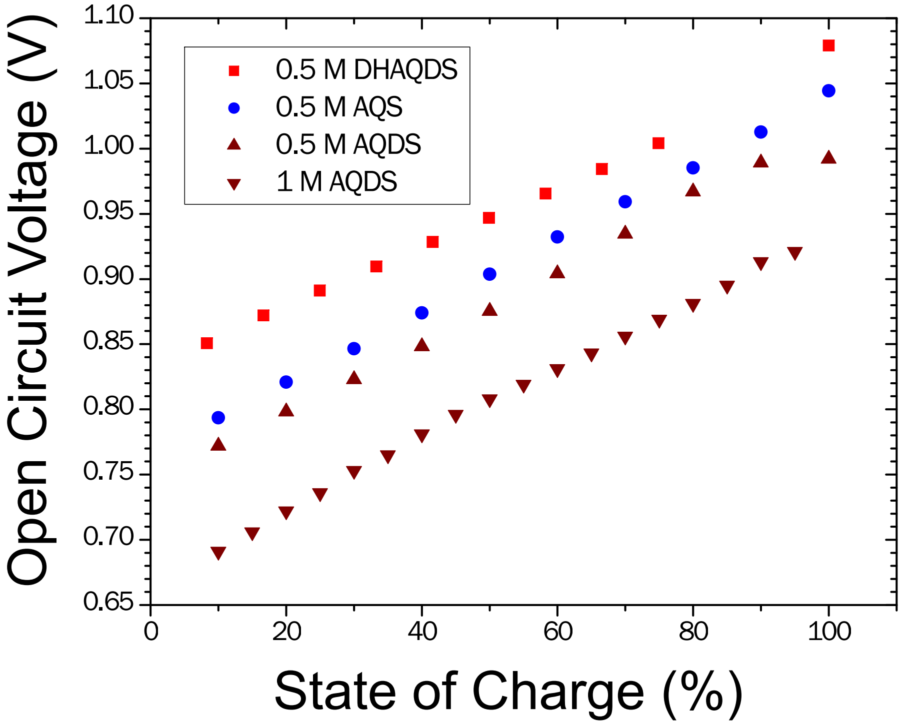


AQS
$E^0 = 0.193$ V
17 mV OCV gain



AQDS
$E^0 = 0.210$ V





Preliminary results from DHAQDS and AQS flow cells against HBr/Br_2 show open circuit voltage rising above 1.0 V at high state of charge.

Michael Gerhardt (unpublished)

1.0 V Quinone-Quinone Cell

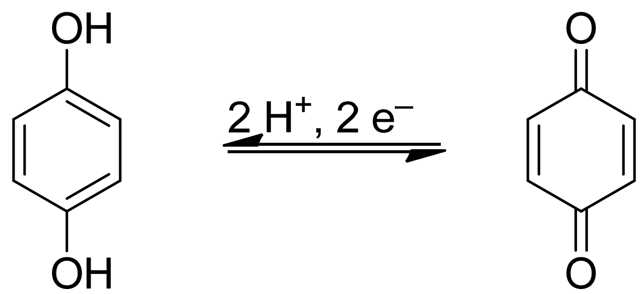
0.1 M in H_2O
Open Circuit Potential = 1.03 V
Peak power density = 50 mA cm^{-2}
>99% current Efficiency

High cell resistance
due (primarily?) to low ion conc.

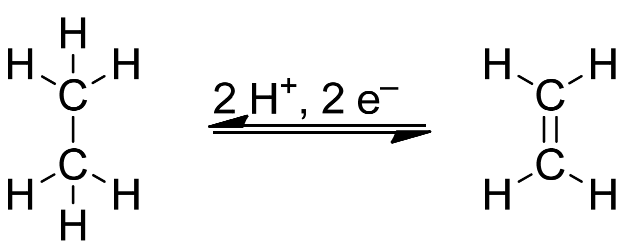
Michael Marshak, Liuchuan Tong (unpublished)

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



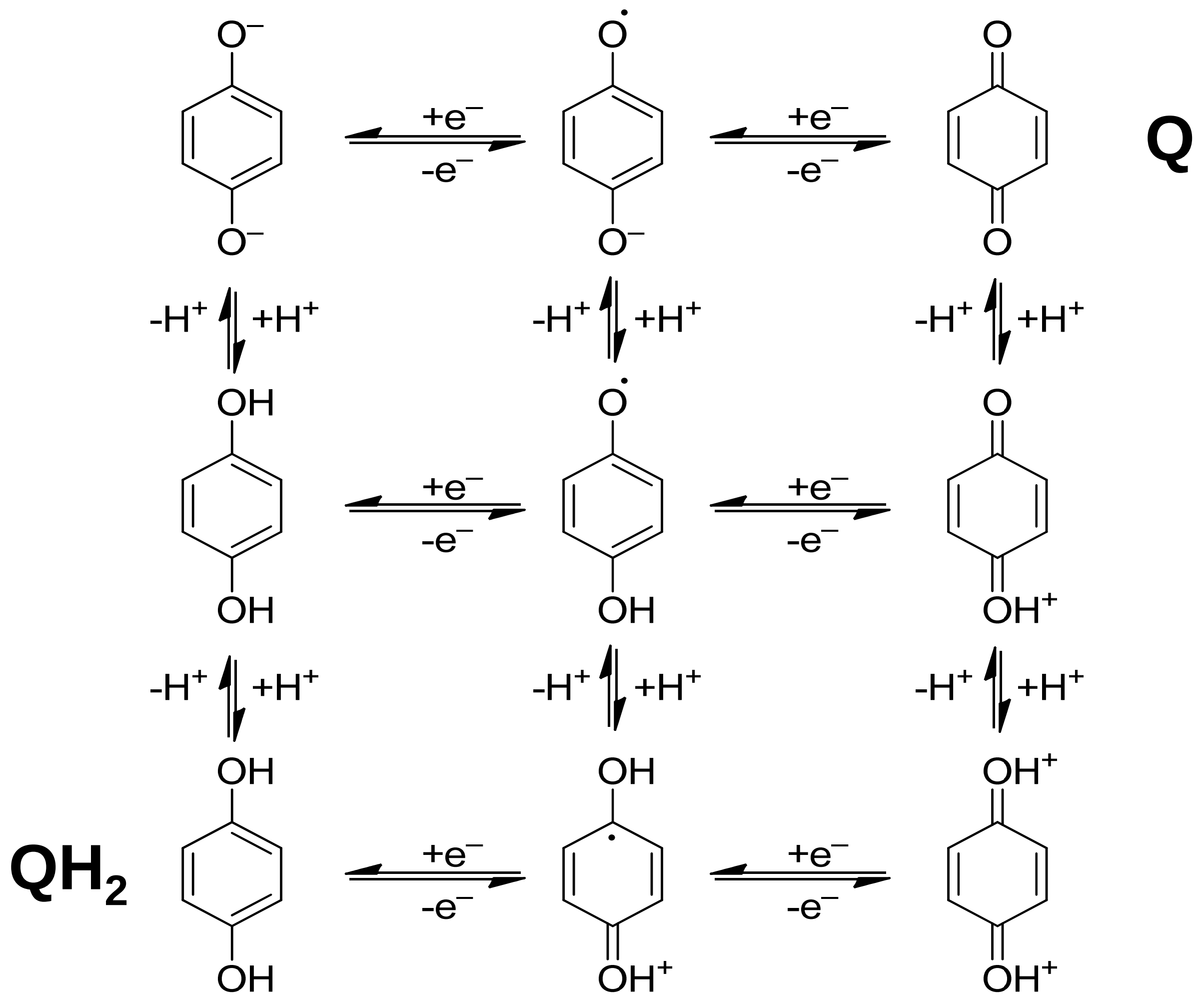
ethane ethylene

J. B. Conant

L. F. Fieser

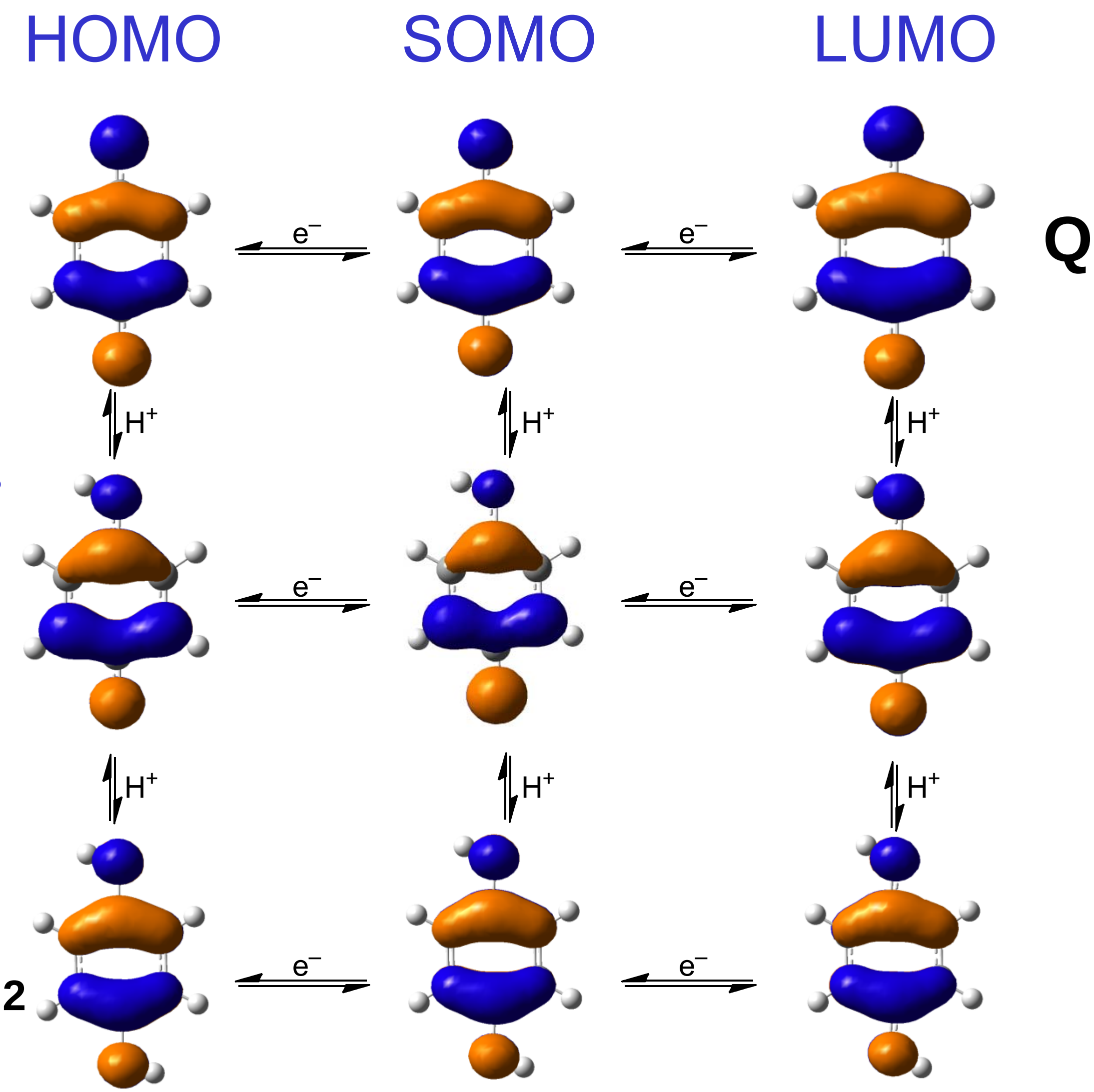
J.B. Conant, H.M. Kahn, L.F. Fieser, S.S. Kurtz,, *J. Am. Chem. Soc.* **44**, 1382 (1922).

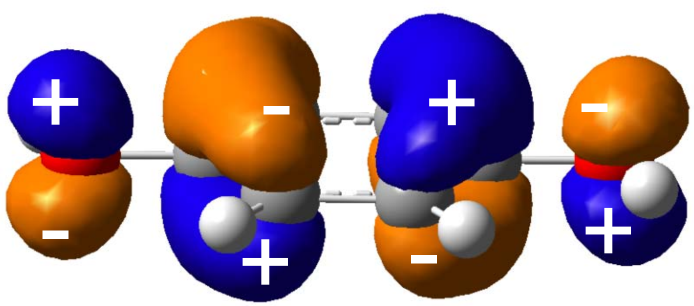
Quinone Redox Scheme



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



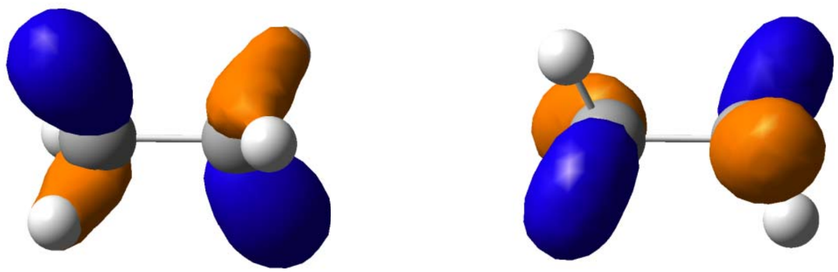


QH_2

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

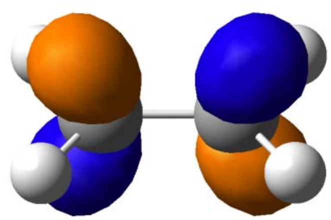
Ethane/Ethylene Orbitals

C_2H_6



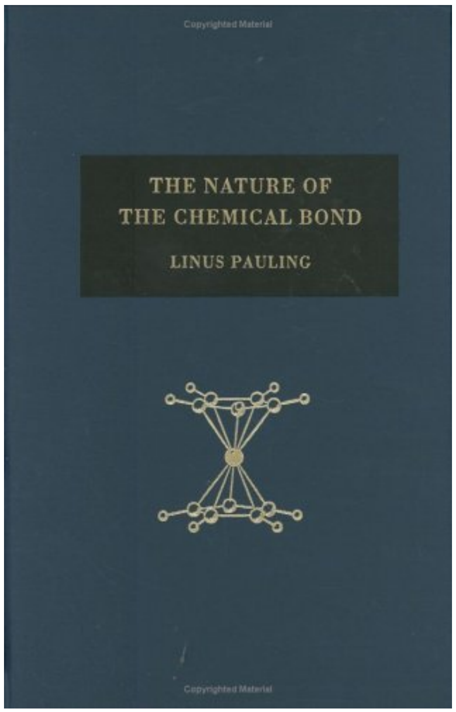
Degenerate HOMO of Ethane consists of C−H σ bonds

C_2H_4



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

Outlook

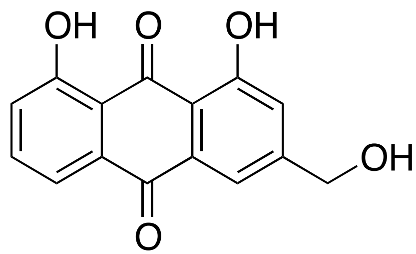


- Cost and tunability of redox-active organics look promising for E storage, other apps?
- High power density, low cost quinone-bromine Redox Flow Batt proves the concept
- There is plenty of room for improvement
  - molecules
  - separators
  - porous electrodes and fluidics
- How low can the capital cost be?

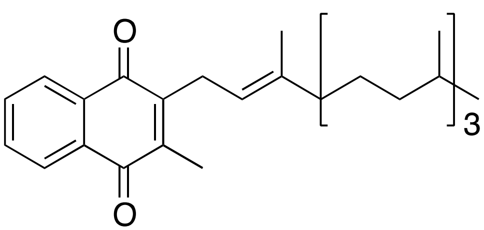
Fun Facts about Quinones

Hydroquinone cream is used to bleach dark spots, moles, etc off of skin

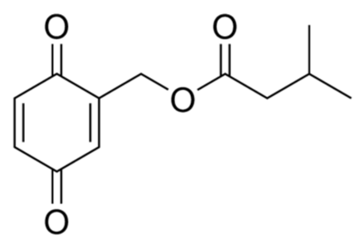
Emodin is found in Aloe Vera

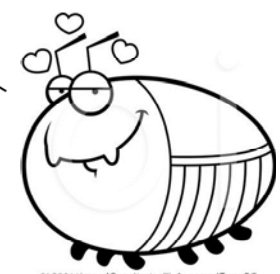


Vitamin K_1 is part of the electron transport chain in photosystem I, found in all green plants



Blatellaquinone is a sex pheromone female cockroaches use to attract males





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Acknowledgments

Harvard U Ctr for the Environment,
Harvard School of Engrg & Appl Sci
Harvard Physics Department,
NSF Grad Rsch Fellowship Program,
DOE ARPA-E award DE-AR0000348

Not pictured: Dr. Brian Huskinson, Professor Theodore Betley, Saraf Nawar, Rachel Burton, Cooper Galvin, Sidharth Chand, Tyler Van Valkenburg, Bilen Aküzüm, Ryan Duncan, Dr. Süleyman Er, Dr. Xudong Chen, Phil Baker, Dr. Trent Molter

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Second Row**: Jessa Piaia, Drew Wong, Kaixiang Lin, Prof. Xin Li, Dr. David Hardee, Dr. Michael Marshak**

Third Row: **Jennifer Wei, Dr. Qing Chen, Michael Gerhardt, Liuchuan Tong, Xinyou Ke**

Front Row: **Dr. Ed Pyzer-Knapp, Dr. Changwon Suh, Lauren Hartle, Prof. Michael Aziz, Prof. Roy Gordon**

Not pictured**: Prof. Theodore Betley, Saraf Nawar, Bilen Aküzüm, Rachel Burton, Cooper Galvin, Sidharth Chand, Phil Baker, Dr. Trent Molter, Dr. Brian Huskinson, Ryan Duncan, Dr. Süleyman Er, Dr. Xudong Chen**

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