Durability and Reactivity in Flow Battery Systems: Advances, Challenges and Prospects

Sri Narayan

University of Southern California, Los Angeles, CA

DoE- OE Workshop

Santa Fe, NM

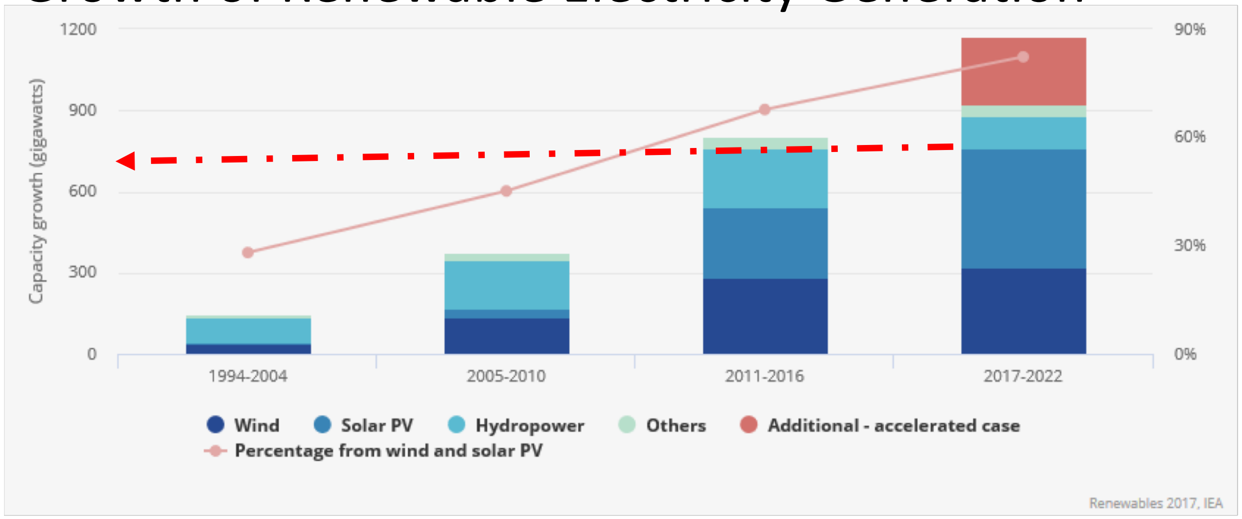
January 30-31, 2019

USC University of Southern California

The Demand for Large-Scale Energy Storage

USC
University of
Southern California

Growth of Renewable Electricity Generation



Renewables 2017, IEA

- Storing 20% of today’s renewable generation: i.e. 700 GWx 0.2 x 5 hours = 700 GWh /day
- With batteries with a specific energy of 100Wh/kg, it is 7 million metric tons of batteries.
- To meet all the global energy needs our generation capacity has to increase to 16000 GW, and at 20% storage, 160 million metric tons of batteries

Comparison of Battery Materials

Battery Materials	Price, $/kg	Global Reserves in Millions of tons	Toxicity
Lithium	70, Very High	53	High
Vanadium	27, Very High	63	High
Chromium	10, High	1.8	High
Antimony	13.7, High	1.8	High
Bromine	0.60, low	15,000 as NaBr	High
Lead	2.2, Moderate	95	High
Zinc	2.2, Moderate	150	Moderate
Manganese	3.2, Moderate	630	Low to None
Iron	0.20, Low	100,000 of iron ore	None
Oxygen(Air)	“Almost Free”	Practically Unlimited	None
Chloride/Sodium	0.20-0.50 Low	55 Billion, Practically unlimited in sea water	None
Carbon Materials	0.3 to 1, Low	Practically Unlimited	None

Sustainable Choices for Large-Scale Energy Storage

Unsustainable Choices

- Lithium reserves : 53 million metric tons; $70/kg
- Vanadium reserves: 63 million metric tons. $35/kg

Sustainable Choices : Abundant raw materials, manufactured using renewable energy

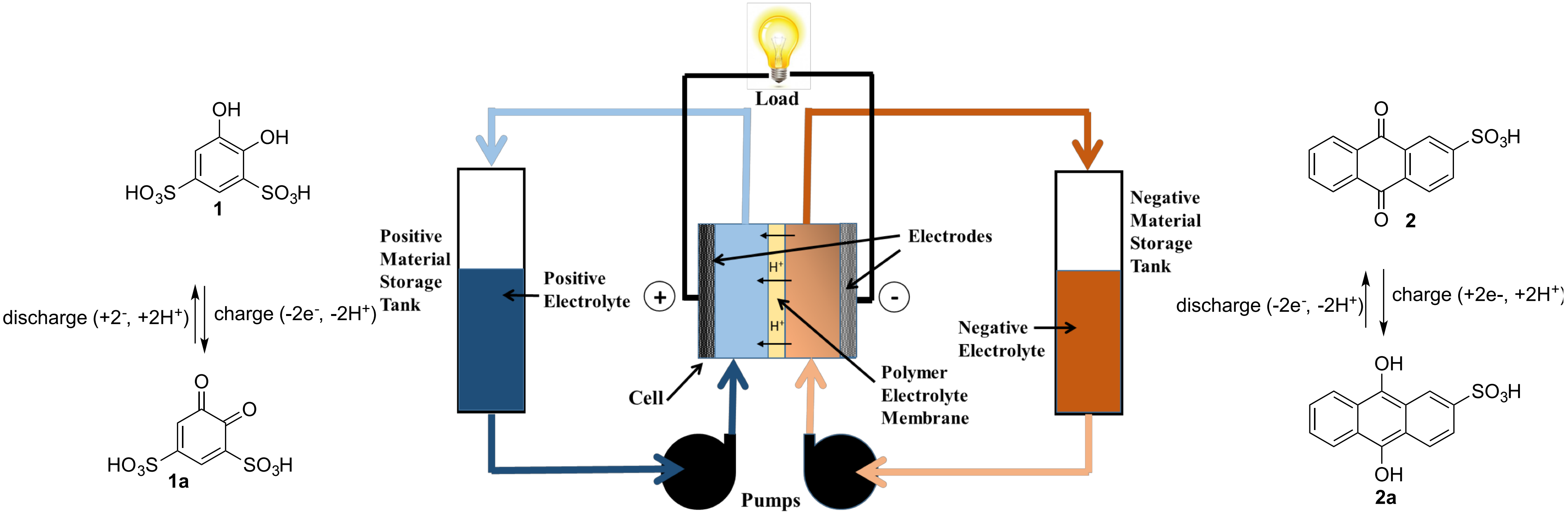
- We make 1700 million metric tons of steel/ year at $0.60 /kg
- Small organic molecules
  - Methanol: 110 million tons/year at $0.50/kg
  - Polyester : 75 million tons/year at $5-8/kg.
  - Phenol: 10 million tons/year at $2/kg.
- Combine hydrogen from efficient water electrolysis with carbon dioxide to make useful organic molecules (hydrogen at $4/kg)

Batteries based on abundant and sustainable materials

Three Battery Types:

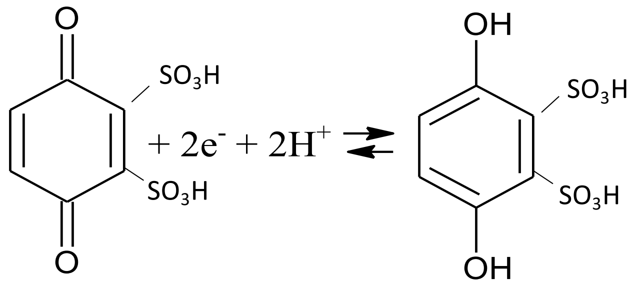
- Iron-based Alkaline Batteries : Iron-Air, Nickel-Iron, Iron-MnO_2
- Iron-Chloride Flow Battery
- Organic Redox Flow Battery

Aqueous Organic Redox Flow Battery



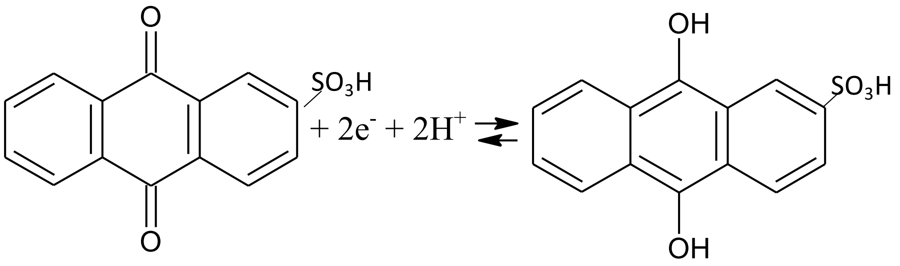
Yang, B.; Hoober-Burkhardt, L. E.; Wang, F.; Prakash, G. K. S.; Narayanan, S. R. *J. Electrochem. Soc.* **2014**, *161*, A1371

Features of the Quinone-based System



Benzoquinone disulfonic acid (BQDS)

$E^o = +0.70$ V

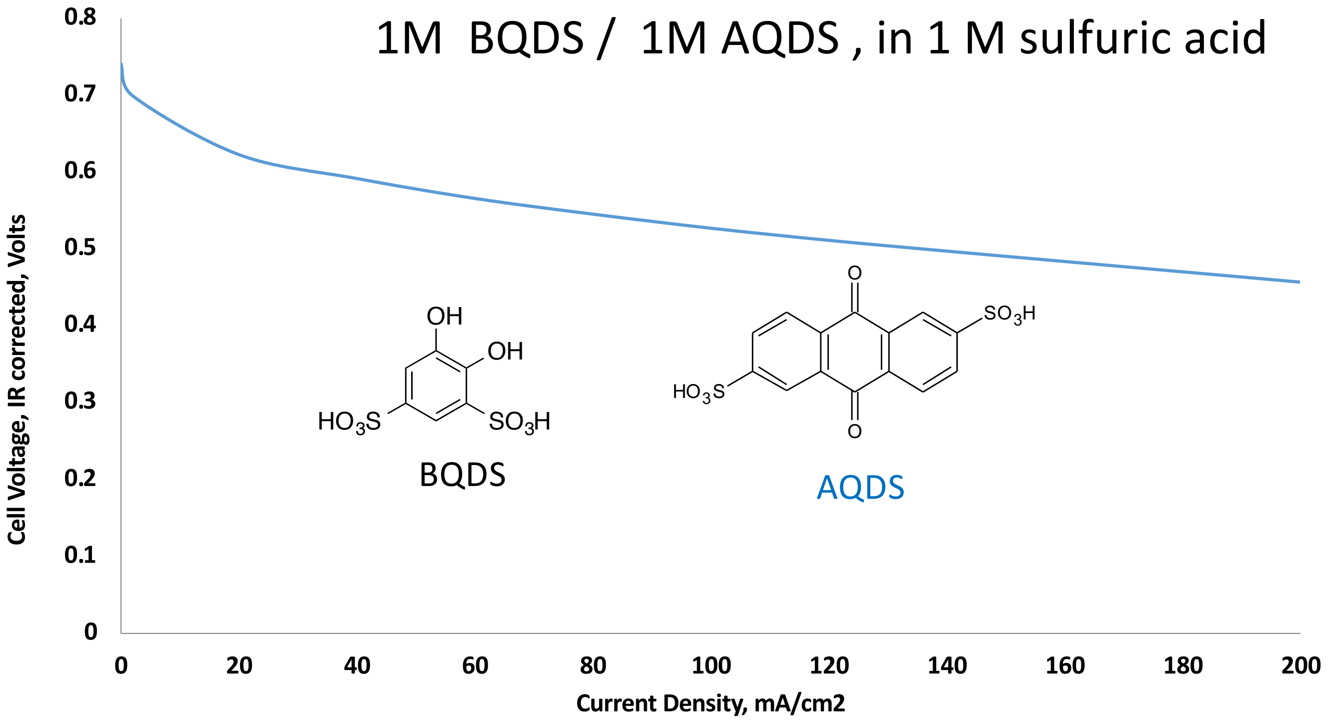


Anthraquinone sulfonic acid (AQDS)

$E^o = +0.16$ V

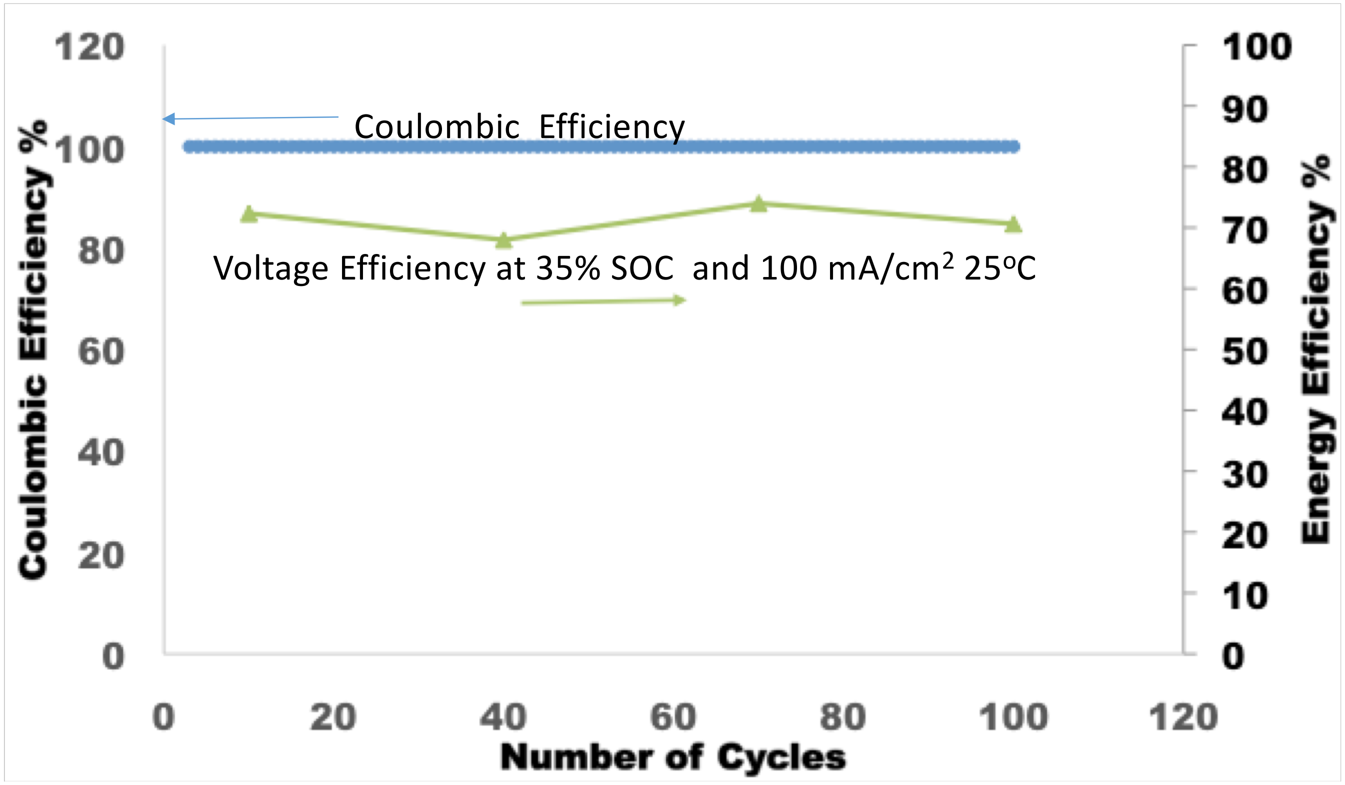
- Water Soluble (1-2 M solutions)
- Fast charge-transfer kinetics: $k_0 = 3\text{x}10^{-3}\text{cm s}^{-1}$
- Acceptable mass transport characteristics: $D_0 = 3\text{x}10^{-6}\text{ cm}^2\text{s}^{-1}$
- Standard Reduction potentials are tunable based on substitution.
- .Charge capacity in the range of 200-490 Ah/kg , 2e- reaction
- Manufactured cost : $ 5-10/kg

Polarization Characteristics of BQDS /AQDS Cell



Current densities as high as 200 mA/cm^2 is achieved with minimal polarization losses

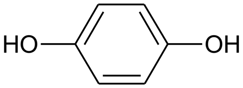
Coulombic and Energy Efficiency of 1M BQDS/AQDS Cell



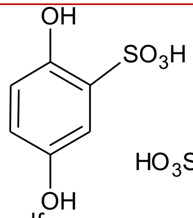
Substituent Effects on Electrochemical Properties

	Substituent type	Effect on Electrode Potential, mV	Effect on Solubility
Electron-Withdrawing	**Sulfonic acid - SO_3H**	+70	increases
	Chloro -Cl	+10 to +46	decreases
Electron-donating	**Hydroxyl -OH**	-100	increases
	Methoxyl –OCH_3	-90	decreases
	Ring addition (4-carbon)	-220	decreases
	Methyl -CH_3	-50	decreases
	-ortho to –para quinone	-130	no change

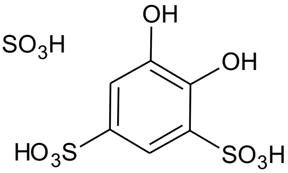
Benzoquinone Redox Couples



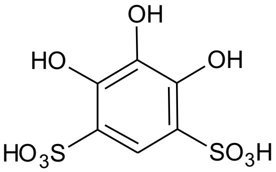
Hydroquinone



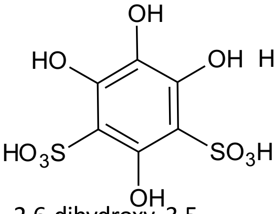
2-sulfo, p-benzoquinol



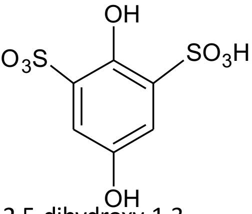
3,5-disulfo,o-benzoquinol



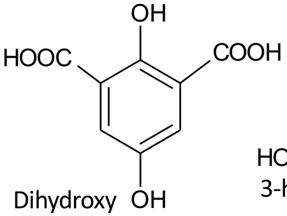
3-hydroxyl, 4,6-disulfo, o-benzoquinol



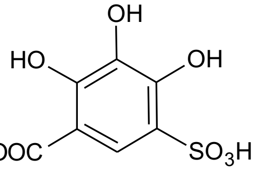
2,6-dihydroxy, 3,5-disulfo, p-benzoquinol



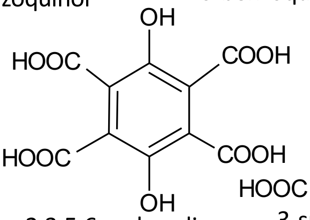
2,5-dihydroxy-1,3-benzenedisulfonic acid



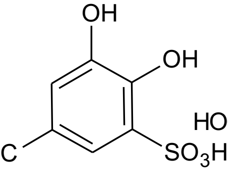
Dihydroxy dicarboxylic acid



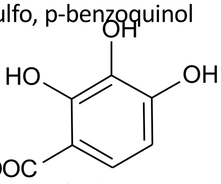
3-hydroxy, 4-sulfo, 6-carboxylic, o-benzoquinol



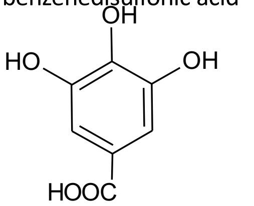
2,3,5,6-carboxylic acid, p-benzoquinone



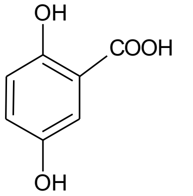
3-sulfo, 5-carboxylic, o-benzoquinol



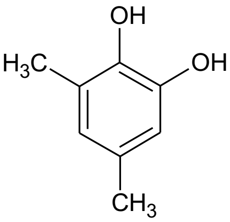
3-hydroxy,4-carboxlylic, o-benzoquinol



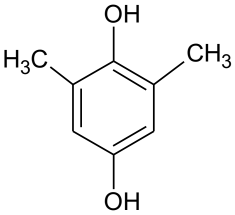
3-hydroxy,5-carboxylic, o-benzoquinol



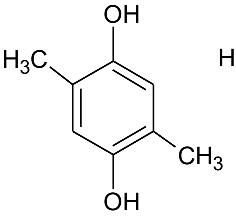
Dihydroxybenzoic acid



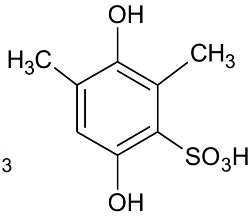
4,6-dimethyl o-benzoquinol



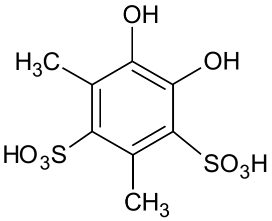
3,5-Dimethyl p-benzoquinol



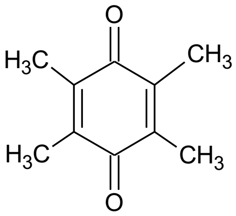
3,6-Dimethyl p-benzoquinol



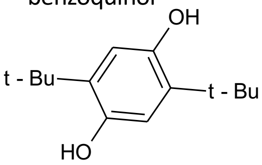
3,5-Dimethyl, 6-sulfo, p-benzoquinol



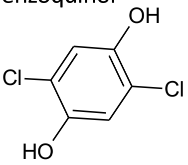
3,5-disulfo,4,6-dimethyl, o-benzoquinol



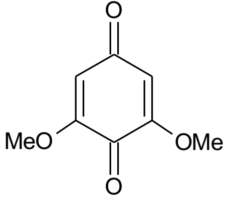
duroquinone



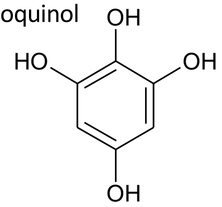
2,5-di-tert-butyl hydroquinone



2,5-dichloro hydroquinone

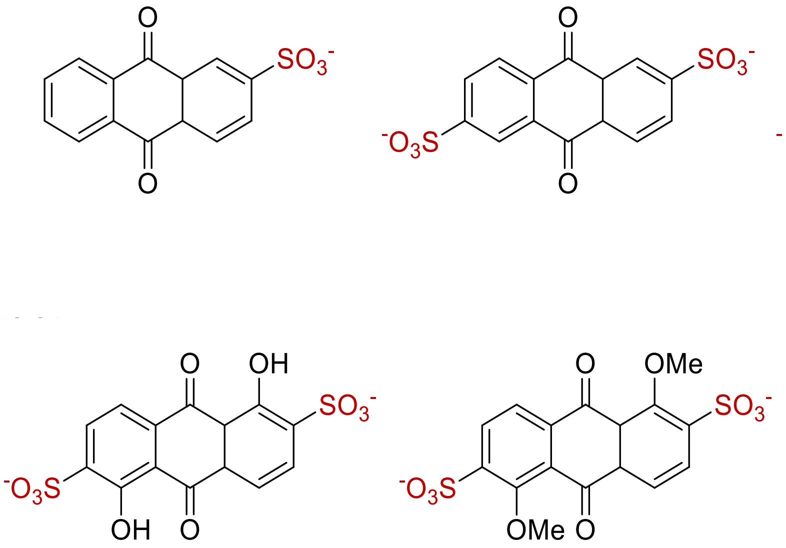


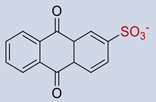
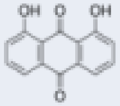
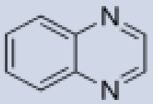
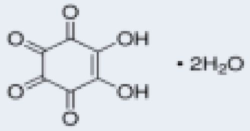
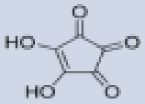
3,5-methoxy, p-benzoquinone



2,6-dihydroxy, p-benzoquinol

Negative Electrode Materials



Compound Name	**Molecular Structure**
Anthraqunione sulfonic acid	
Dihydroxyanthraquinone	
Quinoxaline, **2-methyl quinoxaline** **6-methyl quinoxaline**	
Rhodozonic acid	
Croconic acid	

Specific Requirements for Commercial Systems

Levelized Cost of Energy Storage(LCOS):

$$\frac{System\ Cost\ (\$)}{Total\ Energy\ Output\ Over\ lifetime\ (kWh)}$$

Example: LCOS target for Large-Scale Energy Storage = $0.05/kWh

A 1kWh system costing $200, needs to put out 4000 kWh over its lifetime.

4000 days of system lifetime : *~11 years*

On a 5 hour charge/5 hour discharge per day, we demand *40,000 hours of operational durability*,.

LCOS for automobile Tesla Model 3 battery

Over 100,000 miles, 34000 kWh: $17000/ 34000 kWh = $0.50/kWh

Economic Drivers for commercial large-scale energy storage systems:

Low System Cost, Long Operational Durability (active), and long passive lifetime

What determines System Cost ?

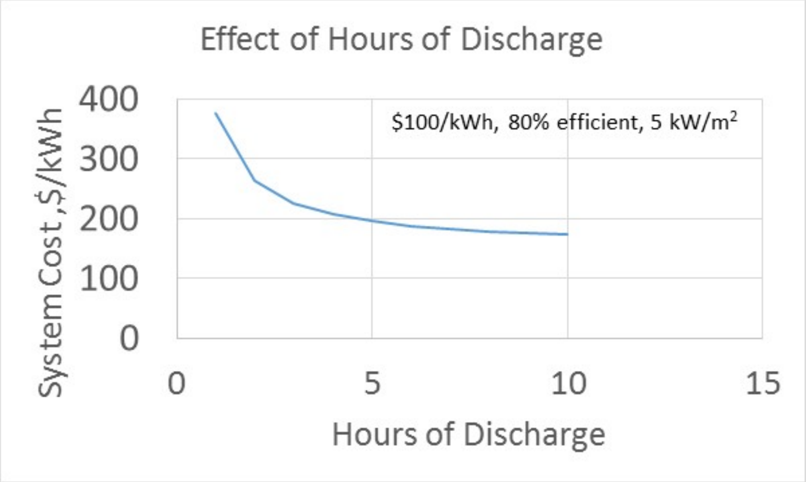
System Cost ($/kWh) = Materials Cost + Stack Cost + Balance of Plant Cost

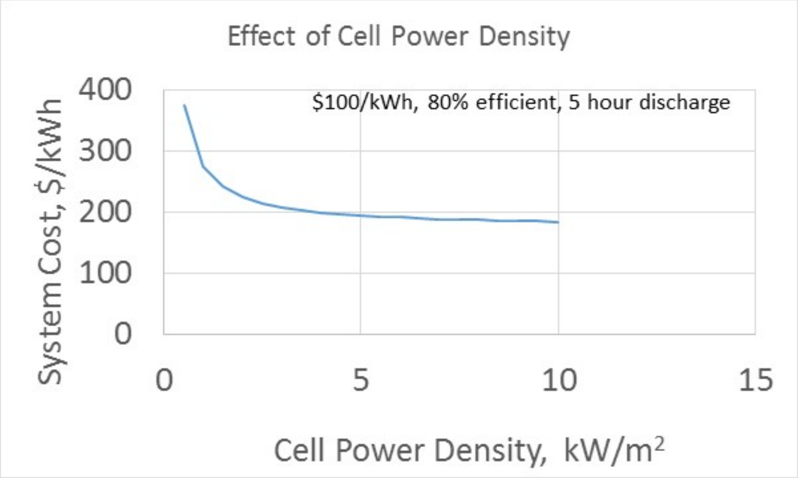
$$Materials\ Cost\left(\frac{\$}{kWh}\right) = Primary\ Materials\ Cost\ \left(\frac{\$}{kWh}\right) * \left(\frac{1}{Roundtrip\ \ Efficiency}\right) * Multiplier\ to\ offset\ degradation$$

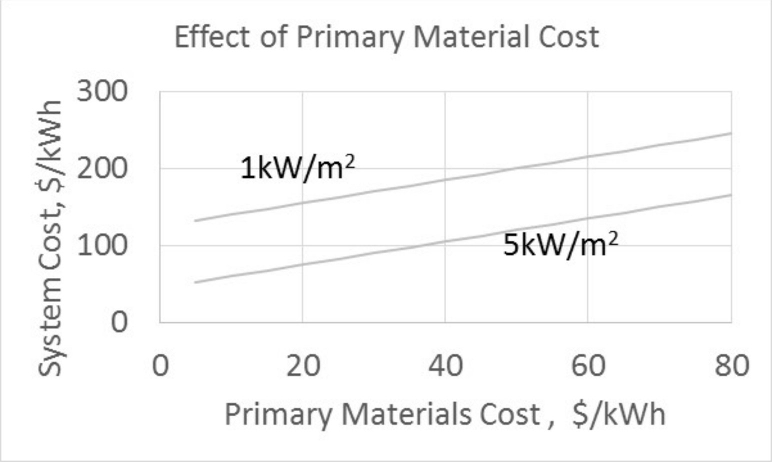
$$Stack\ Cost(\frac{\$}{kWh}) = \frac{Cell\ Cost\ (\frac{\$}{m2})}{Cell\ Power\ Density\ (\frac{kW}{m2})} * \frac{1}{Hours\ of\ Discharge}$$

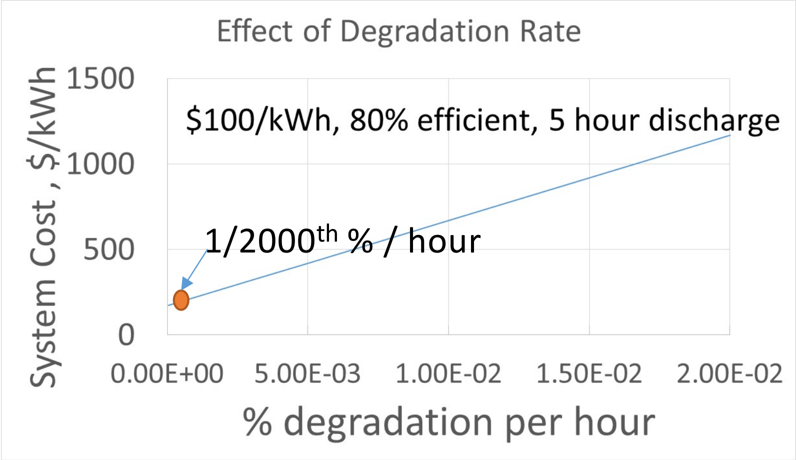
$$Balance\ of\ Plant\ Cost\ \left(\frac{\$}{kWh}\right) = \frac{Specific\ BOP\ Cost(\frac{\$}{kW})}{(1-Efficiency)} * \frac{1}{Hours\ of\ Discharge}$$

Key Variables Affecting System Cost


Effect of Hours of Discharge


Effect of Cell Power Density


Effect of Primary Material Cost


Effect of Degradation Rate

Addressing Low System Cost

Selecting low-cost redox molecules that are water soluble.

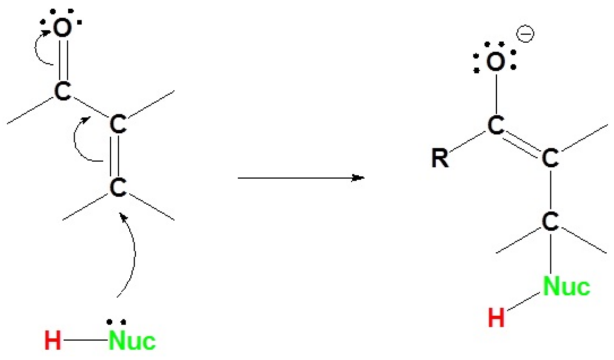
Making Power density and Durability improvements, specific to the redox flow battery chemistry.

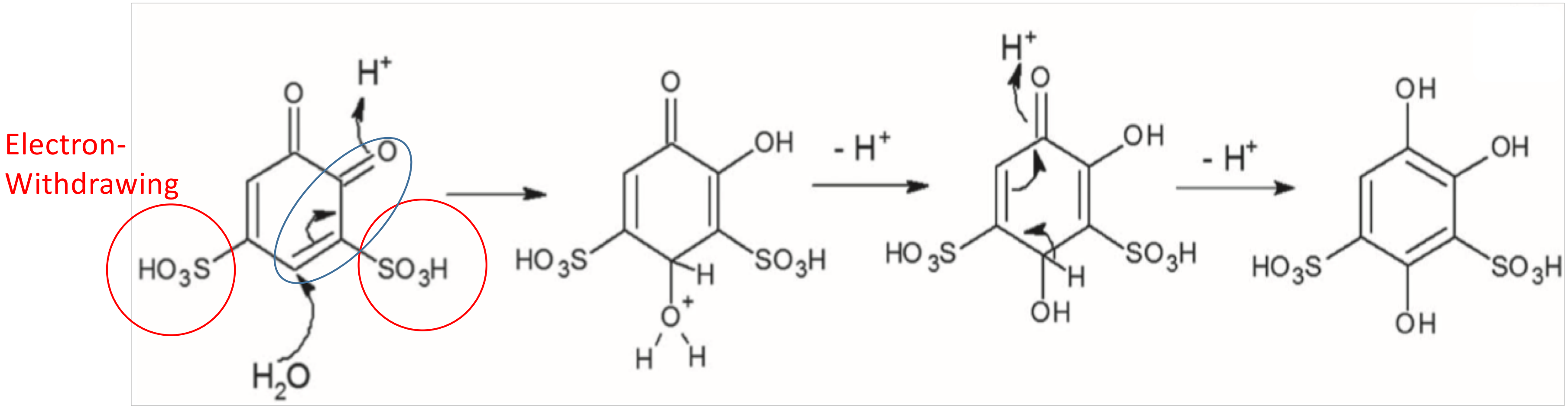
Improve Electrode and flow field designs- applicable across various redox flow battery systems.

Water is a safe and low-cost solvent

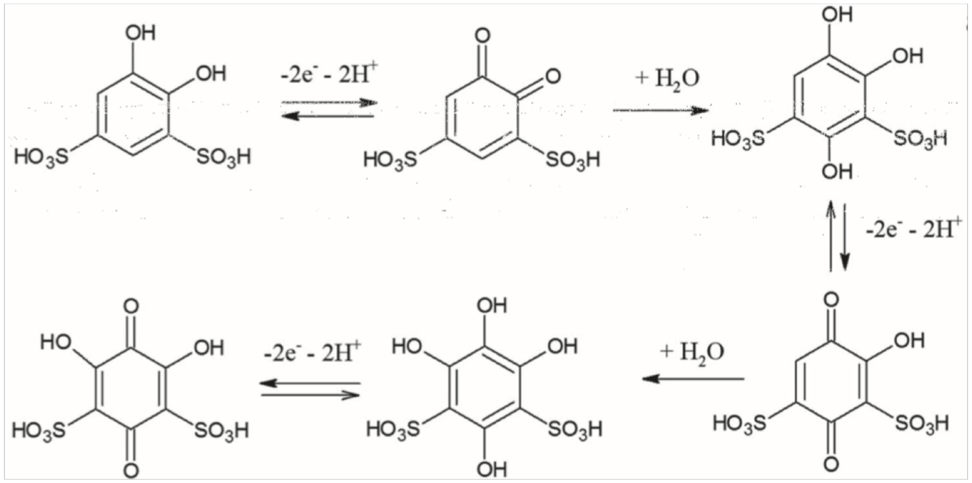
- Dipolar properties of water are useful in enhancing solubility , but…
- Nucleophilic properties can be a challenge to the stability of molecules.
- For example: Water reacts with quinones through 1,4- Michael Addition reaction.

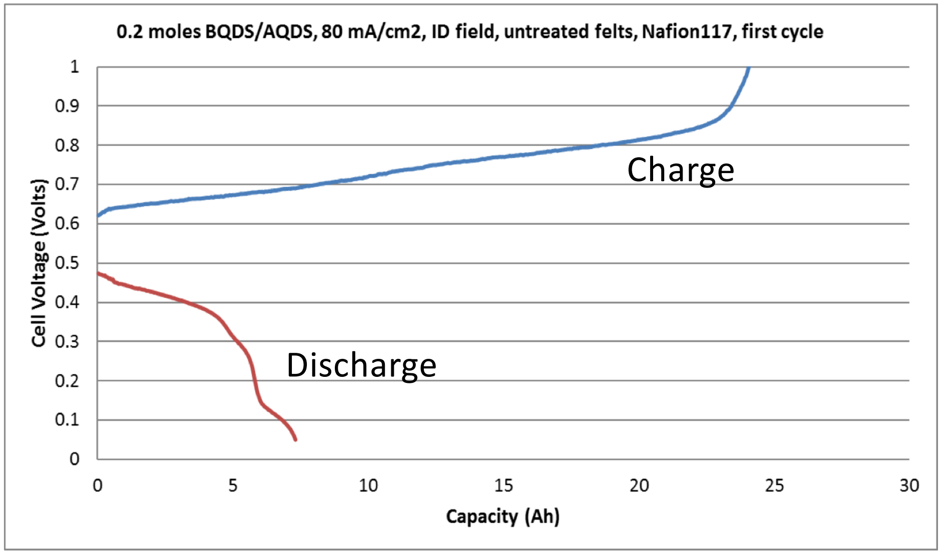
Product Transformation by the Michael Reaction





Consequences of the Michael Addition of Water to BQDS

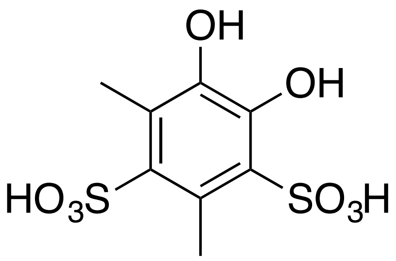




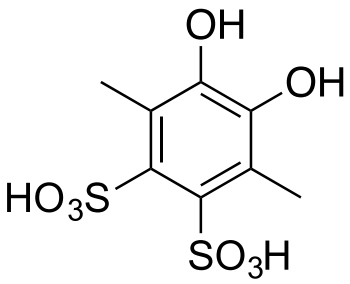
Xu, Y.; Wen, Y.; Cheng, J.; Yanga, Y.; Xie, Z.; Cao, G. *Non-Grid-Connected Wind Power and Energy Conference*, *IEEE*, **2009**

- Requires 3 equivalents of negative material.
- Hydroxylation also reduces the cell voltage by 200 mV

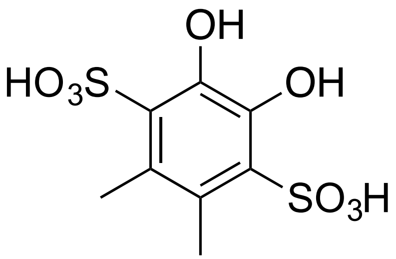
Alternatives to BQDS, Not Prone to the Michael Reaction



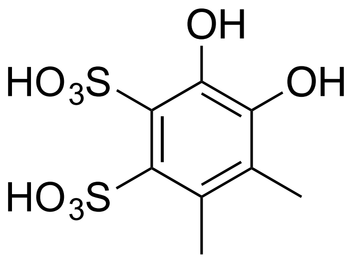
I



II



III



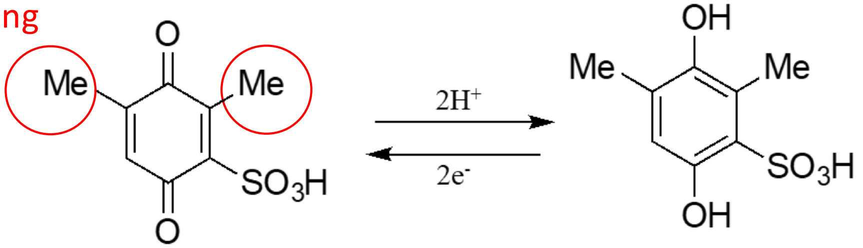
IV

- Di-sulfonation is not easily accomplished
- Some precursor compounds are not readily available, and hence scale up and cost could be a problem
- Full substitution may not be necessary

DHDMBS overcomes Reactivity with Water

3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid

Electron-donating

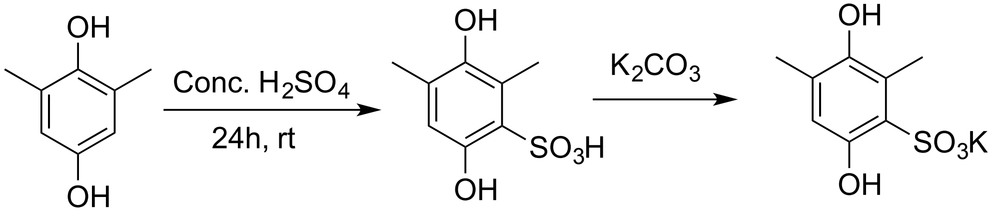


$E_{1/2}$ vs MSE: + 0.15 V

DHDMBS

Solubility up to 2 M

Sulfonation of the Commercial Precursor

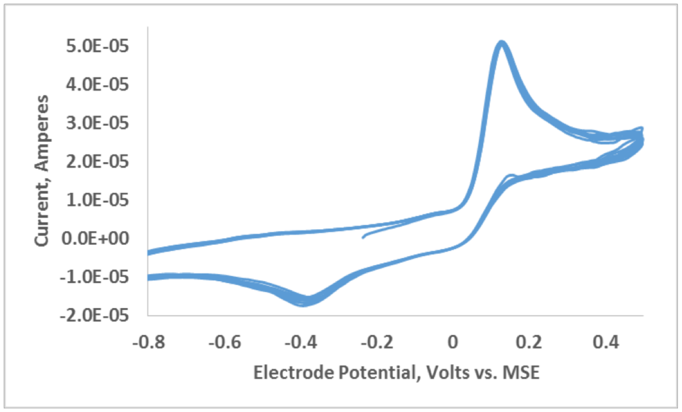


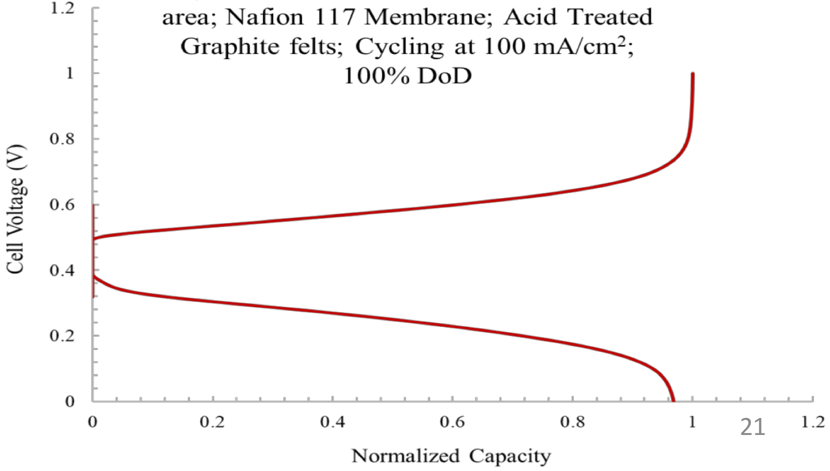
7, 50g scale

100% conv., **7a**

7a', 85%

L. Hoober-Burkhardt, S. Krishnamoorthy, B. Yang, A. Murali, A. Nirmalchandar, G. K. Surya Prakash, S. R. Narayanan, *J. Electrochem. Soc.*, **164**, A600 (**2017**)





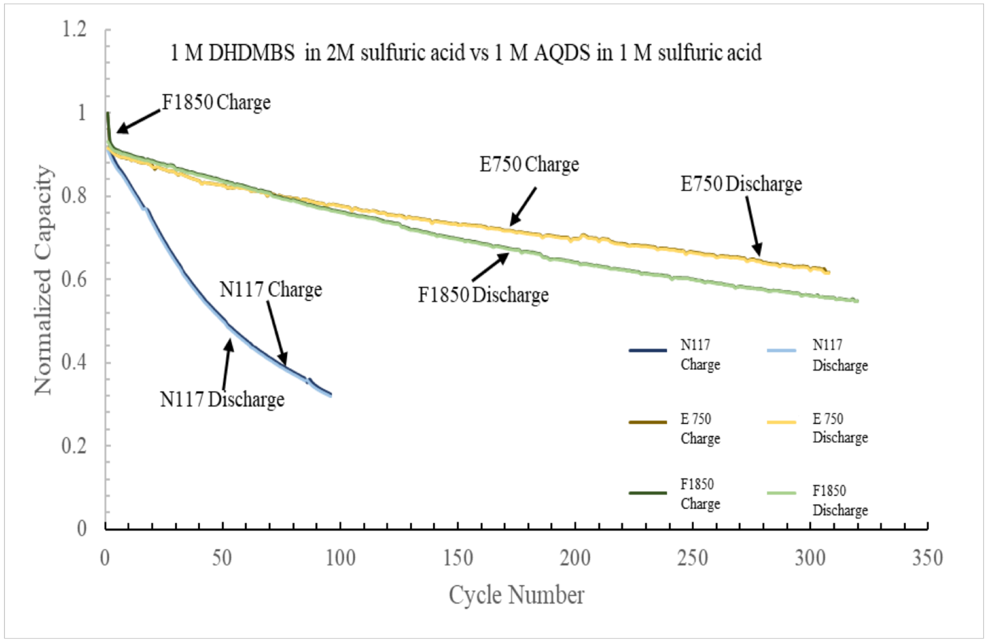
1 M DHDMBS in 2 M Sulfuric Acid vs 1 M AQDS in 1 M Sulfuric Acid; 25 cm^2 active area; Nafion 117 Membrane; Acid Treated Graphite felts; Cycling at 100 mA/cm^2; 100% DoD

New Challenges with DHDMBS

Unlike BQDS, DHDMBS was not fully ionized in solution.

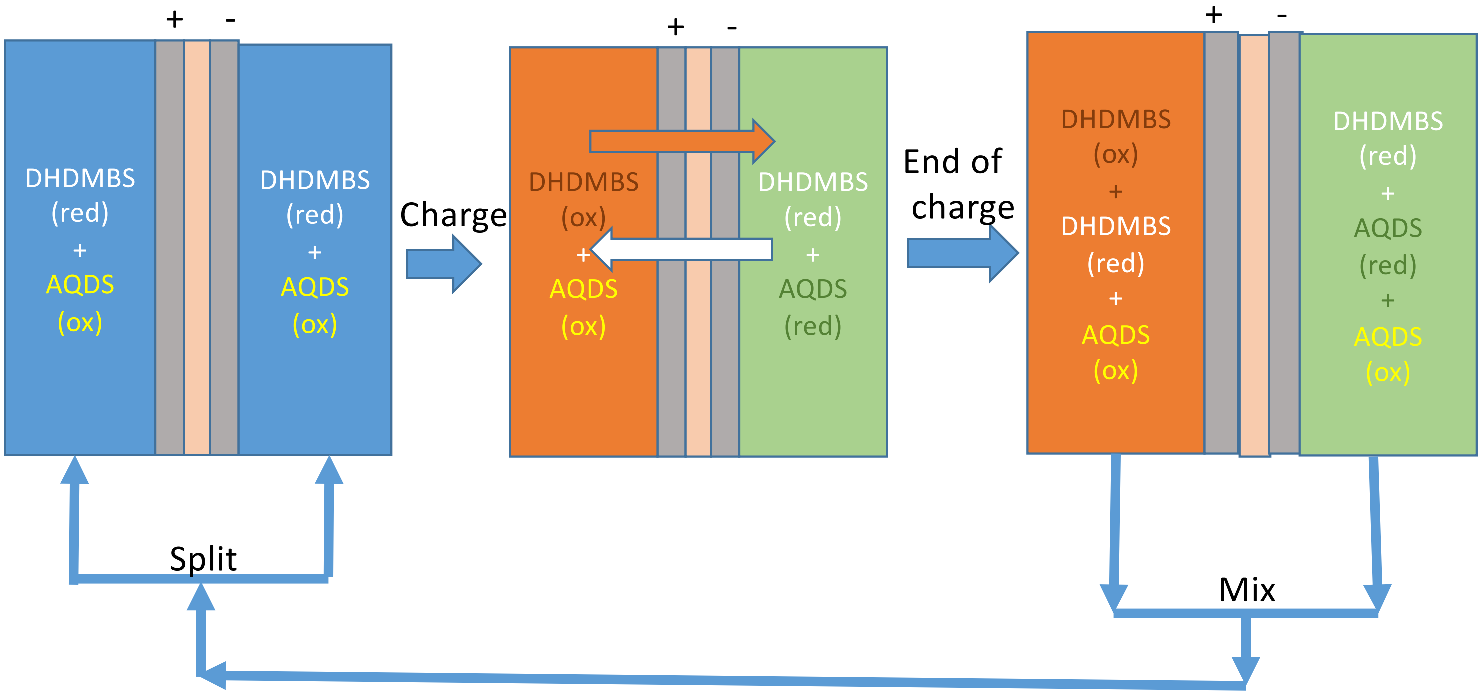
Thus, DHDMBS in its unionized form was more prone to crossover.

Various membranes were tested and E750- HPEEK membrane proved to have the lowest diffusion coefficient.



Membrane Type	D_{app}, Apparent Diffusion Coefficient (cm^2s^{-1})	Normalized Diffusion Coefficient for thickness (D_{app}*thickness in µm)
Nafion 117	3.12E-06	5.46E-04
F1850 (Fumatech)	1.66E-06	8.3E-05
E750 (Fumatech)	**1.63E-07**	**8.15E-06**

Mixed Electrolyte (Symmetric) Configuration



\+ -

DHDMBS
(red)
\+
AQDS
(ox)

DHDMBS
(red)
\+
AQDS
(ox)

Charge

\+ -

DHDMBS
(ox)
\+
AQDS
(ox)

DHDMBS
(red)
\+
AQDS
(red)

End of charge

\+ -

DHDMBS
(ox)
\+
DHDMBS
(red)
\+
AQDS
(ox)

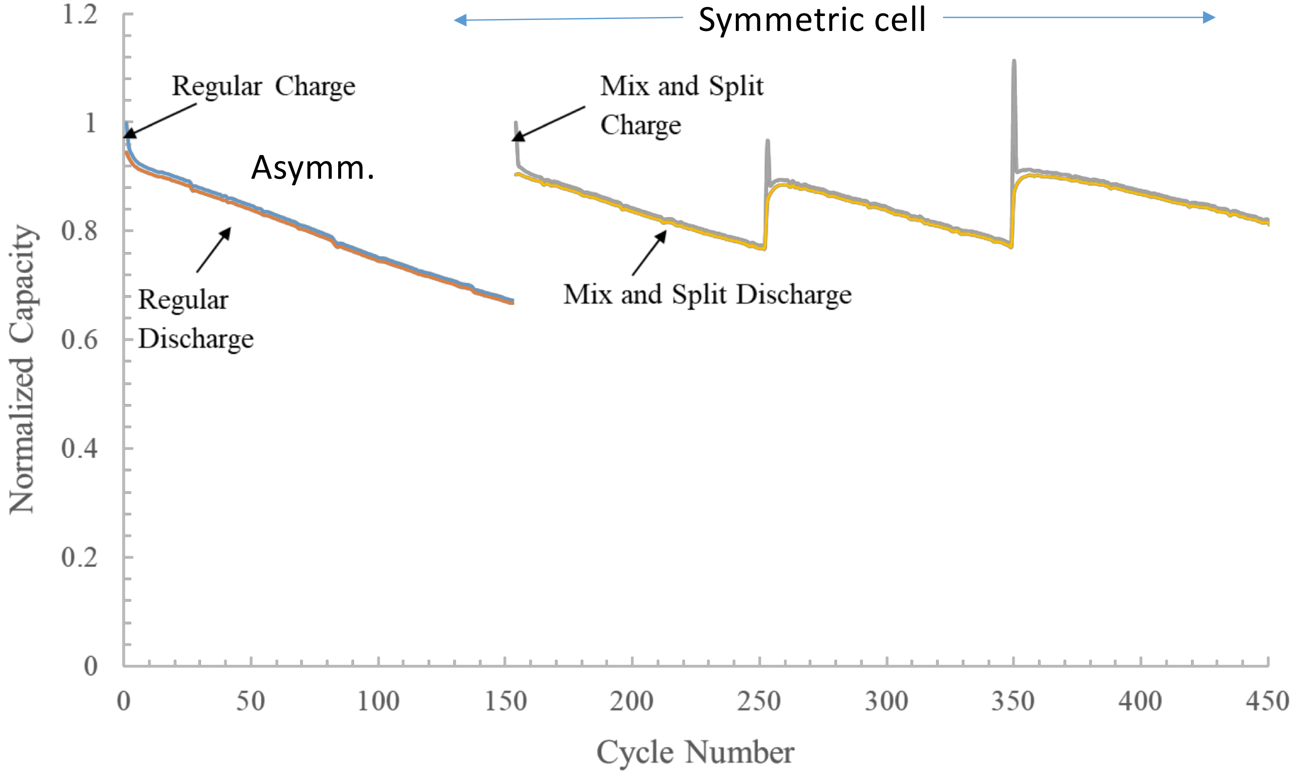
DHDMBS
(red)
\+
AQDS
(red)
\+
AQDS
(ox)

Split

Mix

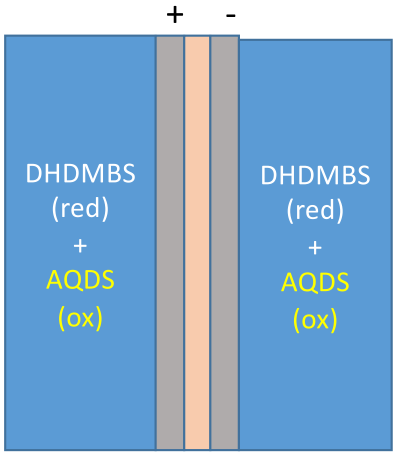
Symmetric Mixed Electrolyte Cells Avoid Permanent Capacity Loss

0.5 M DHDMBS/0.5 M AQDS in 1 M Sulfuric Acid; 25 cm^2 active area; N117 Membrane; Acid Treated Graphite felts; Cycling at $100 mA/cm^2$; 100% DoD



- Mix and Split restores capacity to starting levels.

Symmetric Mixed Electrolyte Configuration
To mitigate effects of crossover



<u>Benefits</u>

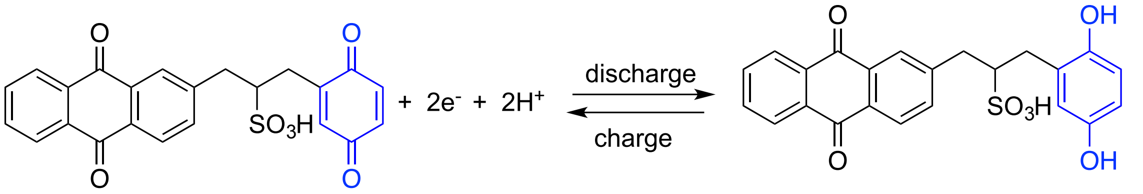
- Minimizes the drastic fall in capacity during initial cycles due to crossover.
- Maintains a balanced osmotic pressure during cycling, avoiding major water transfer issues.
- We can focus on just ionic conductivity, without the need to optimize barrier properties of the membrane.

<u>Disadvantages</u>

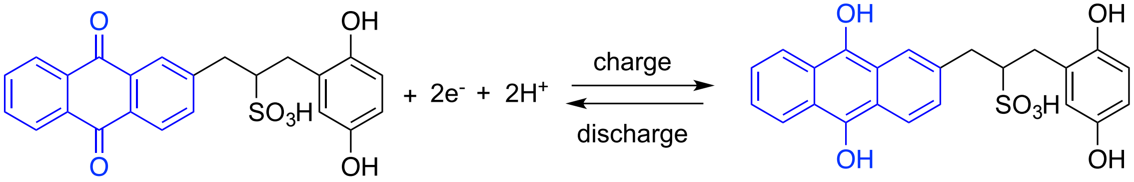
- Increases the cost of materials and size of tanks.
- Reduces the concentration of the dissolved materials
- Requires additional BOP for mix-and-split operations.

Another Approach to Mitigate Crossover : Redox Reaction of the Di-couple

- Positive electrode reaction

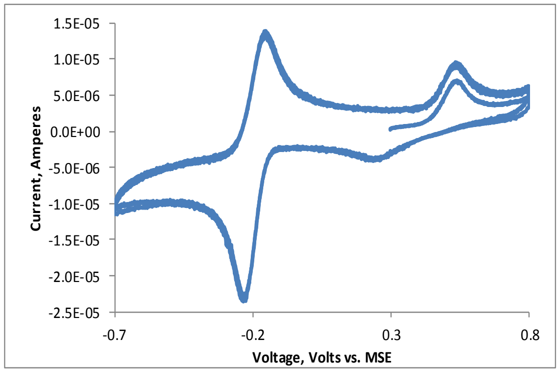


- Negative electrode reaction

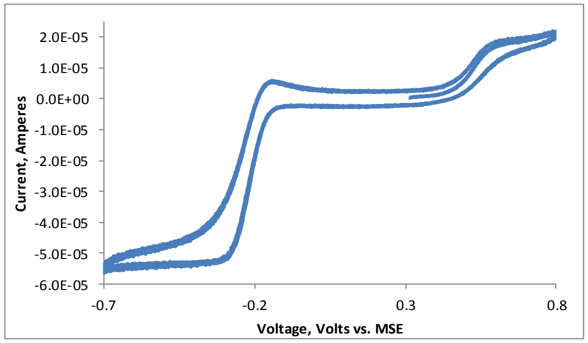


Increased molecular size could prevent crossover and avoid the need for mix and split operations

a) CV

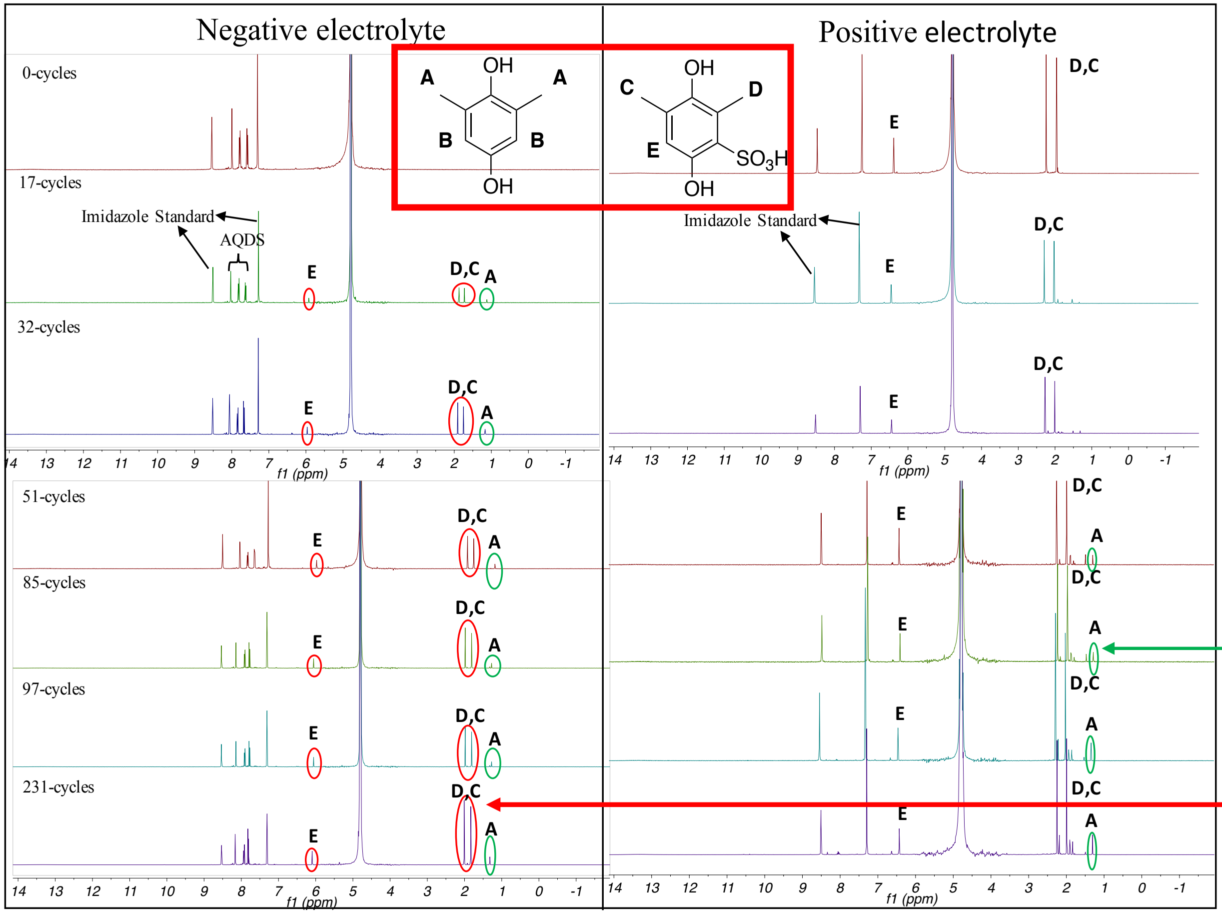


a) RDE



Analysis of Solutions after Extended Discharge

^{1}H-NMR

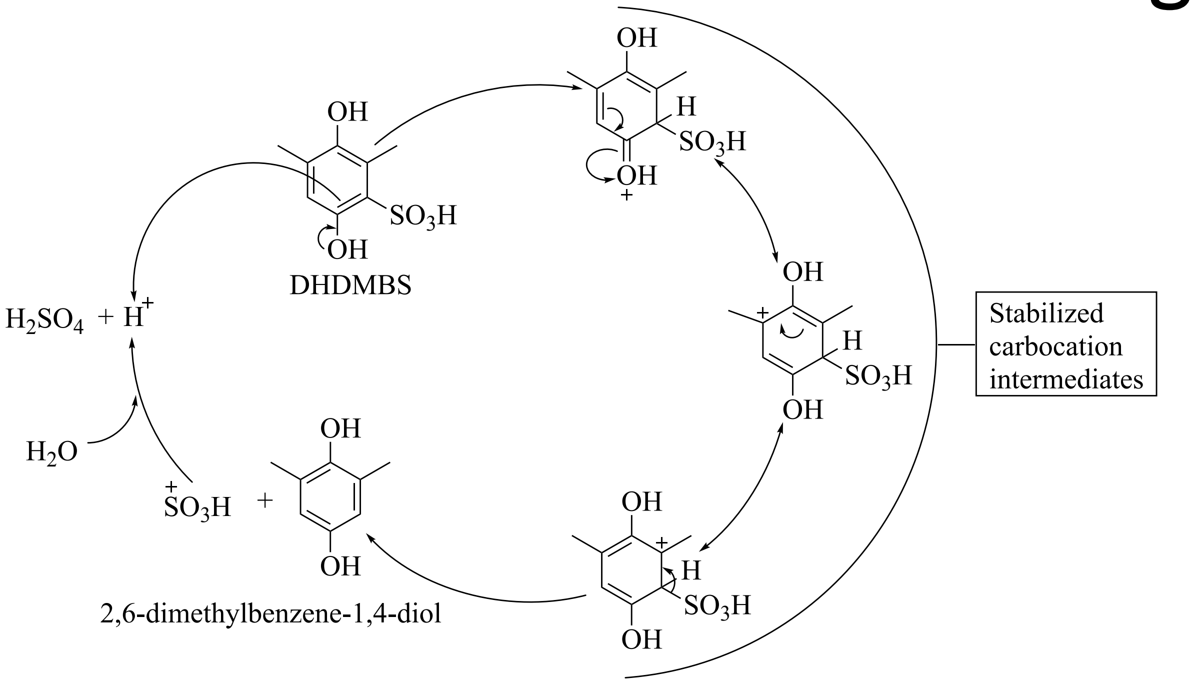


- ^{1}H-NMR of samples from the cell at the end of various cycles: positive electrolyte.
- Capital notations of A, B, C, D and E refer to the protons in the molecular structures shown in the inset.

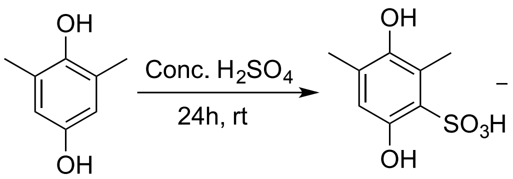
Protodesulfonation

Crossover

Proto-desulfonation in strongly acidic media



Reverse of the Synthesis reaction



7, 50g scale

100% conv., **7a**

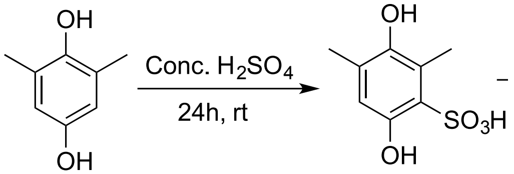
Rate of protodesulfonation = $k_{PDS}\ C_{DHDMBS}\ C_{H+}$

Pseudo First order Rate Constant at 1M sulfuric acid $k'_{PDS} = 2.96 \times 10^{-6}\ s^{-1}$

Working at low acid concentration was essential for avoiding proto-desulfonation or passive degradation

S. R. Narayanan et al , *J. Electrochem. Soc.,* **164**, A1193 (**2018**)

Scale up of DHDMBS/AQDS- 1 kWh System



7, 50g scale   100% conv., **7a**

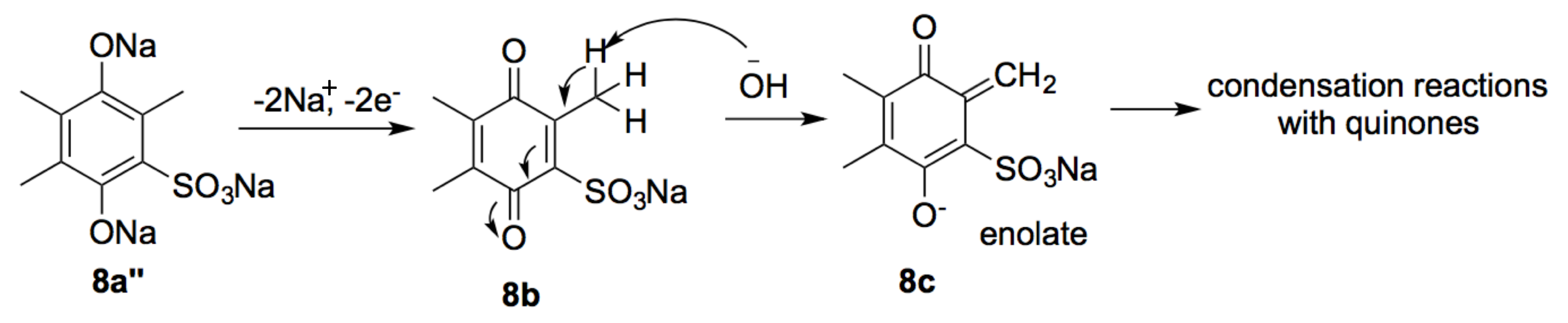
Scaled up 1kWh system Conducted by ITN

DHDMBS scaled up to 35 kg with external vendor; Zero-free acid and > 1M solution. AQDS obtained from Riverside Specialty; Symmetric electrolyte tanks.

- 4000 Ah/ cycle, 100% coulombic efficiency
- Utilization of 77% charge at 200 mA/cm^2 and discharge at 100 mA/cm^2
- >1 kWh
- Energy Efficiency ~ 45% (IR losses were high)
- 400 cycles, 1700 hours, over 120 days,
- 0.01% per hour of cycle time (4.5 h).

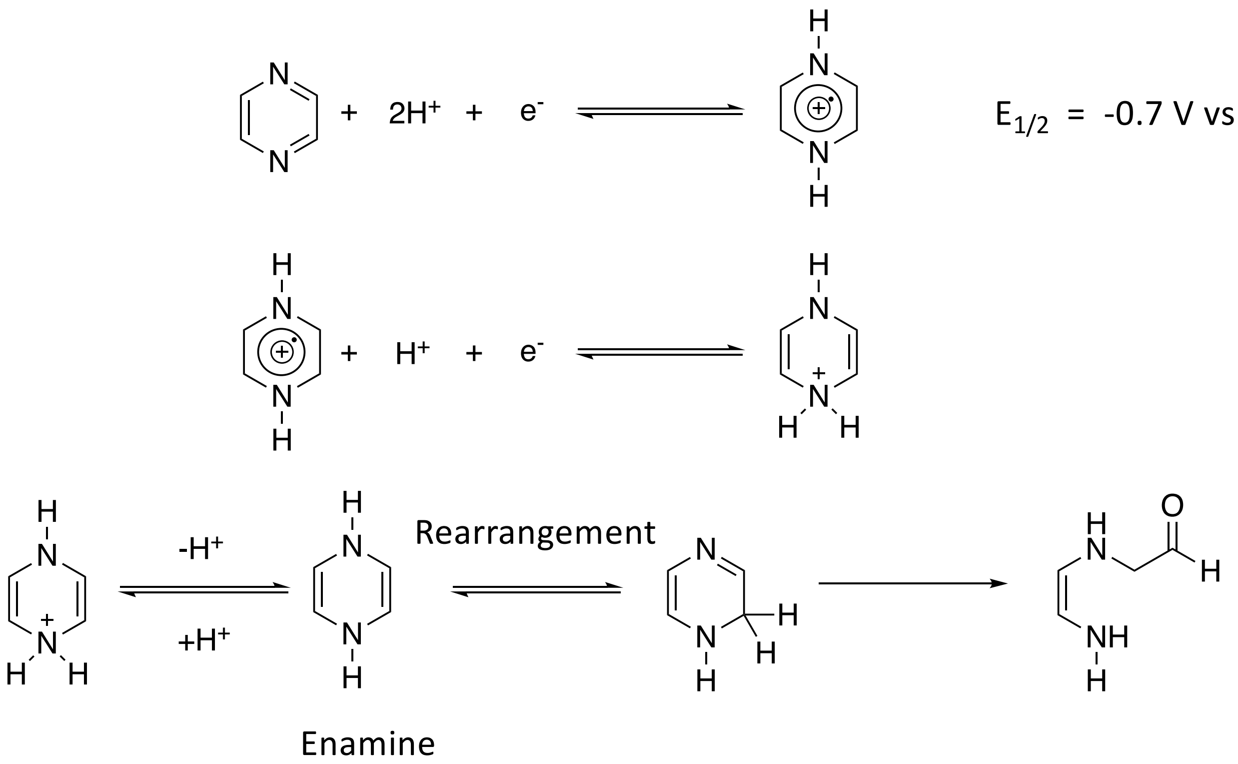
Challenge for Benzoquinones in Alkaline Media

- Hydroxide ion is a strong nucleophile.
- Michael Reaction will occur at the electron deficient site.
- Methyl-substituted quinones undergo transformation to quinone methide



Many researchers have chosen to work with ferricyanide/ferrocyanide for the positive electrode in alkali where the stability is better.

Durability Challenges with Nitrogen-containing redox materials (heteroaromatics) in acid media

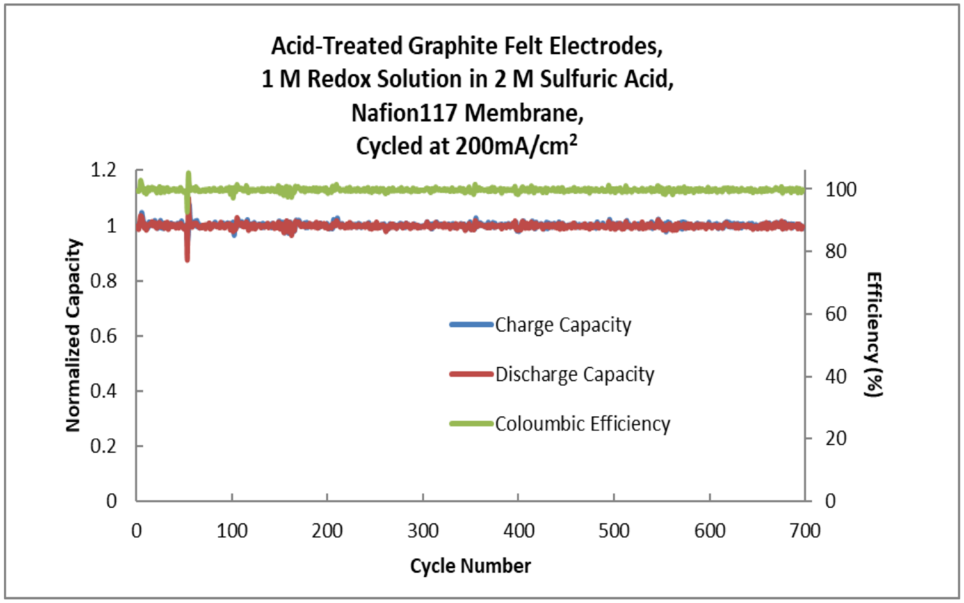


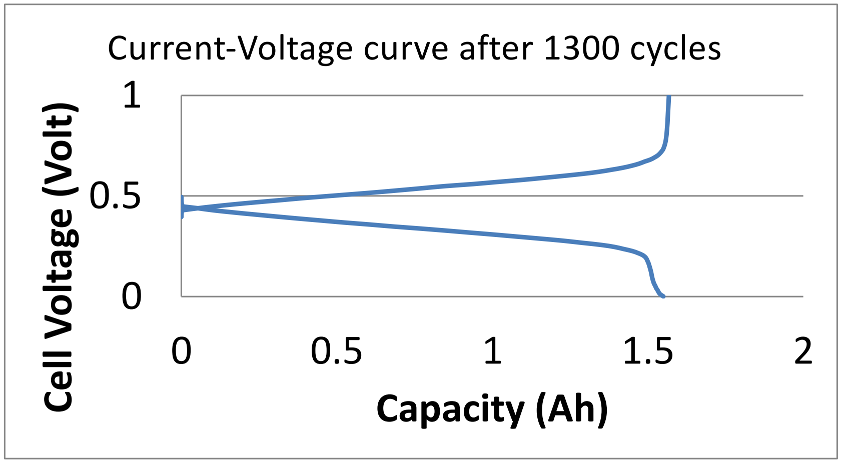
$E_{1/2}$ = -0.7 V vs. MSE.

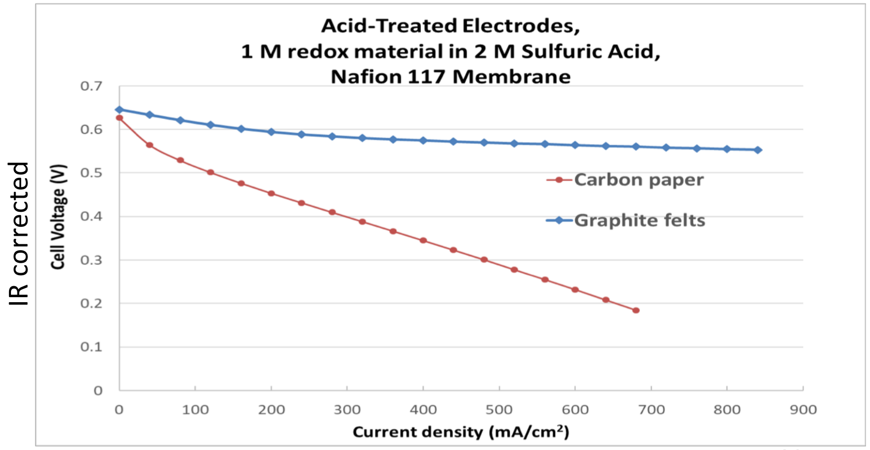
New Materials to meet Ultra-Low Cost Requirements

Material Cost : $22/kWh

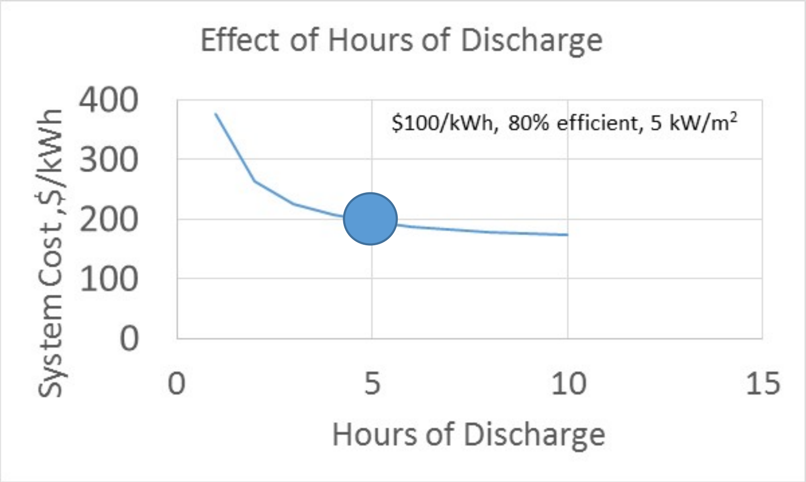
Stable Chemistry

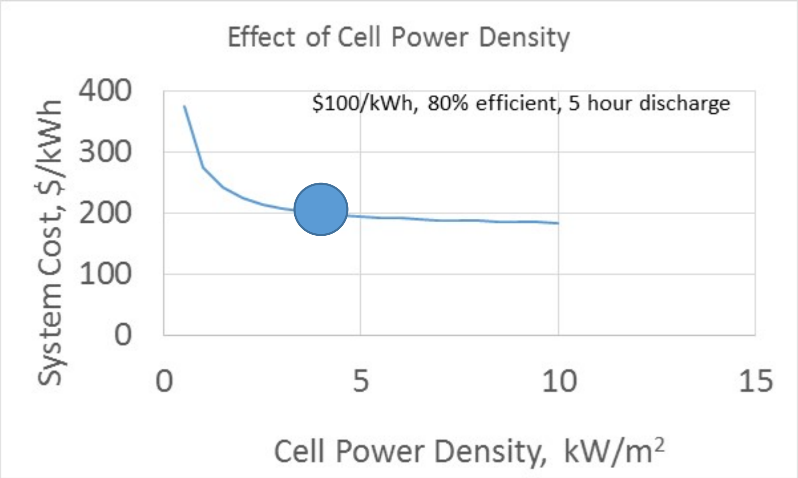


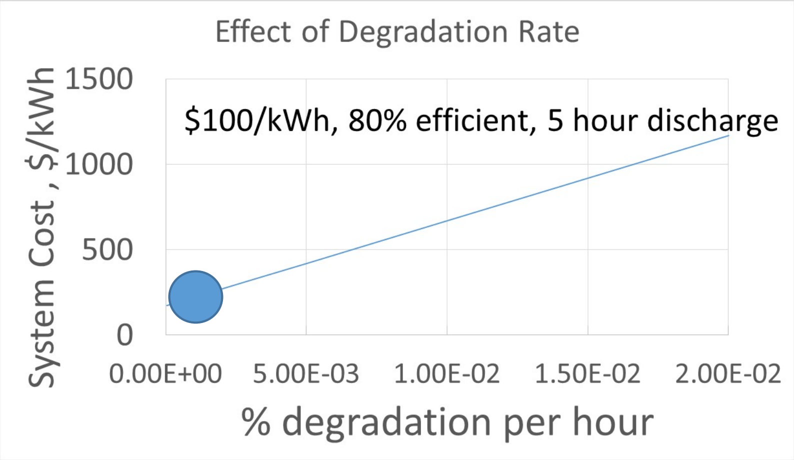


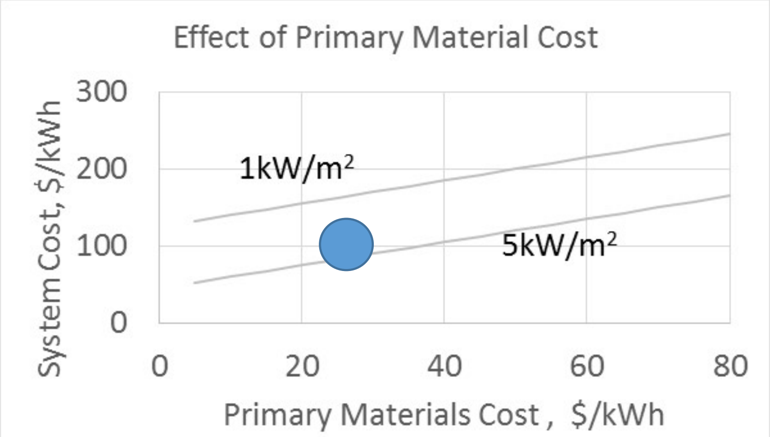


Key Variables Affecting System Cost









The USC Organic Flow Battery Team

USC
University of
Southern California

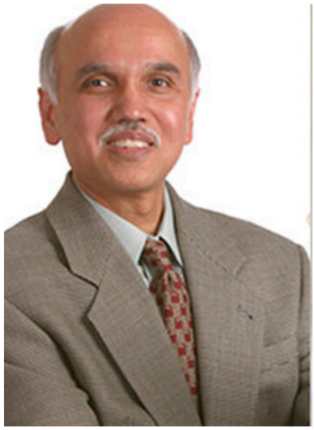
Dr. Lena Hoober

Dr. Bo Yang

Dr. Sankarganesh
Krishnamoorthy

Advaith Murali

Archith
Nirmalchandar



Prof. Surya
Prakash

Dr. Robert Aniszfeld

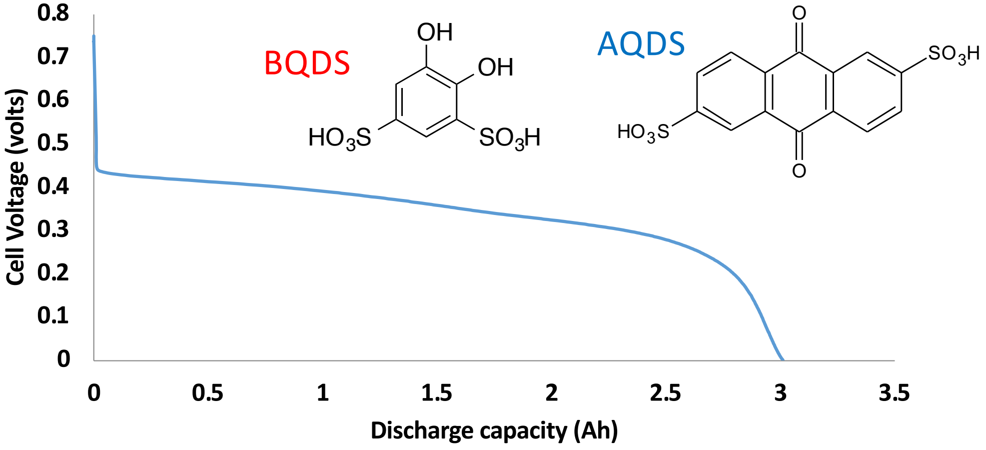
Acknowledgements

- ARPA-E Contract DE-AR0000337 for supporting this work
- ITN Energy Systems who have participated in the ARPA-E sponsored research
- Guidance and suggestions from Dr. Grigorii Soloveichik at critical junctures in this project
- Loker Hydrocarbon Research Institute and USC for additional financial support.

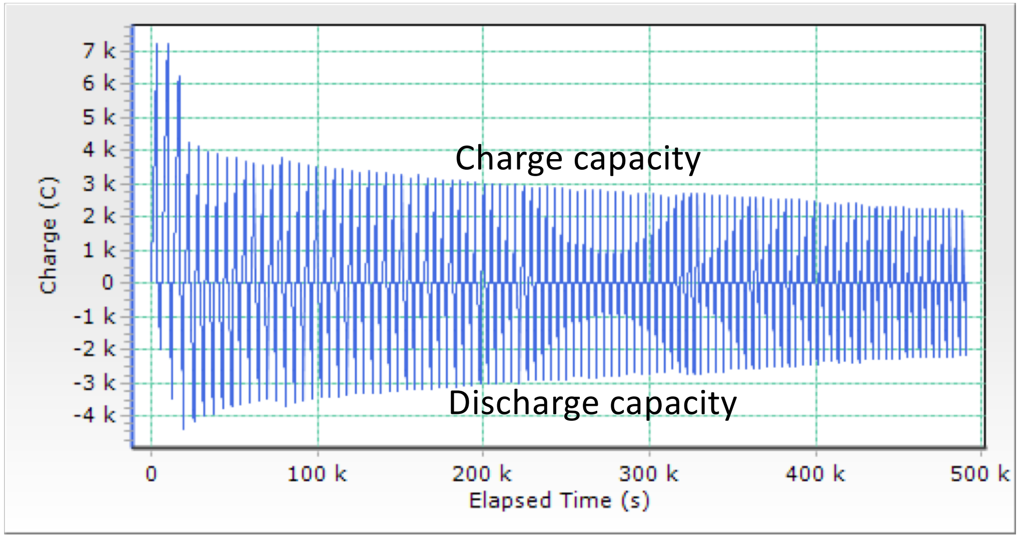
Thank you !

Charge/Discharge Performance for BQDS/AQDS Cell

1M BQDS, 1M AQDS, discharge at 100 mA/cm^2

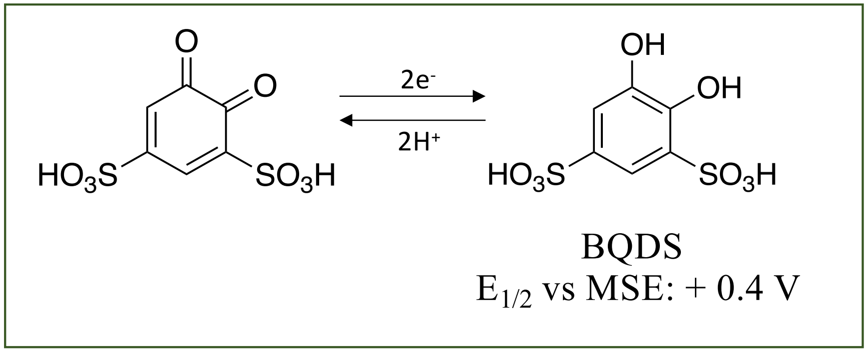


>1000 cycles were achieved at 80mA/cm^2,
Slow capacity decrease



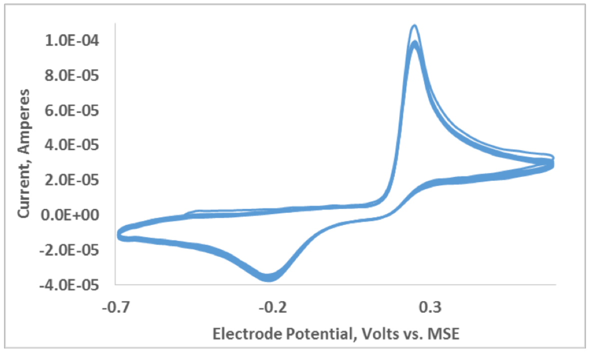
Favorable Properties of BQDS as a Positive Electrode Material

4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS)

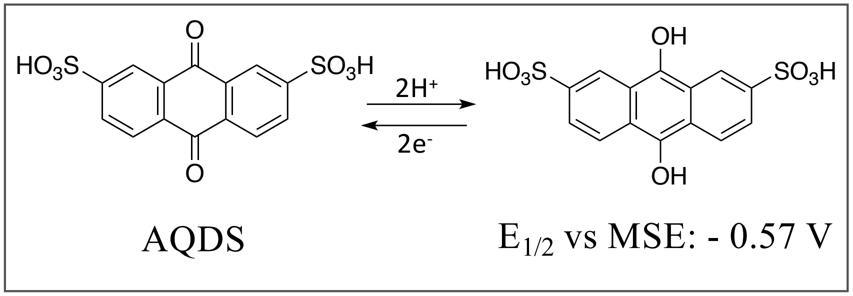


BQDS

$E_{1/2}$ vs MSE: + 0.4 V

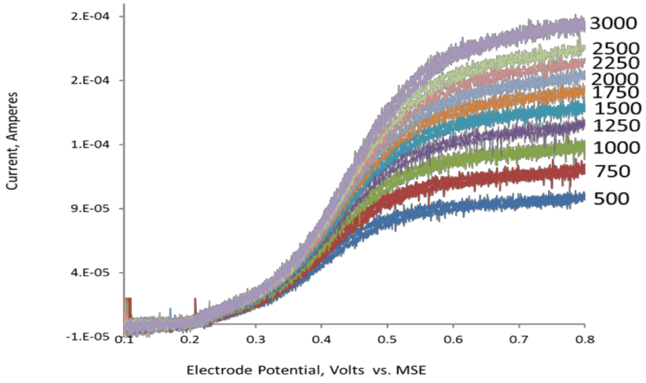


Anthraquinone-2,7-disulfonic acid



AQDS

$E_{1/2}$ vs MSE: - 0.57 V



Yang, B.; Hoober-burkhardt, L.; Krishnamoorthy, S.; Murali, A.; Prakash, G. K. S.; Narayanan, S. R. *J. Electrochem. Soc.* **163**, A1442 (**2016**)