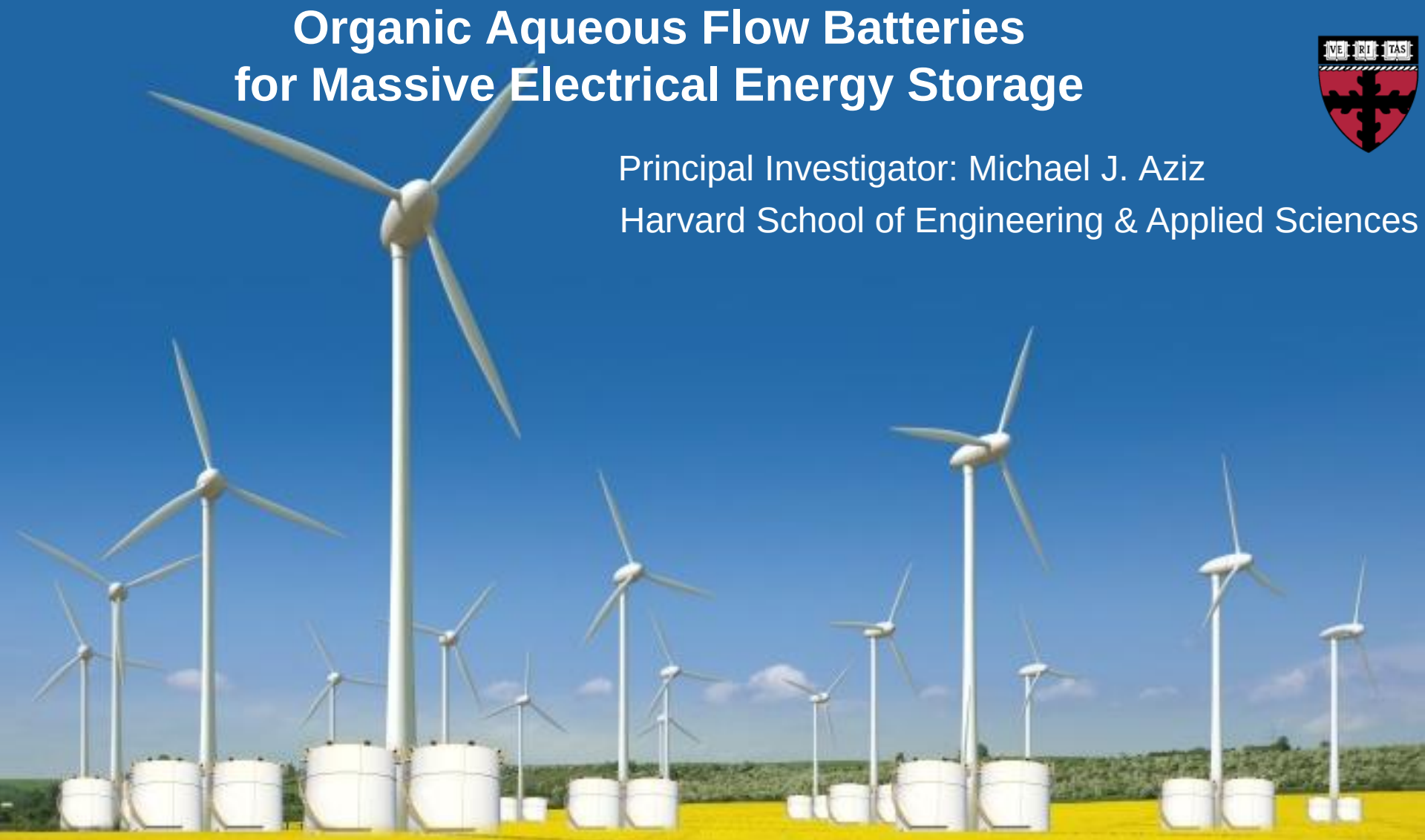
Organic Aqueous Flow Batteries for Massive Electrical Energy Storage

Principal Investigator: Michael J. Aziz
Harvard School of Engineering & Applied Sciences



Research reported here supported by Office of Electricity Delivery and Energy Reliability (OE)
Dr. Imre Gyuk
DE-AC05-76RL01830
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7/1/2016-

U.S. DEPARTMENT OF ENERGY

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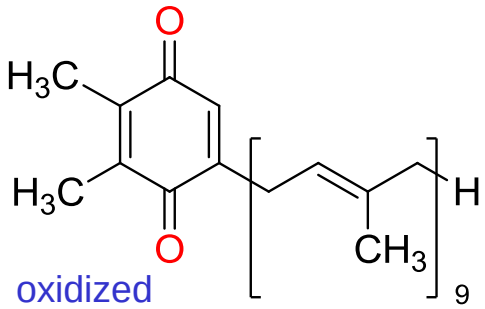
DOE/OE PEER REVIEW 2016
September 25-28, 2016 • Washington DC

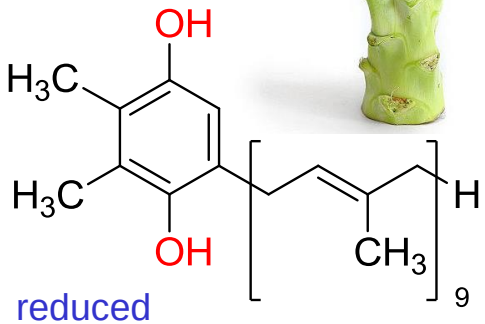
Redox-Active Organics for Battery Storage

Plastoquinone
in photosynthesis



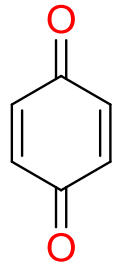
oxidized

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

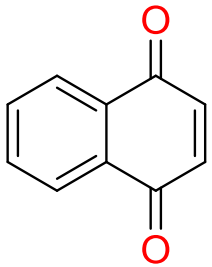


reduced

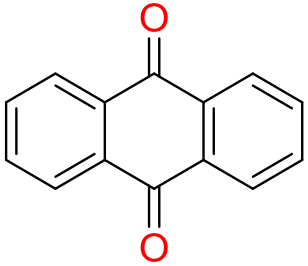
simplest
quinone



Benzoquinone



Naphthoquinone

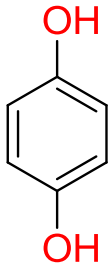


Anthraquinone

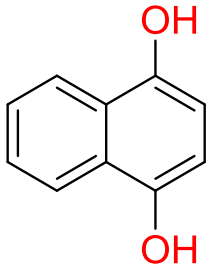
$+2\ H^+,$
$+2\ e^-$

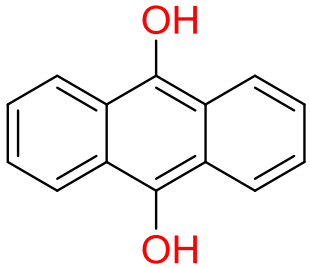
$+2\ H^+,$
$+2\ e^-$

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

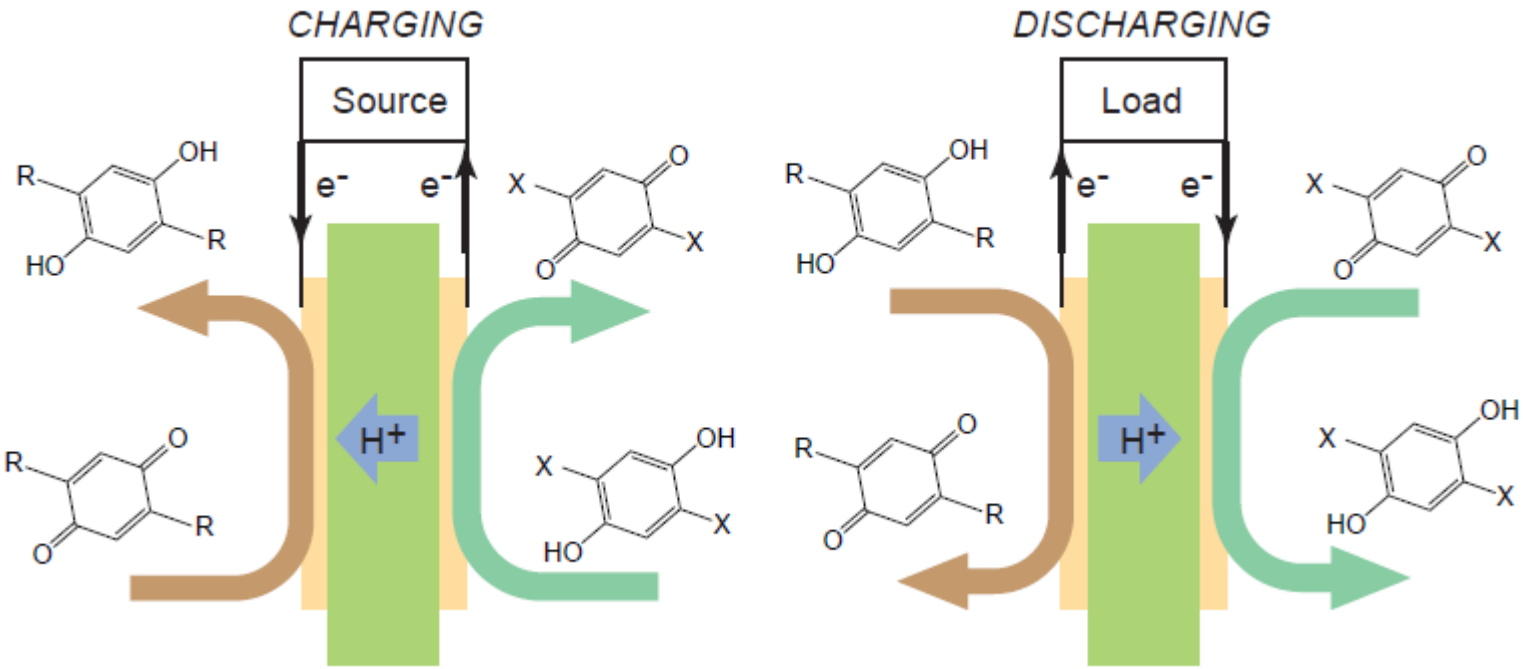


Hydroquinone





Organic-Based Aqueous Flow Batteries

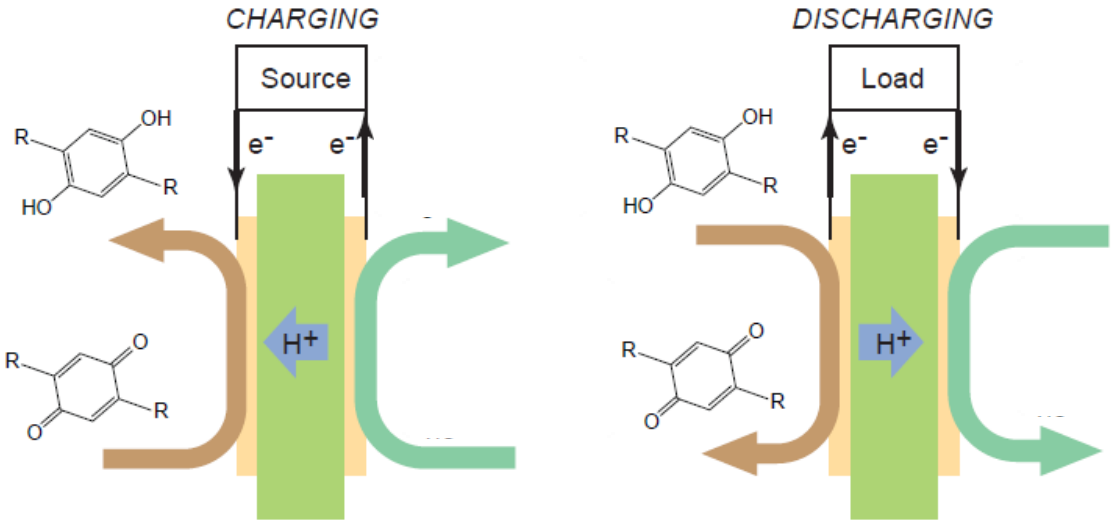


Primary requirements:

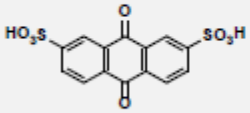
- Reduction potential
- Aqueous Solubility
- Redox kinetics
- Stability
- Cost

Aqueous-Soluble Organics (ASOs) 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



History of High Performance ASO RFBs

Negative Electrolyte	Positive Electrolyte	No. of Cycles (Condition)	Capacity Retention per Cycle (%)	Energy Density (Wh/L)	Voltage (V)	Year Institution (Sponsor)	Merit (limitation)
 anthraquinone-2,7-disulfonic acid	bromine / hydrobromic acid	10	99	16	0.86	2014 Harvard (ARPA-E)	Low cost; highest power density (toxic bromine)
		750	99.84	16		2014 Harvard (ARPA-E)	

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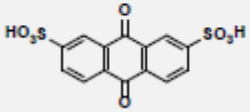 anthraquinone-2,7-disulfonic acid	bromine / hydrobromic acid	10	99	16	0.86	2014 Harvard (ARPA-E)	Low cost; highest power density (toxic bromine)
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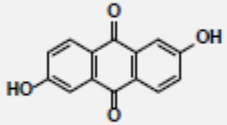
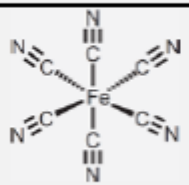
 2,6-dihydroxy-anthraquinone	 ferrocyanide	100	99.1	6.8	1.2	2015 Harvard (ARPA-E)	Non-toxic and less corrosive electrolyte (reduced ion conductivity w.r.t. proton; modest $Fe(CN)_6$ solubility)

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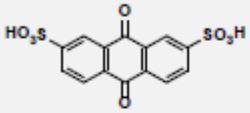 anthraquinone-2,7-disulfonic acid	bromine / hydrobromic acid	10	99	16	0.86	2014 Harvard (ARPA-E)	Low cost; highest power density (toxic bromine)
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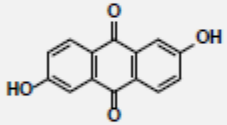
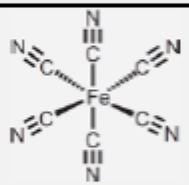
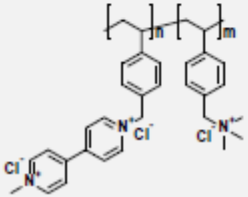
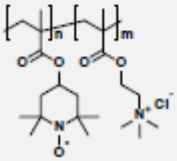
 2,6-dihydroxy-anthraquinone	 ferrocyanide	100	99.1	6.8	1.2	2015 Harvard (ARPA-E)	Non-toxic and less corrosive electrolyte (reduced ion conductivity w.r.t. proton; modest $Fe(CN)_6$ solubility)
 viologen polymer	 TEMPO polymer	100	~ 99.75[b]	10	1.15	2015 Friedrich Schuller U. (EFRE)	Cheap dialysis membrane (high electrolyte viscosity)
		10,000 (non-flow cell)	> 99.99				

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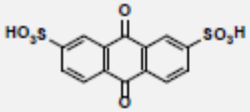 anthraquinone-2,7-disulfonic acid	bromine / hydrobromic acid	10	99	16	0.86	2014 Harvard (ARPA-E)	Low cost; highest power density (toxic bromine)
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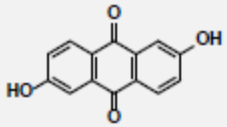
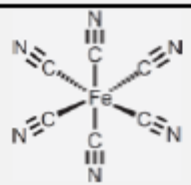
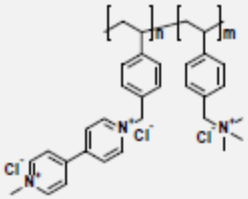
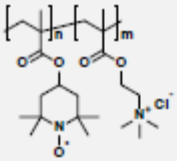
 2,6-dihydroxy-anthraquinone	 ferrocyanide	100	99.1	6.8	1.2	2015 Harvard (ARPA-E)	Non-toxic and less corrosive electrolyte (reduced ion conductivity w.r.t. proton; modest $Fe(CN)_6$ solubility)
 viologen polymer	 TEMPO polymer	100	~ 99.75[b]	10	1.15	2015 Friedrich Schuller U. (EFRE)	Cheap dialysis membrane (high electrolyte viscosity)
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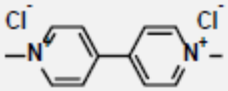
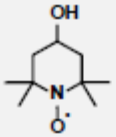
 methyl viologen	 4-hydroxy-TEMPO	100 (low conc.)	> 99.99	8.4	1.25	2015 PNNL (DOE/OE)	Neutral pH (low current density; stability)
		100 (high conc.)	>99.89				

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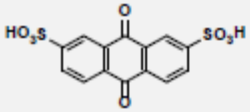 anthraquinone-2,7-disulfonic acid	bromine / hydrobromic acid	10	99	16	0.86	2014 Harvard (ARPA-E)	Low cost; highest power density (toxic bromine)
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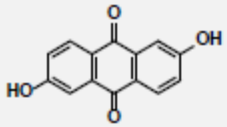
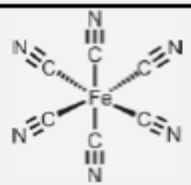
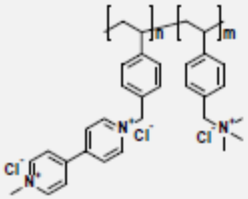
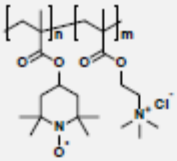
 2,6-dihydroxy-anthraquinone	 ferrocyanide	100	99.1	6.8	1.2	2015 Harvard (ARPA-E)	Non-toxic and less corrosive electrolyte (reduced ion conductivity w.r.t. proton; modest $Fe(CN)_6$ solubility)
 viologen polymer	 TEMPO polymer	100	~ 99.75[b]	10	1.15	2015 Friedrich Schuller U. (EFRE)	Cheap dialysis membrane (high electrolyte viscosity)
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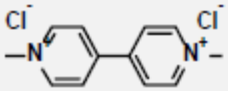
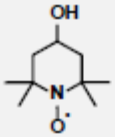
 methyl viologen	 4-hydroxy-TEMPO	100 (low conc.)	> 99.99	8.4	1.25	2015 PNNL (DOE/OE)	Neutral pH (low current density; stability)
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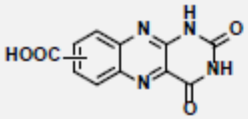
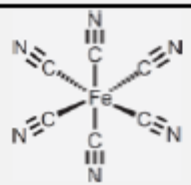
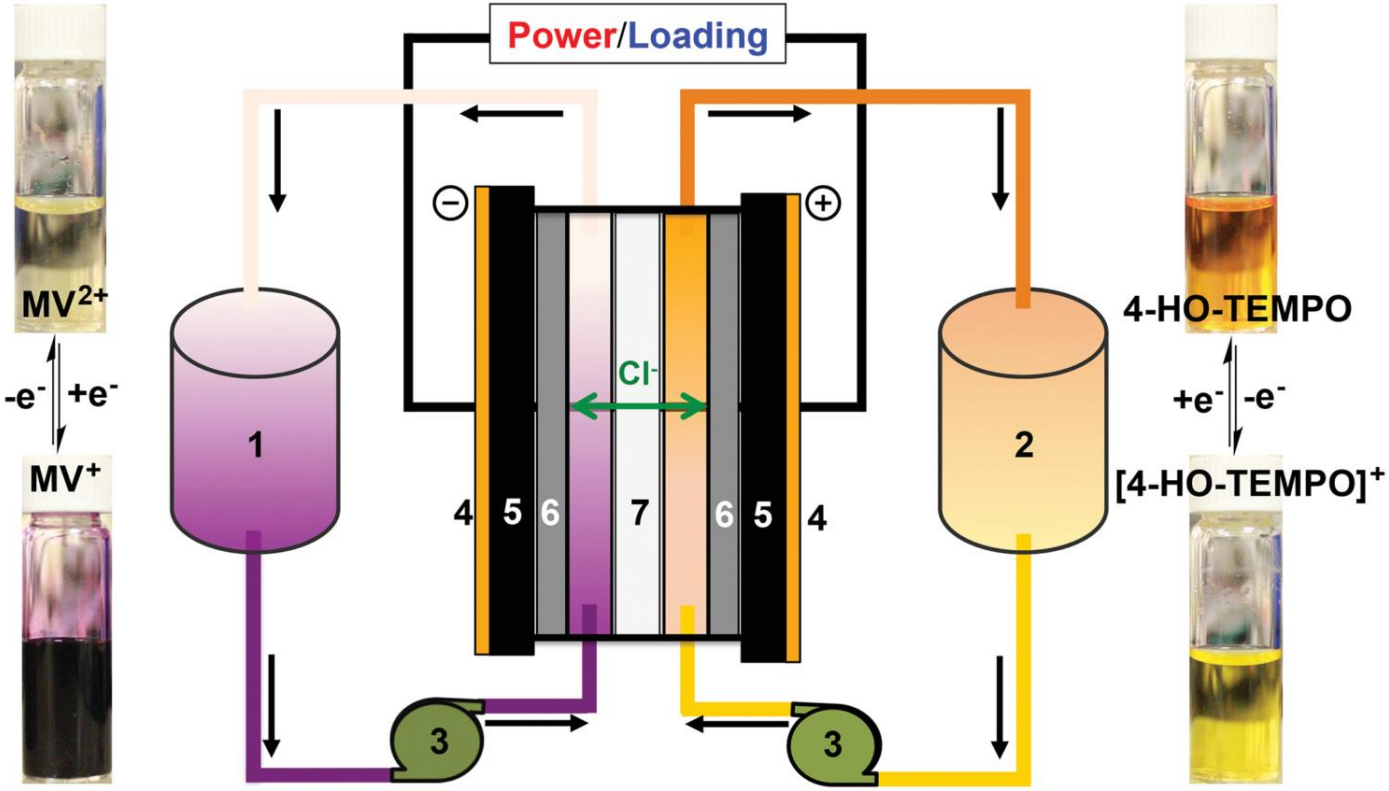
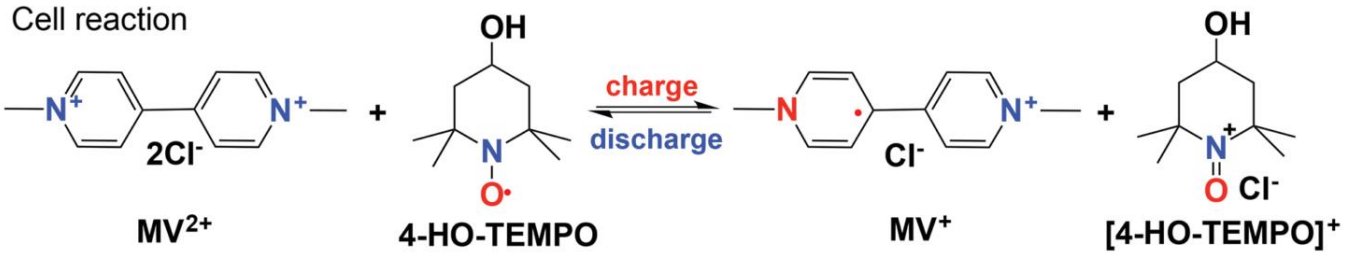
 alloxazine carboxylic acid	 ferrocyanide	400	99.987	10.3	1.23	2016 Harvard (ARPA-E & NSF)	High current efficiency, high ACA solubility (ACA stability; modest $Fe(CN)_6$ solubility)

PNNL pH 7 Aqueous Flow Battery



Cell reaction



T. Liu, X. Wei, Z. Nie, V. Sprenkle, and W. Wang,
"A Total Organic Aqueous RFB Employing a Low Cost and Sustainable Methyl Viologen Anolyte and 4-HO-Tempo Catholyte",
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Low Capacity Fade at Low Reactant Concentrations

0.1 M MV
1.0 M NaCl

0.1 M HO-TEMPO
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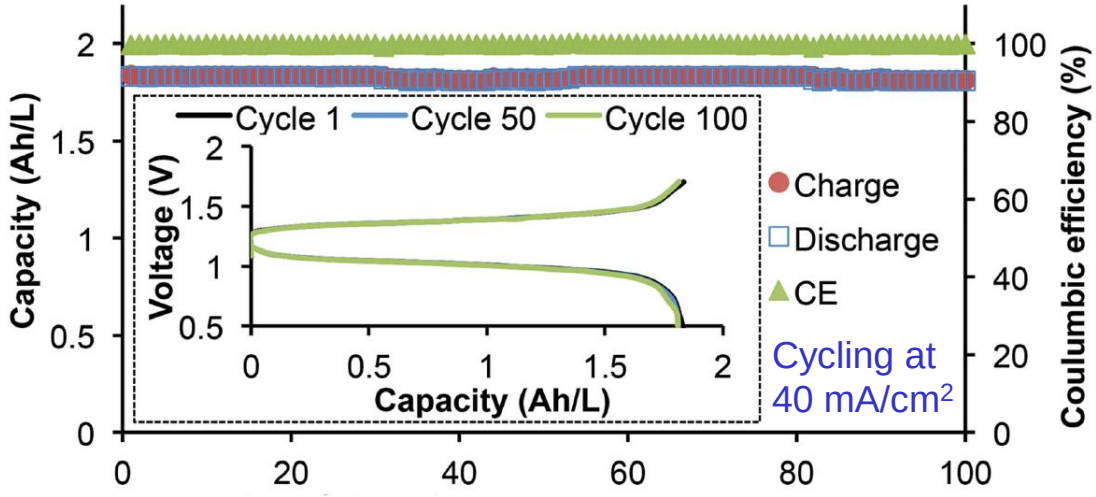

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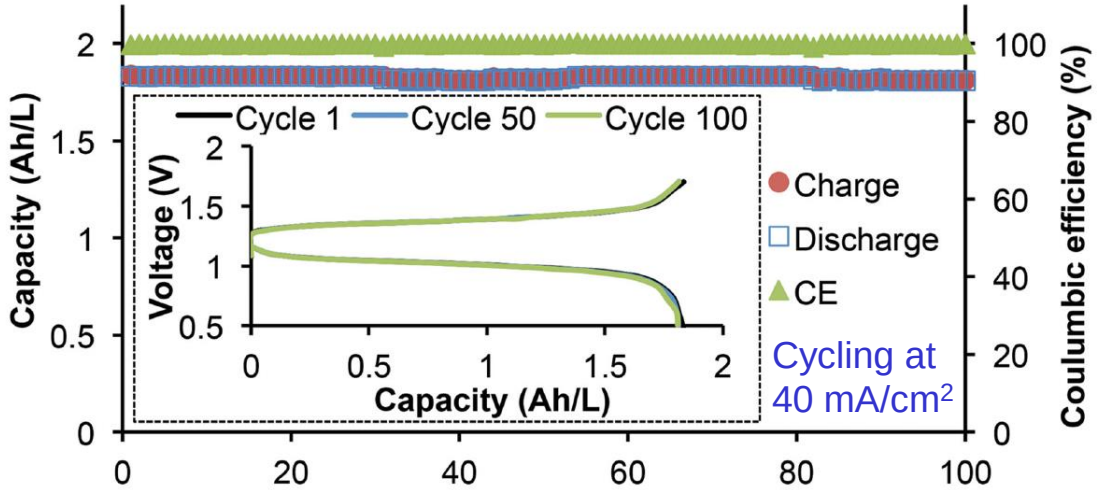
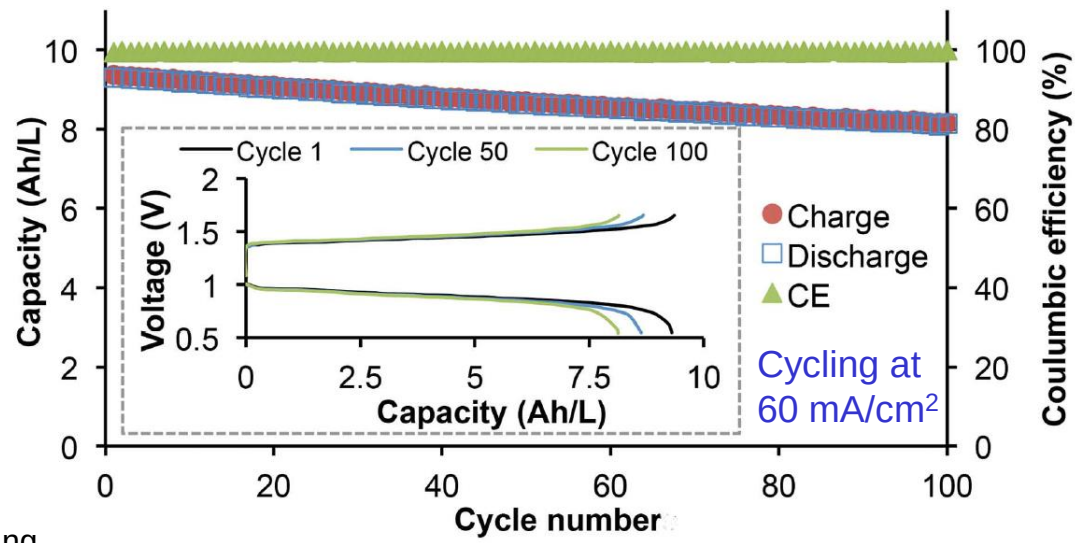


0.5 M MV
1.5 M NaCl

0.5 M HO-TEMPO
1.5 M NaCl



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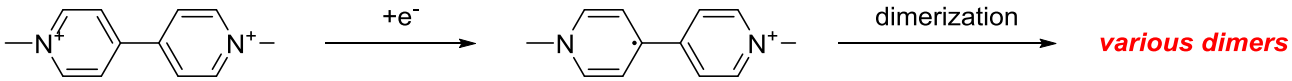
Our Hypothesized Decomposition Mechanisms of MV



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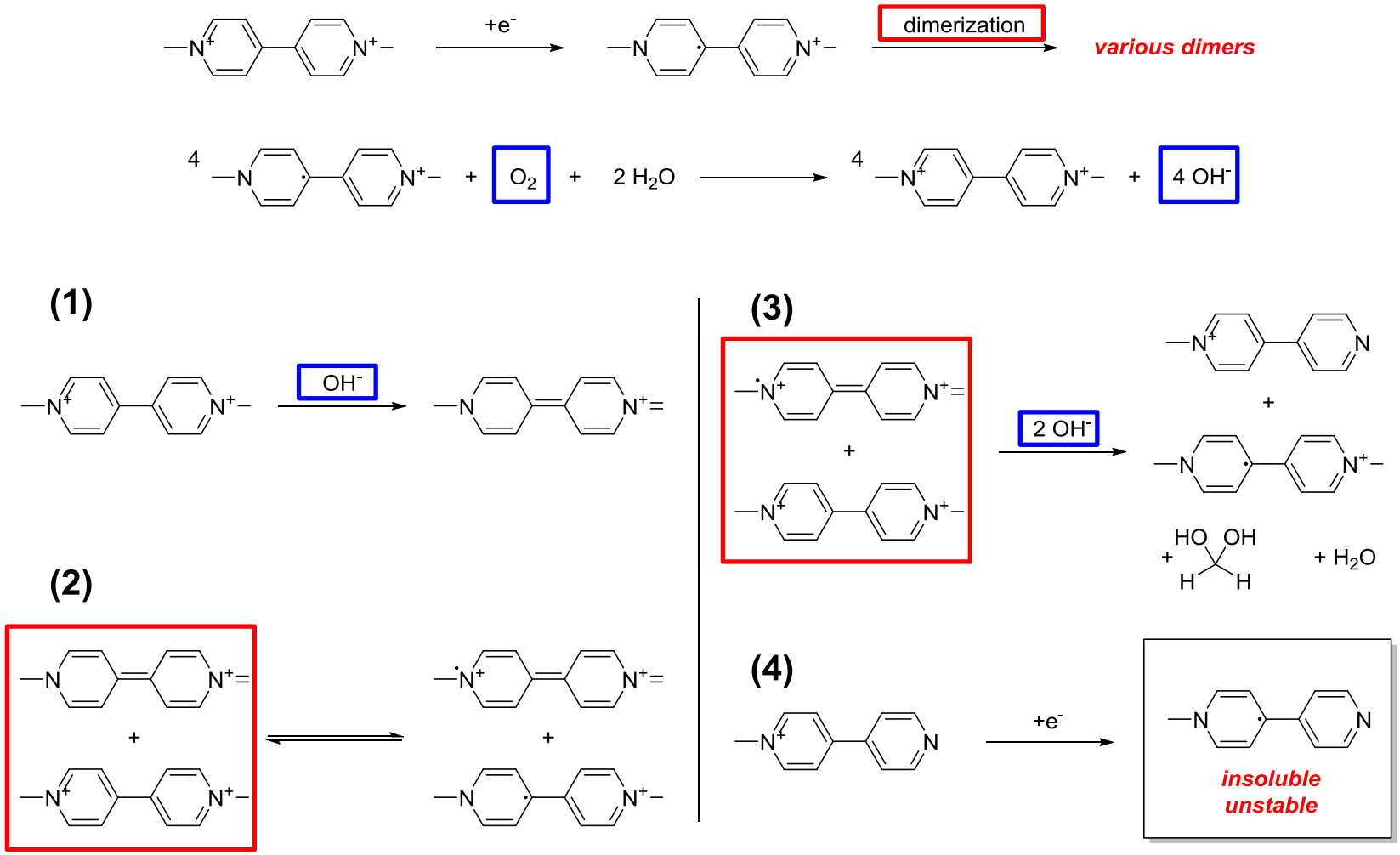
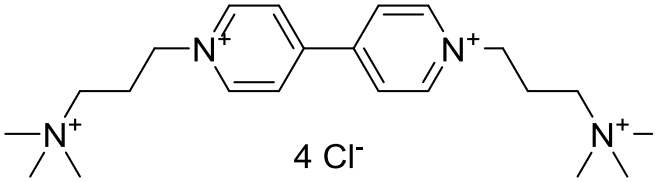


Chem. Asian. J. **2015**, *10*, 56–68
J. Org. Chem. **1988**, *53*, 1481–1485

A pH 7 Aqueous Flow Battery with High Capacity

BTMAP-Viologen

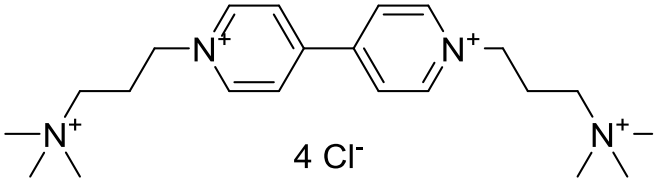


B T M A P

Bis(**T**ri**M**ethyl**A**mmonio)**P**ropyl

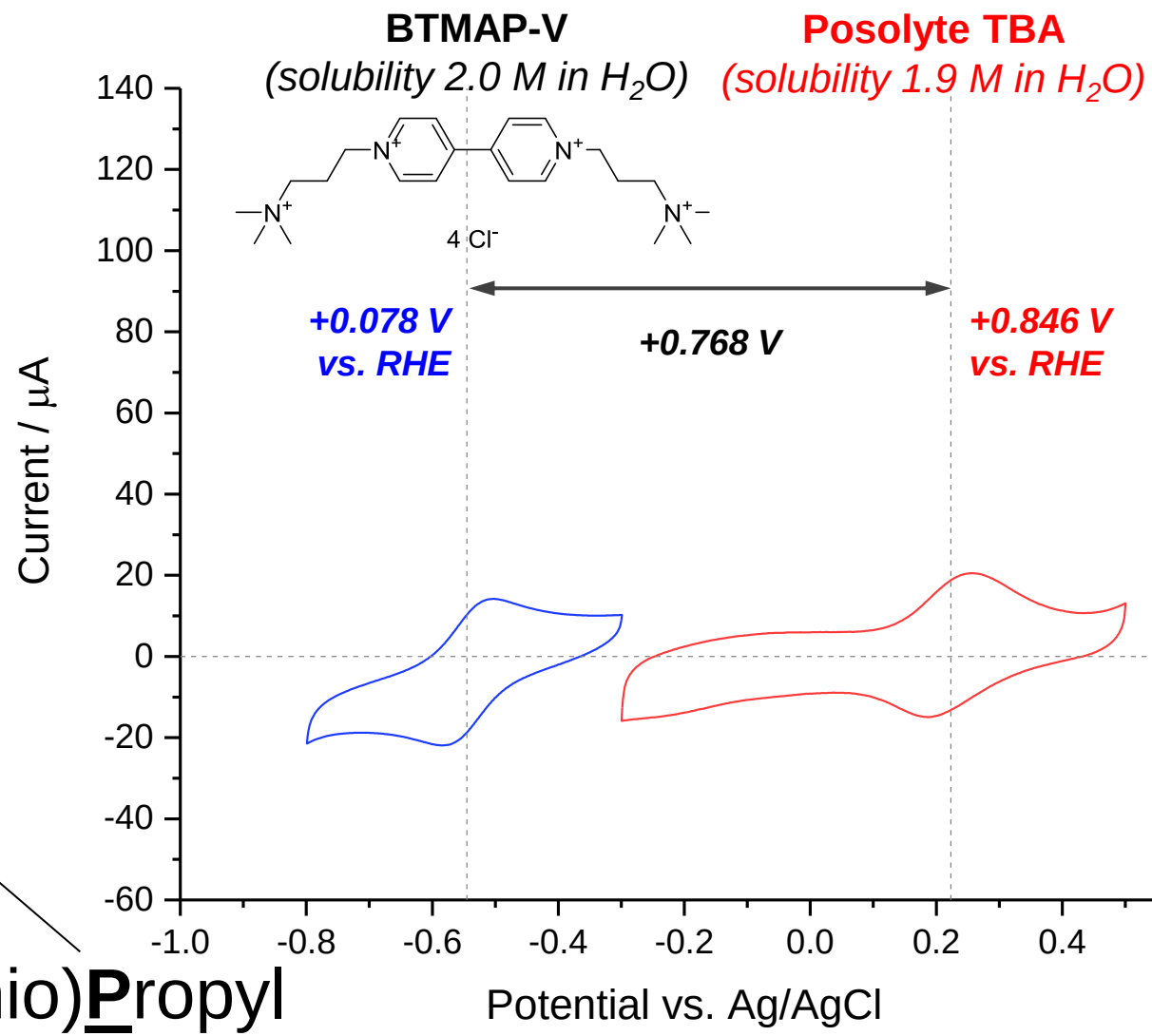
A pH 7 Aqueous Flow Battery with High Capacity

BTMAP-Viologen



B T M A P

Bis(TriMethylAmmonio)Propyl

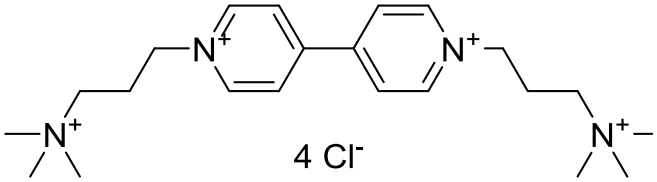


A pH 7 Aqueous Flow Battery with High Capacity

Negolyte:	**0.5 M BTMAP-V** *(13.4 Ah/L)*, **14.5 mL**
Posolyte:	**TBA, 1.0 M** *(26.8 Ah/L)*, **5.5 mL**
Flow plates:	**Serpentine, sealed**
Electrodes:	**3 × 39AA, baked**
Membrane:	**Selemion AMV, 5 cm^2**
Pumps:	**Peristaltic, speed "60"**

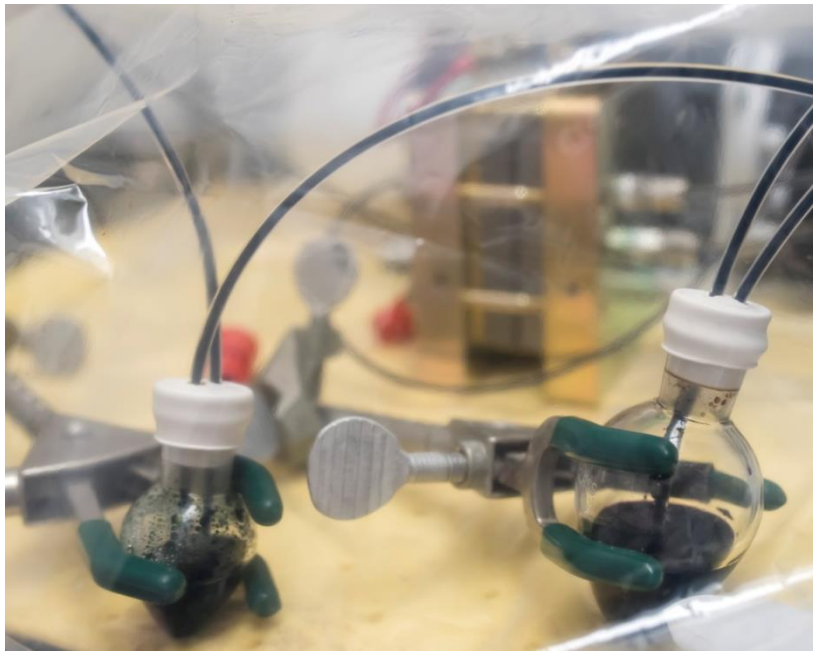
OCV:	***0.72 V at 50% SOC***
	0.84 V at 100% SOC
ASR:	***4.5 Ω cm^2 (EIS)***
	5.1 Ω cm^2 (polarization)

BTMAP-Viologen



B T M A P

Bis(**T**ri**M**ethyl**A**mmonio)**P**ropyl



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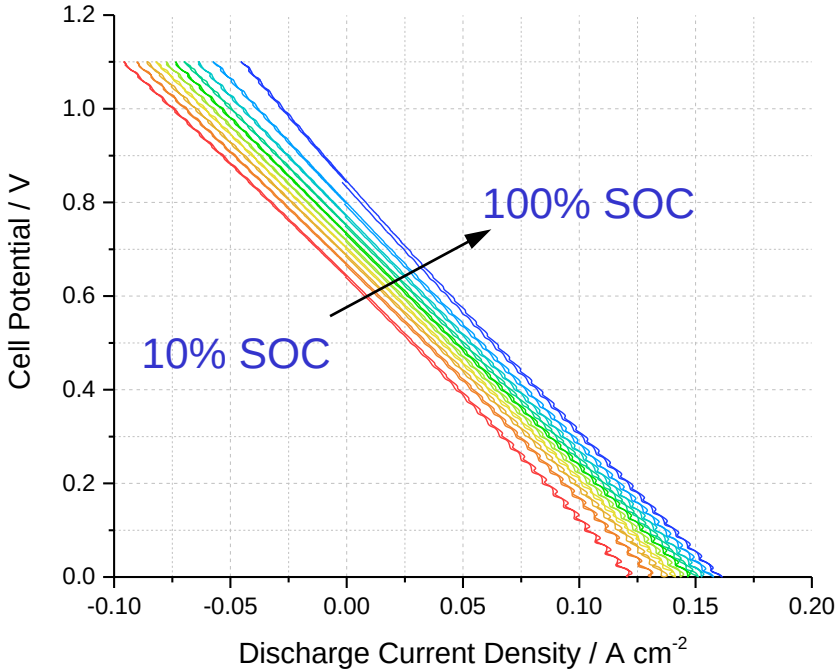
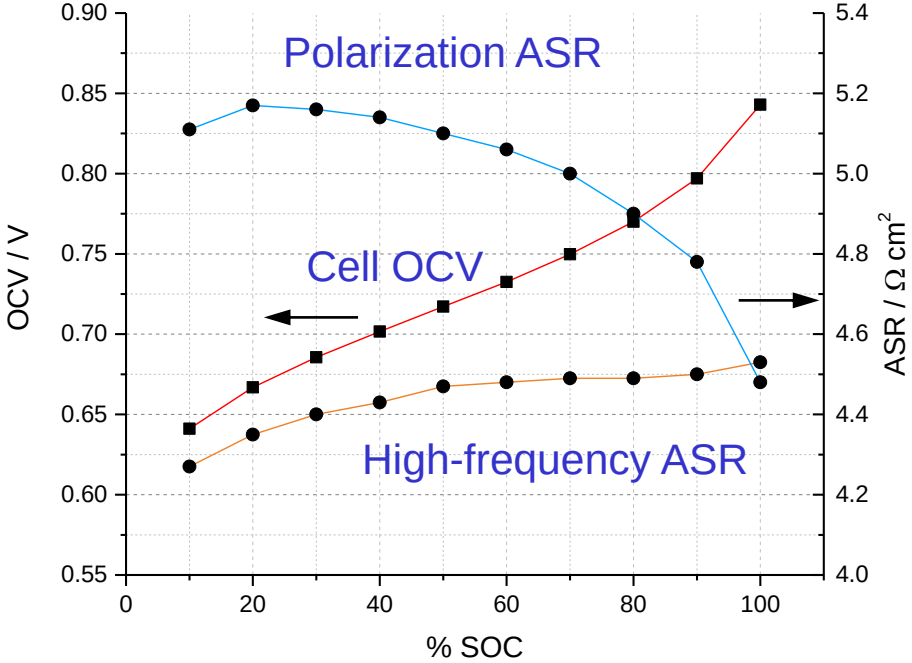
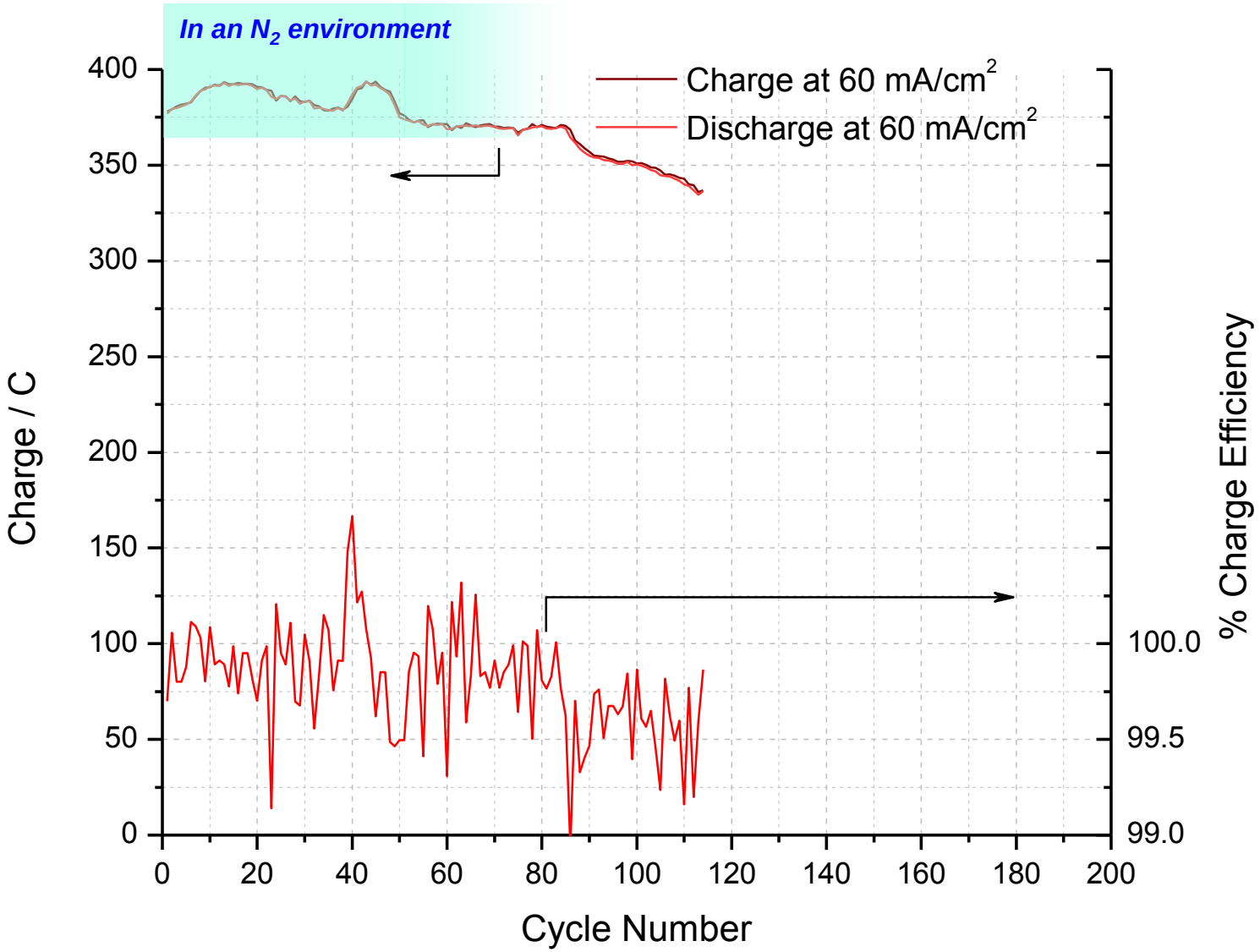
OCV: ***0.72 V at 50% SOC***
0.84 V at 100% SOC

ASR: ***4.5 Ω cm² (EIS)***
5.1 Ω cm² (polarization)





Cycling Performance, BTMAP-Viologen vs. ASO TBA



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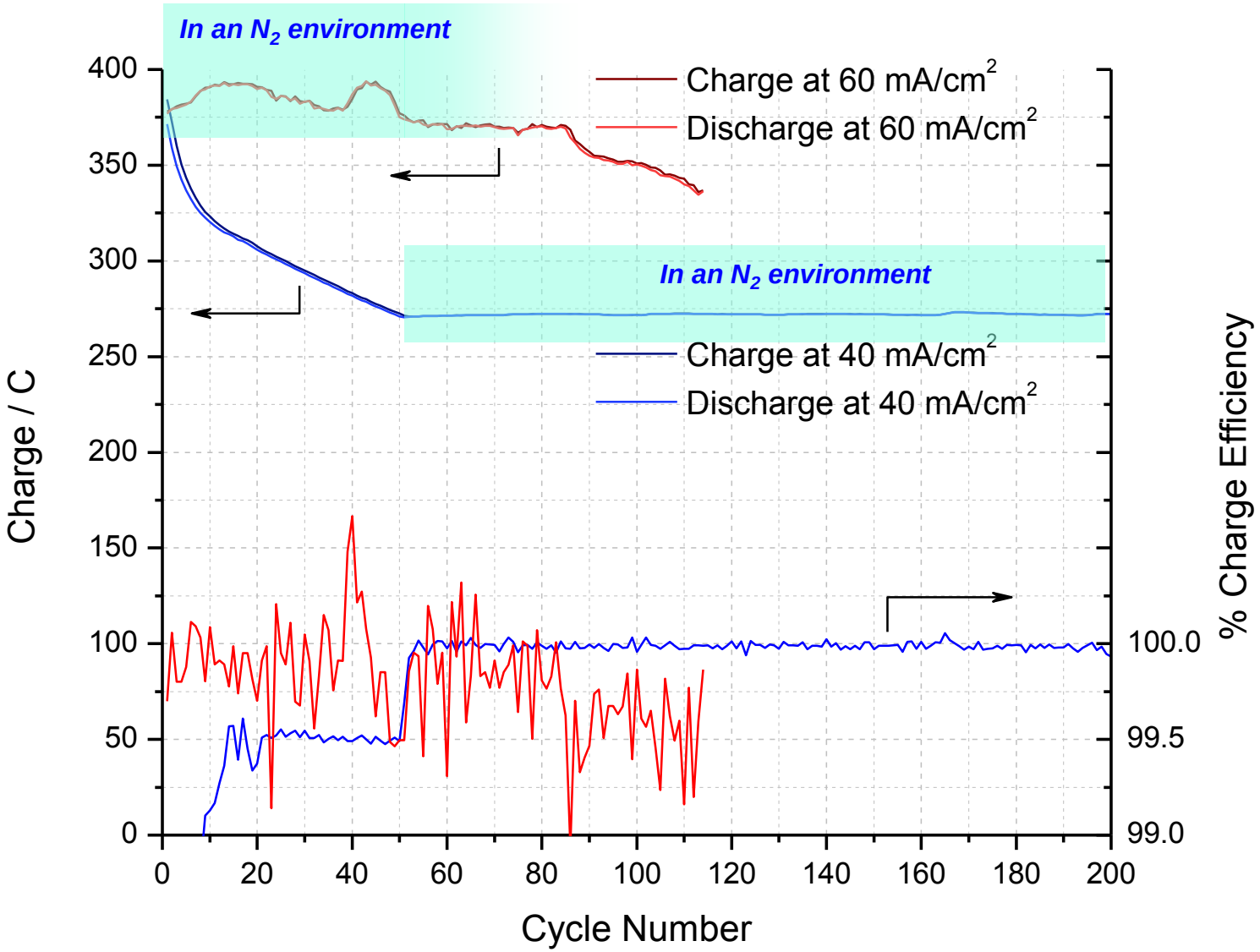


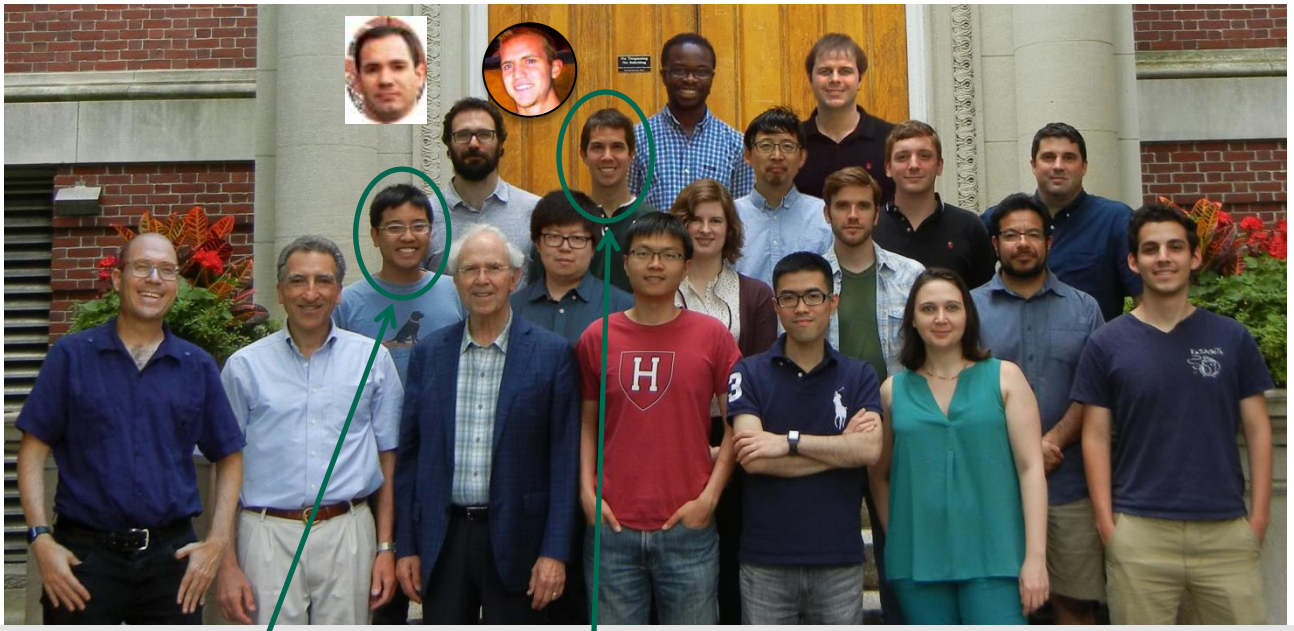
Outlook

- Cost, tunability, and stability of ASOs look promising for electrical energy storage
- High performance, low cost quinone-bromide RFB suitable for utility & industrial applications
- High voltage, low toxicity alkaline organic Redox Flow Batt more suitable for residential, commercial use
- First pH 7 high-capacity ASO flow battery that cycles stably
- Neutral pH enables wide variety of membrane chemistries
- BTMAP functionalization suppresses MV dimerization / decomp. that leads to insoluble or inactive species
- BTMAP functionalization *should* also reduce crossover
- There is still room for improvement
  - molecules
  - separators
  - porous electrodes and fluidics
- Priorities:
  - reduce membrane resistance
  - evaluate crossover

Harvard Department of Chemistry & Chemical Biology

HARVARD John A. Paulson School of Engineering and Applied Sciences

Acknowledgments



Not pictured: Professor Ted Betley, Saraf Nawar, Rachel Burton, Cooper Galvin, Rebecca Gracia, Sidharth Chand, Tyler Van Valkenburg, Bilen Aküzüm, Ryan Duncan, Dr. Süleyman Er, Dr. Xudong Chen, Phil Baker, Dr. Trent Molter, Dr. Junling Huang, Prof. Maurizio Salles, Dhruv Pillai, Dr. Changwon Suh, Louise Eisenach, Jennifer Wei

Back to front, left to right:

- **Dr. Michael Marshak, Dr. Brian Huskinson, Dr. David Kwabi, Dr. Danny Tabor**
- **Dr. Rafa Gómez-Bombarelli, Andrew Wong, Dr. Sungjin "James" Kim, Michael Gerhardt, Joel Veak**
- **Dr. Eugene Beh, Kaixiang Lin, Lauren Hartle, Dr. Marc-Antoni Goulet, Prof. Sergio Granados-Focil**
- **Prof. Alán Aspuru-Guzik, Prof. Michael Aziz, Prof. Roy Gordon, Liuchuan Tong, Qing Chen, Diana DePorcellinis, Alvaro Valle**

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