Organic Aqueous Flow Batteries for Massive Electrical Energy Storage

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

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Dr. Imre Gyuk
DE-AC05-76RL01830 through PNNL subcontract 304500
7/1/2016-
Redox-Active Organics for Battery Storage

Plastoquinone in photosynthesis

oxidized

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

reduced

simplest quinone

Benzoquinone

Naphthoquinone

Anthraquinone

Hydroquinone
Organic-Based Aqueous Flow Batteries

**Primary requirements:**
- Reduction potential
- Aqueous Solubility
- Redox kinetics
- Stability
- Cost
## Aqueous-Soluble Organics (ASOs) for Energy Storage

<table>
<thead>
<tr>
<th>Feature</th>
<th>Benefit</th>
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<tbody>
<tr>
<td>Low chemicals cost:</td>
<td>Enables low cost/kWh</td>
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<td>Rapid redox kinetics:</td>
<td>Enable low area/kW (\rightarrow) low cost/kW</td>
</tr>
<tr>
<td>All-liquid storage:</td>
<td>Enables inexpensive BOS and high cycle life</td>
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<td>Aqueous electrolyte:</td>
<td>Enables fireproof operation</td>
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<td>Non-toxic:</td>
<td>Ideal for commercial, residential markets</td>
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<td>Scalability:</td>
<td>Enables rapid chemistry scaleup</td>
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<td>Tunability:</td>
<td>Enables performance improvements</td>
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<td>Small organic molecules:</td>
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![Diagram of charging and discharging processes](image)
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<td>100 (low conc.)</td>
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<td>100 (high conc.)</td>
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<td>Cl$^-$</td>
<td></td>
<td>400</td>
<td>99.987</td>
<td>10.3</td>
<td>1.23</td>
<td>2016 Harvard (ARPA-E &amp; NSF)</td>
<td>High current efficiency, high ACA solubility (ACA stability; modest Fe(CN)$_6^-$ solubility)</td>
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Low Capacity Fade at Low Reactant Concentrations

0.1 M MV
1.0 M NaCl

0.1 M HO-TEMPO
1.0 M NaCl

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",
*Advanced Energy Materials* 6, 1501449 (2016)
High Capacity Fade at High Reactant Concentrations

0.1 M MV
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0.5 M MV
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Our Hypothesized Decomposition Mechanisms of MV
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Chem. Asian. J. 2015, 10, 56–68
A pH 7 Aqueous Flow Battery with High Capacity

BTMAP-Viologen

BTMAP

Bis(TriMethylAmmonio)Propyl
A pH 7 Aqueous Flow Battery with High Capacity

BTMAP

BTMAP-V
(solubility 2.0 M in H₂O)

Posolyte TBA
(solubility 1.9 M in H₂O)

Bis(TriMethylAmmonio)Propyl

BTMAP-Viologen

Current / μA

Potential vs. Ag/AgCl
Negolyte: 0.5 M BTMAP-V \((13.4 \, \text{Ah/L})\), 14.5 mL
Posolyte: TBA, 1.0 M \((26.8 \, \text{Ah/L})\), 5.5 mL
Flow plates: Serpentine, sealed
Electrodes: 3 \times 39\text{AA}, baked
Membrane: Selemin AMV, 5 cm²
Pumps: Peristaltic, speed “60”

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

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

BTMAP-Viologen

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Cycling Performance, BTMAP-Viologen vs. ASO TBA
Cycling Performance, BTMAP-Viologen vs. ASO TBA

In an N₂ environment

Charge at 60 mA/cm²
Discharge at 60 mA/cm²

Charge at 40 mA/cm²
Discharge at 40 mA/cm²

% Charge Efficiency

Cycle Number

Charge / C
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
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