Pacific Northwest
NATIONAL LABORATORY

Improve the Kinetics of the Ketone-based Aqueous Organic Redox Flow Batteries

Presentation # 603

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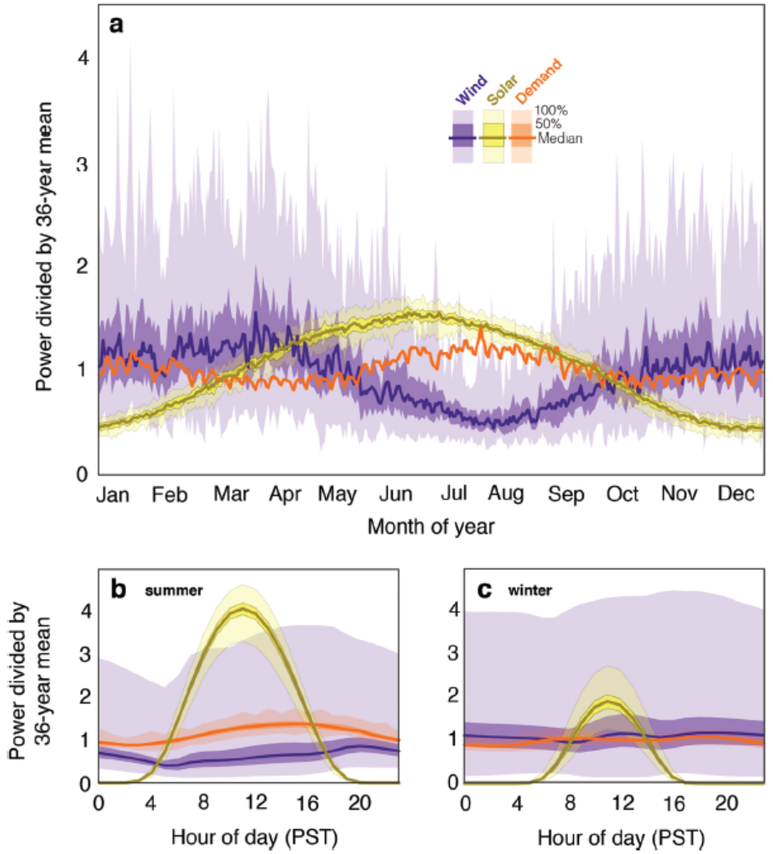
U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

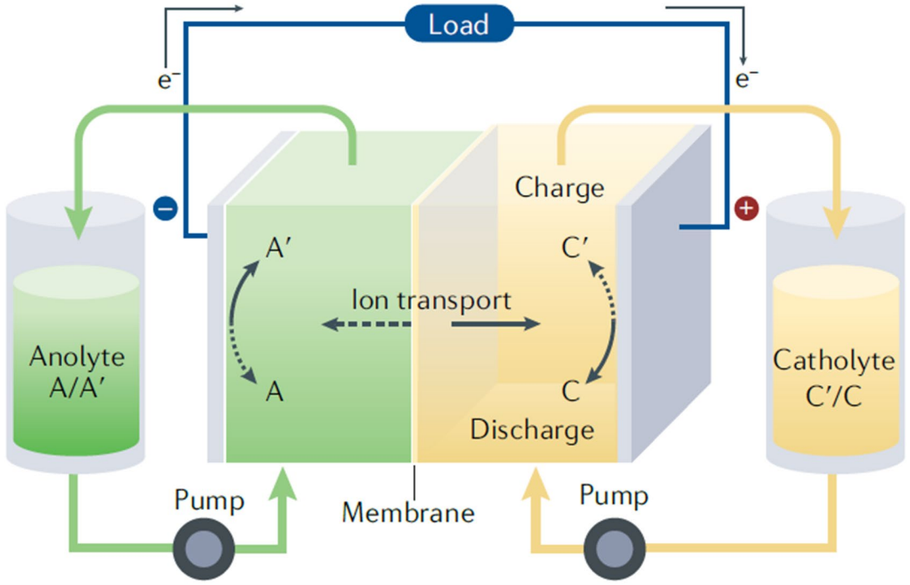
Low-carbon electricity system
With renewable energy

>20% of renewable energy in grid, energy storage system is needed for grid stabilization



Fluctuation of solar and wind resources
Miss match of supply and demand

Nat. Chem. **2016**, *8* (3), 204-206; *Energy Environ. Sci.* **2018**, *11* ,914-925.

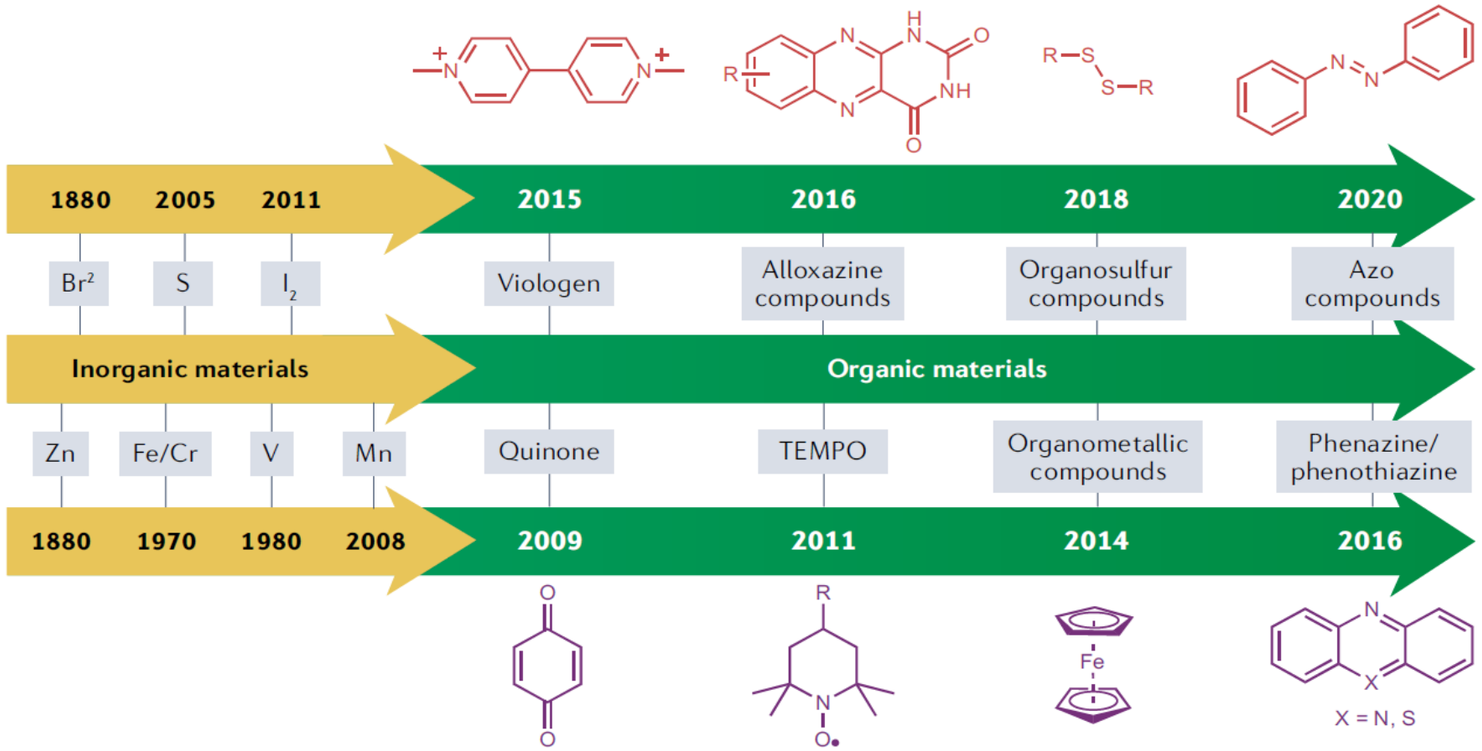


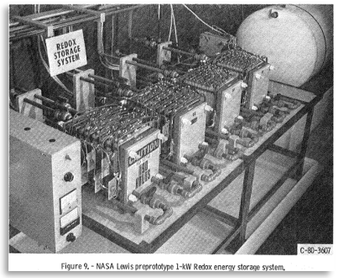
flow battery configuration

Modular structure

- fluidic electrolyte
- spatial separation of energy storage and power generation
- individually tuning of energy capacity and power capability

Nat. Rev. Chem. **2022**, *6*, 524–543.



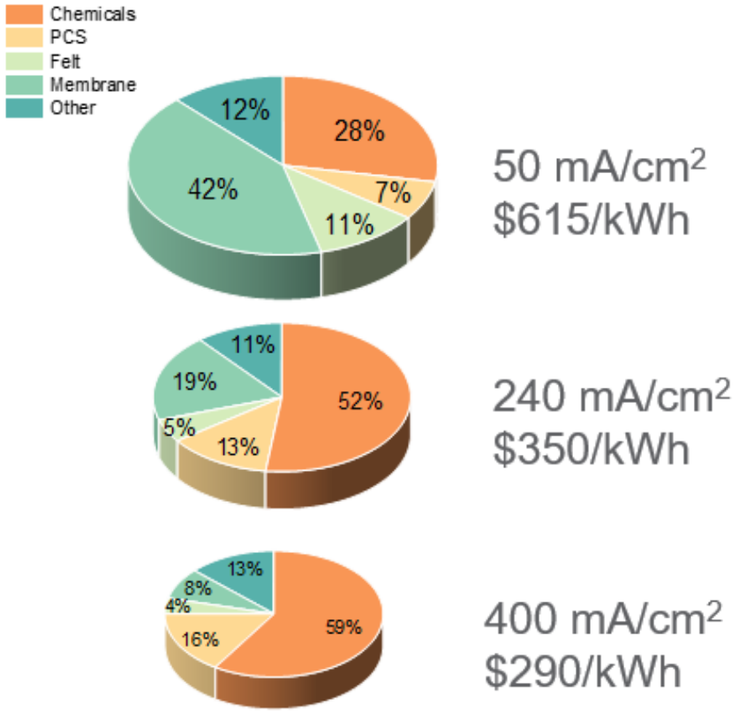


NASA Redox Storage System Development Project

ESS inc. iron flow battery

Nat. Rev. Chem. **2022**, *6*, 524–543.

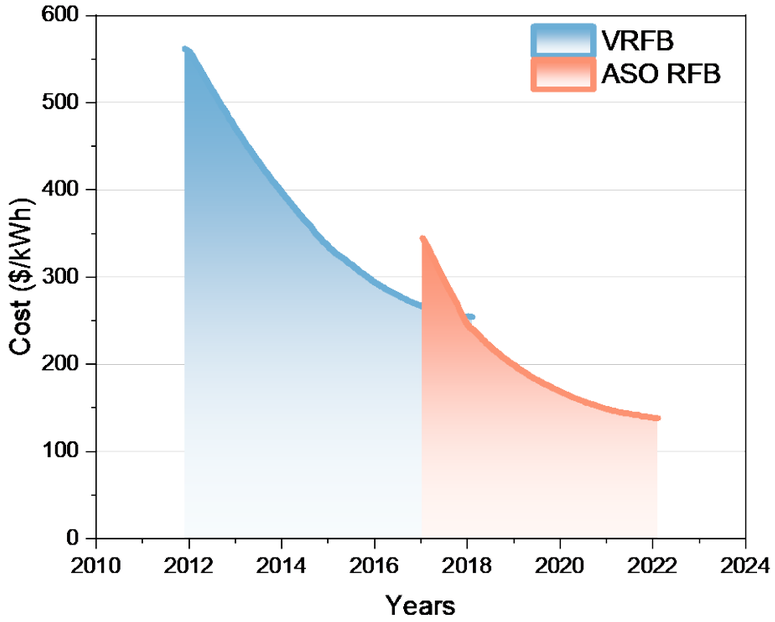
Vanadium redox flow battery cost



50 mA/cm^2
$615/kWh

240 mA/cm^2
$350/kWh

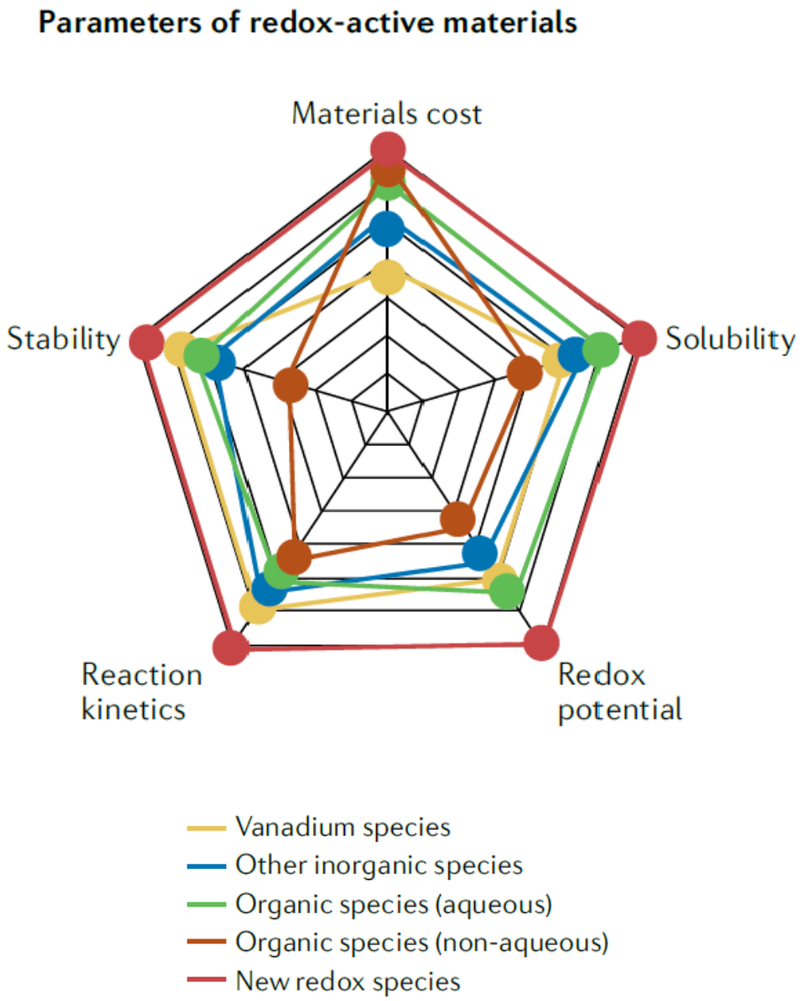
400 mA/cm^2
$290/kWh



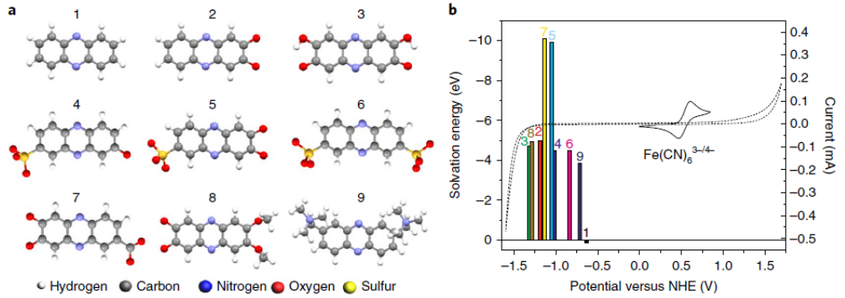
Benefits of Organic Materials

- lower material cost on large scale
- **tunability** of electrolyte
- multi-electron transfer redox events

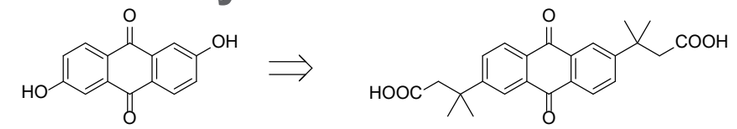
Material driven approach: tunability of organic molecule



Redox potential / Solubility

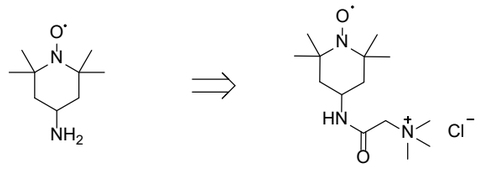


Stability

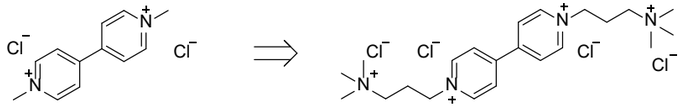


Science, **2015**, *349 (6255)*, 1529.
Chem, **2020** *6 (6)*, 1432-1442.

Nat. Energy **2018**, *3* (6), 508-514.
Joule **2021**, *5* (9), 2437-2449.

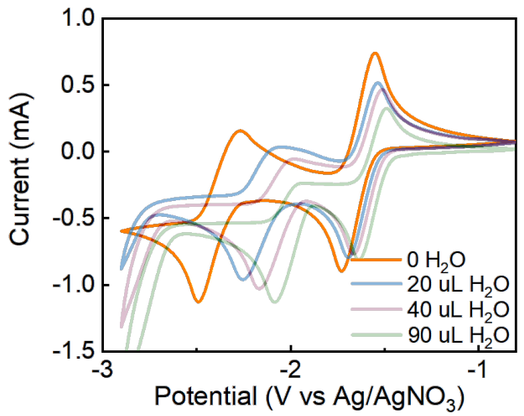


Adv. Funct. Mater. **2022**, 2203032.

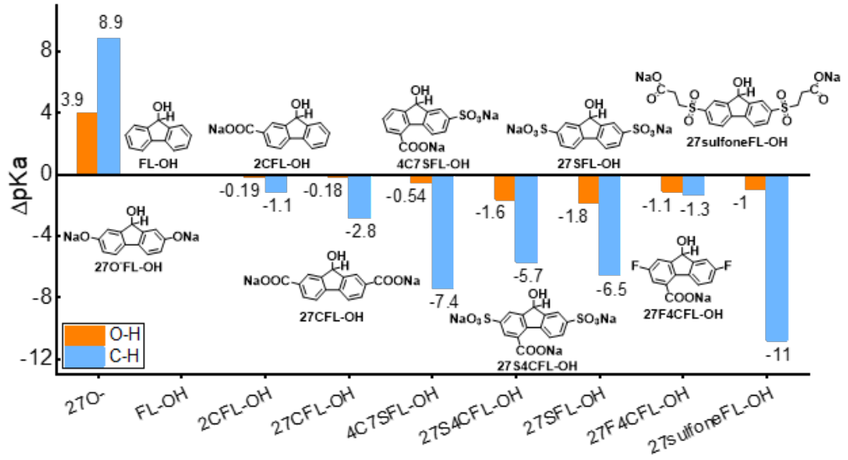


Chem. Commun. **2018**, *54* (50), 6871-6874.

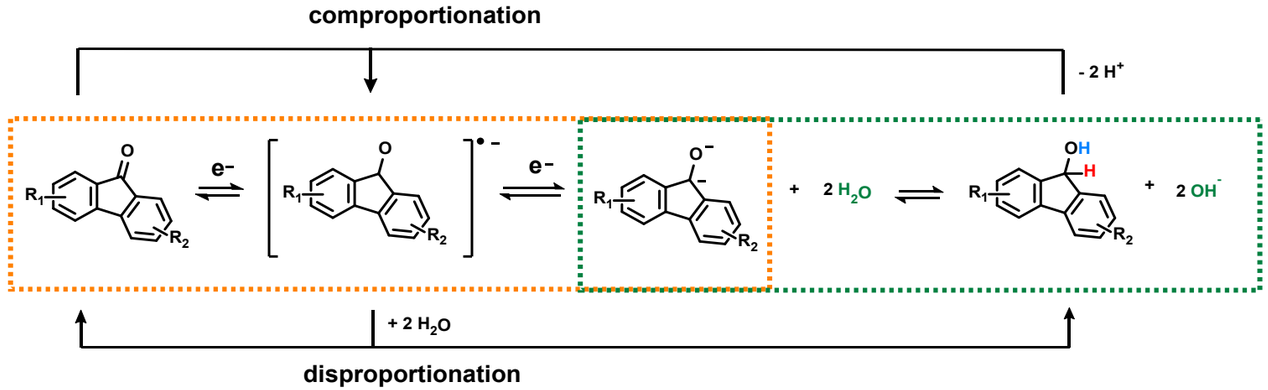
Activate reversibility with molecular engineer



Ketone hydrogenation in water



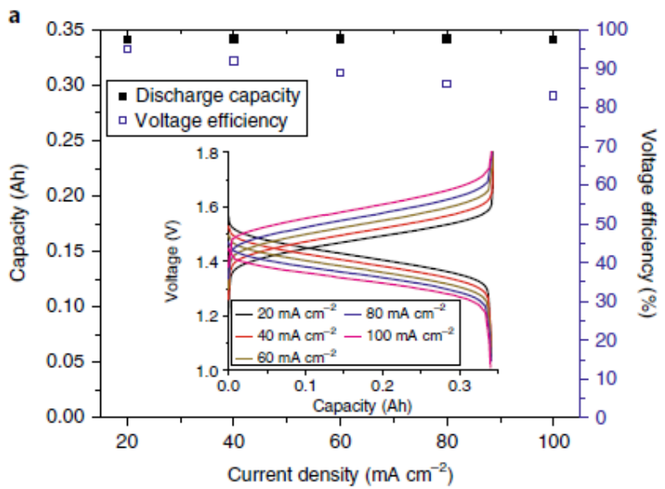
Activate reversibility with functional groups



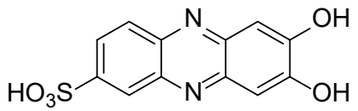
coupled chemical electrochemical process

Science, **2021**, *372*, 836-840.

FL kinetics comparing to other organic systems

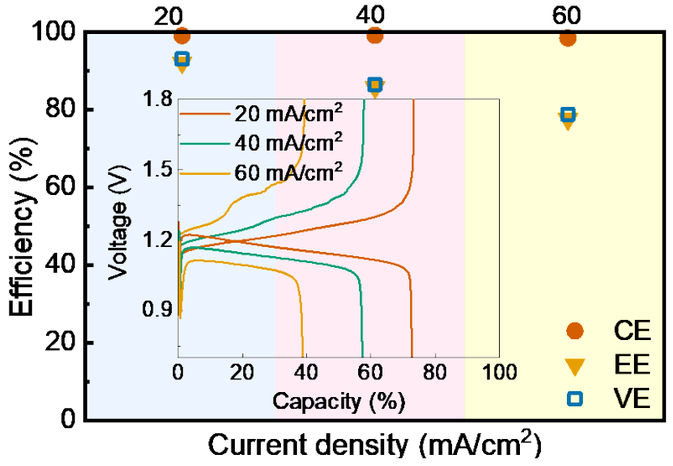


DHPS 75 Ah/L

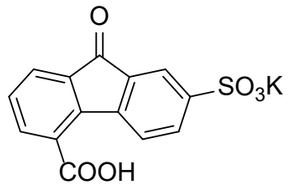


Nat. Energy **2018**, *3* (6), 508-514.

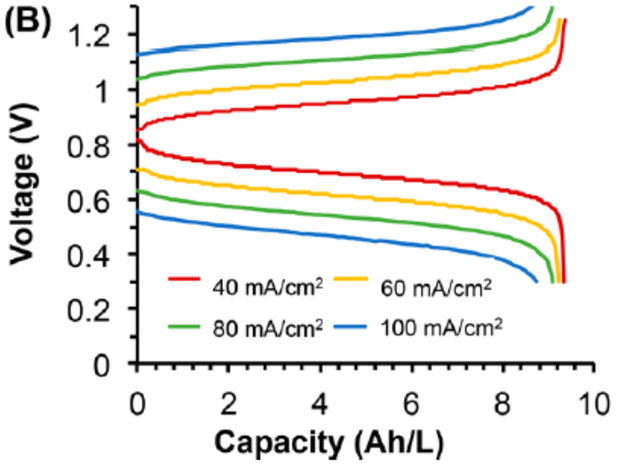
Alkaline system



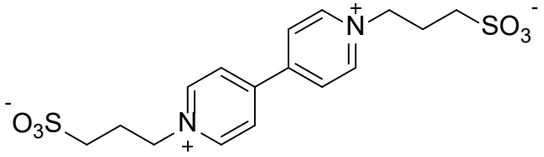
4C7SFL 73 Ah/L



Alkaline system



$(SPr)_2V$ 13.4 Ah/L

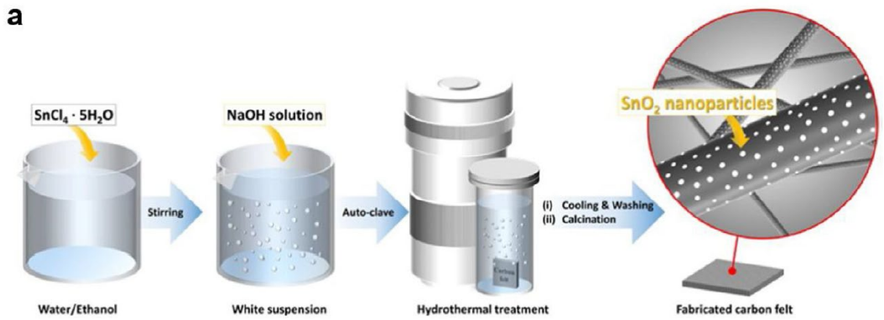


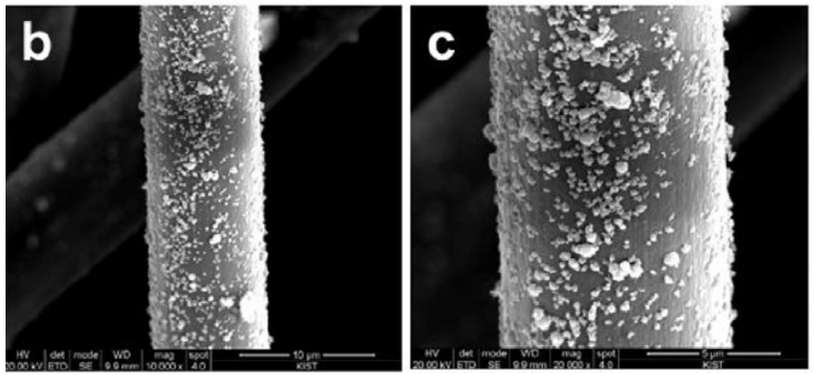
ACS Energy Lett. **2018**, *3*, 663–668.

neutral system

In redox flow battery
For a fixed material, tune kinetics?

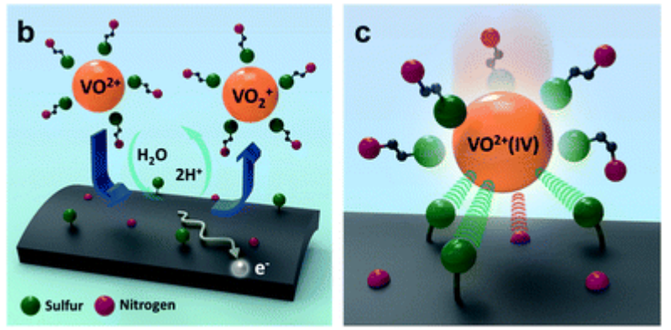
Electrode modification with metal/metal oxide electrocatalyst



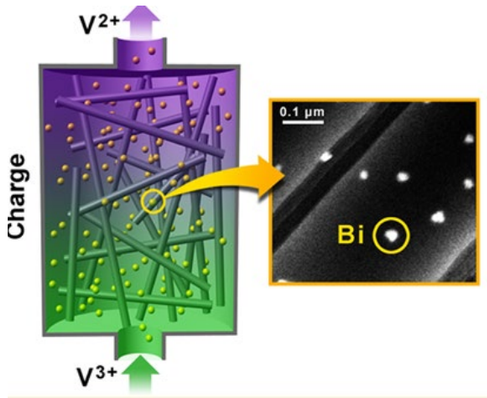


J. Mater. Sci. Technol. **2021**, *75* , 96–109.

Additives in electrolyte leading to electrode modification

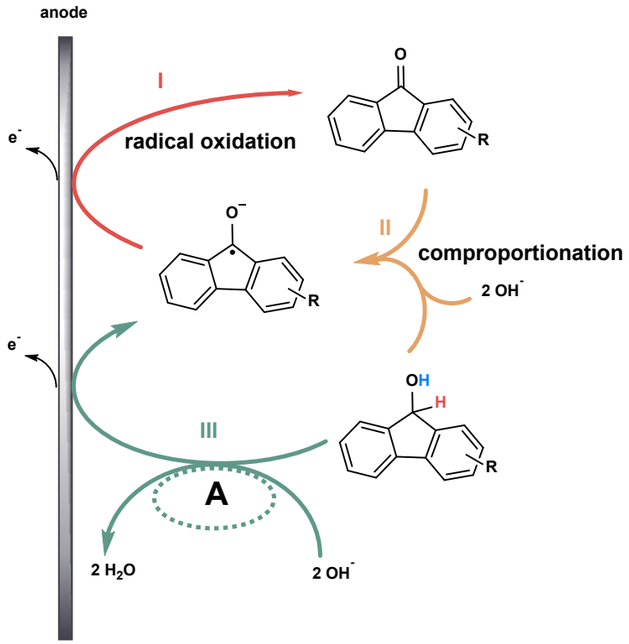


J. Energy Chem. **2018**, *27*, 1269-1291.

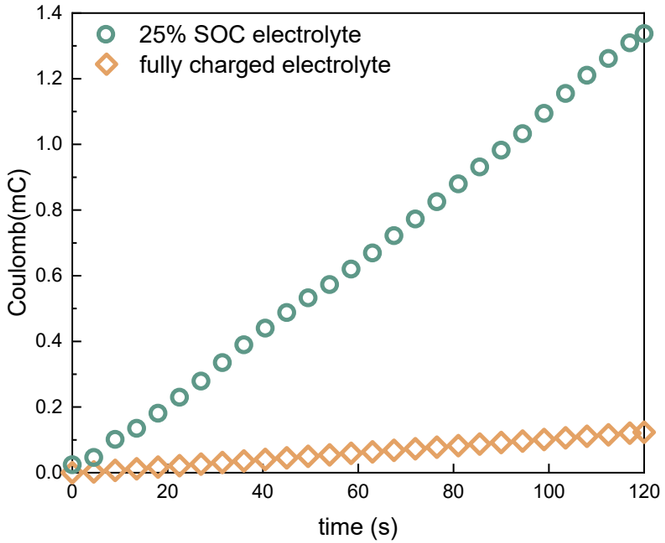


Nano Lett. **2013**, *13*, 1330−1335

For fluorenone: mechanism-informed approach



On discharge
accelerate the radical anion supply



Chronocoulometry in H-cell
potential held at -0.65V *vs* Hg/HgO

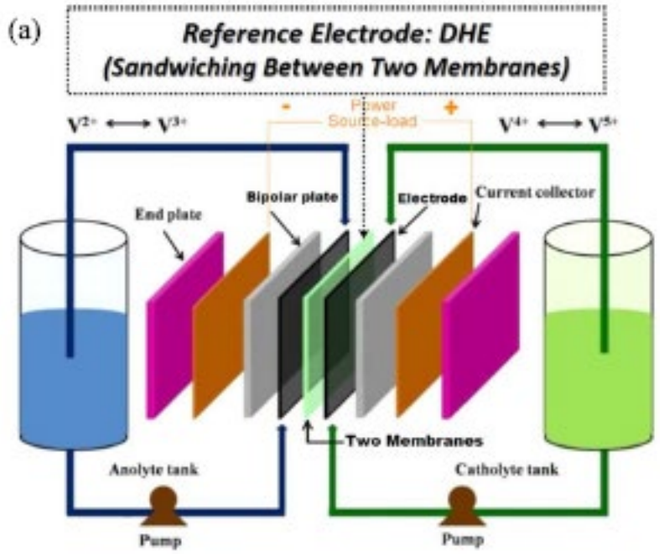
Unpublished result

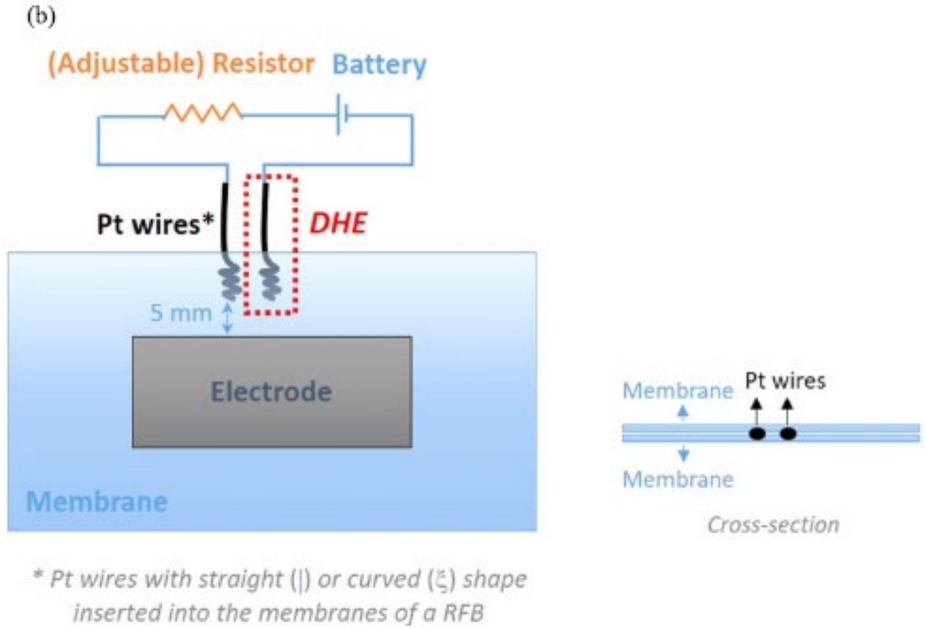
Battery validation: current response test

Objective:

Battery electrode potential being held at certain potential against selected reference
Check the discharge current
Higher the current, faster the kinetics

Method: Dynamic Hydrogen Reference Electrode





* Pt wires with straight (|) or curved (ξ) shape inserted into the membranes of a RFB

J. Electrochem. Soc. **2020**, *167*, 160541

Battery validation: current response test

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Check the discharge current
Higher the current, faster the kinetics

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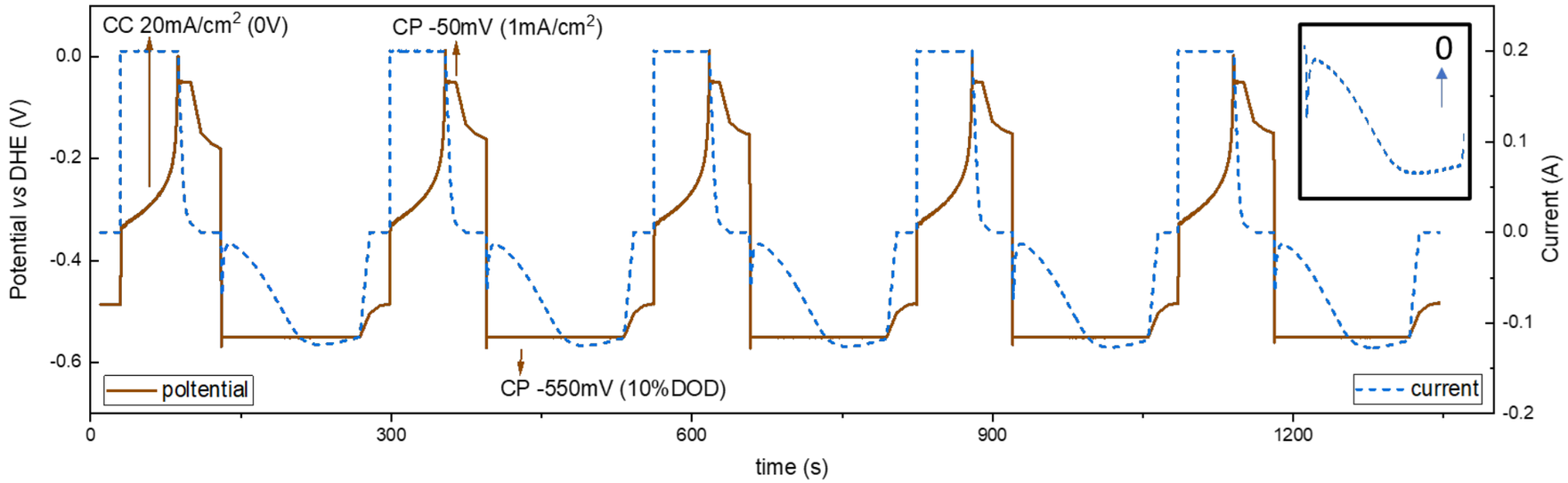


Charge

CC at 20 mA/cm^2 until 0 V cutoff
CP at -50 mV *vs* DHE until 1mA/cm^2

Discharge

CP at -0.55 V *vs* DHE until 10% DOD

- alkaline condition
- reference electrode potential drift

Unpublished result

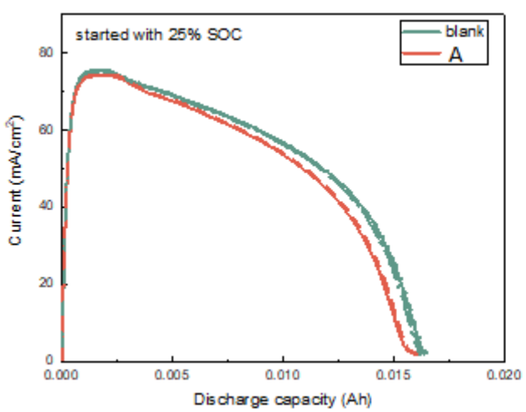
Battery validation: current response test

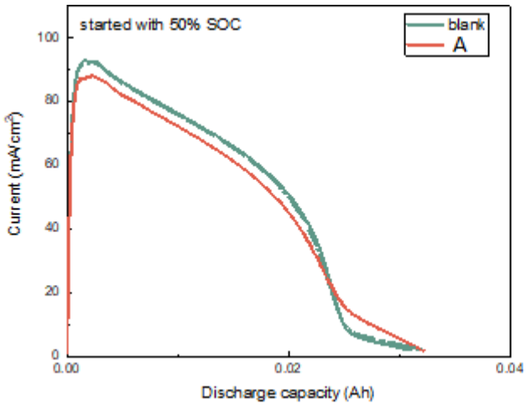
Objective:

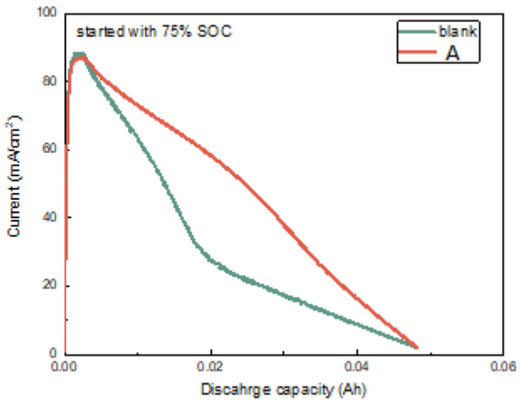
Battery electrode potential being held at certain potential against selected reference
Check the discharge current
Higher the current, faster the kinetics

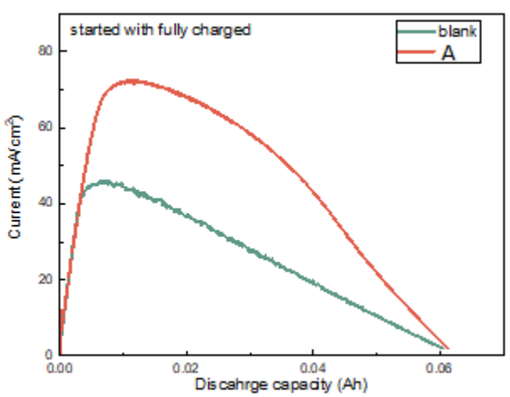
Method: pseudo reference

Battery assembled with large excess catholyte, catholyte solution SOC maintained minimal fluctuation during tests, battery discharge at held voltage against catholyte, similar effect to anode held at fixed potential against reference





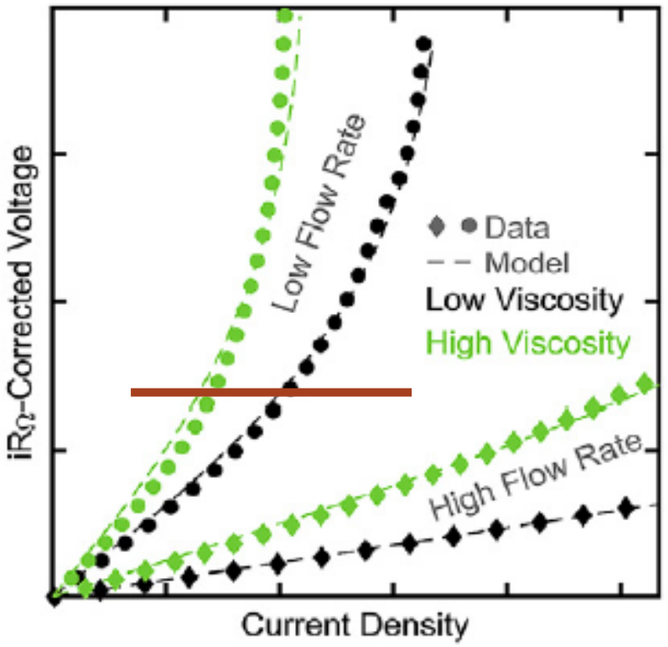




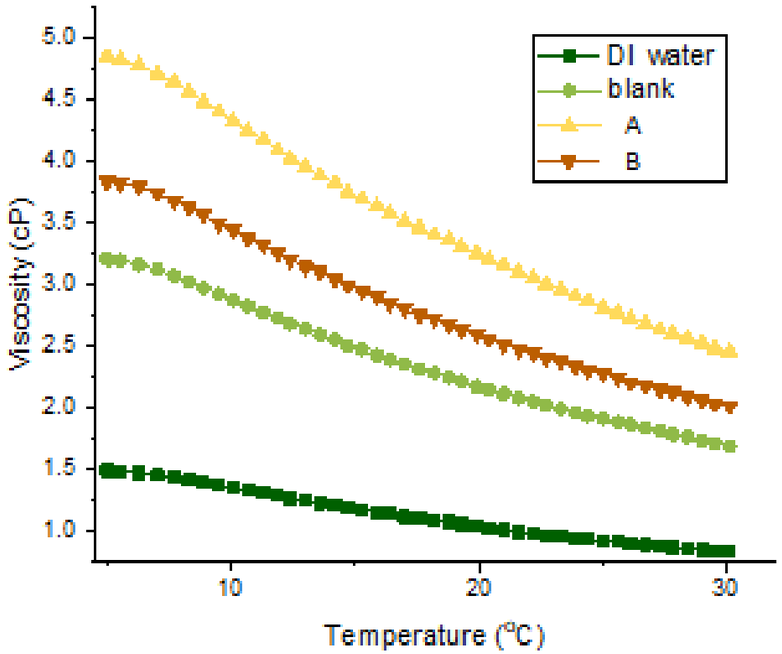
Charge
CP at 1.4 V until desired SOC
Discharge
CP at 0.9 V, recording the current response

Unpublished result

first: viscosity influence on flow battery

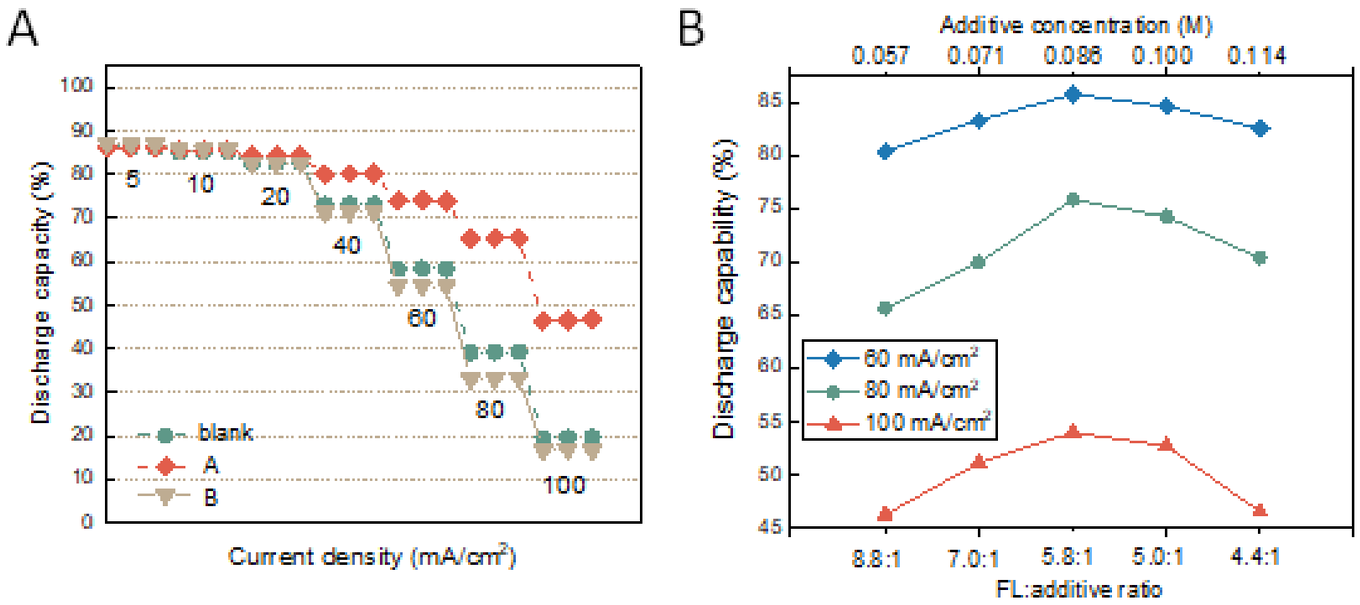


J. Power Sources **2018** ,*399*, 133-143



Unpublished result

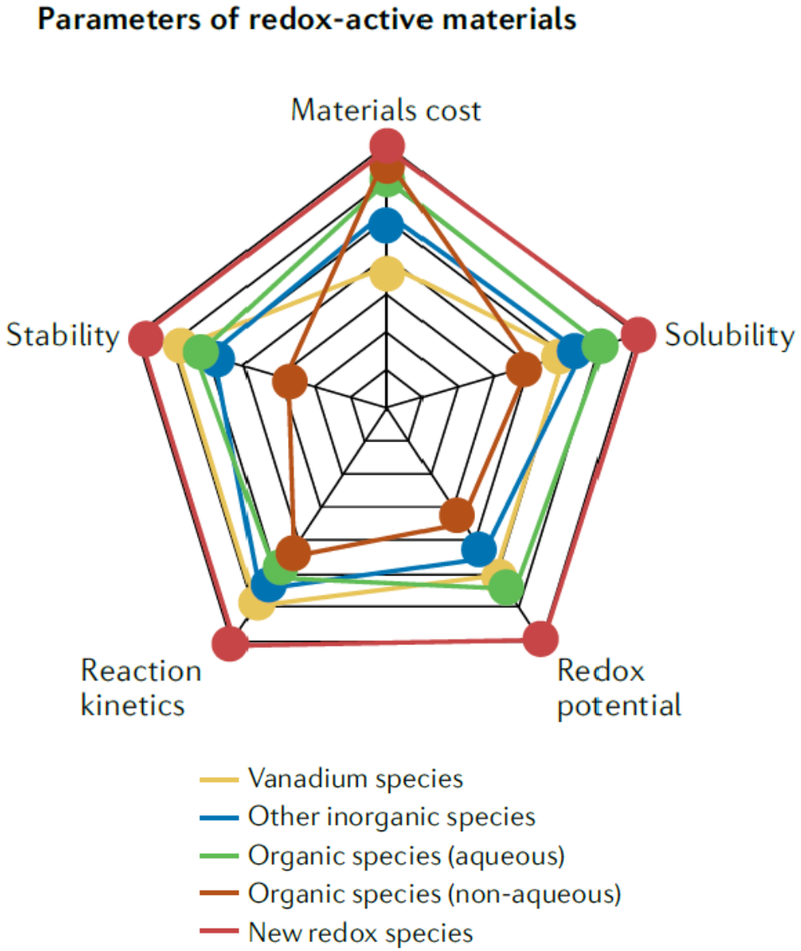
Battery performance



- Net positive effect
- *Kinetic enhancement* outcompete *viscosity negative impact*
- Optimal ratio

Unpublished result

Summary



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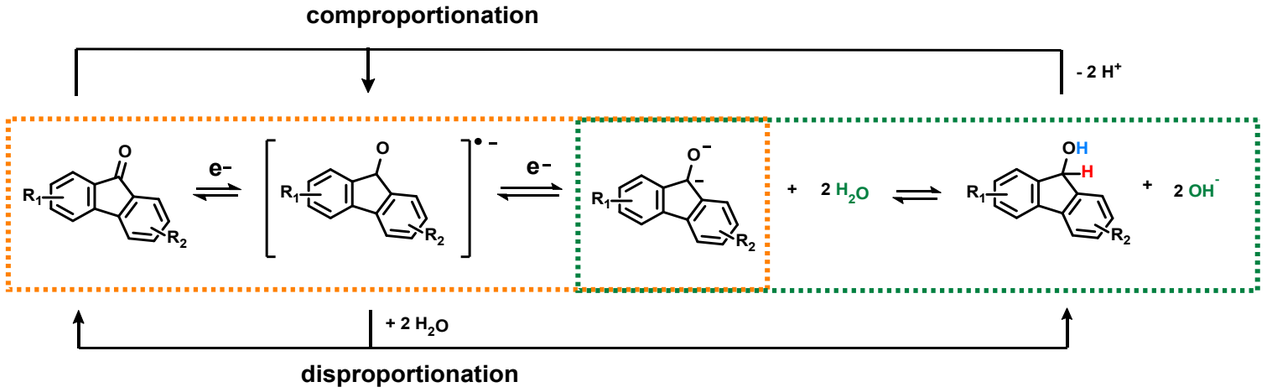

molecular engineer

- **activate** traditionally considered redox-inactive material
- coupled chemical reaction electrochemical process
- taking advantage of highly stable organic molecule core

electrolyte design

- higher battery power capability
- One-step closer to practical application
- **Ground-breaking approach for kinetic enhancement**

Acknowledgement

- US DOE-Office of Electricity under Dr. Imre Gyuk

- Wei Wang, Yuyan Shao, Aaron Hollas, Xin Zhang, Ying Chen, Vijayakumar Murugesan, Yangang Liang, Litao Yan, Qian Huang, David Reed, Vince Sprenkle, etc

- Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy.

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- The DFT calculations of relative free energies were performed at Yale University and were supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.