Fluorenone-based material development for redox flow batteries

2025 OE Peer Review

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Project Overview

- **Project Goal:**

  This task aims to develop anolyte materials for redox flow batteries,

  which are **low-cost**, **stable**, and **high-energy density**

- **Current Practice:**
  - Vanadium-based electrolyte: high cost, low energy density
  - Zn-based flow system (hybrid system): dendrite, limited areal capacity of Zn anode

- **Why PNNL:**
  - Extensive IPs on organic and redox-active materials (FL, viologens, TEMPOs, phenazines)
  - Materials Innovation through Robotics and AI Lab (MIRAL)
  - Grid Storage Launchpad: the most advanced energy storage facility

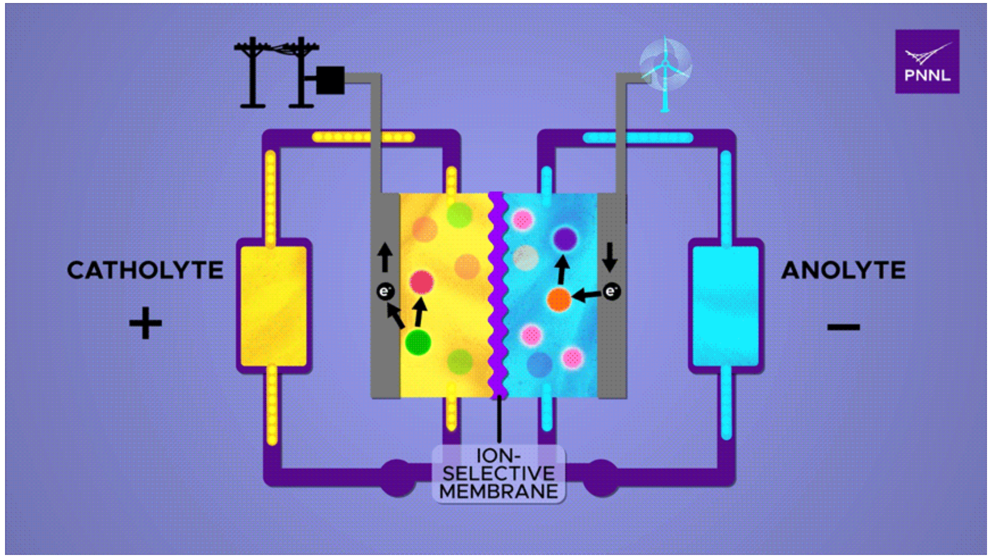
- **Innovation:**
  - **Enabling technology** that takes advantage of traditionally considered non-viable materials
  - Reversible hydrogenation and dehydrogenation **without a noble metal catalyst**

- **Impact:**
  - Lower energy storage cost for grid-scale energy storage
  - Support electricity grid resilience and stability

- **Alignment:**
  - This project is accelerating the development and testing of a new energy storage technology that is more cost-effective, safe, and durable, which is crucial to meeting the Administration's goal of providing reliable, affordable, secure, and resilient energy.

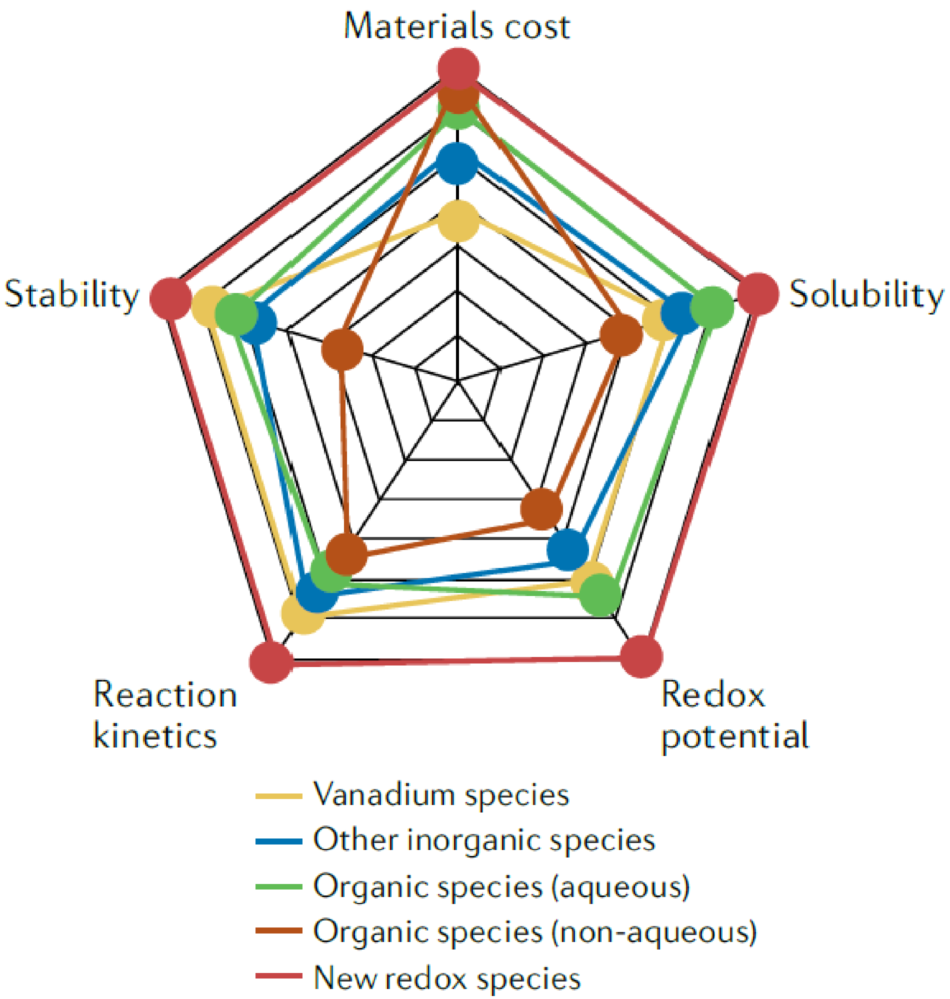
MIRAL

Redox flow batteries: electrolyte development



- energy carried in liquid electrolyte format and stored in an external tank
- decoupled power generation and energy storage

Parameters of redox-active materials



Fluorenone-based electrolyte research at PNNL

2021	• Science: coupled chemical electrochemical mechanism	Enabling
2022	• Nat. Rev. Chem. : ASO material development perspectives, mechanism insights, and characterization techniques	Strategy
2023	• Joule: “Sugar” enhanced battery kinetics via PCET mechanism regulation • Cell Rep. Phys. Sci. : robotics-assisted material energy density optimization	Acceleration
2024	• JES: FL redox activity modulation via π-π stacking for capacity control • JES: miniaturize the redox flow battery for accelerated materials discovery	Multi-electron
2025	• Manuscript in prep : mediating strategy for battery voltage enhancement **[poster]** • Manuscript in prep : solvation structure modulation for battery kinetics control	Power

Science, **2021**, *372, 836-840;* Nat. Rev. Chem. **2022,** 6, 524–543; Joule, **2023**, 7, 1609-1622; *Cell Rep. Phys. Sci.* **2023**, *4(10)*, 101633; J. Electrochem. Soc. **2024**, 171 (9), 090501; J. Electrochem. Soc. **2024**, 171 (12), 120532.

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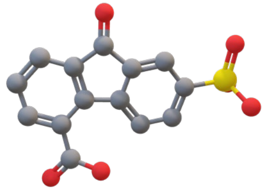
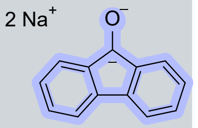
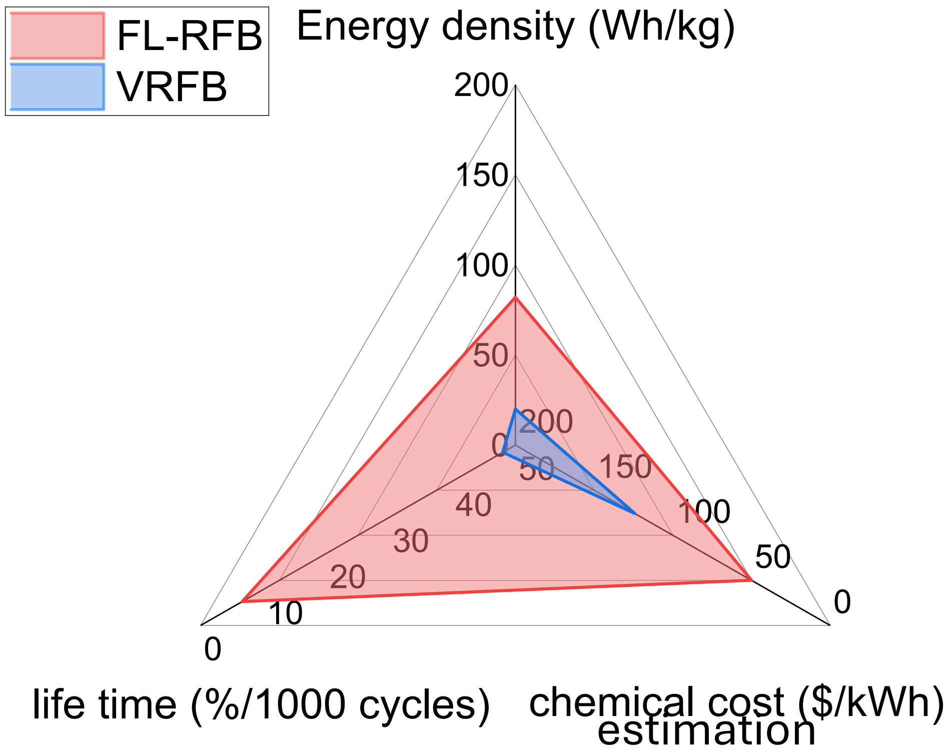
Fluorenone electrolytes



material cost	stability	energy density
• diphenic acid **$0.1/kg*** • EDTA ligand **$0.1/kg*** • vanadium sulfate hydrate **$6.6/kg***	• Extreme thermal stability** • Longest demonstrated ASO flow battery in lab	• Enabled by high solubility • Up to 4 M electron concentration • ~107Ah/L (record)





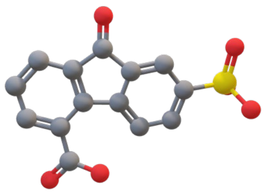
* Chemical cost from CHEMI.com for wholesale suppliers

** 1999 report from the Institute for Fundamental Research of Organic Chemistry (IFOC) Japan

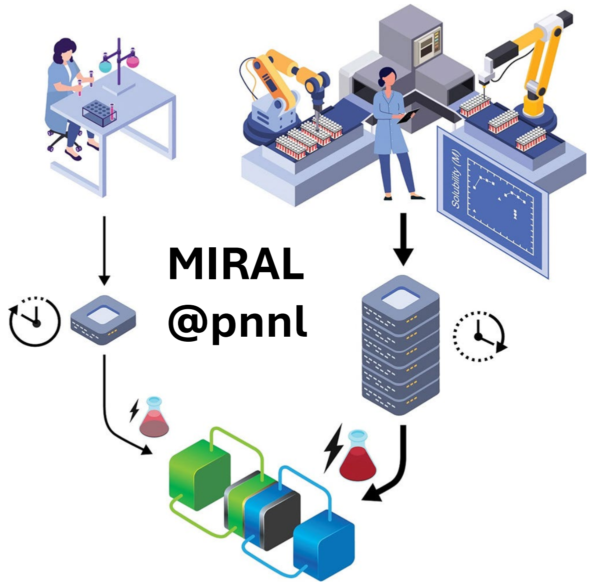
Journal of Power Sources **2021**, *499*, 229965

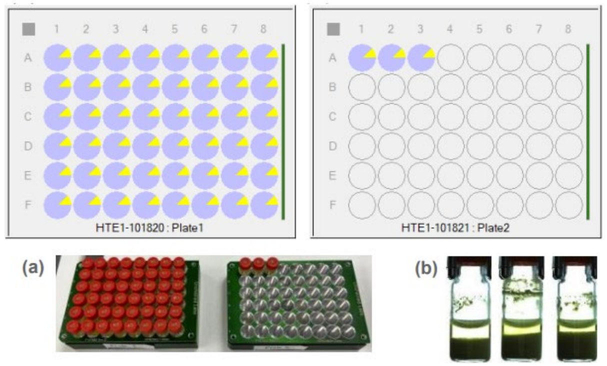
Transl. Mater. Res. **2018**, *5*, 034001

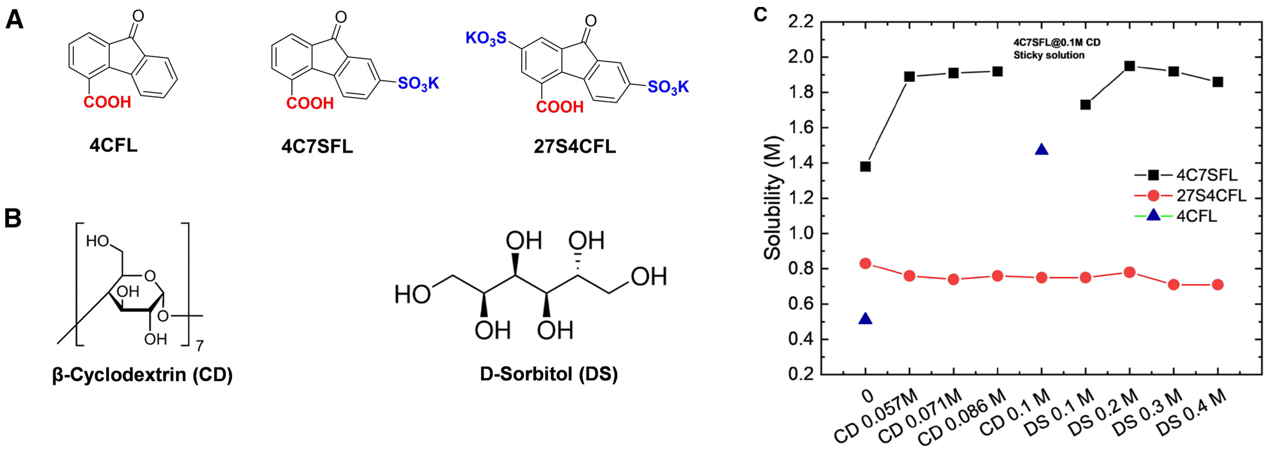
Accelerating material research through MIRAL

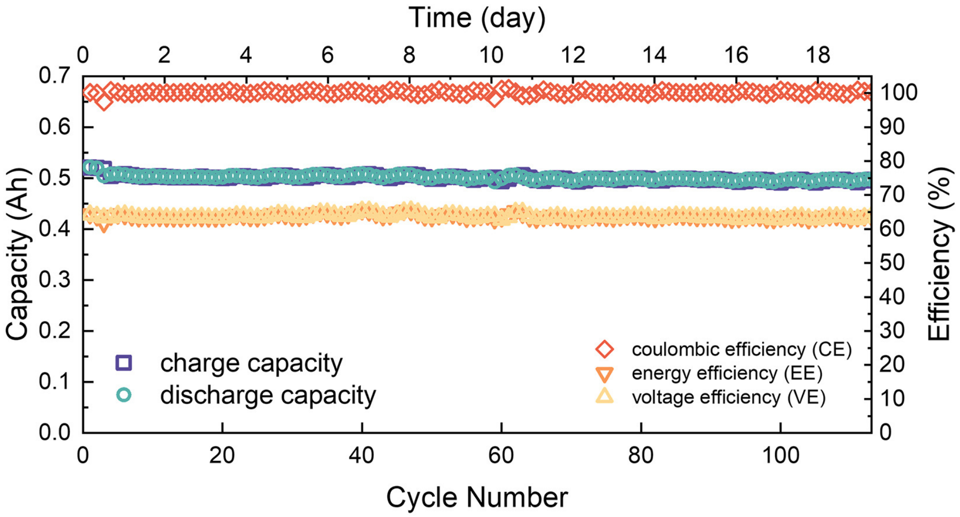


faster data collection



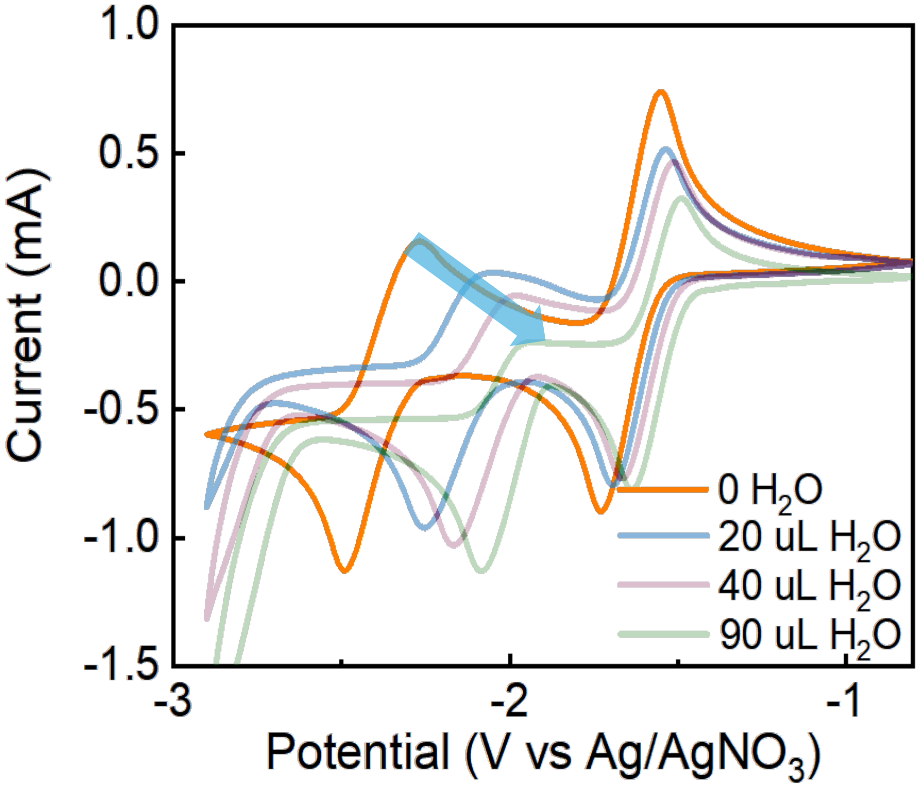




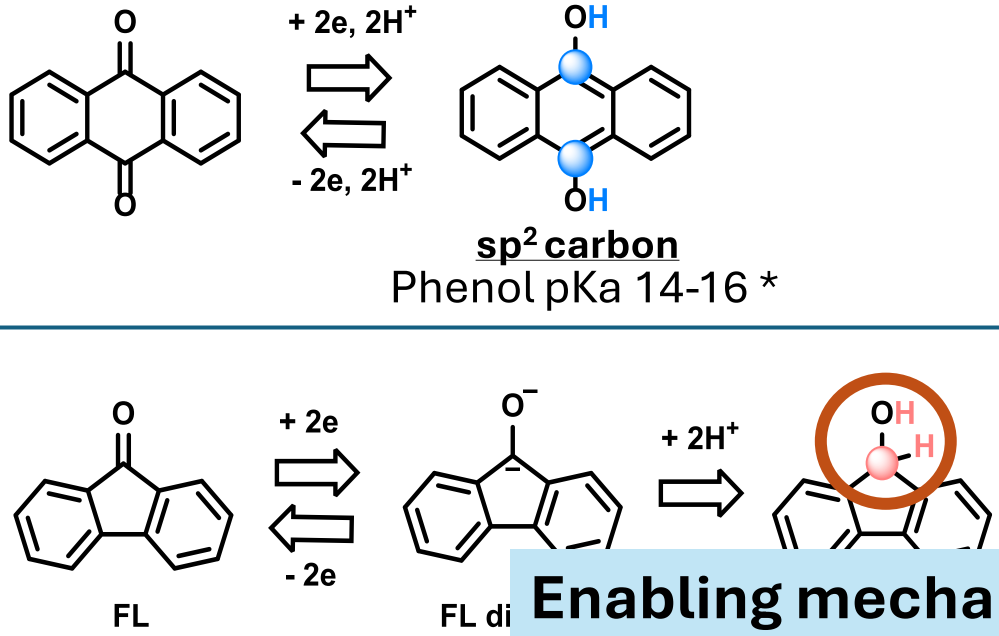


Cell Rep. Phys. Sci. **2023**, *4(10)*, 101633

Difference between fluorenone (FL) vs anthraquinone (AQ)



FL in ACN, NaTFSI supporting electrolyte



Phenol pKa 14-16 *

1e/ketone

Only O-H

2e/ketone

Both the C-H and O-H

are

ed

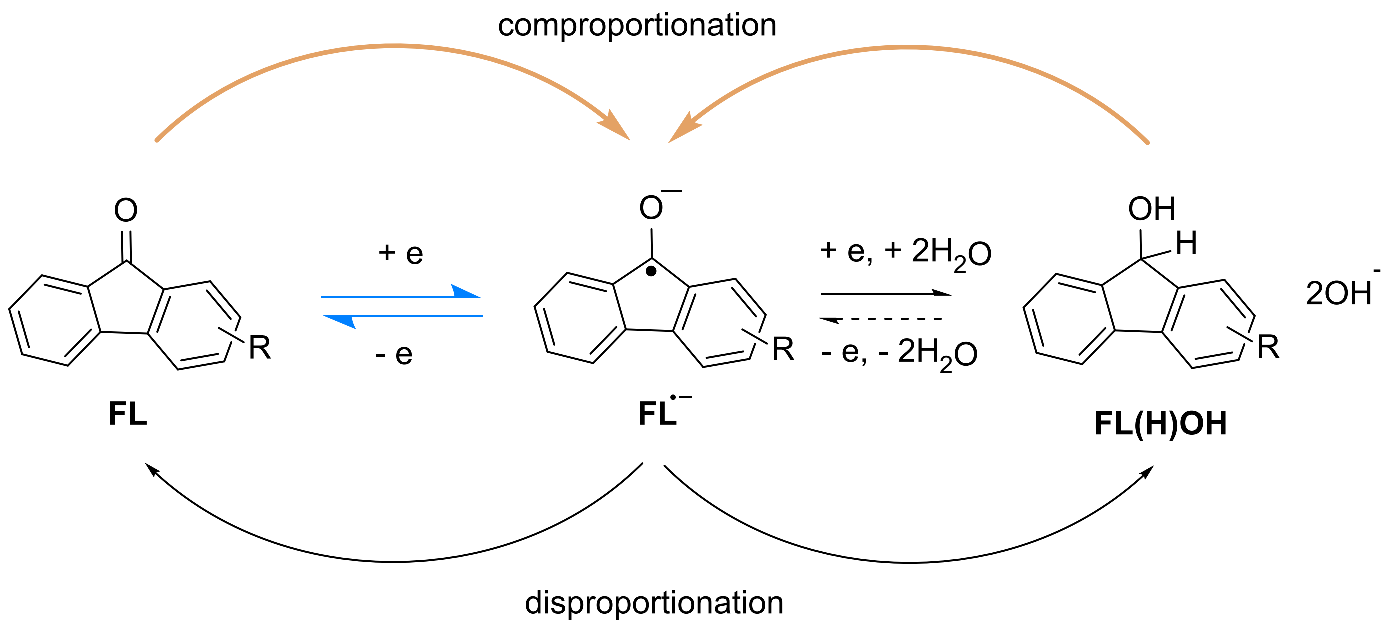
Enabling mechanism for reversible C-H bond formation and breakage

Science **2021**, *372* (6544), 836–840.

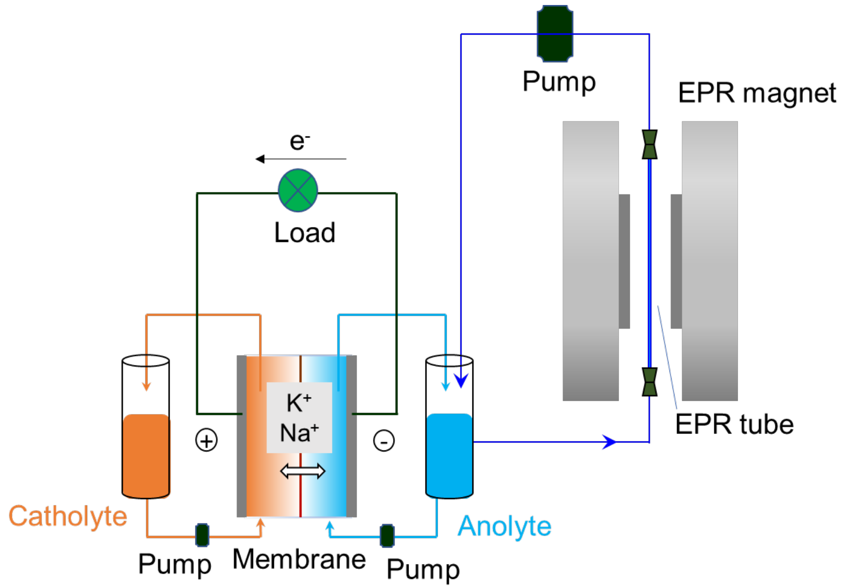
* Bodwell pKa Table, DMSO solvent

Development of in situ Electron Paramagnetic Resonance (EPR)

coupled chemical-electrochemical process

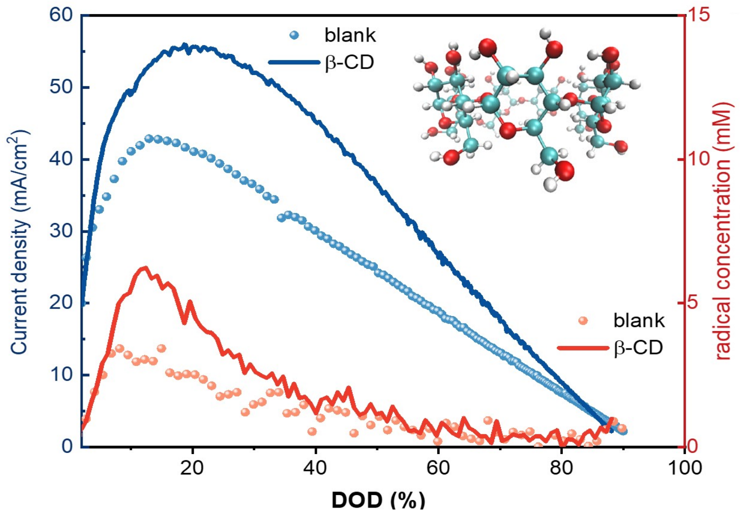


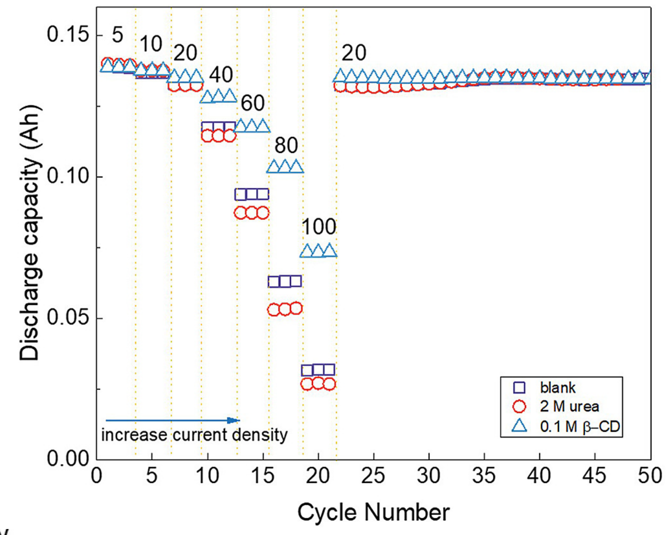
Science **2021**, *372* (6544), 836–840.



In-situ electron paramagnetic resonance (EPR)

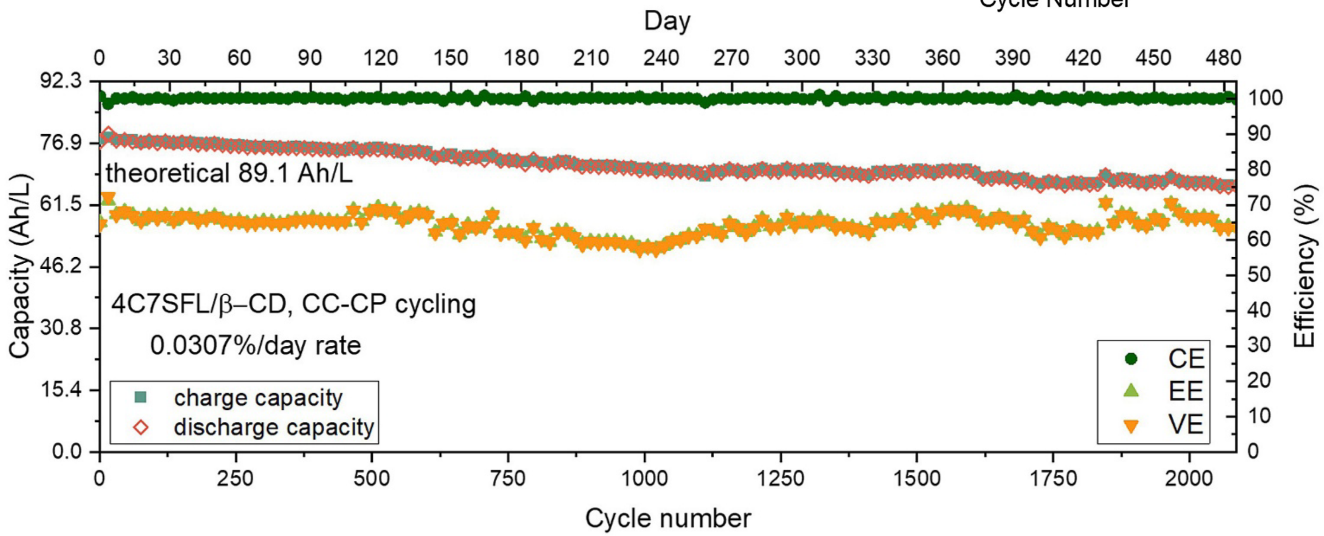
Increase battery power density via homogeneous catalysis strategy





Using pseudo reference under controlled potential

- Higher current density
- Higher intermediate (radical) concentration
- Faster kinetics



Post-NMR confirmed the capacity decay not from material

Joule, **2023**, 7, 1609-1622; *Cell Rep. Phys. Sci.* **2023**, *4(10)*, 101633

New strategy for battery power density: Solvation structure modulation/EDL modulation

Electrical Double Layer (EDL)

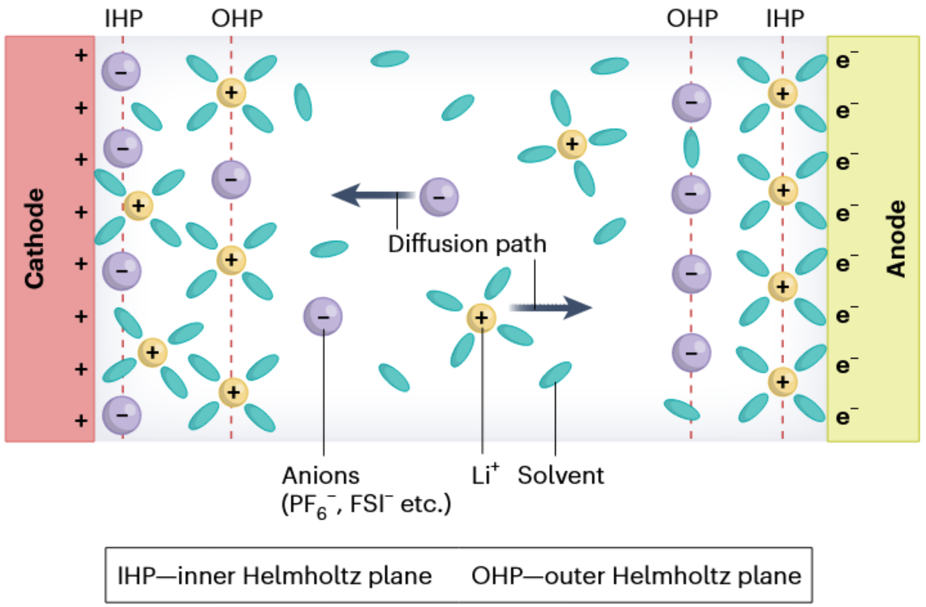


Fig. 3 | Electrical double layers formed on positive electrode (cathode in battery) and negative electrode sides (anode in battery) during charge process. The constituents in the IHL are related to the later formed passivation layers on positive and negative electrodes, which can be used to help develop better electrolytes or additives to tune CEI or SEI properties.

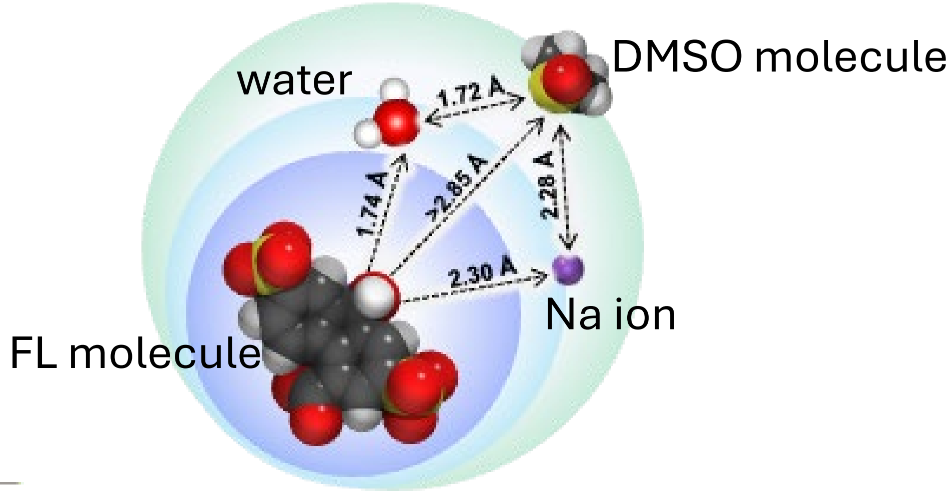
Jie Xiao etc., *Nature Energy* **2024** *9*, 1463–1473

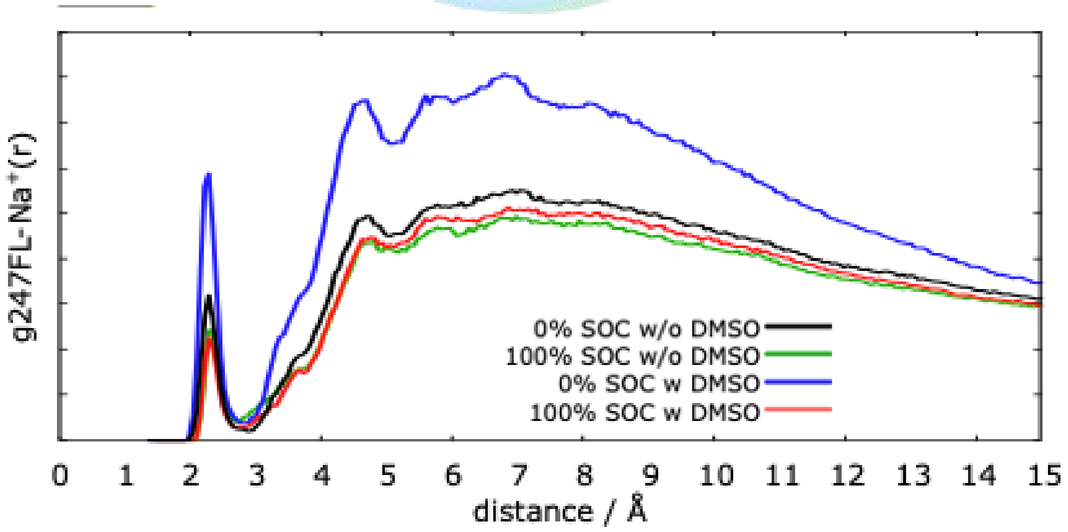
Long-ignored effect in ASO RFB

- Highly charged redox-active molecules repulsion to electrode surface
- Negative impact on battery power density

- Solvation structure modulation to alter the repulsion
- Increase molecules accessibility to electrode surface

Solvation structure modulation strategy

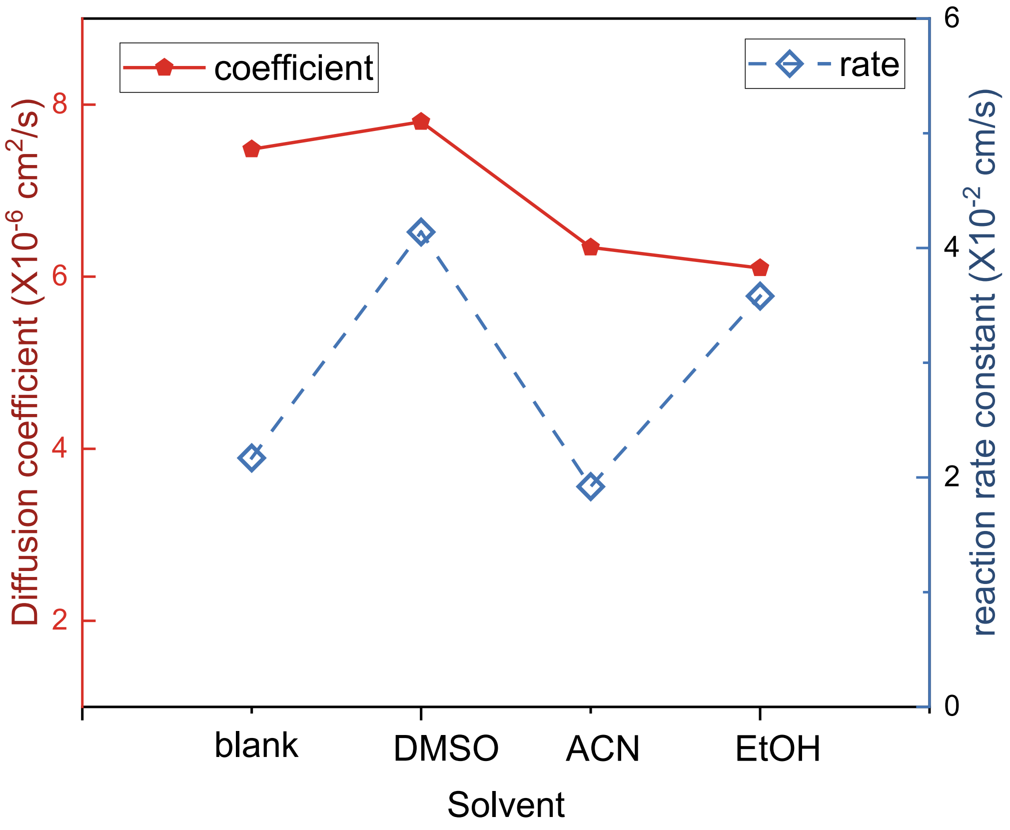


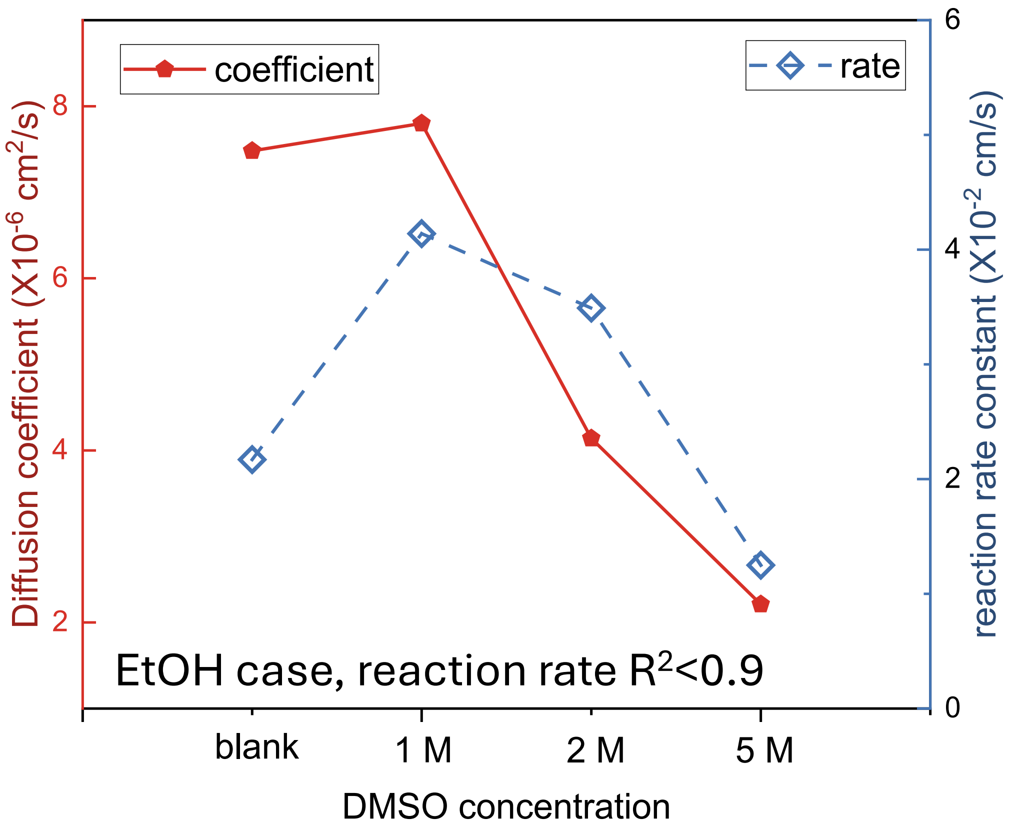


MD simulation of the solvation shell of ASO

- DMSO as a co-solvent
- Push Na^{+} ion closer to negatively charged species
- Less repulsion to the electrode surface EDL
- Beneficial to battery power density

Electrochemical performance of the molecule





With DMSO co-solvent

- Faster **charge transfer rate constant**
- On par **diffusion coefficient** with pure aq.

Randles-Sevcik equations

Nicolson's method

Chem. Commun., **2019**, *55*, 12247;
ACS Appl. Energy Mater. **2021**, *4*, 8765−8773

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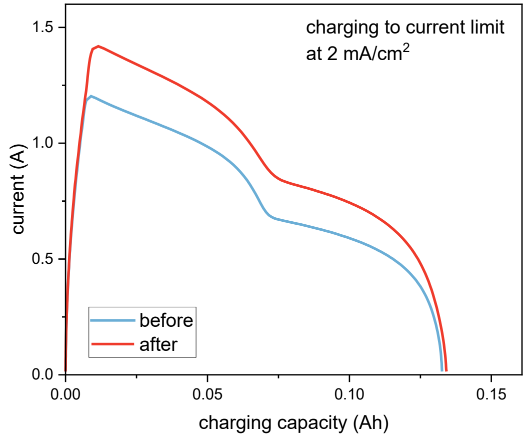
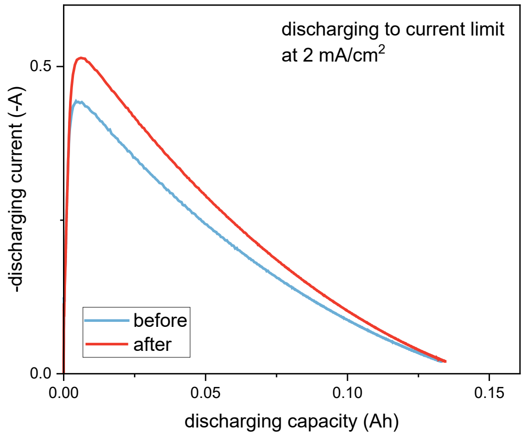
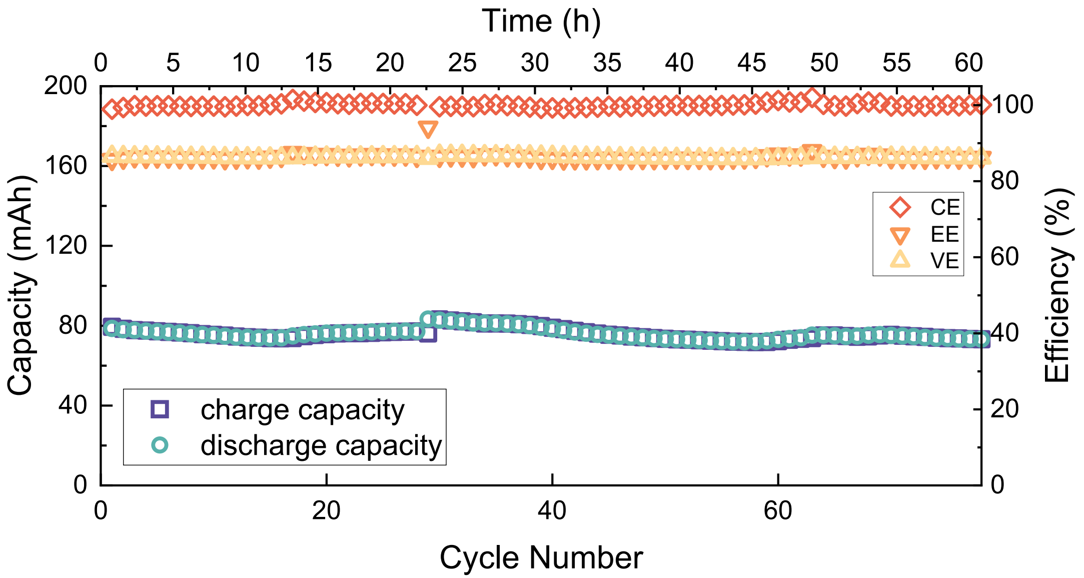
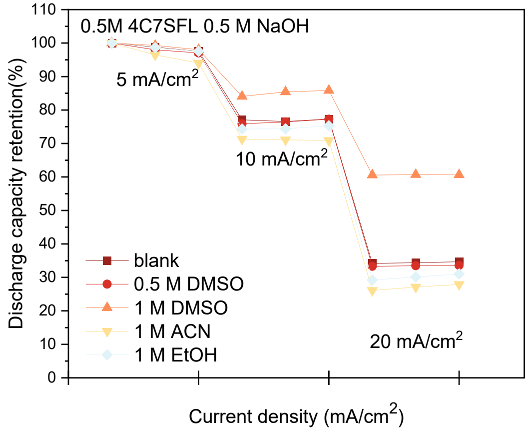
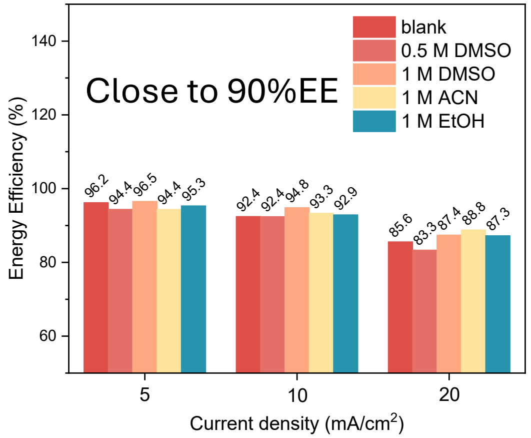
Solvation structure modulation strategy











- ➢ Effective on both charging and discharging on FL-electrolyte
- ➢ Stable operation with co-solvent on both anolyte and catholyte side

Acknowledgment

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