Fluorenone-based electrolyte for flow batteries

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Project Overview

- Goal:
  - This task aims to develop high-performance anolyte materials for redox flow batteries [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)
  - ✓ Grid Storage Launchpad: the most advanced energy storage facility
- Innovation:
  - ✓ Enabling technology that takes advantage of traditionally considered non-viable materials
  - ✓ Byproducts from the coal industry, domestic manufacturing with low cost and no critical materials
- Duration: FY21-FY26, from **Chemistry Discovery → Electrolyte Engineering**
- Impact:
  - ✓ Low Levelized cost of storage using domestic manufacturing of organic materials
  - ✓ Robust battery technology supporting electricity grid resilience and stability
- Vertical/Investment Area:
  - ✓ Materials and Systems Innovation
- Alignment/Supports Strategic Pathway:
  - ✓ 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.

2021
- Science: coupled chemical electrochemical mechanism
- **[Discovery of a brand-new working mechanism for flow battery]**

2022
- Nat. Rev. Chem. : ASO material development perspectives, mechanism insights, and characterization techniques

2023
- Joule: "Sugar" enhanced battery kinetics via PCET mechanism regulation
- Cell Rep. Phys. Sci. : robotics-assisted material energy density optimization

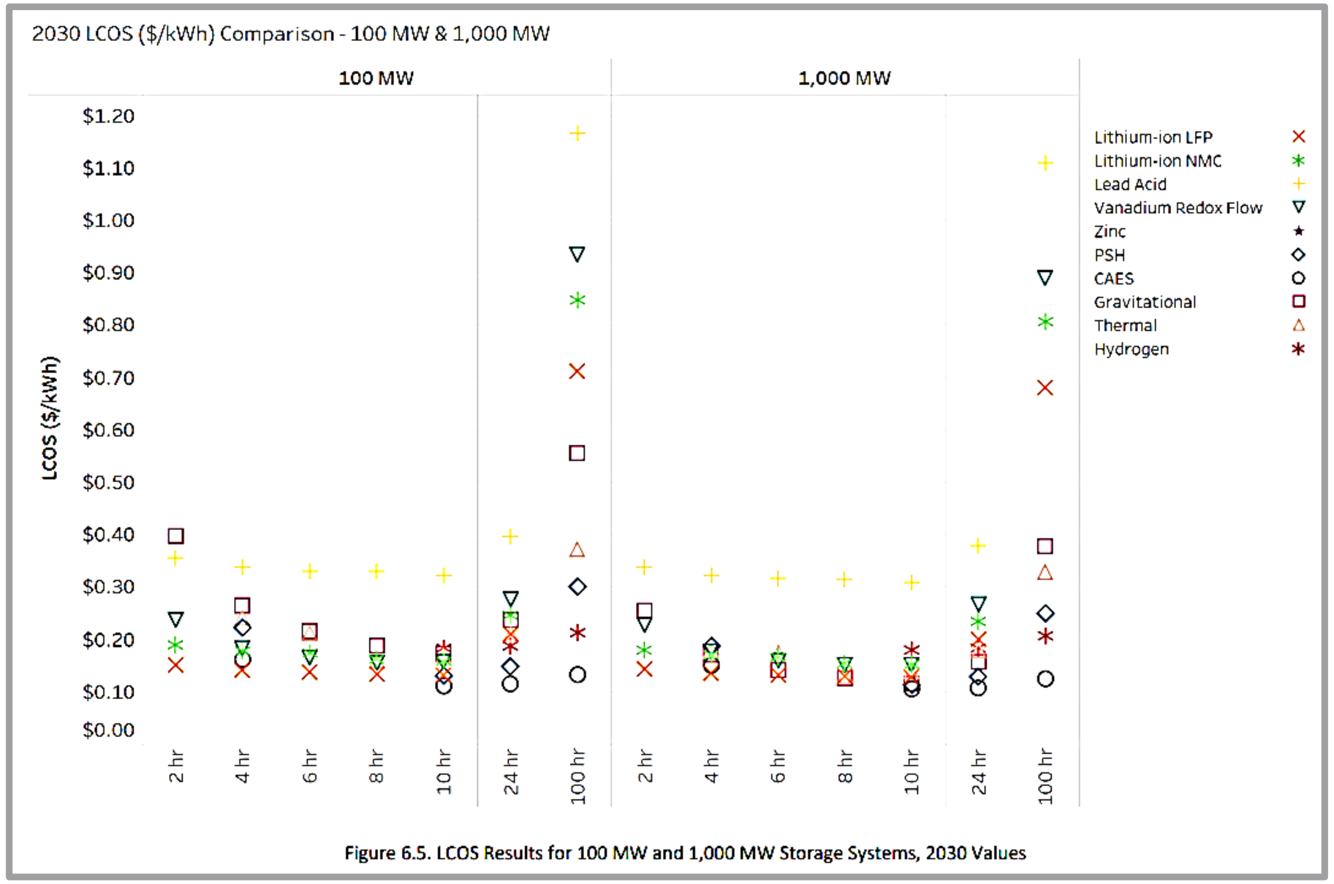
2024
- JES: FL redox activity modulation via π-π stacking for capacity control; JES: miniaturize the redox flow battery
- **[Accelerated materials innovation]**

2025
- Solvation structure modulation for battery kinetics control
- Electrolyte engineering

2026
- Mediating strategy for battery voltage enhancement [under review]
- Proton regulation for enhanced performance [under review]

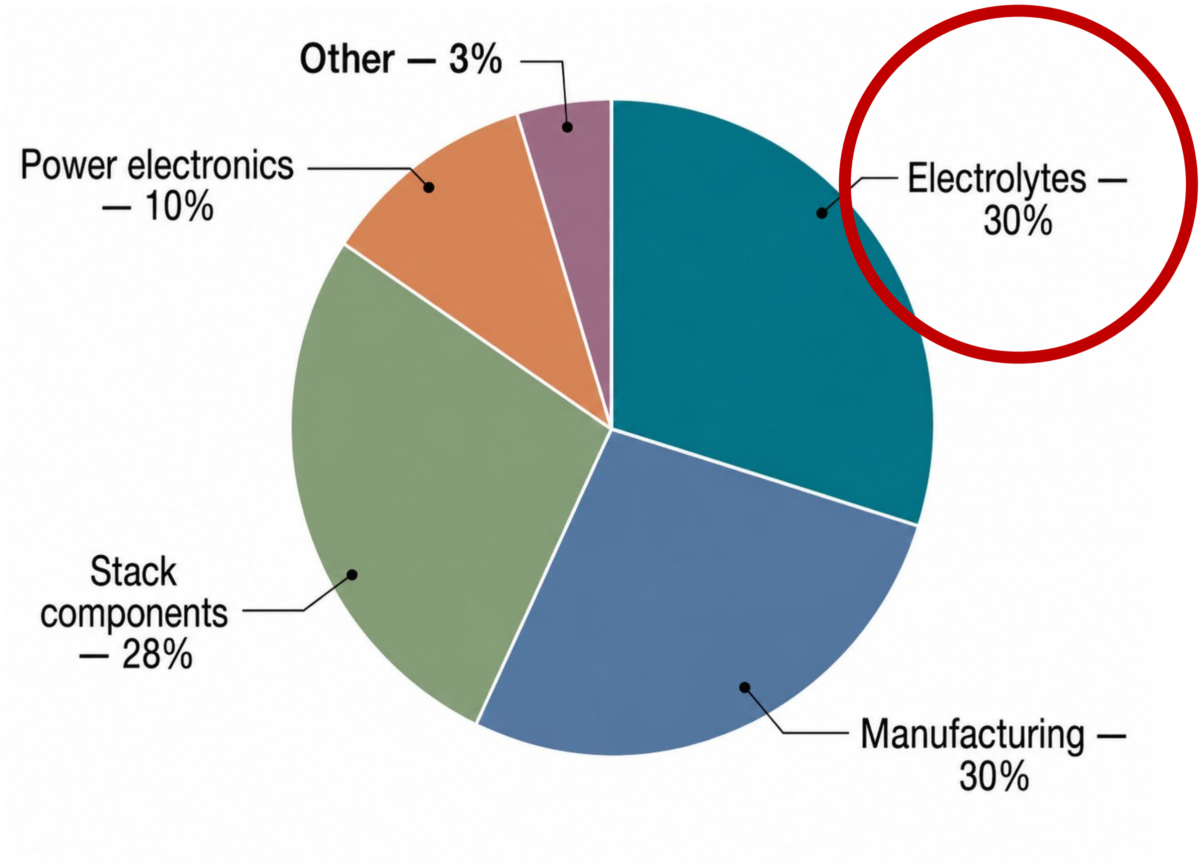
Science, **2021**, *372, 836-840;* Nat. Rev. Chem. **2022,** 6, 524–543; Joule, **2023**, 7, 1609-1622; *Cell Rep. Phys. Sci.* **2023**, *4(10)*, 101633; J. Electrochem. Soc. **2024**, 171 (9), 090501; J. Electrochem. Soc. **2024**, 171 (12), 120532.

Redox flow battery cost reduction challenge



2022 Grid Energy Storage Technology Cost and Performance Assessment Vilayanur Viswanathan, Kendall Mongird, Ryan Franks, Xiaolin Li, Vincent Sprenkle*, Pacific Northwest National Laboratory.

https://www.energy.gov/cmei/2022-grid-energy-storage-technology-cost-and-performance-assessment

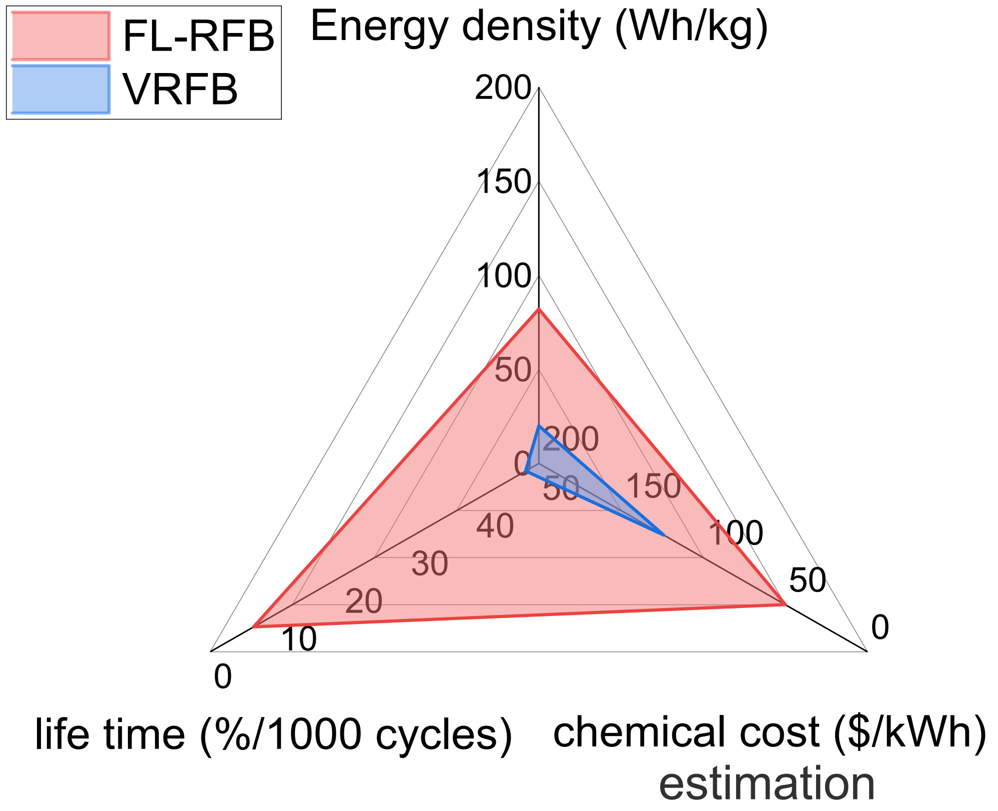


The most promising cost reduction opportunities

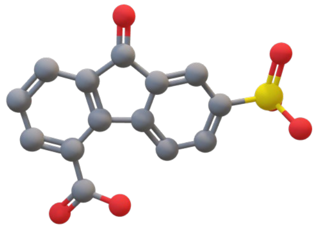
(Flight Paths listening session, January 12, 2023)

https://www.energy.gov/oe/storage-innovations-2030

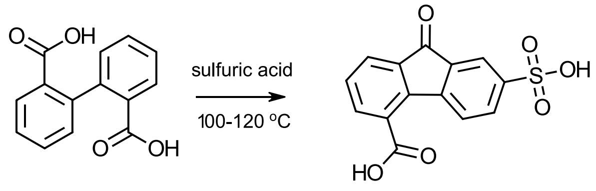
Aqueous organic electrolytes fluorenone case study



Journal of Power Sources **2021**, *499*, 229965
Transl. Mater. Res. **2018**, *5*, 034001



- One-step synthesis
- Water processing



biphenic acid

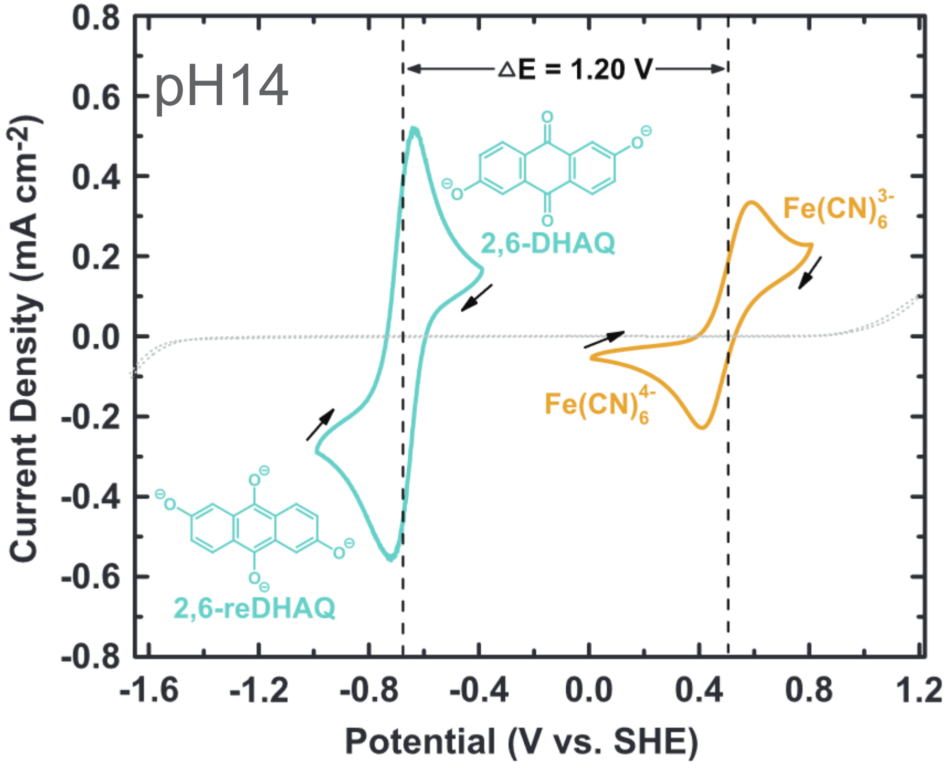
4C7SFL

Material Cost	Stability	Energy Density
• biphenic 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)

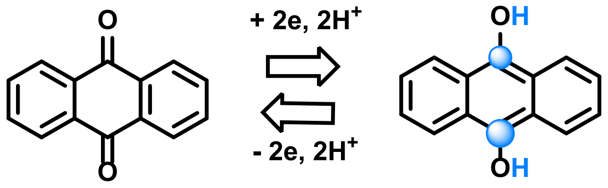
* Chemical cost from CHEMI.com for wholesale suppliers
** 1999 report from the Institute for Fundamental Research of Organic Chemistry (IFOC) Japan

Fluorenone is completely **different** from anthraquinone

1e/ketone
Only O-H

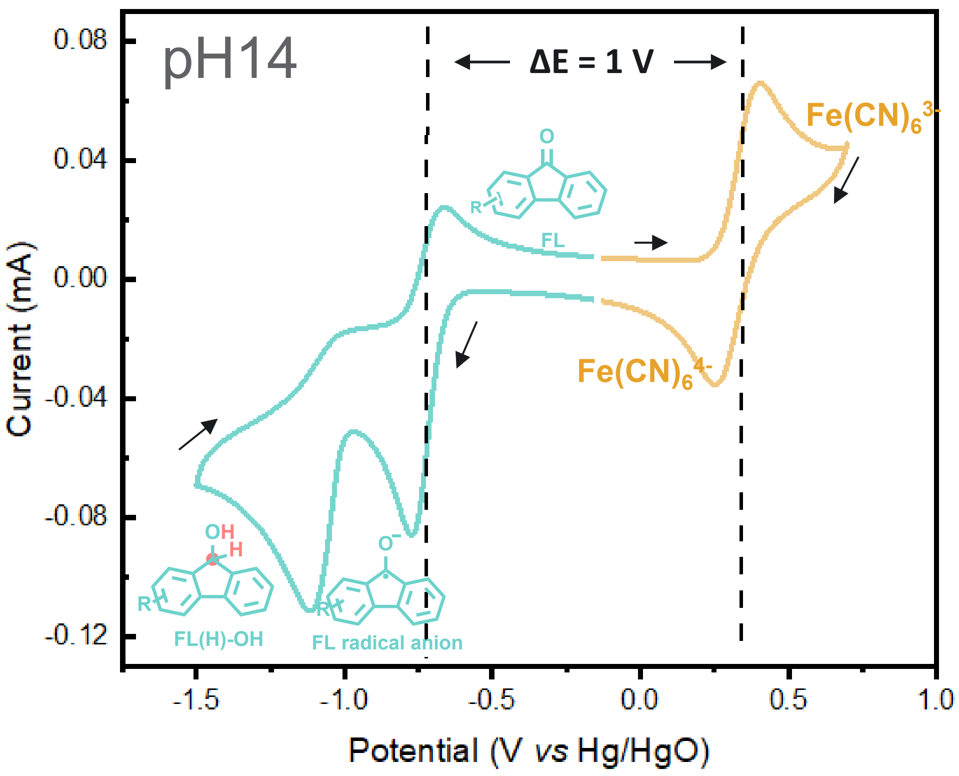


Science **2015**, *349 (6255)*, 1529. **MIT**

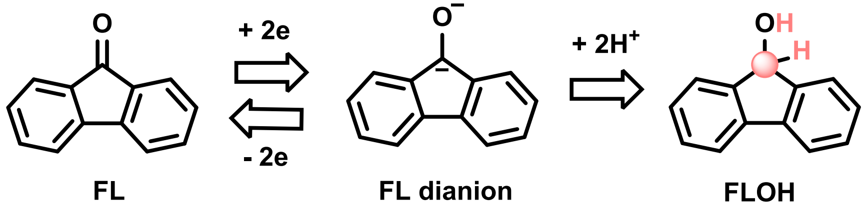


sp^2 carbon

2e/ketone
Both the C-H and O-H bonds are involved



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

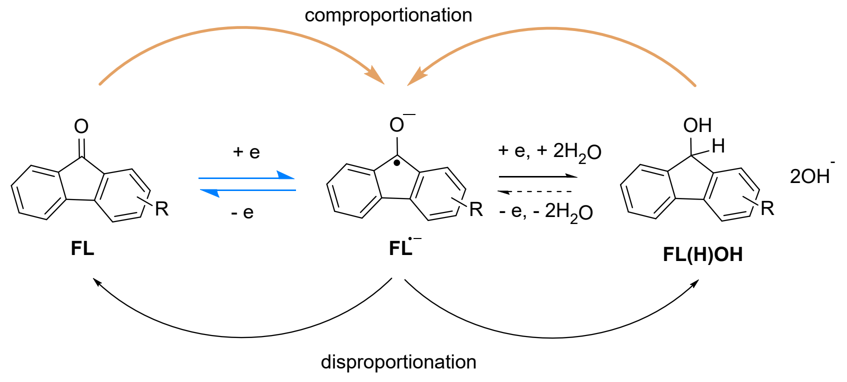


sp^3 carbon

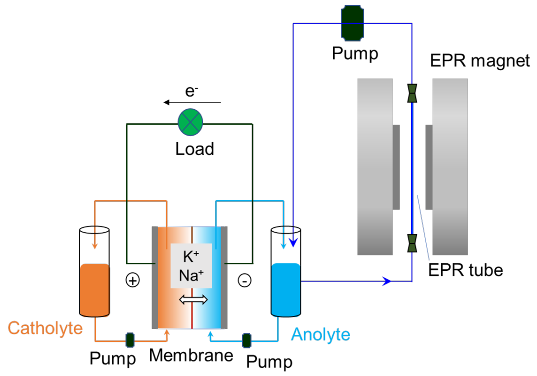
Enabling technology

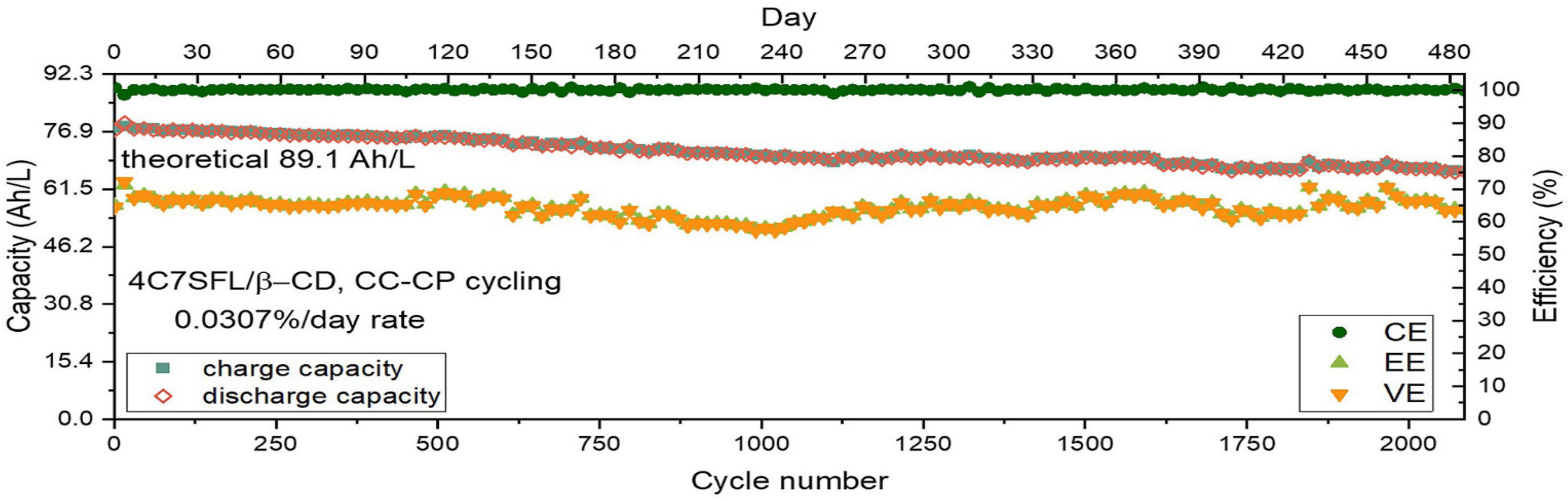
Take advantage of traditionally considered non-viable materials

Coupled chemical electrochemical mechanism



In-situ electron paramagnetic resonance (EPR)

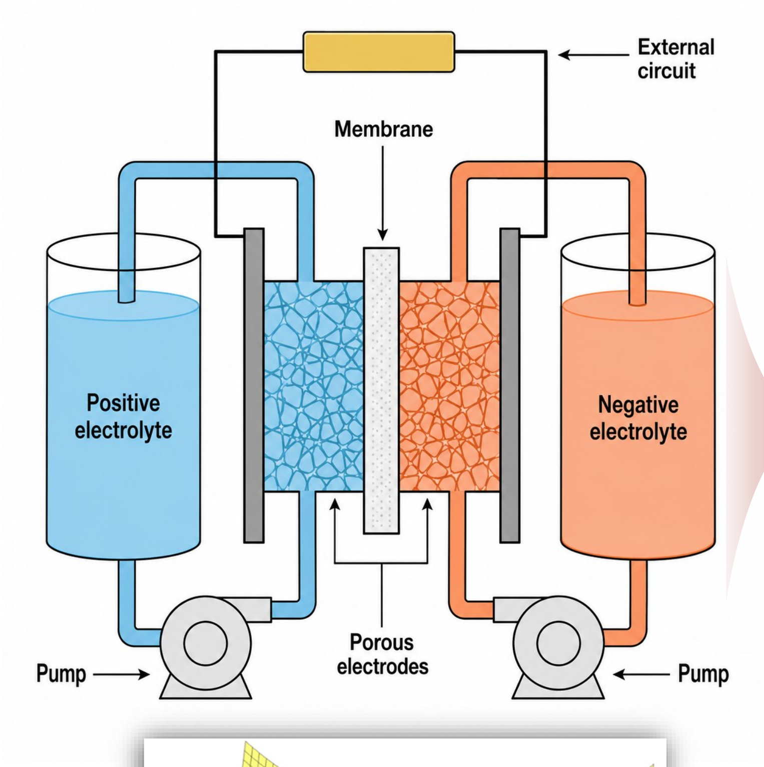


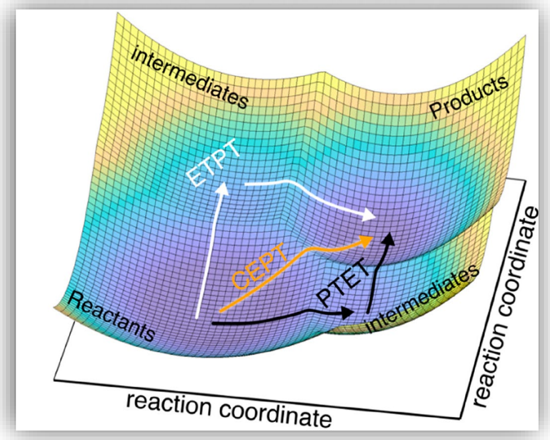


Postmortem NMR and MS (electrolyte exposure to air)
No material degradation by the detection error limit

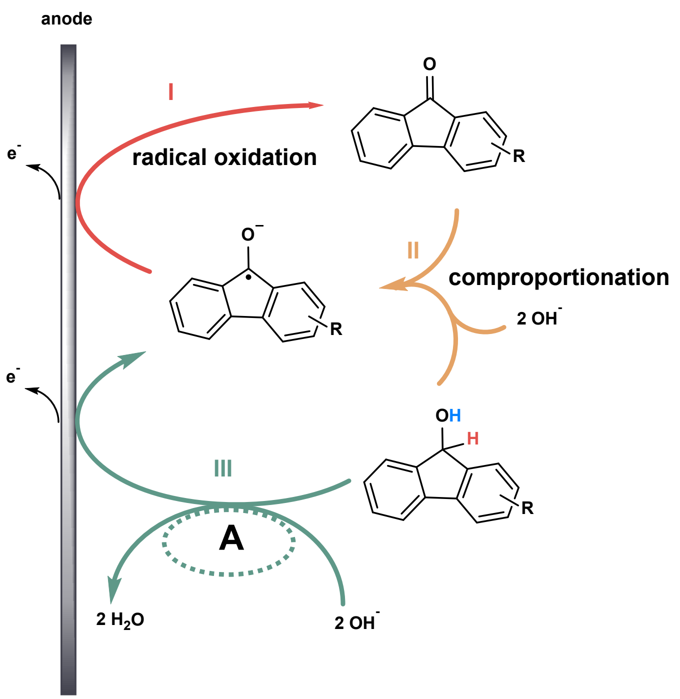
Science **2021**, *372* (6544), 836–840. *Joule*, **2023**, *7*, 1609-1622;

Mechanism informed electrolyte engineering



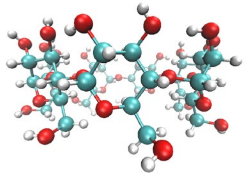


Reaction pathway tuning
Kinetic enhancement

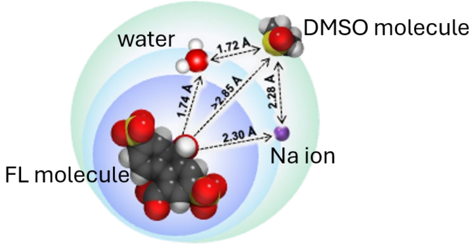


Strategies

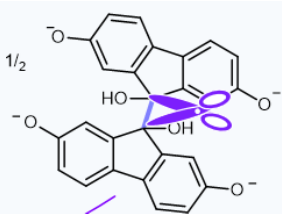
- Redox-inert additives



- Solvation engineering



- Mixed functionalization



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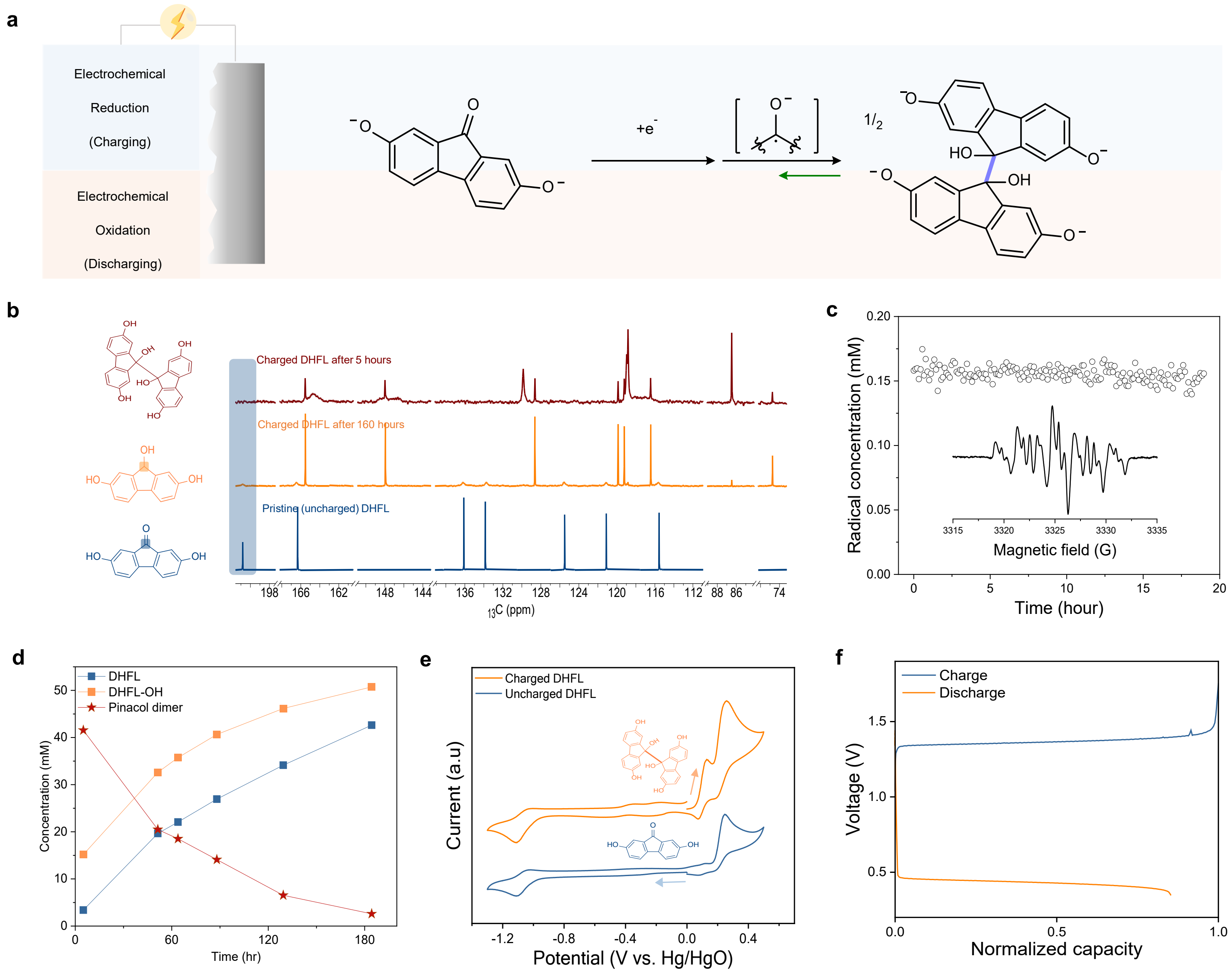
Science, **2021**, *372, 836-840;* Nat. Rev. Chem. **2022,** 6, 524–543; Joule, **2023**, 7, 1609-1622; *Cell Rep. Phys. Sci.* **2023**, *4(10)*, 101633; J. Electrochem. Soc. **2024**, 171 (9), 090501; J. Electrochem. Soc. **2024**, 171 (12), 120532.

Functionalization effect on FL chemistry



Chemistry origin

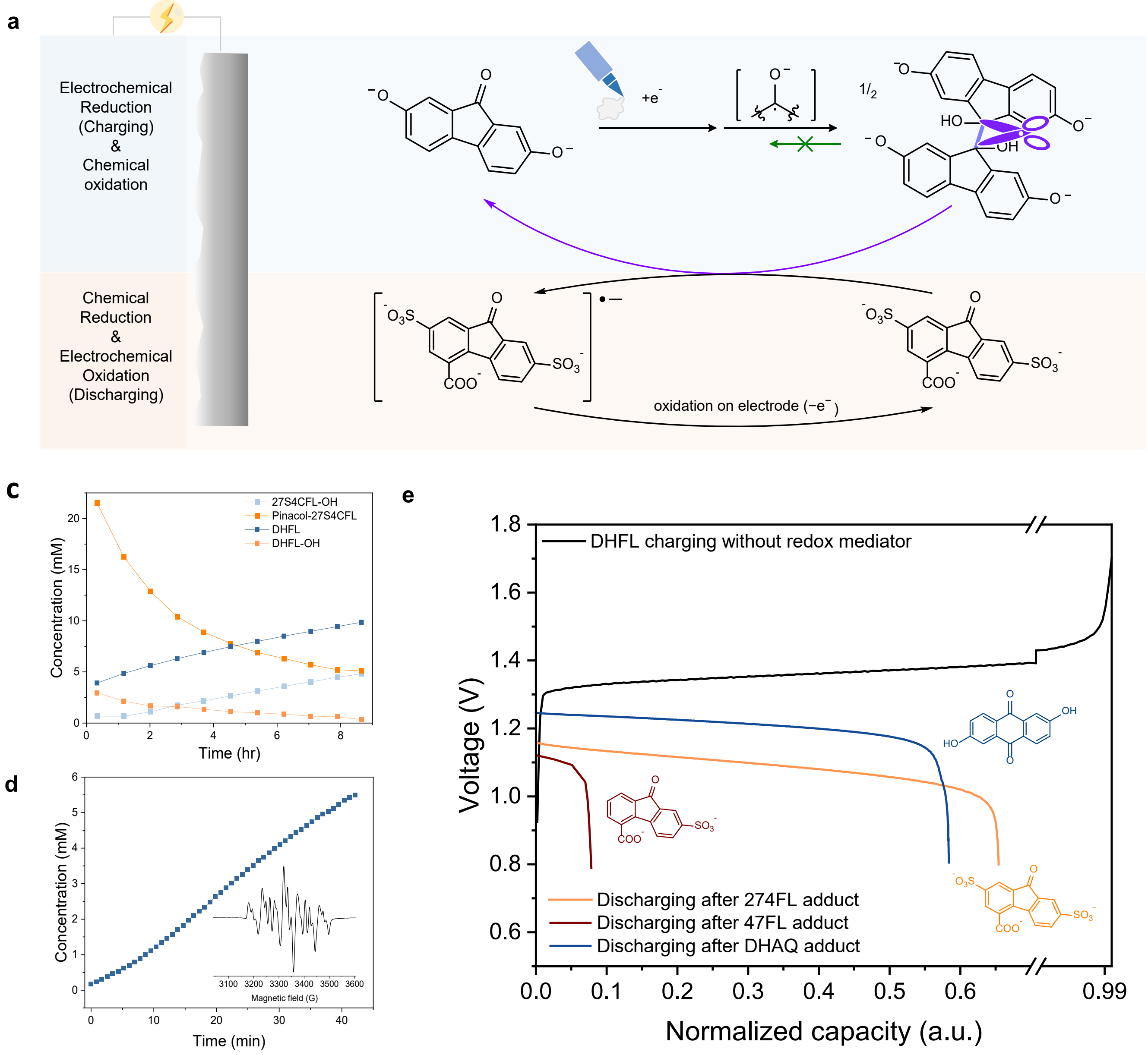
- Electron-donating groups lead to a dimerization reaction
- Shut off the redox process
- Leads to one-electron transfer per molecule

Battery outcome

- Half the capacity
- 0.5 V battery discharge voltage
- energy efficiency (EE) of ~27 %

Manuscript under review

Voltage recovery strategy by mixed electrolytes



Chemistry origin

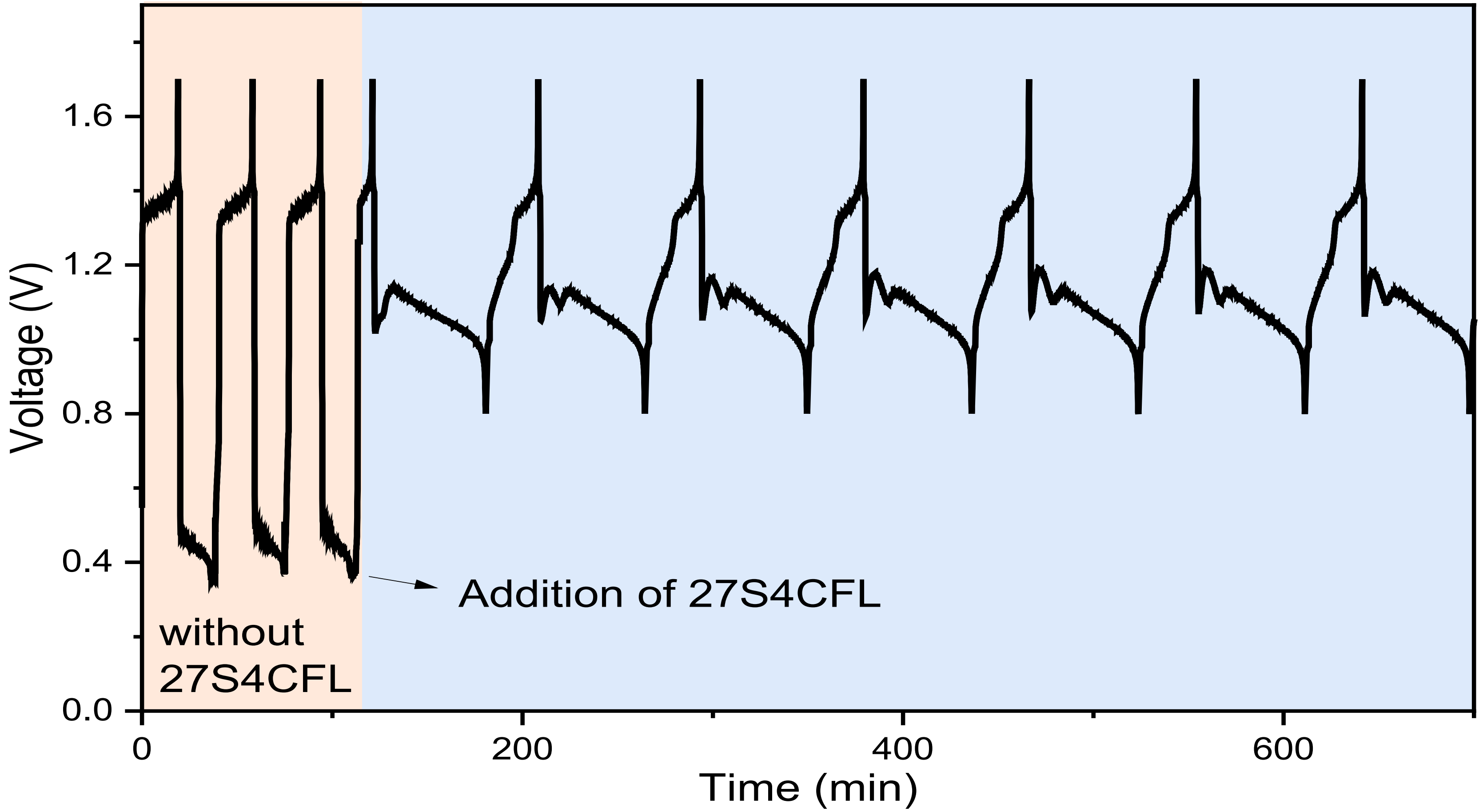
- Mixed electrolytes shuttle electrons
- Overcome the electrochemical kinetic barrier of C-C bond cleavage

Battery outcome

- Increased capacity from both contributors
- ~ 1 V battery discharge voltage
- energy efficiency (EE) of ~80 %

Manuscript under review

Very effective battery voltage modulation



- Addition of EWG functionalized FL into EDG functionalized FL
- Voltage increase from ~0.5 V to ~1 V
- EE increased from ~30% to ~ 80%
- Strategy broadly applicable to other mediators

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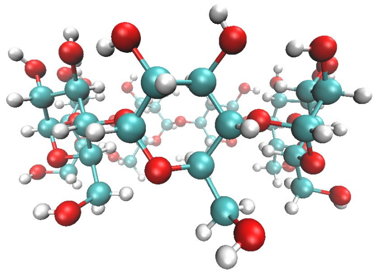
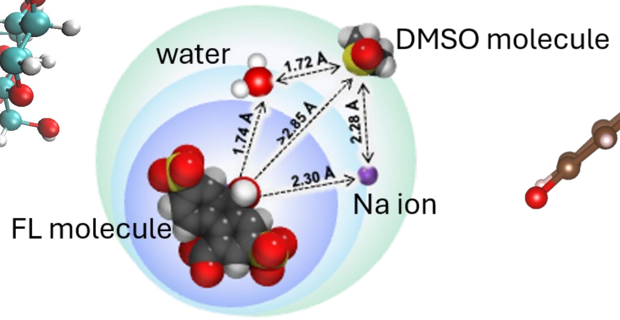
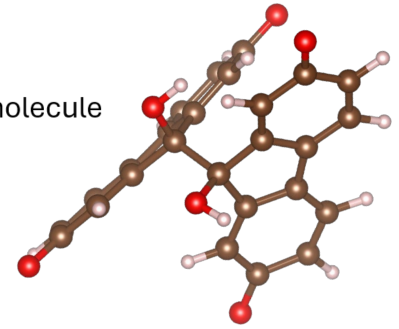
Summary and Future Direction
Data-driven innovation

Materials innovation strategies

- ✓ Homogeneous catalysis
- ✓ Solvation engineering
- ✓ Molecular engineering







Future direction

- ❑ Design principles establishment
  - o Complete picture of knowledge
  - o Electrolytes library expansion
- ❑ Technology use cases
  - o Working temperature window
  - o System operation
- ❑ Knowledge application in broader electrolytes/energy storage systems

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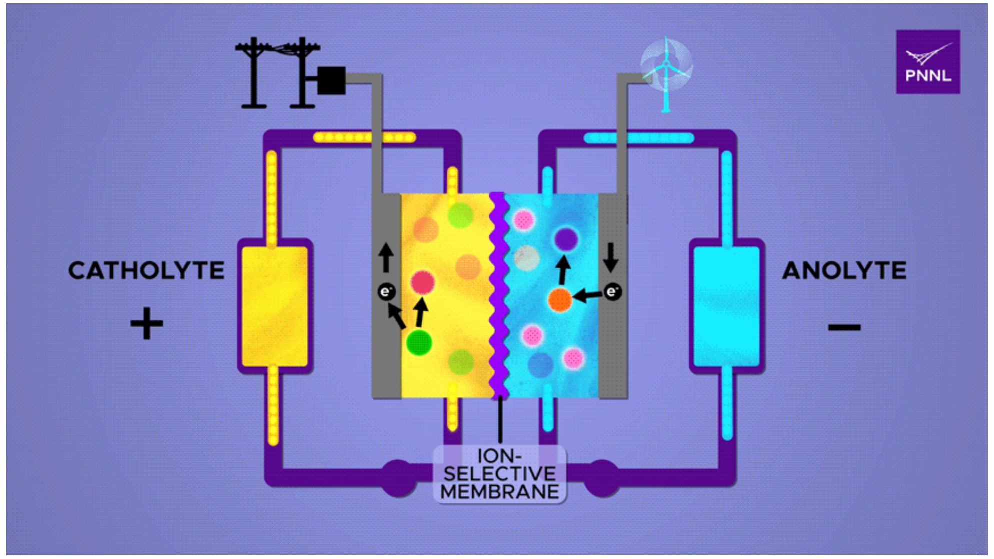
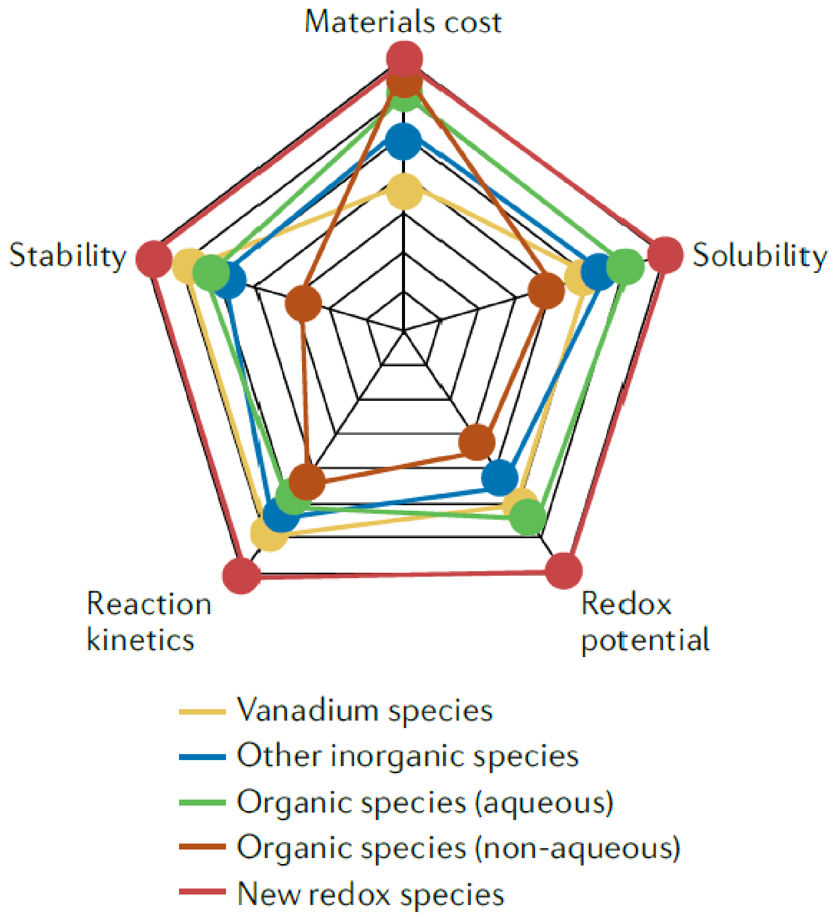
Project Impact

- ✓ Enabling low-cost, chemically robust electrolytes for next-generation flow batteries
- ✓ Establishing transferable design principles for flow battery electrolyte engineering
- ✓ Advancing fundamental understanding of organic redox materials broadly applicable to many energy storage systems
- ✓ Directly supporting DOE OE's mission for the energy storage supply chain toward earth-abundant, low-cost resources



Parameters of redox-active materials



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