Voltage Modulation Strategy of Deactivated Fluorenone Anolyte via Electron Abstraction by Redox Mediator

Jong-Hwa Shon, Ruozhu Feng, Ying Chen, Peter Rice, Wei Wang
Pacific Northwest National Laboratory, Richland, WA

Alignment

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

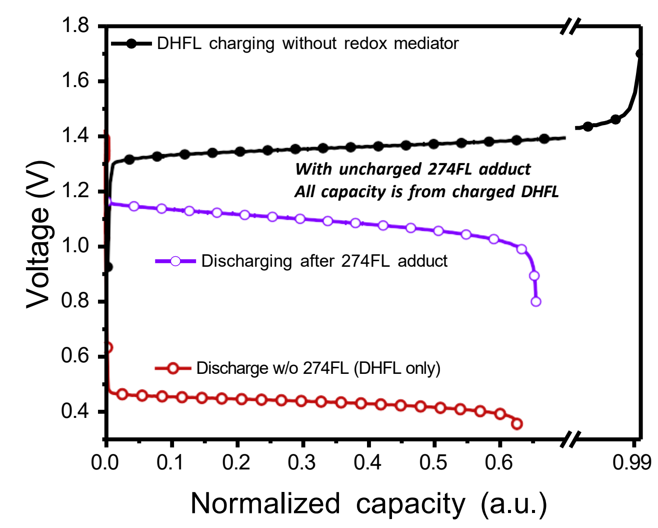
Objective and Approach

Objective: Develop low-cost, stable ASO electrolytes for long-duration energy storage with enhanced cell voltage

Approach: Utilize a redox mediator via an electron abstraction mechanism to boost battery discharge voltage

Introduction

Aqueous Soluble Organic (ASO) materials in aqueous redox flow batteries offer a promising route to significantly reduce material costs. For long-duration energy storage applications, developing electrolytes that are low-cost, stable, and possess high energy density is essential. Although side reactions are often unavoidable, they are a major contributor to chemical instability and reduced battery life. In our work, without employing precious metal catalysts or external energy input, we have strategically utilized a side product inherent to fluorenone chemistry. This approach not only mitigates capacity loss but also provides the additional benefit of voltage modulation.

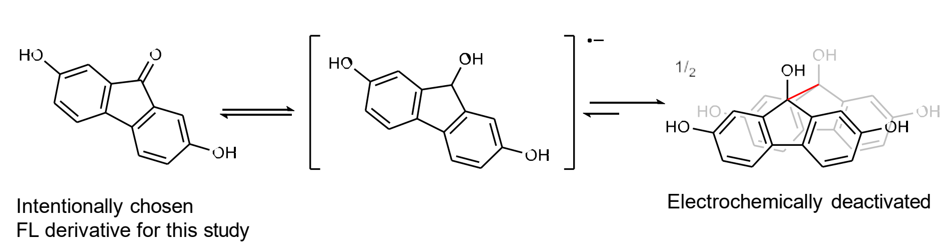


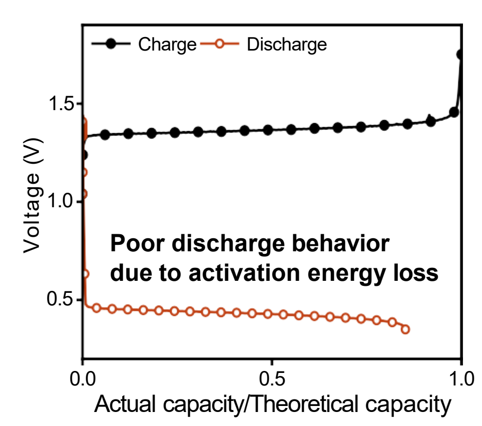
- Charged DHFL forms pinacol dimer that is discharging at low voltage.
- Redox mediator adduction to abstract the electron from the pinacol dimer
- Higher power density is achieved by enhancing discharging voltage through redox mediation.

Result

Dimerization of fluorenone derivative during redox reaction

- 2,7-dihydroxy-9-fluorenone (DHFL) is used as a model compound to investigate the dimerization behavior during the charge–discharge process

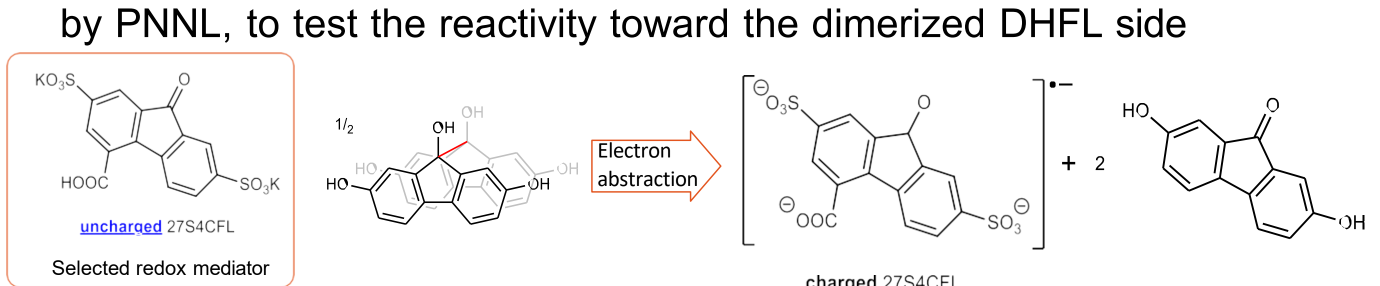




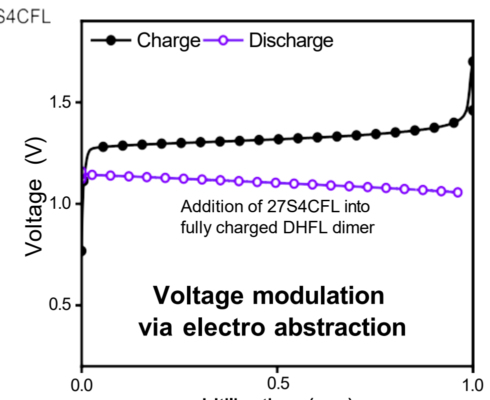
- Formed dimer – pinacol – is not electrochemically active due to the requisition of high activation energy to break the C-C pinacol bond, resulting in a low battery discharge voltage (**~0.5 V**).

Voltage modulation strategy from dimerized side product

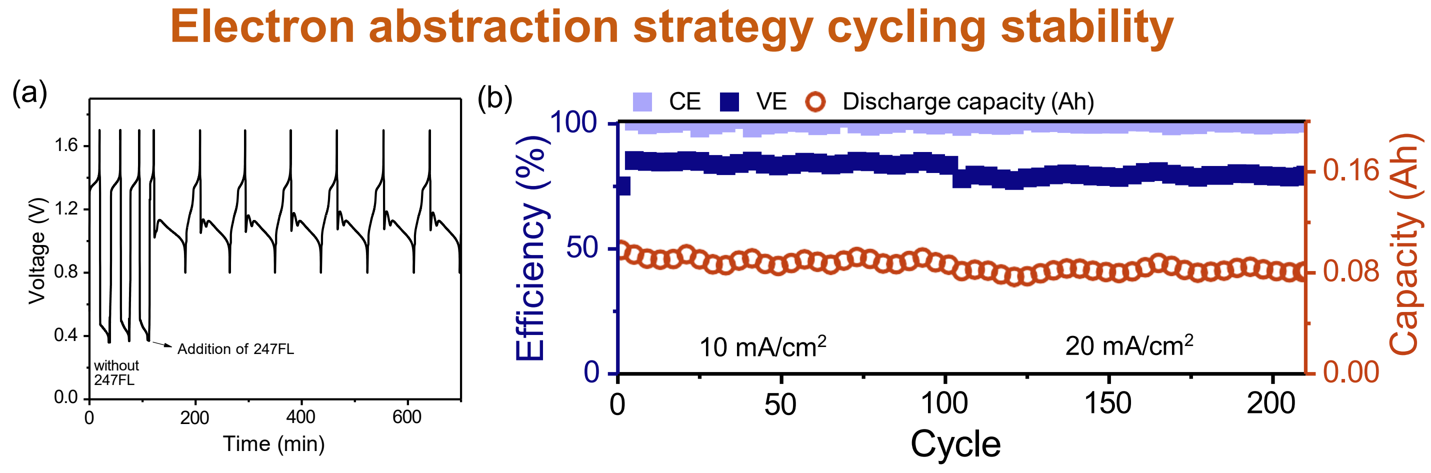
- redox mediator 27S4CFL is selected, which was previously invented by PNNL, to test the reactivity toward the dimerized DHFL side



- 27S4CFL can fully abstract the electron from the dimer during the discharging step
- Battery discharge at **~1.1 V** is recovered
- **Performance metric**: More than a **twofold increase** in discharge voltage compared to the earlier state



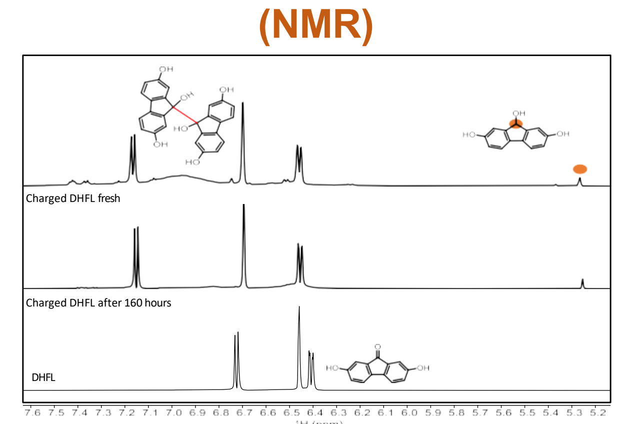
Electron abstraction strategy cycling stability



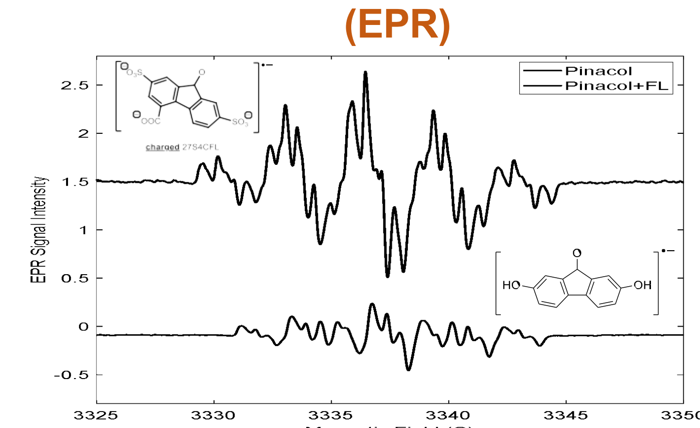
- V-T plot during cycling w/o and w/ redox mediator (a) and long-term cycling (b)
- **Performance metric**: 94% capacity retention with 84 % (10 mA/cm^2) voltage efficiency

Characterization

Nuclear Magnetic Resonance (NMR)

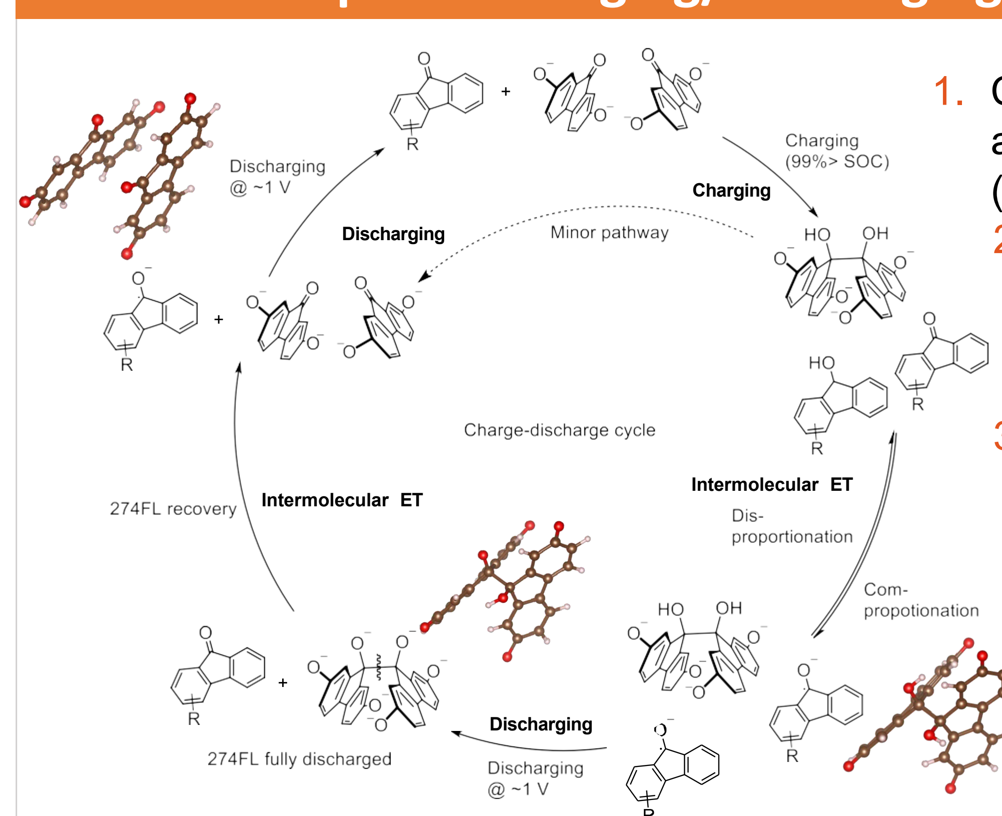


Electron paramagnetic resonance (EPR)



- NMR confirms the formation of the pinacol – C-C bond formation
- EPR confirms the electron abstraction mechanism
- EPR identifies the product of the electron abstraction process

Proposed charging/discharging mechanism



1. Charging: Both 27S4CFL and DHFL are charged (DHFL dimer formed).
2. Charged 27S4CFL is discharged first and forms uncharged 27S4CFL.
3. Uncharged 27S4CFL abstracts the e- from dimer and discharged at modulated voltage.
4. The DHFL dimer is recovered to DHFL to store electron for next cycle.

- Associated PCET steps were studied by DFT calculation. Major pathway of DHFL dimer formation (or dissociation) is ET-PT-PT-ET (ET: electron transfer, PT: proton transfer). C-C bond cleavage happens during 2nd proton removal step.

Summary and Perspective

- A voltage modulation strategy is developed by utilizing a redox mediator
- More than a twofold increase in discharge voltage is achieved via an electron abstraction mechanism
- EPR, NMR, and DFT methods are employed to investigate the electron abstraction mechanism
- The design principle of mediators' capability for such an electron abstraction process will be investigated.

Acknowledgement

- This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.
- PNNL is a multi-program national laboratory operated by Battelle for the US Department of Energy under contract DE-AC05-76RL01830

Reference

1. Feng, Wei et al. *Science* **2021**, *372*, 836-840.
2. Feng, Wei et al. *J. Electrochem. Soc.* **2024**, *171*, 090501
3. Aziz et al. *Nature Energy* **2016**, *1*, 16102.

For additional information, contact:

Jong-Hwa Shon
Tel: (509) 371-6988
Email: jong.shon@pnnl.gov

U.S. DEPARTMENT of ENERGY BATTELLE

Pacific Northwest NATIONAL LABORATORY
www.pnnl.gov