High-voltage Electrolyte Design for Sodium-ion Batteries

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Introduction

Sodium-ion batteries (SIBs) are a cost-effective alternative to lithium-ion batteries, making them suitable for energy storage applications. However, hard carbon (HC)||NFM111 Na-ion batteries using carbonate electrolytes still suffer from short cycle life, low power and energy density due to Na plating and low anodic stability of carbonate electrolytes. High-voltage & Na-tolerant electrolytes are crucial for the success of SIBs. We reported the electrolyte design principle for SIBs and demonstrated it by developing all anion electrolytes.

Objectives

- ❑ Propose electrolyte design principles for SIBs.
- ❑ Guide by electrolyte design principles to develop high voltage Na-stable electrolytes for HC||NMC622 and HC||NFM111 full cells to achieve long-cycle performance.

Electrolyte Design Principle

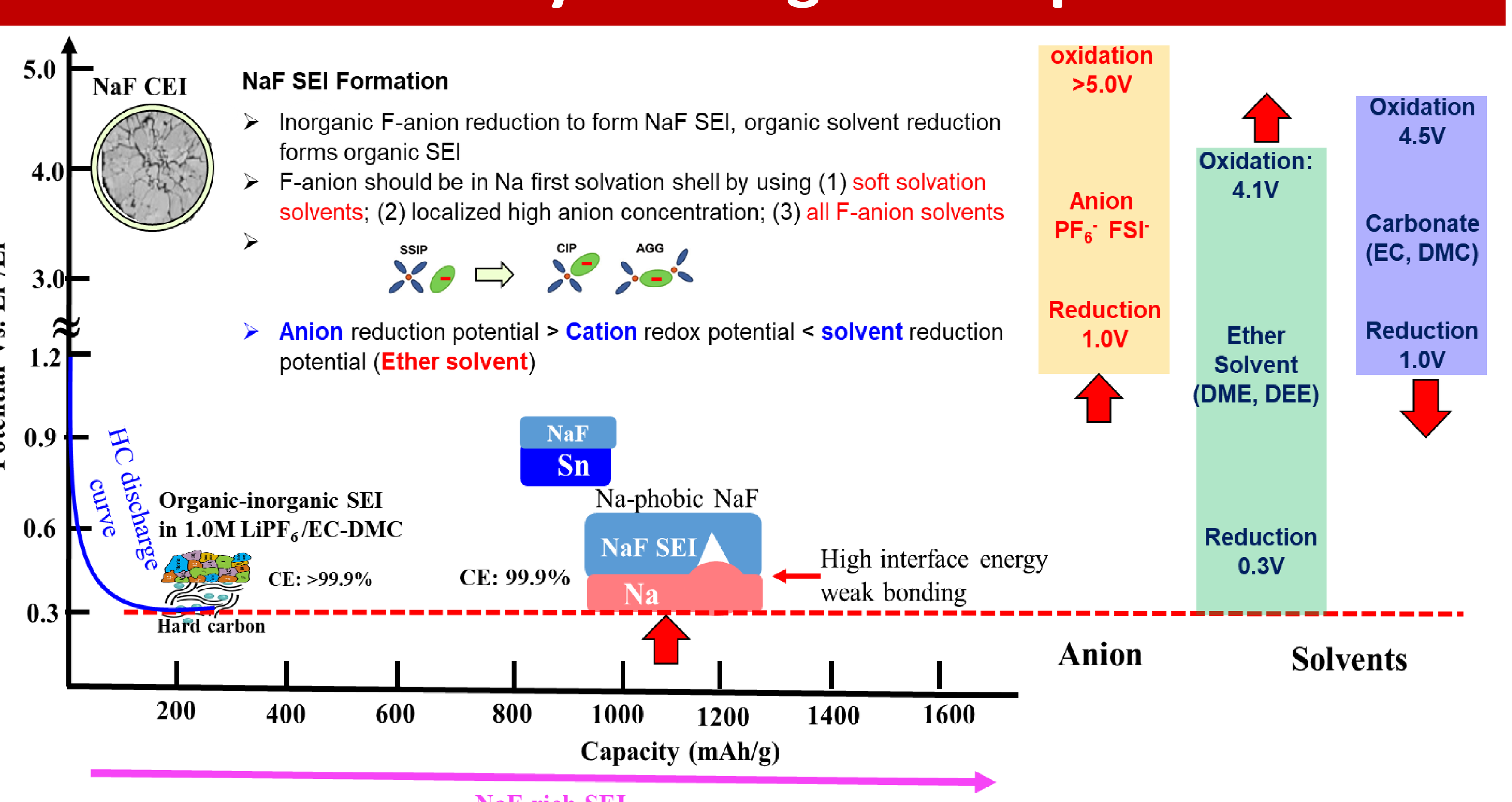

Figure 1. Electrolyte design principle. The low Na-insertion potential of hard carbon (HC) will induce Na plating at fast-charging and low-temperature operation. The organic-rich SEI formed in carbonate electrolytes promotes the growth of Na dendrites on HC. Ether electrolytes can form Na-phobic NaF-rich SEI on HC due to promoted anion reduction (forming NaF) and suppressed ether solvent reduction (forming organic SEI), which inhibits Na dendrite growth due to high interface energy at NaF/Na interface. The low voltage of ether electrolytes can be enhanced by using sulfonate electrolytes and pre-salt sulfonamide electrolytes. Formation of NaF SEI requires electrolytes to have a CIP and AGG solvation structure, and the cation redox potential is higher than the solvent reduction potential but is lower than the anion reduction potential

Soft Sulfonate Electrolytes (I)

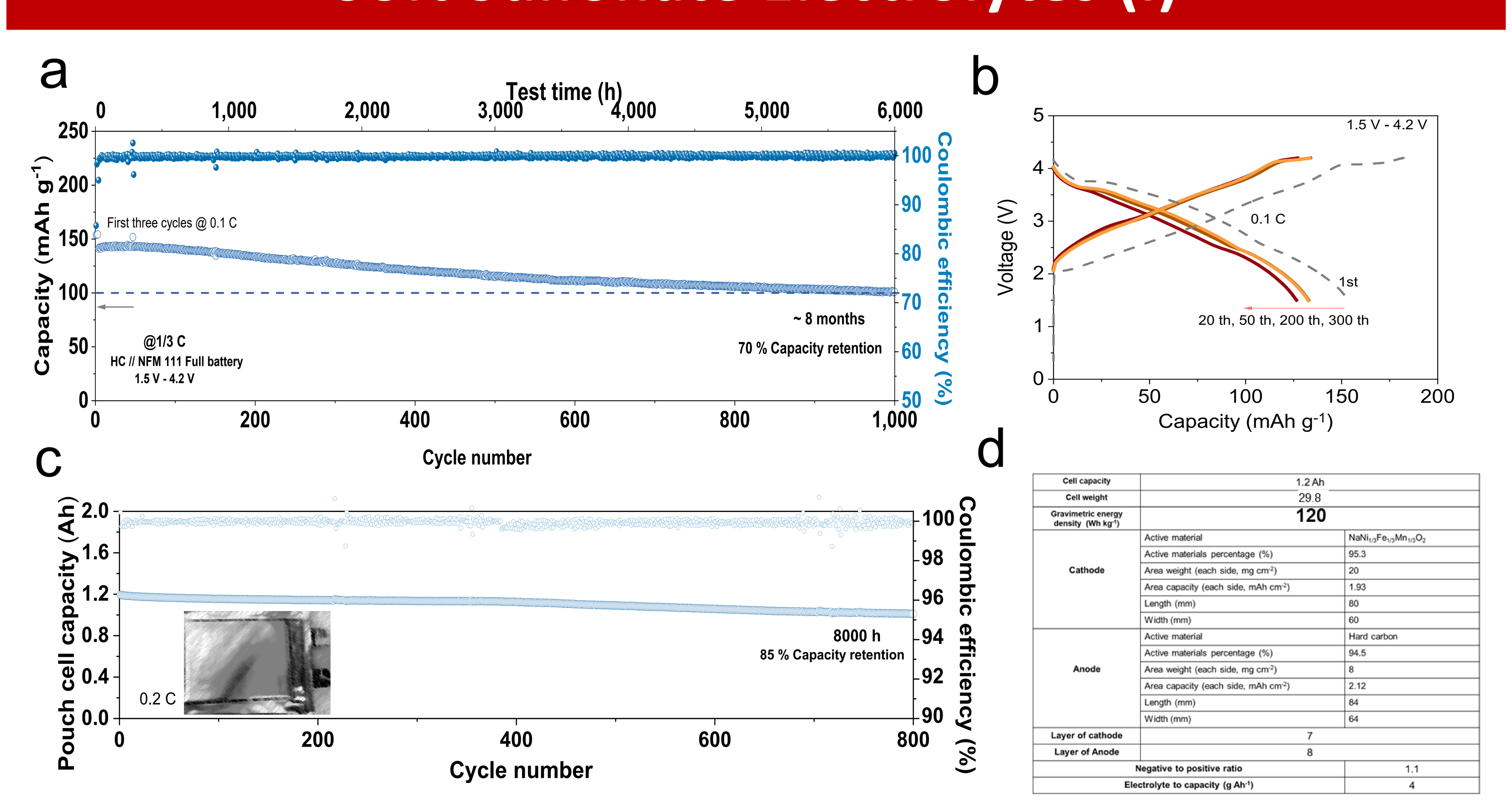

Figure 2. (a) Cycle performance and (b) voltage profiles of the HC||$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ Coin cell (1.5 mAh/cm^2 and N/P=1.04) in sulfonate electrolytes in a voltage range of 1.5 - 4.2V at 0.3 C. (c) Cycling performance of HC||$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ pouch cells using the sulfonate electrolyte at a cut-off voltage of 4 V and a capacity of 1.2 Ah @ 0.2 C. (d) Detailed cell parameters.

Soft Sulfonate Electrolytes (II)

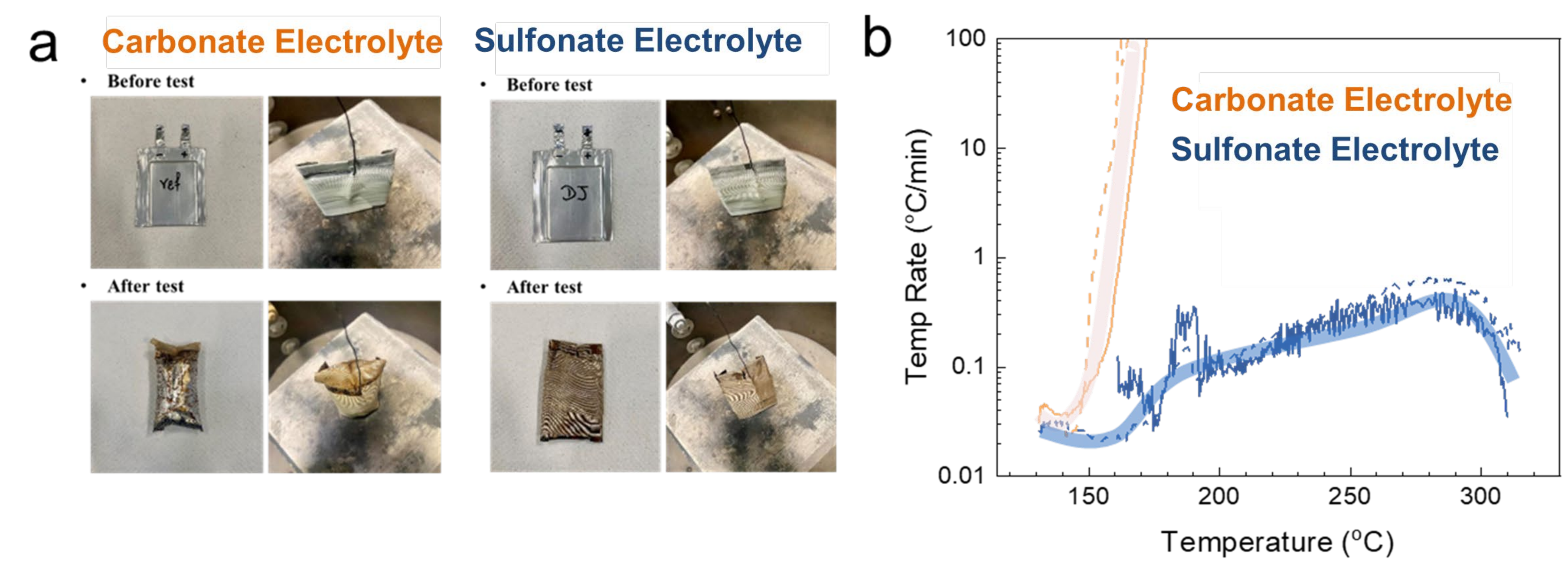

Figure 3. (a) Pictures of pouch cells before and after ARC testing using the carbonate and sulfonate electrolytes. (b), SHR as a function of temperature for HC// $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ pouch cells (500 mAh) using commercial and sulfonate electrolytes at 4.2 V after formation cycles. Each ARC test was conducted with two pouch cells.

Na plating tolerant Pre-salt Sulfonamide Electrolyte

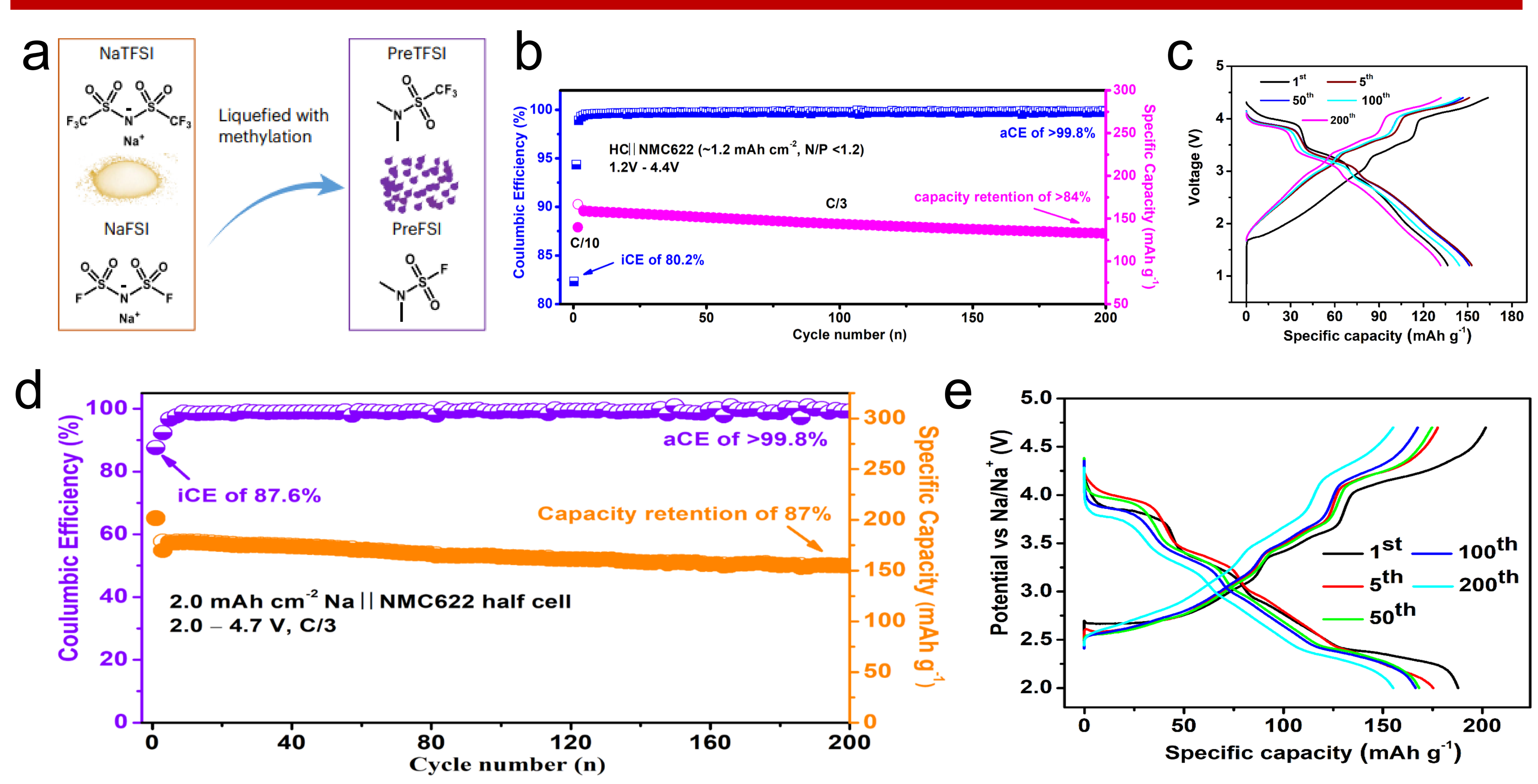

Figure 4. (a) Pre-salt sulfonamide solvent structure; (b) Cycle performance and (c) charge/discharge profile of 1.2 mAh cm^{-2} HC||$NaNi_{0.6}Mn_{0.2}Co_{0.2}$ full cells between 1.2 V and 4.4 V at C/3 rate in 0.5 M NaFSI/PreTFSI electrolyte; (d) cycle performance and (e) charge/discharge profiles of 2.0 mAh cm^{-2} Na|| $NaNi_{0.6}Mn_{0.2}Co_{0.2}$ full cells between 1.2 V and 4.7V at C/3 in 0.5 M NaFSI/PreTFSI electrolyte.

Conclusion and Future Work

- ❑ We developed the Na-ion battery electrolyte design principle and two high-voltage electrolytes. The Na-plating tolerant pre-salt sulfonamide electrolytes enable the HC||NMC622 cells to retain 84% at 4.4 V after 200 cycles, and the Na‖NMC622 cells to retain 87% at 4.7 V after 200 cycles. Soft sulfonate electrolyte enables HC||NFM111 pouch cells to achieve 120 Wh kg^{-1} (1.2 Ah, 4 V, 800 cycles, 1 year) without thermal runaway using the ARC test.
- ❑ We will refine all anion electrolytes for high-energy sodium-ion batteries and evaluate hard carbon and Sn anodes (> 3.5 mAh cm^{-2}, high ICE) in pre-salt sulfonamide electrolytes under lean conditions (E/C < 4). We will utilize AI tools to stabilize defluorinated products of pre-salt sulfonamide electrolytes, thereby achieving high safety, long cycle life, and low cost.

Publications

1. Ai-Min Li, Peter Y. Zavalij, Fred Omenya, Xiaolin Li, and Chunsheng Wang. "Salt-in-presalt electrolyte solutions for high-potential non-aqueous sodium metal batteries." ***Nature Nanotechnology*** 20, 3 (2025) 388-396.
2. Ai-Min Li, Travis P. Pollard, Zeyi Wang, Nan Zhang, Fred Omenya, Sha Tan, Enyuan Hu, Xiao-Qing Yang, Xiaolin Li, Oleg Borodin, and Chunsheng Wang. "Electrolyte Design with Non-fluorinated Solvents for High-Voltage Anode-free Sodium Metal Batteries ." ***Nature Sustainability***; 2025, In Press.

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