High-voltage Electrolyte Design for Sodium-ion Batteries

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PROJECT PROFILE
Topic: Sodium ion batteries | Vertical: Electrolyte
Strategic Pathway: Solvation structure and interphase design
Project start and finish: FY26-FY27

PROBLEM

Sodium-ion batteries (SIBs) are a cost-effective alternative to lithium-ion batteries for large-scale energy storage applications. However, hard carbon (HC)||NFM111 full cells using conventional carbonate electrolytes suffer from short cycle life, low power capability, and narrow operating temperatures due to the side reaction of plated Na with the carbonate electrolyte. In addition, the positive potential shift from Li to Na-ion batteries also requires the electrolytes to have a high anti-oxidation potential. The development of high-voltage and Na-compatible electrolytes is critical for SIBs. Here, we report an electrolyte design principle for sodium-ion batteries and demonstrate its effectiveness using all-anion electrolytes.

APPROACH

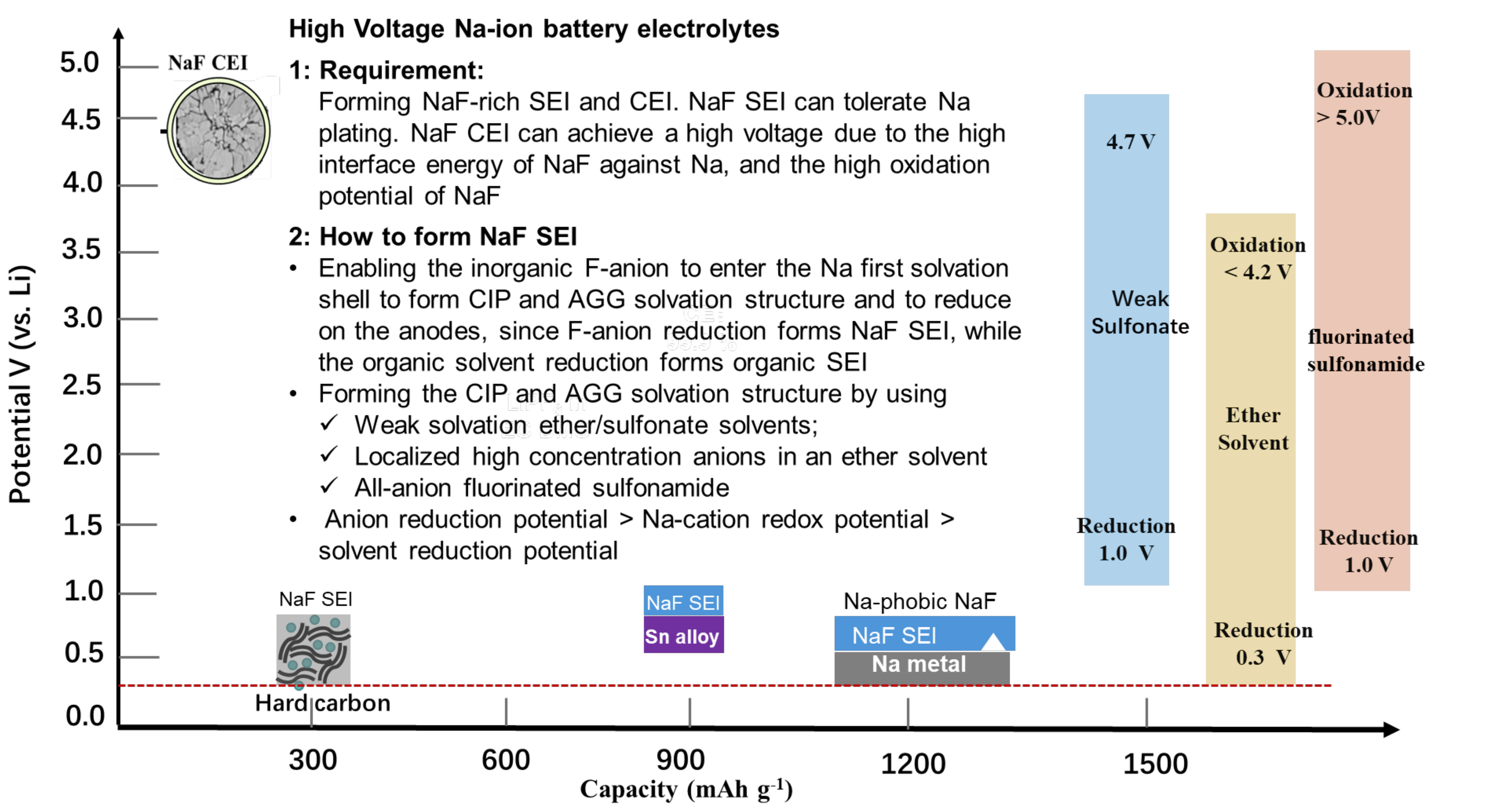

Figure 1. Electrolyte design principle. The similar Na-insertion potential of hard carbon (HC) to Na redox potential induces Na plating during fast charging and low-temperature operation. The organic-rich SEI formed in carbonate electrolytes promotes the growth of plated Na into dendrites on HC. Ether electrolytes can form an NaF-rich SEI on HC with a low reduction potential of ether, which inhibits Na dendrite growth due to the high interfacial energy at the 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 solvent reduction potential is lower than the anion reduction potential.

Weak Solvation Sulfonate Electrolytes (I)

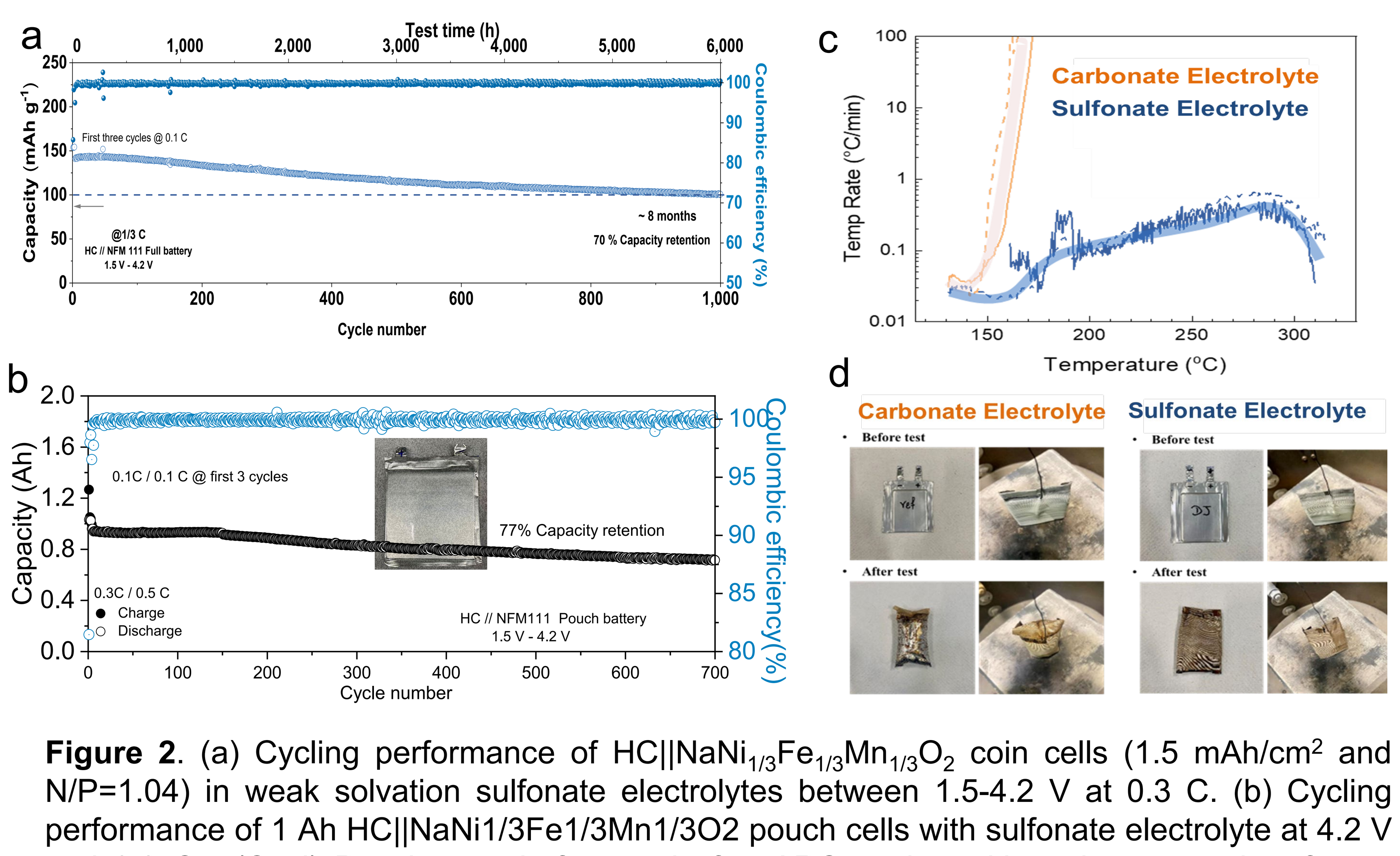

Figure 2. (a) Cycling performance of HC||$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ coin cells (1.5 mAh/cm^2 and N/P=1.04) in weak solvation sulfonate electrolytes between 1.5-4.2 V at 0.3 C. (b) Cycling performance of 1 Ah HC||NaNi1/3Fe1/3Mn1/3O2 pouch cells with sulfonate electrolyte at 4.2 V and 0.3 C. (C, d) Pouch cells before and after ARC testing with carbonate and sulfonate electrolytes. Self-heating rate versus temperature for HC// $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ (500 mAh) pouch cells using commercial carbonate and sulfonate electrolytes at 4.2 V after formation. Each ARC test used two pouch cells.

Weak Solvation Ether Electrolytes (II)

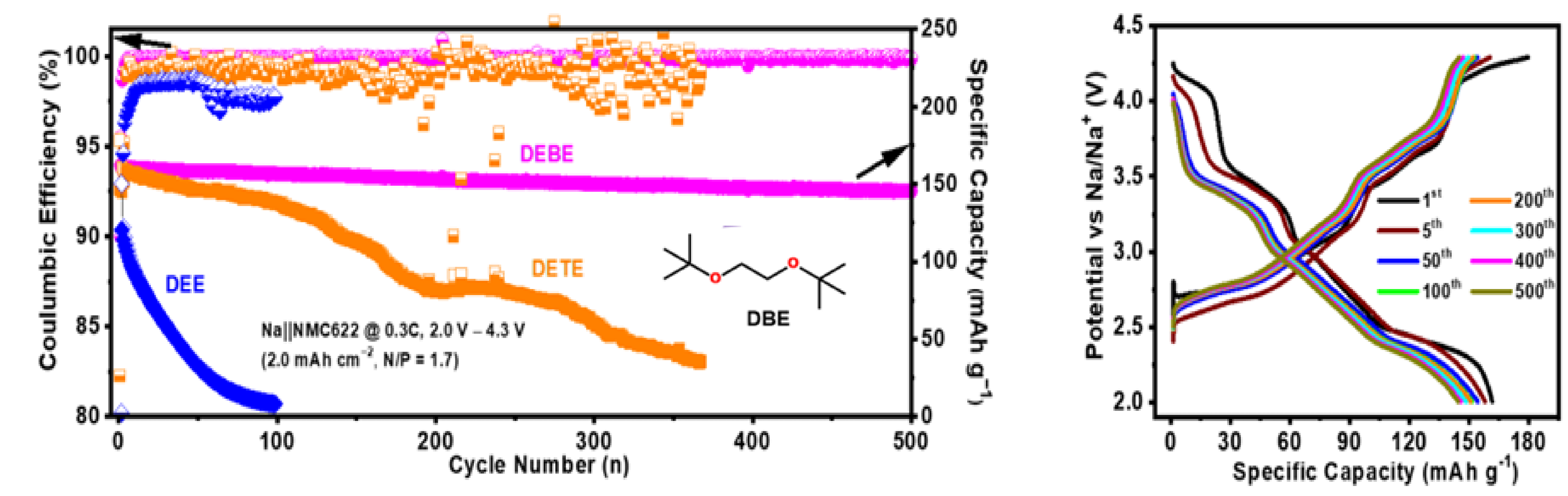

Figure 3. Electrochemical performance of Na||$NaNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) full cells. a, Capacity retention and CE of 2.0 mAh cm^{-2} Na||NMC622 (N/P = 1.7) full cells cycled in different electrolytes. The cells were cycled between 2.0 V 4 and 4.3 V at 0.3C with one formation cycle at C/10

Na plating tolerant Fluorinated Sulfonamide Electrolyte (III)

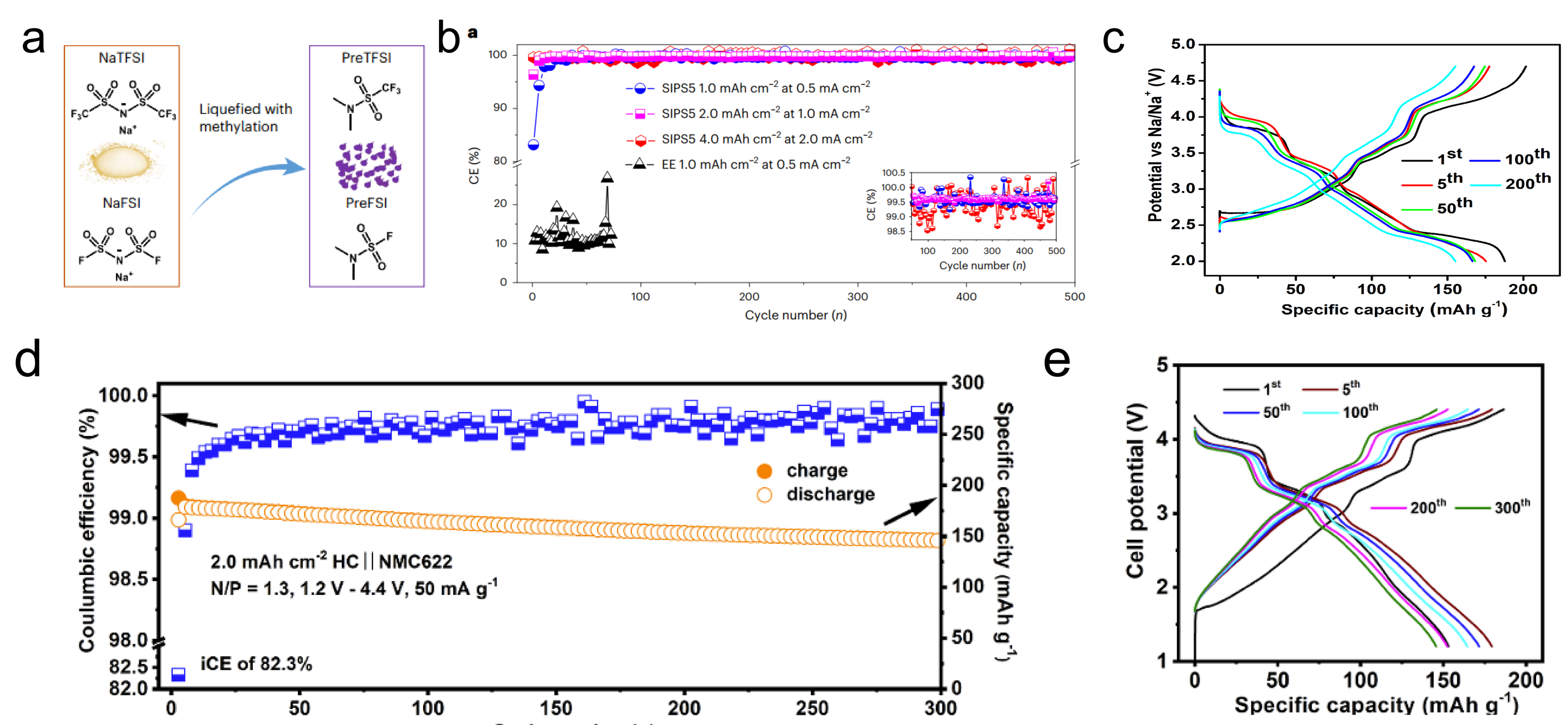

Figure 4. Performance of Na batteries in fluorinated sulfonamide electrolyte (0.5 M NaFSI/PreTFSI). (a) Molecular structure of the fluorinated sulfonamide solvent. (b) Na anode performance and (c) cycling performance of Na||$NaNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cells at 4.7 V and C/3. (d) Cycling performance and voltage profiles of HC||$NaNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cells at 4.4 V.

CONCLUSIONS & IMPACT

We developed Na-ion electrolyte design principles and two high-voltage electrolytes. The Na-plating-tolerant pre-salt sulfonamide electrolyte delivers 99.7% CE in Na||Al half cells, 87% retention for Na||NMC622 cells at 4.7 V after 200 cycles, and 84% retention for HC||NMC622 cells at 4.4 V after 300 cycles. The soft sulfonate electrolyte enables HC||NFM111 pouch cells to achieve 700 cycles at 4.2 V without thermal runaway in ARC tests.

FUTURE DIRECTIONS

We will optimize fluorinated sulfonamide electrolytes for high-energy sodium-ion batteries and evaluate full cells with hard carbon and Sn anodes (> 3.0 mAh cm-2, high ICE) in these electrolytes under lean-electrolyte conditions (E/C < 5). AI-assisted design will be used to stabilize defluorinated products, enabling safer, longer-life, and lower-cost sodium-ion batteries.

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*** 9.2 (2026): 306-316.

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