Electrolytes and Interfaces for Stable High-Energy Na-Ion Batteries

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Pacific Northwest National Laboratory

2021 DOE VTO Annual Merit Review

June 21-25, 2021

Project ID #bat429

Overview

Timeline

- Start date: Oct. 1, 2018
- End date: Sept. 30, 2021
- Percent complete: 90%

Budget

- Project funding
  - DOE share 100%
- Funding for FY20: $430K
- Funding for FY21: $430K

Barriers

- Short cycle life: Need functional electrolyte enabling stable electrolyte/electrode interface
- High cost: Need low cost and sustainable anode and cathode material to enable electric vehicle (EV) battery cost < $100/kWh

Partners

- Argonne National Laboratory
- Lawrence Berkeley National Laboratory

Relevance/Objectives

- New electrolytes compatible for high-capacity anode and high-voltage cathode materials can enable high energy Na-ion batteries (NIBs) as an alternative, low-cost battery solution for EV applications.
- Establish a fundamental understanding on the correlation between electrolyte/electrode interface and electrochemical performance of NIBs.
- Tailor electrolyte formulations (salt/solvent/additives) to improve their electrochemical stability in NIBs.
- Increase energy density and cycle life of NIBs by developing high-capacity anode coupling with high-voltage cathode materials.

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Milestones

Date	Milestone Name/Description	Status
Dec. 31, 2020	Optimize the synthesis condition of high-capacity anode (> 450 mAh g^{-1}) to further improve its capacity	Completed
Mar. 30, 2021	Develop high voltage electrolytes to enable stable and safe cycling of high energy density NIBs in full cells	Completed
June 30, 2021	Design new electrolytes that are compatible with conventional polymer separators	On track
Sept. 30, 2021	Investigate both electrochemical and physicochemical properties of new electrolytes	On track

Approaches

1. Investigate the synthesis conditions and electrochemical performance of high-capacity carbon anode with optimized electrolyte.

2. Develop dual-additive based-carbonate and phosphate-based localized high concentrated electrolytes for NIBs.

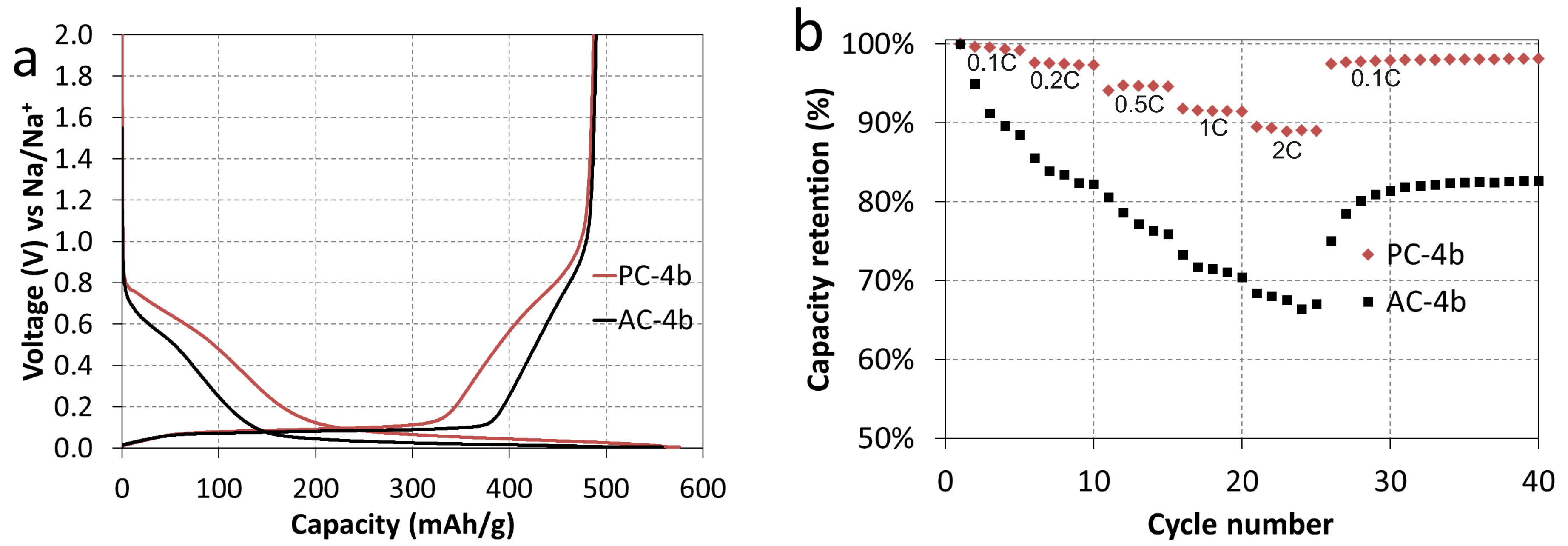
3. Design electrolytes with good wetting properties toward polymer separator.

4. Investigate both electrochemical and physicochemical properties of new electrolytes.

Technical Accomplishments

1. Development of high-capacity anode for NIBs

Performance of carbon anode synthesized by thermal treatment of different precursors

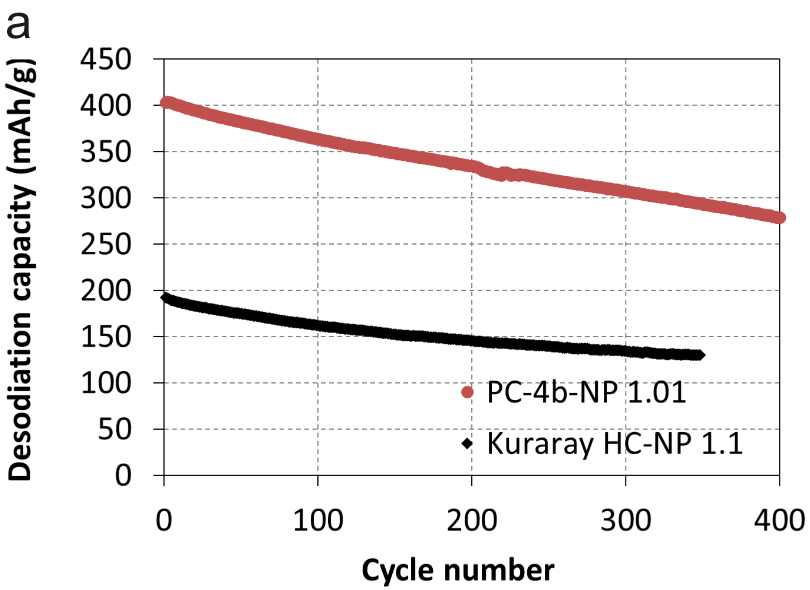


(a) 1st cycle voltage profile in voltage and (b) the rate performance of Na half-cell with 1 M $NaPF_6$/EC-DMC

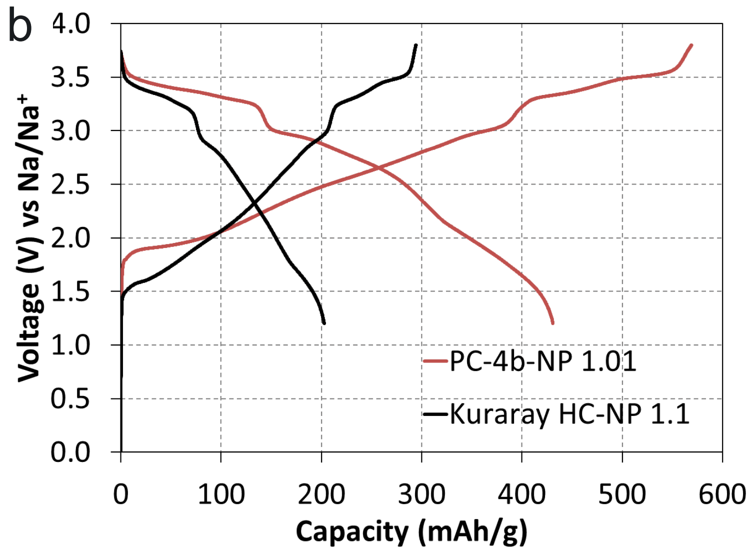
a. PC-4b exhibits much higher initial capacity (489 mAh g^{-1}) and high-rate capability than those of state-of-the-art carbon anode (Kuraray HC, ~300 mAh g^{-1}).
b. AC-4b exhibits a sodiation potential too close to the sodium plating potential and poor hight rate capability.

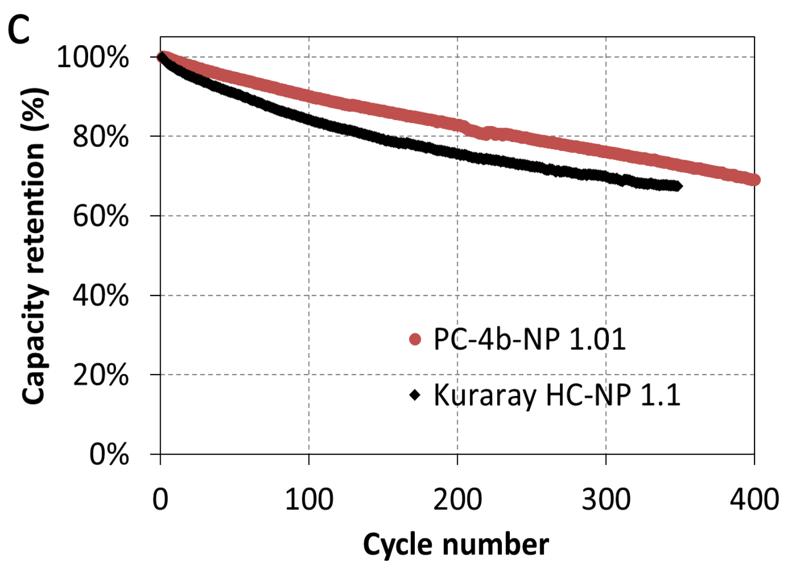
Technical Accomplishments

Electrochemical performance of new carbon anode



(a) Capacities and cycle stability of Na||C half cells using different carbon anodes





Initial voltage profiles (b) and cycle stability (c) of C|| $NaNi_{0.68}Co_{0.1}Mn_{0.22}O_2$ full cells using different carbon anodes. Electrolyte: NaFSI-TEP/TTE electrolyte (1:1.5:2 in mole)

a. Na||PC-4b cell exhibits 79% ICE and 440 mAh g^{-1} capacity compared to 69% ICE and 202 mAh g^{-1} for Na|| Kuraray HC (typical hard carbon anode used for NIBs).
b. PC-4b||NaNMC full cell has a capacity twice as much as those of Kuraray HC|| NaNMC full cell
c. Na||PC-4b cell has better cycling stability than Na|| Kuraray HC cell.

Technical Accomplishments

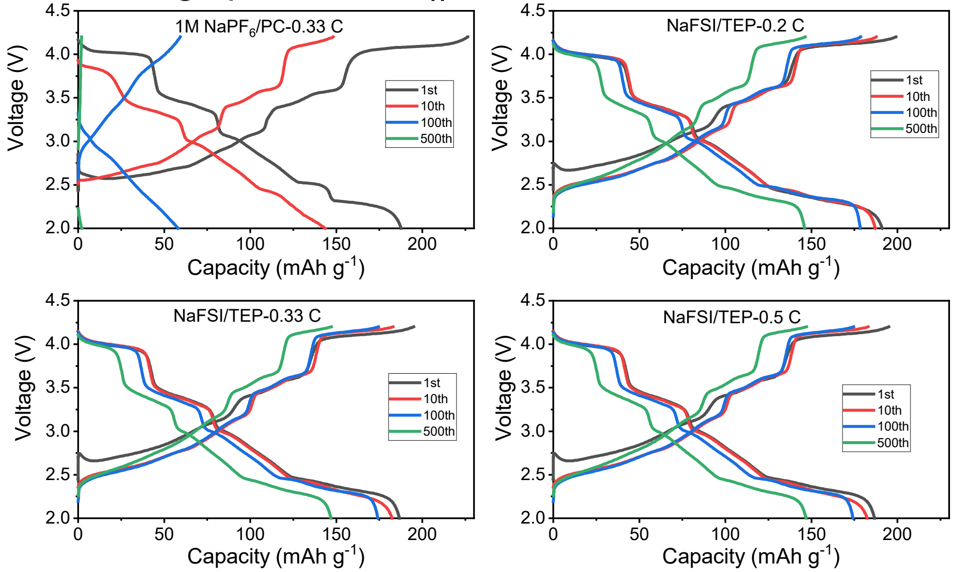
2. Nonflammable phosphate-based high-concentration electrolytes

Triethyl phosphate (TEP)

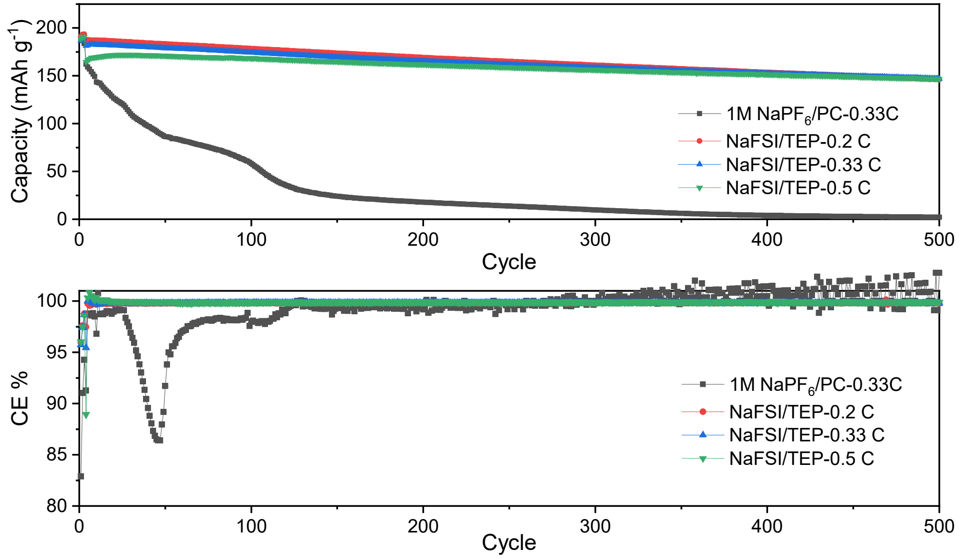
- ✓ High oxidization window
- ✓ High thermal stability
- ✓ **<u>Nonflammable</u>**

Electrolyte	Density, g/ml	Molar concentration	Ion conductivity (mS cm^{-1}), 30 °C
1M $NaPF_6$ in PC (Baseline)	1.2804	1.0	7.60
NaFSI: TEP = 1:1.5 in mole	1.3275	2.79	1.10

Voltage profile of Na||NaNMC cells at different C rate



Long-cycling performance Na||NaNMC cells at different C rate



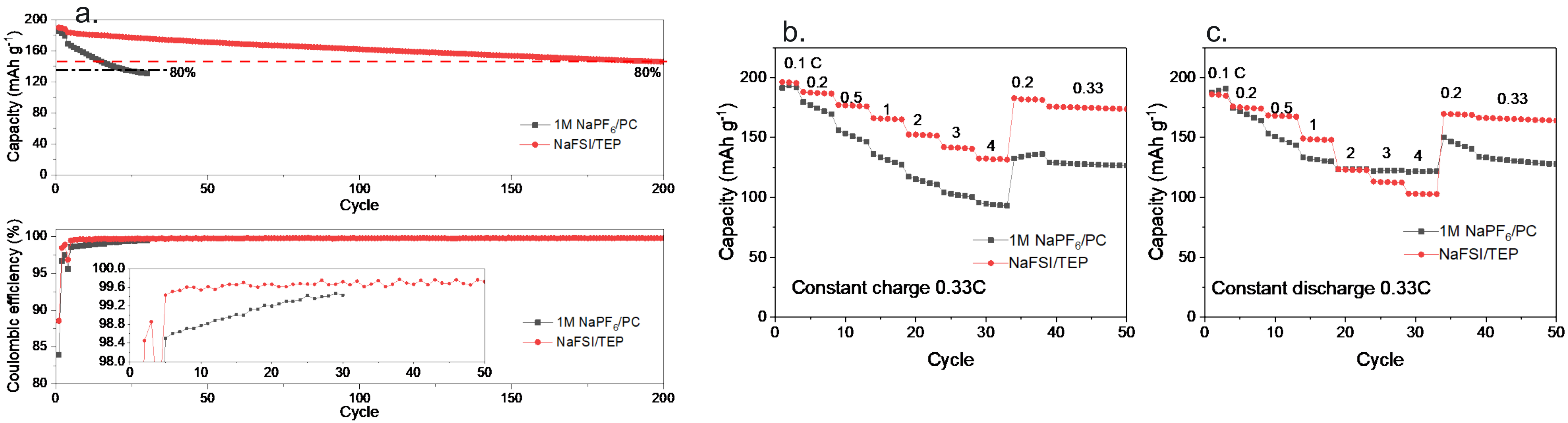
Note: Na||NaNMC half cells, cathode : NaNMC: PVDF: CB=85:5:10, mass loading: 4-5 mg/cm^2

- ➢ HCE is stable with NMC cathode at 4.2 V.
- ➢ Capacity retention of cells with HCE (81%, 500 cycle, 0.33C) is much larger than those with baseline electrolyte (18%, 130 cycle, 0.33C).

Technical Accomplishments

Nonflammable phosphate-based High-Concentration Electrolytes

Full-cell HC|| NaNMC operating in voltage range of 2.0 – 4.2 V



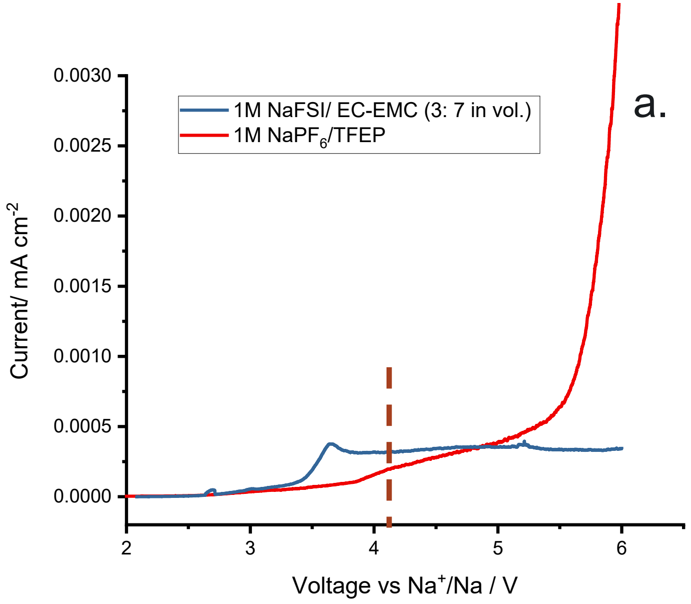
a. In nonflammable HCE, capacity retention is 80% after 200 cycles which is much better than those in baseline (80 % for less than 30 cycle).
b. Nonflammable HCE leads to higher discharge rate.
c. Nonflammable HCE electrolytes also leads to higher charge rate.

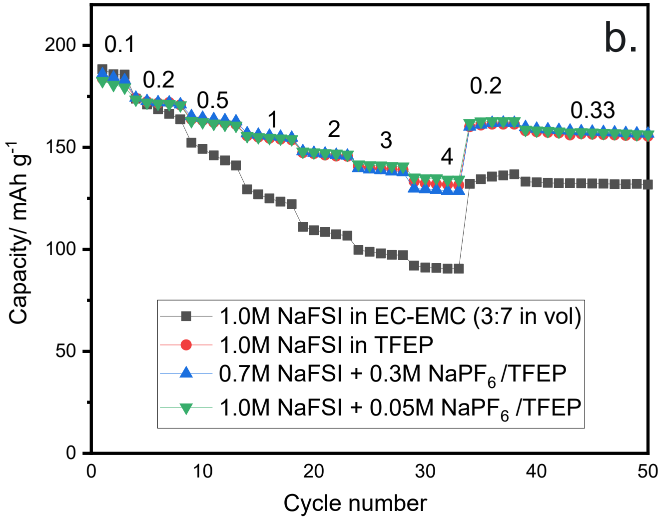
Technical Accomplishments

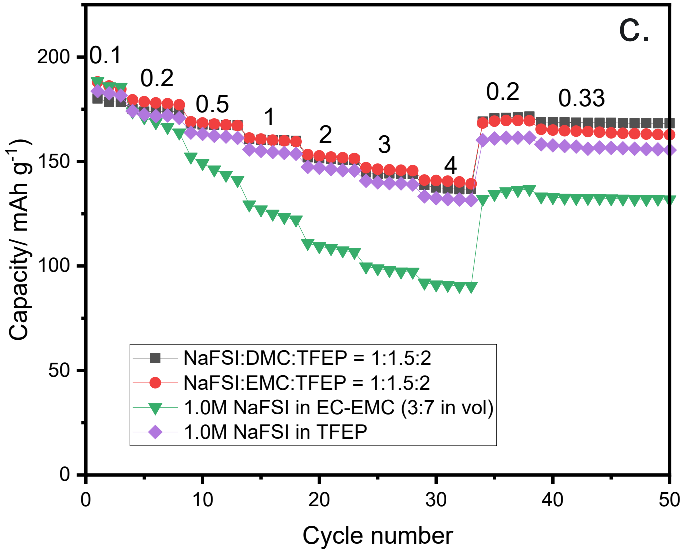
3. Nonflammable, high voltage electrolyte for NIBs

Fluorinated phosphates (TFEP)

- ✓ High oxidization window; High thermal stability
- ✓ **Nonflammable; Compatible with PE separator**
- × Low ionic conductivity (vs. carbonate based-electrolyte)





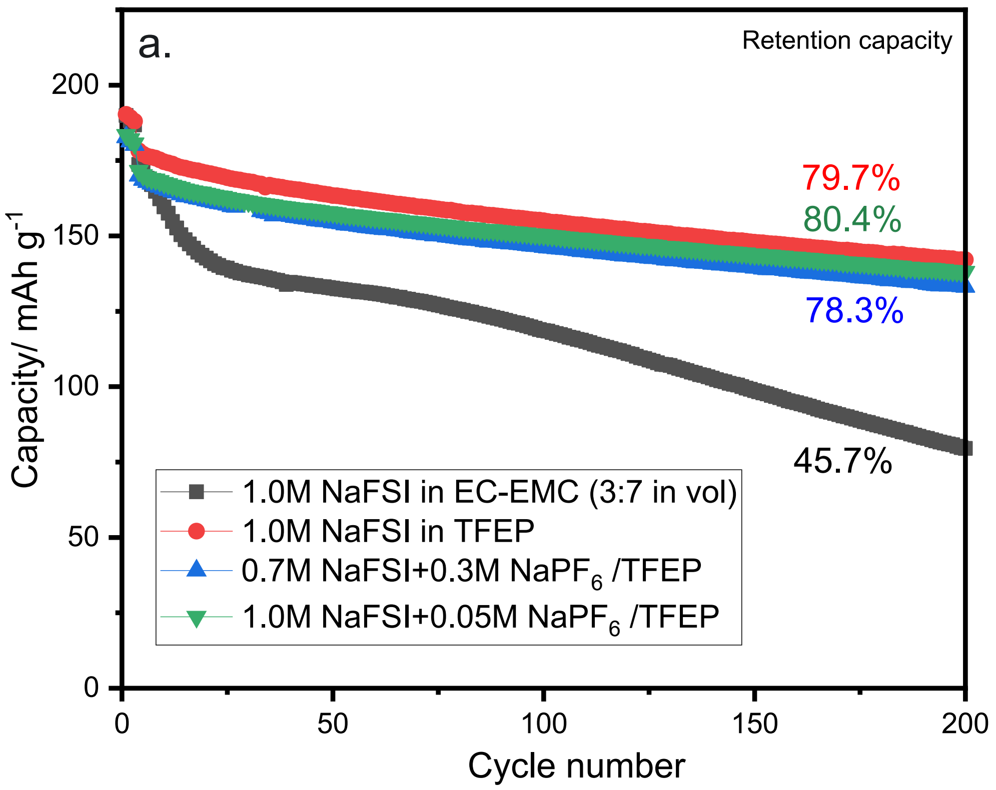


a. TFEP based electrolyte is more stable at high voltage then baseline electrolyte.
b. Dual-salt in electrolyte improves the rate capability of HC||NaNMC cell.
c. Co-solvent in TFEP based electrolyte further enhances high-rate performance.

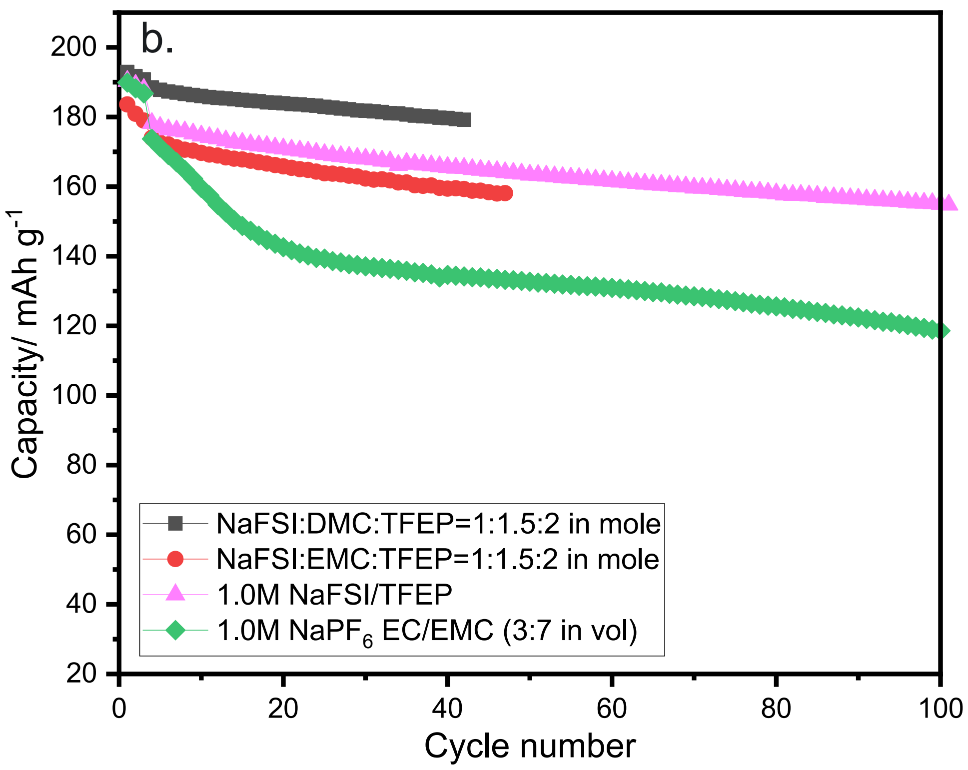
Technical Accomplishments

Cycling stability of NIBs using TFEP based electrolytes

Dual-salt effect



Co-solvent effect



a. TFEP based-electrolyte show higher capacity retention for high voltage full cell than baseline electrolyte
b. Co-solvent leads to more stable cycling than dual salt.

Note: HC ‖ NaNMC full-cell. capacity loading 0.65 mAh cm^{-2}

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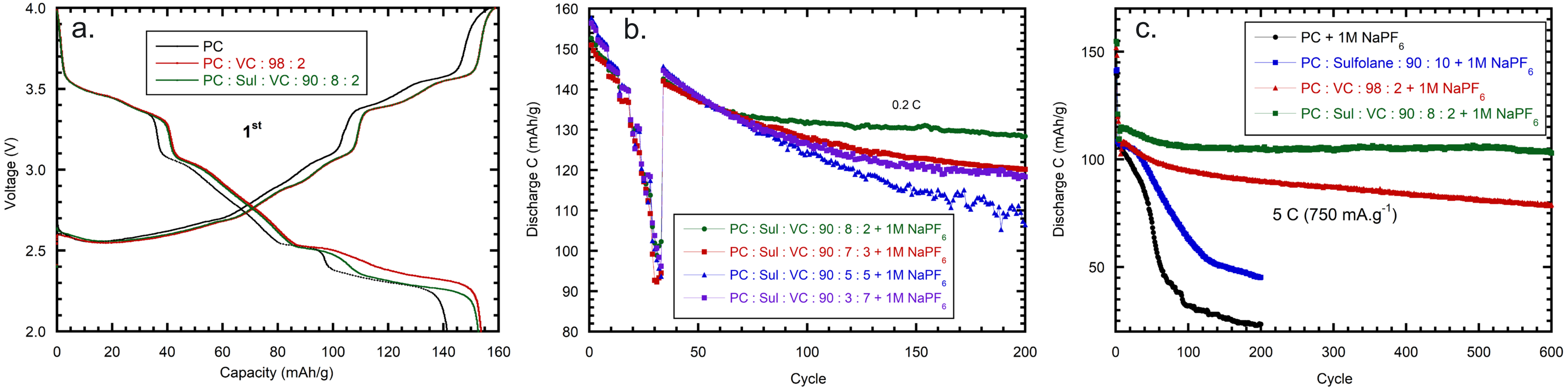
Technical Accomplishments

4. Dual-additive based carbonate electrolyte

Na ǁ NaNMC, loading: ~4-5 mg/cm^2 ; Baseline electrolyte: PC + 1 M $NaPF_6$



a. Electrolyte with dual-additives (Sul:VC = 8:2) exhibits the best performance.

b. Optimized electrolyte leads to good stability at 0.2 C for 200 cycles.

c. After 600 cycles, cells with dual-additive based electrolyte still retains 94 % of initial capacity.

Proposed Future Works

- Optimize electrolyte co-solvent/additives to tailor the solvation structures to improve high-voltage and full cell electrochemical performance
- Investigate the thermal stability of electrolyte using ARC and DEMS
- Explore the feasibility of anode-free NIBs using new electrolytes/additives

Any proposed future work is subject to change based on funding levels.

Summary

- Developed high-capacity carbon anode with a specific capacity of 485 mAh g^{-1} which is 60% more than the conventional hard carbon anode (300 mAh g^{-1}, Kuraray HC).
- Nonflammable phosphate (TEP)-based high concentration electrolytes demonstrates high voltage (4.2V) stability with $NaNi_{0.68}Mn_{0.22}Co_{0.1}O_2$ cathode and capacity retention of 81% after 500 cycles at 0.33 C.
- Novel TFEP based nonflammable electrolytes are highly stable at high voltage and compatible with PE separator. Addition of carbonate co-solvent in TFEP based electrolyte significantly enhances high-rate and long-cycling performance of HC||NMC full-cells.
- Dual-additive VC-sulfolane leads to excellent high-rate performance for Na ||NaNMC cells.

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Collaboration and Coordination

- Dr. Chongmin Wang (PNNL) for TEM and STEM images, etc.
- Dr. Biwei Xiao (PNNL) for providing high voltage Na-ion cathode material electrodes
- Dr. Mark Engelhard (PNNL) for XPS analysis.
- Dr. Patrick El-Khoury (PNNL) for Raman analysis.
- Dr. Kee Sung Han (PNNL) for NMR analysis.

Acknowledgements

- Support form DOE/EERE/VTO/BMR program is highly appreciated.

- Team members: Thanh D. Vo, Yan Jin, and Ran Yi

Responses to Previous Year's Reviewers' Comments

- This project was not reviewed last year.

Remaining Challenges and Barriers

Key Challenges

- The compatibility of electrolytes with high-voltage cathode and anode to achieve safety operation and long-cycling performance
- Thermal stability of the electrolytes
- High-cost of high-voltage cathode materials for NIB

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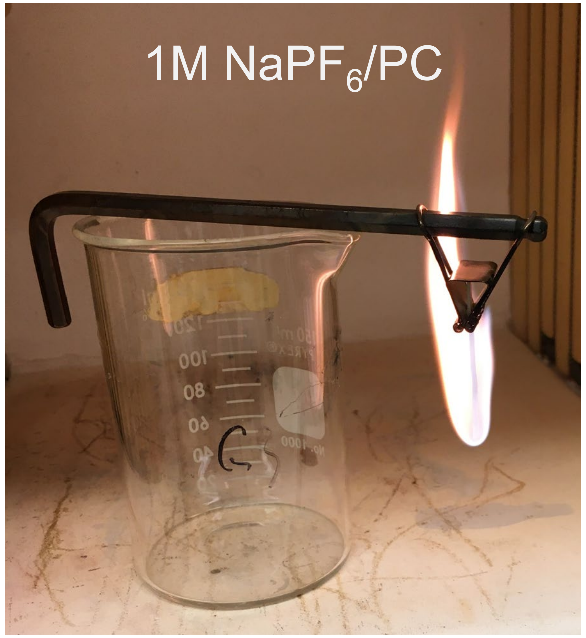
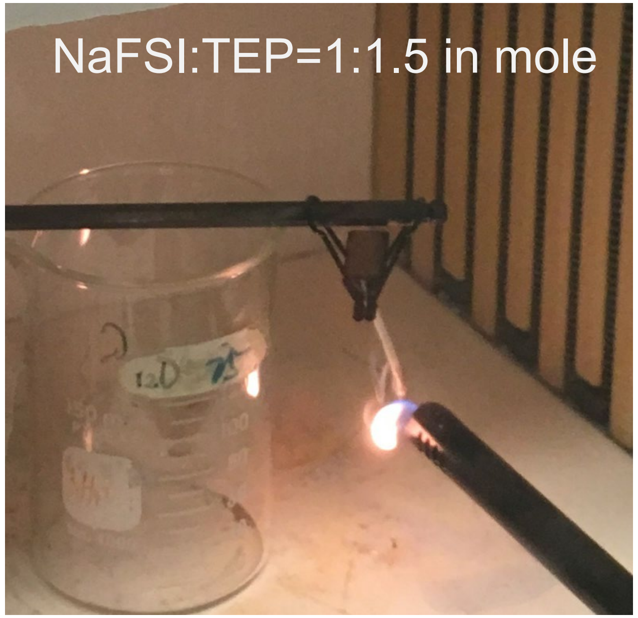
Technical Backup Slides

Technical Accomplishments

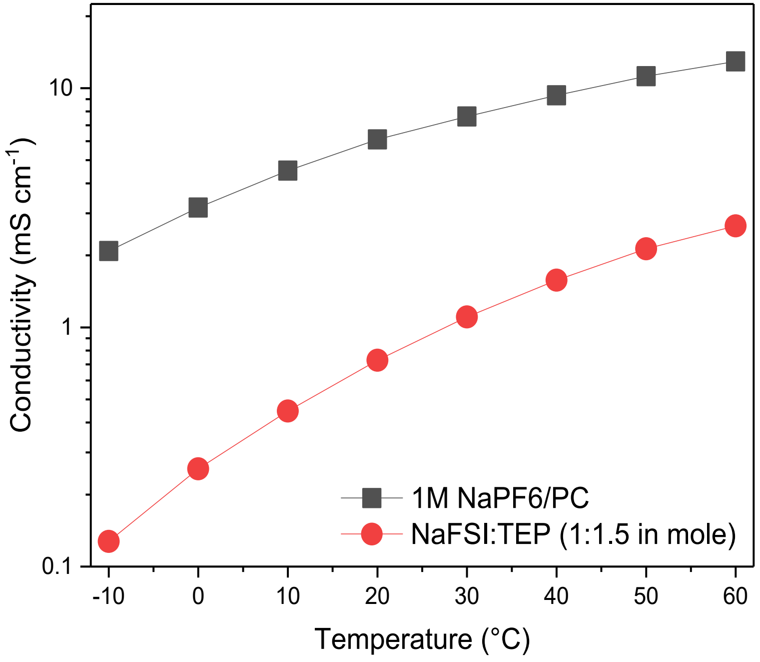
Non-flammable of Phosphate Based-Electrolyte

Flammability test





Ionic conductivity

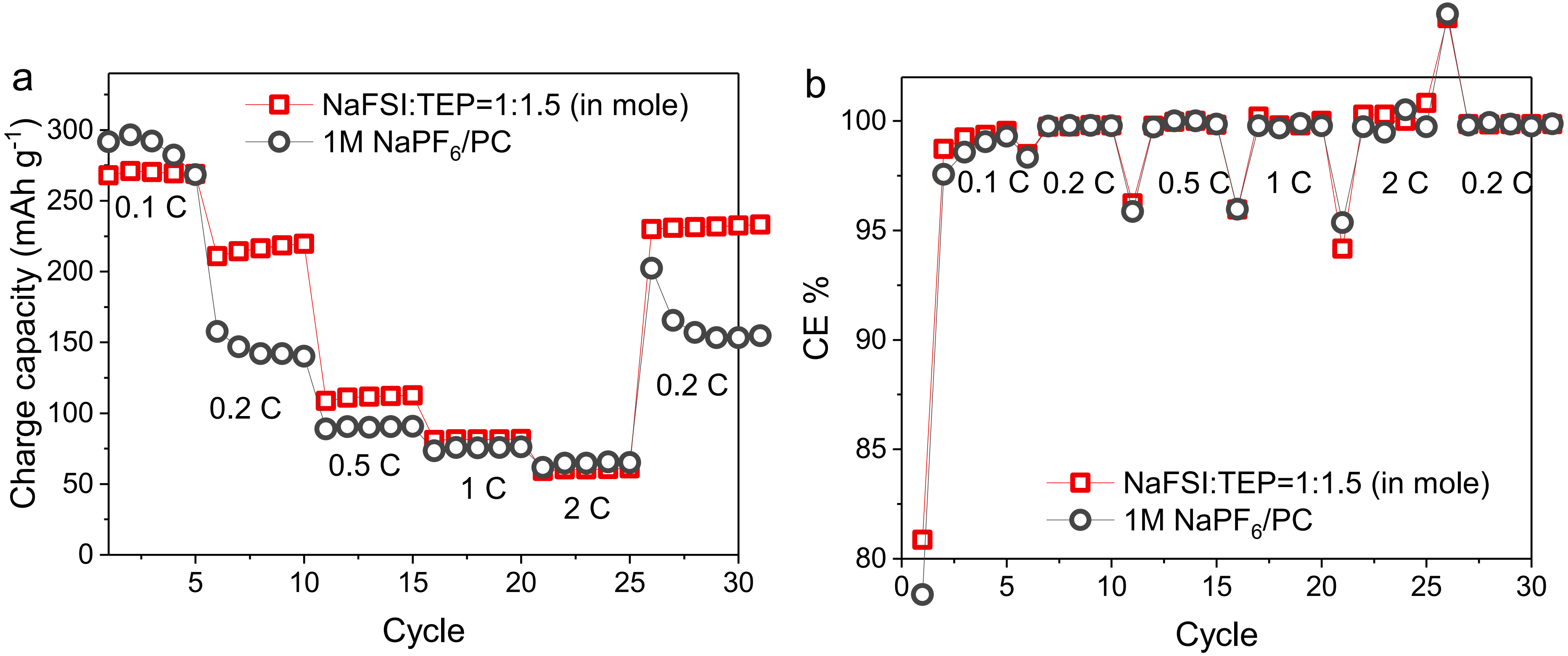


- Self-extinguish time of conventional electrolyte (1M NaPF6/PC): 101 s/g
- High concentration phosphate electrolyte is nonflammable.

Technical Accomplishments

Non-flammable of Phosphate Based-Electrolyte

Rate performance of HC anodes in different electrolytes



High-concentration electrolyte NaFSI:TEP=1:1.5 demonstrates better rate-performance than baseline electrolyte.

Note: NaǁHC half cells, HC electrode: HC:PVDF:CB=90:5:5, mass loading: 2–3 mg/cm^2

Technical Accomplishments

Dual-additive based carbonate electrolyte

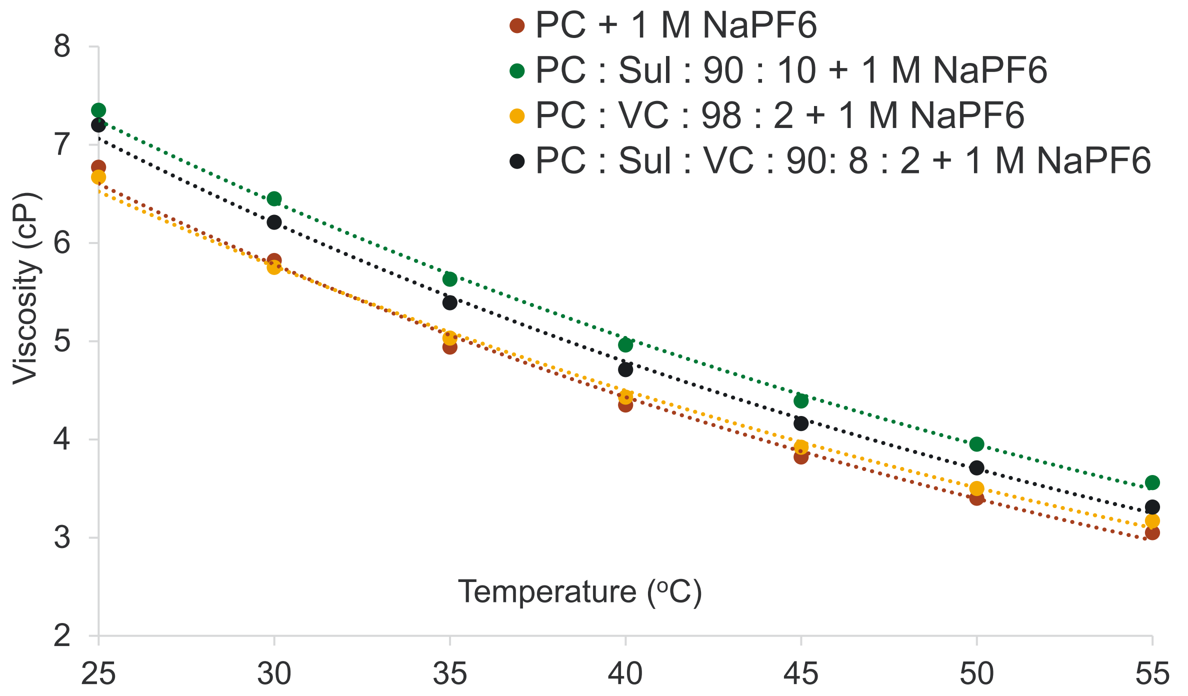
Viscosity and ionic conductivity

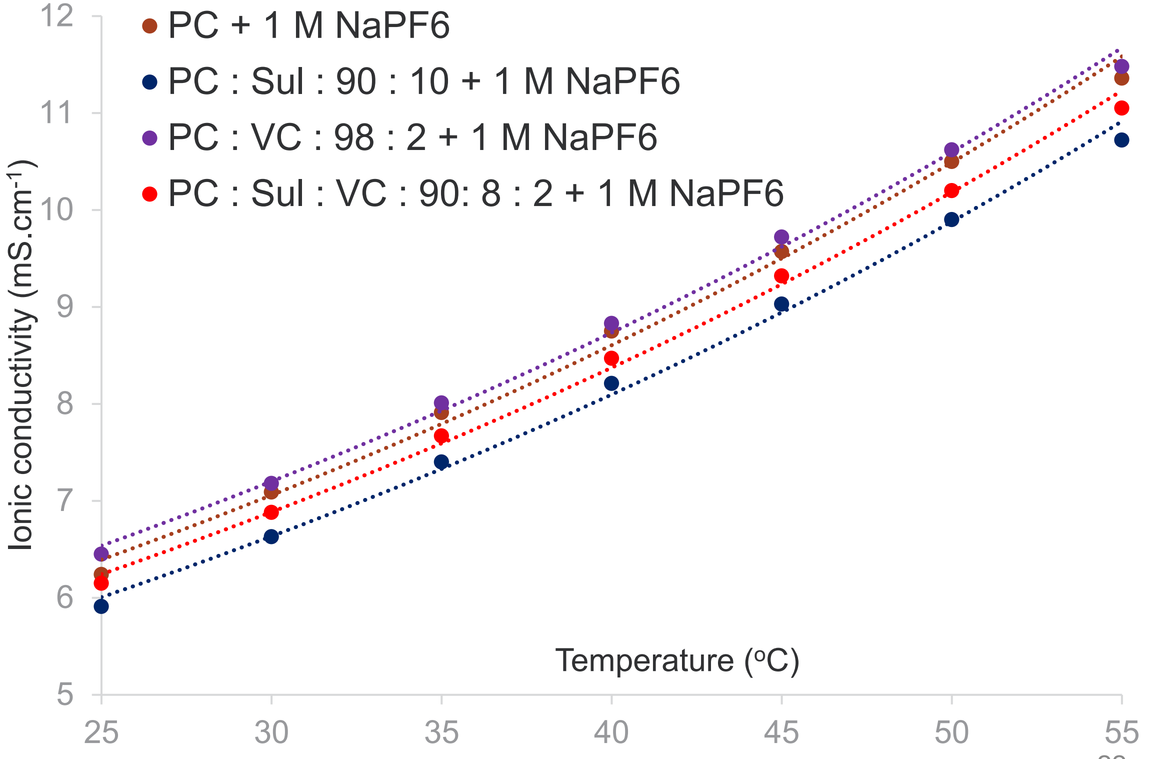
Electrolyte: **PC + 1M $NaPF_6$**

PC: Sulfolane 90: 10 + 1M $NaPF_6$ (Without VC)

PC: VC 98: 2 + 1M $NaPF_6$ (Without Sulfolane)

PC: Sulfolane: VC 90: 8: 2 + 1M $NaPF_6$

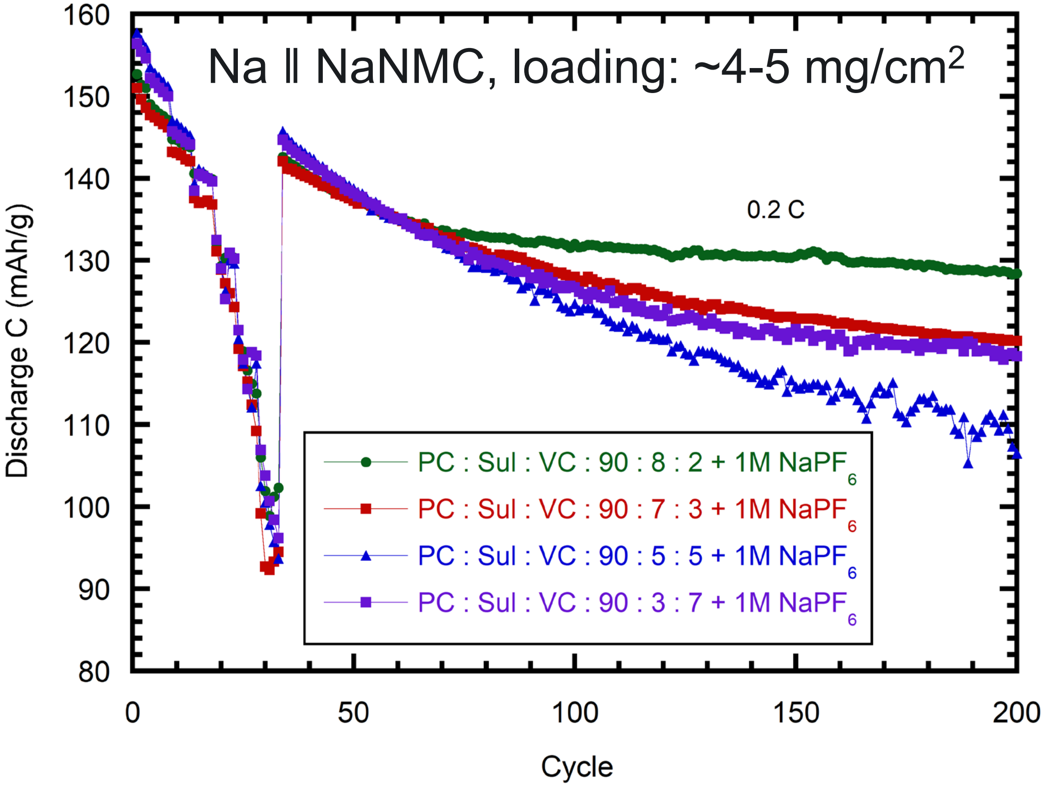


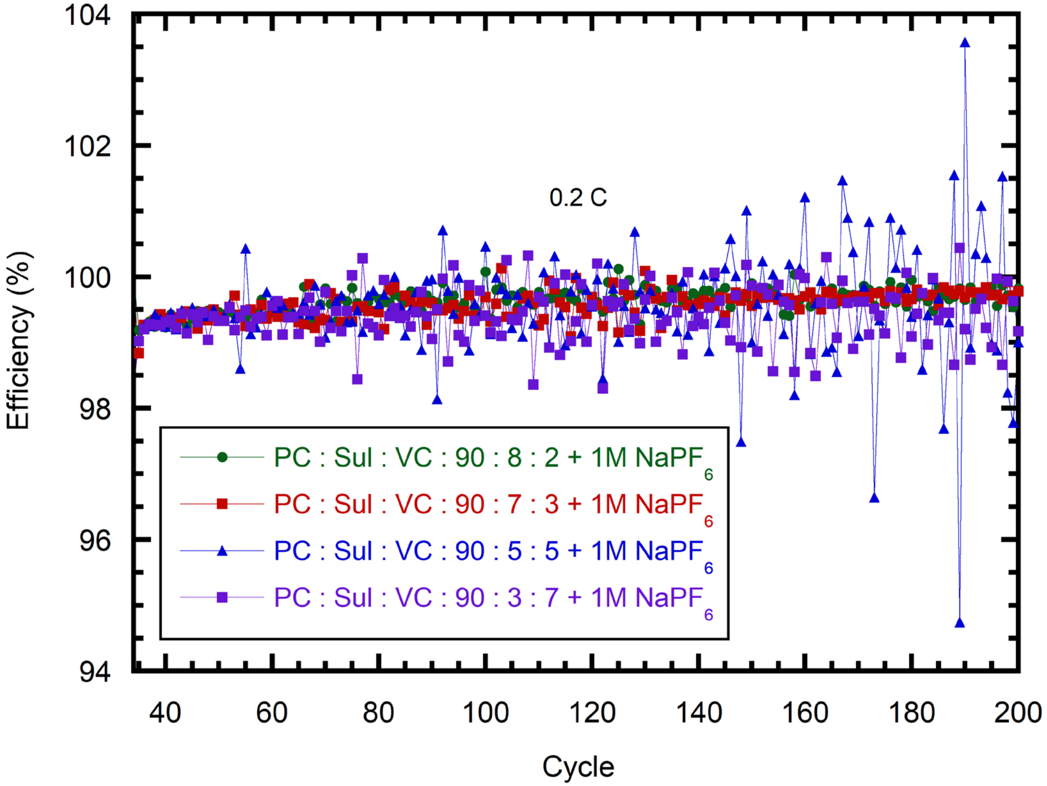


Technical Accomplishments

Dual-additive based carbonate electrolyte

-Optimized additive ratio



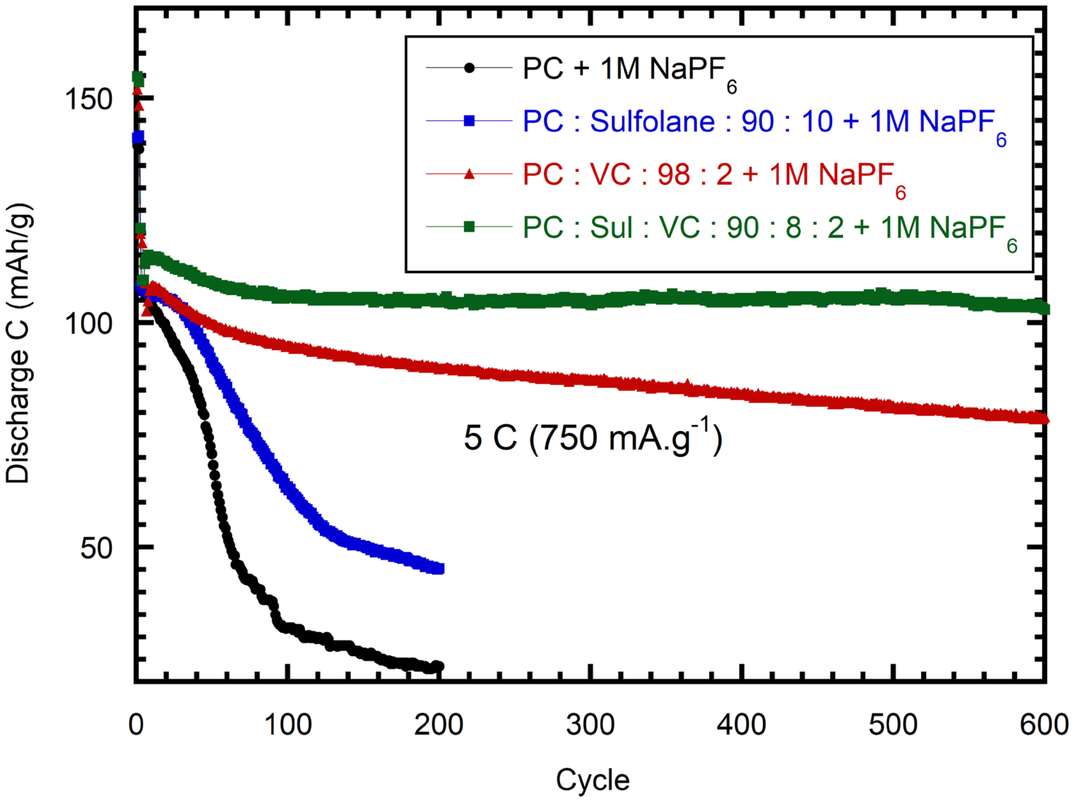


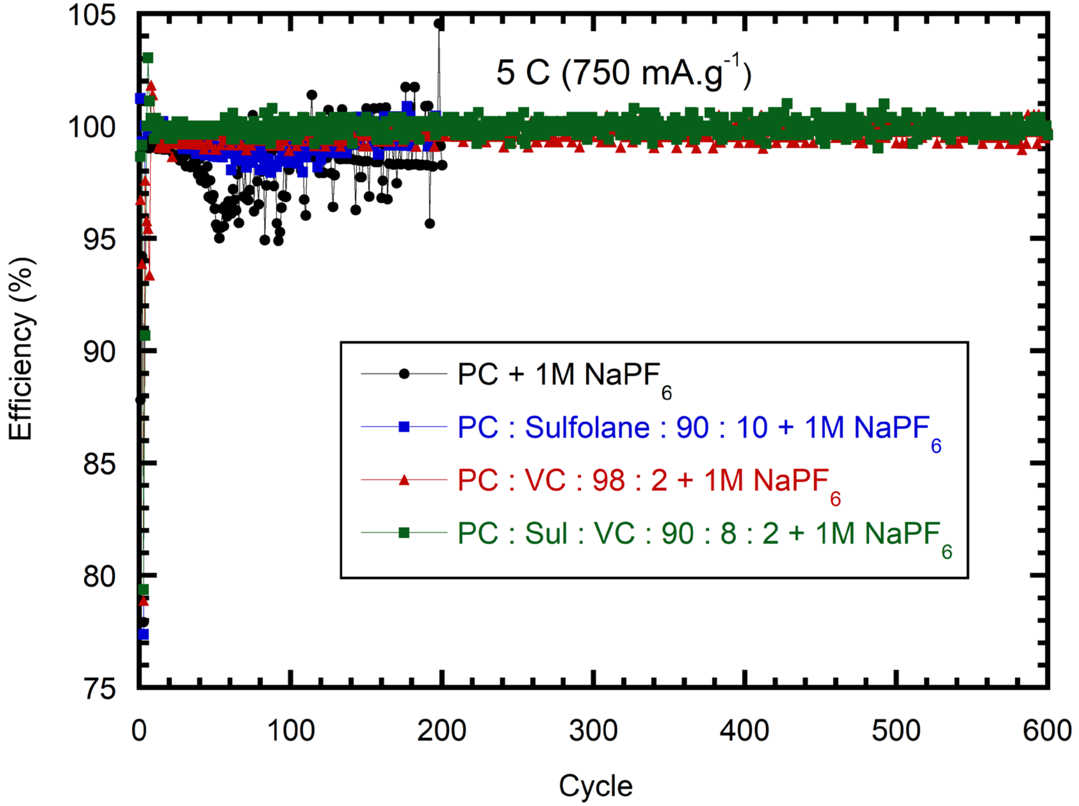
- **PC:Sul:VC 90:8:2 + 1M $NaPF_6$** has an optimized ratio of Sulfolane : VC = 8 : 2
- Excellent stability at 0.2 C for 200 cycles

Technical Accomplishments

Dual-additive based carbonate electrolyte

High-rate Performance (5 C)





- **PC:Sul:VC 90:8:2 + 1M $NaPF_6$** shows a superior performance compared to single and without additive.
- After 600 cycles, cells with dual-additive based electrolyte still shows high capacity (103 mAh g^{-1}), high ICE (99.9 %) and retains 94 % of initial capacity.