

Low-cost and Long-life Cathodes for Sodium-ion Batteries



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Background

Sodium-ion battery market opportunities are rapidly expanding, propelled by advantages such as low-cost raw materials, environmental friendliness, and shared manufacturing pathways with lithium-ion chemistry. Among various cathode options, layered oxides derived from non-critical, earth-abundant transition metals stand out for their improved performance, structural stability, and low materials cost. In this work, we developed a fluorinated $\text{Na}_{0.67}\text{Mn}_x\text{Fe}_y\text{Ti}_{1-x-y}\text{O}_2$ cathode featuring large single-crystalline particles, which suppress particle fracture during electrode fabrication and maintain high structural integrity through a phase-pure P2 structure. A thin, single-layer Na nanograin, composed of Na salts and voids, forms on the particle surface, stabilizing surface properties and reducing interfacial side reactions. We have also developed a robust co-precipitation route capable of synthesizing a wide range of Mn-rich compositions, yielding secondary particles with controlled morphology and a narrow particle size distribution. Furthermore, we have developed electrolyte formulations that enhance cycling stability by facilitating reversible phase transitions in layered oxide and NASICON-type cathode materials.

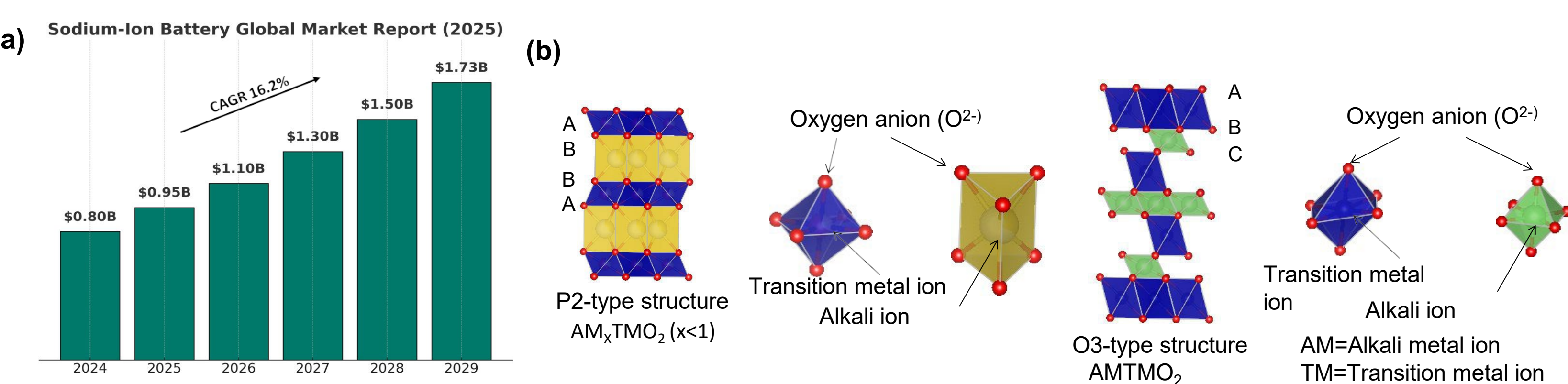


Figure 1. (a) Market growth rate of Sodium-ion batteries (b) Structure of P2-type and O3-type layered oxide sodium cathodes

Results and Discussion

Cathode materials synthesis and optimization

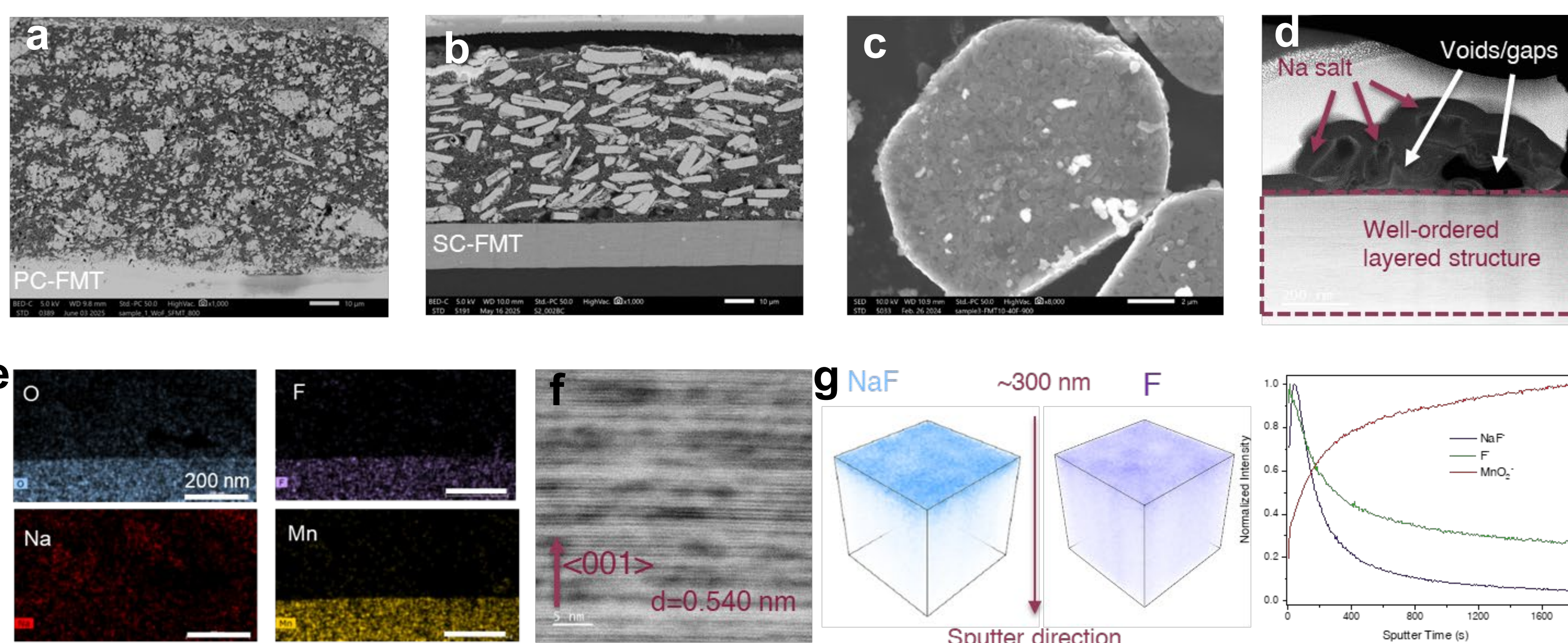


Figure 2. (a) Cross-sectional SEM images of electrodes of (a) PC-FMT (b) SC-FMT (c) SEM image, (d) Cross-sectional HAADF-STEM image, (e) mapping scan results of related elements, and (f) enlarged view of dashed box from (d) of F incorporated SC-FMT (g) Individual spatial distributions of the selected secondary ions and normalized (to their maximum) depth profiles

- Polycrystalline FMT with smaller particles is prone to breakdown during electrode fabrication, whereas single-crystal FMT offers a denser morphology and superior mechanical stability
- Fluorinated sample shows a plate-like morphology with a thickness of 2 μm and a diameter of 10-15 μm
- F forms a concentration gradient from the surface to the internal (no surface F loss during washing)
- It shows a well-ordered layered structure in the bulk

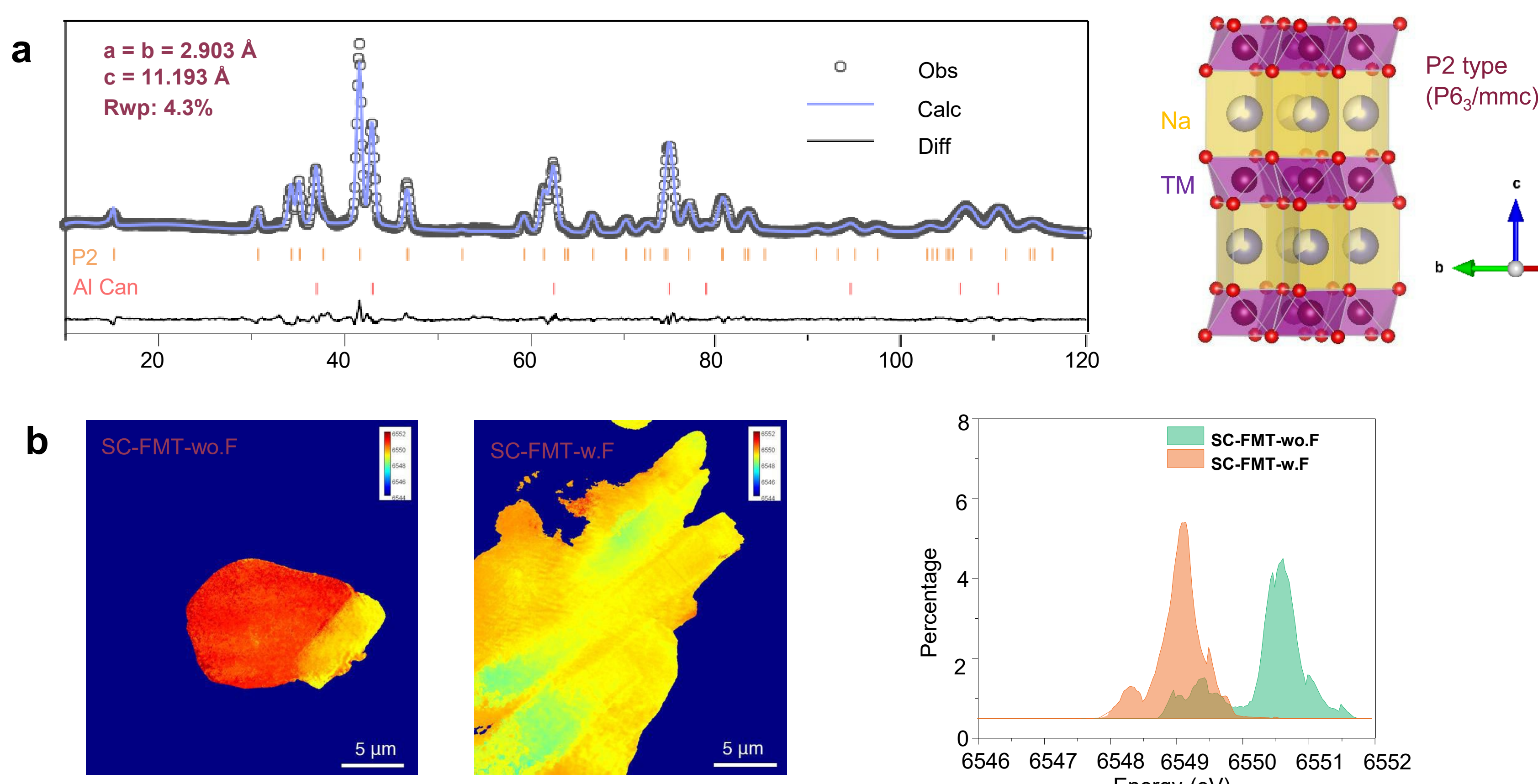


Figure 3. (a) Rietveld refinement of the XRD pattern of F incorporated SC-FMT and schematic illustration of the structure. (b) 2D Mn valence state distribution of FMT and histograms of Mn valence distribution in SC-FMT with and without F.

- Pure P2 phase after F incorporation
- Fluorine incorporation reduces the Mn oxidation state by charge compensation

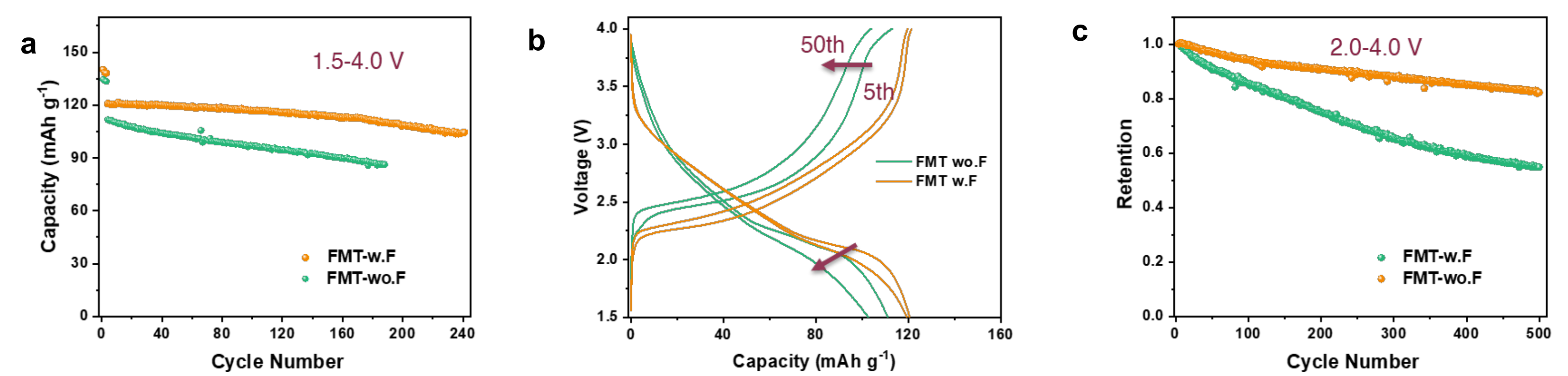
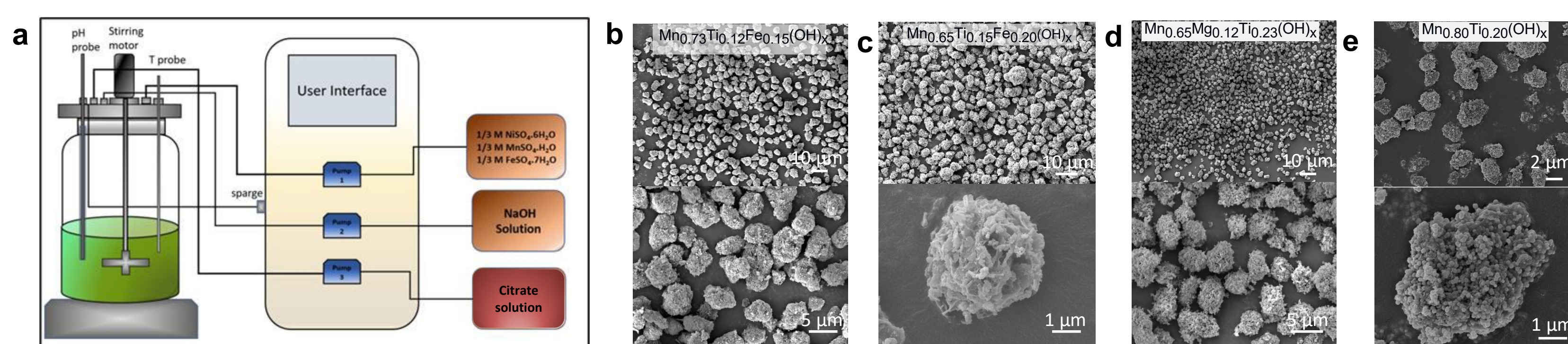


Figure 4. (a) Cycling performance at 0.5 C (1C = 130 mA/g) during 1.5-4.0 V. (b) Charging and discharging profiles of FMT without and with F incorporation at 5th and 50th cycles. (c) Cycling performance at 0.5 C during 2.0-4.0 V.

- Fluorine incorporation is effective in maintaining cycling stability, and mitigating voltage and capacity fade



- Sodium citrate-assisted method provides stronger metal-ligand complexation, leading to well-defined secondary particle morphology with narrow particle size distribution across diverse Mn-rich compositions

Electrolyte Engineering

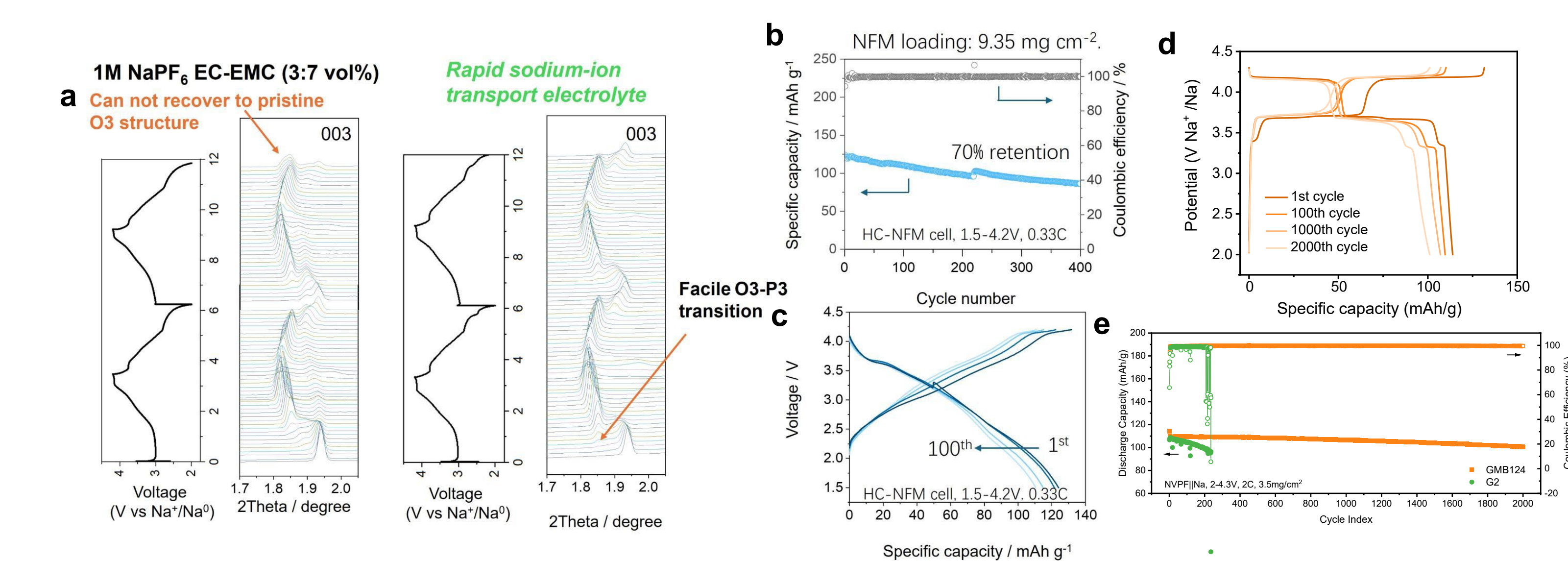


Figure 6: (a) In-situ synchrotron XRD reveals enhanced reversible O3-P3 phase transition in NFM|Na cells, (b) cycling stability, and (c) voltage profile with rapid Na^+ ion transport electrolyte, and (d) voltage profiles and (e) cycling stability of NVPF|Na cells with GMB electrolyte

- Rapid sodium-ion transport electrolyte enable facile O3-P3 transition during cycling
- HC-NFM cells retained 70% of their capacity after 400 cycles
- GMB electrolyte has 92.9% retention after 2,000 cycles, providing better stability than G2-based electrolyte

Conclusion and Perspective

- A molten salt method was employed to tailor cathode particle morphology, leading to fast Na-ion transport in dense plate-like microstructure and high structural integrity
- A thin surface layer, resulting from partial fluorination, suppresses interfacial side reactions and promote longer cycle life
- A solid-state, dry synthesis method produces phase-pure, carbon-coated NVPF crystals with well-defined 2-3 μm particle size, preserving structural integrity and delivering high capacity
- The ether-based high-voltage-tolerant GMB124 electrolyte sustains a long cycle life for the NVPF cathode with a 99.9% average Coulombic efficiency and a 92.9% retention after 2,000 cycles.
- Rapid sodium-ion transport electrolyte enable facile O3-P3 transition to suppress irreversible capacity loss.
- HC-NFM full cells retained 70% capacity after 400 cycles.
- Future work will involve leveraging AI capabilities to engineer cathode structure to mitigate mechanical degradation and local hotspot of safety concerns and improvement of full cell performance for rare, extreme conditions, such as mechanical shock, and wide temperature swing.

Acknowledgements

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