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Supporting Information

Inhibition of sodium dendrite by solvent structural reorganization for non-flammable high-performance sodium-metal batteries

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Keywords: Sodium-metal batteries; Sodium dendrite; In-situ optical visualization; High-safety electrolyte, Electrolyte simulation

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1. Experimental Section

1.1 Raw materials

Na metal stored in kerosene was purchased from Sigma-Aldrich. Triethyl phosphate (TEP), Ethylene carbonate (EC), Diethyl carbonate (DEC), fluoroethylene carbonate (FEC), and hexafluorophosphate ($NaPF_6$) were purchased from DoDo Chem (China). Other chemical reagents were provided by Sinopharm Chemical Reagent Co. Ltd.

1.2 Electrolyte preparation

1 M $NaPF_6$ was dissolved in TEP with 5 vol% BSTFA, and 5 vol% FEC. All electrolytes were prepared inside a glovebox with O_2 and H_2O content $\leqslant$ 0.05 ppm (Vigor, China).

1.3 General Characterization

The morphologies and microstructures of the Na surface were characterized by using a field emission scanning electron microscope (FESEM, Hitachi S4800) and energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was operated by using an ESCALAB_250Xi X-ray photoelectron spectrometer. To avoid direct contact with air, the samples containing Na metal were all transferred in a homemade device filled with pure Ar.

1.4 Electrochemical Measurement

All cells (CR20332 type) were assembled in a glovebox filled with Ar, which O_2 and H_2O content $\leqslant$ 0.05ppm. Cyclic voltammograms (CV) were carried out in an electrochemical workstation (DH7000, DONGHUA, China). CV of Na/NVP full cell was scanned from 2.6 to 3.8 V at a scan rate of 0.1 mV s^{-1}. The ionic conductivities of the different electrolytes were measured by a Benchtop conductivity meter (LeiCi, China).

1.5 Preparation of Full cells and Symmetric cells

$Na_3V_2(PO_4)_3$ (NVP) was synthesized according to the literature[1]. The NVP cathode electrodes used for full cells were fabricated by maxing the NVP, super P, and PVDF binder at a mass ratio of 7:2:1 on Al foil (～1.1 mg cm^{-2}). Na anode electrode was made from purchased sodium blocks pressed into 10mm sodium sheets. The Na/NVP full cells were cycled between 2.6-3.8V (1C was defined as 117.6 mA g^{-1}).

2. Supplementary data

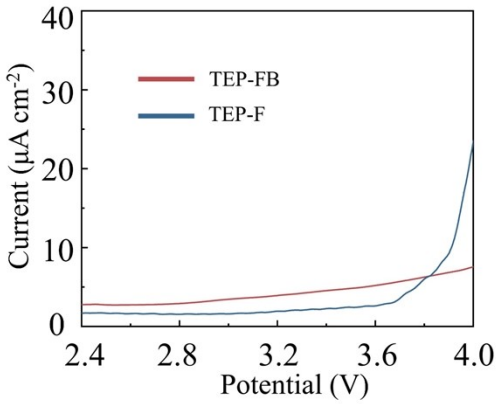

Fig. S1 Oxidation stabilities for the TEP-FB and TEP-F electrolytes in symmetrical stainless-steel cells at a scan rate of 0.1 mV s^{-1}.

Fig. S2 Nonwoven fabric morphology after self-extinguishing experiment using TEP-F electrolyte.

Fig. S3 The radial distribution function plots of Na-O_{PF6^-}, Na-O_{FEC}, and Na-O_{TEP} pairs in the TEP-F electrolyte.

Fig. S4 The mean square displacement of Na^+ in TEP-FB and TEP-F electrolytes.

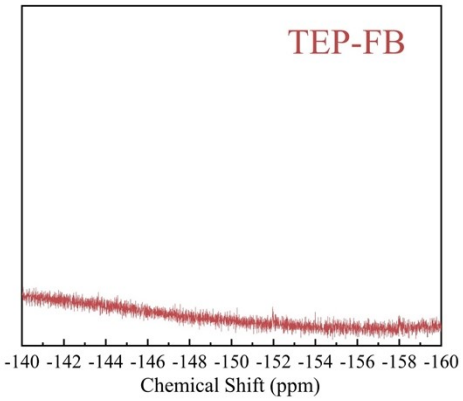

Fig. S5 ^{19}F NMR spectra of TEP-FB.

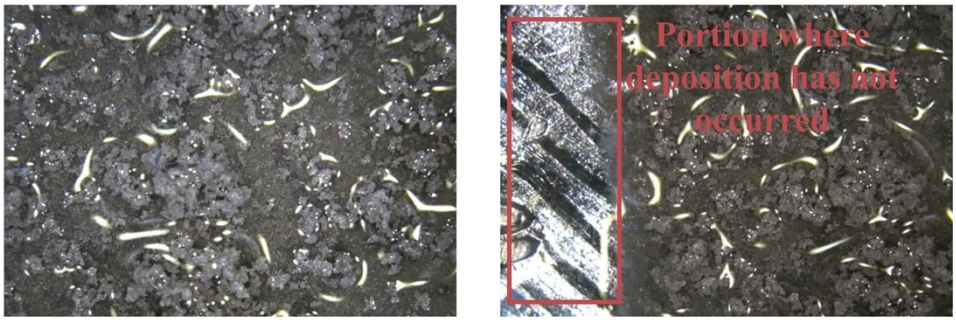

Fig. S6 Enlarged view of the sodium electrode measurement after completion of the reaction.

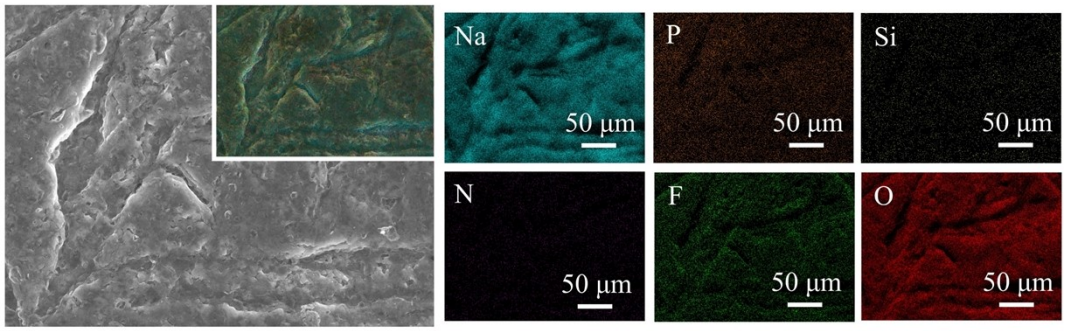

Fig. S7 EDS mapping images of Na anode with TEP-F electrolyte.

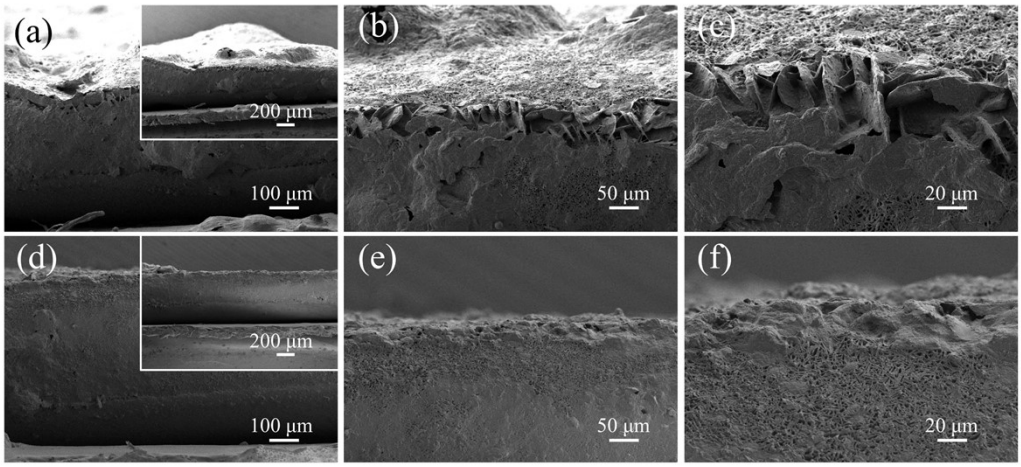

Fig. S8 SEM image of sodium anode side, (a-b) TEP-F and (d-f) TEP-FB.

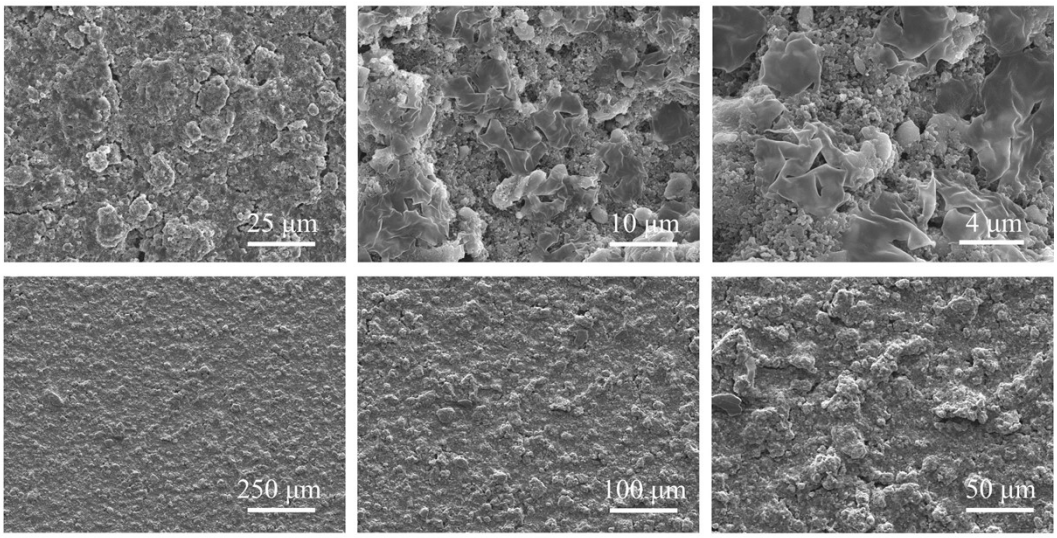

Fig. S9 SEM images of the CEI layer obtained after a complete cell cycle using sodium metal and NVP in TEP-FB electrolytes.

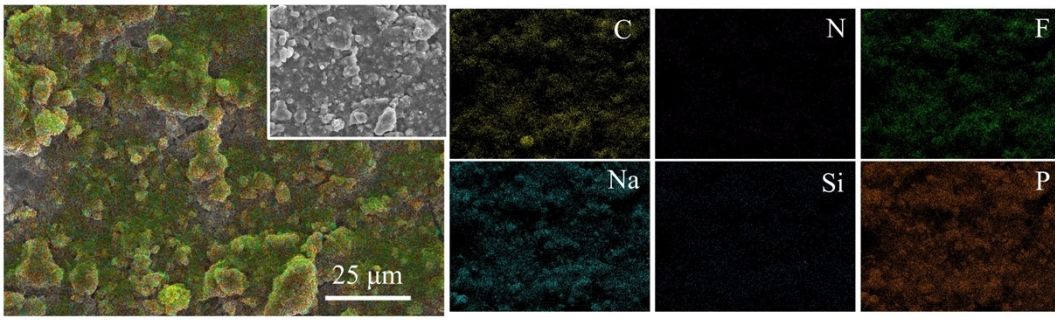

Fig. S10 EDS mapping of the CEI layer obtained after a full cell cycle with sodium metal and NVP in TEP-FB electrolytes.

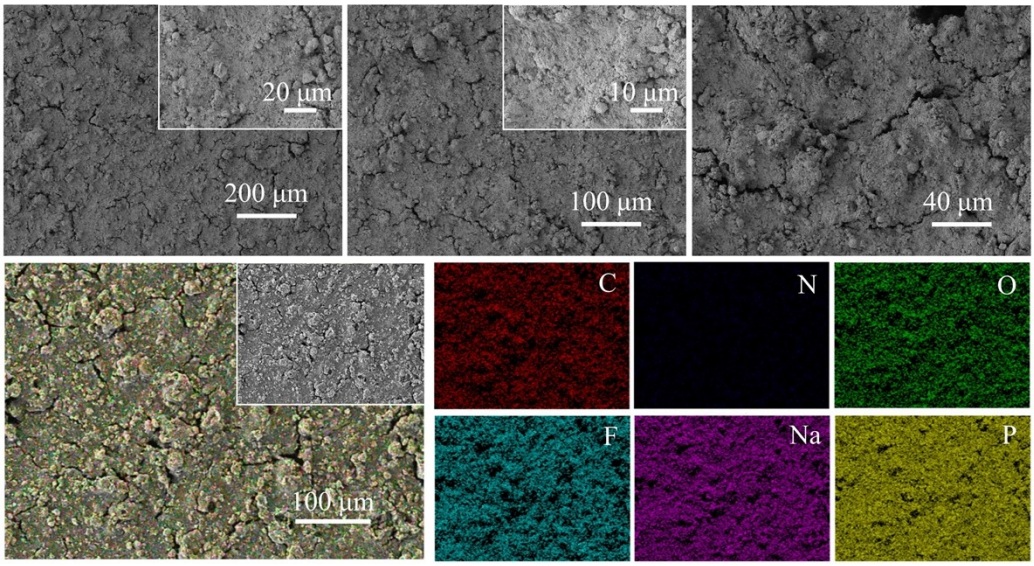

Fig. S11 SEM images and EDS mapping of the CEI layer obtained after a complete cell cycle using sodium metal and NVP in TEP-F electrolytes.

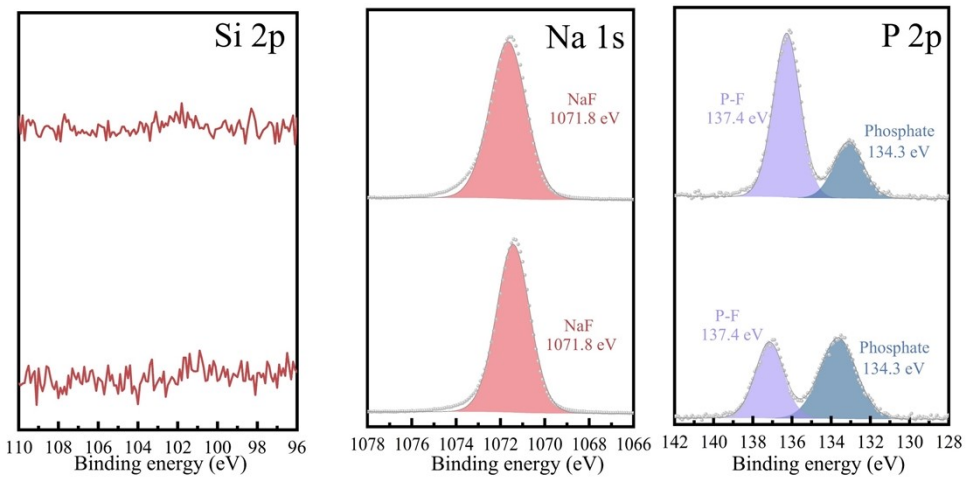

Fig. S12 (a) Si 2p, (b) Na 1s, and (c) P 2p peaks of TEP-F and TEP-FB electrolytes.

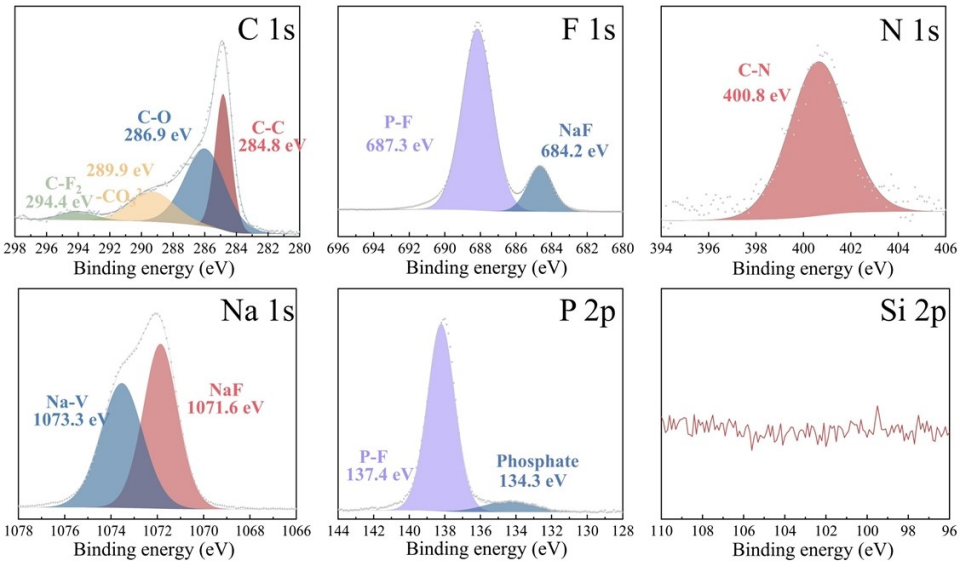

Fig. S13 XPS characterization of the NVP cathode with TEP-FB electrolyte.

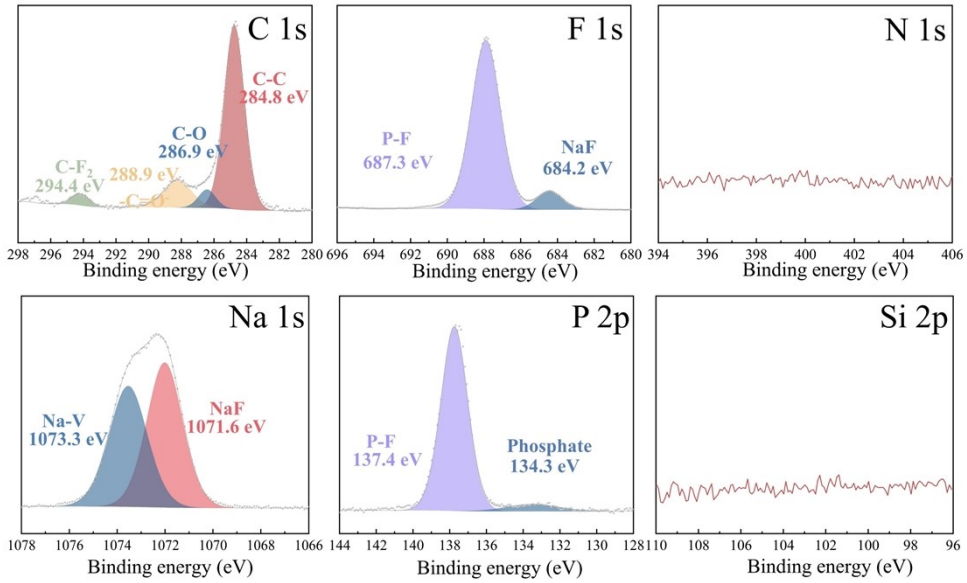

Fig. S14 XPS characterization of the NVP cathode with TEP-F electrolyte.

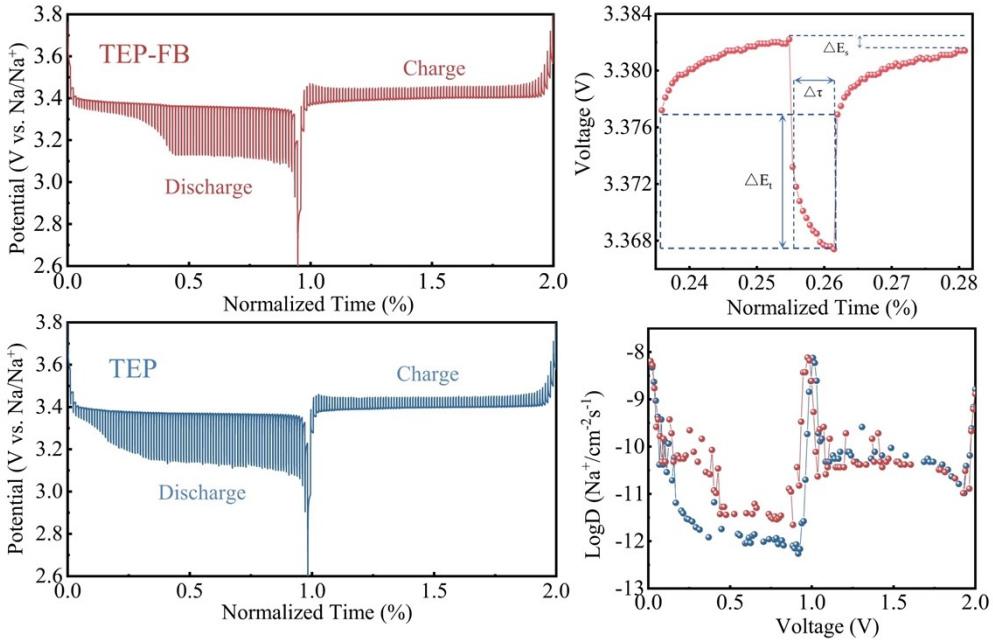

Fig. S15 GITT testing of TEP-F and TEP-FB electrolytes.

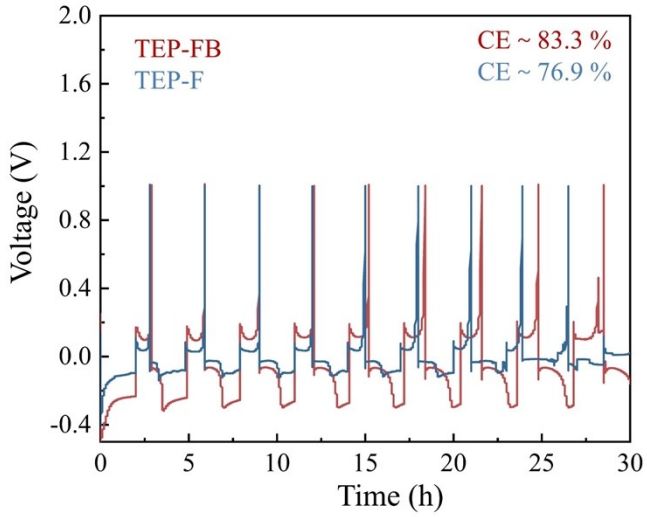

Fig. S16 Coulombic efficiency of Cu/Na cells with TEP-FB and TEP.

References

1. T. Wei, G. Yang and C. Wang, *Nano Energy*, 2017, **39**, 363-370.