

Supporting Information

Solvation Structure Fine-Tuning Enables High Stability Sodium

Metal Batteries

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1. Experimental Section

1.1 Raw materials

Na metal stored in kerosene was purchased from Sigma-Aldrich. 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 EC, DEC, and FEC (1:1:0.05, in volume ratio, EDF) solvent, and EC, DEC, FEC, and PMS (1:1:0.05:0.03, in volume ratio, EDF/PMS) solvent. All electrolytes were prepared inside a glovebox with O_2 and H_2O content \leq 0.05 ppm (Vigor, China).

1.3 General Characterization

The morphologies and microstructures of sodium metal 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, all 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 \leq 0.05ppm. The LSV (2.5 to 6.0 V with Na/steel cells at 0.5 mV s^{-1}) measurements were carried out in an electrochemical workstation (DH7000, DONGHUA, China).

1.5 Preparation of Full cells and Symmetric cells

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) was synthesized according to the literature [1]. The NVP cathode electrodes used for full cells were fabricated by maxing NVP, super P, and PVDF binder at a mass ratio of 7:2:1 on Al foil ($\sim 1.14 \text{ mg cm}^{-2}$). Na anode electrode was made from purchased sodium blocks pressed into 15.9 mm sodium sheets. The Na/NVP full cells were cycled between 2.6-3.8V (1C was defined as 117 mA g^{-1}).

2. Supplementary data

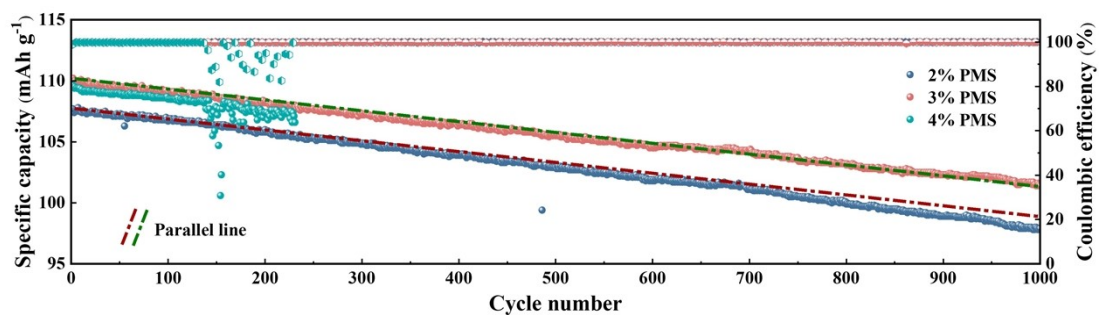


Fig. S1. Cyclability with different electrolytes additive concentrations of Na||NVP full cells at 2C.

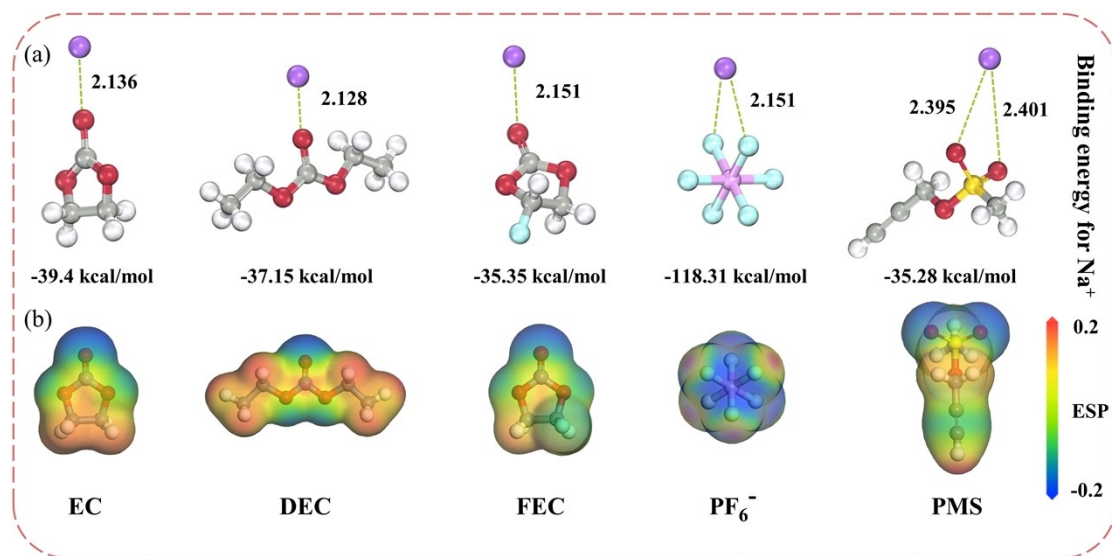


Fig. S2. (a) Adsorption energies and bond length of Na⁺ with solvent molecules and anions. (b) Electrostatic potential map (ESP) of solvent molecules and anions.



Fig. S3. Schematic of the electrochemical deposition of EDF electrolyte at 100th second in 50 mA cm⁻².

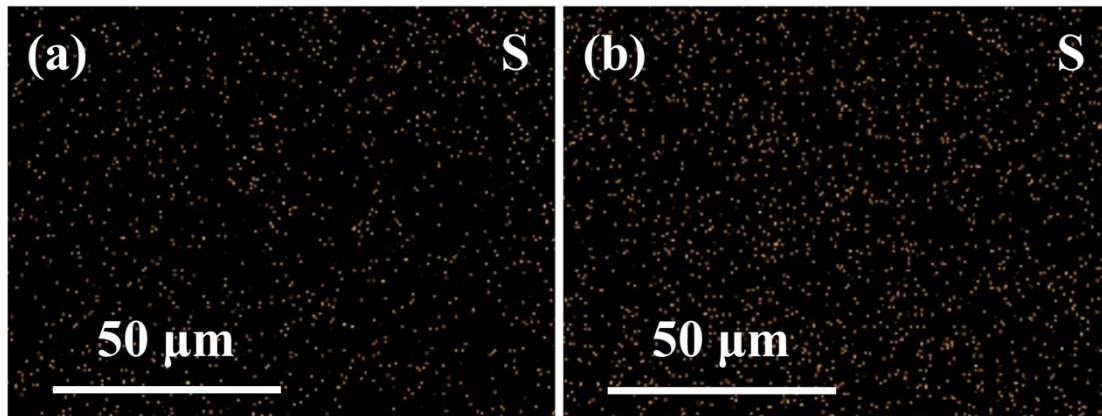


Fig. S4. Enlarged mapping image of S element on (a) EDF-80r and (b) EDF/PMS-80r SEI films.

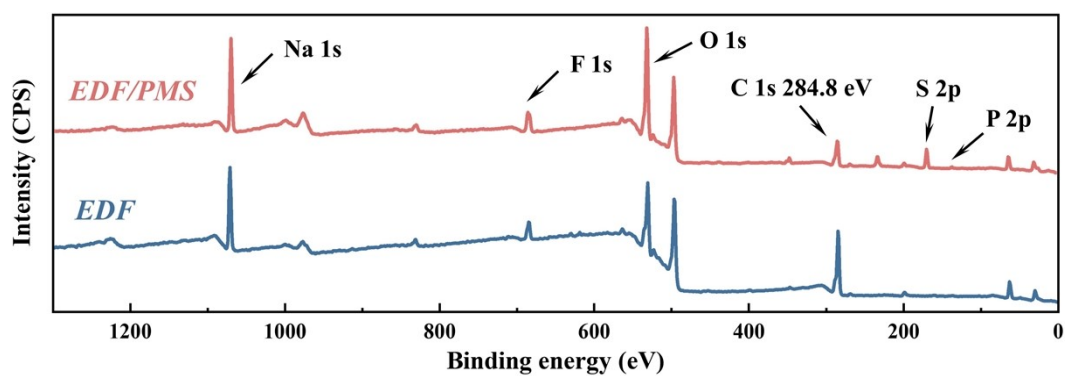


Fig. S5. XPS full spectrum of SEI films in EDF and EDF/PMS electrolytes.

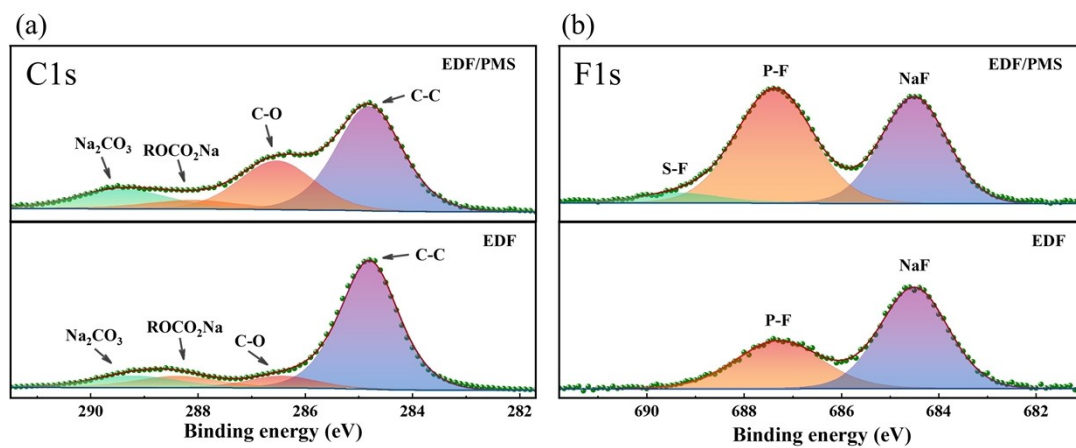


Fig. S6. (a) C 1s and (b) F 1s peaks of EDF and EDF/PMS.

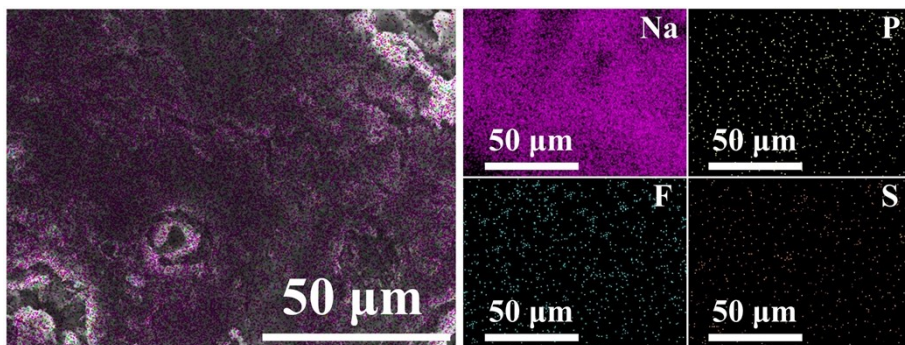


Fig. S7. EDS mapping of Na anode surface after 1000 cycles in Na||NVP full cells with EDF/PMS electrolyte.

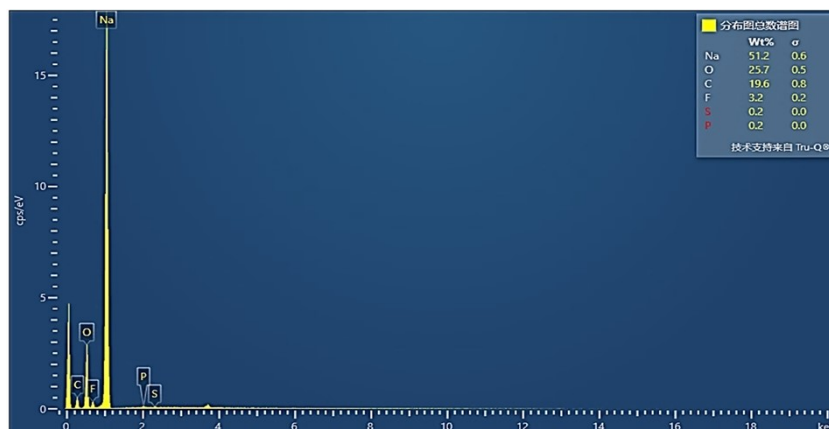


Fig. S8. Element content of Na anode surface after 1000 cycles in Na||NVP full cells with EDF/PMS electrolyte.

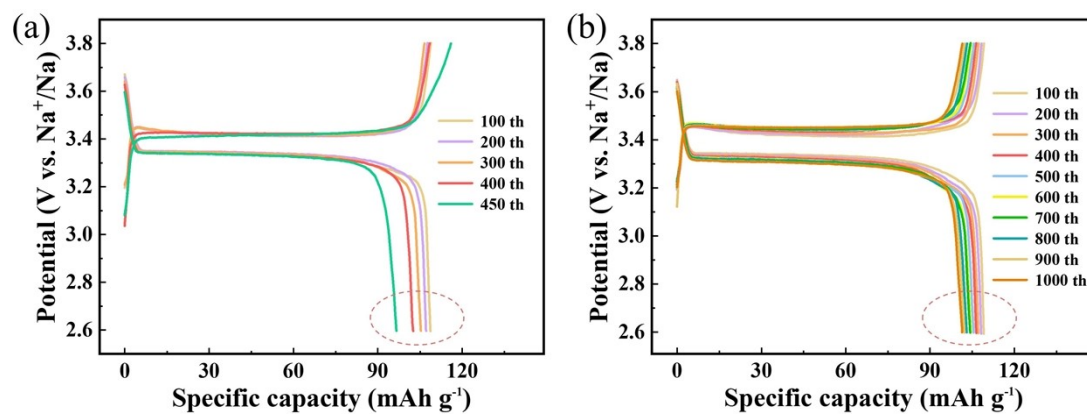


Fig. S9. Charge-discharge voltage curves of (a) EDF and (b) EDF/PMS at different cycles.

References

- [1] R. Klee, M.J. Aragón, R. Alcántara, J.L. Tirado, P. Lavela, High-Performance $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Cathode for Sodium-Ion Batteries Prepared by a Ball-Milling-Assisted Method, *Eur. J. Inorg. Chem.* 2016 (2016) 3212-3218.