

## Supporting Information

### **Methyl Propionate–Dominant Electrolyte for Enhanced Kinetics and Low-Temperature Performance of Prussian Blue Analogue Rechargeable Sodium-Ion Batteries**

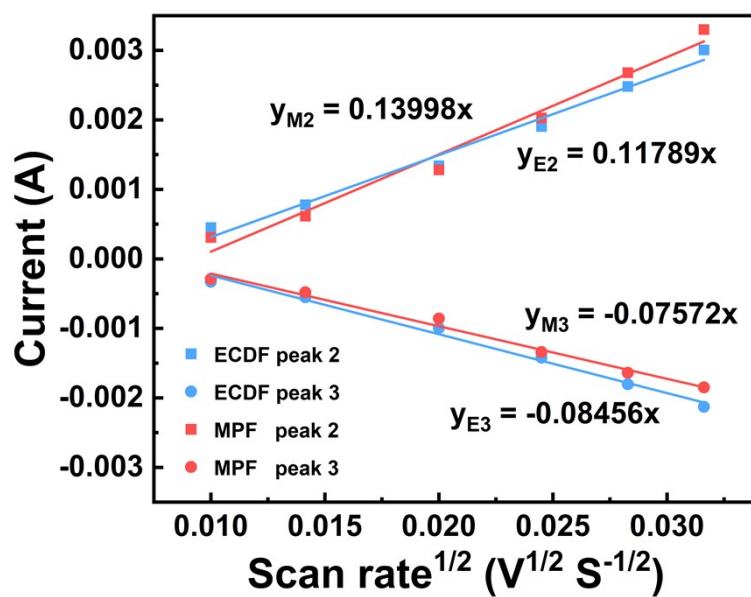
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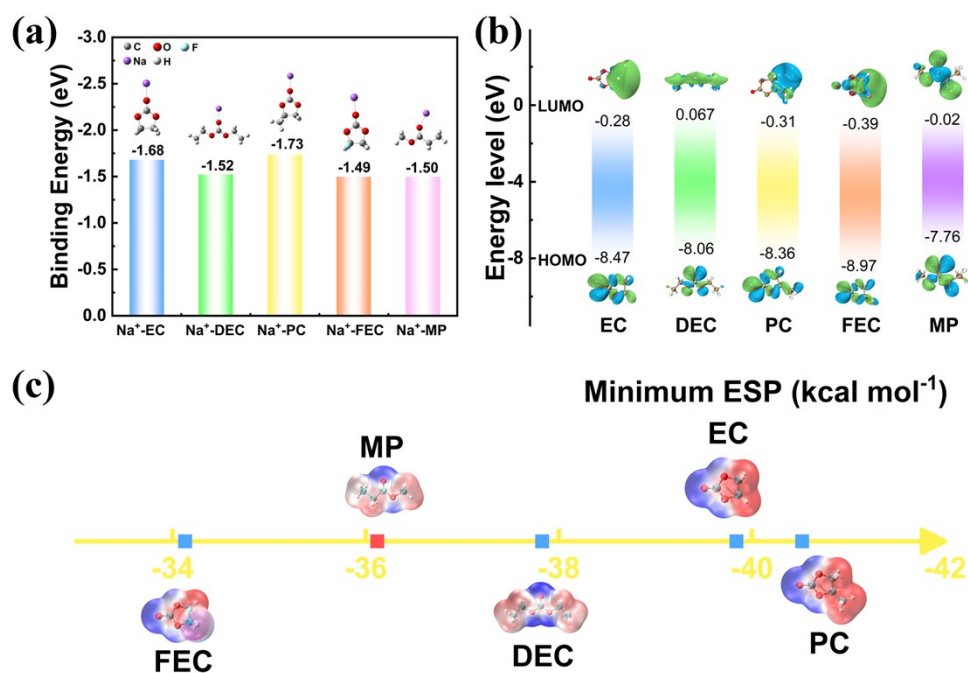
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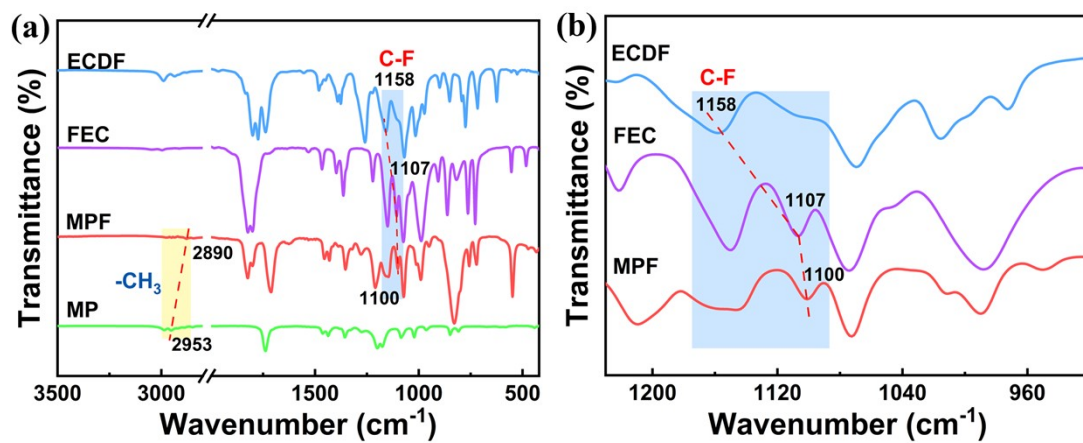
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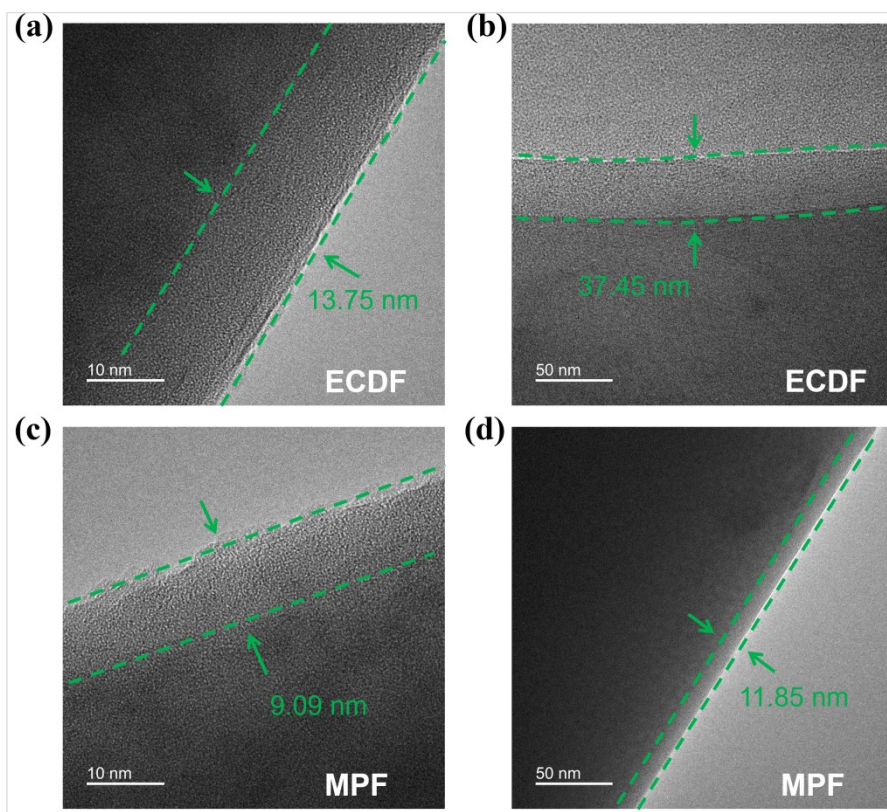
**Fig. S1.** PBA|ECDF|Na and PBA|MPF|Na half-cells linear relationship between current and  $v^{1/2}$  (scan rate)



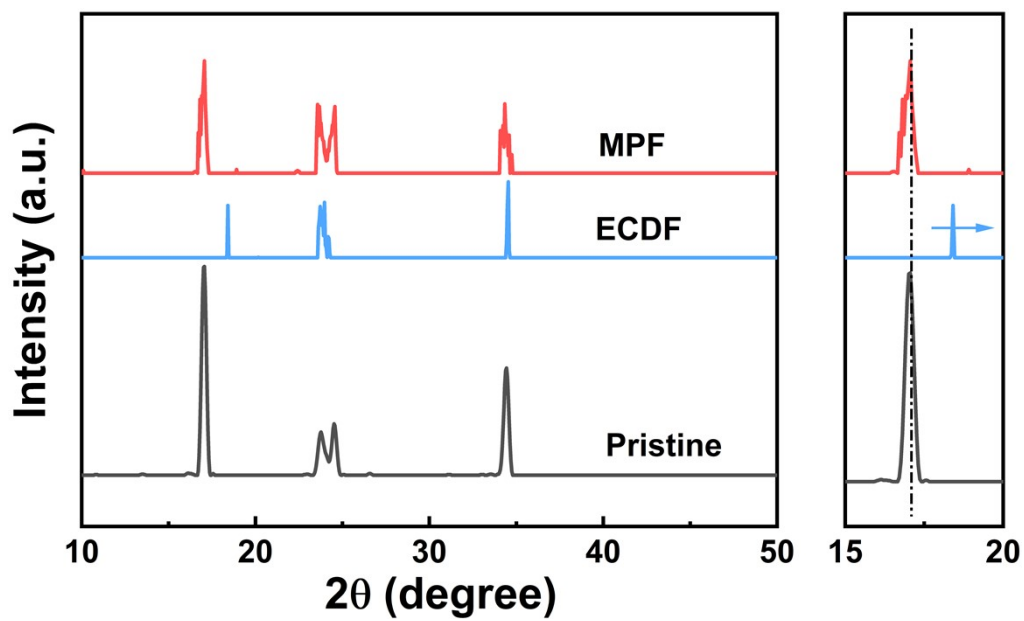
**Fig. S2.** DFT calculations. (a) Binding energies and corresponding structural models of different solvents with Na<sup>+</sup>. (b) HOMO and LUMO energy levels of different solvents. (c) ESP<sub>min</sub> values of various solvents.



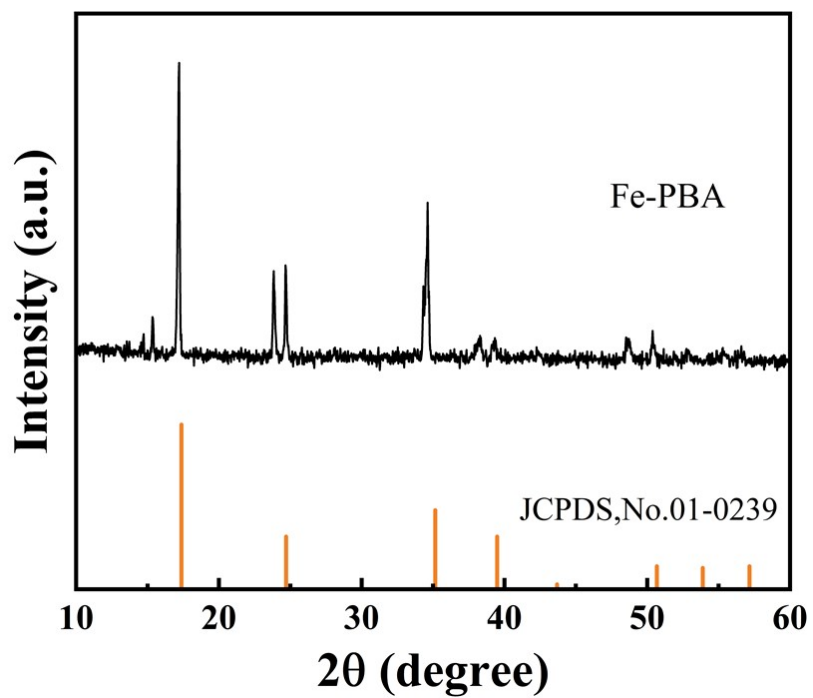
**Fig. S3.** (a) FTIR spectra of individual solvents and their various combinations, and (d) their local enlarged view.



**Fig. S4.** TEM image of cycled PBA cathode in (a, b) ECDF electrolyte and (c, d) MPF electrolyte.



**Fig. S5.** Comparison of XRD patterns for the PBA cathode in its initial state and after cycling.



**Fig. S6.** XRD pattern of the as-synthesized Fe-PBA cathode material.

**Table S1** Electrochemical properties of PBA-sodium-ion batteries with various designs

Electrode	Electrolyte	Specific capacity (mAh g <sup>-1</sup> )	Wide-Temp. Performance: Capacity retention, cycle @ C (°C)	Ref.
PBA  Na (fluorine-rich CEI)	1 M NaPF <sub>6</sub> in MP /FEC (9:1)	155 @1C	80.57%, 100@ 1C (50°C); 83.4%, 200@ 1C (25°C); 86.68%, 300@ 1C (-20°C)	This work
PBA  Na (Cs <sup>+</sup> /Zn <sup>2+</sup> co-doped)	1 M NaClO <sub>4</sub> in EC/DEC (1:1), 8% FEC	108 @5C (-20°C)	79.63%, 5400@5C (-20°C)	[1]
FePB  HC (FePB@S-CEI)	1 M NaClO <sub>4</sub> in EC/DEC (1:1), 2 % 1-propene-1,3sultone (PS)	124@0.1C	92.7%, 400@1C (0°C) 80.7%, 400@1C (60°C)	[2]
FeVO-PBA  Na	1 M NaPF <sub>6</sub> in DEG-DME	148.9@0.5C	92.6%, 400@ 5C (60°C); ~100%, 300@ 1C (-30°C)	[3]
I-PB  Na (ice-assisted)	1 M NaClO <sub>4</sub> in EC/DEC (1:1), 4% FEC	123@15 mA g <sup>-1</sup>	72.6%, 100@ 150 mA g <sup>-1</sup> (60°C); ~100%, 100@ 150 mA g <sup>-1</sup> (-10°C)	[4]
M5-PBA  HC (M=Mn, Fe, Co, Ni, Cu)	1 M NaClO <sub>4</sub> in EC:PC:FEC (47.5 :47.5:5)	142.4@0.1C	82.9%, 500@ 1C (30°C);	[5]
M-BA  Na	1 M NaClO <sub>4</sub> in EC/DEC (1:1), 5% FEC	131.1@0.1C	94.8%, 200@ 1C (25°C)	[6]
FeNi-MnHCF  Na	1 M NaPF <sub>6</sub> in PC/EMC, 4% /FEC+1 wt% ETFA	107.1@0.1C	92.1%, 1120@(1C, 77.4 mAhg <sup>-1</sup> (-20°C)	[7]
Na <sub>2</sub> Fe[Fe(CN) <sub>6</sub> ]·2H <sub>2</sub> O  Na	1 M NaPF <sub>6</sub> in tetraglyme	145@0.1C	>70%, 140@30 mA g <sup>-1</sup> (25°C)	[8]
NiMnFe-PBA  Na	1 M NaClO <sub>4</sub> in PC, 5% FEC	122.8@10 mA g <sup>-1</sup>	71.35%, 300@100 mA g <sup>-1</sup> (25°C)	[9]
NaKMhCF  Na	1 M NaClO <sub>4</sub> in PC, 5% FEC	129.3@10 mA g <sup>-1</sup>	77.0%, 500@500 mA g <sup>-1</sup> (25°C)	[10]
Zn-substituted Fe- PBA  Na	1 M NaPF <sub>6</sub> in EC/DEC (1:1)	114.56@10 mA g <sup>-1</sup>	80.27%, 350@200 mA g <sup>-1</sup> (25°C)	[11]
NaMHCF  Na	1 M NaPF <sub>6</sub> in PC/EC (1:1),	159.2 @0.1C	90%, 300@350 mA g <sup>-1</sup> (25°C); 65%, 300@0.5C (-20°C)	[12]

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