

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

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In this study, we focus on modifying the interface using methyl propionate (MP)-based electrolytes to reduce the thickness of the cathode electrolyte interphase (CEI) and to improve both the stability and rate capacity. The results of our work are compared with those of previous studies, which are listed below.

**Table 1** 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 @0.1C                                | 80.57%, 100@ 1C (50°C); 83.4%, 200@ 1C (25°C); 86.68%, 300@ 1C (-20°C) | <b>This work</b> |
| 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  | 148.9@0.5C                               | 92.6%, 400@ 5C (60°C);   | [3]              |

|  |  |                              |  |      |
|--|--|------------------------------|--|------|
|  | DEG-DME  |                              | ~100%, 300@ 1C (-30°C)   |      |
| I-PB  Na<br>(ice-assisted)   | 1 M NaClO <sub>4</sub> in<br>EC/DEC (1:1), 4%<br>FEC         | 123@15 mA g <sup>-1</sup>    | 72.6%, 100@ 150 mA g <sup>-1</sup><br>(60°C);<br>~100%, 100@ 150 mA g <sup>-1</sup><br>(-10°C) | [4]  |
| M5-<br>PBA  HC (M=<br>Mn, Fe, Co, Ni,<br>Cu)                       | 1 M NaClO <sub>4</sub> in<br>EC:PC:FEC (47.5:<br>47.5:5)     | 142.4@0.1C                   | 82.9%, 500@ 1C (30°C);   | [5]  |
| M-BA  Na   | 1 M NaClO <sub>4</sub> in<br>EC/DEC (1:1), 5%<br>FEC         | 131.1@0.1C                   | 94.8%, 200@ 1C (25°C)  | [6]  |
| FeNi-<br>MnHCF  Na   | 1 M NaPF <sub>6</sub> in<br>PC/EMC, 4%<br>/FEC+1 wt%<br>ETFA | 107.1@0.1C                   | 92.1%, 1120@(1C, 77.4 mAhg <sup>-1</sup><br>(-20°C)  | [7]  |
| Na <sub>2</sub> Fe[Fe(CN) <sub>6</sub> ]<br>·2H <sub>2</sub> O  Na | 1 M NaPF <sub>6</sub> in<br>tetraglyme                       | 145@0.1C                     | >70%, 140@30 mA g <sup>-1</sup> (25°C)   | [8]  |
| NiMnFe-<br>PBA  Na   | 1 M NaClO <sub>4</sub> in PC,<br>5% FEC                      | 122.8@10 mA g <sup>-1</sup>  | 71.35%, 300@100 mA g <sup>-1</sup><br>(25°C)   | [9]  |
| NaKMnHCF  Na   | 1 M NaClO <sub>4</sub> in PC,<br>5% FEC                      | 129.3@10 mA g <sup>-1</sup>  | 77.0%, 500@500 mA g <sup>-1</sup> (25°C)   | [10] |
| Zn-substituted<br>Fe- PBA  Na                                      | 1 M NaPF <sub>6</sub> in<br>EC/DEC (1:1)                     | 114.56@10 mA g <sup>-1</sup> | 80.27%, 350@200 mA g <sup>-1</sup><br>(25°C)   | [11] |
| NaMnHCF  Na  | 1 M NaPF <sub>6</sub> in<br>PC/EC (1:1), 10%<br>FEC          | 159.2 @0.1C                  | 90%, 300@350 mA g <sup>-1</sup> (25°C);<br>65%, 300@0.5C (-20°C)                               | [12] |

EC: Ethylene carbonate; DEC: Diethyl carbonate; FEC: Fluoroethylene carbonate; PC: propylene carbonate; ETFA: 2,2,2-trifluoroethyl acetate; EMC: ethyl methyl carbonate

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