Supplementary information

A safe and non-flammable sodium metal battery based on an ionic liquid electrolyte

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Supplementary Figures

Supplementary Figure 1. Na plating/stripping profiles of a Na/Pt cell using buffered Na-Cl-IL electrolyte without [EMIm]FSI additive at a current density of 0.5 mA cm\(^{-2}\).
Supplementary Figure 2. Morphology of Na plating at different current densities. a, b, SEM images of Na-plated Cu foils in Na/Cu cells at a current density and of 0.5 and 1.5 mA cm$^{-2}$, respectively. Specific capacity, 0.5 mAh cm$^{-2}$. The cells were cycled for 5 cycles and stopped at discharge state (Na plating on Cu) prior to characterization. Scale bars in a and b, 10 μm.
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![Graph showing galvanostatic charge-discharge curves of Na/NVP@rGO cells with different loadings.]
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91.2\% after 363 cycles
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Supplementary Figure 19. Surface XPS spectrum of a Na anode from a Na/NVP@rGO cell with the NVP@rGO mass loading of 5.0 mg cm\(^{-2}\) at fully charged state. Prior to XPS measurement, the cell was cycled for 20 cycles at 100 mA/g for sufficient formation of SEI.
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Supplementary Figure 21. Capacity and Colombic efficiency retention of a Na/NVP@rGO cell using 1 M NaFSI in [EMIm]FSI IL electrolyte at 150 mA g\(^{-1}\).
Supplementary Figure 22. Capacity and Colombic efficiency retention of a Na/NVP@rGO cell using NaFSI/N-propyl-N-methylpyrroldinium bis(fluorosufonyl)imide (molar ratio of 2:8) IL electrolyte. Current density, 150 mA g\(^{-1}\).
**Supplementary Figure 23.** Galvanostatic charge-discharge curves of a Na/NVP@rGO cell using NaFSI/N-propyl-N-methylpyrrolidinium bis(fluorosufonyl)imide (molar ratio of 2:8) IL electrolyte at varied current densities from 25 to 400 mA g\(^{-1}\).
### Suppementary Table 1. Comparison of representative Na metal battery performances based on IL electrolytes.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>$C_{sp}$ (mAh g$^{-1}$)</th>
<th>CE</th>
<th>Cyclic stability</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>Discharge voltage (V)</th>
<th>$E$ (Wh kg$^{-1}$)</th>
<th>$P$ (W kg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaFePO$_4$</td>
<td>1 M NaBF$_4$ in BMP-TFSI</td>
<td>92</td>
<td>-</td>
<td>67%@100 cycles</td>
<td>~ 1.9</td>
<td>~ 2.8</td>
<td>~ 253</td>
<td>~ 66</td>
<td>1</td>
</tr>
<tr>
<td>NaFePO$_4$</td>
<td>1 M NaClO$_4$ in BMP-TFSI</td>
<td>79</td>
<td>-</td>
<td>62%@100 cycles</td>
<td>~ 1.9</td>
<td>~ 2.8</td>
<td>~ 217</td>
<td>~ 34</td>
<td>1</td>
</tr>
<tr>
<td>NaFePO$_4$</td>
<td>1 M NaPF$_6$ in BMP-TFSI</td>
<td>44</td>
<td>-</td>
<td>57%@100 cycles</td>
<td>~ 1.9</td>
<td>~ 2.8</td>
<td>~ 121</td>
<td>~ 12</td>
<td>1</td>
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<tr>
<td>Na$_{0.44}$MnO$_2$</td>
<td>1 M NaBF$_4$ in BMP-TFSI</td>
<td>84</td>
<td>-</td>
<td>40%@100 cycles</td>
<td>-</td>
<td>~ 2.7</td>
<td>~ 227</td>
<td>~ 28</td>
<td>1</td>
</tr>
<tr>
<td>Na$_{0.44}$MnO$_2$</td>
<td>1 M NaClO$_4$ in BMP-TFSI</td>
<td>97</td>
<td>-</td>
<td>65%@100 cycles</td>
<td>-</td>
<td>~ 2.7</td>
<td>~ 262</td>
<td>~ 52</td>
<td>2</td>
</tr>
<tr>
<td>Na$_{0.44}$MnO$_2$</td>
<td>1 M NaTFSI in BMP-TFSI</td>
<td>92</td>
<td>-</td>
<td>50%@100 cycles</td>
<td>-</td>
<td>~ 2.7</td>
<td>~ 248</td>
<td>~ 37</td>
<td>2</td>
</tr>
<tr>
<td>Na$_{0.44}$MnO$_2$</td>
<td>1 M NaPF$_6$ in BMP-TFSI</td>
<td>38</td>
<td>-</td>
<td>33%@100 cycles</td>
<td>-</td>
<td>~ 2.7</td>
<td>~ 103</td>
<td>~ 9</td>
<td>2</td>
</tr>
<tr>
<td>NVP@C</td>
<td>1 M NaFSI in Py$_{13}$FSI</td>
<td>89</td>
<td>99%</td>
<td>~99%@50cycles</td>
<td>-</td>
<td>~ 3.3</td>
<td>~ 294</td>
<td>~ 1620</td>
<td>3</td>
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<tr>
<td>Na$<em>{0.45}$Ni$</em>{0.22}$Fe$_{0.11}$O$_2$</td>
<td>0.2 M NaTFSI in Py$_{14}$TFSI</td>
<td>~ 150</td>
<td>98%</td>
<td>~ 93%@5 cycles</td>
<td>1.0</td>
<td>~ 3</td>
<td>~ 450</td>
<td>~ 30</td>
<td>4</td>
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<tr>
<td>Na$<em>{0.45}$Ni$</em>{0.22}$Co$<em>{0.1}$Mn$</em>{0.66}$O$_2$</td>
<td>0.45 M NaTFSI in Py$_{14}$TFSI</td>
<td>~ 220</td>
<td>-</td>
<td>~80%@100 cycles</td>
<td>~ 2.5</td>
<td>2.7</td>
<td>550</td>
<td>~ 30</td>
<td>5</td>
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<tr>
<td>NaCrO$_2$</td>
<td>NaFSI in Py$_{13}$FSI (2: 8 in molar)</td>
<td>92</td>
<td>99.7%</td>
<td>-</td>
<td>~ 2.9</td>
<td>~ 267</td>
<td>~ 64</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>NVP@rGO</td>
<td>Buffered Na-Cl-IL</td>
<td>98</td>
<td>99.9%</td>
<td>~ 96%@460 cycles</td>
<td>3.0</td>
<td>~ 3.3</td>
<td>323</td>
<td>~ 1650</td>
<td>This work</td>
</tr>
<tr>
<td>NVPF@rGO</td>
<td>Buffered Na-Cl-IL</td>
<td>114</td>
<td>99.0%</td>
<td>~ 90.6%@710 cycles</td>
<td>3.0</td>
<td>~ 3.75</td>
<td>~ 420</td>
<td>~ 1766</td>
<td>This work</td>
</tr>
</tbody>
</table>

$C_{sp}$, CE, E and P represent specific discharge capacity, Coulombic efficiency, energy density and power density, respectively. BMP, N-butyl-N-methylpyrrolidinium. Py$_{13}$, Py$_{14}$.
N-methyl-N-propylpyrrolidinium. Py$_{14}$, N-butyl-N-methylpyrrolidinium. FSI, bis(fluorosulfonylimide. TFSI, bis(trifluoromethanesulfonylimide.
Supplementary Methods

Preparation of graphene oxide. 1 g flake graphite powder was pre-oxidized in the mixture of 30 mL sulfuric acid and 10 mL nitric acid under stirring for 24 h. After washing with deionized water and drying, the obtained powder was exfoliated in a tube furnace at 1000°C for 10 s, followed by reacting with 60 mL oleum, 0.84 g K₂S₂O₈ and 1.3 g P₂O₅ at 80°C for 5 h under stirring. After cooling down to room temperature, 500 mL deionized water was slowly added to the suspension, and the dried products were obtained by vacuum filtrating and washing for 3 times, and dried in a vacuum oven. The resulted powder was added to 50 mL oleum in ice bath, followed by adding 3 g KMnO₄ slowly under vigorous stirring, during which the temperature was kept below 20°C. The mixture was then heated to 35°C and stirred for another 2 h, and diluted with 500 mL deionized water and added with 2 mL 30 wt% H₂O₂. The dispersion was left overnight, and the brown gel at bottom was washed with deionized water, followed by centrifuging with 1 M HCl solution for 5 times, and then washing with deionized water until the decantate turned nearly neutral.

Details of battery assembly and testing. We found that the powders of NVP@rGO and NVPF@rGO are best to store in an Ar-filled glove box to avoid possible contaminations and absorption of moisture in air. Freshly prepared NVP@rGO and NVPF@rGO electrodes are preferable for good battery performances. Sufficient contact between electrode and separator is important for good rate and cycling performances. The pouch cell was placed under vacuum for 15 min after injecting the electrolyte to enhance the electrolyte permeation into separator and electrodes. The edges of the pouch cells were flattened, and the pouch was further clamped using two clips (0.75 inch, Clipco) between two hardboards for 30 min, realizing a good contact between the electrode and separator. The clips were then removed and no extra pressure was applied on the battery during testing.
Supplementary References


