1 2	Supplementary information
3	A safe and non-flammable sodium metal battery based on an
4	ionic liquid electrolyte
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8 Supplementary Figures

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11 Supplementary Figure 1. Na plating/stripping profiles of a Na/Pt cell using buffered

12 Na-Cl-IL electrolyte without [EMIm]FSI additive at a current density of 0.5 mA cm⁻².



15 Supplementary Figure 2. Morphology of Na plating at different current densities. a, b,

16 SEM images of Na-plated Cu foils in Na/Cu cells at a current density and of 0.5 and 1.5 mA

17 cm^{-2} , respectively. Specific capacity, 0.5 mAh cm⁻². The cells were cycled for 5 cycles and

- 18 stopped at discharge state (Na plating on Cu) prior to characterization. Scale bars in **a** and **b**,
- 19 10 μm.
- 20



- 21
- 22 Supplementary Figure 3. Cross-section morphology of Na plating. a, b, SEM images of a
- 23 Na particle before (**a**) and after (**b**) cutting via focused ion beam. Scale bars in **a** and **b**, 5 μm.
- 24



26 **Supplementary Figure 4.** SEM and the corresponded element mapping images of the cross

27 section of a Na particle via FIB cutting. The Na particle was plated on a Cu foil at a current

28 density of 0.5 mA cm⁻² in a Na/Cu cell. The cell was first cycled for 10 cycles and stopped at

29 discharge state (Na plating on Cu) prior to characterization. Scale bar, 5 μ m.



Supplementary Figure 5. XRD patterns of NVP@rGO.



35 Supplementary Figure 6. Morphology of NVP@rGO. a, b, SEM images of NVP@rGO at

- 36 low and high magnifications, respectively. Scale bars in **a** and **b** are 500 nm and 200 nm,
- 37 respectively.
- 38



- 40 Supplementary Figure 7. TEM images of NVP@rGO. a, b, TEM and High-resolution
- 41 TEM images of NVP@rGO, respectively. Scale bars in **a** and **b** are 200 nm and 5 nm,
- 42 respectively.



Supplementary Figure 8. TGA of NVP@rGO within a temperature range of 25-800 °C with

46 a heating rate of 5 $^{\circ}$ C min⁻¹ in air.



48

Supplementary Figure 9. Variation of specific discharge capacity of NVP@rGO on IL electrolytes with different molar ratios of AlCl₃ and EMIC. Current density, 25 mA g⁻¹. The specific capacity of Na-NVP@rGO battery showed a dependence with the molar ratio of AlCl₃/[EMIm]Cl. Increasing the molar ratio from 1.2 to 1.5 enhanced the specific capacity due to the increased Na ion concentration. However, when the molar ratio further reached 1.6, the specific capacity decreased slightly likely due to increased viscosity.



Supplementary Figure 10. Cyclic stability of a Na/NVP@rGO cell using conventional
organic electrolyte consisting of 1 M NaClO₄ in ethylene carbonate/diethyl carbonate
(EC/DEC, 1:1 by vol) with 5% FEC at a current density of 150 mA g⁻¹.



Supplementary Figure 11. Galvanostatic charge-discharge curves of Na/NVP@rGO cells
with different NVP@rGO loadings of 3.0, 5.0 and 8.0 mg cm⁻² at a current density of 25 mA
g⁻¹.



Supplementary Figure 12. XRD patterns of NVPF and NVPF@rGO.



70 Supplementary Figure 13. SEM image of NVPF@rGO. Scale bar, 500 nm.



Supplementary Figure 14. TGA of NVPF@rGO within a temperature range of 25-800 °C
with a heating rate of 5 °C min⁻¹ in air. The temperature range used for determining rGO
percentage is 180-460 °C.



78 Supplementary Figure 15. CV curve of a Na/NVPF@rGO cell using Na⁺-C-IL electrolyte at

79 a scan rate of 0.1 mV s⁻¹.

80



Supplementary Figure 16. Variety of specific capacity and energy density on different mass
 loadings from 3 to 8 mg cm⁻². The inset showed corresponding galvanostatic
 charge-discharge curves with different loadings 50 mA g⁻¹.



Supplementary Figure 17. Cyclic stability of a Na/NVPF@rGO cell with a NVPF@rGO
mass loading of 5.3 mg cm⁻² using buffered+EtAlCl₂/[EMIm]FSI additive IL electrolyte.
Current density, 150 mA g⁻¹.



92 Supplementary Figure 18. Cyclic stability of a Na/NVPF@rGO cell using buffered
93 Na⁺-C-IL electrolyte without EtAlCl₂ additive at 150 mA g⁻¹ for 300 cycles. The mass
94 loading of NVPF@rGO was 3.0 mg cm⁻².



96

97 Supplementary Figure 19. Surface XPS spectrum of a Na anode from a Na/NVP@rGO cell

98 with the NVP@rGO mass loading of 5.0 mg cm⁻² at fully charged state. Prior to XPS

- 99 measurement, the cell was cycled for 20 cycles at 100 mA/g for sufficient formation of SEI.
- 100





102 Supplementary Figure 20. High-resolution XPS spectra for N 1s of the Na anode from a

103 Na/NVP@rGO cell with the NVP@rGO mass loading of 5.0 mg cm⁻² at different depths.

104 Prior to XPS measurement, the cell was cycled for 20 cycles at 1 C for sufficient formation of

105 SEI.



108 Supplementary Figure 21. Capacity and Colombic efficiency retention of a Na/NVP@rGO

- 109 cell using 1 M NaFSI in [EMIm]FSI IL electrolyte at 150 mA g⁻¹.
- 110



111

112 Supplementary Figure 22. Capacity and Colombic efficiency retention of a Na/NVP@rGO

113 cell using NaFSI/N-propyl-N-methylpyrrolidinium bis(fluorosufonyl)imide (molar ratio of

114 2:8) IL electrolyte. Current density, 150 mA g^{-1} .



117 Supplementary Figure 23. Galvanostatic charge-discharge curves of a Na/NVP@rGO cell

118 using NaFSI/N-propyl-N-methylpyrrolidinium bis(fluorosufonyl)imide (molar ratio of 2:8)

119 IL electrolyte at varied current densities from 25 to 400 mA g^{-1} .

124 Supplementary Tables

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126	Supplementary	Table 1.	Comparison	of represent	ative Na met	tal battery	performances	based on IL	electrolytes.
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Cathode	Electrolyte	C _{sp}	CE	Cyclic stability	Loading	Discharge	Е	Р	Ref.
		$(mAh g^{-1})$			$(mg cm^{-2})$	voltage (V)	$(Wh kg^{-1})$	(W kg ⁻¹)	
NaFePO ₄	1 M NaBF ₄ in BMP-TFSI	92	-	67%@100 cycles	~ 1.9	~ 2.8	~ 253	~ 66	1
NaFePO ₄	1 M NaClO ₄ in BMP-TFSI	79	-	62%@100 cycles	~ 1.9	~ 2.8	~ 217	~ 34	1
NaFePO ₄	1 M NaPF ₆ in BMP-TFSI	44	-	57%@100 cycles	~ 1.9	~ 2.8	~ 121	~ 12	1
Na _{0.44} MnO ₂	1 M NaBF ₄ in BMP-TFSI	84	-	40%@100 cycles	-	~ 2.7	~ 227	~ 28	1
Na _{0.44} MnO ₂	1 M NaClO ₄ in BMP-TFSI	97	-	65%@100 cycles	-	~ 2.7	~ 262	~ 52	2
$Na_{0.44}MnO_2$	1 M NaTFSI in BMP-TFSI	92	-	50%@100 cycles	-	~ 2.7	~ 248	~ 37	2
$Na_{0.44}MnO_2$	1 M NaPF ₆ in BMP-TFSI	38	-	33%@100 cycles	-	~ 2.7	~ 103	~ 9	2
NVP@C	1 M NaFSI in Py ₁₃ FSI	89	99%	~99%@50cycles	-	~ 3.3	~ 294	~ 1620	3
$Na_{0.6}Ni_{0.22}Fe_{0.11}$	0.2 M NaTFSI in Py14TFSI	~ 150	98%	~ 93%@5 cycles	1.0	~ 3	~ 450	~ 30	4
$Mn_{0.66}O_2$									
$Na_{0.45}Ni_{0.22}Co_{0.1}$	0.45 M NaTFSI in Py ₁₄ TFSI	~ 220	-	~80%@100 cycles	~ 2.5	2.7	550	~ 30	5
$_{1}Mn_{0.66}O_{2}$									
NaCrO ₂	NaFSI in Py ₁₃ FSI (2: 8 in	92	99.7%	-	-	~ 2.9	~ 267	~ 64	6
	molar)								
NVP@rGO	Buffered Na-Cl-IL	98	99.9%	~ 96%@460 cycles	3.0	~ 3.3	323	~ 1650	This work
NVPF@rGO	Buffered Na-Cl-IL	114	99.0%	~ 90.6%@710 cycles	3.0	~3.75	~ 420	~ 1766	This work

127 C_{sp}, CE, E and P represent specific discharge capacity, Coulombic efficiency, energy density and power density, respectively. BMP, *N*-butyl-*N*-methylpyrrolidinium. Py₁₃,

N-methyl-*N*-propylpyrrolidinium. Py₁₄, N-butyl-N-methylpyrrolidinium. FSI, bis(fluorosulfonyl)imide. TFSI, bis(trifluoromethanesulfonyl)imide.

130 Supplementary Methods

131

132 **Preparation of graphene oxide.** 1 g flake graphite powder was pre-oxidized in the mixture 133 of 30 mL sulfuric acid and 10 mL nitric acid under stirring for 24 h. After washing with 134 deionized water and drying, the obtained powder was exfoliated in a tube furnace at 1000 °C 135 for 10 s, followed by reacting with 60 mL oleum, 0.84 g K₂S₂O₈ and 1.3 g P₂O₅ at 80 °C for 5 136 h under stirring. After cooling down to room temperature, 500 mL deionized water was 137 slowly added to the suspension, and the dried products were obtained by vacuum filtrating 138 and washing for 3 times, and dried in a vacuum oven. The resulted powder was added to 50 139 mL oleum in ice bath, followed by adding 3 g KMnO₄ slowly under vigorous stirring, during 140 which the temperature was kept below 20 °C. The mixture was then heated to 35 °C and 141 stirred for another 2 h, and diluted with 500 mL deionized water and added with 2 mL 30 wt% 142 H₂O₂. The dispersion was left overnight, and the brown gel at bottom was washed with 143 deionized water, followed by centrifuging with 1 M HCl solution for 5 times, and then 144 washing with deionized water until the decantate turned nearly neutral.

145

146 Details of battery assembly and testing. We found that the powders of NVP@rGO and 147 NVPF@rGO are best to store in an Ar-filled glove box to avoid possible contaminations and 148 absorption of moisture in air. Freshly prepared NVP@rGO and NVPF@rGO electrodes are 149 preferable for good battery performances. Sufficient contact between electrode and separator 150 is important for good rate and cycling performances. The pouch cell was placed under 151 vacuum for 15 min after injecting the electrolyte to enhance the electrolyte permeation into 152 separator and electrodes. The edges of the pouch cells were flattened, and the pouch was 153 further clamped using two clips (0.75 inch, Clipco) between two hardboards for 30 min, 154 realizing a good contact between the electrode and separator. The clips were then removed 155 and no extra pressure was applied on the battery during testing.

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158 Supplementary References

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