Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Suitability of ionic liquid electrolyte for room-temperature sodium-ion battery applications

Chueh-Han Wang,[a] Cheng-Hsien Yang[a] and Jeng-Kuei Chang*[abc]

[a] Institute of Materials Science and Engineering, National Central University, Taiwan

[b] Department of Mechanical Engineering, National Central University, Taiwan

[c] Department of Chemical and Materials Engineering, National Central University, Taiwan

*Corresponding author

Telephone: +886-3-4227151 ext. 34908

Fax: +886-3-2805034

E-mail: jkchang@ncu.edu.tw

Address: 300 Jhong-Da Road, National Central University, Taoyuan,
Taiwan

Experimental procedure

Preparations of electrode materials and electrolytes

The $Na_{0.44}MnO_2$ was synthesized using a solid-state reaction method. Mn_2O_3 (99.9 wt%, Aldrich) and Na_2CO_3 (99.9 wt%, Aldrich) precursors were mixed in a molar ratio of 1:0.484 (10% excess of Na). The mixture was hand-ground, pelletized, and heated at 500 °C under air for 5 h. Then, the pellet was re-ground, re-pelletized, and heated again at 900 °C under air for 12 h. After the two-step calcination followed by pulverization of the pellet, the oxide powder was obtained. Carbon-coated $LiFePO_4$ powder was synthesized using a carbothermal reduction method at 700 °C involving the precursors of ferric oxide (99 wt%, Taiwan Polychem Co. Ltd.), ammonium dihydrogen phosphate (99 wt%, First Chemical Works Co. Ltd.), and lithium carbonate (99 wt%, First Chemical Works Co. Ltd.) in the required stoichiometric ratio. In the calcination, polyethylene glycol (M_W = 6000, Huacheng Industrial Co. Ltd.) was used as a reduction agent as well as a carbon source. $FePO_4$ was then prepared by delithiation of the prepared $LiFePO_4$. Acetonitrile solution with nitronium tetrafluoroborate (NO_2BF_4, 97 wt%, Acros Organics) was used as the delithiation agent. A mixture of the $LiFePO_4$ powder (1 g), NO_2BF_4 (1.7 g), and acetonitrile (100 mL) was stirred for 24 h at 25 °C with continuously purged argon. The obtained powder was repeatedly washed with distilled water. After centrifugation, the precipitated $FePO_4$ was collected and dried at 80 °C in a vacuum oven overnight before use. The $NaFePO_4$ electrode was prepared by electrochemical sodiation of the $FePO_4$ electrode. Hard carbon was purchased from Kureha Battery Materials Japan Co., Ltd. Graphite powder was provided by China Steel Chemical Corporation.

PMP–FSI IL (99.5 wt%, Solvionic) was dried under vacuum at 60 °C for 24 h before use. NaFSI (99.7 wt%, Solvionic) with a concentration of 1 M was dissolved in the IL to provide Na^+ conduction. A conventional organic electrolyte, consisting of 1:1 (by volume) ethylene carbonate (EC, 99 wt%, Alfa Aesar) and diethyl carbonate (DEC, 99 wt%, Alfa Aesar) as co-solvent and 1 M $NaClO_4$ solute, was also prepared for comparison. Each mixture was continuously stirred by a magnetic paddle for 24 h to ensure uniformity. All the chemicals were stored and handled in an argon-filled glove box (Innovation Technology Co. Ltd.), where both the moisture content and oxygen content were maintained at below 1 ppm. The electrolyte water contents, measured using a Karl Fisher titrator, were less than 100 ppm.

Cell assembly

An electrode slurry was prepared by mixing 75 wt% active material powder, 20 wt% carbon black, and 5 wt% poly(vinylidene fluoride) in N-methyl-2-pyrrolidone solution. The slurry was pasted onto Al (for cathodes) or Cu (for anode) foil and vacuum-dried at 80 °C for 8 h. The typical active material loading on each electrode was 1.5(±0.2) mg cm^{-2}. Then, the electrode was roll-pressed and punched to match the required dimensions of a CR2032 coin cell. For Na half cells, Na foil and a glassy fiber membrane were used as the counter and the separator, respectively. The $Na_{0.44}MnO_2$/hard carbon full cells were also prepared with an active material weight ratio of 1:1. The assembly of the coin cells was performed in the argon-filled glove box.

Material and electrochemical characterizations

The charge−discharge performance (in terms of capacity, high-rate capability, and cyclic stability) of various cells was evaluated using an Arbin BT-2043 multi-channel battery tester. Electrochemical impedance spectroscopy (EIS) analyses were conducted at the open-circuit potentials. The AC amplitude of 10 mV was adopted.

The $Na_{0.44}MnO_2$/hard carbon full cells with the IL and conventional organic electrolytes were disassembled after 100 charge−discharge cycles. The electrode morphologies were examined using scanning electron microscopy (SEM; FEI Inspect F50). X-ray photoelectron spectroscopy (XPS; VG Sigma Probe) was employed to study the chemical compositions of the solid-electrolyte-interphase films.

Table S1 Discharge capacities (mAh g^{-1}) of various cells measured at various rates with 1 M NaFSI/PMP−FSI IL electrolyte and conventional 1 M NaClO$_4$/EC/DEC electrolyte.

	NMO/Na		**HC/Na**		**NMO/HC**	
Discharge-charge Rate	IL electrolyte	Organic electrolyte	IL electrolyte	Organic electrolyte	IL electrolyte	Organic electrolyte
30 mA/g	107	117	280	290	120	117
50 mA/g	98	108	228	244	109	109
100 mA/g	78	101	153	208	104	103
500 mA/g	45	73	79	121	79	77
1 A/g	20	46	51	99	70	50

Table S2 R_s and R_{ct} values of various cells measured using EIS with 1 M NaFSI/PMP−FSI IL electrolyte and conventional 1 M $NaClO_4$/EC/DEC electrolyte.

Cell	**Electrolyte**	**R_s (Ω)**	**R_{ct} (Ω)**
NMO/Na	IL electrolyte	4.3	550
	Organic electrolyte	2.5	140
HC/Na	IL electrolyte	4.3	510
	Organic electrolyte	2.5	75
Na/Na	IL electrolyte	4.3	1120
	Organic electrolyte	2.5	170
NMO/NMO	IL electrolyte	4.3	3.4
	Organic electrolyte	2.5	55
HC/HC	IL electrolyte	4.3	2
	Organic electrolyte	2.5	3

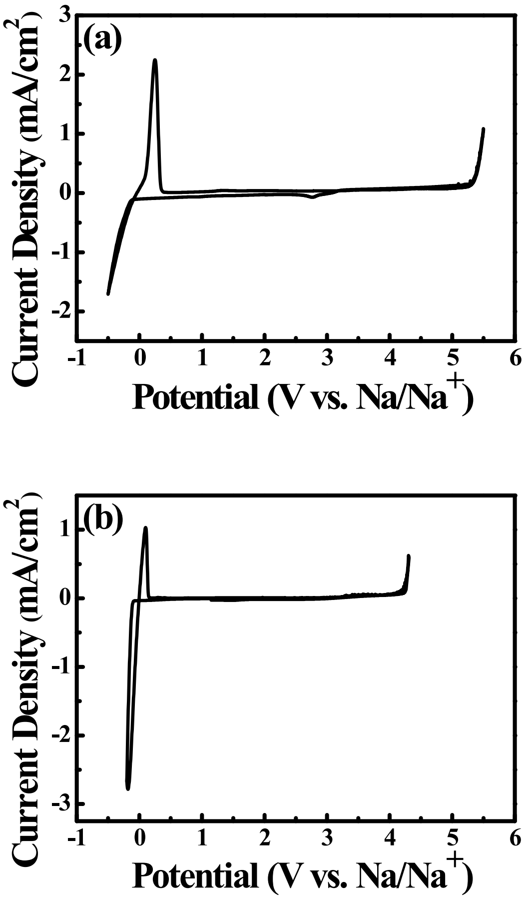

Fig. S1 Cyclic voltammograghs of (a) IL electrolyte and (b) conventional organic electrolyte recorded at Pt electrodes with a potential scan rate of 3 mV s^{-1}.

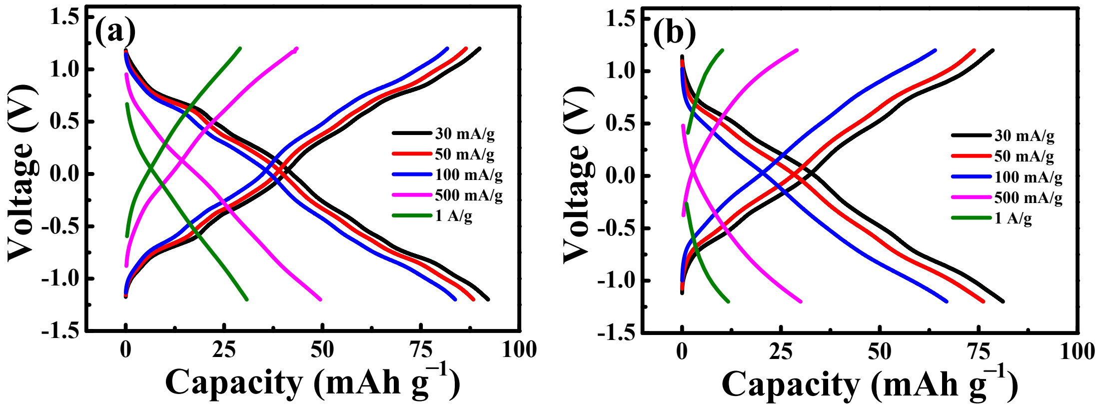

Fig. S2 Charge–discharge curves of NMO/NMO cells with (a) IL electrolyte and (b) conventional organic electrolyte recorded at 25 °C.

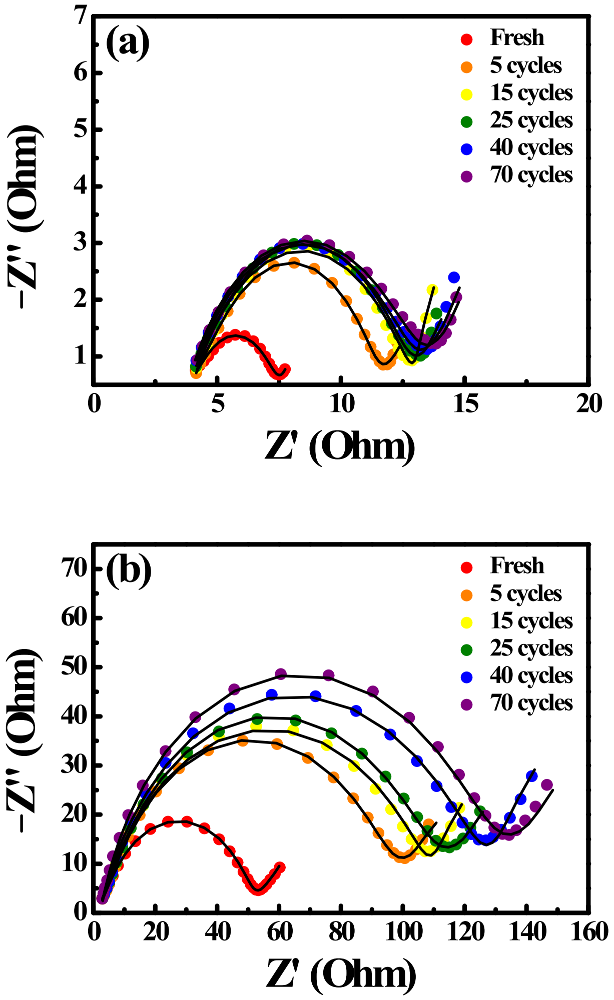

Fig. S3 EIS spectra of NMO/NMO cells with (a) IL electrolyte and (b) conventional organic electrolyte recorded after certain charge–discharge cycles. The solid lines are data fitting results.

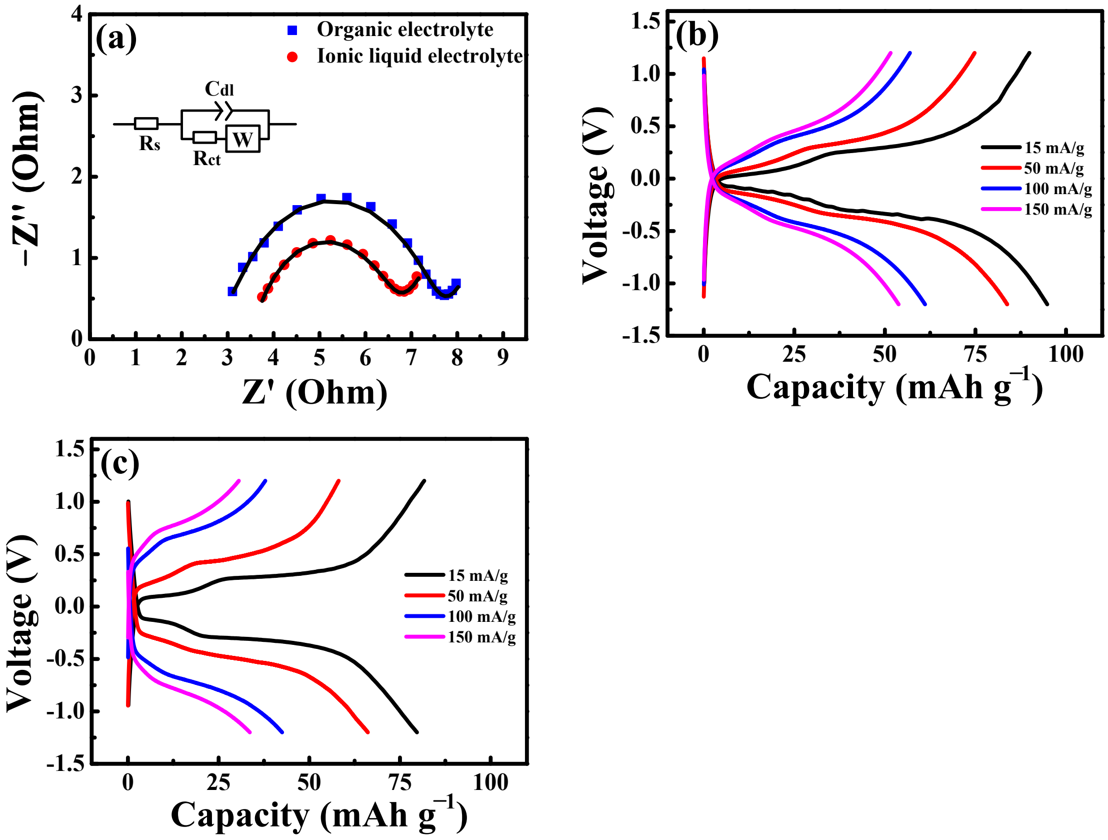

Fig. S4 (a) EIS spectra of NFP/NFP cells with IL and conventional organic electrolytes (solid lines are the data fitting results). Charge–discharge curves of $FePO_4$/NFP cells with (b) IL electrolyte and (c) conventional organic electrolyte. Measurements were performed at 25 °C.

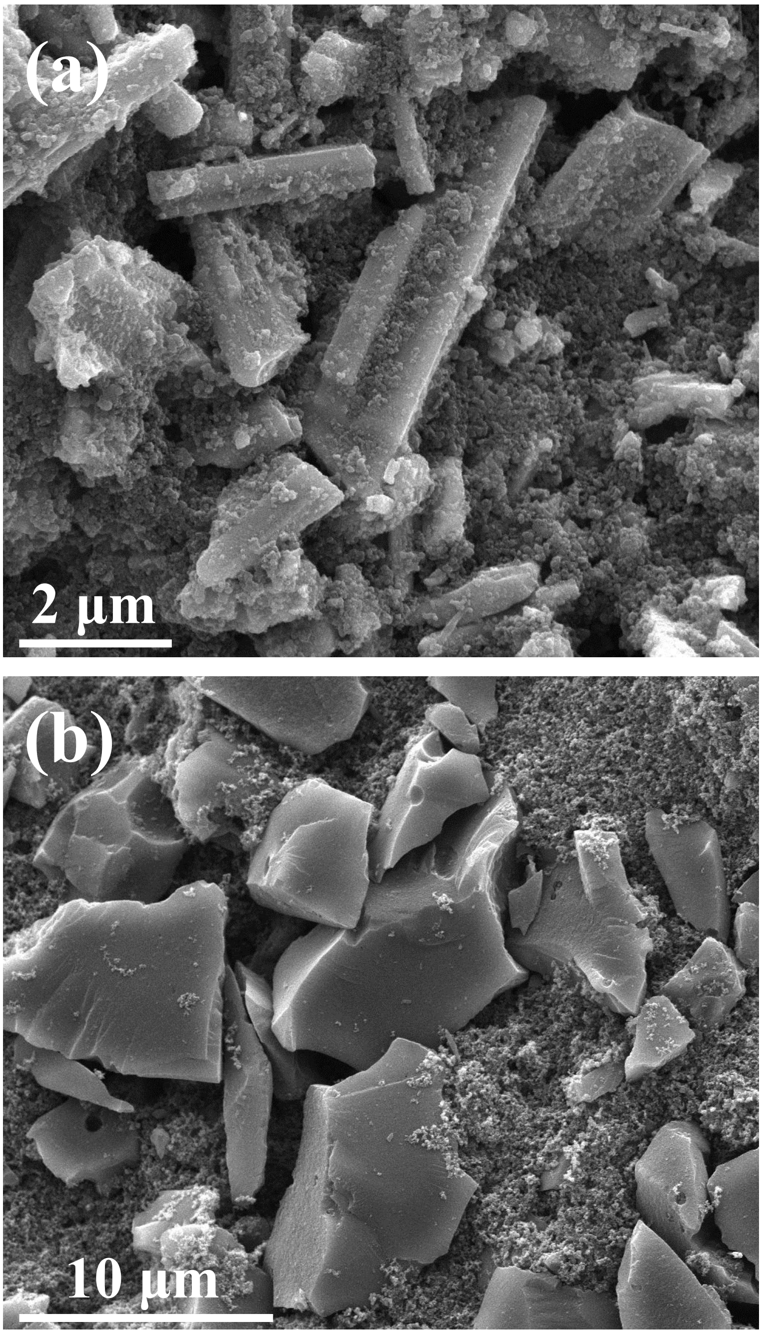

Fig. S5 SEM micrographs of pristine (a) NMO and (b) HC electrodes.

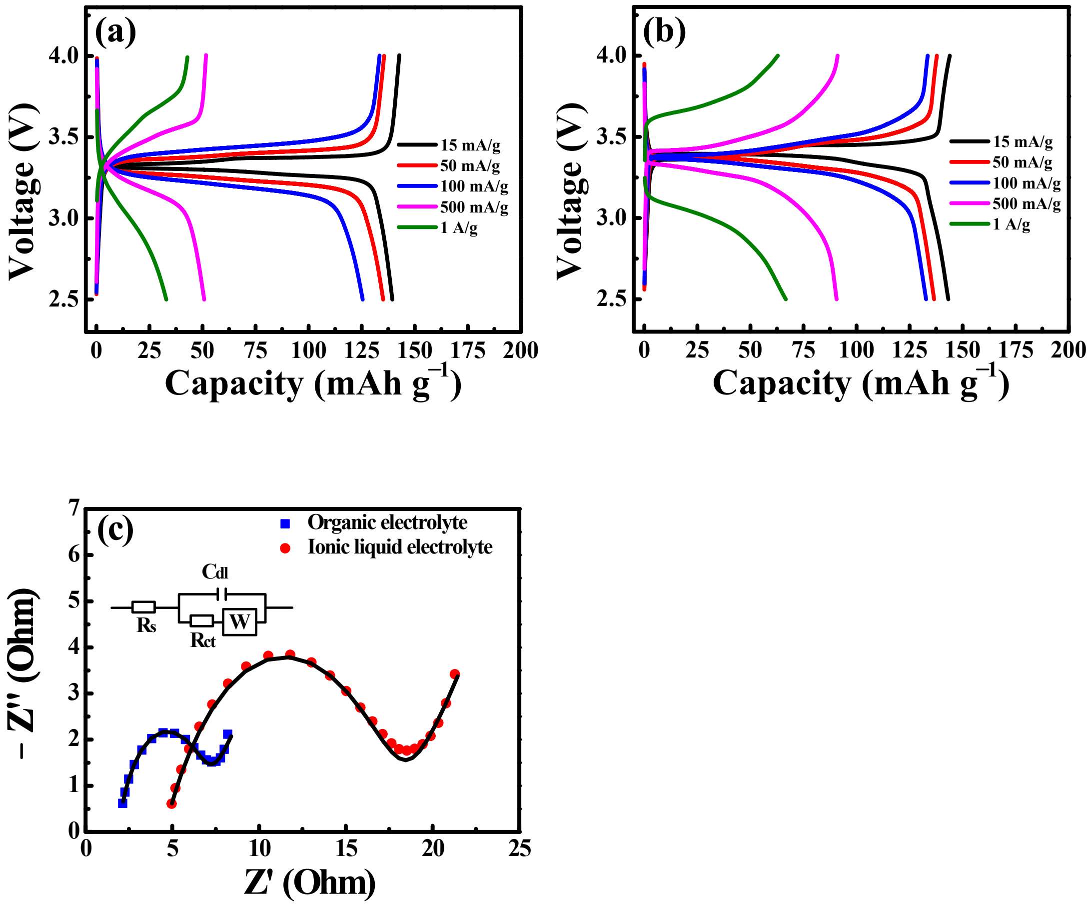

Fig. S6 Charge–discharge curve of LiFePO$_4$/graphite full cells with (a) 1 M LiFSI/PMP–FSI IL electrolyte and (b) conventional 1 M LiPF$_6$/EC/DEC electrolyte. (c) EIS spectra of the above two cells (solid lines are the data fitting results). Measurements were performed at 25 °C.