Robust interphase derived from a dual-cation ionic liquid electrolyte enabling exceptional stability of high-nickel layered cathodes

Fanglin Wu,[1,2,3] Haolin Tang,[1] Jian Wang,[2,3] Xilai Xue,[2,3] Thomas Diemant,[2,3] Shan Fang,[4] Huihua Li,[2,3] Ziyuan Lyu,[2,3] Hao Li,[1] En Xie,[1] Hongzhen Lin,[5] Jae-Kwang Kim,[6] Guk-Tae Kim,[2,3,6,7]* Stefano Passerini[2,3,8]**

[1] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei 430070, China*

[2] *Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, Ulm 89081, Germany*

[3] *Karlsruhe Institute of Technology (KIT), P.O. Box 3640, Karlsruhe 76021, Germany*

[4] *School of Physics and Materials Science, Nanchang University, Nanchang, Jiangxi, 330031, China*

[5] *i-Lab & CAS Key Laboratory of Nanophotonic Materials and Device Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu 215123, China*

[6] *Department of Energy Convergence Engineering, Cheongju University, Cheongju, Chungbuk, 28503, Republic of Korea*

[7] *Il Chem Co., Ltd, 282, Hagui-ro, Dongan-gu, Anyang-si, Gyeonggi-do, Republic of Korea*

[8] *Austrian Institute of Technology (AIT), Center for Transport Technologies, Giefinggasse 4, 1220, Wien, Austria*

E-mail: thln@whut.edu.cn; guk-tae.kim@kit.edu; stefano.passerini@kit.edu

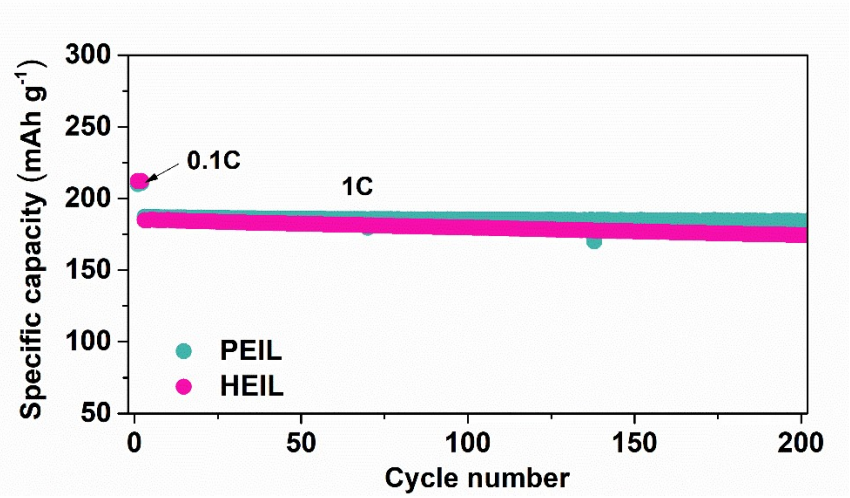

Fig. S1 Cycling behaviour of Li||NCM83 cells using PEIL or HEIL as the electrolyte at 1C and 20 °C after activation for two cycles at 0.1C.

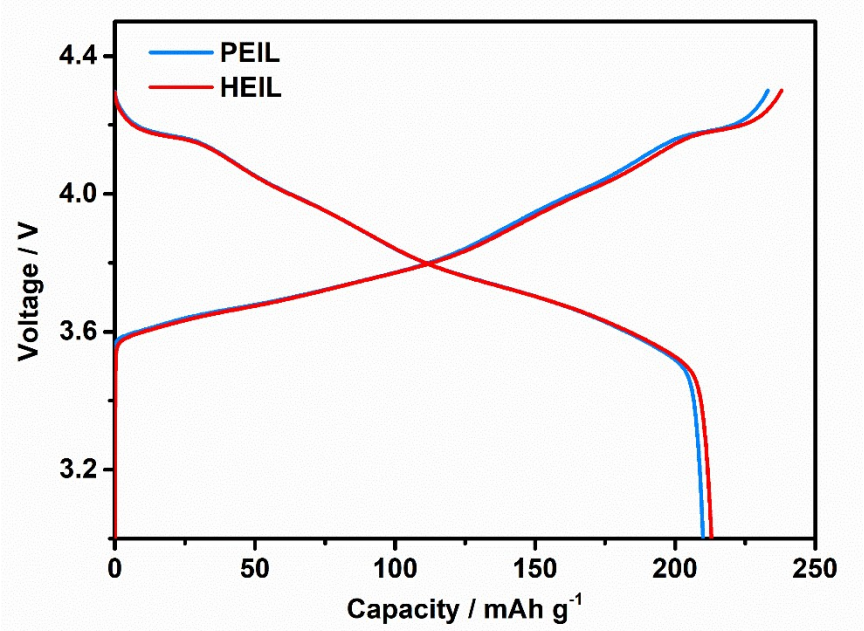

Fig. S2 Charge/discharge profile during the first cycle of Li||NCM83 cells with PEIL and HEIL as the electrolyte.

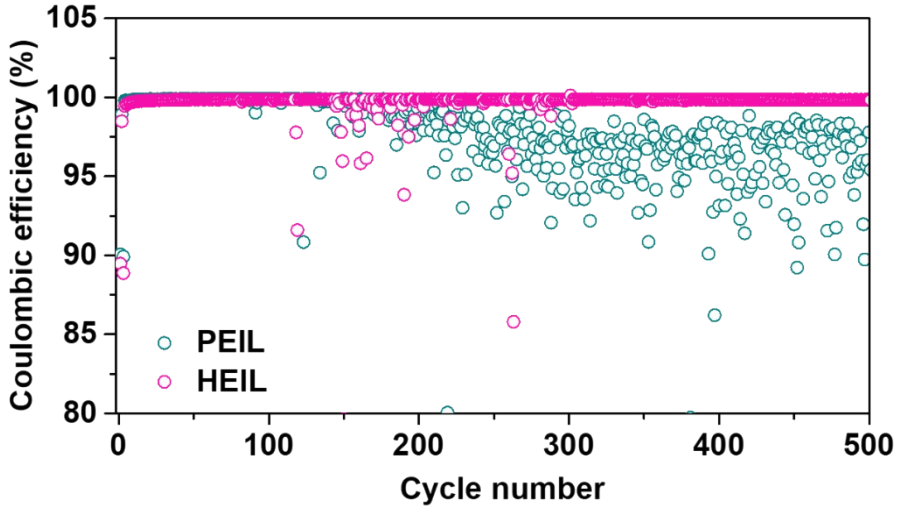

Fig. S3 Coulombic efficiency during prolonged cycling of Li||NCM83 cells with PEIL or HEIL as the electrolyte.

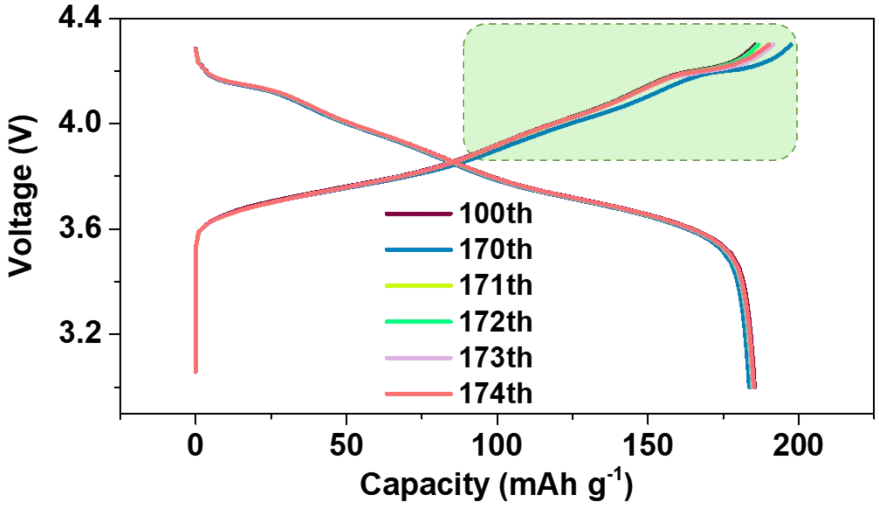

Fig. S4 Selected voltage curves of Li||NCM83 cell with PEIL as the electrolyte.

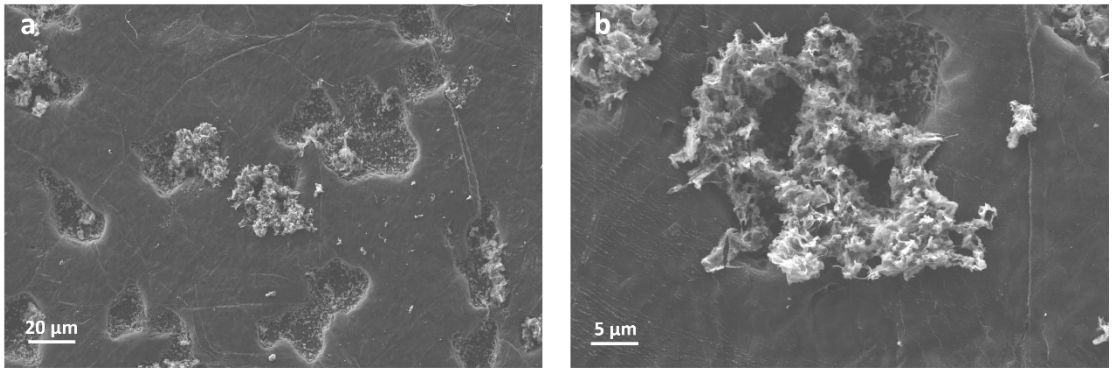

Fig. S5 SEM images depicting the morphology of a lithium metal electrode after stripping/plating for 10 cycles in Li||Li symmetric cells employing PEIL.

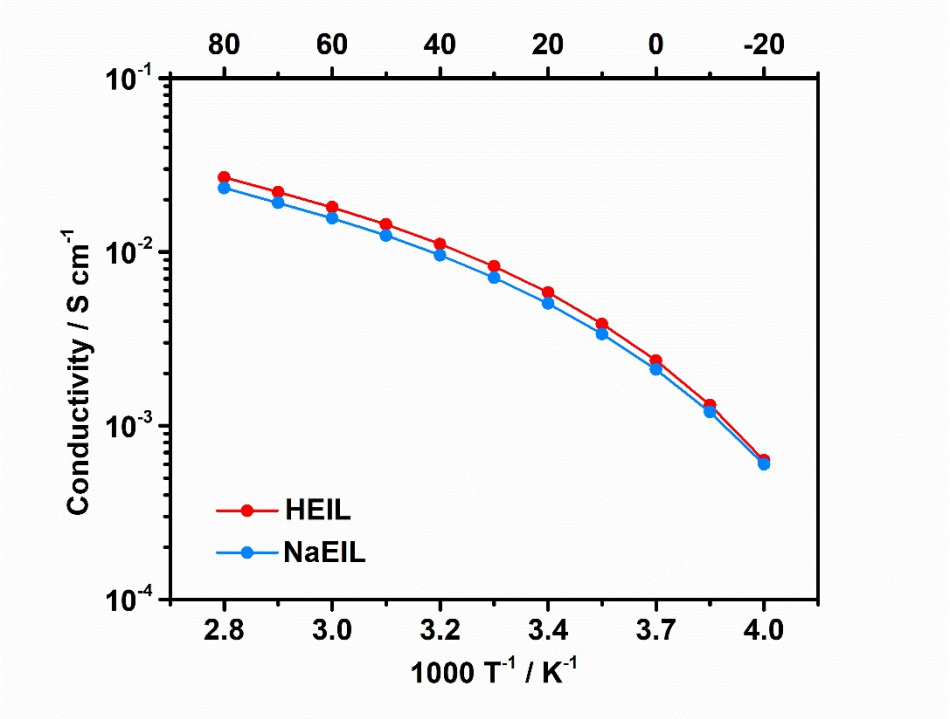

Fig. S6 Ionic conductivity of HEIL and NaEIL.

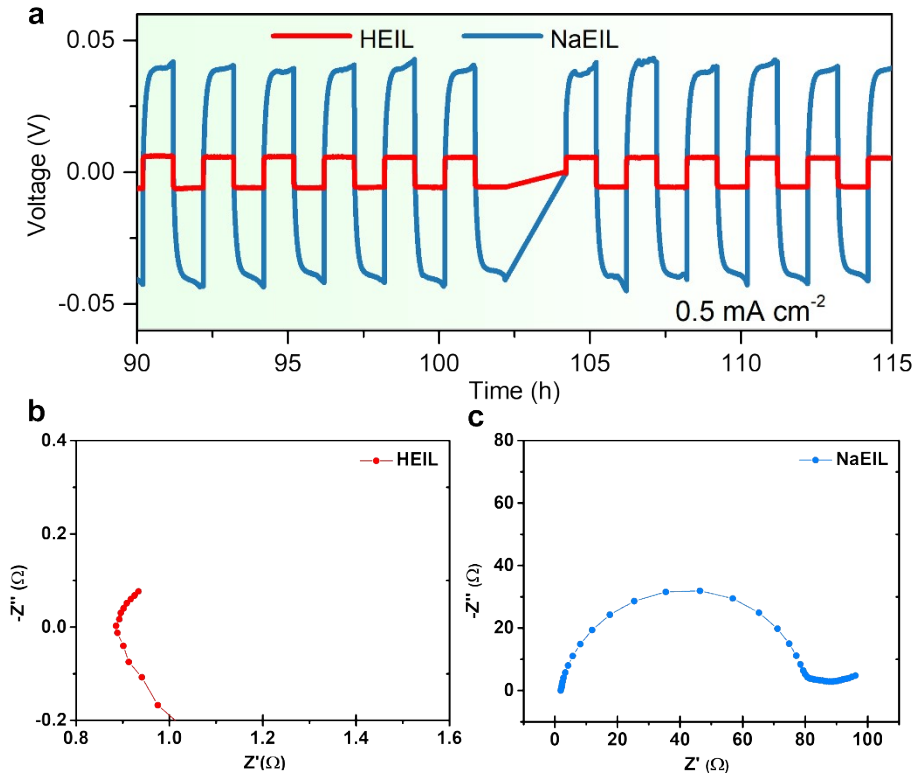

Fig. S7 a) Magnification of the stripping/plating overvoltage behaviour displayed in **Fig.2c.** EIS spectra of the cell employing HEIL (b) and NaEIL (c) taken after 100 hours of cycling.

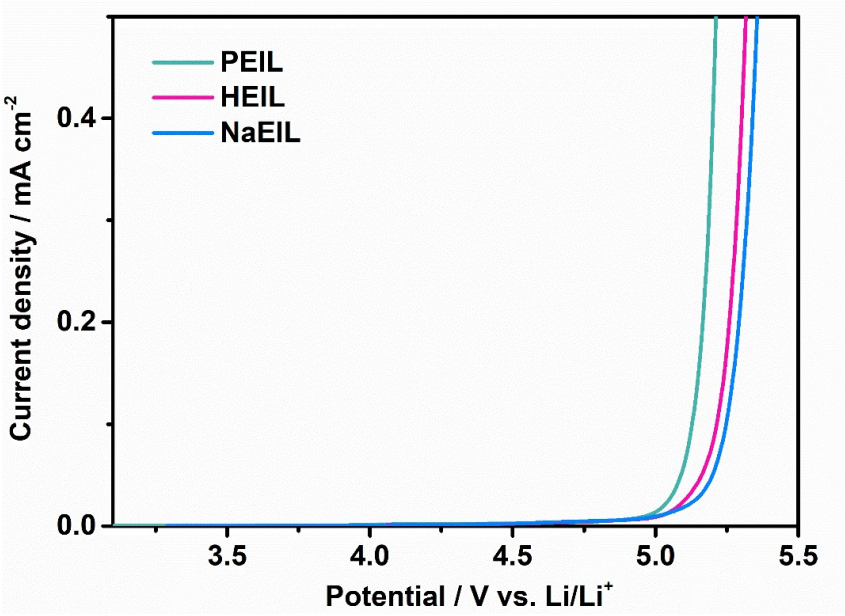

Fig. S8 LSV measurements of the investigated electrolytes.

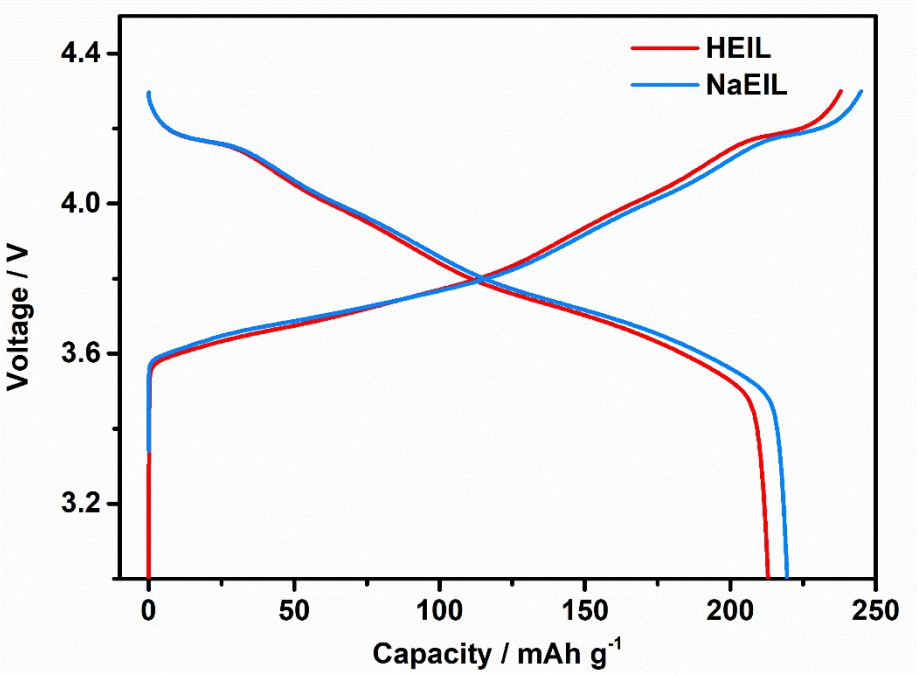

Fig. S9 Initial charge/discharge profile of Li||NCM83 cells employing HEIL or NaEIL as the electrolyte.

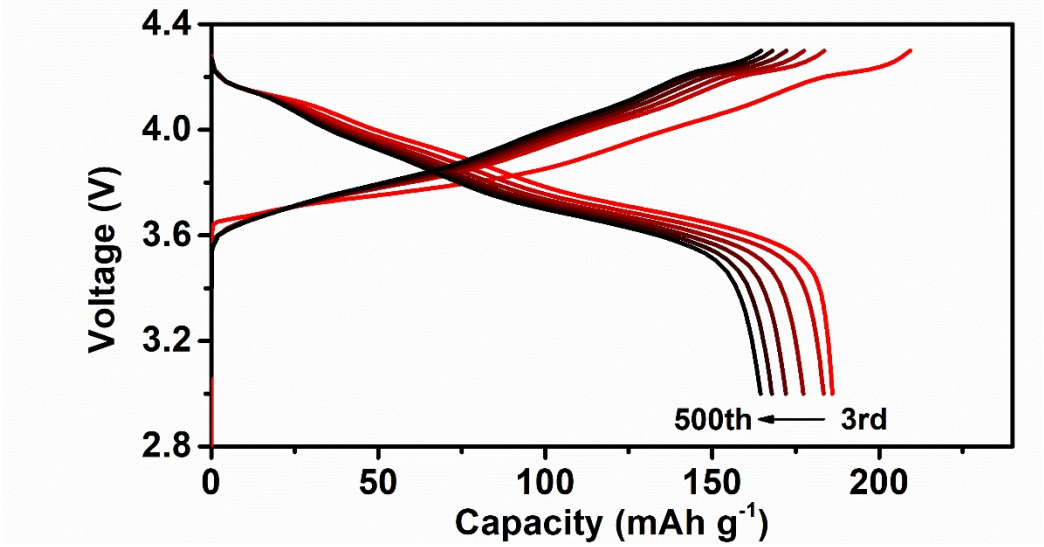

Fig. S10 Selected voltage curves of a Li||NCM83 cell employing HEIL within the 3rd and 500th cycle.

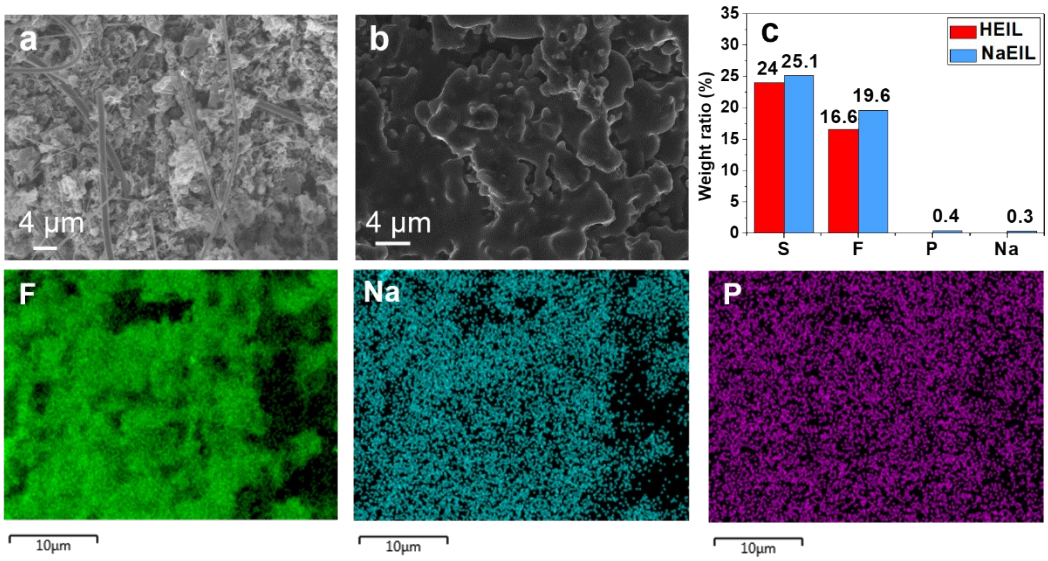

Fig. S11 SEM morphology of lithium metal after 200 cycles in (a) HEIL or (b) NaEIL. c) Weight ratio of a few elements on the surface of lithium metal electrodes cycled in HEIL and NaEIL. The corresponding EDX mapping of F, Na and P elements for the electrode cycled in NaEIL are shown in the lower images.

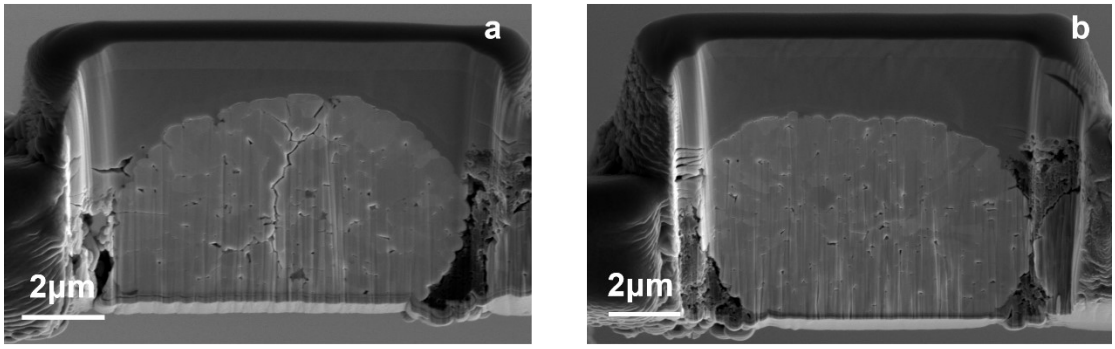

Fig. S12 Cross sectional morphology of NCM83 particles after cycling in (a) HEIL or (b) NaEIL.

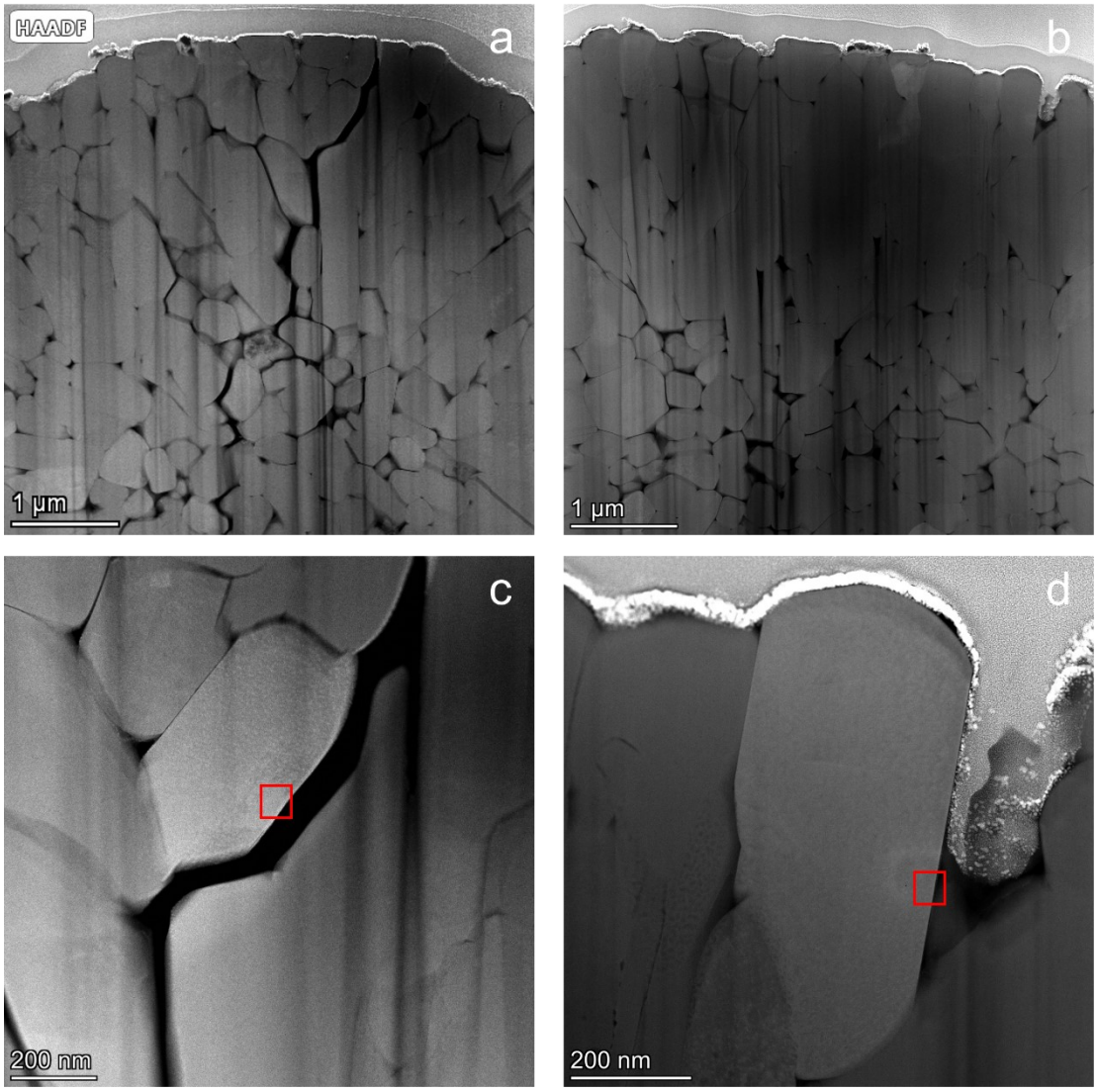

Fig. S13 HAADF images of NCM83 particles after cycling in (a,c) HEIL and (b,d) NaEIL.

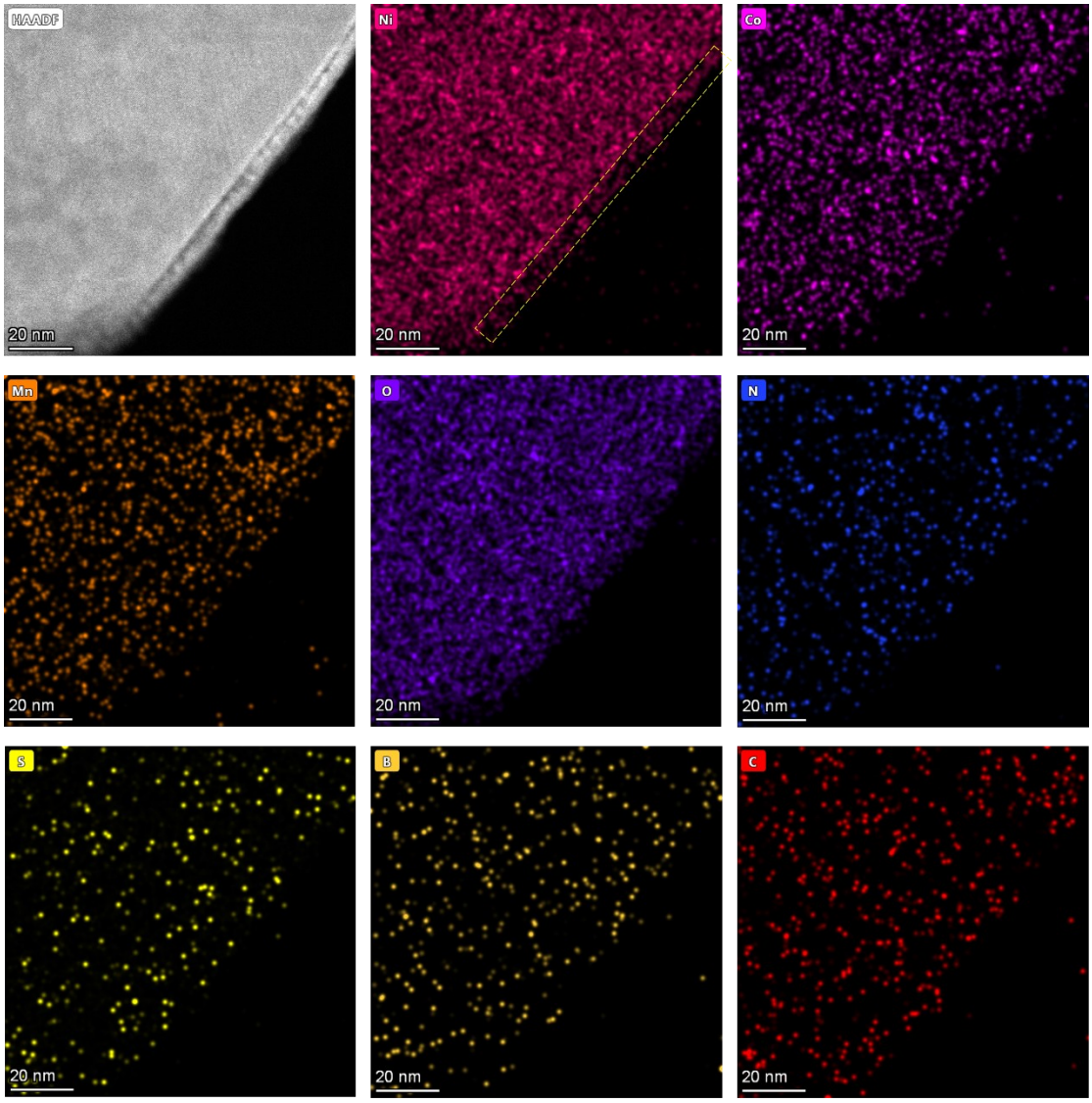

Fig. S14 STEM-EDX mapping of different elements of NCM83 electrodes after cycling in HEIL.

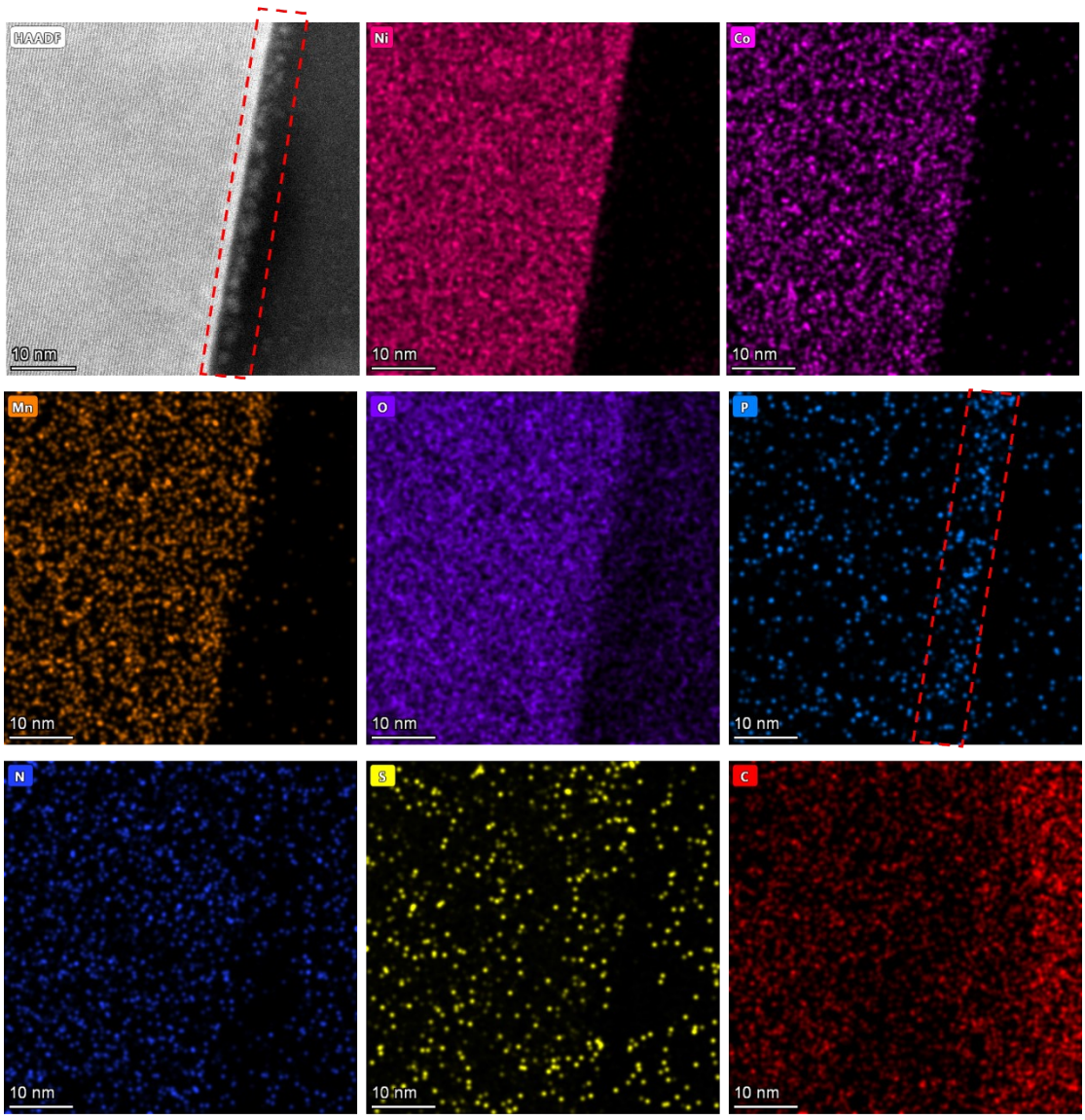

Fig. S15 STEM-EDX mapping of different elements of NCM83 electrodes after cycling in NaEIL.

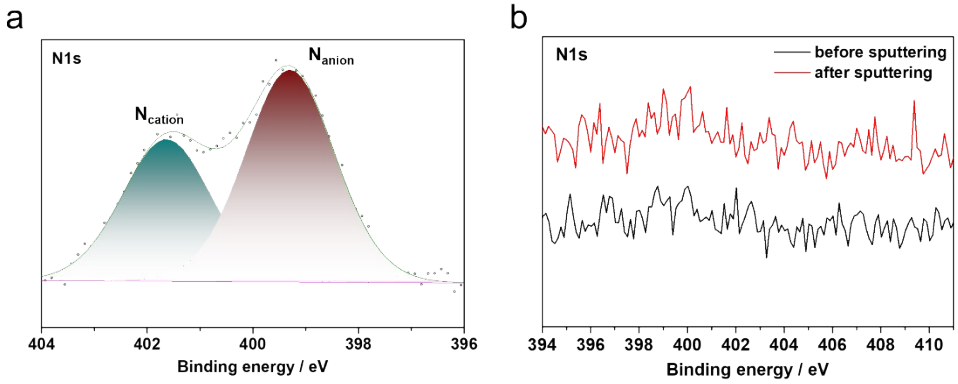

Fig. S16 XPS detail spectra in the N1s region taken from NCM83 electrodes after cycling in (a) HEIL and (b) NaEIL.

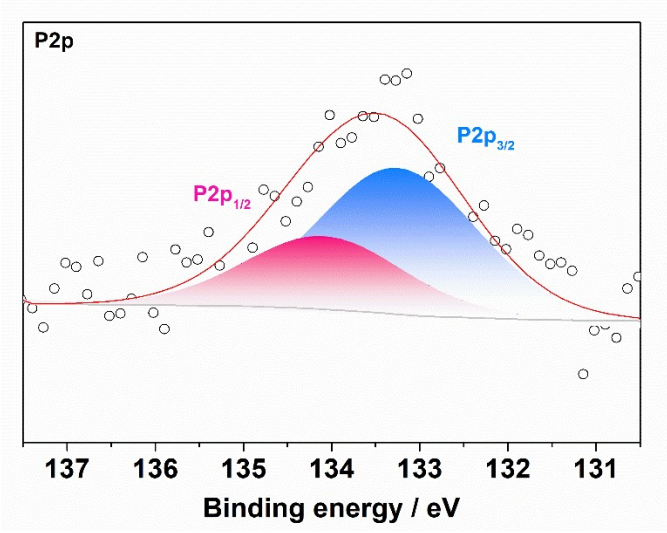

Fig. S17 XPS detail spectra in the P2p region taken from an NCM83 electrode after cycling in NaEIL.

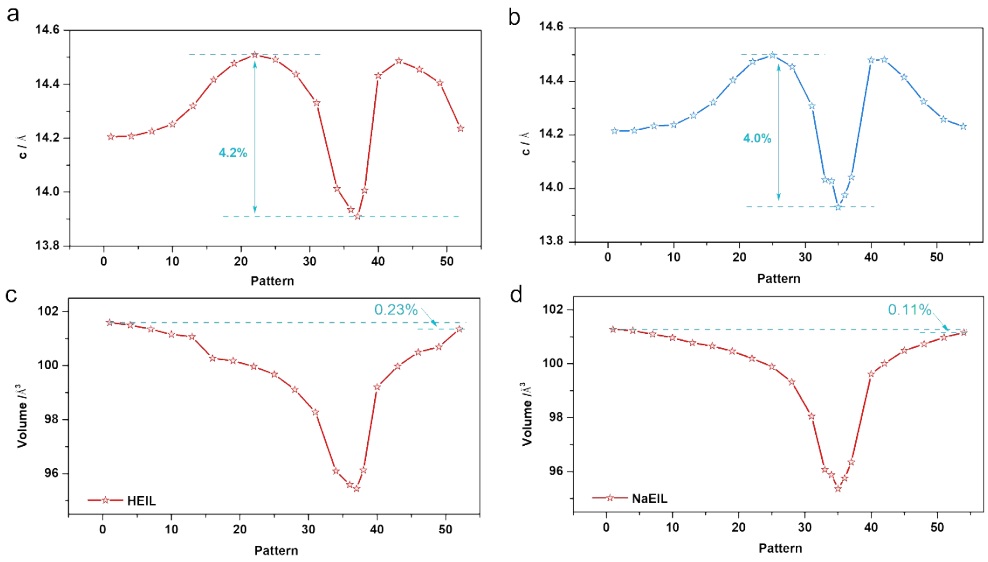

Fig. S18 Variation of the lattice parameter and the unit cell volume of NCM83 during the first-charge process in (a,c) HEIL and (b,d) NaEIL.

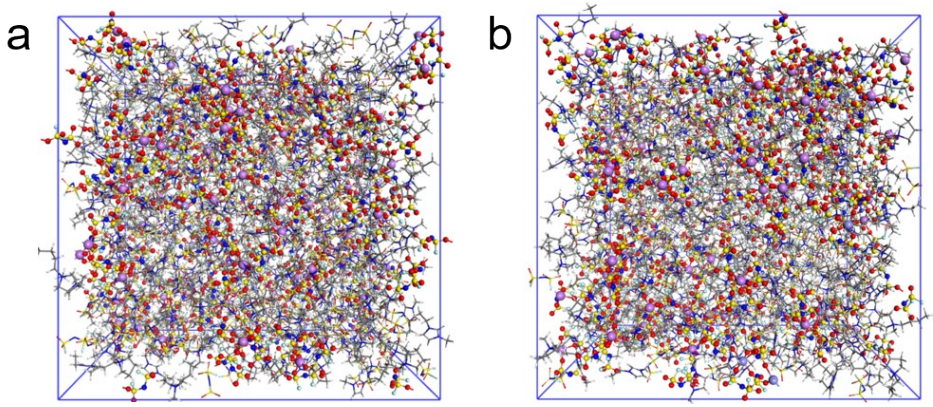

Fig. S19 Representative snapshots of solvent structure in (a) HEIL and (b) NaEIL.

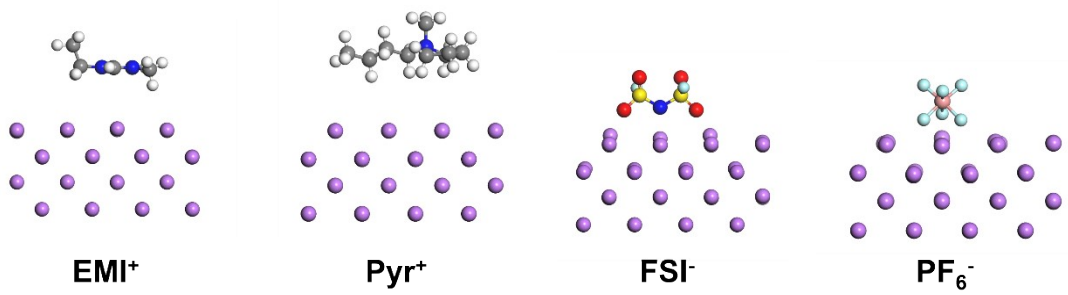

Fig. S20 Adsorption model of different cations and anions on the (100) surface of lithium metal.

Table S1. Performance comparison of reported state-of-the-art IL-based electrolytes employed in nickel rich cathodes.

Number	Electrolyte	Cell information	Strategy	Current density	Charge Rate	Cyclability	Reference
1	$[LiTFSI]_1[Pyr_{14}FSI]_1[TCM]_2$	Half cell: Li||NCM811 3.0-4.3 V	TCM as co-solvent	1 mA cm^{-2}	1C	81.6% after 500 cycles	*Adv. Mater.* **2024**, *36*, 2400537
2	2M LiTFSI/LiDFOB in DFPyrTFSI/DMC	Half cell: Li||NCM811 2.8-4.5 V	Fluorination of the IL' cations	0.45 mA cm^{-2}	C/3	90.5% after 200 cycles	*Angew. Chem.* **2024**, *136*, e202317148
3	$[LiFSI]_1[EmimFSI]_2[BnOCF]_{0.55}$	Half cell: Li||NCA 2.8-4.4 V	BnOCF as co-solvent	0.67 mA cm^{-2}	C/3	93% after 450 cycles	*Adv. Mater.* **2024**, *36*, 2309062
4	1M LiFSI/0.3M $LiNO_3$ in $PP_{13}TFSI$ and DME (v:v = 1:4)	Half cell: Li||NCM811 3.0-4.3 V	IL tuned the solvation structure of ethereal electrolyte	1.62 mA cm^{-2}	5C	75% after 600 cycles	*Adv. Energy Mater.* **2023**, 2302443
5	3.2 mol kg^{-1} LiFSI in C3mpyrFSI:DME (wt : wt =80 : 20)	Full cell: Li||NCM811 (Li thickness: 50 µm) 2.8-4.4 V	Ether aided ILE	0.5 mA cm^{-2}	0.5C	81% after 300 cycles	*Energy Environ. Sci.*, 2022, 15, 1907–1919
6	$[LiFSI]_1[EmimFSI]_2[dFBn]_2$	Half cell: Li||NCM811 2.8-4.4 V	dFBn as co-solvent	0.67 mA cm^{-2}	C/3	93% after 500 cycles	*Adv. Energy Mater.* **2022**, 2200862
7	$[LiTFSI]_1[Pyr_{14}FSI]_4$	Half cell: Li||NCM88 3.0-4.3 V	Dual anions in ILE	0.168 mA cm^{-2}	0.3C	88% after 1000 cycles	*Joule 5, 2177-2194*
8	$[LiTFSI]_1[Pyr_{14}FSI]_4$	Full cell: Li||NCM88 (Li thickness: 50 µm) 3.0-4.3 V	Dual anions in ILE	0.3 mA cm^{-2}	0.5C	88.3% after 300 cycles	*Joule 5, 2177-2194*
9	5M LIFSI/0.16M NaTFSI in EMIMFSI	Half cell: Li||NCM811	High concentration ILE with NaTFSI as	1 mA cm^{-2}	0.5C	94% after 200 cycles	*Adv. Mater.* **2020**, 2001741

		2.8-4.4 V	additive				
10	5M LIFSI/0.16M NaTFSI in EMIMFSI	Half cell: Li||NCM811 2.8-4.4 V	High concentration ILE with NaTFSI as additive	1.4 mA cm^{-2}	0.7C	74% after 500 cycles	*Adv. Mater.* **2020**, 2001741
11	1M LiDFOB TEP/$Pyr_{13}TFSI$	Half cell: Li||NCM90 2.8-4.3 V	TEP as co-solvent	0.2 mA cm^{-2}	0.2C	91% after 100 cycles	*Adv. Funct. Mater.* ***2023**, 33, 2215065*
12	1 M LiPF6 in EC/EMC/DMC +0.6 wt% LiHMDS	Half cell: Li||NCM811 2.8-4.3 V	LiHMDS as additive	~0.5 mA cm^{-2}	~1C	71.24% after 1000 cycles	*Nat. Commun., 2022, 12,6966*
13	1M LiPF6 in EC/EMC (wt:wt=3:7)+2% LTBA	Li||NCM86 2.5-4.3 V	LTBA as additive	~0.5 mA cm^{-2}	C/3	66% after 240 cycls	*Adv. Energy Mater.* ***2024**, 14, 2402051*
14	1M LiPF6 in EC/EMC (wt:wt=3:7)+VC+DMVC-OCF3+DMVC-OTMS	Si-C||NCM811 2.5-4.3 V	fluorinated and silylated additives	2.7 mA cm^{-2}	1C	81.5% after 400 cycles	*Nat. Commun., 2021, 12, 838*
15	$[NaPF_6]_{0.2}[LiFSI]_{1.8}[EMIFSI]_4[Pyr_{14}FSI]_4$	Half cell: Li||NCM83 3.0-4.3 V	Dual-cation with $NaPF_6$ additive	0.5 mA cm^{-2}	1C	95.2% after 500 cycles	This work
16	$[NaPF_6]_{0.2}[LiFSI]_{1.8}[EMIFSI]_4[Pyr_{14}FSI]_4$	Half cell: Li||NCM83 3.0-4.3 V	Dual-cation with $NaPF_6$ additive	0.5 mA cm^{-2}	1C	80.4% after 1500 cycles.	This work