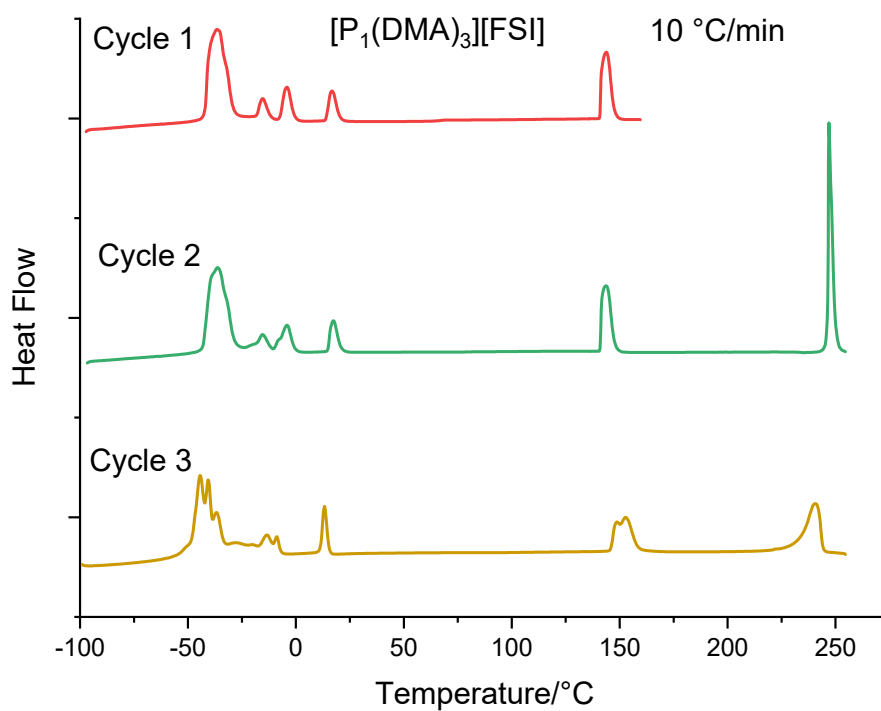
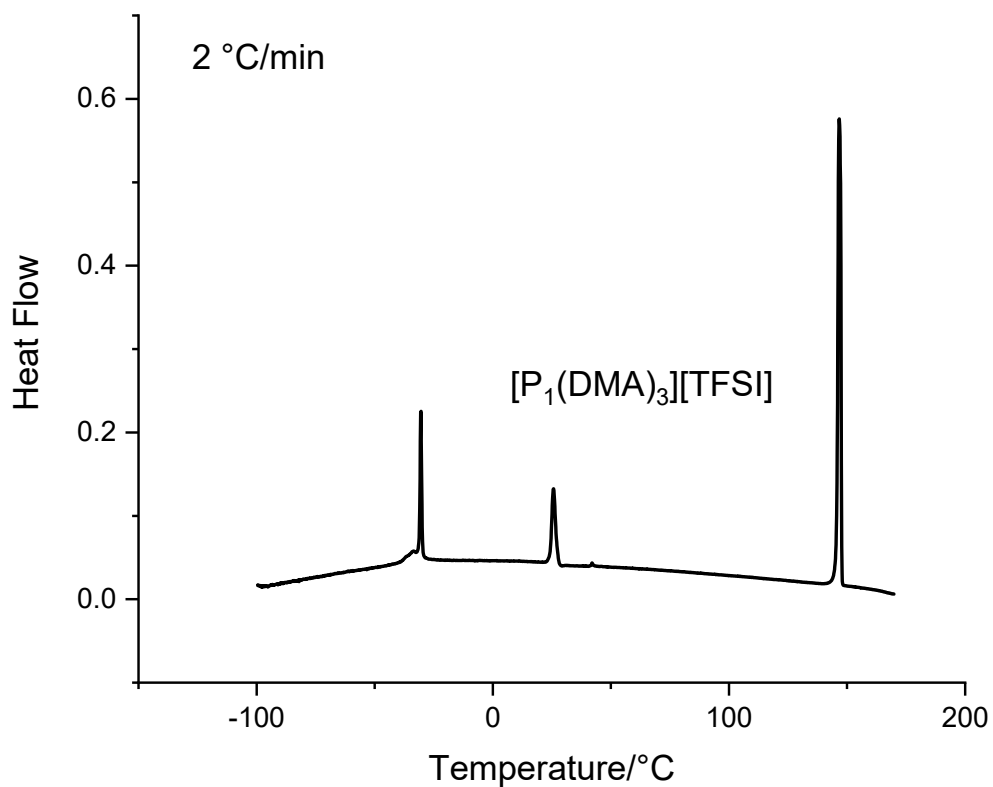


## Supporting Information

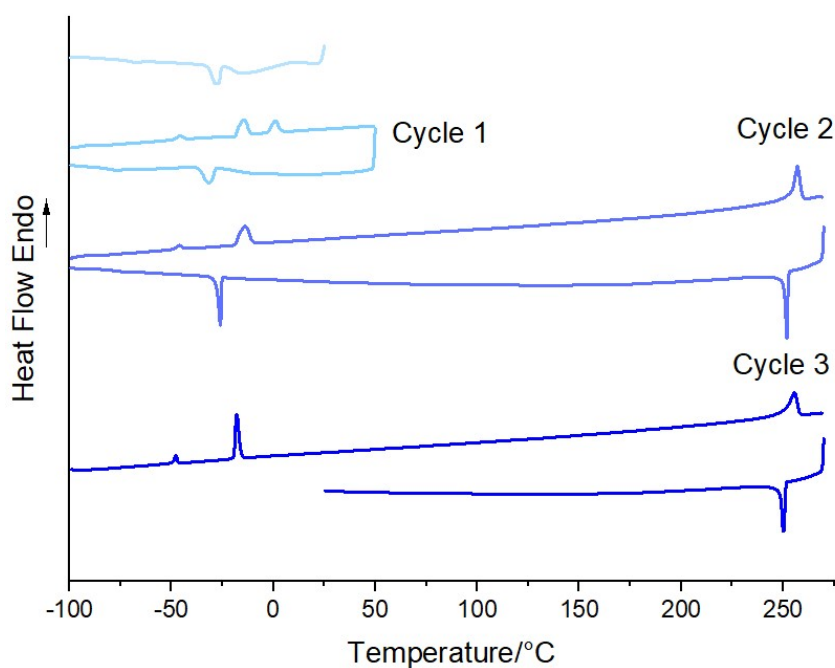
The Supporting Information is available free of charge



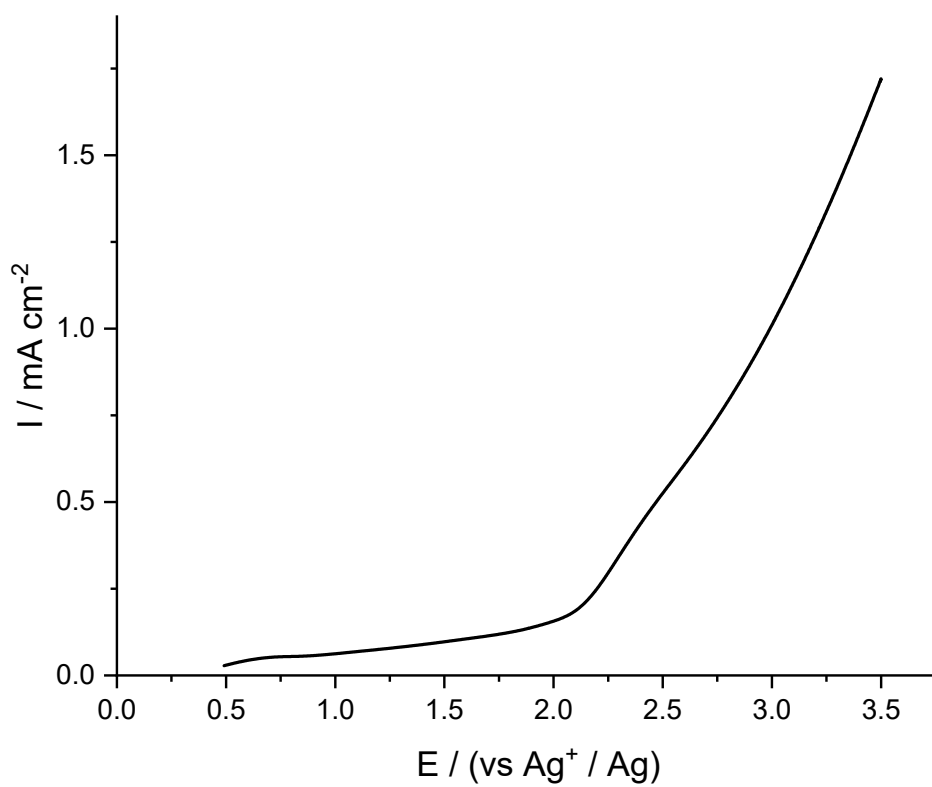
**Figure S1.** DSC of  $[P_1(\text{DMA})_3][\text{FSI}]$  showing three heating cycles that indicate a change in the solid-solid transitions after melting.



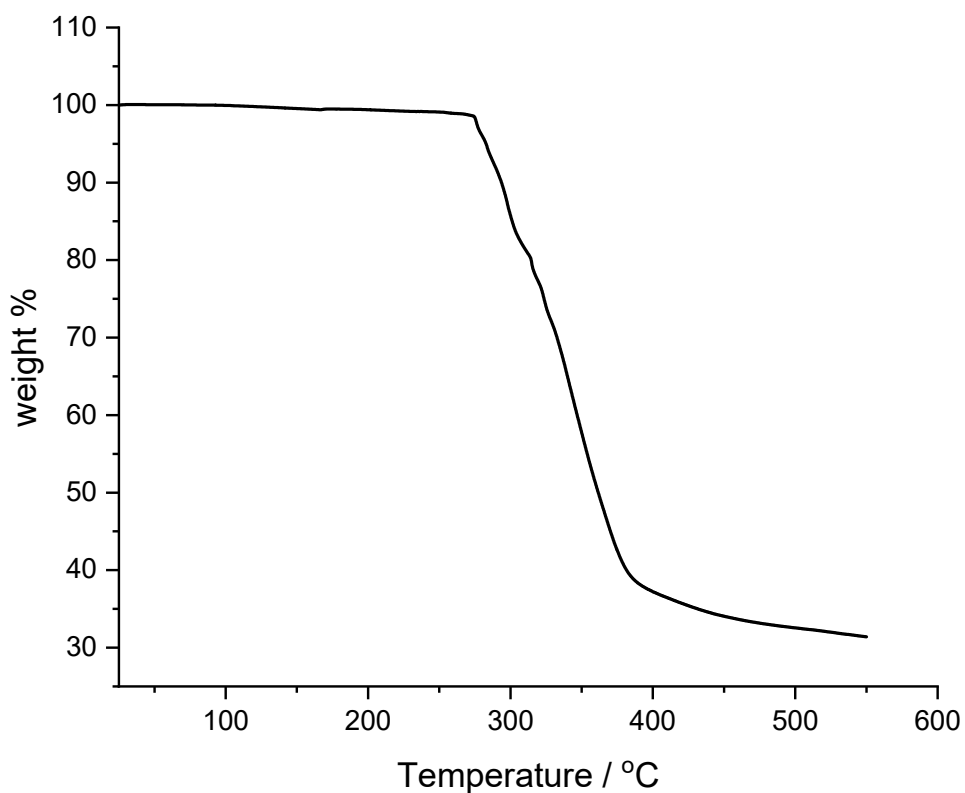
**Figure S2.** DSC of  $[P_1(\text{DMA})_3][\text{TFSI}]$  at a scan rate of 2 °C/min reflecting a single peak at 46 °C



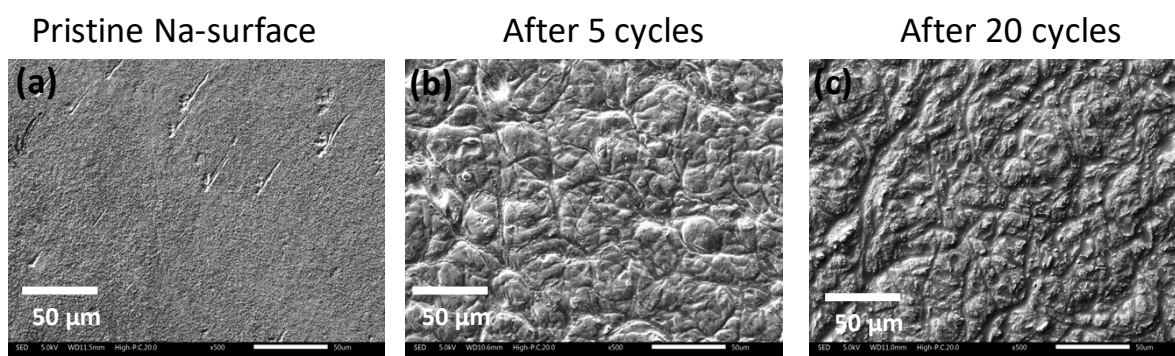
**Figure S3.** DSC of  $[P_1(\text{DEA})_3][\text{FSI}]$  showing the change of the solid-solid transition (near 0 °C) between cycle 1 and cycle 2



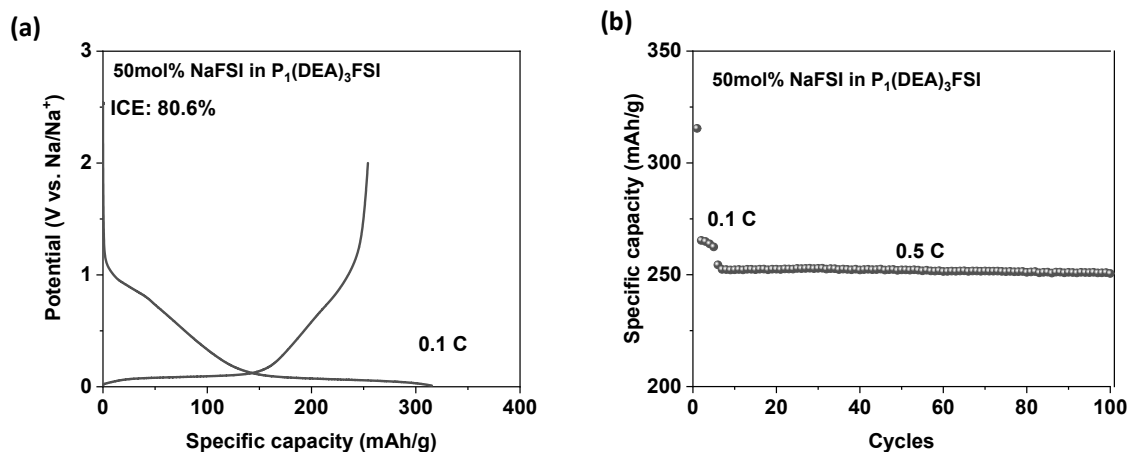
**Figure S4.** LSV curve of 50mol% NaFSI/[P1(DEA)3][FSI] using Cu as WE, Pt as CE and Ag<sup>+</sup>/AgOTf as RE at a scan rate of 10 mV/s.



**Figure S5.** TGA thermograms of the 50mol% NaFSI/[P1(DEA)3][FSI], recorded at a heating rate of 10°C/min.



**Figure S6.** SEM images (50  $\mu\text{m}$ ) of the Na metal (d) at pristine state, (e) after 5 cycles and (f) after 20 cycles under 0.5 mA cm<sup>-2</sup> with 1 h plating/stripping



**Figure S7.** Cycling stability of Na/HC half-cell in 50 mol% NaFSI/P<sub>1</sub>(DEA)<sub>3</sub> electrolyte. (a) initial galvanostatic charge/discharge curve at C/10 (1C = 300 mAh/g); (b) cycling stability of 5 formation cycles at C/10, followed by 1/5 C for long term cycling.

**Table S1.** Electrochemical comparison of Na/Na symmetrical cell in different ionic liquid electrolytes at 50 °C

ILs	Salt	Concentration (mol %)	Current density (mA cm <sup>-2</sup> )	Polarization time (h)	Cycles	Over potential (V)	Ref
P1(DEA) <sub>3</sub> FSI	NaFSI	50	0.5/ 0.5	1/2	120/75	0.06/ 0.07	This work
C <sub>3</sub> mpyrFSI	NaFSI	50	0.5	0.13	20	0.13	J. Phys. Chem. C 2016, 120, 4276–4286
C <sub>3</sub> mpyDCA	NaFSI/ NaDCA/ NaTFSI/ NaFTFSI	19/ 18/ 18/ 18	0.1	1	25/ 25/ 25/ 25	0.1/ 0.08/ 3.2/ 3	ACS Appl. Mater. Interfaces 2019, 11, 46, 43093–43106
Dry C <sub>3</sub> mpyrFSI (< 30 ppm)	NaFSI	50	1	1	100	0.139	ACS Appl. Mater. Interfaces

							2022, 14, 15784-1 5798
Wet C <sub>3</sub> mpyrFSI (~1000ppm)	NaFSI	50	1	1	100	0.083	ACS Appl. Mater. Interfaces 2022, 14, 15784-1 5798
Dry P <sub>111i4</sub> FSI (< 30 ppm)	NaFSI	42	1	1	100	0.131	ACS Appl. Mater. Interfaces 2022, 14, 15784-1 5798
Wet P <sub>111i4</sub> FSI (~1000 ppm)	NaFSI	42	1	1	100	0.081	ACS Appl. Mater. Interfaces 2022, 14, 15784-1 5798
C <sub>3</sub> mpyrFSI	NaFSI	50	0.05	1	50	0.03	ChemSus Chem201 9,12,1700 -1711