Supplementary

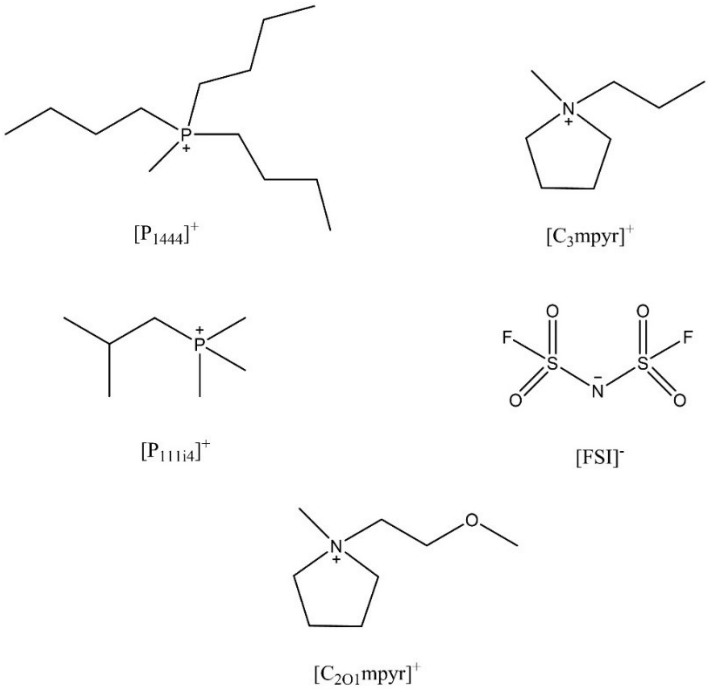

Figure S1. Structures of the ionic liquids

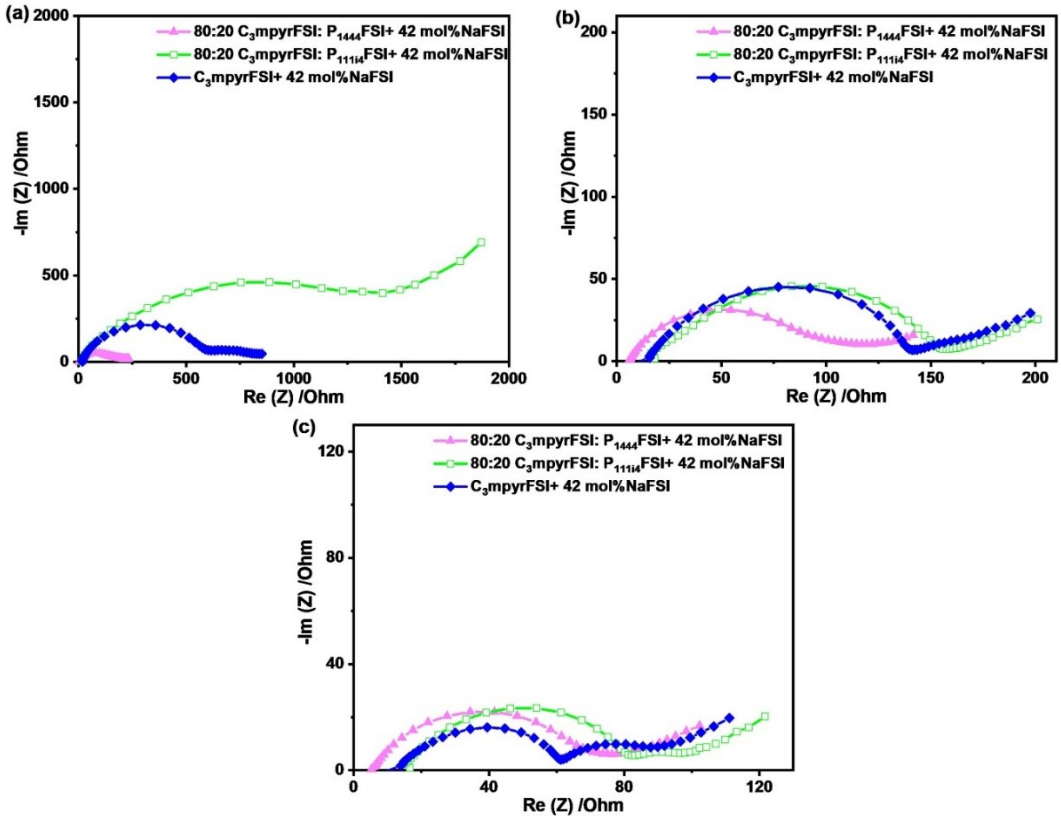

Figure S2. Nyquist plot from Na/Na cells (a) before cycling (b) after first cycle (c) after 10th cycle

Table S1. Equivalent circuit fitting results of Na/Na symmetrical cells after first cycle (SI)

Sample (with 42 mol% NaFSI)	R_b (Ω)	C_{SEI} (F)	R_{SEI} (Ω)	C_{CT} (F)	R_{CT} (Ω)	W ($\Omega.s^{-1/2}$)
80:20 C_3mpyrFSI: P_{1444}FSI	5.2	2.9×10^{-6}	63.6	3.5×10^{-3}	57.0	8.6
80:20 C_3mpyrFSI: P_{111i4}FSI	13.8	1.7×10^{-7}	65.9	7.1×10^{-7}	96.3	28.4
C_3mpyrFSI	14.1	8.6×10^{-7}	57.3	3.9×10^{-7}	68.8	58.9

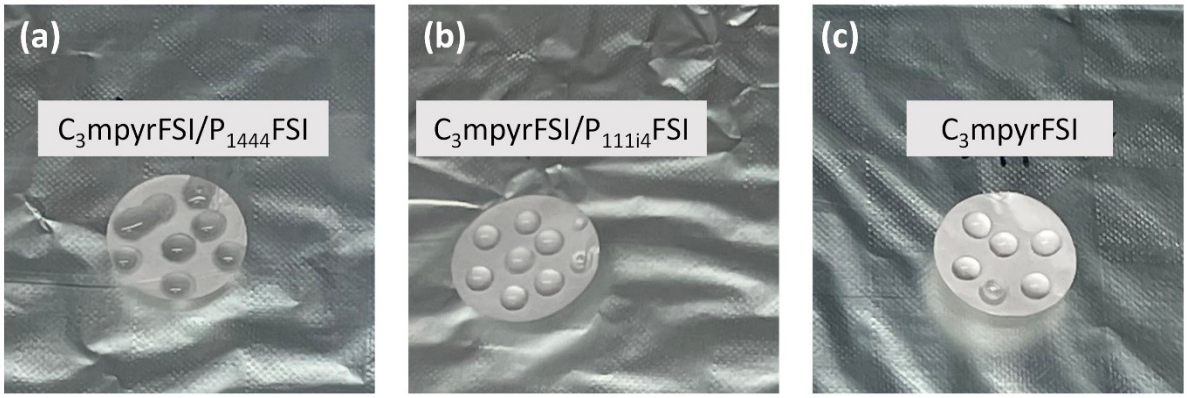

Figure S3. Wettablity of the Solupor seperator with (a) C_3mpyrFSI/P_{1444}FSI mixture (b) C_3mpyrFSI/P_{111i4}FSI mixture (c) C_3mpyrFSI, all containing 42 mol% NaFSI

Table S2. Neutron Scattering Length Density estimated for the used materials SI

Material	**SLD (10^{-6} Å^{-2})**
C_3mpyrFSI	1.18
P_{111i4}FSI	0.83
P_{1444}FSI	0.5
NaFSI	1.6
C_3mpyr^+	-0.38
P_{111i4}^+	-0.96
P_{1444}^+	-1.27
FSI^-	4
Si	2.07
SiO2	3.5
Cr	3
Au	4.5
Na^+	-

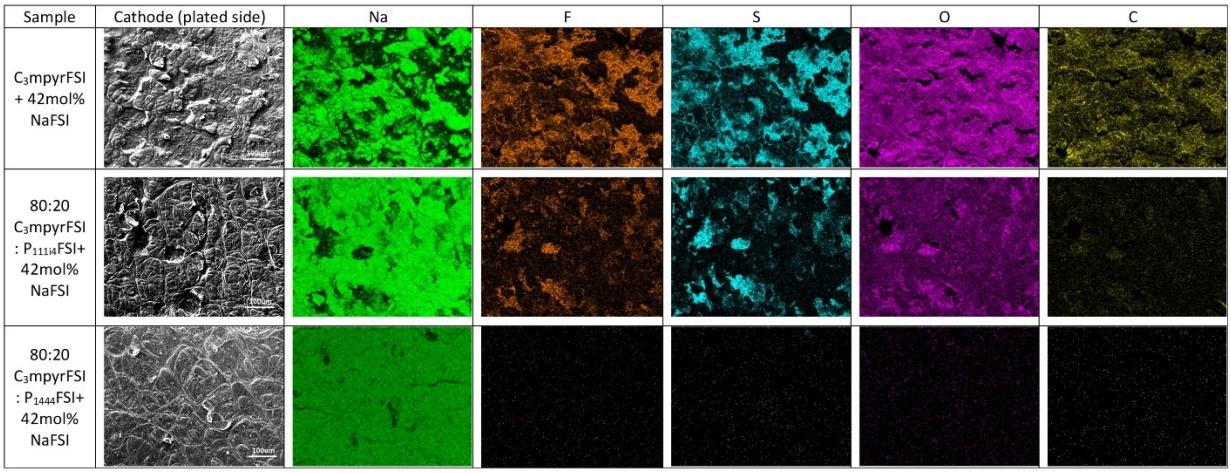

Figure S4. SEM of the plated sodium electrode after 20 cycles.

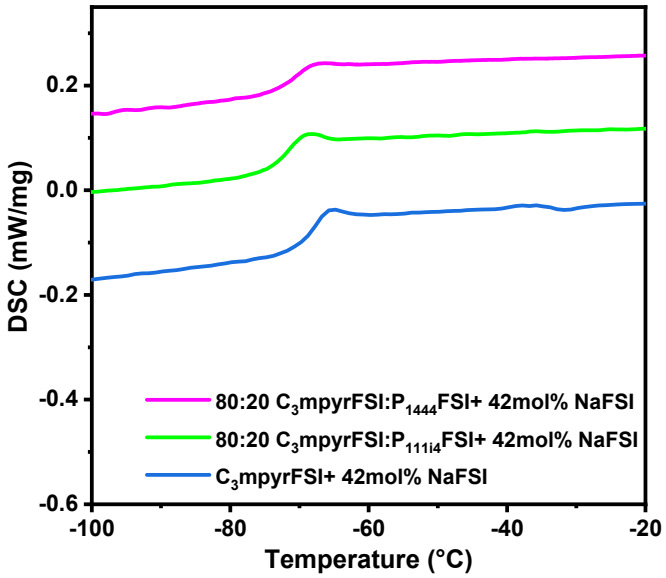

Figure S5. DSC heating traces of the mixed P111i4FSI, P1444FSI and C3mpyrFSI with 42 mol% NaFSI system.

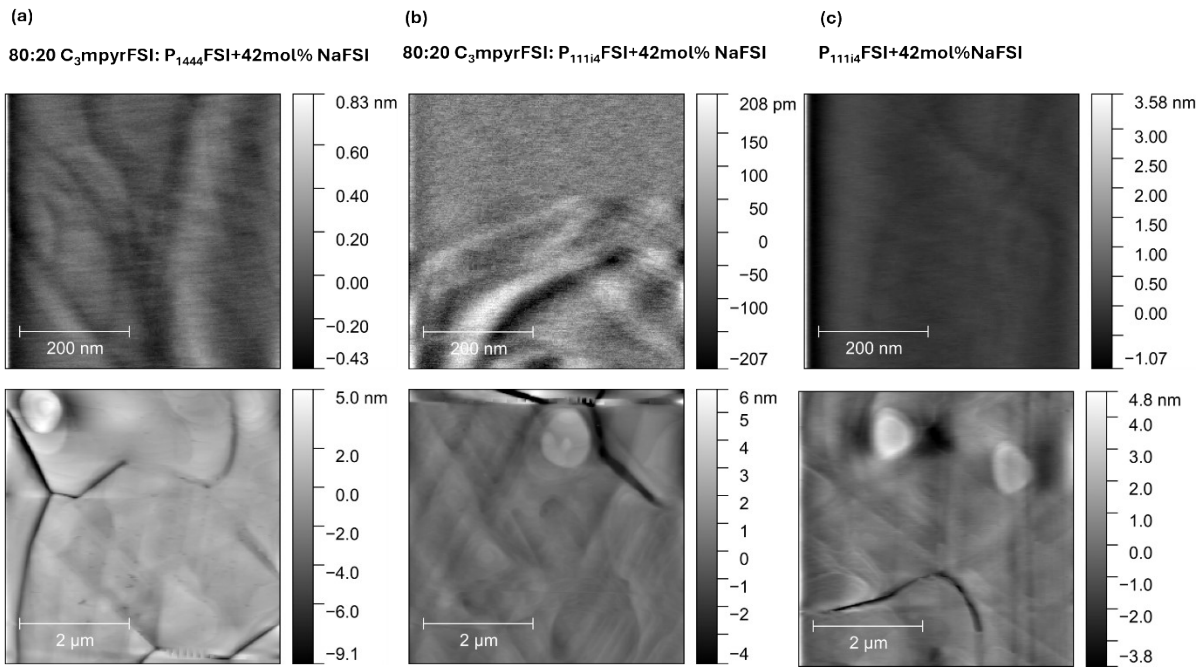

Figure S6. Surface morphology of the Au surface through AFM surface imaging at OCP-0.7 V before SEI formation for (a) C_3mpyrFSI/P_{1444}FSI mixture, (b) C_3mpyrFSI/P_{111i4}FSI mixture and (c) P_{111i4}FSI + 42 mol% NaFSI.