N-ethyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide-electrospun polyvinylidene fluoride composite electrolytes: characterization and lithium cell studies

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[C_2mpyr][FSI] synthesis procedures:

[C_2mpyr][FSI] was synthesized as follows: 9.73 g (0.05 mol) of *N*-ethyl-*N*-*m*ethylpyrrolidinium bromide ([C_2mpyr]Br) and 12.05 g (0.055 mol) of potassium bis(fluorosulfonyl)imide (KFSI) were separately dissolved in distilled water. The KFSI solution was then added dropwise into the [C_2mpyr]Br solution. [C_2mpyr][FSI] was obtained as a waxy white solid after the water was removed with rotary evaporation. For purification, [C_2mpyr][FSI] was first dissolved in acetone (Scharlau HPLC grade), and filtered, and the acetone then removed by rotary evaporation. To further remove any KBr impurity, the [C_2mpyr][FSI] was dissolved in distilled water by heating at 80°C. The solution was put in the refrigerator for an hour to recrystallize the [C_2mpyr][FSI]. After that, the clear liquid was tested with $AgNO_3$ solution. A precipitate indicated the existence of Br^- and the solid was separated from the water. This recrystallization process was repeated six times until there was no precipitate when testing with $AgNO_3$ solution. In the end, 9.99 g (0.034 mol) of [C_2mpyr][FSI] was dried under vacuum on a Schlenk line at 50°C for over 48 hours and then stored in an argon glovebox. The yield was 68%.

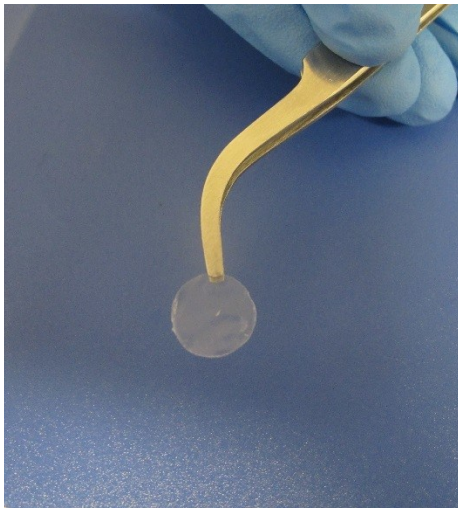
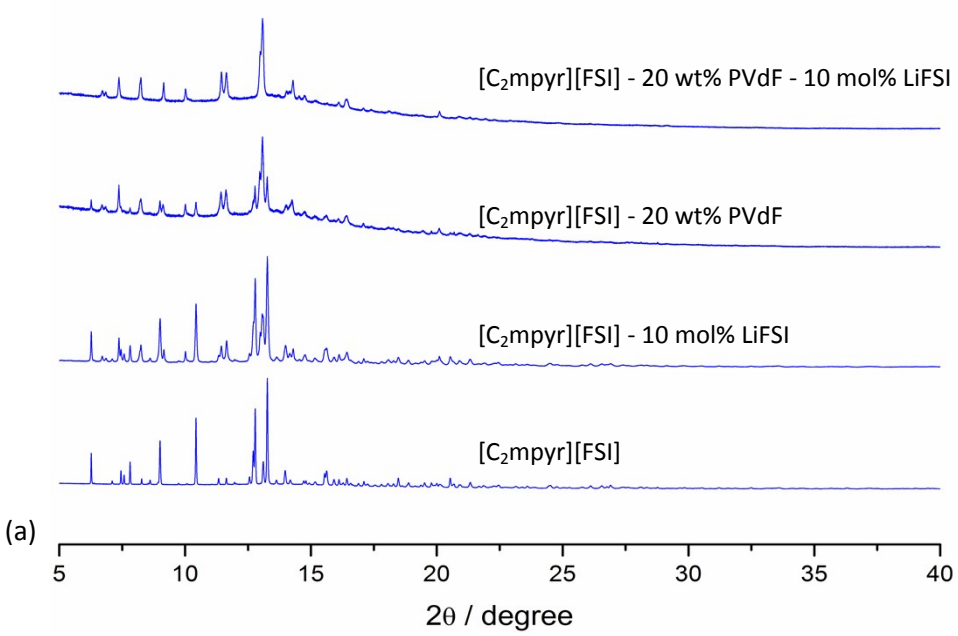


Fig S1. The flexible, solid, free-standing [C_2mpyr][FSI] - 10 wt% PVdF - 10 mol% LiFSI composite electrolyte.

Phase III: -100 ℃



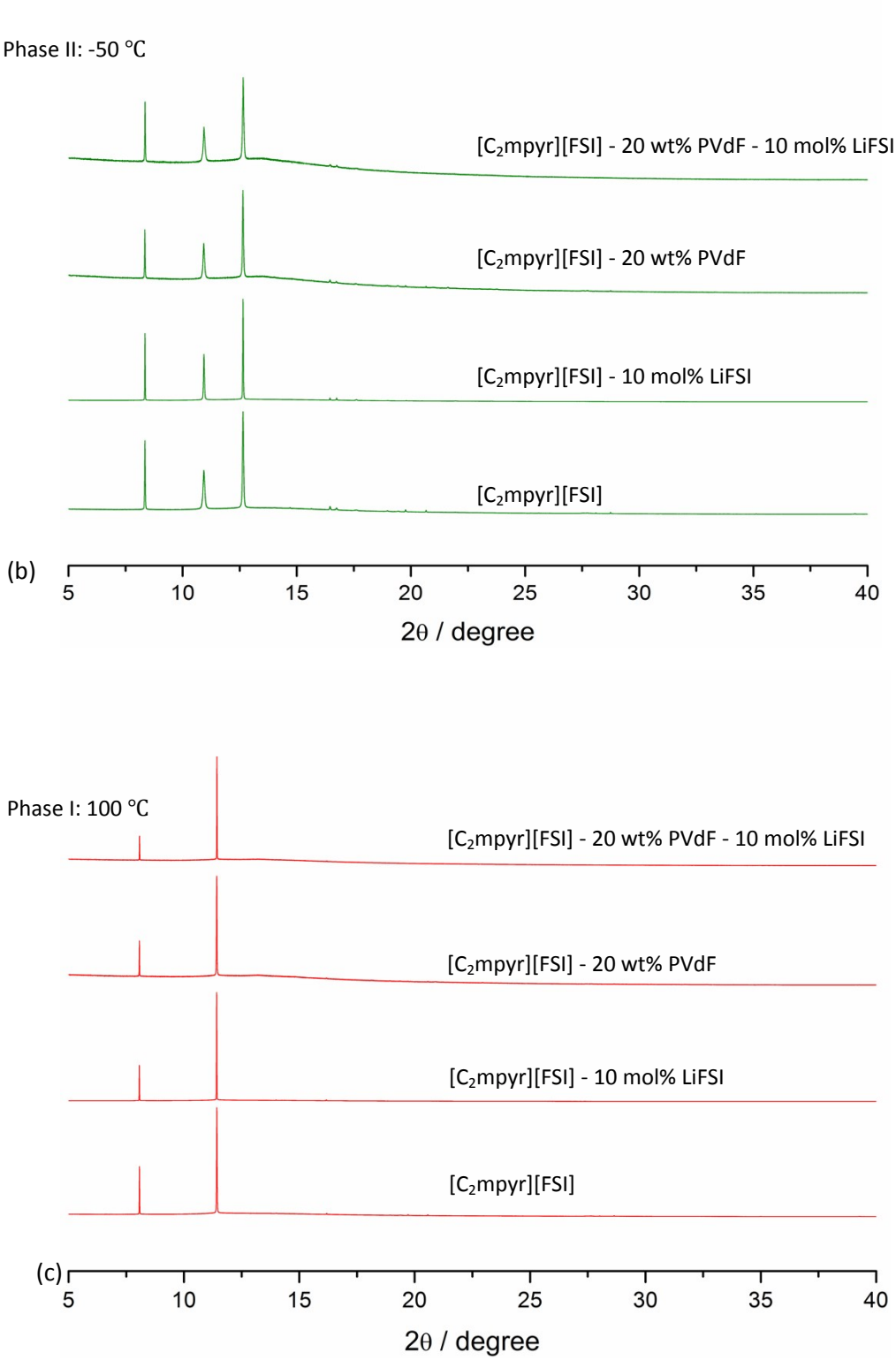


Fig S2. Synchrotron XRD patterns of (a) phase III, -100°C (b) phase II, -50°C (c) phase I, 100°C of the four systems, [C_2mpyr][FSI], [C_2mpyr][FSI] - 10 mol% LiFSI, [C_2mpyr][FSI] - 20 wt% PVdF, and [C_2mpyr][FSI] - 20 wt% PVdF - 10 mol% LiFSI.

Table S1 The space group and unit cell parameters including a, b, c, α, β, γ, and unit cell volume of [C_2mpyr][FSI], [C_2mpyr][FSI] - 10 mol% LiFSI, [C_2mpyr][FSI] - 20 wt% PVdF, [C_2mpyr][FSI] - 20 wt% PVdF - 10 mol% LiFSI.

Material	phase	Space Group	a(Å)	b(Å)	c(Å)	a(°)	β (°)	γ (°)	Unit cell volume(Å^3)
[C_2mpyr][FSI]	III	C2/m (monoclinic)	7.6352(5)	10.5337(8)	12.1091(4)	90	126.(2)	90	785.5(4)
	II	P6/mmm (trigonal)	12.5128(2)	12.5128(2)	11.9220(8)	90	90	120	1616.5(7)
	I	Fmmm (orthorhombic)	12.4552(0)	14.6151(2)	15.8127(8)	90	90	90	2878.4(7)
[C_2mpyr][FSI] - 10 mol% LiFSI	III	C2/m	7.9810(3)	10.7128(7)	10.9286(3)	90	104.(8)	90	903.4(7)
	II	P6/mmm	20.9631(4)	20.9631(4)	3.7092(6)	90	90	120	1409.1(9)
	I	Fmmm	8.7032(3)	16.4164(4)	18.6101(4)	90	90	90	2658.9(5)
[C_2mpyr][FSI] - 20 wt% PVdF	III	C2/m	6.7247(7)	10.9855(4)	9.3244(2)	90	91.(8)	90	688.5(2)
	II	P6/mmm	12.7998(7)	12.7998(7)	11.8938(6)	90	90	120	1687.5(8)
	I	Fmmm	12.2543(9)	14.4071(5)	15.6677(0)	90	90	90	2766.1(5)
[C_2mpyr][FSI] - 20 wt% PVdF - 10 mol% LiFSI	III	C2/m	6.7019(1)	11.0569(2)	11.3358(6)	90	123.(4)	90	701.3(5)
	II	P6/mmm	12.3874(8)	12.3874(8)	14.1728(0)	90	90	120	1883.4(4)
	I	Fmmm	11.0418(4)	16.1326(2)	16.3924(2)	90	90	90	2920.4(1)

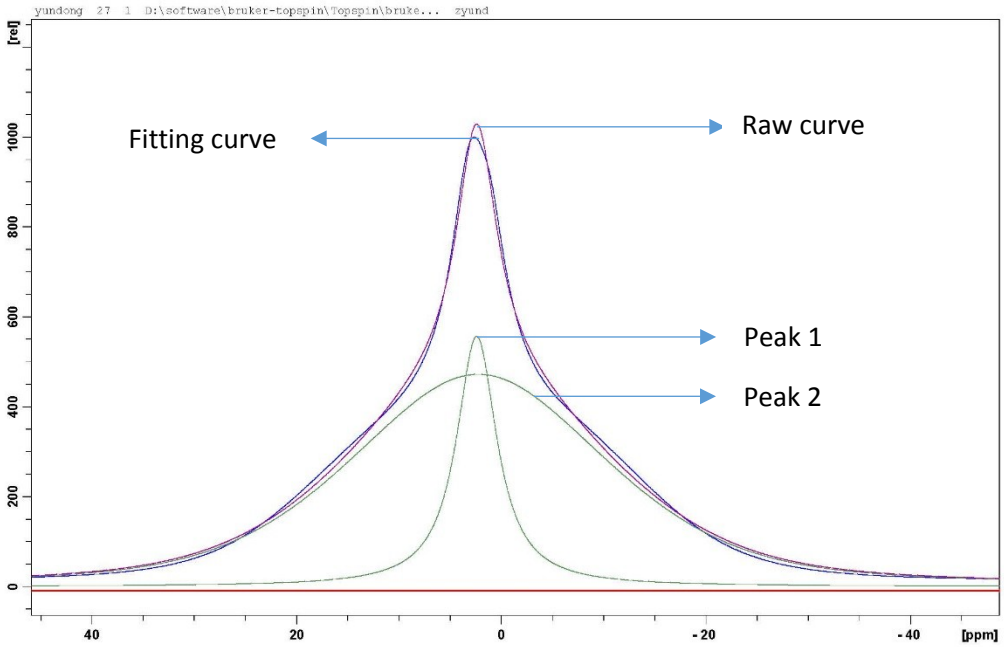


Fig S3. One fitting example of ^{1}H for [C_2mpyr][FSI] - 10 mol% LiFSI at 223K. The areas under Peak 1 (mobile species) and Peak 2 (rigid species) were calculated to work out the percent each compromised.

Table S2. The percent and full width at half maximums (FWHM) of each peak for (a) [C_2mpyr][FSI], (b) [C_2mpyr][FSI] - 10 mol% LiFSI, (c) [C_2mpyr][FSI] - 10 wt% PVdF - 10 mol% LiFSI at 223K and 293K. Fitting error less than 10%.

(a)

[C_2mpyr][FSI]		^{1}H		^{19}F	
		Percent(%)	FWHM(Hz)	Percent(%)	FWHM(Hz)
223K	Peak 1	100	10069	100	7550
293K	Peak 1	100	3686	100	2854

(b)

[C_2mpyr][FSI] - 10 mol% LiFSI		^{1}H		^{19}F		^{7}Li	
		Percent(%)	FWHM(Hz)	Percent(%)	FWHM(Hz)	Percent(%)	FWHM(Hz)
223K	Peak 1	22	1439	100	6589	100	302
	Peak 2	78	8878	-	-	-	-
293K	Peak 1	85	1000	10	82	100	27
	Peak 2	15	1692	90	1285	-	-

(c)

[C_2mpyr][FSI] - 10 wt% PVdF - 10 mol% LiFSI		^{1}H		^{19}F		^{7}Li	
		Percent(%)	FWHM(Hz)	Percent(%)	FWHM(Hz)	Percent(%)	FWHM(Hz)
223K	Peak 1	100	8833	100	6973	100	612
293K	Peak 1	100	1809	100	1408	100	366

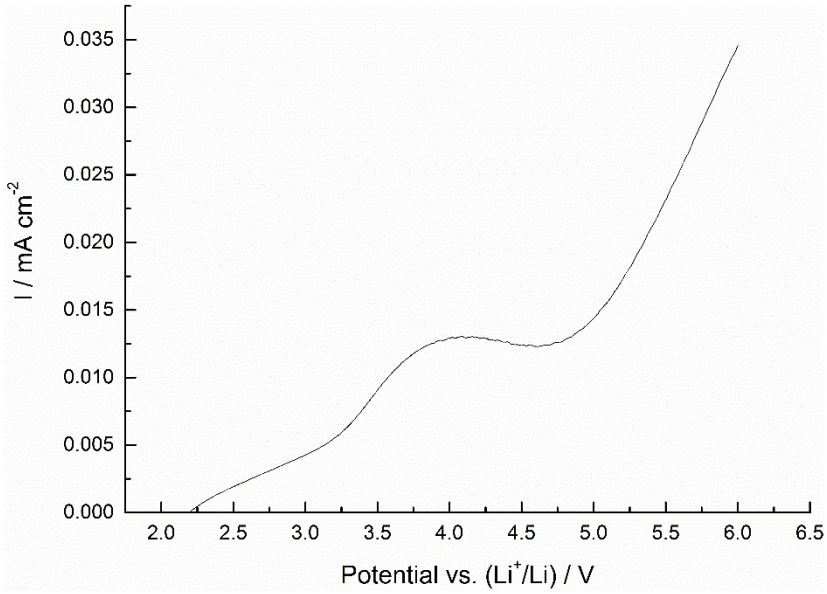


Fig S4. Linear scanning voltammogram of [C_2mpyr][FSI] - 10 wt% PVdF - 10 mol% LiFSI composite electrolyte.

To measure the lithium transference number, a Li / [C_2mpyr][FSI] - 10 wt% PVdF - 10 mol% LiFSI / Li symmetric coin cell was galvanostatically cycled at 0.13 mA cm^{-2} at room temperature for 200 cycles until the impedance became stable. Then a 10 mV potential was applied to the cell for 1.5h at room temperature until the current became stable.

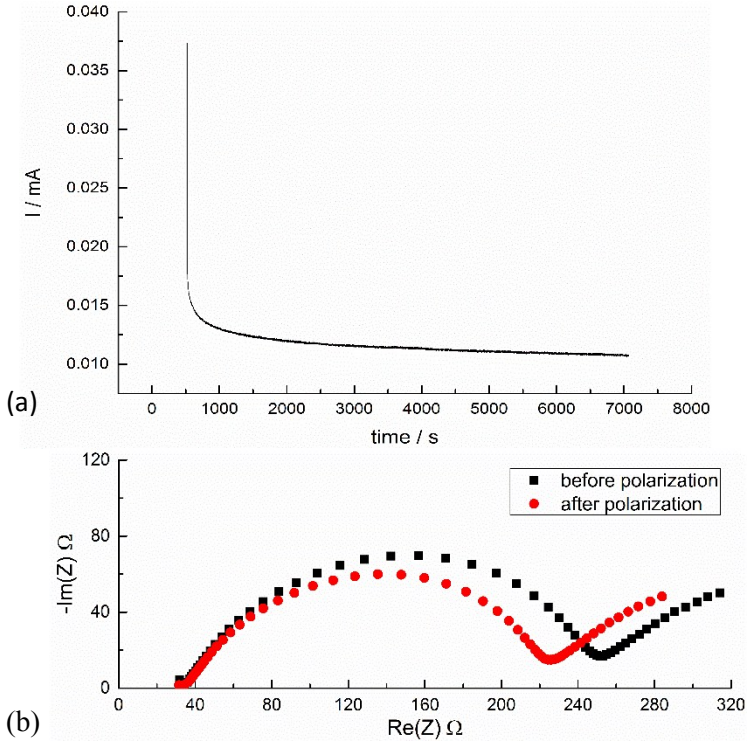


Fig S5. The (a) current vs time and (b) impedance before polarization and after stabilization. The I_0 (initial current) was 0.037 mA. The I_s (stable current) was 0.011 mA. The R_0 (impedance before polarization) was 194 $\pm$ 4 Ω. The R_s (impedance after stabilization) was 220 $\pm$ 4 Ω. The transference number of the lithium ions was calculated to be 0.104 $\pm$ 0.006.