Supporting information

[BMIM]BF_4 modified PVDF-HFP composite polymer electrolyte for high-performance solid-state lithium metal battery

Kaixiong Huang,[a] Yanyi Wang,[a] Hongwei Mi,[a] Dingtao Ma,[a] Bo Yong[a] and Peixin Zhang*[a]

[a] College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China.

E-mail: pxzhang@szu.edu.cn

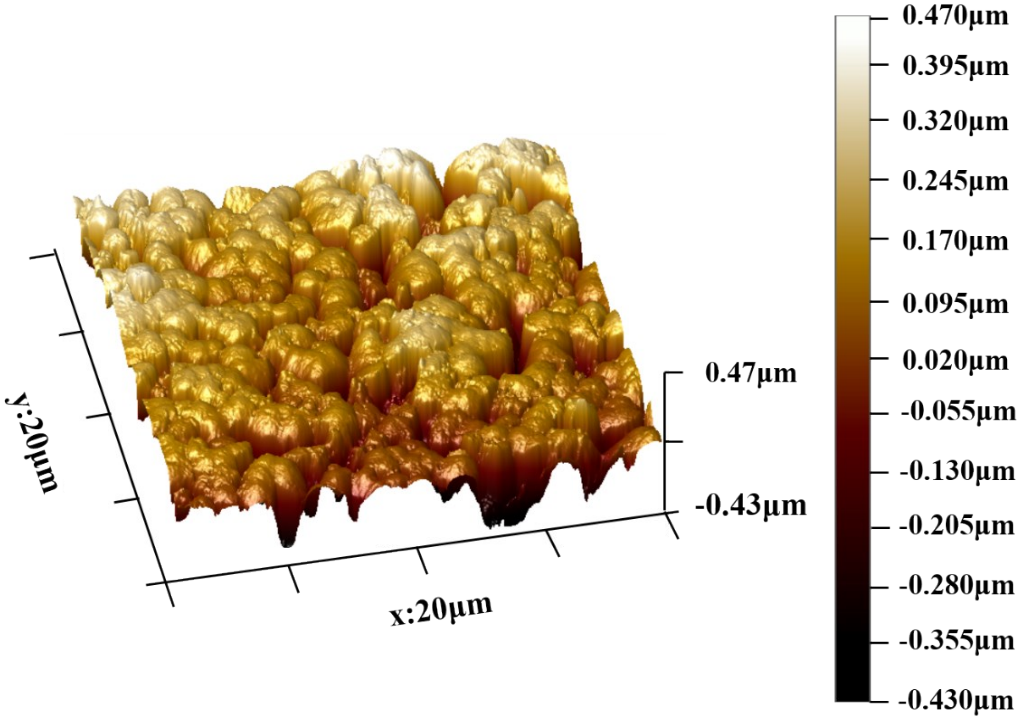

Figure S1. Atomic force microscope (AFM) photograph of PPEB212 electrolyte.

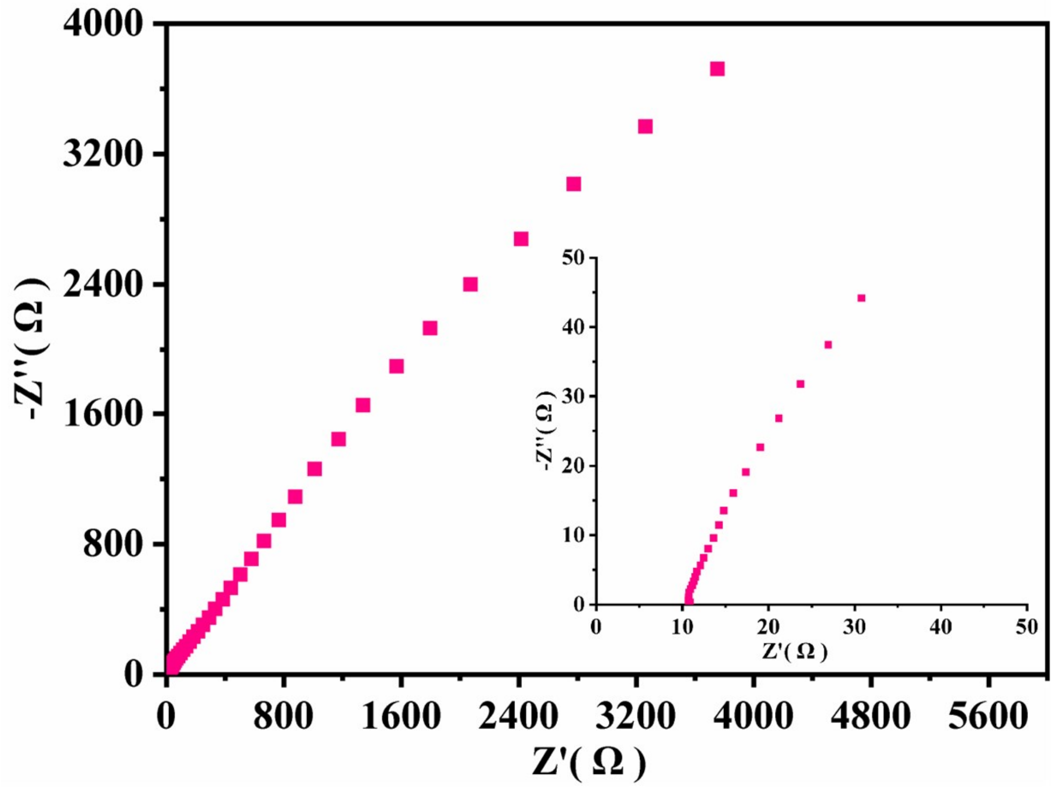

Figure S2. Impedance measurement of solid polymer electrolyte that only consist of PVDF-HFP, LiTFSI and $[BMIM]BF_4$.

The ionic conductivity of solid polymer electrolyte that only consist of PVDF-HFP, LiTFSI and [BMIM]BF_4 was calculated to be about 7.07×10^{-4} S cm^{-1} at 25℃.

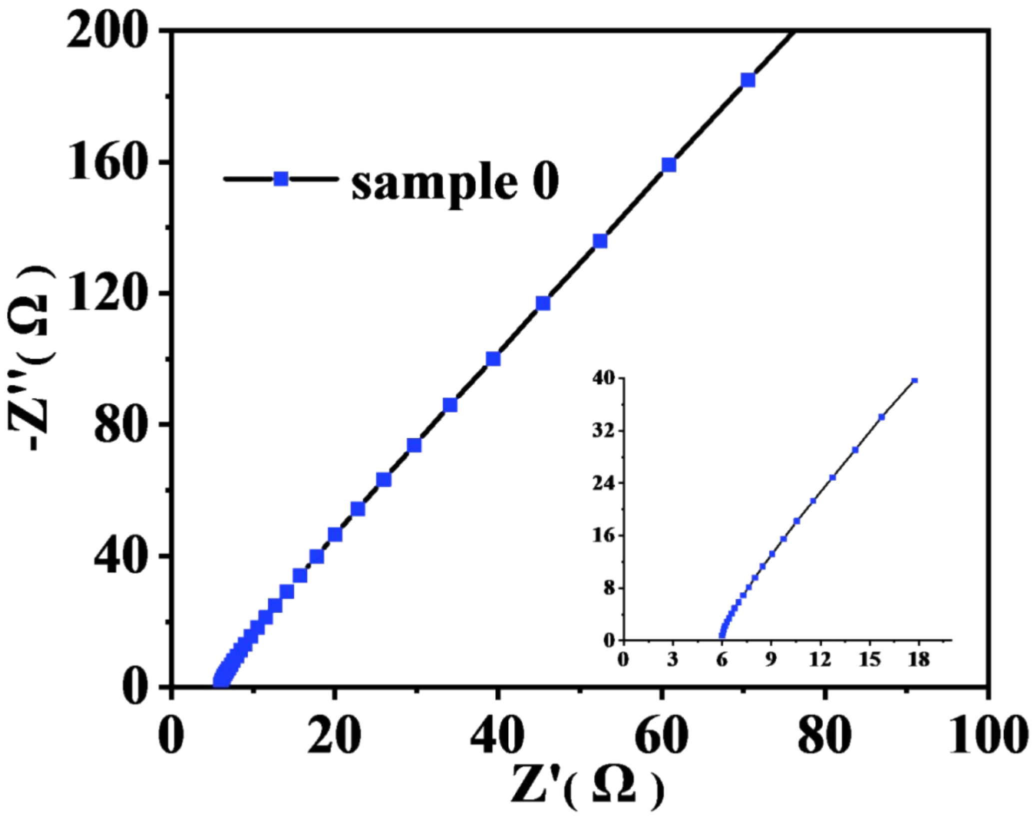

Figure S3. The impedance spectra of sample 0 at 25 °C. The sample 0 (PVDF-HFP: LiTFSI : PC : EC = 1.0 g : 0.4 g : 1.0 g : 0.5 g) shows a general ionic conductivity of 1.76 mS cm^{-1}.

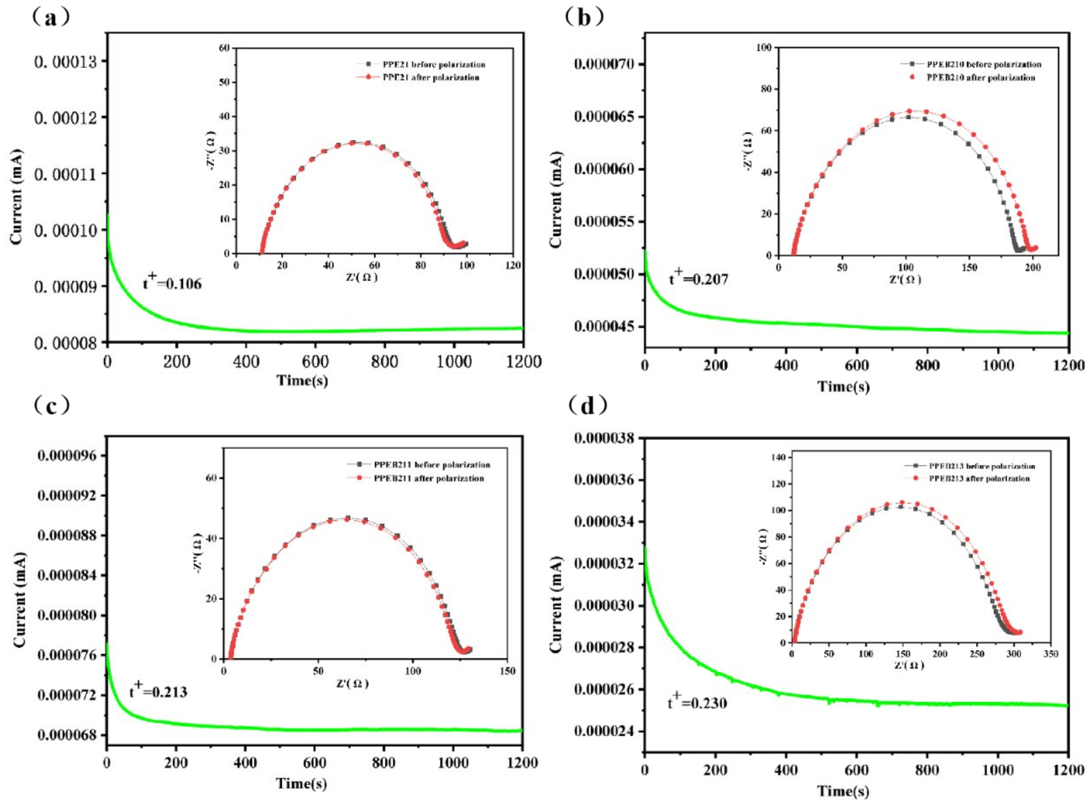

Figure S4. Li-ion transference number (t_{Li+}) of (a) PPE21, (b)PPEB210, (c)PPEB211, and (d) PPEB213.

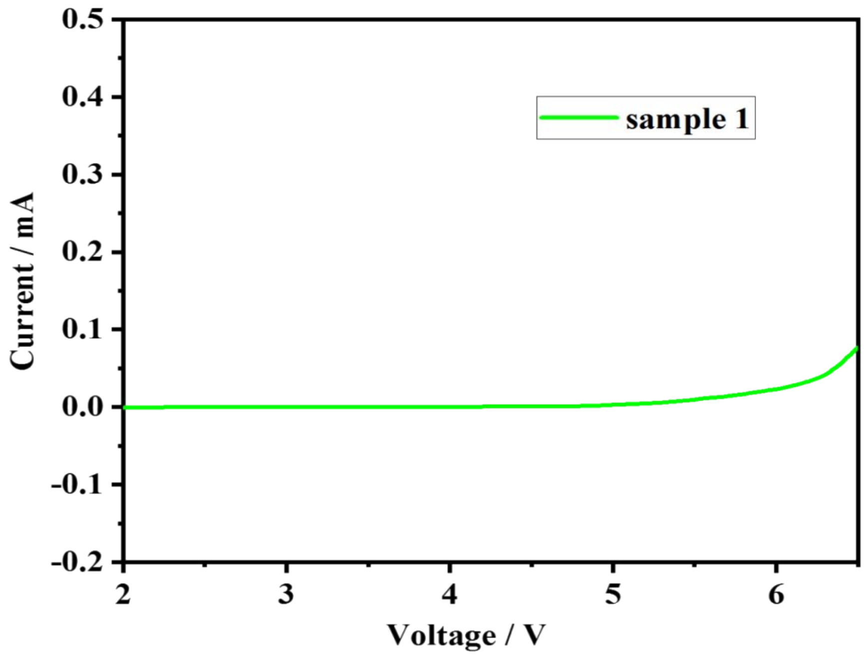

Figure S5. Linear sweep voltammograms of the sample 1(continue adding 0.4 g LiTFSI in PPEB212) sample 1 shows a higher decomposition potential of 5.8V.

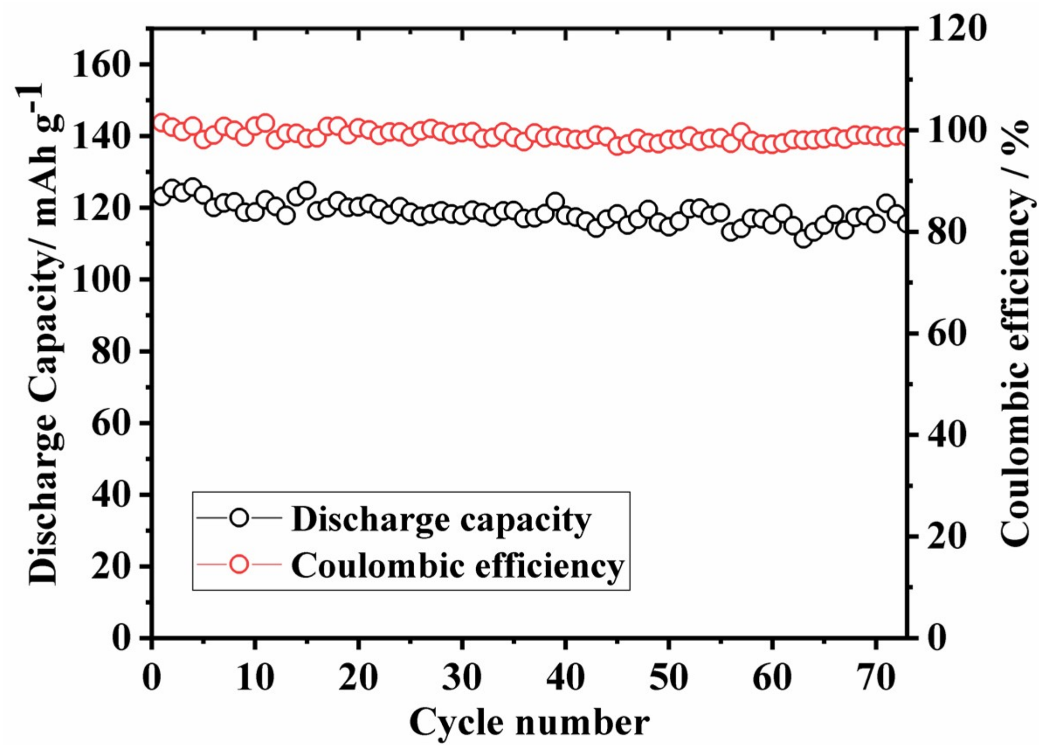

Figure S6. Electrochemical performance of solid polymer electrolyte that only consist of PVDF-HFP, LiTFSI and $[BMIM]BF_4$ at 0.2 C.

The battery constructed of the above-mentioned solid polymer electrolyte shows a lower discharge capacity of 120 mAh g^{-1}, which implies that the high viscosity $[BMIM]BF_4$ is not suitable for polymer electrolyte lonely.

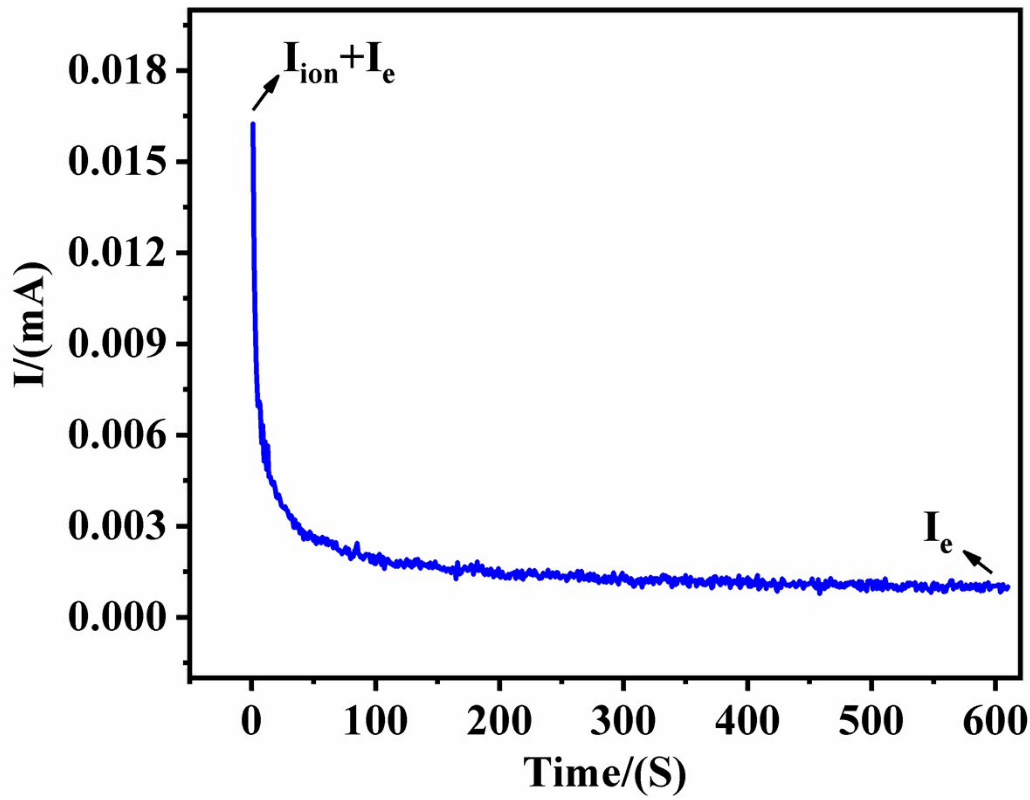

Figure S7. The plot of direct current (DC) test.

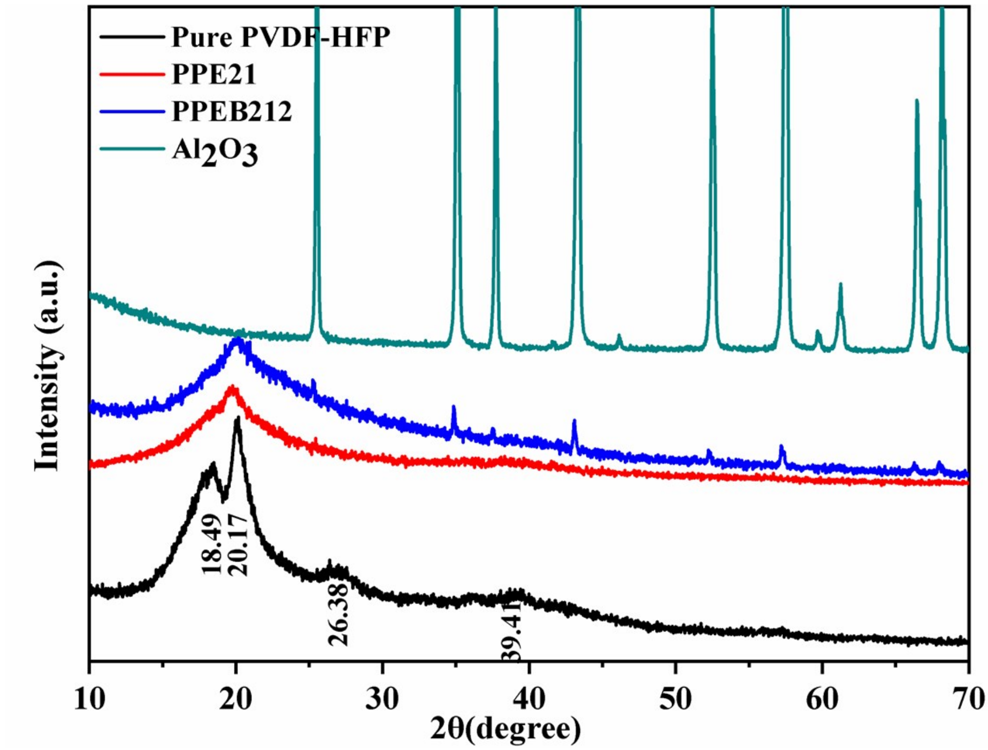

Figure S8. XRD patterns of the pure PVDF-HFP, Al_2O_3 particle, PPEB21 and PPEB212 ILCPE.

The ionic conductivity of polymer electrolyte would be greatly influenced by their crystallinity. Generally, increasing the amorphicity of films can lead to an increment of ionic conductivity. X-ray diffraction (XRD) was conducted to investigate the crystallinity phase of the as-prepare membrane as shown in Figure S8. The result obviously shows that the diffraction peaks located at around 18.5, 20.2, 26.4 and 39.4^{o} are corresponding to characteristic peaks of pure PVDF-HFP. After adding the plasticizers, it can be seen that most of peaks of PPE21 disappear or become broader. Such phenomenon indicates that the crystallinity of pure PVDF-HFP decreases with the increasing content of plasticizers. On the other hand, after embedding the [BMIM]BF_4 in the PVDF-HFP based ILCPE, the diffraction peaks at 39.41^{o} also disappear, which implies the further reduction of crystallinity degree of the ILCPE.

Table S1. The EIS fitting results of Li|PPEB210|$LiFePO_4$ cell after different cycling number at room temperature.

	R_b (Ω)	R_{ct1} (Ω)	R_{ct2} (Ω)	W (Ω)
1st	6.347	123.4	0.6938	113.7
3rd	6.382	4.86	128.1	107.3
5th	6.502	412.5	144.8	88.99
7th	6.336	149.2	26.76	82.21
9th	6.529	34.24	126.7	80.39
11th	6.755	168.3	31.37	64.4
13th	6.765	12.59	166.5	79.98
15th	5.693	170	291.6	42.08
17th	5.502	164.8	0.983	69.13
19th	6.536	23.08	152.8	66.08

Table S2. The EIS fitting results of Li|PPEB212|$LiFePO_4$ cell after different cycling number at room temperature.

	R_b (Ω)	R_{ct1} (Ω)	R_{ct2} (Ω)	W (Ω)
1st	5.248	230.8	1.399	135.9
3rd	5.752	160.9	98.18	118.5
5th	5.676	269.2	51.4	133.2
7th	5.527	52.33	292.9	95.82
9th	5.804	244.3	34.93	132
11th	5.574	284	50.01	97.97
13th	5.516	288.5	223.1	64.55
15th	5.648	259	31.84	128
17th	5.528	55.35	277.7	92.42
19th	5.819	263.8	61.54	97.25

Table S3. The comparison of electrochemical performance with the Li/$LiFePO_4$ cells assembled with various polymer electrolyte membranes in the previous literatures.

Samples	**Discharge capacity ($mAh\ g^{-1}$)**	**Capacity retention/%**	**Ref.**
PVDF-HFP/ PET/PVDF-HFP	120 (1 C, 1st) 103 (1 C, 100th)	86	1
PVDF/PP microfiber	141 (0.1 C, 1st) 96 (0.1 C, 50th)	68	2
PVDF-HFP/LiTFSI/LLZO	119 (0.5 C, 1st) 113 (0.5 C, 150th)	93	3
PVDF-HFP/LiTFSI/LLATO/ Li_3PO_4	130 (0.5 C, 1st) 114.7 (0.5 C, 160th)	87.8	4
PVDF-HFP porous separators	140 (0.5 C, 1st) 130 (0.5 C, 100th)	94	5
PVDF-HFP/PC/EC/LiTFSI/ Al_2O_3/[BMIM]BF_4	130 (2 C, 1st) 124.2 (2 C, 300th)	95.5	This work

Reference

1. Y.-S. Wu, C.-C. Yang, S.-P. Luo, Y.-L. Chen, C.-N. Wei and S. J. Lue, *Int. J. Hydrogen Energ.*, 2017, **42**, 6862-6875.

2. J. Hao, Q. Xiao, G. Lei, Z. Li and L. Wu, *Electrochim. Acta*, 2014, **125**, 450-456.

3. Y. Li, W. Zhang, Q. Dou, K. W. Wong and K. M. Ng, *J. Mater. Chem. A*, 2019, **7**, 3391-3398.

4. H. Yang, J. Bright, B. Chen, P. Zheng, X. Gao, B. Liu, S. Kasani, X. Zhang and N. Wu, *J. Mater. Chem. A*, 2020, **8**, 7261-7272.

5. J. Heo, Y. Choi, K. Y. Chung and J. H. Park, *J. Mater. Chem. A*, 2016, **4**, 9496-9501.