Supporting Information

Chemical Interaction and Enhanced Interfacial Ion Transport in Ceramic Nanofiber-Polymer Composite Electrolyte for All-Solid-State Lithium Metal Battery

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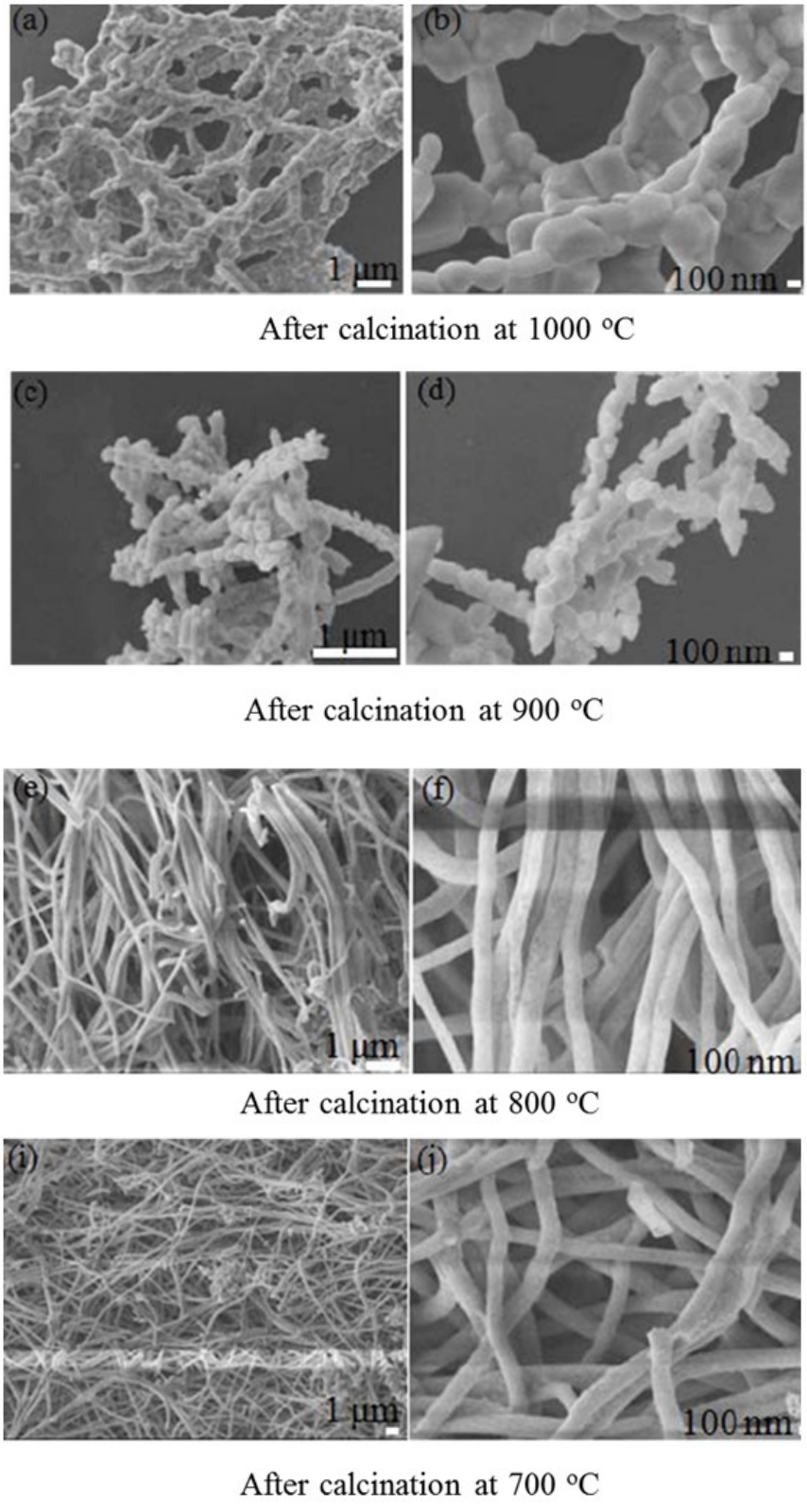

Figure S1. SEM images of the LLTO nanofibers after calcination at different temperatures

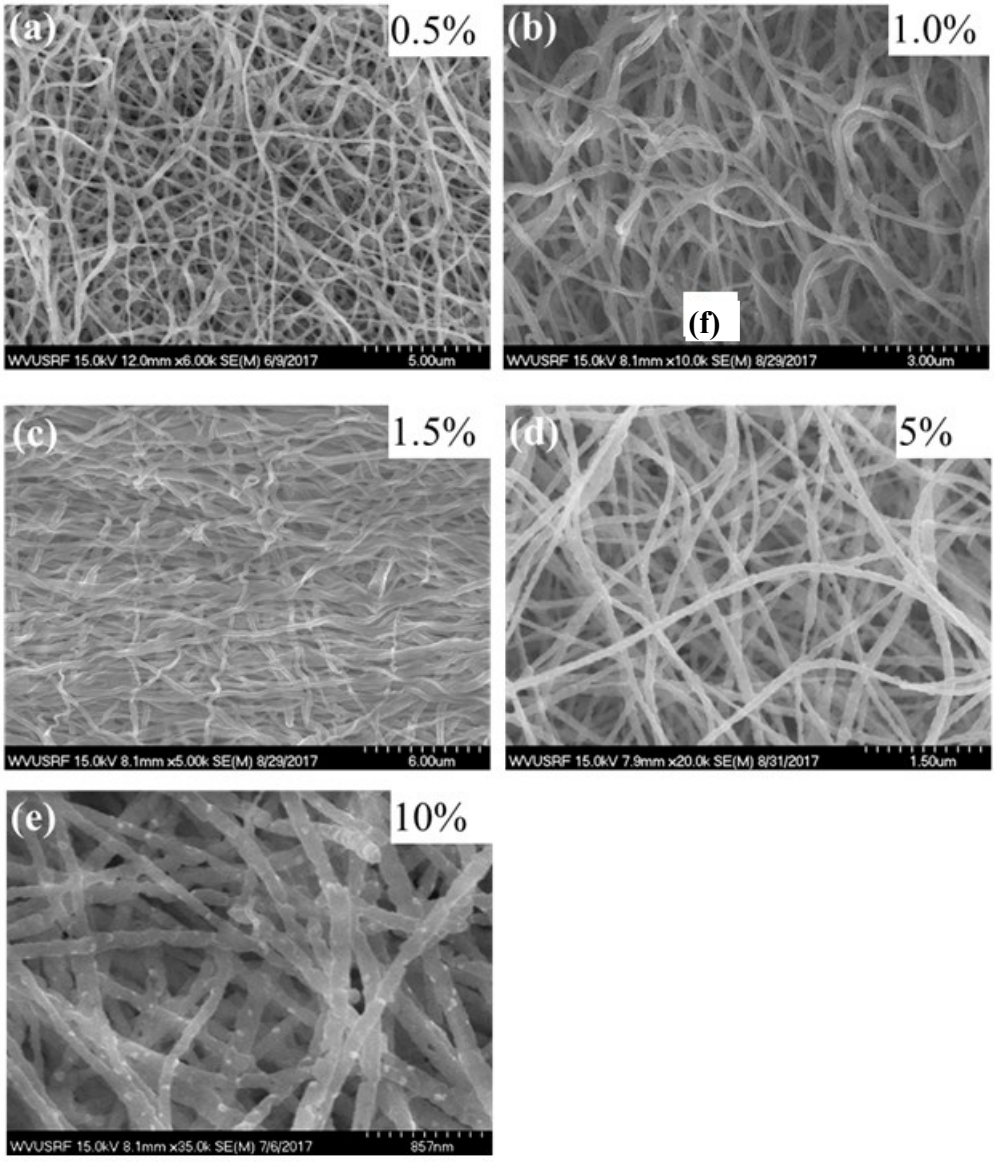

Figure S2. SEM images of Al-doped LLTO nanofibers. (a) LLATO, (b) LLATO-1, (c) LLATO-2, (d) LLATO-3, and (e) LLATO-4.

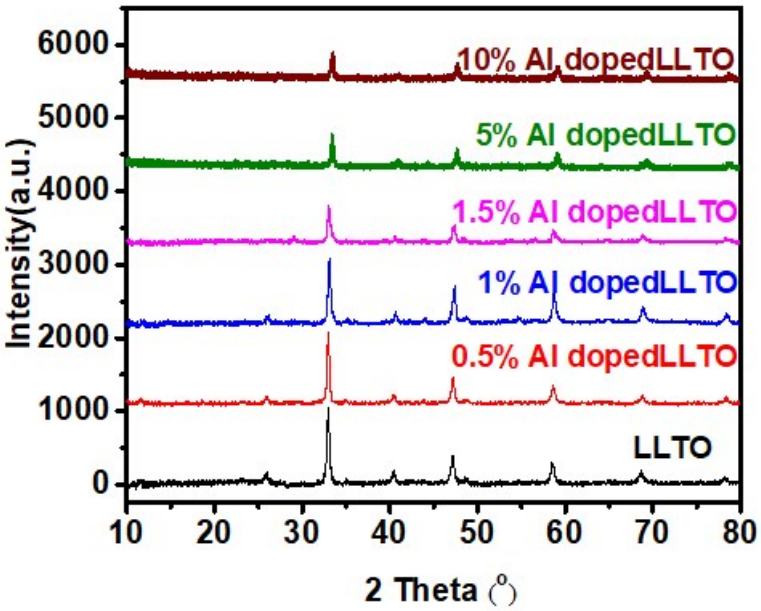

Figure S3. XRD spectra of 0.5-10% Al-doped LLTO nanofibers.

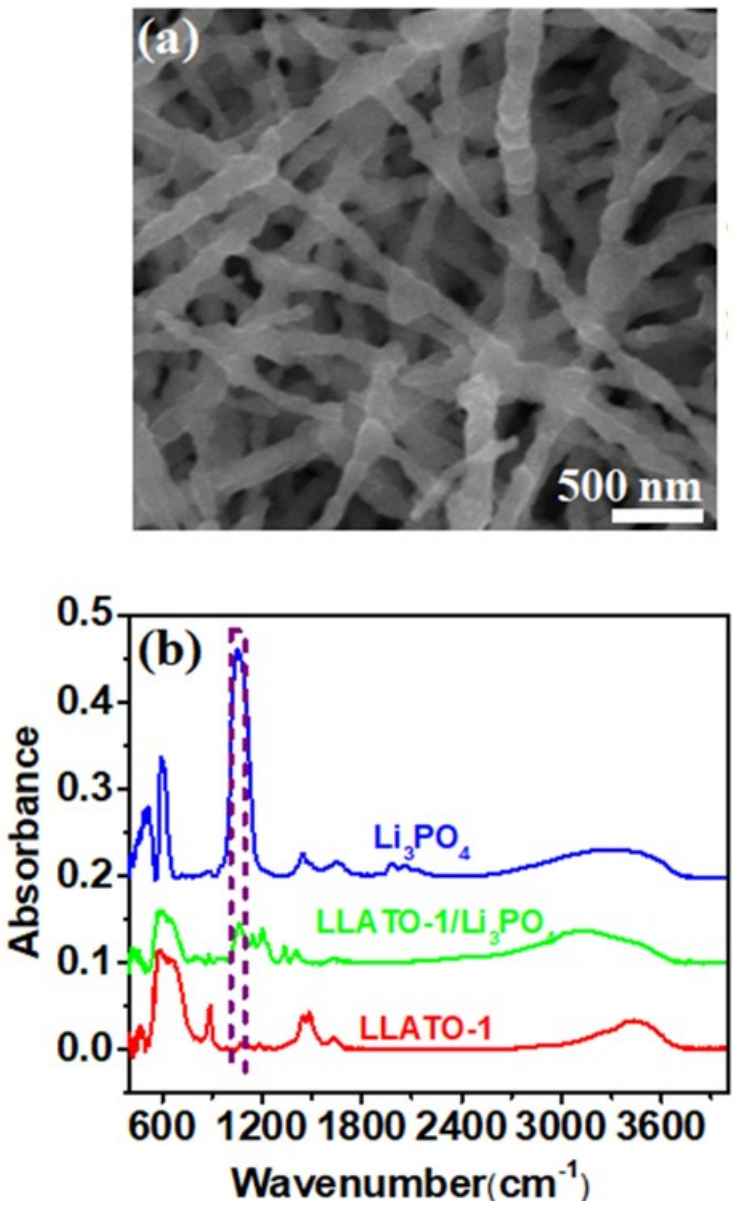

Figure S4. (a) SEM images of Li_3PO_4-modified LLATO nanofibers, (b) FTIR spectra.

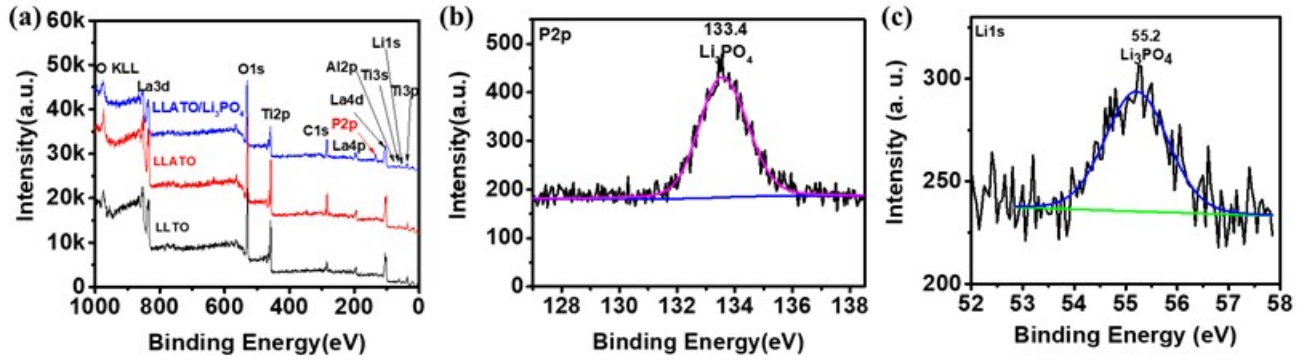

Figure S5. (a) XPS survey scan of Li_3PO_4-modified LLATO nanofibers, (b) P 2p core-level spectrum, (c) Li 1s core-level spectrum.

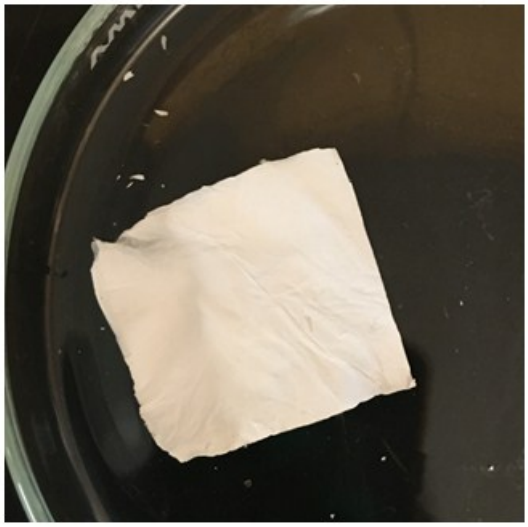

Figure S6. Optical image of PVDF-HFP/LiTFSI/LLATO composite electrolyte.

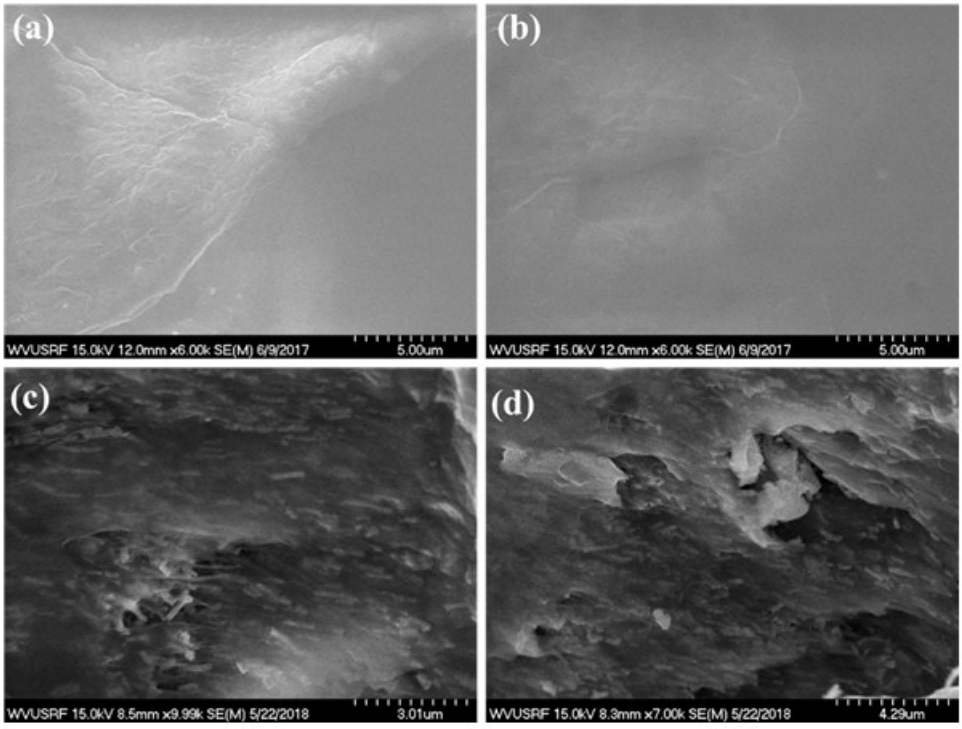

Figure S7. SEM imgaes of surface of PVDF-HFP/LiTFSI/LLATO membrane at different spots (a) (b), SEM image of inside of the PVDF-HFP/LiTFSI/LLATO membrane at different spots (c) (d).

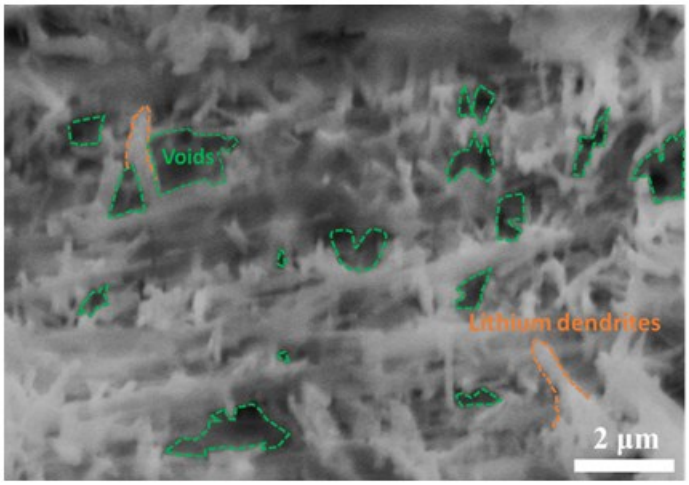

Figure S8. SEM image of the PVDF-HFP/LiTFSI0/40%LLATO membrane. The dendrites are grown at a current density of 0.5 mA/cm^2 with areal capacity of 0.25 mAh/cm^2 at room temperature.

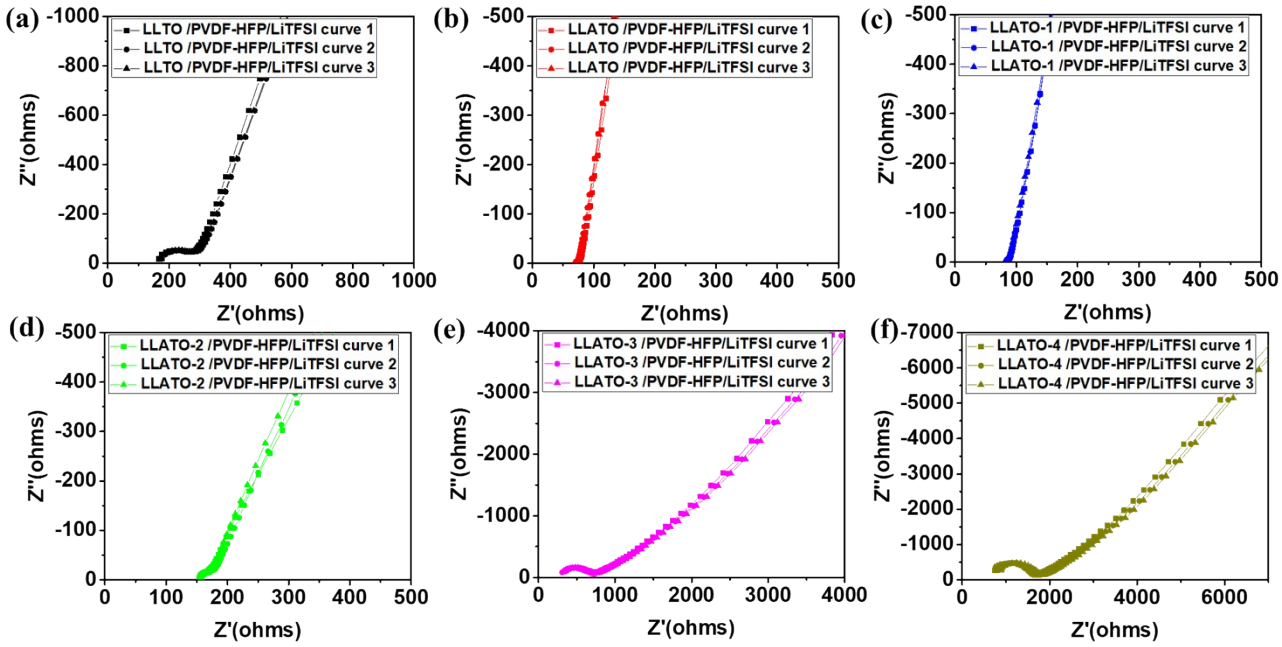

Figure S9. EIS plots of composite electrolytes based on LLTO nanofibers with different contents of aluminum doping. (a) LLTO/PVDF-HFP/LiTFSI, (b) LLATO/PVDF-HFP/LiTFSI, (c) LLATO-1/PVDF-HFP/LiTFSI, (d) LLATO-2/PVDF-HFP/LiTFSI, (e) LLATO-3/PVDF-HFP/LiTFSI, (f) LLATO-4/PVDF-HFP/LiTFSI.

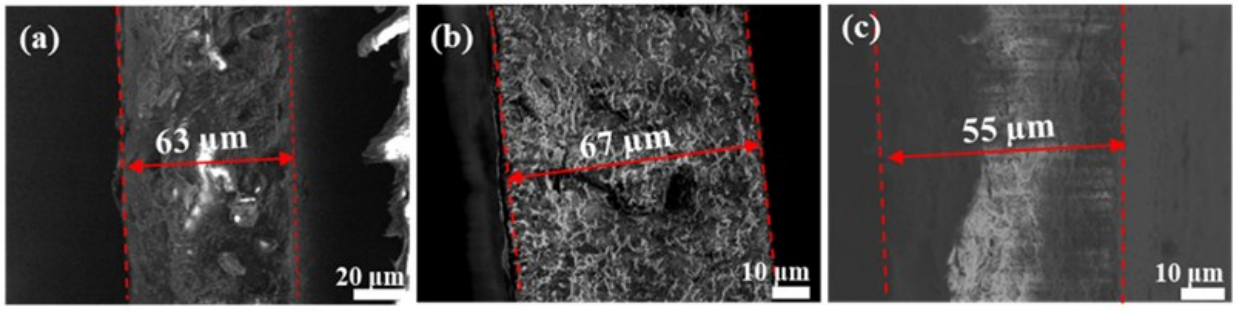

Figure S10. Thickness of composite electrolyte membrane for symmetric Li|Electrolyte|Li cell. (a) PVDF-HFP/LiTFSI, (b) PVDF-HFP/LiTFSI/LLATO (c) PVDF-HFP/LiTFSI/LLATO/Li_3PO_4.

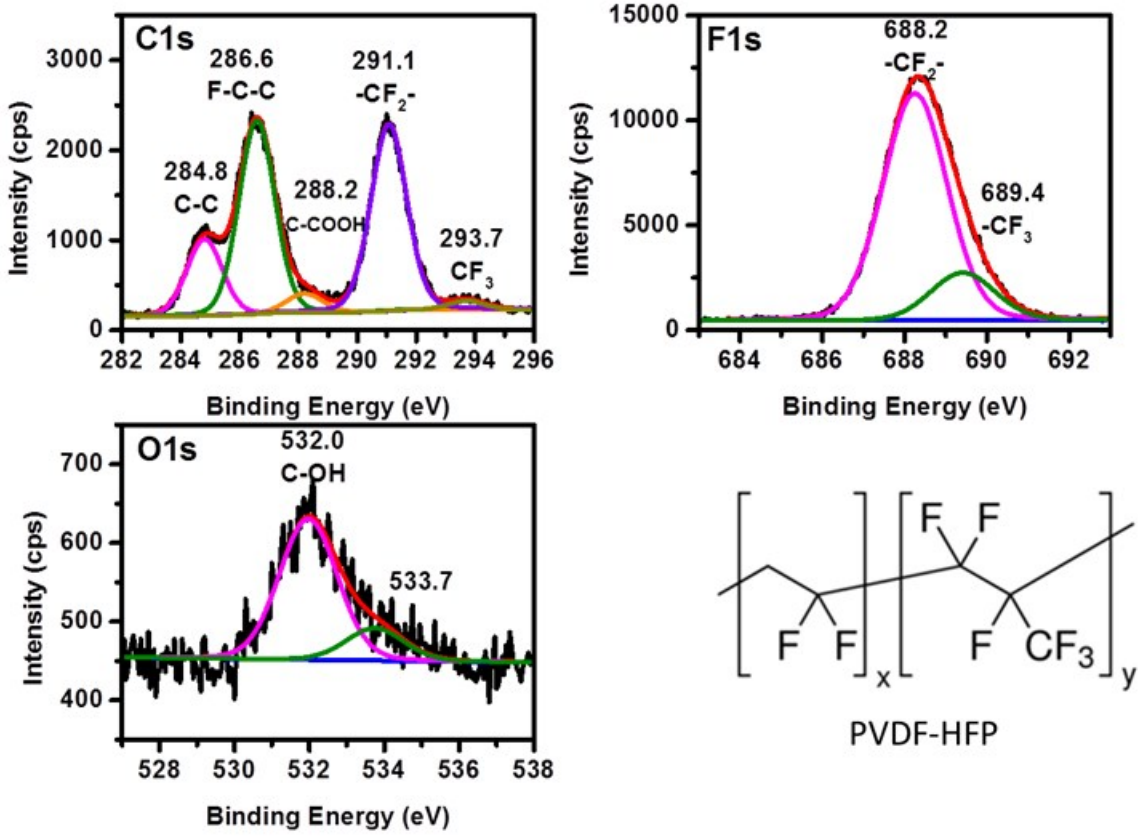

Figure S11. XPS spectra of PVDF-HFP.

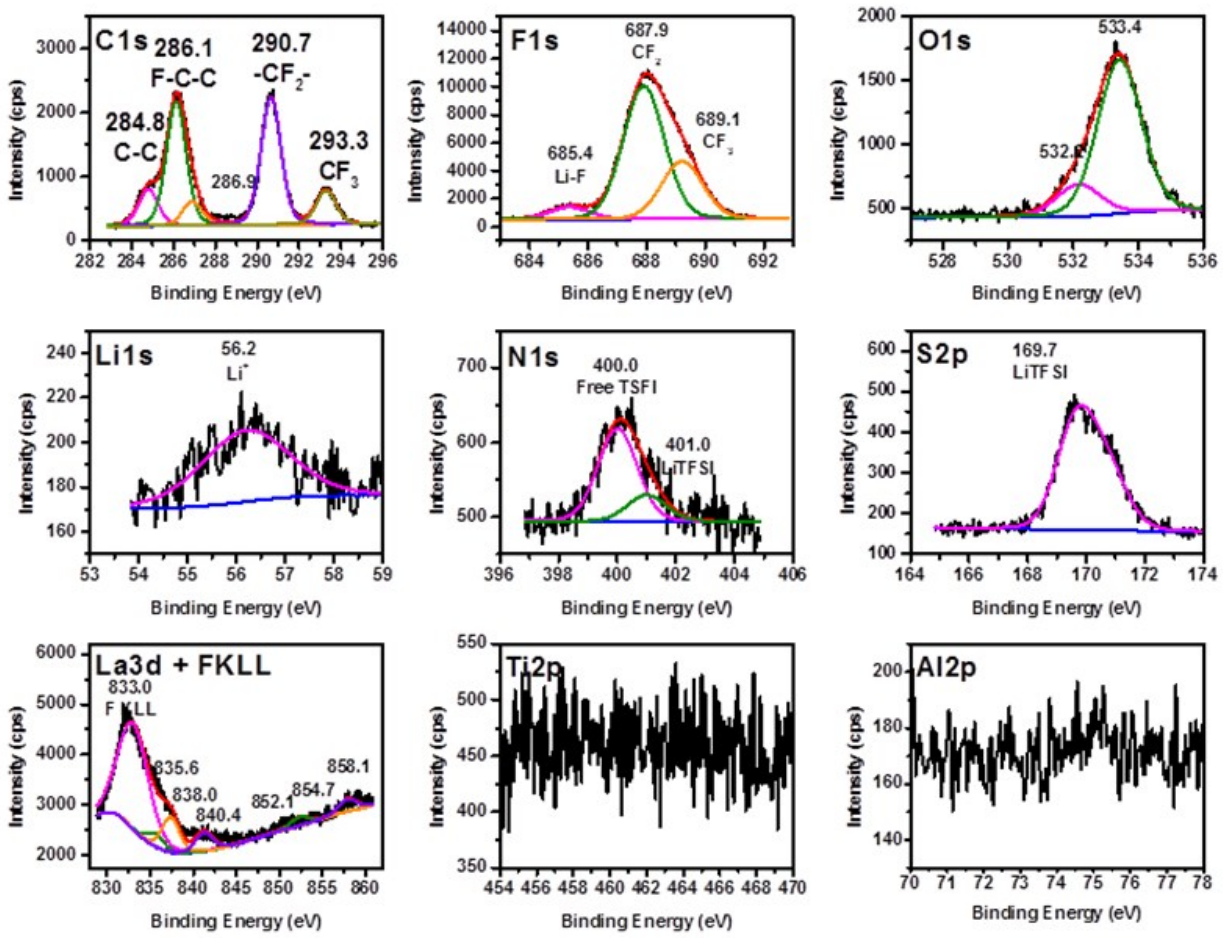

Figure S12. XPS of PVDF-HFP/LiFTSI composite electrolyte.

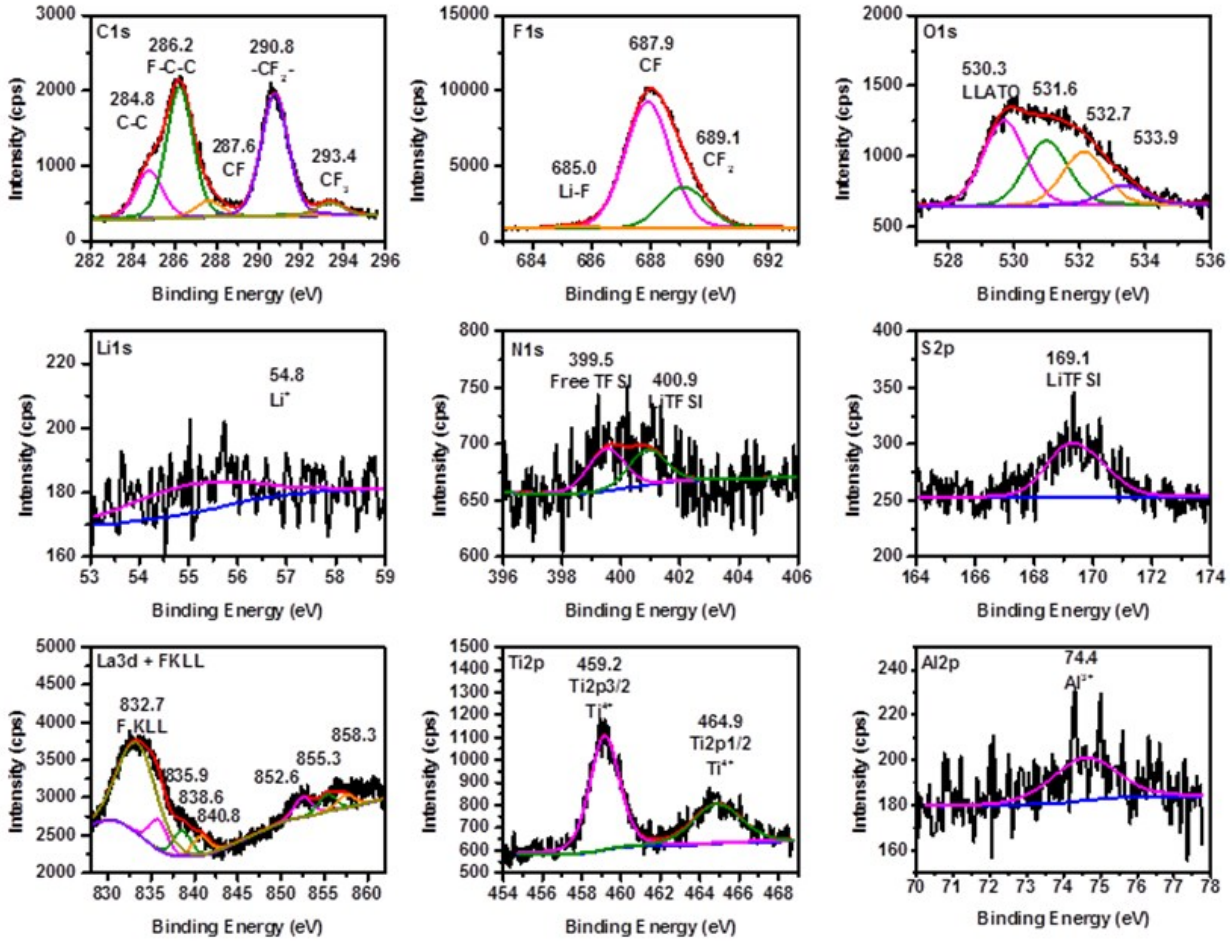

Figure S13. XPS of PVDF-HFP/LiTFSI/30%LLATO composite electrolyte.

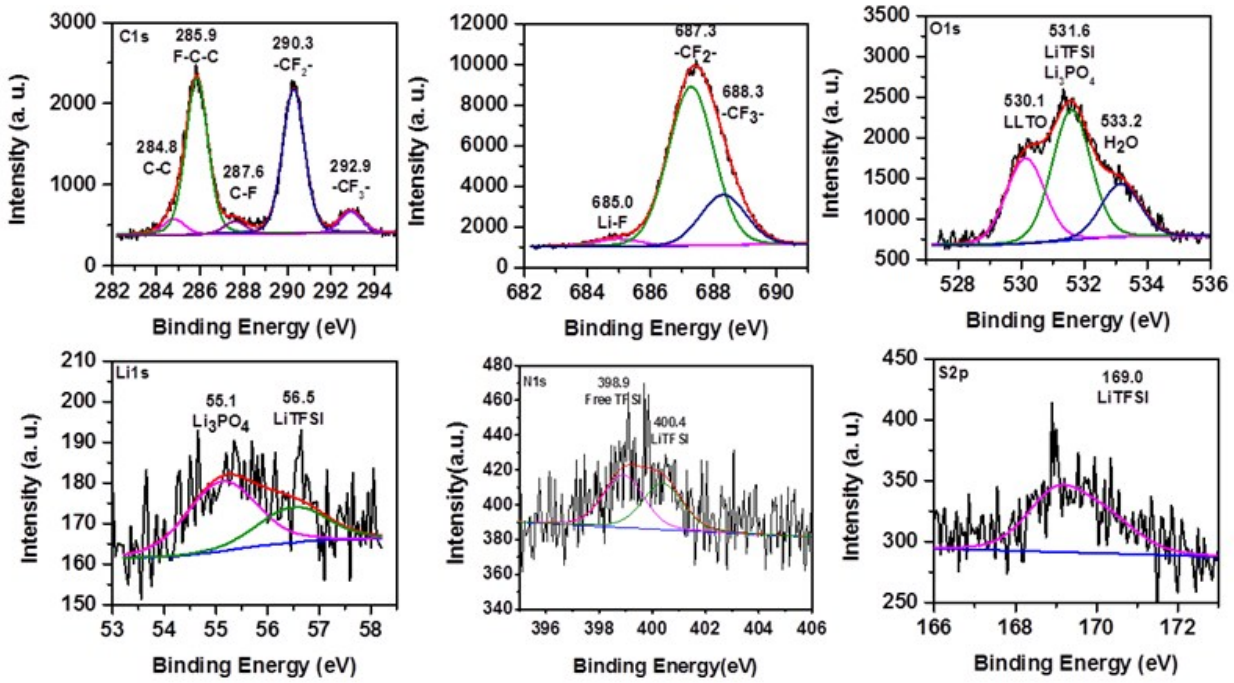

Figure S14. XPS of PVDF-HFP/LiTFSI/30%LLATO/Li_3PO_4 composite electrolyte.

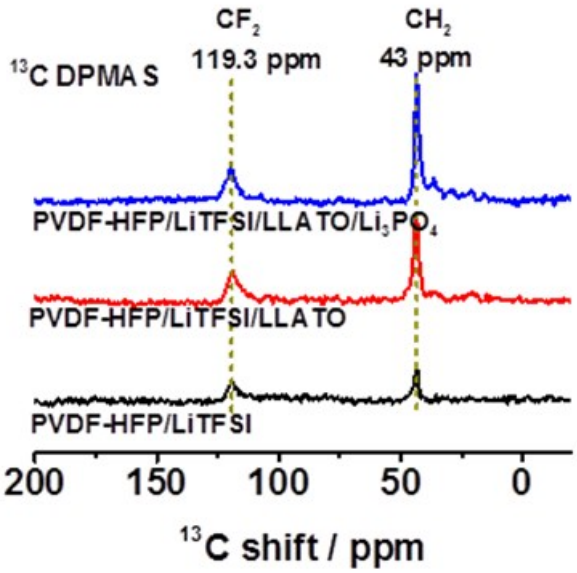

Figure S15. ^{13}C NMR spectra of PVDF-HFP/LiTFSI, PVDF-HFP/LiTFSI/LLATO, and PVDF-HFP/LiTFSI/LLATO/Li_3PO_4.

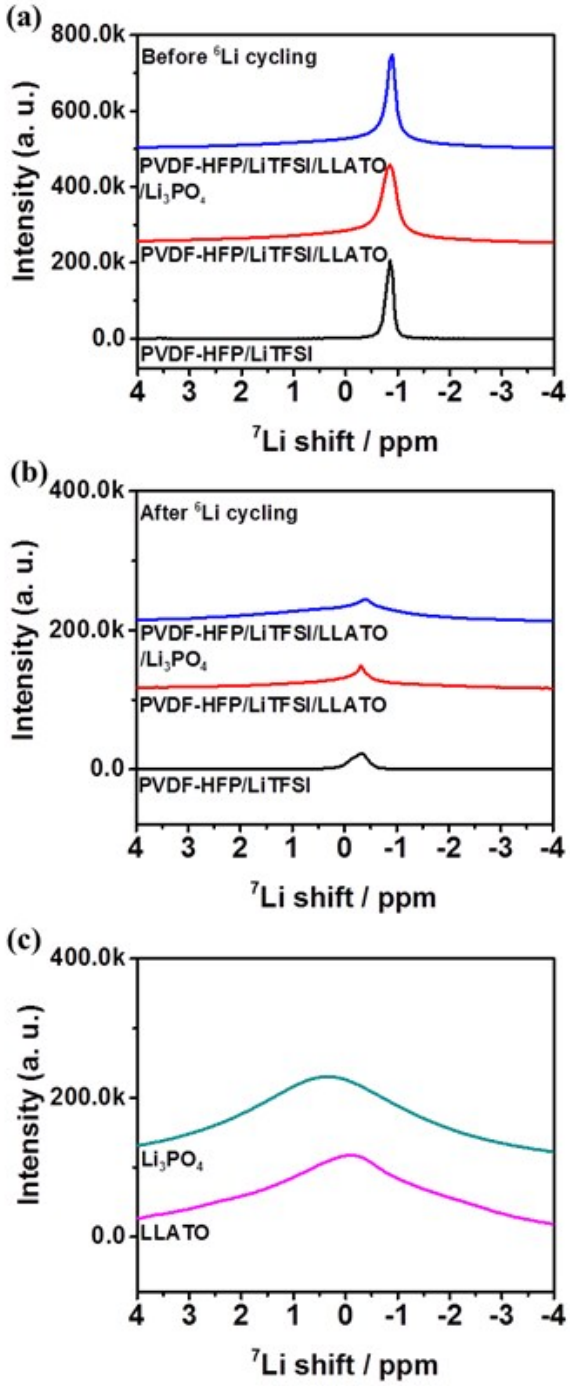

Figure S16. (a)^{7}Li NMR spectra of HFP/LiTFSI, PVDF-HFP/LiTFSI/LLATO, and PVDF-HFP/LiTFSI/LLATO/Li_3PO_4 before ^{6}Li cycling, (b)^{7}Li NMR spectra of PVDF-HFP/LiTFSI, PVDF-HFP/LiTFSI/LLATO, and PVDF-HFP/LiTFSI/LLATO/Li_3PO_4 after ^{6}Li cycling, (c) ^{7}Li NMR spectra of pure Li_3PO_4 and LLATO nanofibers.

Table S1. Calculated lithium transference numbers.

	I_0 (μA)	I_{SS} (μA)	R_0 (Ω)	R_{SS} (Ω)	t_{Li+}
PVDF-HFP	0.11	0.02	219	1401	0.18
10%	2.7	0.9	913	1122	0.28
20%	0.15	0.06	903	1192	0.40
30%	10.2	4.6	544	553	0.45
30% +Li_3PO_4	2.7	1.4	281	431	0.46

Table S2. Spectral simulation, assignment and quantification results of ^{6}Li NMR spectra of PVDF-HFP/LiTFSI/LLATO after electrochemical cycling

PVDF-HFP/LiTFSI/LLATO	**ppm**	**Height**	**Width(Hz)**	**Area**	**percentage %**
LLATO	2.45	35869.68	42	795570.1	15.1
LLATO	2	5190.17	20	41682.36	0.8
Interface	1.09	10980.61	76	350630.58	6.7
LLATO	0.19	95125.74	42	2185075.1	41.5
LLATO	-0.33	68933.26	22	807272.44	15.3
LiTFSI	-0.16	26581.46	20	284079.74	5.4
LLATO	-0.72	47379.85	31	804413.42	15.3

Table S3. Spectral simulation, assignment and quantification results of ^{6}Li spectra of PVDF-HFP/LiTFSI/LLATO/Li_3PO_4 after electrochemical cycling

PVDF-HFP/LiTFSI/LLATO/Li_3PO_4	**ppm**	**Height**	**Width (Hz)**	**Area**	**percentage %**
LLATO	2.44	7930.38	280	197707.09	5.9
LLATO	1.86	7623.13	300	198818.29	5.9
Interface	1.09	11485.77	361	388768.91	11.5
Li_3PO_4	0.42	62709.61	140	836839.55	24.8
LLATO	0.11	37953.61	119	408001.61	12.1
LiTFSI	-0.13	12890.36	96	123372.22	3.7
LLATO	-0.35	43528.1	201	869639.91	25.8
LLATO	-0.71	5604.02	109	59247.993	1.8
Decomposed LLATO	-1.51	4682.26	626	292631.21	8.7