

## Supplementary Information

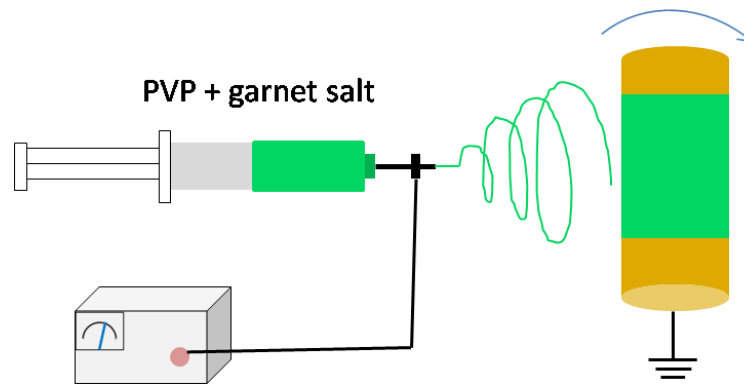
# Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> ceramic nanofiber-incorporated composite polymer electrolytes for lithium metal batteries

*Yang Li,<sup>†</sup> Wei Zhang,<sup>†</sup> Qianqian Dou, Ka Wai Wong and Ka Ming Ng<sup>\*</sup>*

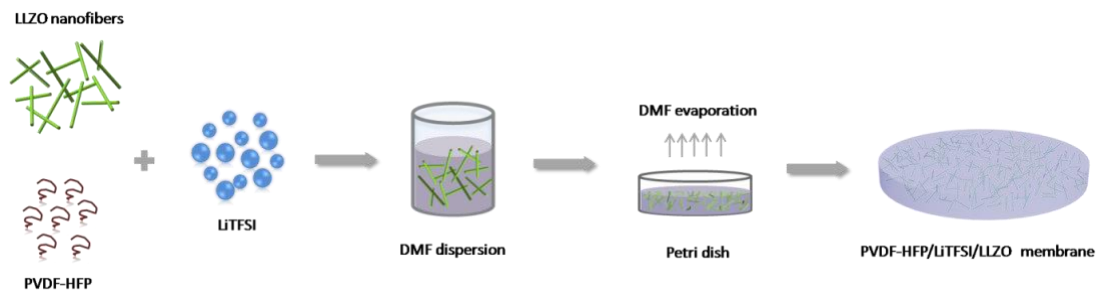
Department of Chemical and Biological Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong 999077, China.

\*Corresponding Author: Ka Ming Ng (kekmng@ust.hk), Fax: +852-23580054; Tel: +852-23587238

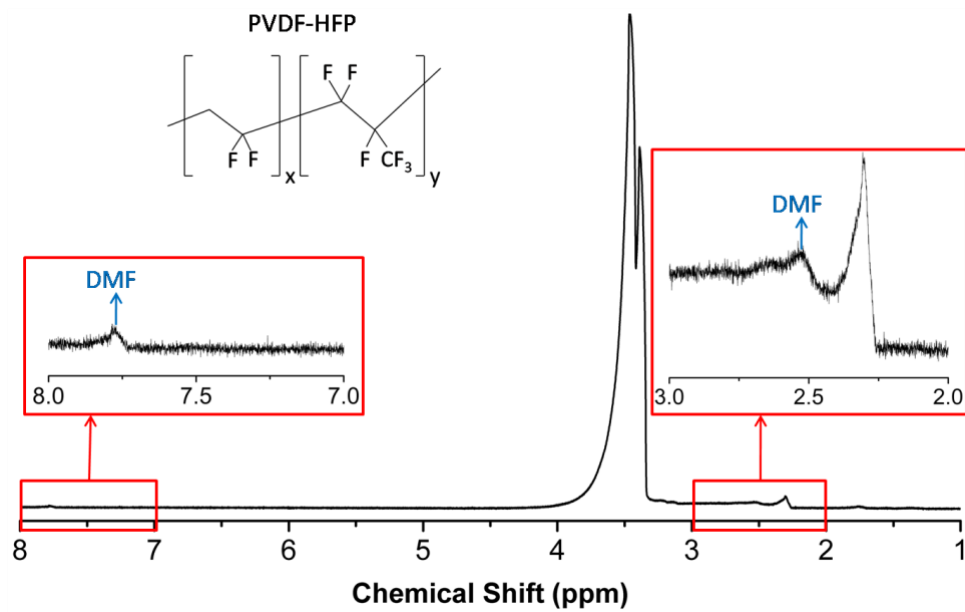
<sup>†</sup>The authors contributed equally.



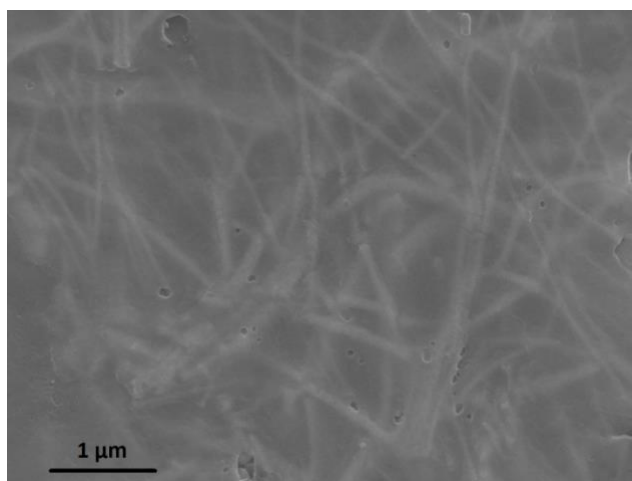
**Scheme S1.** Schematic electrospinning setup of garnet-PVP nanofibers.



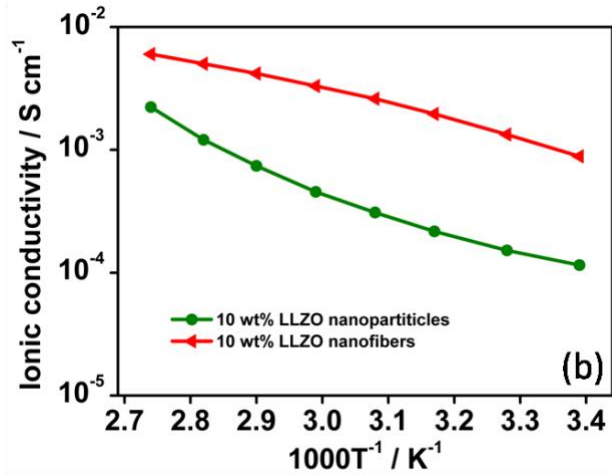
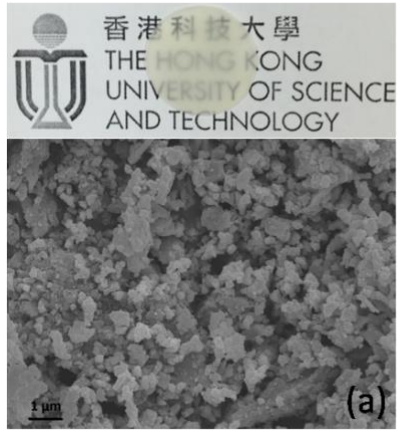
**Scheme S2.** Schematic procedure for the fabrication of the PVDF-HFP/LiTFSI/LLZO membranes.



**Fig. S1.**  $^1\text{H}$  NMR measurement of PVDF-HFP/LiTFSI/LLZO membrane.



**Fig. S2.** SEM image of the PVDF-HFP/LiTFSI/LLZO membrane with 20 wt% LLZO nanofibers.



**Fig. S3.** (a) SEM image of LLZO nanoparticles, and photo of PVDF-HFP-based electrolyte with LLZO nanoparticles. (b) Comparison of ionic conductivity of CPEs containing LLZO nanofibers and LLZO nanoparticles.

**Table S1.** Liquid electrolyte uptakes in PVDF-HFP/LiTFSI/LLZO CPEs.

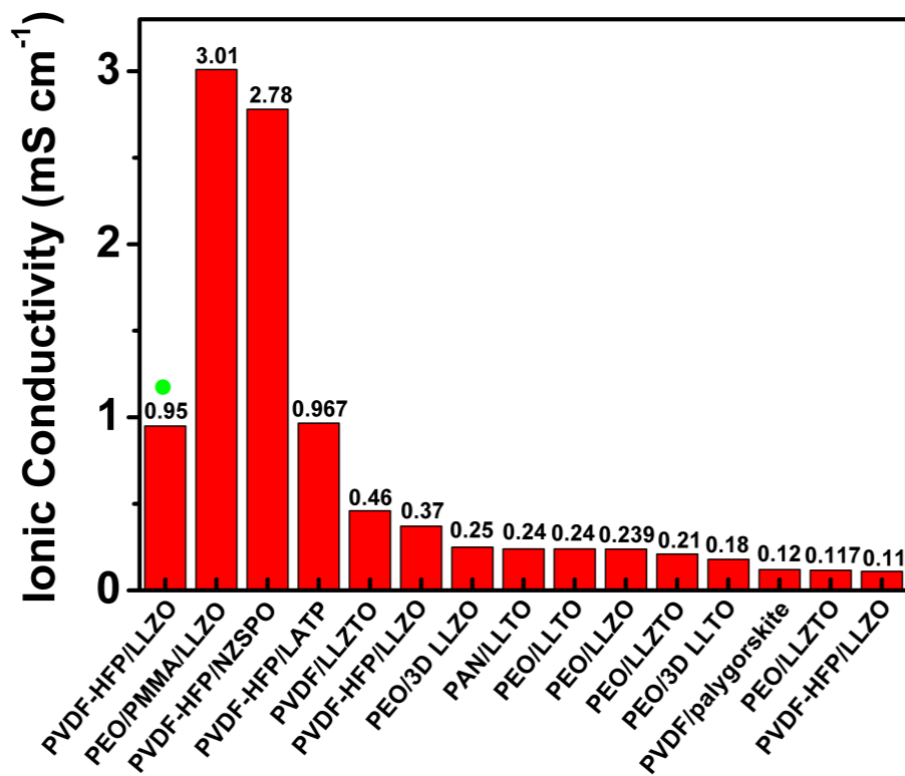
Sample	W <sub>0</sub> (g)	W <sub>1</sub> (g)	Uptake
1	0.072	0.08	11.1%
2	0.067	0.074	10.4%
3	0.075	0.082	9.3%

Liquid electrolyte uptakes were measured by weighting method. First, the dry PVDF-HFP/LiTFSI/LLZO CPE membranes were cut into round pieces and weighted as W<sub>0</sub>. After soaked in PC/LiTFSI liquid electrolyte solution for 20 min, the excess electrolyte solution on the surface of the membranes was removed by wiping with a tissue paper, and then weighted as W<sub>1</sub>. The liquid uptake is calculated by the following equation:

$$\text{Uptake (\%)} = (W_1 - W_0) / W_0 \times 100\%$$

**Table S2.** A comparison of ionic conductivities and mechanic properties of PVDF or PVDF-based gel or solid polymer electrolytes (GPE or SPE) from representative works and ours.<sup>1-8</sup>

	<b>Electrolyte</b>	<b>Liquid electrolyte uptake (%)</b>	<b>Ionic conductivity (mS cm<sup>-1</sup>)</b>	<b>Stress (MPa)/ Stress (%)</b>
	PVDF-HFP/LLZO	10	0.95	5.3/25
<b>GPE</b>	PVDF/cellulose	267	1.33	2.83/5.92
	PVDF-HFP/Al <sub>2</sub> O <sub>3</sub>	371	0.7	17/20
	PVDF-HFP/TiO <sub>2</sub>	125	0.98	9.69/74.4
	PVDF-HFP/BaTiO <sub>3</sub>	462	0.104	—/—
	PVDF-HFP/PEO/GO	368	2.1	—/—
	PVDF-HFP/PEO/PMMA	75	0.81	—/—
	PVDF/polymer-blend	81	3.5	—/—
<b>SPE</b>	PVDF/PMMA	0	0.031	—/—
	PVDF-HFP	0	0.078	—/—



**Fig. S4.** A comparison of ionic conductivities of ceramic nanofiller-incorporated composite polymer electrolytes from representative works and ours.<sup>9-22</sup>

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