

## Supporting Information

### $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ ceramic nanofiber-enhanced polyethylene oxide-based composite polymer electrolyte for all-solid-state lithium batteries

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Table S1. Comparison between our research and the reported work in literature.

	<b>Crystallinity of polymer matrix after adding of fillers</b>	<b>Concentration of nanofiber fillers in the polymer matrix</b>	<b>Proposed main conduction mechanism</b>	<b>Ionic conductivity (<math>S\text{ cm}^{-1}</math>)</b>	<b>Stability and voltage window of Li/composite electrolyte/Li cell</b>
LLTO nanofiber + PAN (Ref 14)	Not changed	Compared 5 LLTO concentrations (0%, 5%, 10%, 15% and 20%)	1. Fast ion transport on LLTO nanofiber surface; 2. 3D ion-conducting network	$2.4 \times 10^{-4}$	No information
LLZO nanofiber + PEO (Ref 15)	No information	One LLZO/PEO ratio (1:4)	3D structure provides long-range ion transfer	$2.5 \times 10^{-4}$	Voltage value of around $\pm 300\text{ mV}$ at $0.5\text{ mA cm}^{-2}$ over 1000 h
LLZO nanofiber + PAN (Ref 27)	Not changed	Compared 6 LLZO concentrations (0%, 1%, 2.5%, 5%, 10% and 15%)	1. Increased $\text{Li}^+$ dissociation from the $\text{ClO}_4^-$ anion; 2. Preferred $\text{Li}^+$ diffusion at the LLZO/polymer interface	$1.31 \times 10^{-4}$	Voltage value of around $\pm 400\text{ mV}$ at $50\text{ }\mu\text{A cm}^{-2}$ over 89 h
Our work	The crystallinity of PEO was lowered.	Compared 4 LLTO concentrations (0%, 5%, 10%, 15% and 20%)	1. Creation of more amorphous region in the PEO matrix 2. Continuous ionic conductive pathways provided by 1D LLTO nanofibers	$2.4 \times 10^{-4}$	Voltage value of around $\pm 115\text{ mV}$ at $0.5\text{ mA cm}^{-2}$ over 720 h

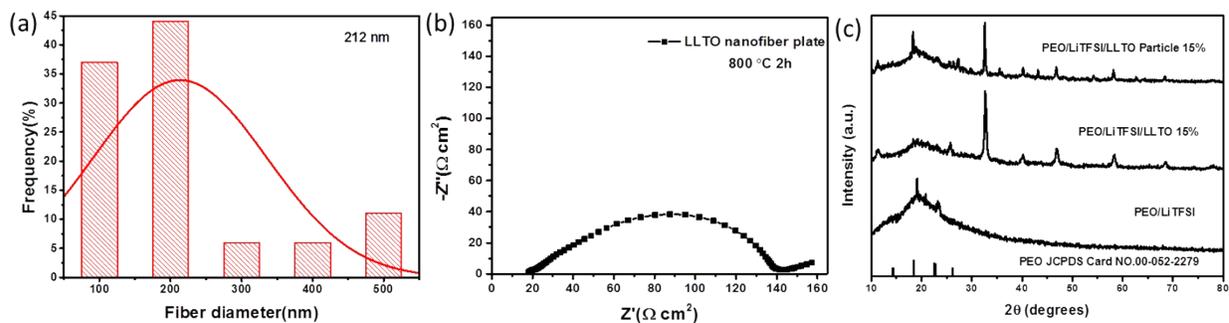


Figure S1. (a) Diameter distributions and average diameters of LLTO nanofibers calcined at 900 °C for 2 h. (b) EIS curve of LLTO plate at room temperature. (c) XRD patterns of the PEO/LiTFSI/LLTO solid composite electrolytes without and with 15% LLTO nanofiber/particle, showing the influence of LLTO morphology on the crystalline phase of PEO.

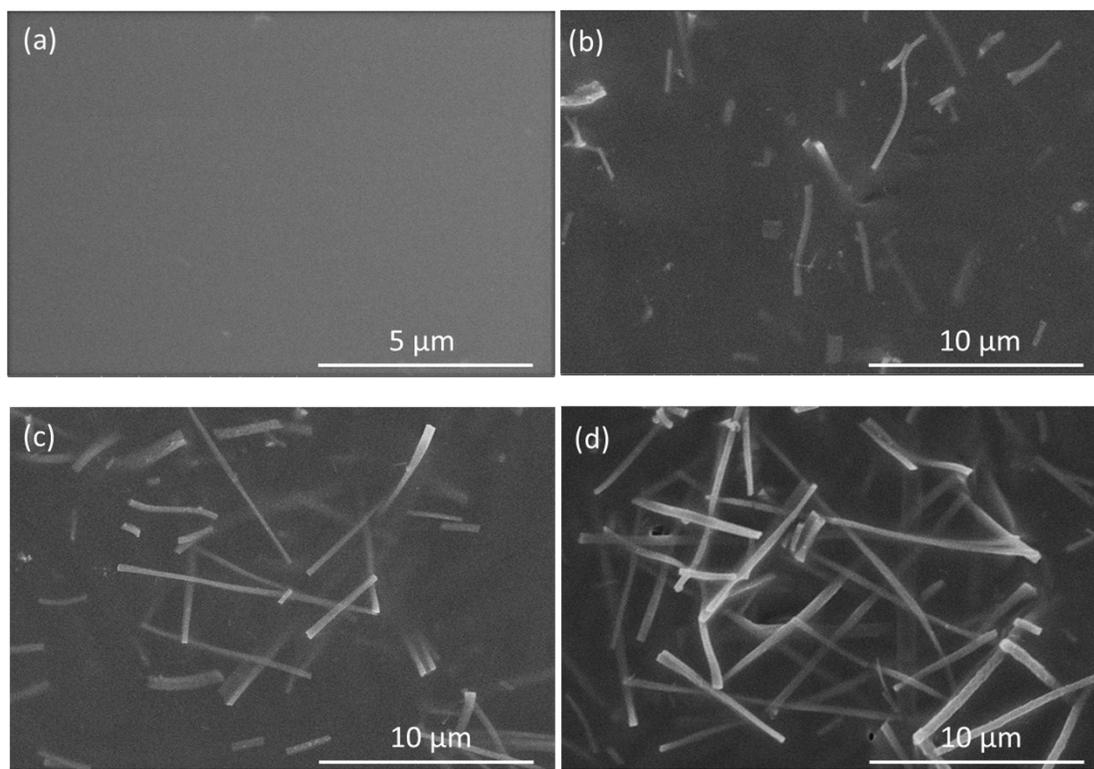


Figure S2. SEM images of (a) PEO/LiTFSI, (b) PEO/LiTFSI/LLTO 10 wt.%, (c) PEO/LiTFSI/LLTO 15 wt.%, and (d) PEO/LiTFSI/LLTO 20 wt.% solid electrolytes.

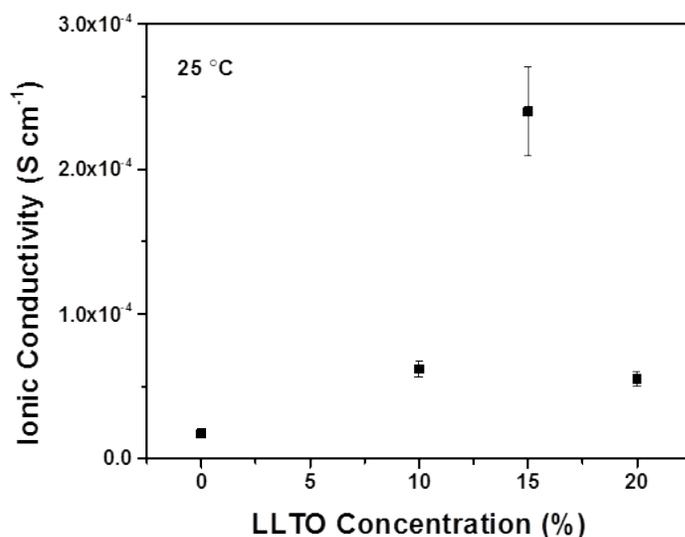


Figure S3. Ionic conductivities of the PEO/LiTFSI/LLTO solid composite electrolytes with different LLTO nanofiber contents at room temperature.

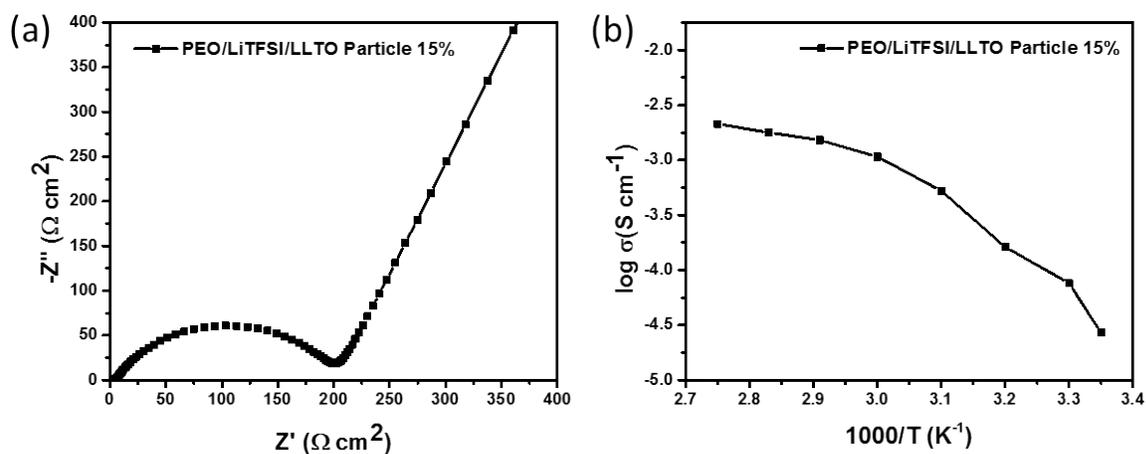


Figure S4. (a) EIS result of the PEO/LiTFSI/LLTO particle solid composite electrolyte with 15% LLTO particles at room temperature. (b) Arrhenius plot of the PEO/LiTFSI/LLTO particle solid composite electrolyte with 15% LLTO particles.