

Study of composite polymer electrolytes incorporating LLZO particles in PEO matrix in high voltage all solid-state lithium batteries

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Table S1. Recent studies of high-voltage Li-metal batteries using PEO-based electrolytes.

Cathode and potential window	Temperature	Rate	Initial discharge capacity	Cycling retention	Reference
Li NCM811 Up to 4.2 V	60 °C	0.1 C	115 mAh g ⁻¹	70% after 150 cycles	This work
Li NCM811 Up to 4.2 V	60 °C	0.4 C	164.5 mAh g ⁻¹	63% after 400 cycles	[1]
Li NCM811 up to 4.3 V	60 °C	0.2 C	171.3 mAh g ⁻¹	80% (100 cycles), 62.3% (200 cycles); PC baseline 44.7% (100 cycles)	[2]
Li NCM811 4.1/4.2/4.3 V cutoffs	NR	NR	NR	96.0% (100 cycles, 4.1 V); 84.6% (4.2 V); 76.8% (4.3 V)	[3]
Li NCM811 Up to 4.3V	60 °C	0.2 C	123 mAh g ⁻¹	50% after 1000 cycles	[4]
Li LATP-NCM811 Up to 4.2 V	NR	0.5 C	185 mAh g ⁻¹	81% after 100 cycles	[5]
Li NCM811 Up to 4.3 V	60 °C	0.5 C	142.4 mAh g ⁻¹	85.7 % after 100cycles	[6]
Li NCM811 Up to 4.2 V	40 °C	0.025 C	180 mAh g ⁻¹	92 % after 40 cycles	[7]

Table S2. Summary of the physical properties of the samples and the impurities introduced through the different synthesis routes.

LLZO solid filler	Synthesis route	Particle size Ave (µm)	Particle morphology	Impurity phases in crystalline structure	Carbon content (g of C/100 g of sample)
S1 Al-doped LLZO	Electrospinning	19	Flake-like	Minor impurities La ₂ Zr ₂ O ₇ and Li ₂ CO ₃	1.7
S2 Al-doped LLZO	Conventional solid-state reaction	10	Granular	Minor impurities such as La ₂ Zr ₂ O ₇ and Li ₂ CO ₃	0.82
S3 Ta/Nb-doped LLZO	Conventional solid-state reaction	12	Granular	Impurities such as La ₂ Zr ₂ O ₇ and Li ₂ CO ₃	1.35
Ref Commercial LLZO	NR	6	Granular	Impurities such as La ₂ Zr ₂ O ₇ and Li ₂ CO ₃	NR

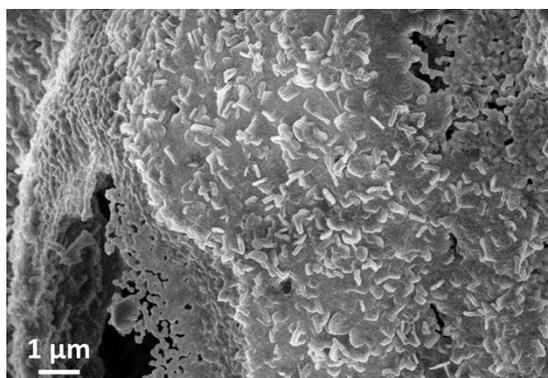


Figure S1. SEM image of S1 particle at higher magnification, where the nanorods are visible.

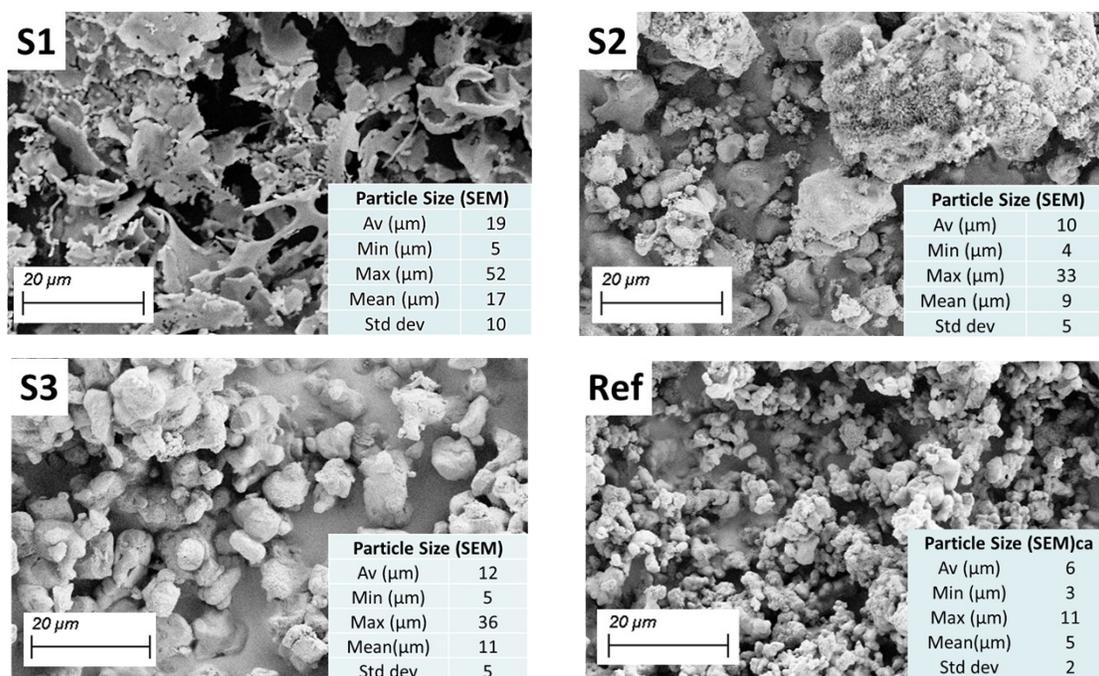


Figure S2. SEM morphology and particle size analysis of LLZO particles from different sources: **S1**- Al-doped LLZO, synthesized via electrospinning, **S2**- bulk Al-LLZO, **S3**- bulk Ta/Nb-LLZO and **Ref**- commercial LLZO.

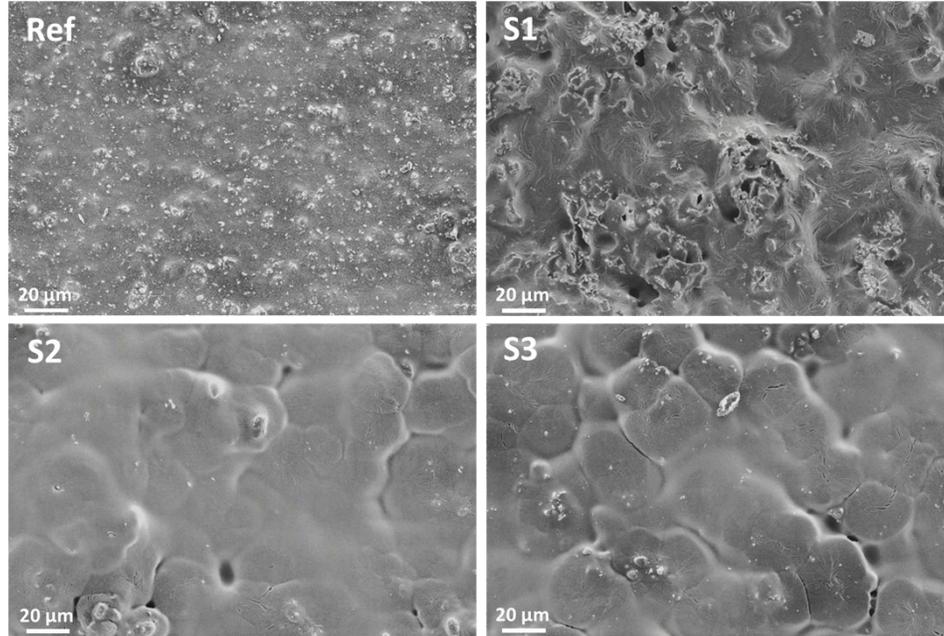


Figure S3. SEM images of the surfaces of composite polymer electrolytes made by embedding 40 wt% LLZO particles in PEO (PEO:LiTFSI = 16:1). Each panel shows a different composite depending on the LLZO filler type: **Ref** – commercial LLZO; **S1** – electrospun Al-doped LLZO; **S2** – bulk Al-doped LLZO; and **S3** – bulk Ta/Nb-doped LLZO.

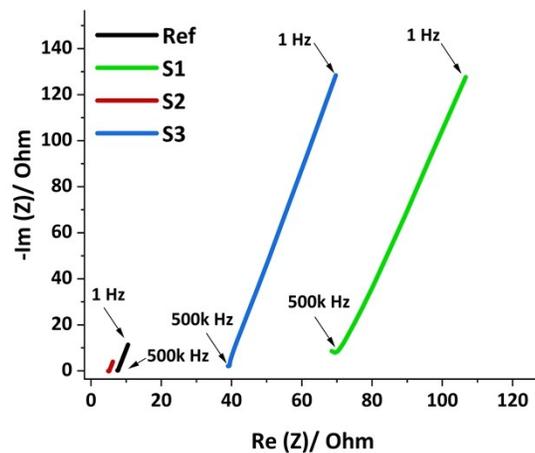


Figure S4. Impedance data of the composite polymer electrolytes measured at 60 °C over a frequency range from 500 kHz to 1 Hz.

The XRD results have been analyzed using the Crystallography Open Database (COD). The COD standard reference codes used for phase identification were 1545083 for LLZO, 9009643 for Li_2CO_3 , and 1544470 for $\text{La}_2\text{Zr}_2\text{O}_7$.

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