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Electronic Supplementary Information

Li-ion transport in a representative ceramic-polymer-plasticizer composite electrolyte: $Li_7La_3Zr_2O_{12}$-polyethylene oxide-tetraethylene glycol dimethyl ether

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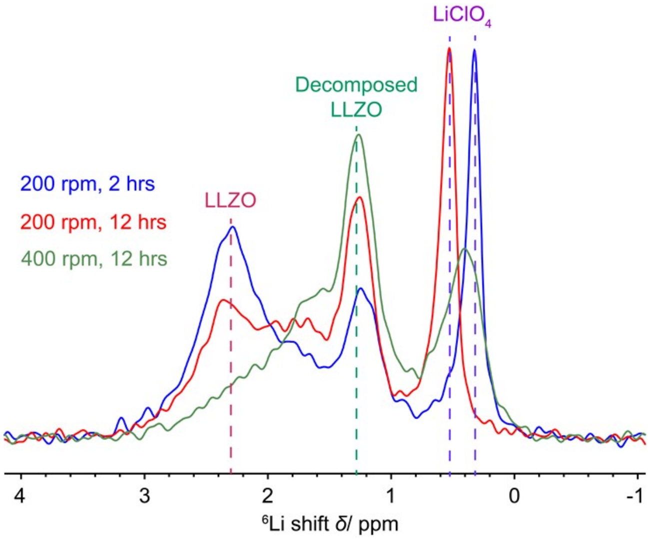

Fig. S1. ^{6}Li NMR spectra of the LLZO-PEO ($LiClO_4$) composite electrolytes using different ball-mill conditions during preparation.

Ball-milling process has great effects on the composite electrolytes. Fig. S1 shows ^{6}Li NMR spectra of the LLZO-PEO ($LiClO_4$) composite electrolytes under different ball-mill conditions. With higher ball-mill speed and longer ball-mill time, the peak for LLZO decreases and the peak at 1.2 ppm increases. At 400 rpm, the signal of $LiClO_4$ is much broader compared with 200 rpm.

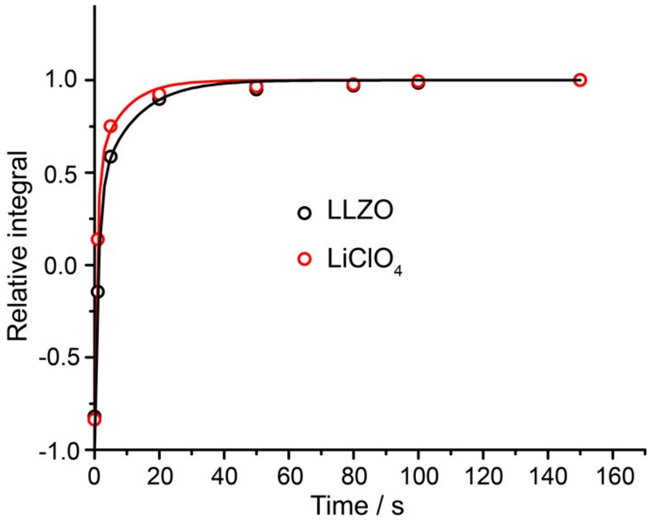

Fig. S2. ^{7}Li T_1 NMR fitting plot of the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte.

Table S1. ^{7}Li T_1 NMR fitting results of LLZO and PEO/LLZO interface, decomposed LLZO in TEGDME, $LiClO_4$ in PEO/TEGDME complex, and $LiClO_4$ in TEGDME.

Components	LLZO and PEO/LLZO interface	Decomposed LLZO in TEGDME	$LiClO_4$ in PEO/TEGDME complex	$LiClO_4$ in TEGDME
mol %	62.9	21.0	6.0	10.1
T_1 (s)	1.14	11.26	8.24	0.79

Fig. S2 and Table S1 show T_1 results of the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte. T_1 of LLZO is short, 1.14 s, while that of LLZO in TEGDME is much longer, 11.26 s.

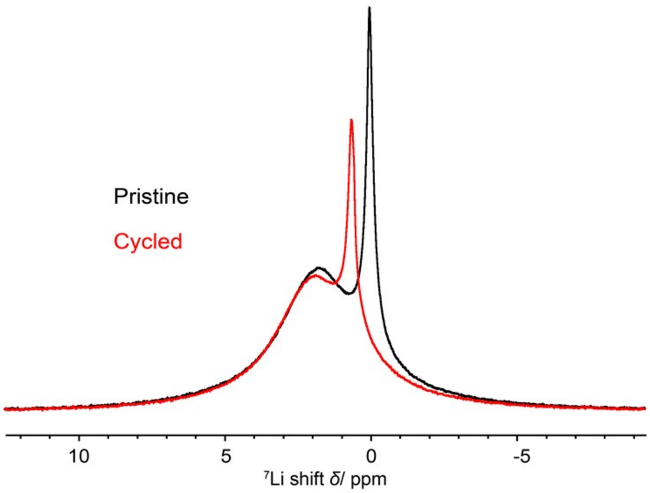

Fig. S3. ^{7}Li NMR spectra of the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolytes before and after cycling.

After LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte was cycled using ^{6}Li metal foils, ^{7}Li NMR spectrum was collected and compared with the pristine sample (Fig. S3). The signal at 0 ppm in the pristine sample shifts to 0.5 ppm after cycling, and the integral decreases, which means part of ^{7}Li was replaced by ^{6}Li.

Table S2. The increase in the ^{6}Li amount of each component (LLZO, PEO/LLZO interface, decomposed LLZO in TEGDME, and $LiClO_4$ in PEO/TEGDME complex) after cycling for fresh composite electrolyte and 2 days and 5 days after the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte was made.

Increase / mol %	LLZO	PEO/LLZO interface	Decomposed LLZO in TEGDME	$LiClO_4$ in PEO/TEGDME complex
Fresh	0.7	1.5	10.1	9.5
2 days	6.6	1.0	19.4	14.9
5 days	0.2	3.8	22.5	16.7

Table S2 lists the enhancement of ^{6}Li after cycling for fresh, 2 days and 5 days samples. They all show increase in decomposed LLZO in TEGDME and $LiClO_4$ in PEO/TEGDME complex. All three samples consistently confirm that Li ion conduction is through the TEGDME-associated phases. Better solvation of decomposed LLZO in TEGDME and $LiClO_4$ in PEO/TEGDME complex may be achieved with time, which facilitates ^{6}Li/^{7}Li exchange, thus increased ^{6}Li amount with time.

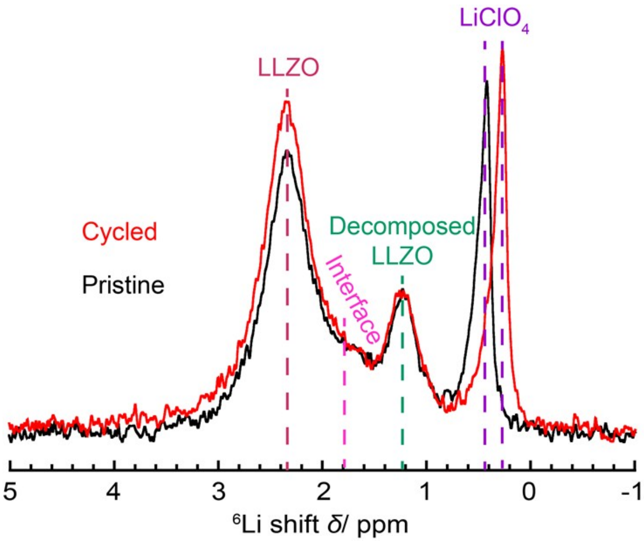

Fig. S4. Comparison of ^{6}Li NMR spectra of the LLZO-PEO ($LiClO_4$)-5 wt % TEGDME composite electrolyte before (pristine) and after (cycled) ^{6}Li → ^{7}Li replacement

Table S3 Increase in the ^{6}Li amount of each Li environment (LLZO, PEO/LLZO interface, decomposed LLZO in TEGDME, and $LiClO_4$ in PEO/TEGDME complex) in the LLZO-PEO ($LiClO_4$)-5 wt % TEGDME composite after ^{6}Li → ^{7}Li replacement.

	LLZO	PEO/LLZO interface	Decomposed LLZO in TEGDME	$LiClO_4$ in PEO/TEGDME complex
Increase / mol %	18.1	1.8	0.8	3.0

The integral of the LLZO peak increased by 18.1 mol % after ^{6}Li -> ^{7}Li replacement, while that of the PEO/LLZO interface, decomposed LLZO and $LiClO_4$ in PEO/TEGDME complex did not show obvious enrichment. This result indicates that Li ions mainly pass through LLZO in the LLZO-PEO ($LiClO_4$)-5 wt % TEGDME composite, similar to LLZO-PEO ($LiClO_4$) without TEGDME, and components in the PEO or TEGDME phase does not make significant contribution to Li-ion conduction.

Higher concentration of TEGDME often leads to higher ionic conductivity. However, when the ratio of PEO to liquid plasticizers TEGDME is larger than 2:1, *i.e.*, the content of TEGDME is > 20 wt % in the composites, the composite electrolytes fail to form a solid film, based on our study and other's reports.[1] In addition, TEGDME is only intended as a minor additive in solid electrolytes; a higher concentration will render the electrolyte to be liquid like.

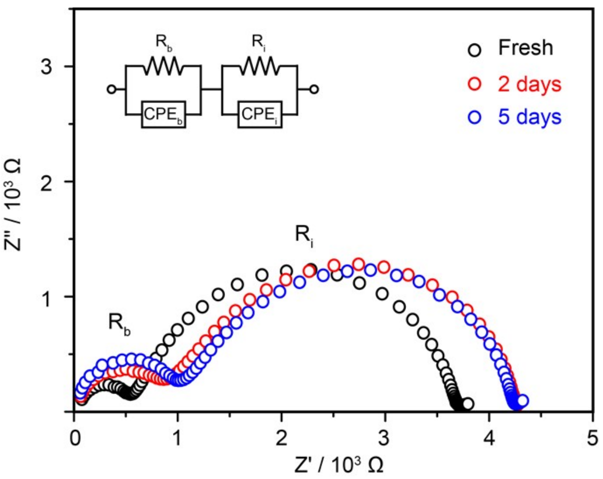

Fig. S5. EIS measurements of the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolytes after 0, 2, and 5 days. The equivalent circuit is included. R_b and CPE_b are the resistance and the constant element for the bulk; R_i and CPE_i are the resistance and the constant element for the interface.

Table S4. Evolution of the bulk resistance (R_b) of the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte and Li/electrolyte interfacial resistance (R_i) with time

	R_b 10^2 / Ω	R_i 10^3 / Ω
Fresh	5.83	3.12
2 days	9.44	3.34
5 days	1.12	3.49

The bulk resistance (R_b) of the composite electrolyte and the Li/electrolyte interface resistance (R_i) are clearly resolved in the EIS measurements (Fig. S5). The R_b and R_i values from the analysis of the EIS measured are listed in Table S4.

The composite film was stored in Argon-filled glovebox, without contact with Li metal. Samples were extracted from the same film after it was freshly made, 2 days, and 5 days. The extracted films were then assembled with Li metal for impedance tests. The bulk impedance increased from 582 Ω to 944 Ω during the first 2 days, and then kept at around 1 kΩ to 5 days. R_i values are similar for the three measurements.

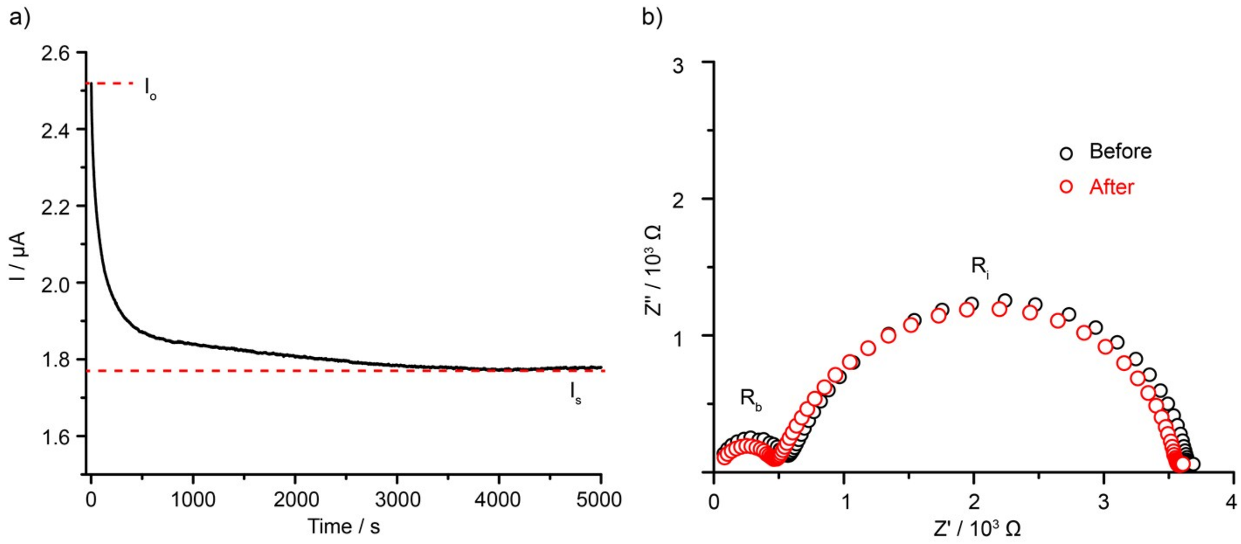

Fig. S6. (a) The evolution of electric current with time after the application of a 10-mV DC polarization potential to the LLZO-PEO ($LiClO_4$)-TEGDME composite electrolyte. (b) EIS measurements on the LLZO-PEO ($LiClO_4$)-TEGDME composite before and after the polarization.

Table S5. The results of T_{Li}^+ measurements for LLZO-PEO ($LiClO_4$)-TEGDME.

I_0 / μA	I_s / μA	R_o^i / Ω	R_s^i / Ω	ΔV / mV	T_{Li}^+
2.52	1.77	3090	3110	10	0.35

Fig. S6 and Table S5 show the evolution of the electric current, impedance plots and results of Li-ion transference number measurements for LLZO-PEO ($LiClO_4$)-TEGDME. The Li-ion transference number (T_{Li}^+) was calculated based on the Bruce−Vincent−Evans equation[2]

$$T_{Li^+} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)}$$

where I_o and I_s are the initial and steady-state currents, R_o^i and R_s^i are the initial and steady-state interfacial resistances and ΔV is the applied polarization voltage.

The T_{Li}^+ of LLZO-PEO ($LiClO_4$)-TEGDME is determined to be 0.35. From previous studies, PEO ($LiClO_4$) polymer electrolytes exhibited a low T_{Li}^+ value, around 0.2.[3,4] The addition of LLZO and TEGDME improved T_{Li}^+ in composite electrolytes.

References:

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