Supporting Information

A single-ion-conducting polymer and high-entropy Li-garnet composite electrolyte with simultaneous enhancement in ion transport and mechanical properties

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Table S1. Rietveld refinement results of the neutron powder diffraction.

R_{wp} (%)	χ^2	Lattice parameter (Å)	Site	Occupancy	x	y	z
3.58%	3.370	12.902(4)	Li1 (24d)	0.6206	3/8	0	1/4
			Li2 (48g/96h)	0.3322	0.102(1)	0.687(2)	0.578(2)

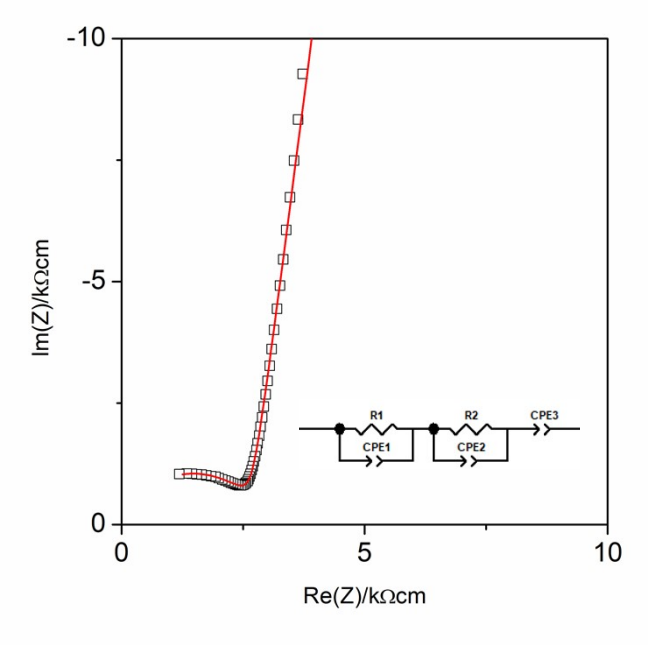

Figure S1. Conductivity of sintered HE Li-garnet pellet at room temperature. The total conductivity is 4×10^{-4} S/cm and the bulk conductivity is over 5×10^{-4} S/cm based on the $(R_{bulk}Q1)(R_{grain\ boundary}Q2)Q3$ circuit.

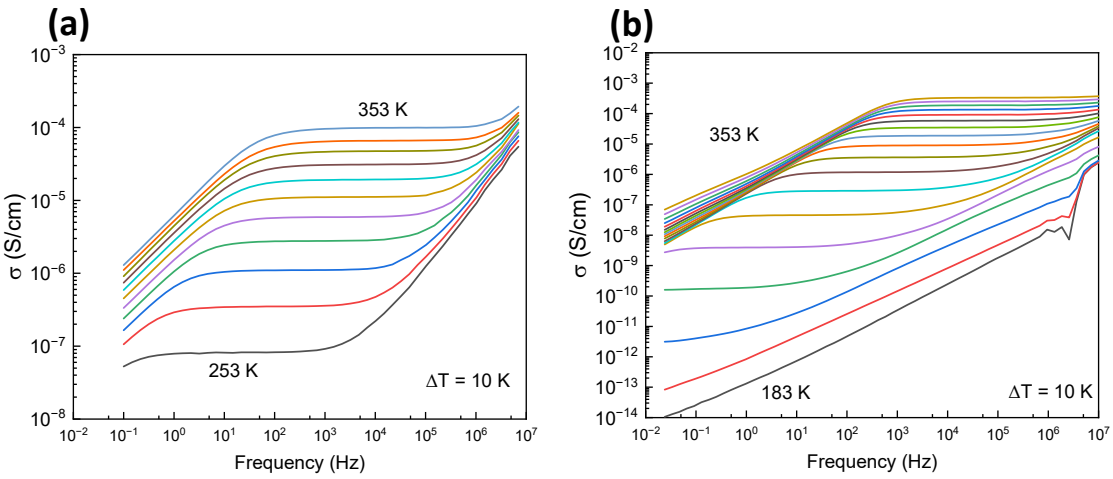

Figure S2. Frequency dependent conductivity spectra at different temperatures: (a) converted EIS data of SIC (Turbula) and (b) SIC-10wt% HE Li-garnet.

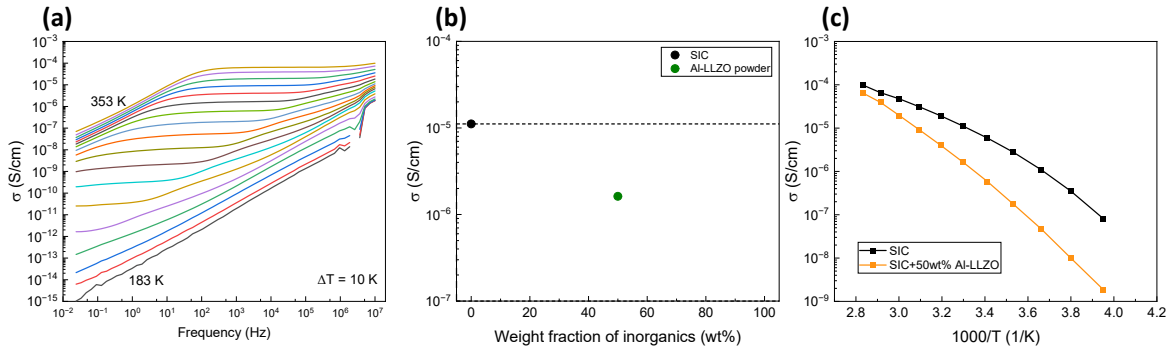

Figure S3. (a) Conductivity spectra of SIC-50wt% Al doped LLZO at different temperatures, (b) conductivity at 30 ºC and (c) Arrhenius plots.

Table S2. XPS analysis of surface composition on Al doped LLZO and HE Li-garnet powder.

	Li	La	Zr	O	Al	C	Nb	Ta	Hf
LLZO-Al	41.0	3.0	2.6	44.3	0.4	8.7	0.00	0.0	0.0
HE-LLZO	37.7	0.7	0.2	41.2	0.0	19.7	0.04	0.5	0.1

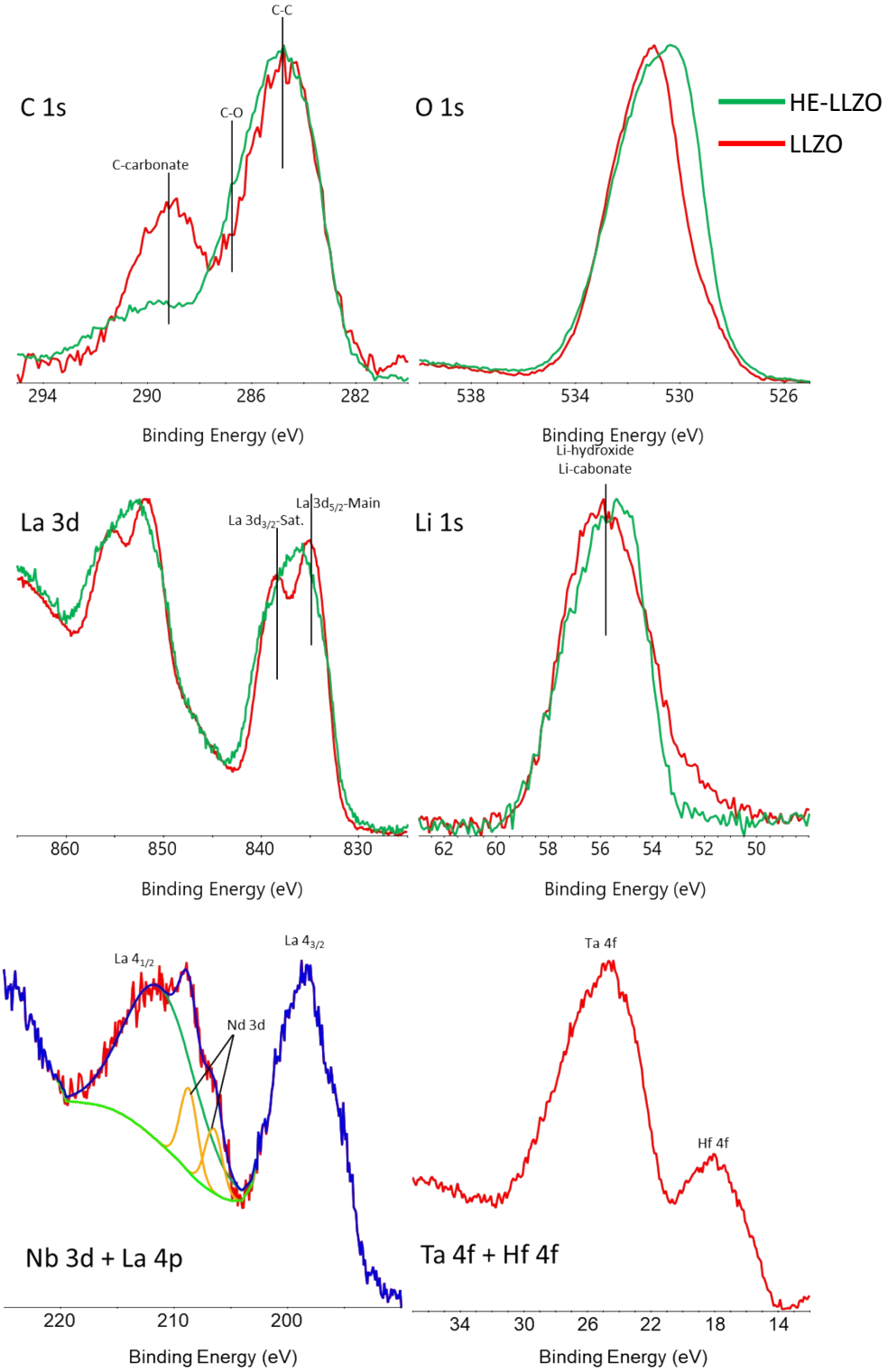

Figure S4. XPS spectra of Al doped LLZO and HE Li-garnet powder.

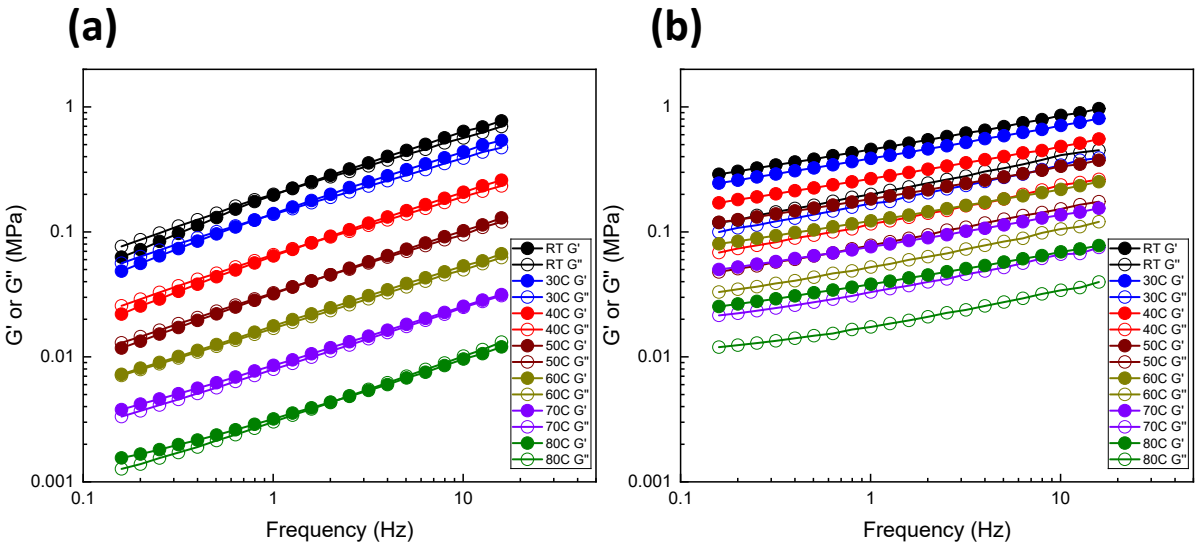

Figure S5. Storage (G') and loss (G'') moduli in SIC (a) and SIC-30wt% HE Li-garnet (b) at different temperatures.

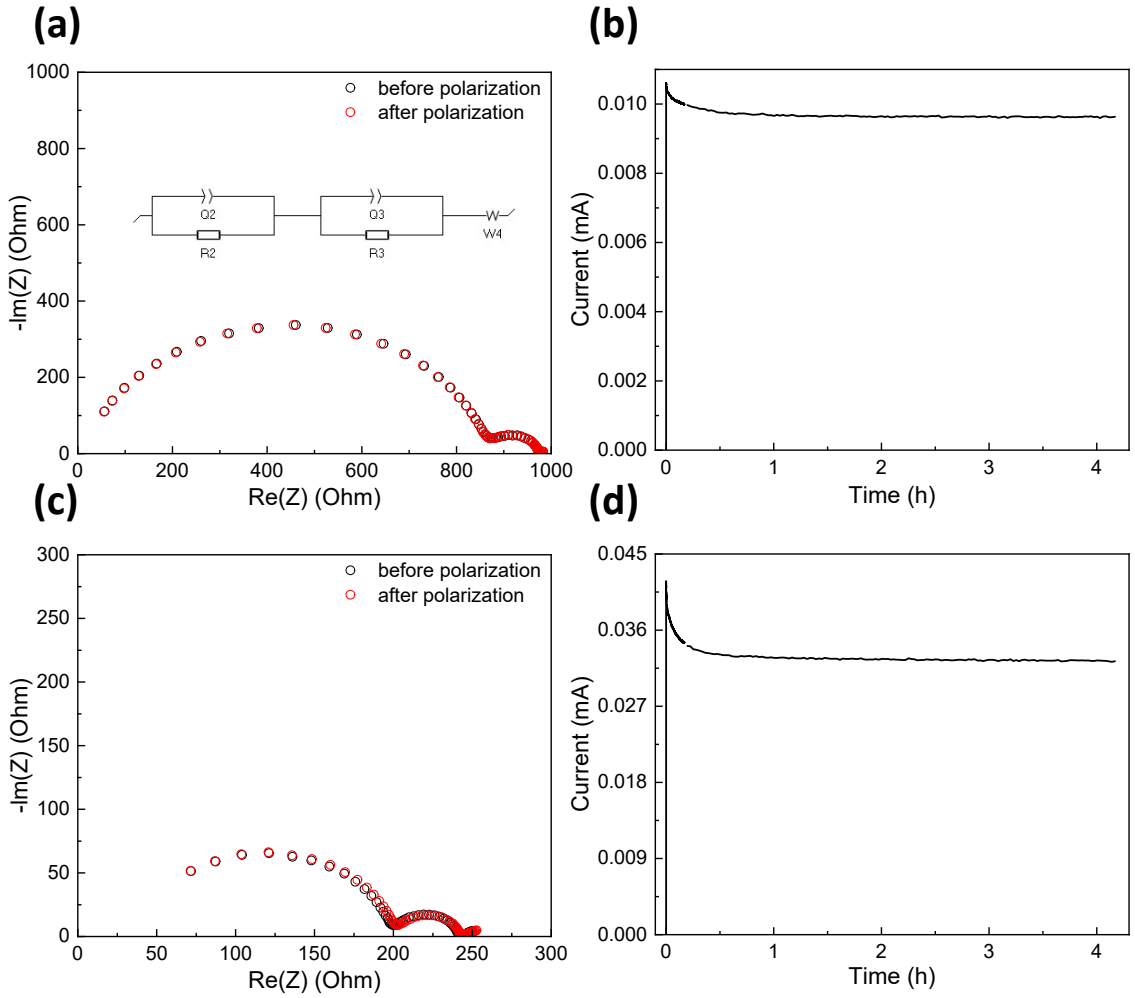

Figure S6. Nyquist plot before/after polarization and polarization graph in the Li symmetric cell with SIC (a-b) and SIC-30wt% HE Li-garnet (c-d). The equivalent circuit shown in the inset was used to fit the results and the solid line represents the fitting result.

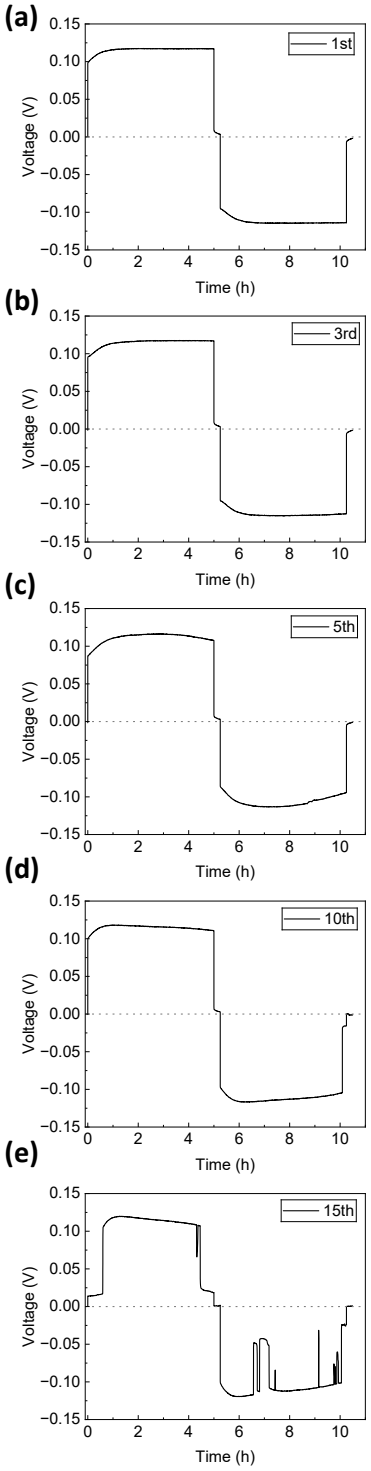

Figure S7. Voltage profile evolution during initial cycling stage of SIC polymer in a Li symmetric cell.

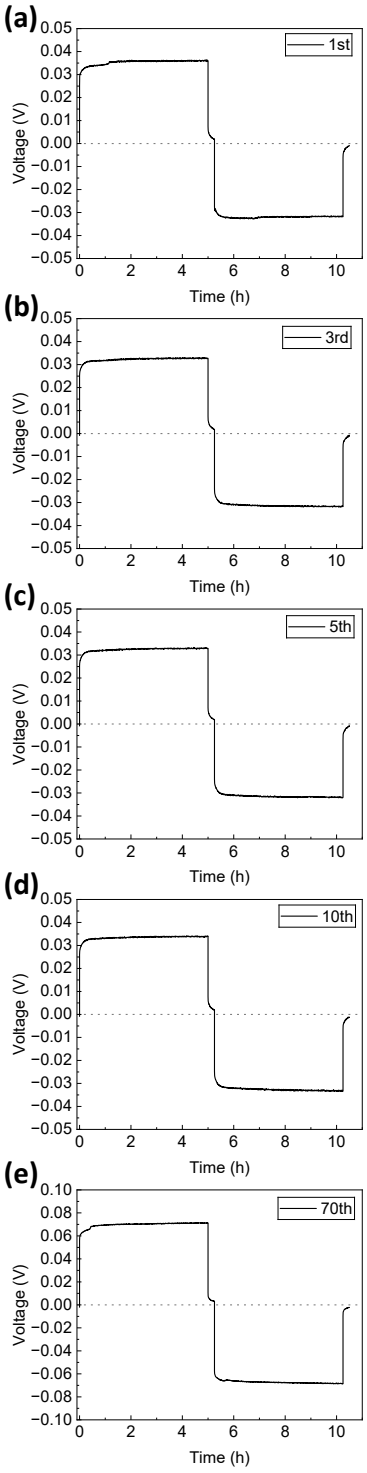

Figure S8. Voltage profile evolution during initial cycling stage of SIC-30wt% HE Li-garnet in a Li symmetric cell.

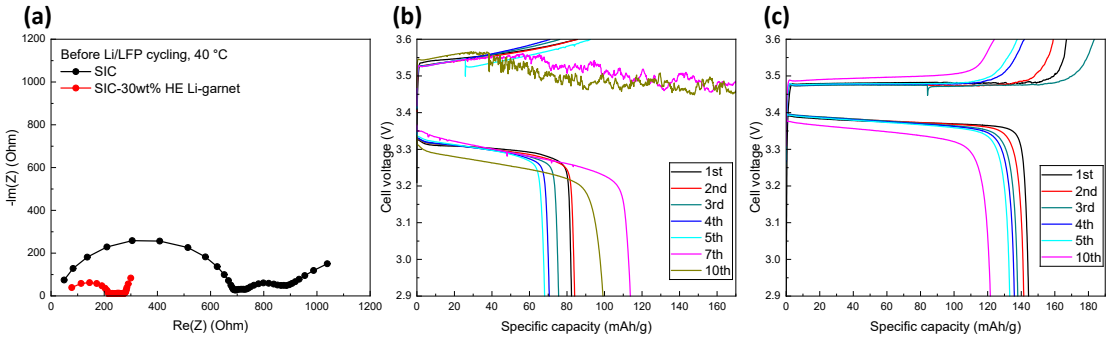

Figure S9. Cell performances of Li/$LiFePO_4$ cells at 40 ºC: (a) Nyquist plots before cycling, and charge/discharge voltage profiles with (b) SIC and (c) SIC-30wt% HE-Li garnet.

Note S1. How to calculate the fraction of the unpolymerized VEC using TGA

SIC: One batch of SIC is composed of 1.00 g VEC and 0.303 g LiMTFSI (with trace amount of AIBN initiator). The weight percentage of VEC is 76.7 %. According to the TGA data, the weight loss corresponding to the unpolymerized VEC is 44.0%. Therefore, the degree of unpolymerized VEC in SIC is (44.0/76.7) (wt%) = 57%. LiMTFSI showed negligible weight loss at this temperature.

SIC-30wt% HE Li-garnet: One batch of SIC-30wt% HE Li-garnet is composed of 1.00 g VEC, 0.303 g LiMTFSI and 0.56 g HE Li-garnet. The weight percentage of VEC is 53.7 %. According to the TGA data, the weight loss corresponding to the unpolymerized VEC is 42 %. Therefore, the degree of unpolymerized VEC in SIC-30wt% HE Li-garnet is (42/53.7) (wt%) = 78 %.