

Supporting information

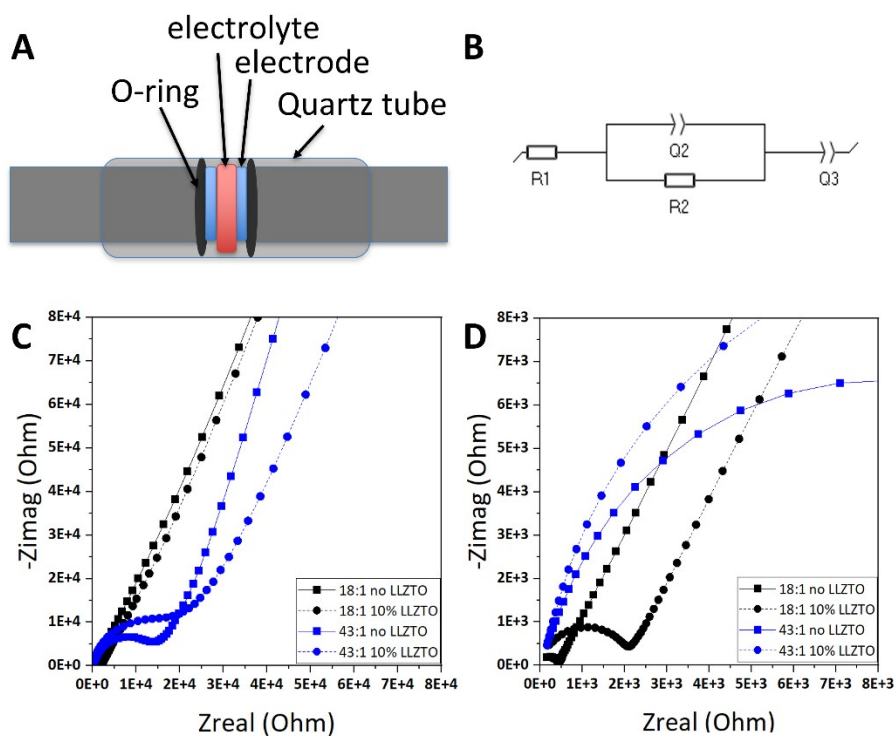


Figure S1. (A) A schematic of a quartz cell sealed with o-rings. This cell was used for Li cycling and LSV tests. (B) Equivalent circuit model (R1: contact resistance, R2 and Q2 (constant phase element, CPE): bulk resistance and capacitance of electrolyte, Q3: capacitance of the electrolyte and the stainless steel spacers) used to fit the Nyquist plot (C, D). Impedance plots of solid-state electrolytes (C) and their magnified versions (D).

	1466/ 1109	1340/ 1360	1190/ 1109	1109/ 1109	962/ 1109	841/ 1109	739/ 1109
18:1 no LLZTO	0.18	0.79	0.81	1	0.26	0.19	0.06
18:1 10% LLZTO	0.16	0.87	0.58	1	0.22	0.19	0.05
43:1 no LLZTO	0.26	1.55	0.28	1	0.35	0.33	0.03
43:1 10% LLZTO	0.28	1.75	0.27	1	0.41	0.38	0.03

Table S1. Normalized peak heights of FTIR spectra against the height of the peak at 1109 cm⁻¹.

The peaks at 1340 cm⁻¹ and 1360 cm⁻¹ were compared to each other to derive relative intensities, while other peak heights were normalized by dividing them by the peak height at 1109 cm⁻¹.

Sample	T _m (C)	ΔH _m (J/g)	X _c (%)
43:1 No LLZTO	62.6	87.1	49.4
	61.5	86.5	49.0
43:1 5 μm 10%	62.3	88.4	55.8
	62.3	94.3	59.4
18:1 No LLZTO	53.9	45.6	30.6
	52.9	48.6	32.7
18:1 5 μm 10%	54.2	45.3	33.9
	53.7	42.8	32.0

Table S2. T_m, ΔH_m, and χ_c values obtained from DSC for four types of solid-state electrolytes.

Image Analysis Details

The spherulite size and area fraction were analyzed at four distinct sites on a representative specimen for each of the four CPE compositions using ImageJ processing software. Initially, the images were processed by enhancing the contrast with 0.3% saturated pixels and equalizing the histogram. Subsequently, a threshold was applied to define the boundaries of the spherulites. The thresholding process did not always accurately outline the spherulite boundaries, necessitating manual intervention. In such cases, the original image was overlaid using 50% transparency, allowing for the manual drawing of outlines on the thresholded image. After manual corrections were made, the overlaid image was removed. The image was then converted to binary, rendering the amorphous regions in white and the spherulites in black. Additionally, to eliminate holes that might have arisen from the thresholding step, the “fill holes” command was used. At this stage, the area fraction of the amorphous area was measured. Further analysis involved measuring spherulite area and quantity, utilizing ImageJ’s “Analyze Particles” function, with edges excluded to ensure including all whole spherulites. To determine the spherulite diameters, a perfect circularity assumption was made, and these values were calculated based on the spherulite areas. Quantitative analysis in the main text is thus based on a total of four sites for each type of electrolyte.