Supporting Information for

Melt Crystallization and Segmental Dynamics of Poly(ethylene oxide) Confined in a Solid Electrolyte Composite

Yage Huang[1], Mingchao Ma[1], and Yunlong Guo*[,1,2,3]

[1]University of Michigan – Shanghai Jiao Tong University Joint Institute, [2]The State Key Lab of Metal Matrix Composites, and [3]School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

The blend of PEO and different ratios of LLZO were dissolved in acetonitrile with a 3 wt% concentration and then prepared via blade coating. The film was transferred into an oven and annealed at 50 ℃ under vacuum for 24 h to remove residual solvent. To examine the quality of the membrane samples, Fourier transform infrared spectroscopy (FTIR) tests were performed and the results showed no remaining solvent in the film and no water was absorbed during the sample preparation as shown in Figure S1.

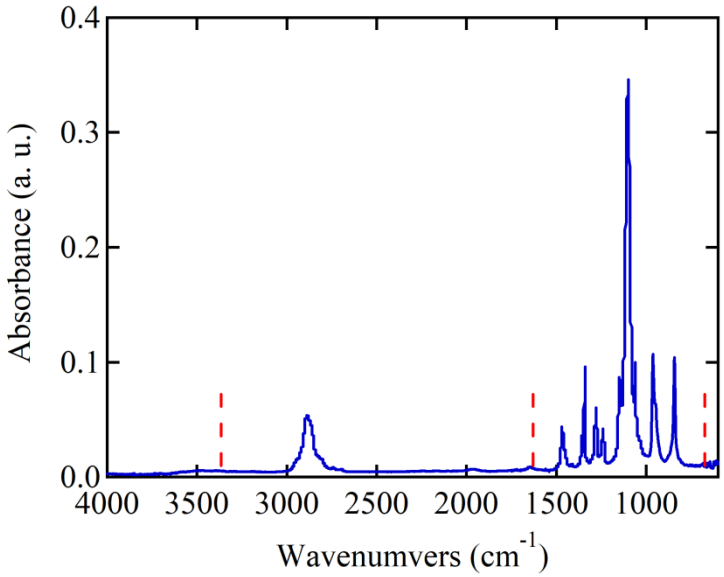

Figure S1. FTIR spectra for sample #3. The dash lines are absorption band for water.

To analyze the isothermal crystallization kinetics and corresponding segmental dynamics, the sample

was heated to melting temperature T_m = 80 ℃ with a constant ramp rate of 10 ℃/min and annealed thereat for 10 min to ensure that it melted completely, and then quenched to T_c = 52 ℃ or 55 ℃ to crystallize isothermally for various times. The temperature protocol is shown in Figure S2.

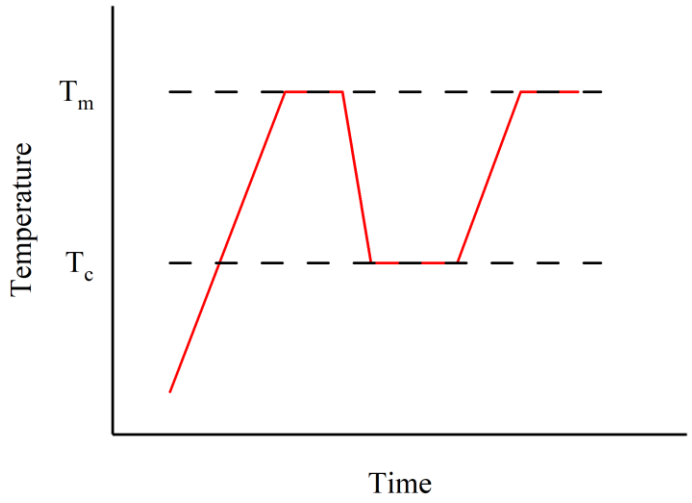

Figure S2. Temperature protocol of test.

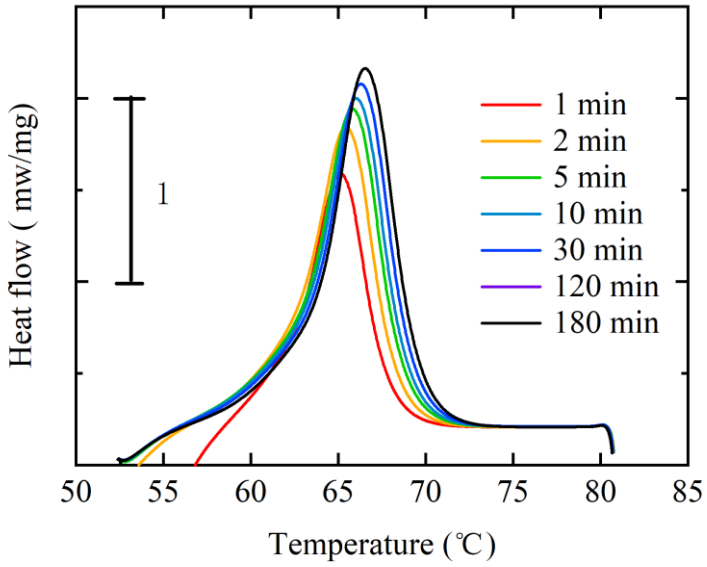

Figure S3. DSC curves of sample #2 as a function of temperature.

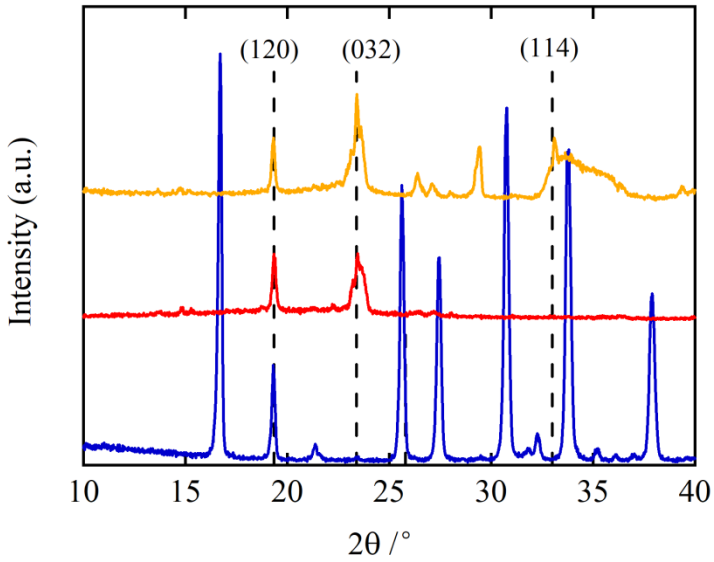

Figure S4. WAXS intensity profile for sample #1 crystallized at T_c = 55 ℃ for 3 h (yellow), 52 ℃ (red). Blue curve shows the LLZO WAXS spectrum. The peaks of PEO and LLZO overlap at reflection (120).

Table S1 shows average particle radius *r* and volume percentage ϕ_2 which are extracted from Nano CT scans (Figure 9). ϕ_2 is smaller than theoretical values since the film is porous, as shown in Figure S4, thus air volume contained in the film is counted.

Table S1: Results of the Dielectric Experiments on Blends

Sample	ϕ_2(%)	***r***(μm)	X_t[a](%)	X_t[b](%)
#2	0.17	2.12	70.5	73.0
#3	2.02	3.91	74.4	77.2
#4	2.31	4.18	69.3	71.8
#5	2.84	4.06	61.8	65.6
#6	8.92	4.03	59.0	62.6
#7	7.99	3.50	52.7	56.8

[a] and [b] represent overall crystallinity after isothermal crystallization at 52 ℃ and 55 ℃ for 3h, respectively

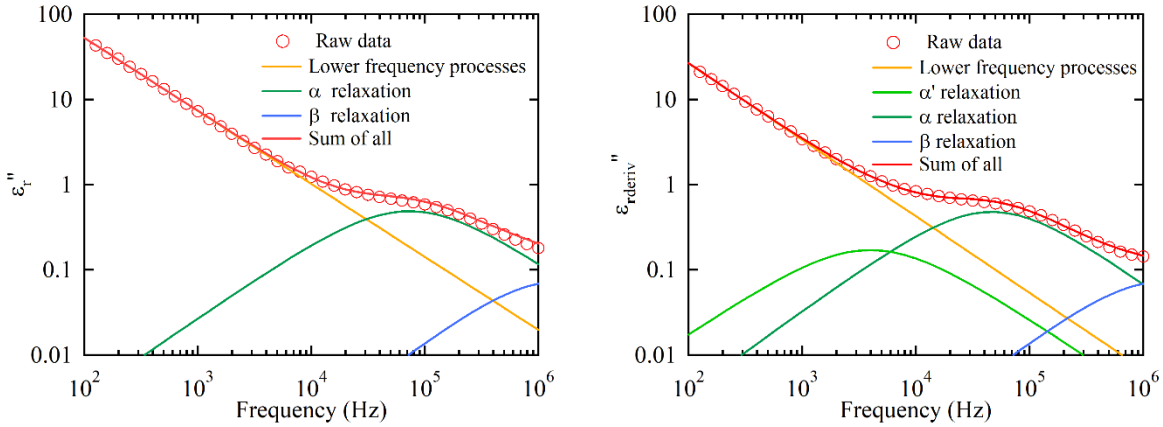

Figure S5. Dielectric loss spectra of sample #3 versus frequency for different crystallization time at 52 °C (left: t = 0 s, right: t = 3 h). Solid lines are model fitting results.

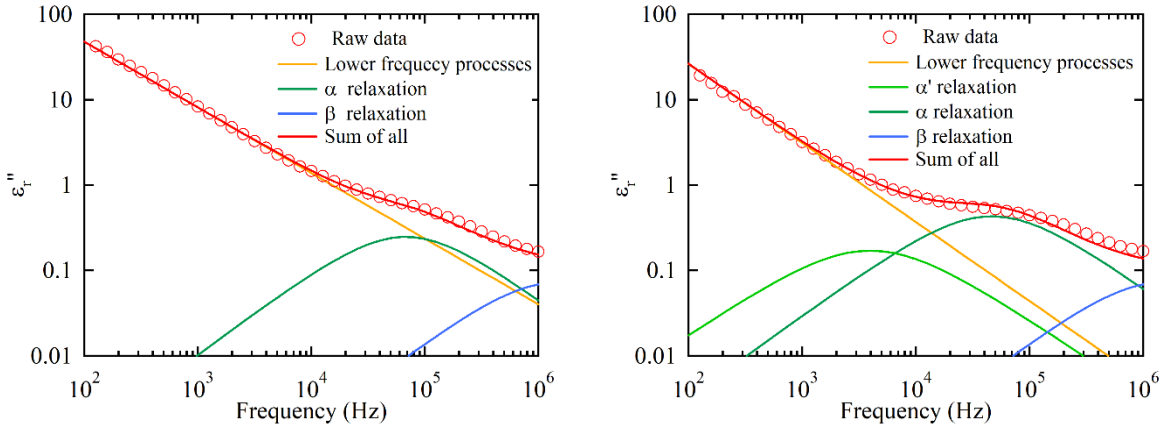

Figure S6. Dielectric loss spectra of sample #4 versus frequency for different crystallization time at 52 °C (left: t = 0 s, right: t = 3 h). Solid lines are model fitting results.

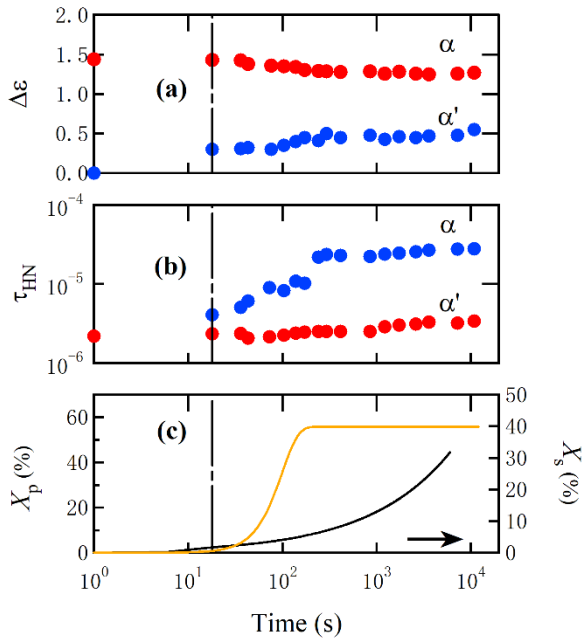

Figure S7. Summary of physical parameters of sample #4 as a function of the crystallization time at 52 ℃: time evolution of (a) Δε, (b) τ_{HN}, (c) primary crystallinity (left) and secondary crystallinity rate (right). Vertical dash dot lines represent the beginning of secondary crystallization determined from DSC DRS results.

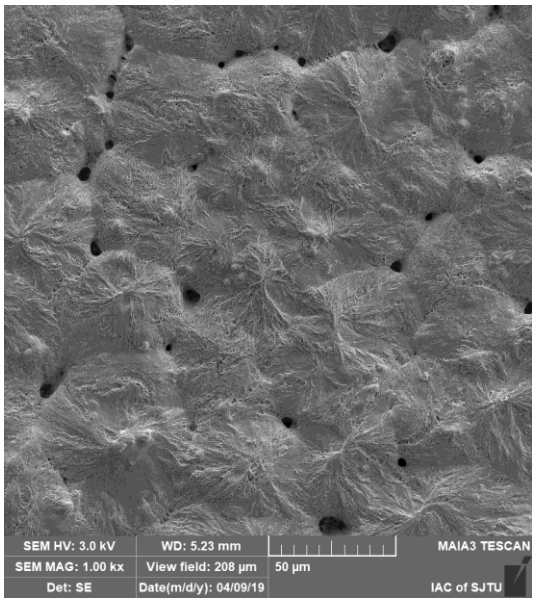

Figure S8. SEM micrographs of Sample #4. It can be seen that there are open channels on the film surface.

Bulk compositional analysis of the composite was carried out using a TA Instruments thermal gravimetric analyzer (SDT/SDT-Q600). Raw TGA thermograms and their first-order derivative curves are shown in Figure S8. Samples are heated from 30 ℃. Final heating temperatures are carefully chosen to avoid emission of Li.

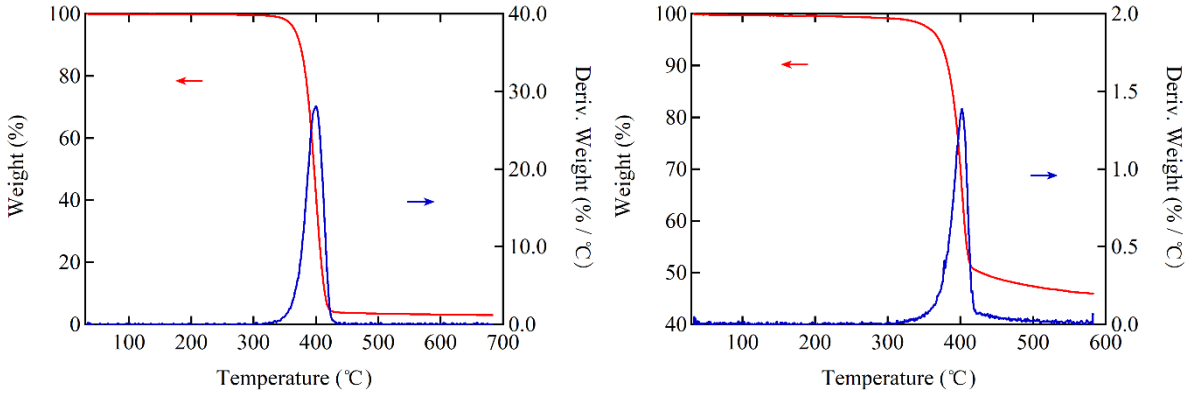

Figure S9. TGA curves for sample #1 (left), and sample #6 (right).

Real-time melting and crystallization were monitored by polarized optical microscopy as mentioned in the paper and represented in Figure S10, S11, and S12. Green dots observed in neat PEO films and the composite might be impurities. The shape and growth rate of spherulites vary with sample composition and crystallization temperature.

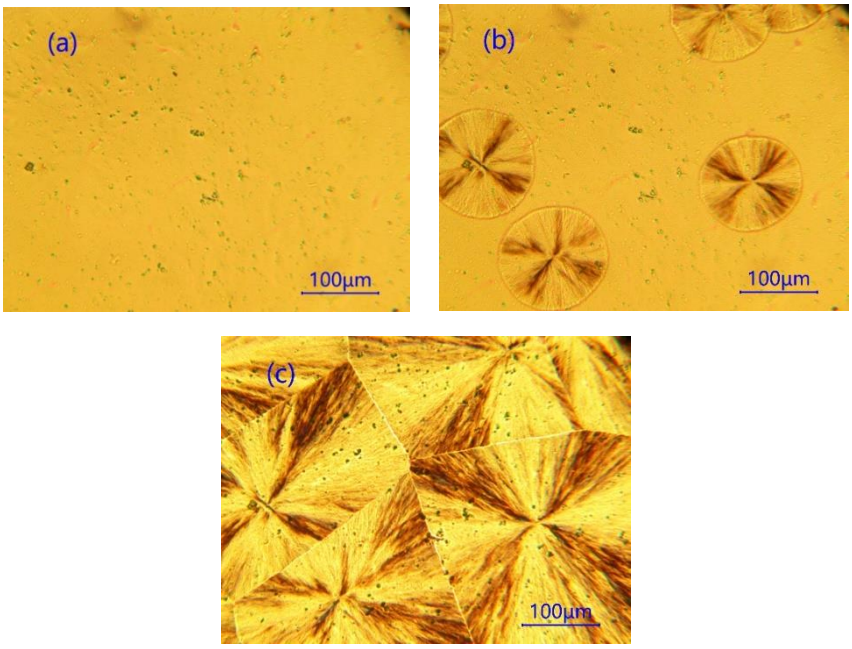

Figure S10. OM images of sample #1 isothermally crystallized at T_c = 52 ℃ for (a) 0 min, (b) 15 min, and (c) 3h.

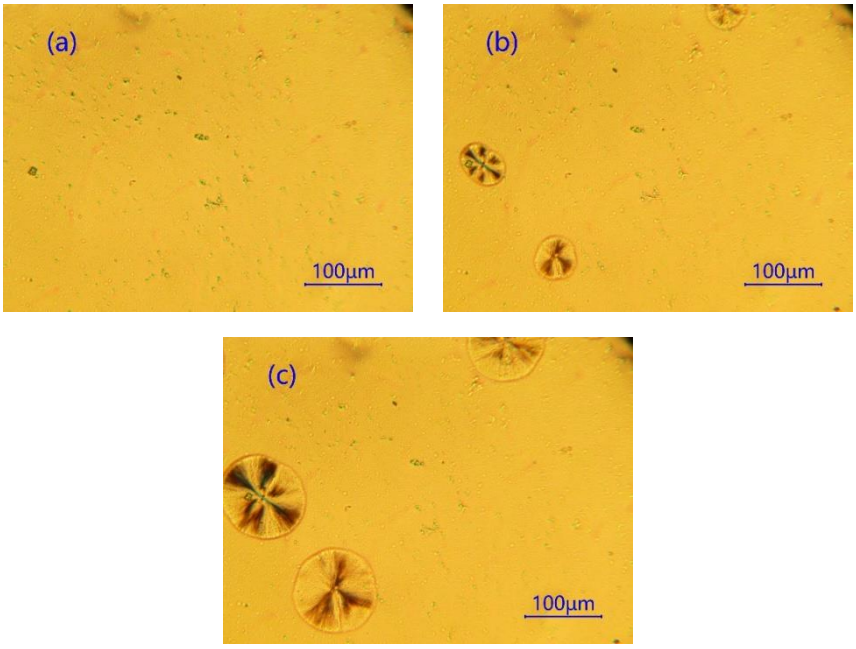

Figure S11. OM images of sample #1 isothermally crystallized at T_c = 55 ℃ for (a) 0 min, (b) 1h, and (c)

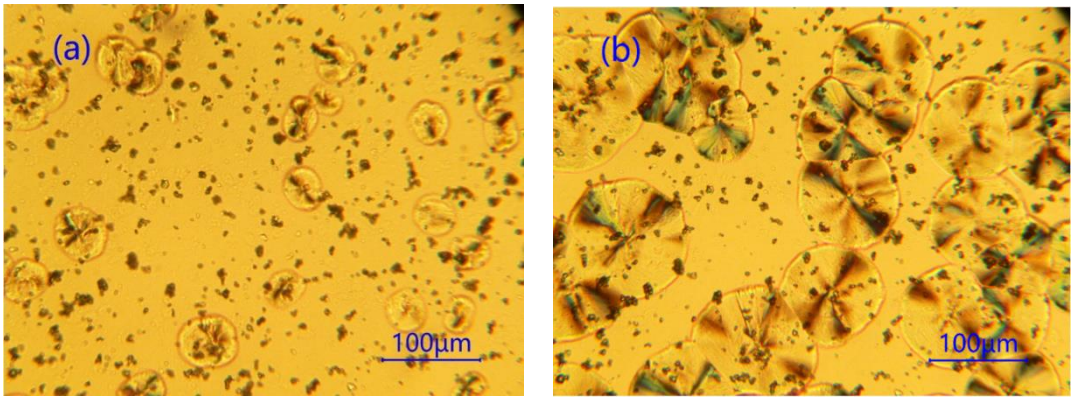

Figure S12. Optical microscopy images of sample #2 isothermally crystallized at 55 ℃ for (a) 5 min, and (b) 3 h.

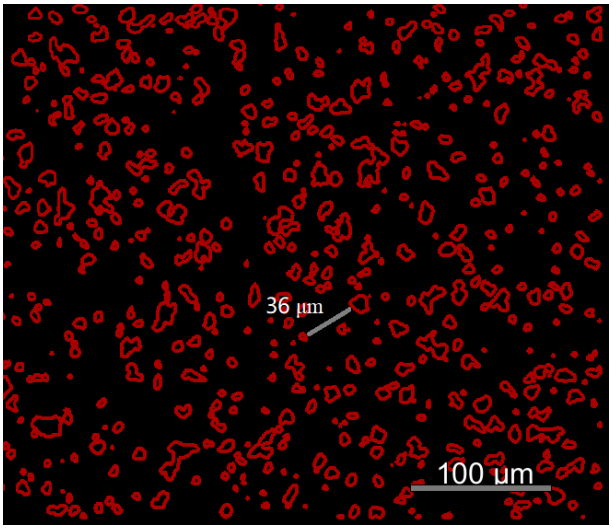

Figure S13. A Nano CT image of sample #3 showing spatial distribution of LLTO particles in the solid composite electrolytes. The space dyed in red displays the space occupied by LLTO ceramic particles.