Supporting Information

In-Situ Thermally Polymerized Solid Composite Electrolytes with Broad Electrochemical Window for All-Solid-State Lithium Metal Batteries

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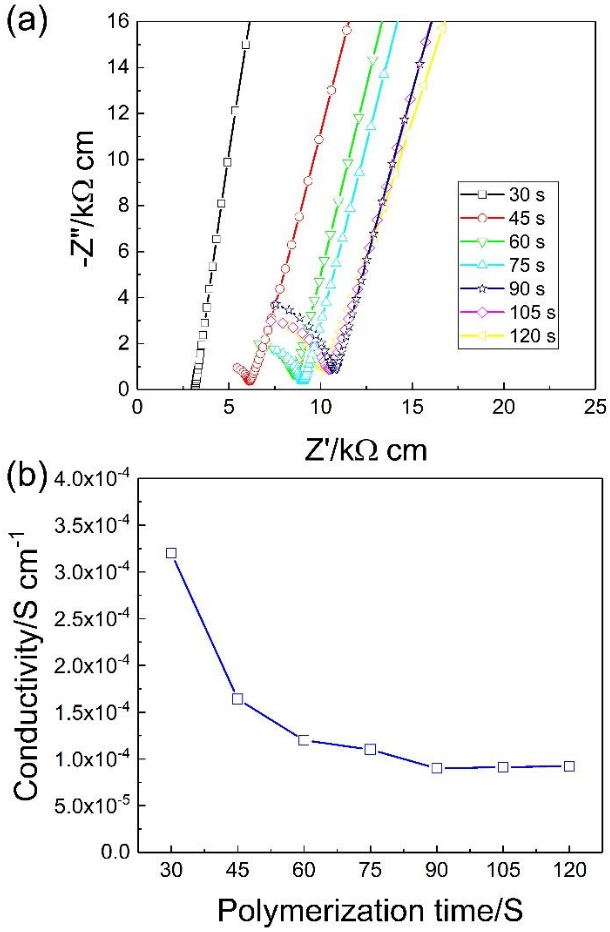

Figure S1. (a) Impedance spectra of the polymer electrolyte for different polymerization time; (b) ionic conductivity of the polymer electrolyte for different polymerization time.

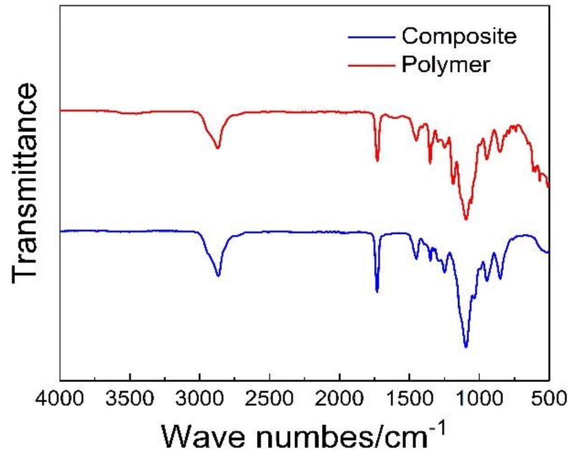

Figure S2. FTIR spectra of polymerized solid electrolytes (polymer and composite electrolytes).

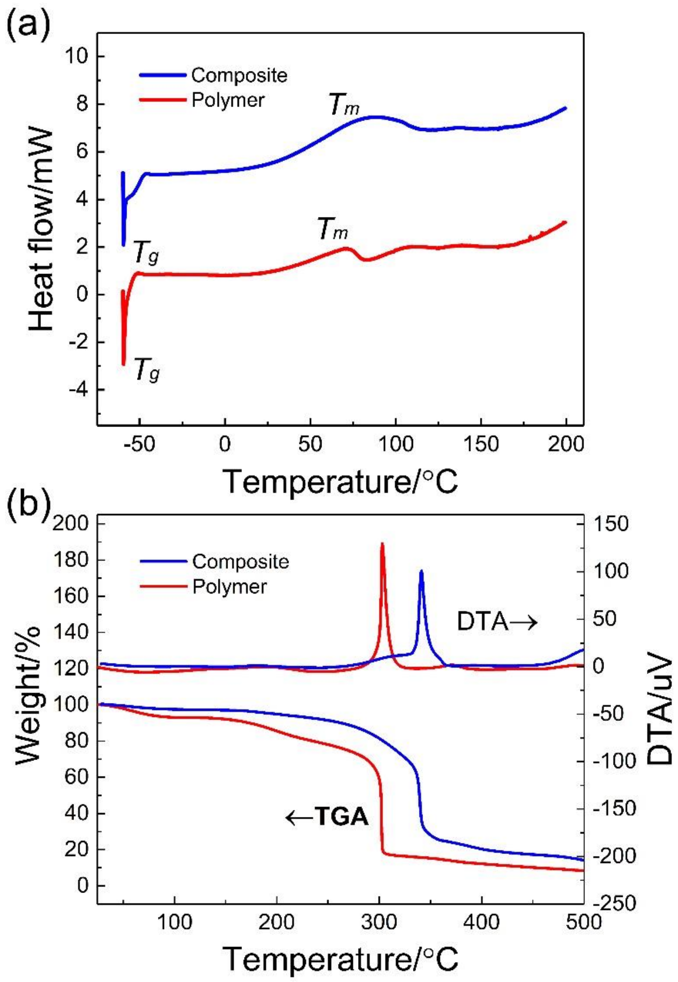

Figure S3. Thermal performances of the polymerized electrolytes (polymer and composite electrolytes): (a) DSC curves, (b) TG-DTA curves.

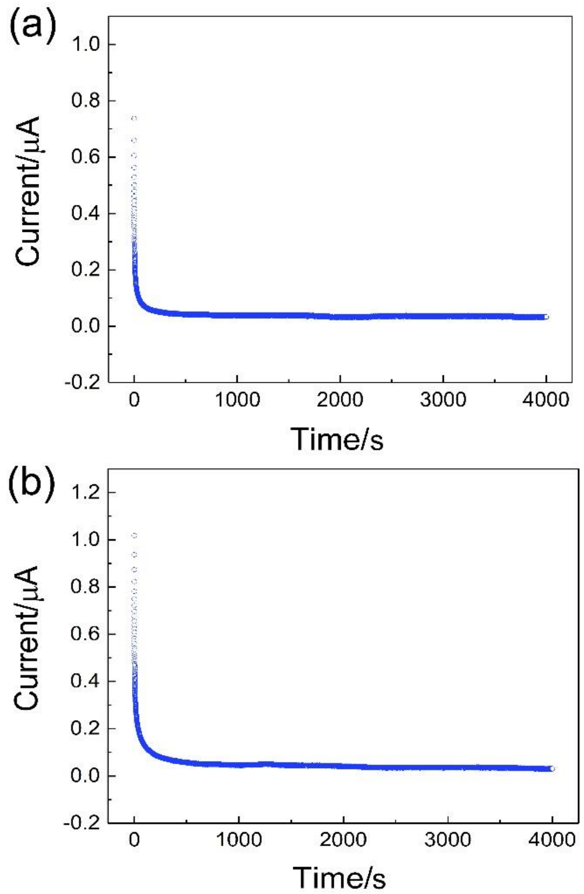

Figure S4. DC polarization curves of the polymerized electrolytes based on stainless steel/electrolyte/stainless steel symmetric cells. (a) Polymerized composite electrolytes with 10% LLZO, (b) polymerized polymer electrolytes without LLZO fillers.

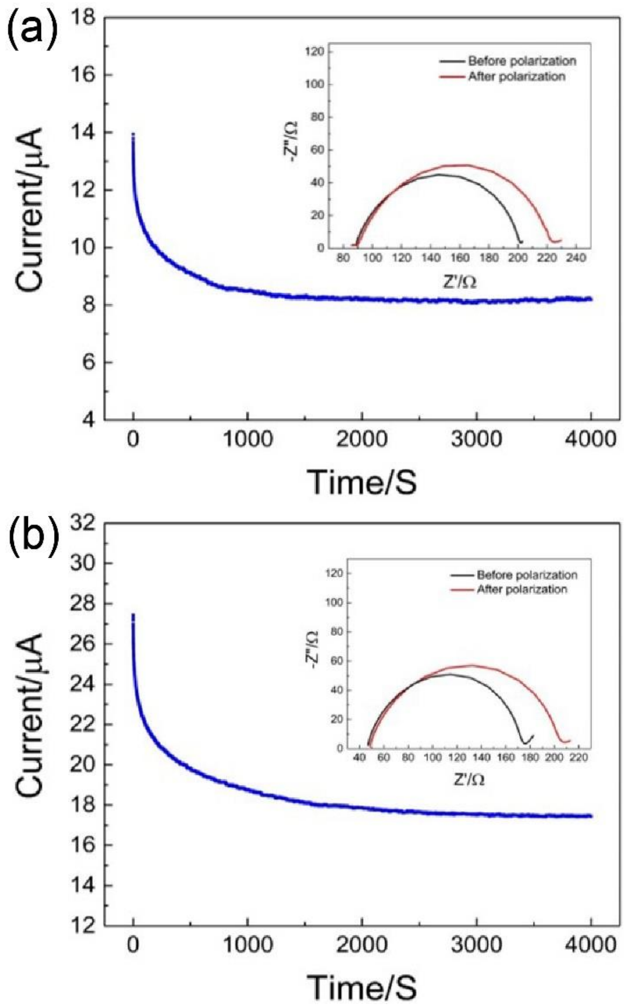

Figure S5. DC polarization curves of the polymerized electrolytes based on Li/electrolyte/Li symmetric cells. Insets: impedance spectra of the cells before and after polarization. (a) Polymerized composite electrolytes with 10% LLZO, (b) polymerized polymer electrolytes without LLZO fillers.

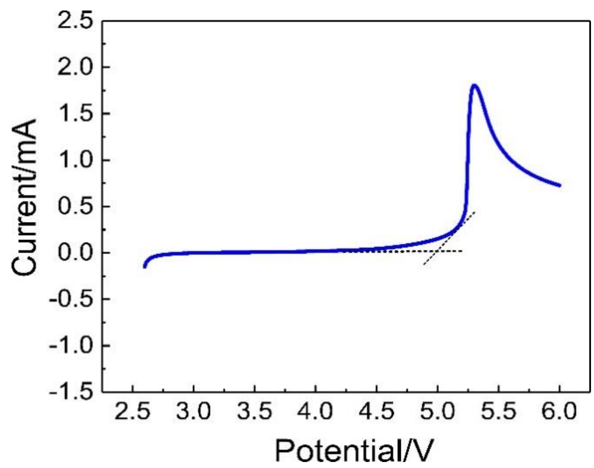

Figure S6. LSV curves of the polymer electrolyte without LLZO fillers.

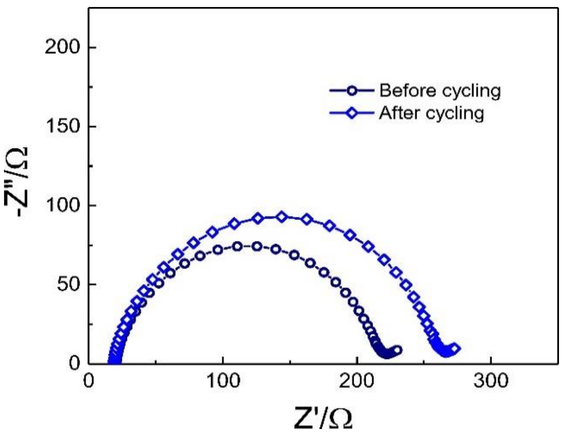

Figure S7. Impedance spectra of the Li/PCE-10/Li symmetric cell before and after 500 cycles at a current density of 0.5 mA cm^{-2}.

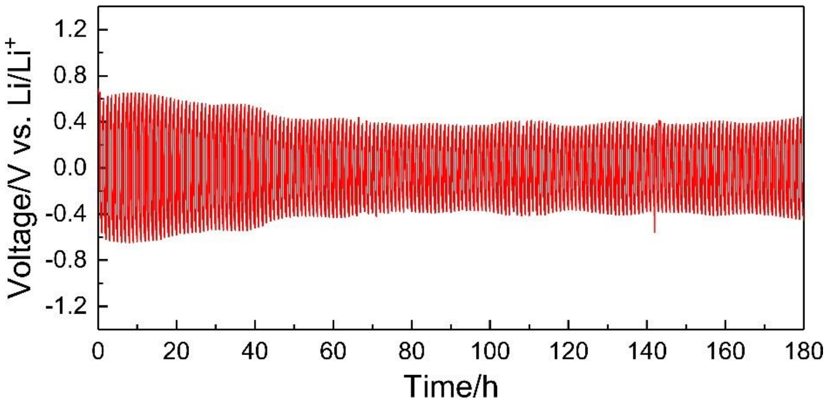

Figure S8. Voltage profiles of the Li/PCE-10/Li symmetric cell at a current density of 0.6 mA cm^{-2}.

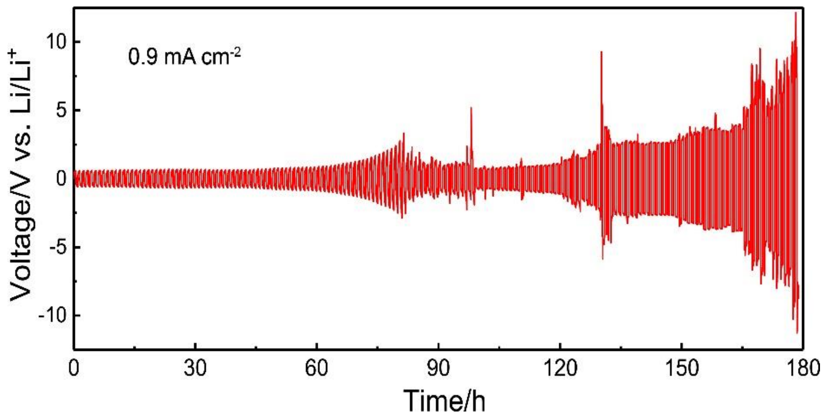

Figure S9. Voltage profiles of the Li/PCE-10/Li symmetric cell at a current density of 0.9 mA cm^{-2}.

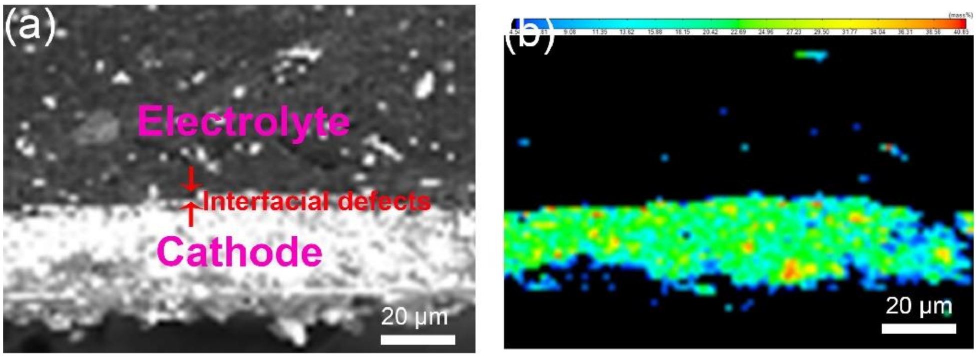

Figure S10. (a) EPMA image, and (b) WDS mapping of the interface between the cathode and the ex-situ polymerized composite electrolyte.

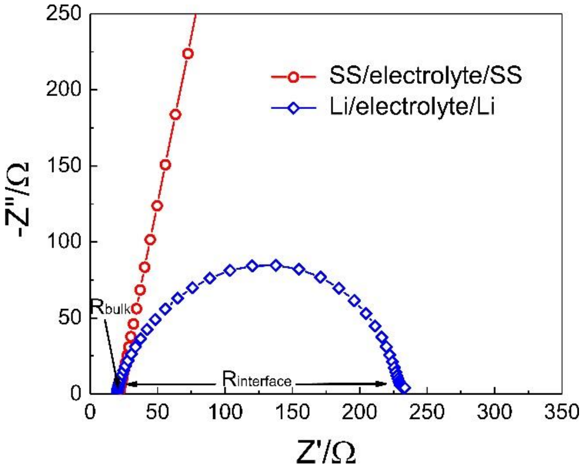

Figure S11. Impedance spectra of PCE-10 with blocking electrodes (stainless steel, SS) and reversible electrodes (metallic Li).

To differentiate the bulk and interfacial resistances, we measured the impedance of PCE-10 samples with blocking electrodes (stainless steel, SS) and non-blocking electrodes (metallic Li); both samples have the same size, ~60 μm in thickness and 15 mm in diameter. As shown in Figure S11, the impedance spectrum of the sample with the blocking electrodes shows an inclined line, which is typical for blocking electrodes; therefore, the intersection at high frequencies represents the bulk resistance (R_{bulk}). However, the impedance spectrum of the sample with the non-blocking electrodes shows a semicircle, whose capacitance is on the scale of 10^{-6} F, which is much too large for the bulk, but typical for electrodes; therefore, the intercept of the semicircle at intermediate frequencies corresponds to the interfacial resistance ($R_{interface}$) between the electrolyte and electrodes. Please also note that for both samples the intersections at high frequencies are coincident, both represent the bulk resistance (R_{bulk}).

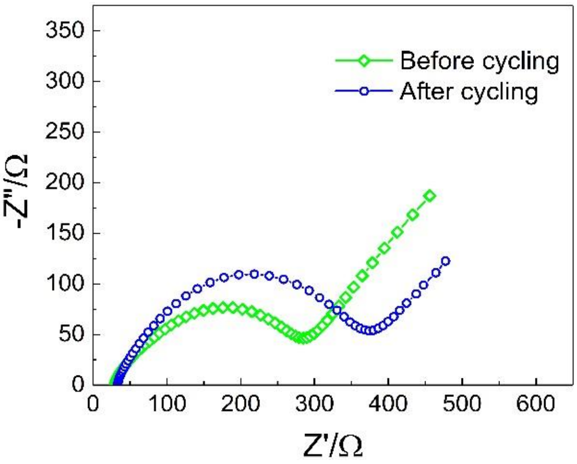

Figure S12. Impedance spectra of the Li/PCE-10/NCA battery before and after cycling at a rate of 0.3 C.

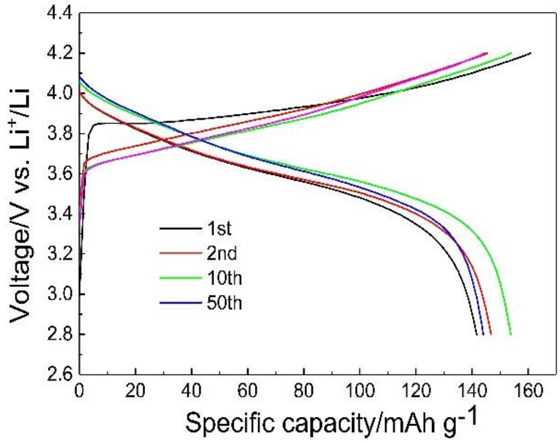

Figure S13. Typical charge/discharge profiles of Li/PCE-10/NCM622 solid-state battery in the voltage range of 2.8 to 4.2 V under 0.5 C.

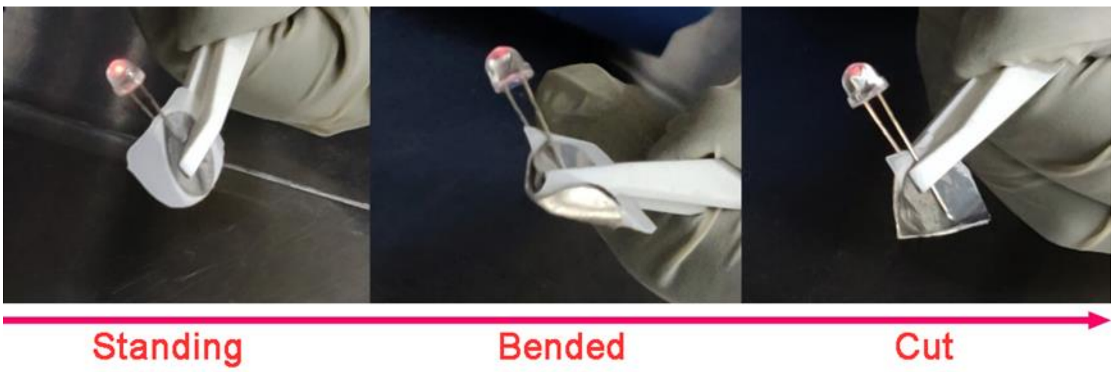

Figure S14. Safety evaluation of solid-state battery Li/PCE-10/NCM622 under destructive conditions: standing, bended, and cut.

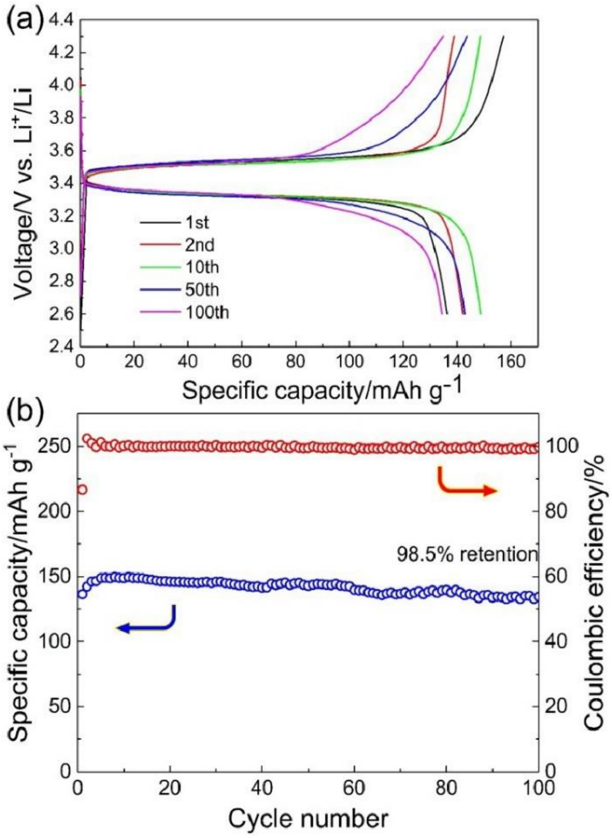

Figure S15. (a) Typical charge/discharge profiles, and (b) cycling stability and Coulombic efficiency of Li/PCE-10/$LiFePO_4$ solid-state battery in the voltage range of 2.6 to 4.3 V under 0.2 C.