RESEARCH ARTICLE

In-situ photo-polymerized elastomeric composite electrolytes containing $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ particles for stable operation in lithium metal batteries

Seung Ho Kwon ¹ Seongmin Kim	1	Jinseok Park ¹	Michael J. Lee ² 🗅	I
Youyoung Byun ³ Hyun Jung Kim ¹	Ι	Young Min Baek ⁴ 🗅	Jaegyeom Kim ⁴	
Eunji Lee ³ Seung Woo Lee ⁵	Bι	ımjoon J. Kim ¹ 💿		

¹Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea ²Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin, Republic of Korea

³School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea

⁴Future Technology Institute, Lotte Chemical Co., Seoul, Republic of Korea

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⁵George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA

Correspondence

Bumjoon J. Kim, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea. Email: bumjoonkim@kaist.ac.kr

Seung Woo Lee, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA. Email: seung.lee@me.gatech.edu

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Abstract

Composite polymer electrolytes (CPEs), produced by incorporating inorganic nanoparticles (NPs) into polymer matrices, have gained significant attention as promising candidates for solid-state lithium metal batteries (LMBs). However, the aggregation of dense inorganic fillers results in nonuniform CPEs, thereby impeding LMB performance. Here, we fabricated in-situ photo-polymerized CPEs by incorporating different weight ratios (0-20 wt%) of Li_{6.4}La₃Zr_{1.4}-Ta_{0.6}O₁₂ (LLZTO) into a polymer electrolyte system composed of poly(butyl acrylate)-based elastomer and succinonitrile-based plastic crystal phases. The rapid photo-polymerization process (~5 min) enabled homogeneous dispersion of LLZTO within the CPE matrix at 10 wt% LLZTO (L10), resulting in the high ionic conductivity (1.02 mS cm⁻¹ at 25°C) and mechanical elasticity (elongation at break \approx 1250%) compared to those of CPE without LLZTO (L0). As a result, the L10-based LMB with a LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode exhibited a high capacity of 166.7 mAh g^{-1} after 200 cycles at 0.5C, significantly higher than those of L0 (74.0 mAh g^{-1}) and L20 (104.8 mAh g^{-1}). In comparison, in-situ thermal polymerized CPE with 10 wt% LLZTO NPs showed aggregation of NPs due to slow polymerization kinetics (~ 2 h), resulting in inferior LMB cycling performance compared to the L10. This work highlights the importance of insitu photo-polymerized CPEs with homogenous dispersion of inorganic NPs to

Seung Ho Kwon and Seongmin Kim contributed equally to this work.

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achieve high ionic conductivity and mechanical robustness suitable for the stable operation of LMBs.

KEYWORDS

composite polymer electrolyte, elastomeric electrolyte, in-situ photo-polymerization, Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂, lithium-metal batteries

1 | INTRODUCTION

The development of lithium (Li) metal batteries (LMBs) has garnered significant attention due to their high energy density.¹ This is attributed to Li metal's superior theoretical specific capacity (3860 mAh g^{-1}) and lower electrochemical potential (-3.04 V vs. the standard hydrogen electrode) compared to conventional graphite anodes.^{2,3} However, LMBs face substantial safety challenges particularly when using flammable liquid electrolytes, due to uncontrolled dendrite formation during cell cycling.⁴⁻⁶ Solid-state electrolytes (SSEs) are promising alternatives to liquid electrolytes due to their nonflammable nature and mechanical properties for inhibiting Li dendrite growth.⁷⁻¹² Among SSEs, solid polymer electrolytes (SPEs) have the advantages of mechanical flexibility, facile processing, and a smooth interface between the electrode and the electrolyte.¹³⁻¹⁹ However, the ionic conductivity of SPEs is significantly lower than that of liquid electrolytes.^{20,21} Moreover, their mechanical properties, such as elasticity, adhesion, and toughness, are often insufficient to accommodate the large volume changes of Li during cycling and prevent dendrite formation.^{22–24}

To overcome the limitations of SPEs, composite polymer electrolytes (CPEs) have emerged as an effective strategy by incorporating inorganic nanoparticles (NPs) into the polymer matrix.^{25–28} CPEs can leverage the combined benefits of both polymer and inorganic components, resulting in enhanced mechanical, thermal, and electrochemical properties.^{29–32} Among various inorganic fillers used in CPEs, sulfide-based NPs, such as Li₁₀GeP₂S₁₂ and Li₆PS₅X are intrinsically unstable, as they react with atmospheric moisture to release toxic H₂S gas and have a narrow electrochemical stability window below 3.0 V (vs. Li/Li⁺).³³⁻³⁵ In contrast, Li-ion (Li⁺)conducting oxide-based Li₇La₃Zr₂O₁₂ (LLZO) NPs are more stable against air and have a wider electrochemical window (>4.0 V vs. Li/Li⁺).^{36,37} However, LLZO NPs encounter poor compatibility with Li metal, which has been addressed by incorporating various dopant species to improve their chemical compatibility with Li metal.^{38,39} For example, tantalum (Ta)-doped LLZO of $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (0.2 < x < 1) (LLZTO) is known for its excellent stability in contact with Li metal and its ability to lower the interfacial resistance between the electrode and electrolyte. $^{40-43}$

Inorganic NPs typically become strongly aggregated, preventing their homogeneous dispersion within the polymer matrix and causing nonuniform Li⁺ flux throughout the CPEs.^{44–46} Therefore, it is crucial to develop a suitable CPE fabrication process for achieving uniform CPE structures and thus improving LMB performances. While ex-situ processing methods, such as hightemperature mixing, hot-pressing, and electrospinning can improve the NP dispersion in a polymer matrix, 47-50ex-situ fabricated CPEs often struggle with poor electrode adhesion and a nonconformal electrolyte/electrode interface compared to in-situ fabricated CPEs.⁵¹ Note that the in-situ approach can form a smooth and conformal interfacial contact with electrodes by injecting a liquid precursor solution into the electrode prior to the polymerization reaction.⁵² However, in-situ thermal polymerization of CPE can lead to NP precipitation and aggregation because of the extended reaction time (i.e., more than 2 h) required for complete monomer conversion.⁵³ In contrast, photo-polymerization offers rapid polymerization kinetics within a few minutes, resulting in a more uniform distribution of inorganic NPs within the polymer matrix.^{54–57} Thus, we envision that photo-polymerization is particularly well-suited for the in-situ fabrication of CPEs and is advantageous for industrial applications.

Herein, we design CPEs through an in-situ photopolymerization process. The rapid photo-polymerization time (\sim 5 min) allows uniform dispersion of LLZTO NPs within an elastomeric electrolyte matrix composed of crosslinked poly(butyl acrylate) (poly(BA)) and ion-conductive succinonitrile (SN) with Li salts, achieving stable operation of LMBs. We note that both the NP fraction and polymerization kinetics are crucial factors in producing homogeneous CPEs through the in-situ process. To understand the structure and properties of CPEs with different weight ratios of LLZTO, several CPEs were formed with 0, 10, and 20 wt% LLZTO. Among them, the CPE containing 10 wt% LLZTO (L10) shows excellent mechanical properties, with an elongation at break $(\varepsilon_{\rm b})$ of 1250% and a high adhesion energy of approximately 10.1 J m⁻² at the CPE/CPE interface, while maintaining a high ionic conductivity (σ) of 1.02 mS cm⁻¹ at 25°C

compared to the CPE without LLZTO. Increasing the LLZTO fraction to 20 wt% resulted in a decrease in both mechanical properties (900%, 6.6 J m⁻²) and σ value (0.76 mS cm⁻¹) due to the increased aggregation of LLZTO NPs. The full-cell performance of L10, using a Li anode and LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) cathode shows excellent cycling stability with 95% capacity retention after 200 cycles at 0.5C and a cutoff voltage of 4.3 V (vs. Li/Li⁺). In contrast, in-situ thermal polymerization causes LLZTO aggregation and strong phase separation from the elastomeric matrix due to the slow polymerization kinetics (~2 h), resulting in inferior LMB performance compared to L10. This work highlights the importance of in-situ photo-polymerization for designing uniform CPEs to achieve highly stable LMBs.

2 | RESULTS AND DISCUSSION

The CPEs were synthesized by in-situ photo-polymerization of precursor solutions containing monomer- and SNbased solutions with LLZTO NPs (Scheme 1). The precursor solutions were prepared by mixing monomer- and SN-based solutions in equal volumes of BA and SN.⁵⁸⁻⁶⁰ Briefly, the monomer-based solution included BA monomer, 1 mol% of poly(ethylene glycol) diacrylate (PEGDA) crosslinker, and 0.5 mol% of 1-hydroxycyclohexyl phenyl ketone (HCPK) photo-initiator. Upon polymerization, the PEGDA crosslinker formed multiple linkages with linear poly(BA) chains, producing a crosslinked polymer network.^{61,62} The SN-based solution was composed of SN, lithium bis(trifluoromethanesulfonic)imide (LiTFSI), and lithium difluoro(oxalato)borate (LiDFOB). A 5 vol% of fluoroethylene carbonate (FEC) additive was added into the SN-based solution to prevent the undesired reactions between SN and Li metal anode.63 The incorporation of LiDFOB helps to prevent the corrosion of the aluminum current collector caused by LiTFSI during cell cycling.64



SCHEME 1 The design of in-situ photo-polymerized CPEs containing LLZTO NPs.

The Li salt concentration was fixed at 0.8 M LiTFSI and 0.2 M LiDFOB within the CPE precursor solutions. The inorganic LLZTO NP with a median particle size (D50) of \sim 500 nm was selected as the inorganic material for the CPE-based LMB system because of its excellent compatibility with Li metal anode, inducing a low interfacial resistance at the Li/CPE interface of CPEs.^{38,65} Each CPE sample was denoted as LX (X = 0, 10, and 20), where X represented the weight ratio of LLZTO added relative to the total weight of the precursor solution. Then, the coin cell assembly employed an in-situ photo-polymerization approach by casting precursor solutions onto the anode and cathode, followed by ultraviolet (UV) light irradiation (Figure S1).

2.1 | Design of CPEs through in-situ photo-polymerization process

The polymerization kinetics of the photo-polymerization process of poly(BA) was monitored by measuring Fouriertransform infrared spectroscopy (FTIR) for the samples with different polymerization times (Figure 1A). The characteristic C=C stretch peak of the acrylate monomer, typically seen at 1620 and 1637 cm^{-1} , disappeared within 5 min under UV irradiation, indicating complete polymerization of crosslinked polymers. In Figure 1B, the precursor solution turned into opaque bulk CPE after the short photo-polymerization process. The fast photo-polymerization kinetics could effectively form a CPE with homogeneously distributed LLZTO NPs by preventing the aggregation of LLZTO and their separation from the polymer matrix. The distribution of LLZTO NPs was characterized by the cross-sectional morphology of CPEs using scanning electron microscopy (SEM) and corresponding energy-dispersive X-ray spectrometer (EDS) mapping (Figure 1C-E and Figure S2). For L0, the wrinkled surface structure of the CPE was observed without any inorganic fillers (Figure 1C). With the addition of 10 wt% LLZTO, L10 exhibited well-dispersed LLZTO NPs throughout the CPE, indicating that rapid photo-polymerization successfully trapped the NPs and prevented their aggregation within the crosslinked polymer matrix (Figure 1D). In contrast, an excessive amount of fillers within L20 led to the aggregated LLZTO NPs within the CPE matrix (Figure 1E). The cross-sectional EDS mapping images for Lanthanum (La) and Zirconium (Zr) elements further supported the agglomeration of LLZTO NPs within the L20 (Figure S2). We performed optical microscopy (OM) and cryogenic transmission electron microscopy (Cryo-TEM) for the L0, L10, and L20 samples to characterize the phase structures of CPEs as well as the



FIGURE 1 (A) FTIR of crosslinked poly(BA) by photo-polymerization according to different processing times. (B) Optical image of the L0 before and after photo-polymerization. Cross-sectional SEM image of CPEs: (C) L0, (D) L10, and (E) L20. Insets display bulk photographs of each electrolyte. Red circles in (E) indicate the aggregated LLZTO NPs.

distribution of LLZTO NPs in the CPEs (Figure S3 and Figure S4). Both the OM and Cryo-TEM images showed the severe aggregations of LLZTO NPs in the L20 and suggested significant differences in the LLZTO distributions between the L10 and L20 samples.

To understand the phase structures of CPEs, we measured ⁷Li solid-state nuclear magnetic resonance (⁷Li NMR) spectroscopy and Cryo-TEM. The ⁷Li NMR spectra of the L0 sample revealed three distinct peaks, corresponding to Li⁺ interactions with the BA-Li, SN-Li, and BA/SN interface (Figure S5A).⁶⁰ This indicates a phaseseparated structure between the crosslinked poly(BA) and SN phases, a result of polymerization-induced phase separation (PIPS) during the photo-polymerization process. This phase-separated structure consisting of an interconnected ion-conducting SN phase within a polymer phase was clearly observed in the Cryo-TEM image (Figure S4A), which is beneficial for enhancing both ionic conductivity and mechanical performance of electrolytes.^{66,67} The LLZTO-containing CPEs, L10, and L20, also exhibited distinct peaks corresponding to the polymer and the SN phases, indicating similar phase separation after photo-polymerization (Figure S5B,S5C). Interestingly, the incorporation of LLZTO NPs induced the migration of a fraction of Li⁺ from the SN to the poly (BA) phase, resulting in the increased Li⁺ concentration in the poly(BA) matrix in L10 and L20 compared to L0 and affecting the Li^+ conductivity in the CPEs.

2.2 | Physiochemical properties of in-situ photo-polymerized CPEs

To investigate the effect of LLZTO NPs on the chemical interaction within CPEs. Raman spectra were obtained in the 1670–1750 cm^{-1} range (Figure 2A), with the full spectra provided in Figure S6. The L0 sample displayed a carbonyl (C=O) stretching band at 1719 cm^{-1} due to the free C=O groups in the poly(BA) phase. The C=O peak was blue-shifted by 3.7 cm^{-1} for L10 and 10.2 cm^{-1} for L20, indicating chemical interactions between the C=O groups and LLZTO NPs. This shift is primarily attributed to the La-ion (La³⁺) in LLZTO fillers, which provided numerous Lewis acid sites that facilitate intermolecular coordination with electron-withdrawing C=O groups in polymer matrix through Lewis acid-base interactions.⁶⁸ For L20, the increased LLZTO content provided more La³⁺ sites for Lewis acid-base interactions, leading to a further peak shift of the C=O groups in the poly(BA) phases. Additionally, Raman spectroscopy was also investigated in the 2220–2300 cm^{-1} range to reveal the intermolecular interaction between LLZTO NPs and the SN phases within the CPEs (Figure 2B). The L0 sample showed a peak at 2262 cm^{-1} , corresponding to the nitrile $(C \equiv N)$ groups of the SN phase. Notably, the C = N peak was shifted by 0.9 cm^{-1} for L10 and 1.6 cm⁻¹ for L20, indicating La-Nitrile interactions between the La³⁺ and the C \equiv N groups within the CPE matrix.⁶⁹ These results

FIGURE 2 Raman shift of the (A) carbonyl (C=O) groups in poly(BA) phase and (B) nitrile (C≡N) groups in SN phase within CPEs. (C) σ value of CPEs determined by electrochemical impedance spectroscopy at 25°C. (D) Stress-strain curves of CPEs at an extension rate of 100 mm min $^{-1}$.



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confirmed that the inorganic LLZTO fillers in CPEs could interact favorably with both the poly(BA) and SN phases.

The Li⁺ transport properties in CPEs were assessed through ionic conductivity measurements using electrochemical impedance spectroscopy (EIS) (Figure 2C). L0 displayed a superior σ value of 1.14 mS cm⁻¹ at 25°C, presumably due to the efficient Li⁺ transport through the SN-based conducting network within the CPEs. For L10, the well-dispersed LLZTO NPs within the CPE matrix resulted in a comparably high σ value of 1.02 mS cm⁻¹. In contrast, the σ value of L20 significantly decreased to 0.76 mS cm^{-1} due to the LLZTO aggregation, which may interrupt the Li⁺ conduction channel of the SN phases within CPEs. This decrease was also partly due to the reduction in Li⁺ concentration within the ion-conducting SN phase, as shown in Figure S5C.

The mechanical adaptability of CPEs is crucial for accommodating the significant volume changes of Li metal during cycling. To assess the impact of LLZTO content on the mechanical properties of CPEs, we evaluated the mechanical elasticity using a universal testing machine (UTM) (Figure 2D). Notably, L10 exhibited remarkably improved elasticity ($\varepsilon_{\rm b} \approx 1250\%$) compared to L0 ($\varepsilon_{\rm b} \approx 400\%$). We attribute the higher mechanical properties of L10 to the uniformly dispersed LLZTO NPs, which bridge the soft polymeric segments via chemical coordination bonding with the C=O groups of poly(BA) This strong coordination matrix (Figure 2A).⁶⁸

interaction between the poly(BA) phase and LLZTO NPs in the CPE matrix could reinforce the mechanical properties including elasticity. Moreover, LLZTO NPs induced the migration of a fraction of Li⁺ from the SN phase to the elastomeric poly(BA) phase (Figure S5B), greatly improving the mechanical elasticity of CPEs. This is due to the formation of a coordinated network between Li⁺ and C=O groups in poly(BA) chains.⁷⁰ Therefore, the excellent elasticity of L10 could accommodate Li volume changes and maintain a conformal contact at the Li/CPE interface during repeated charge/discharge, improving the cycling stability of LMB operation.⁶⁶ In comparison, L20, with aggregated LLZTO fillers, showed reduced elasticity ($\varepsilon_{\rm b} \approx 900\%$), likely due to the nonuniform mechanical properties throughout the CPE.

The electrochemical performances of the CPEs were evaluated in full cells using NCM811 cathodes. As described in the coin-cell assembly process (Figure S1), the CPEs were in-situ photo-polymerized on both the anode and cathode and then sandwiched to fabricate the LMB full cells. This assembly process produced a CPE/CPE interface (Figure S7) that significantly affects the interfacial stability of the assembled cells. To assess the interfacial properties at the sandwiched CPEs with varying LLZTO contents, we measured the adhesion forces using a UTM (Figure S8). For L0, the low G_c of 3.1 Jm^{-2} indicated a relatively weak CPE/CPE interface, which could result in contact loss at the CPE interface

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due to significant dimensional volume change of the CPE during cycling. The instability in physical and electrochemical contact between CPEs could cause a notable increase in cell impedance and disrupt the disconnected Li^+ conduction pathway. In contrast, LLZTO-containing L10 exhibited a significantly improved G_c of 10.1 J m⁻², possibly due to enhanced LLZTO-poly(BA) and LLZTO-SN intermolecular interactions within the CPEs. Therefore, the strong coordination between the C=O group of the polymer phase and LLZTO NPs could promote better physical and electrochemical integration at the CPE interface. In contrast, L20 showed a reduced G_c of 6.6 J m⁻² compared to L10, due to aggregated LLZTO NPs creating nonuniform and rough surfaces at the CPE/CPE interface.

2.3 | Electrochemical performance of in-situ photo-polymerized CPEs

The electrochemical performances of L0, L10, and L20 CPEs were evaluated through cycling tests using 400 μ m-Li metal/CPEs with a polypropylene (PP) separator/NCM811 full cells at 0.5C. As described in the previous

section related to Figure S1, coin cells were constructed by assembling the in-situ polymerized CPEs on both sides of the separator/anode and cathode after casting identical precursor solutions on each side. A detailed full cell fabrication process is provided in Section 3.1. As shown in Figure 3A, the full cell of L0 exhibited a low capacity of 74.0 mAh g^{-1} (50% capacity retention) with an average Coulombic efficiency (CE) of 99.4% after 200 cycles at 0.5C. In contrast, L10, with well-dispersed LLZTO NPs, displayed the highest capacity of 166.7 mAh g^{-1} (95% capacity retention) with an average CE of 99.7% after 200 cycles at 0.5C, demonstrating superior cycling stability for CPE-based LMBs. However, L20, with an excessive amount of LLZTO, showed less stable cycling with a decreased discharge capacity of 104.8 mAh g^{-1} (77% capacity retention) with an average CE of 99.5% after 200 cycles (Figure 3B and Figure S9).

EIS analysis was employed to gain deeper insights into the electrochemical performances of full cells with varying LLZTO contents. Specifically, we monitored changes in impedance at the CPE/CPE interface, which can be closely related to Li⁺ transport through the electrolytes. The Nyquist plot of pristine full cells before cycling (Figure 3C) shows that the semicircle corresponds



FIGURE 3 (A) Cycling performance of 400 μ m-Li/NCM811 (2.5 mg cm⁻²) full cells at 0.5C after three formation cycles at 0.2C in the voltage range of 3.0–4.3 V. (B) Corresponding discharge profiles of composite polymer electrolyte at 200th cycle. (C, D) Nyquist plot of the full cells; (C) Pristine and (D) 200th cycle. (E) Rate capability test of the full cells at different C-rates.

to the combined charge transfer resistance (R_{ct}) from the electrode/CPE and CPE/CPE interfaces (Figure S7). The L10 full cell showed a lower R_{ct} value of 95 Ω compared to L0 (178 Ω) and L20 (122 Ω), indicating the highest interfacial stability of L10 before cycling. In the EIS measurements of the full cells after 200 cycles at 0.5C (Figure 3D), L10 maintained the lowest overall resistance (113 Ω) compared to L0 (413 Ω) and L20 (274 Ω), correlating with the superior cycling performance of the L10-based full cell. Furthermore, L10 showed a higher transference number (t_+) of 0.55, compared to L0 (0.49) and L20 (0.35), which could be due to its low interfacial resistances at CPE/CPE and Li/CPE interfaces while maintaining efficient Li⁺ transport through SN channel (Figure S10).

Moreover, the $R_{\rm ct}$ value influences the rate capability of the full cells (Figure 3E). The L10 delivered higher discharge capacities at all C-rates (i.e., 0.2, 0.5, 1, 2, and 3C) compared to L0 and L20. Notably, at a high rate of 3C, L10 maintained a capacity of 134.8 mAh g⁻¹, whereas L0 and L20 showed significantly reduced capacities of 69.1 and 30.9 mAh g⁻¹, respectively. For L0, the low adhesion energy ($G_c \approx 3.1 \text{ Jm}^{-2}$) disrupted the Li⁺ conduction pathway, resulting in a high $R_{\rm ct}$ (178 Ω) value due to an unstable CPE/CPE junction (Figure S8 and Figure 3C). This poor interfacial stability could impede the rate performance of L0, despite its superior bulk ionic conductivity. In contrast, L10 showed better rate capability than L0 due to a stable CPE/CPE interface with a higher G_c of 10.1 J m⁻² and lower R_{ct} (95 Ω) value.

We summarize the key properties of in-situ photopolymerized CPEs, which include high σ , mechanical elasticity, and interfacial adhesion, all contributing to high LMB performance (Scheme 2). Uniform coordination of LLZTO NPs with polymer and SN phases is crucial for achieving superior mechanical properties of CPEs and stable interfaces in the full cell. First, L0, with a lack of LLZTO NPs and adhesive properties at the CPE/CPE junction, showed an impeded Li⁺ transport due to a disconnected Li⁺ conduction pathway. In contrast, the superior adhesion energy of L10 ($G_{\rm c} \approx$ 10.1 J m⁻²) compared to L0 and L20 was helpful in maintaining stable contact at the CPE/CPE interface. This adhesive property of L10 could mitigate the interfacial resistance at the CPE/CPE junction. These results were attributed to the strong coordination of well-dispersed LLZTO NPs with the poly(BA) and SN phases throughout the CPE. Furthermore, the remarkably enhanced elasticity of L10 ($\varepsilon_{\rm b} \approx 1250\%$) compared to L0 and L20 was beneficial for achieving low impedance at



SCHEME 2 Schematic illustration of LLZTO NPs distribution and coordination interactions in each CPE with different NP ratios. The L10 with uniformly dispersed NPs exhibits strong coordination in CPE matrix, forming stable interfaces by its high σ , enhanced G_c , and ε_b .

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the Li/CPE interface. The high mechanical elasticity of L10 could accommodate the large volume change of the Li metal upon charging and restore its dimension upon discharging.^{59,71} Additionally, the high σ (>1.0 mS cm⁻¹) of L10 also contributed to rapid Li⁺ transport at the CPE/CPE and Li/CPE interfaces. However, with the further increase of LLZTO content, L20 showed the agglomeration of inorganic fillers, resulting in nonuniform Li⁺ flux at the CPE/CPE and Li/CPE interfaces. This aggregation behavior of NPs also led to an increased R_{ct} due to the lower G_c (6.6 J m⁻²) at CPE/CPE interface than that of L10. Thus, L10 shows superior full cell cycling performance by successfully leveraging the advantages of LLZTO and elastomeric electrolytes. These beneficial features are primarily attributed to the well-dispersed LLZTO NPs within the CPE, achievable through in-situ photo-polymerization, which requires only a few minutes for the construction of the CPEs.

2.4 | Characterization of the cycled-Li metal anodes of in-situ photopolymerized CPEs

To further understand the difference in the cycling performance of the full cells in Figure 3A, we investigated the chemical composition of the SEI layer at the Li/CPE

interface. We characterized the cycled-Li metal anodes of the L0, L10, and L20 full cells after 200 cycles at 0.5C using X-ray photoelectron spectroscopy (XPS). In general, inorganic SEI layer species exhibited significantly high shear modulus values, such as LiF (>50 GPa) and Li₂O (>40 GPa), compared with organic SEI compounds (<10 GPa). This high shear modulus is crucial for preventing dendrite growth by forming a robust Li/CPE interface.^{72,73} It is known that Li dendrite growth could be effectively suppressed if the shear modulus of the SEI component is 2-fold greater than that of Li (4.8 GPa).^{74,75} We estimated the integrated peak area ratio of inorganic (Li₂O, LiF) to organic (RCOOLi) compounds. The L10 showed a higher inorganic to organic ratio (10.1) compared to those of L0 (6.4) and L20 (2.5), effectively suppressing dendritic Li metal formation (Figure 4A-C).⁷⁶ The O 1s and F 1s spectra further supported that the inorganic-rich SEI layers of L10 contained a greater amount of inorganic compounds (Li2O, LiF) compared to L0 and L20 (Figure 4D-F and Figure S11). For L10 with well-dispersed LLZTO NPs, the coordination interactions between the polymer matrix and LLZTO contribute to the preferential formation of inorganic-based SEI with the decomposition of Li salts.⁶⁸ Consequently, the inorganic-based SEI layer of the L10 system effectively suppresses Li dendrite growth, resulting in a highly stable full cell cycling performance.



FIGURE 4 (A-C) Li 1s and (D-F) O 1s XPS spectra of cycled-Li metal anodes of full cells with different CPEs after 200 cycles at 0.5C.

2.5 Comparison of in-situ thermal polymerized and photo-polymerized CPEs

The rapid photo-polymerization successfully dispersed 10 wt% LLZTO NPs within the CPE for high-performing LMBs. To highlight the importance of this fast in-situ polymerization kinetics on the NP dispersion in CPE and electrochemical performance, the precursor solution of the CPE containing 10 wt% of LLZTO was subjected to in-situ thermal polymerization, denoted as CPE-heat. For CPE-heat, the composite precursor solutions were made with the same components as the L10, except that azobisisobutyronitrile (AIBN) thermal initiator was used instead of the HCPK initiator. In Figure 5A, in-situ thermal polymerization exhibited significantly slower kinetics (~ 2 h) compared to photo-polymerization (~ 5 min), resulting in the agglomeration of NPs during the formation of the crosslinked poly(BA) network. The CPE-heat exhibited macroscale phase distinction upon thermal processing, due to the slow polymerization kinetics and precipitation of LLZTO NPs (Figure 5B,C). It is noted that to better visualize the vertical distribution of LLZTOs in the sample, we used much thicker CPE-heat and CPE-photo samples compared to the films used in the full cell cycling test. SEM images revealed no NPs on the upper layer, while the bottom layer showed significantly aggregated LLZTO NPs within the polymer matrix (Figure 5D,E). The uneven distribution of NPs could negatively affect the physical and electrochemical properties of CPEs due to nonuniform Li⁺ flux. The macroscopically phase-separated and agglomerated LLZTO NPs in CPE-heat were further evidenced by EDS mapping images in Figure S12. In contrast, there was no significant vertical segregation of LLZTO NPs in CPE-photo samples (Figure S13). Thus, the rapid kinetics of photopolymerization proved to be an effective process for fabricating homogeneous CPEs with uniformly dispersed LLZTO NPs.

To further evaluate the electrochemical performance according to the different polymerization processes, full cell cycling tests of CPE-heat and CPE-photo were conducted using a 40-µm Li foil, a higher loading NCM811 $(\sim 10 \text{ mg cm}^{-2})$ (Figure 5F–H). After 80 cycles at a high current density of 1.0 mA cm⁻² (~0.5C), the CPE-heat revealed a discharge capacity of 50.0 mAh g^{-1} (34%) capacity retention) with an average CE of 98.7%. These results can be attributed to the nonuniform CPE formation caused by the sedimentation of LLZTO NPs, leading to uneven Li⁺ transport. In contrast, CPE-photo maintained a capacity of 136.6 mAh g^{-1} (82% capacity retention) with an average CE of 99.5%. The cycling performance of full cells with CPE-photo was further demonstrated through replicated cells (Figure S14).

3 CONCLUSION

We have developed the CPEs via an in-situ photo-polymerization method, introducing LLZTO inorganic fillers within polymer electrolytes composed of elastomer and plastic crystal phases. The rapid polymerization time $(\sim 5 \text{ min})$ enabled uniform dispersion of LLZTO NPs within the polymer matrix, achieving stable operation of LMBs. By adjusting the weight ratio of LLZTO, the CPE containing 10 wt% LLZTO (L10) exhibited a high σ value, excellent elasticity and adhesion properties with well-distributed LLZTO NPs. Furthermore, L10 demonstrated superior performance in Li/NCM811 full cells, maintaining a capacity retention of 95% after 200 cycles with a specific capacity of 166.7 mAh g^{-1} with an average CE of 99.7% at a 0.5C. These results were attributed to the mechanical enhancement of CPEs by strong coordination between LLZTO and crosslinked polymer matrix, and significantly reduced interfacial resistances at the CPE/CPE and Li/CPE interfaces. We further demonstrated that the prolonged processing time with the in-situ thermal polymerization method results in the sedimentation of LLZTO NPs and non-uniform CPEs, compared to the uniform and high-performing CPEs fabricated by the fast photo-polymerization method. Thus, this work provides a facile design strategy for CPEs using in-situ photo-polymerization to develop highly stable LMBs.

3.1 **Experimental section**

Preparation of electrolytes 3.1.1

The CPEs (i.e., L0, L10, and L20) were fabricated in an argon (Ar)-filled glove box (<0.1 ppm of O₂ and H₂O concentration). BA (≥99%; Sigma Aldrich) was degassed by Ar bubbling for 30 min before use. The BA-based solution was prepared by mixing 1 mol% of PEGDA (average $M_{\rm n}$: 575 g mol⁻¹; Sigma Aldrich), 0.5 mol% of HCPK (Sigma Aldrich) or AIBN (Sigma Aldrich) for initiator in BA liquid. Unlike BA monomer, SN (≥99%; TCI) was utilized after a repeated freeze-pump-thaw procedure for three times. The SN-Li salts solution was prepared by mixing SN with LiTFSI (≥99%; Sigma Aldrich), and LiD-FOB (\geq 99%; Sigma Aldrich) at 60°C. A 5 vol% of fluoroethylene carbonate (FEC) (\geq 98.0%; TCI) additive was added into the SN-based solution to prevent undesired reactions between SN and Li metal anode.^{60,63} The Li salt concentration within the CPE precursor solution was fixed to 0.8 M LiTFSI and 0.2 M LiDFOB. Each BA-based solution and SN-Li salt solution was mixed homogeneously in a 1:1 volume ratio at 40°C to generate the CPE precursor solutions. Then, a desired weight ratio of



FIGURE 5 (A) FTIR spectra of crosslinked poly(BA) by thermal polymerization according to different processing times. (B) Bulk photograph and (C) cross-sectioned SEM images at low magnification of CPE-heat. Cross-sectional SEM images of (D) top and (E) bottom layer of CPE-heat. (F) Cycling performance of 40 μ m-Li/high-loading NCM811 (~10.0 mg cm⁻²) full cells using CPE-heat and CPE-photo in the voltage range of 3.0–4.3 V. The cell was cycled at 1.0 mA cm⁻² after three formation cycles at 0.2 mA cm⁻². Corresponding Galvanostatic charge–discharge (GCD) profiles of (G) CPE-heat and (H) CPE-photo.

LLZTO NPs (D50: \sim 500 nm, MTI Korea) was dispersed in the precursor solutions by magnetic stirring, which were subsequently in-situ photo-polymerized for 5 min to form the CPEs using a UV lamp with a wavelength of 365 nm and a power of 10 W. The vertical distance between the UV lamp and the CPE samples was 15 cm. In the case of in-situ thermal polymerization, CPE precursor solutions were heated in the 70°C oven for 2 h.

3.1.2 | Material characterization

The bulk morphologies of CPEs were observed by fieldemission SEM (Hitachi SU-8320), equipped with an EDS. FTIR spectra were obtained using a Bruker ALPHA-P spectrometer. To investigate the intrinsic polymerization kinetics of thermal and photo-polymerization, FTIR was conducted on the crosslinked poly(BA) matrix. The distribution of LLZTO NPs in CPEs was observed using an optical microscope in the reflection mode (Eclipse L150, Nikon). Raman measurements were taken using a Raman spectrometer (ARAMIS, Horiba Jobin Yvon) at an excitation wavelength of 514 nm. The ⁷Li NMR spectra were obtained using a Bruker Avance III HD 500-MHz solid-state NMR spectrometer at ambient temperature. To address the moisture sensitivity, samples were prepared within an inert glove box and sealed in poly (chlorotrifluoroethylene) rotors. The NMR results were referenced to a 1 M LiCl aqueous solution set at 0 ppm. To investigate the internal morphology of CPEs, a cryo-TEM experiment was performed. The CPEs were cryogenically vitrified in a liquid nitrogen (N₂) chamber for 10 s. A Leica EM FC7 ultramicrotome containing a cryo chamber equipped with a glass knife was utilized to section the vitrified CPEs. The block face for the sample preparation was approximately $200 \times 200 \ \mu$ m. The ultrathin (\sim 50 nm thick) sections were transferred to a 200 mesh carbon-coated copper grid while maintaining temperatures between -90 and -80°C. Cross-sectional images of CPEs were acquired using a JEOL JEM-1400 (JEOL Ltd.) operating at 120 kV equipped with a Gatan 914 cryo-holder (Gatan Inc.). TEM images were recorded by a Veleta charge-coupled device (CCD) camera (EMSIS GnbH) with a 1 s exposure time. Data were analyzed with the RADIUS imaging software. A mechanical tensile test and interfacial adhesion-strength measurements were performed utilizing UTM (Lloyd Instruments LR5K). The tensile stress (y-axis) of the CPEs was expressed as a true stress value. The bulk samples of CPEs were prepared in a dogbone-shaped mold (ASTM D412 Type C). The SEI layer compositions at Li metal interfaces were investigated using XPS (Thermo VG Scientific K-alpha), with

binding energies calibrated with the C 1s peak at 284.8 eV (C—C component).

3.1.3 | Electrode preparation

NCM811 cathode was prepared by a slurry coating process. NCM811 active material, Super P conductive carbon, and polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone for 24 h with a weight ratio of 8:1:1 to fabricate a slurry. The slurry was coated onto a current collector of aluminum foil. The fabricated cathodes were dried at 90°C for 1 h, followed by vacuum drying at 60°C for 24 h. The loading densities of the active material were ~2.5 and ~10 mg cm⁻², respectively.

3.1.4 | Electrochemical measurements

The electrochemical performance tests were evaluated using 2032-type coin cells in a glove box filled with Ar gas (<0.1 ppm of O_2 and H_2O concentration). The CPE precursor solutions were mixed homogeneously and injected onto Li metal with a separator (i.e., Celgard 2500 for Li/ NCM811 full cells and Li symmetric cells, glass fiber (GF/ A) for ionic conductivity analysis). For the full cell fabrication of the in-situ photo-polymerization process (Figure S1), the precursor solutions were cast onto both anode and cathode. For the preparation of CPE on the Li metal anode, we employed a PP separator to increase the wettability of the precursor solution to the Li metal surface. Before coin cell assembly, the UV light was irradiated both the Li anode and NCM811 cathode for 5 min. In the case of in-situ thermal polymerization, the coin cell was assembled before the thermal polymerization at 70°C for 2 h. EIS measurements (BioLogic SP-200) were recorded from 5 MHz to 2 mHz for full cells. The Li⁺ transference number (t_{+}) was measured using Li symmetric cells via the Bruce-Vincent method. The ionic conductivity of CPEs was measured by EIS with stainless steel (SS)/CPE/SS symmetric cells at 25°C within an envichamber. The ronmental 400 µm-Li/CPE/NCM811 $(\sim 2.5 \text{ mg cm}^{-2})$ full cells were conducted by galvanostatic charge/discharge tests in the voltage range of 3.0-4.3 V (Neware battery tester) for 200 cycles at 25°C. The full cell cycling tests were performed at 0.5C after three formation cycles at 0.2C. The rate capability tests were conducted in the same voltage range, with C-rates varying from 0.2 to 3C. The high-loading full cells composed of 40 µm-Li/ CPE/NCM811 (\sim 10.0 mg cm⁻²) were evaluated by galvanostatic charge/discharge tests at current densities of 1.0 mA cm^{-2} after three formation cycles at 0.2 mA cm $^{-2}$.

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AUTHOR CONTRIBUTIONS

Seung Ho Kwon: Conceptualization, experimentation, investigation, formal analysis, writing - original draft. Seongmin Kim: Conceptualization, experimentation, investigation, formal analysis, writing - original draft. Jinseok Park: Methodology, validation, formal analysis, writing - original draft. Michael J. Lee: Methodology, validation, formal analysis, data visualization. Youyoung Byun: Formal analysis, data Visualization. Hyun Jung Kim: Experimentation, data Visualization. Young Min Baek: Validation, data Visualization. Jaegyeom Kim: Validation, data Visualization. Eunji Lee: Methodology, validation, data visualization. Seung Woo Lee: Methodology, validation, supervision, writing - review & editing. Bumjoon J. Kim: Conceptualization, methodology, validation, project administration, supervision, writing review & editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

ORCID

Seung Ho Kwon [©] https://orcid.org/0000-0001-6991-6381 Seongmin Kim [®] https://orcid.org/0009-0006-4604-7746 Jinseok Park [®] https://orcid.org/0000-0002-0389-9707 Michael J. Lee [®] https://orcid.org/0000-0001-5087-3991 Young Min Baek [®] https://orcid.org/0009-0004-9140-5261 Eunji Lee [®] https://orcid.org/0000-0001-7494-1776 Seung Woo Lee [®] https://orcid.org/0000-0002-2695-7105 Bumjoon J. Kim [®] https://orcid.org/0000-0001-7783-9689

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SUPPORTING INFORMATION

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