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Composite Electrode-Hybrid Electrolyte Integration Strategy for Enhanced Ion Transport and Scalable All-Solid-State Lithium Batteries

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ABSTRACT

Achieving both high energy density and long-term cyclability in all-solid-state lithium batteries (ASSBs) remains a formidable challenge, particularly under high-cathode-loading conditions, where interfacial instability and through-plane Li^+ transport limitations compromise performance. This study reports a synergistic design that combines a hybrid solid electrolyte (HSE) and a composite electrode (CE) incorporating ball-milled Al-doped $\text{Li}_{6.28}\text{Al}_{0.24}\text{La}_3\text{Zr}_2\text{O}_{11.98}$ (BM Al-LLZO) to address these bottlenecks. The HSE, containing 3 wt% BM Al-LLZO dispersed in a poly (ethylene oxide)-based, in situ polymerized matrix, exhibits enhanced ionic conductivity ($1.04 \times 10^{-3} \text{ S cm}^{-1}$) and a high Li-ion transference number ($t_+ = 0.661$) owing to uniform filler dispersion and strong polymer–ceramic interfacial synergy. However, particle confinement at the electrode surface limits bulk ion percolation. To overcome this issue, a CE architecture with BM Al-LLZO homogeneously embedded throughout the cathode matrix is proposed. This design significantly reduces ionic resistance and enables continuous transport pathways. Consequently, the CE||SPE||Li cell delivers excellent performance, retaining 71.55 % of its initial capacity after 200 cycles at 0.5C, while a high-loading pouch cell demonstrates scalable applicability with over 90 % coulombic efficiency. These findings underscore the critical role of interfacial engineering in ASSBs and provide a practical route toward high-performance, scalable solid-state battery systems.

1 | Introduction

The rapid electrification of transportation and grid-scale energy storage systems has intensified the demand for next-generation batteries that provide both high energy density and intrinsic safety. Li-ion batteries (LIBs) currently dominate these markets owing to their high ionic conductivity (10^{-2} to $10^{-3} \text{ S cm}^{-1}$) and well-established manufacturing infrastructure [1, 2]. However, the use of flammable liquid electrolytes poses significant safety concerns, including thermal runaway and fire hazards. Moreover, LIBs are approaching their theoretical energy density limits, restricting

their ability to meet the growing performance demands of electric vehicles (EVs) and stationary energy storage systems (ESSs). All-solid-state batteries (ASSBs) have emerged as promising alternatives, replacing liquid electrolytes with solid-state electrolytes, offering superior thermal stability, and enabling the use of Li metal anodes for enhanced energy density [3, 4]. Despite these advantages, the practical implementation of high-energy ASSBs remains limited by sluggish interfacial ion transport and high resistance at the electrode–electrolyte interface, which become more severe as cathode areal loading and thickness increase [5, 6]. Insufficient through-plane Li^+ transport within thick

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cathodes concentrates reaction near the external interface, causing pronounced polarization and underutilization of active material in the electrode interior. Interfacial limitations arising from insufficient contact, void formation, and mechanical mismatches degrade ionic pathways and long-term cycling performance.

To mitigate these challenges, solid polymer electrolytes (SPEs), such as polyethylene oxide (PEO), have been widely studied for their high deformability and their ability to conform to irregular electrode surfaces, thereby reducing interfacial gaps and contact resistance [7–9]. However, their intrinsic ionic conductivity at room temperature remains relatively low, typically approximately 10^{-5} to 10^{-6} S cm $^{-1}$, due to limited segmental motion of polymer chains and strong ion–polymer coordination. Additionally, during long-term cycling, SPEs are prone to Li dendrite penetration, particularly at elevated current densities, thereby compromising both their safety and lifespan [10]. Conversely, inorganic solid electrolytes (ISEs), such as Li $_7$ La $_5$ Zr $_2$ O $_{12}$ (LLZO) and Li $_{1.3}$ Al $_{0.3}$ Ti $_{1.7}$ (PO $_4$) $_3$ (LATP), have attracted attention for their high room-temperature ionic conductivity (10^{-3} to 10^{-4} S cm $^{-1}$) [10, 11], wide electrochemical stability window, and excellent compatibility with Li metal. LLZO is particularly effective due to its high ionic conductivity, chemical stability, and ability to directly interface with Li metal without degradation, unlike other solid electrolytes such as LATP, which can chemically degrade upon contact with Li [12–16]. However, despite their high ionic conductivity, ISEs are often brittle, resulting in poor mechanical flexibility and limited interfacial contact, and they are difficult to process into conformal, defect-tolerant layers over large areas—constraints that become critical in high-loading cathodes where uniform electrolyte access throughout the electrode thickness is required [17, 18].

To exploit the advantages of both materials, hybrid solid electrolytes (HSEs) incorporating inorganic ceramic fillers into polymer matrices have been developed to combine the mechanical flexibility and processability of polymers with high ionic conductivities and electrochemical stabilities of ceramics [19–22]. In such systems, the polymer provides a continuous, flexible framework that facilitates electrode–electrolyte contact, whereas the dispersed ceramic phase contributes fast Li-ion transport pathways and suppresses dendrite propagation [23]. Commonly adopted processing techniques include solution casting, slurry coating, and in situ polymerization through direct injection of the precursor solution into pre-assembled cells, followed by thermal curing [24–26]. While these approaches are advantageous for achieving conformal contact and enabling scalable fabrication, they can unintentionally induce ceramic-filler migration and spatial inhomogeneity during solvent removal and/or curing. Maintaining a uniform nanoscale dispersion of ceramic fillers within a polymer matrix remains a significant challenge across various fabrication methods [27]. Such filler redistribution (e.g., surface enrichment, sedimentation, or aggregation) disrupts the continuity of Li $^+$ -conducting pathways across the membrane thickness and at the cathode interior, producing locally deficient conduction zones, increased tortuosity, and elevated interfacial resistance-effects that are amplified in thick, high-loading electrodes [23, 28]. Additionally, the thermal curing process can induce internal stresses owing to non-uniform shrinkage or gradients in crosslinking density, potentially causing cracking, delamination, or mechanical failure of the membrane. These issues are

further exacerbated in high-loading cathode configurations where ensuring conformal contact and structural compliance is particularly critical. Thus, precise control over dispersion quality, formulation chemistry, and processing kinetics is essential for achieving homogeneous ceramic distribution and stable electrochemical performance in practical ASSB applications.

Composite electrodes (CEs) have emerged as strategically important design elements for advanced ASSB, particularly in systems with high area loading, where interface-confined ion transport is intrinsically insufficient to sustain uniform delithiation through the electrode depth. In conventional electrode architectures, Li-ion flux is largely confined to the vicinity of the electrode–electrolyte interface, resulting in sluggish kinetics, pronounced polarization, and underutilization of active materials deeper within the electrode bulk [29, 30]. These limitations are highly pronounced in thick electrode structures, where tortuosity and low ionic conductivity hinder effective lithiation and delithiation throughout the full volume of the cathode. CEs address these constraints by embedding ion-conductive solid electrolyte particles directly into percolation networks that span the entire electrode thickness. This internalized ion transport network facilitates homogeneous electrochemical activity, minimizes ionic transport bottlenecks, and reduces local overpotentials. Recent investigations have validated the CE approach using various inorganic fillers, such as sulfide-type electrolytes and NASICON-type conductors (such as LATP), demonstrating improvements in reaction uniformity and reductions in interfacial resistance [31, 32]. However, these materials often suffer from limited electrochemical stability, chemical reactivity with Li metal, and compatibility issues with layered oxide cathodes, which can offset the benefits of improved bulk transport.

To further advance the functionality of CEs, the strategic incorporation of garnet-type inorganic solid electrolytes, particularly Al-doped LLZO (Al-LLZO), presents a compelling pathway grounded in electrochemistry and materials science. Among inorganic solid electrolytes, Al-LLZO is unique owing to its high room-temperature ionic conductivity ($\sim 10^{-3}$ S cm $^{-1}$), broad electrochemical stability window (> 6 V), and chemical inertness with both Li metal and Ni-rich cathodes. The aliovalent substitution of Li $^+$ by Al $^{3+}$ in the garnet lattice stabilizes the highly conductive cubic phase and promotes the formation of Li vacancies, thereby facilitating vacancy-mediated Li-ion transport [33–36]. When uniformly integrated into CE structures, Al-LLZO particles can establish continuous ionic pathways within the electrode matrix, reduce tortuosity, and enable uniform charge distribution across thick cathode layers. Unlike sulfide or NASICON-type alternatives, which often suffer from moisture sensitivity, interfacial degradation, or redox instability, Al-LLZO maintains interfacial compatibility and mechanical integrity under demanding cycling conditions [37, 38]. Furthermore, a high shear modulus (> 60 GPa) suppresses the formation of Li dendrite when paired with Li metal anodes, thereby enhancing overall system safety [39, 40]. Nevertheless, realizing these advantages in practical electrodes requires not only selecting a stable ceramic conductor but also ensuring its homogeneous dispersion and functional continuity across the electrolyte–electrode domains.

Owing to its established advantages, Al-LLZO functions not only as a bulk ionic conductor but also as a structural stabilizer within

the CE matrix. The inclusion of Al-LLZO improves percolation pathways across the entire electrode volume while maintaining mechanical compliance under cycling-induced stress. This dual role is particularly valuable for ASSB architectures that require thick, high-capacity electrodes with sustained cycling stability and manufacturability. However, many prior studies have optimized HSEs and composite cathodes in isolation; as a result, the Li^+ -conducting phase is not continuous from the bulk electrolyte into the cathode thickness, creating a through-plane ionic-transport bottleneck that becomes increasingly detrimental at high areal loadings [41, 42]. Although Al-LLZO has been independently employed in HSEs and CEs, its concurrent integration into both components has rarely been realized in a unified manner [43–46]. This disjointed approach often leads to ionic discontinuities at the interface, particularly in thick, high-loading electrodes where continuous through-plane conduction is essential for uniform lithiation.

Herein, we propose a dual-domain (electrolyte and electrode) co-design framework that uses ball-milled Al-doped LLZO (BM Al-LLZO) as a shared ion-conductive phase to establish materials continuity and uninterrupted Li^+ transport pathways across the cell. Specifically, BM Al-LLZO is incorporated into both (i) a hybrid solid electrolyte, where optimized dispersion enhances ionic conductivity and increases the Li^+ transference number, and (ii) a composite cathode, where homogeneous ceramic embedding forms a through-thickness percolation network that reduces ionic resistance and polarization in high-loading electrodes. By aligning the ion-conductive phase in both domains, this strategy directly targets two coupled bottlenecks-

interfacial instability and through-plane transport limitation-using a single, chemically stable garnet conductor. The optimized HSE containing 3 wt% BM Al-LLZO exhibits an ionic conductivity of $1.04 \times 10^{-3} \text{ S cm}^{-1}$ and a Li -ion transference number of 0.661 at 45 °C. Meanwhile, the CE fabricated with the same BM Al-LLZO loading achieves homogeneous filler distribution throughout the electrode thickness, contributing to reduced interfacial resistance (4.26Ω), and improves cycling performance (71.55 % capacity retention after 200 cycles at 0.5C in half-cell configurations). Finally, as a proof-of-concept scale demonstration, the CE concept is evaluated in a high-loading pouch-type cell, highlighting the scalability potential of the proposed co-design strategy for practical energy-storage platforms. These results underscore the importance of unifying material functionality and structural coherence in developing next-generation ASSBs with both high energy density and long-term reliability.

2 | Results and Discussion

2.1 | Synthesis and Structural Characterization of Al-Doped LLZO

To synthesize phase-pure nanosized Al-LLZO solid electrolyte, a nitrate-assisted solid-state reaction method was adopted. This approach was selected to suppress carbonate impurities, improve crystallinity, and optimize ionic conductivity by controlling grain boundary morphology and particle dispersion. X-ray diffraction (XRD) analysis of samples calcinated at 800–1200 °C revealed the phase evolution of Al-LLZO (Figure 1a). At 800 °C and 900 °C,

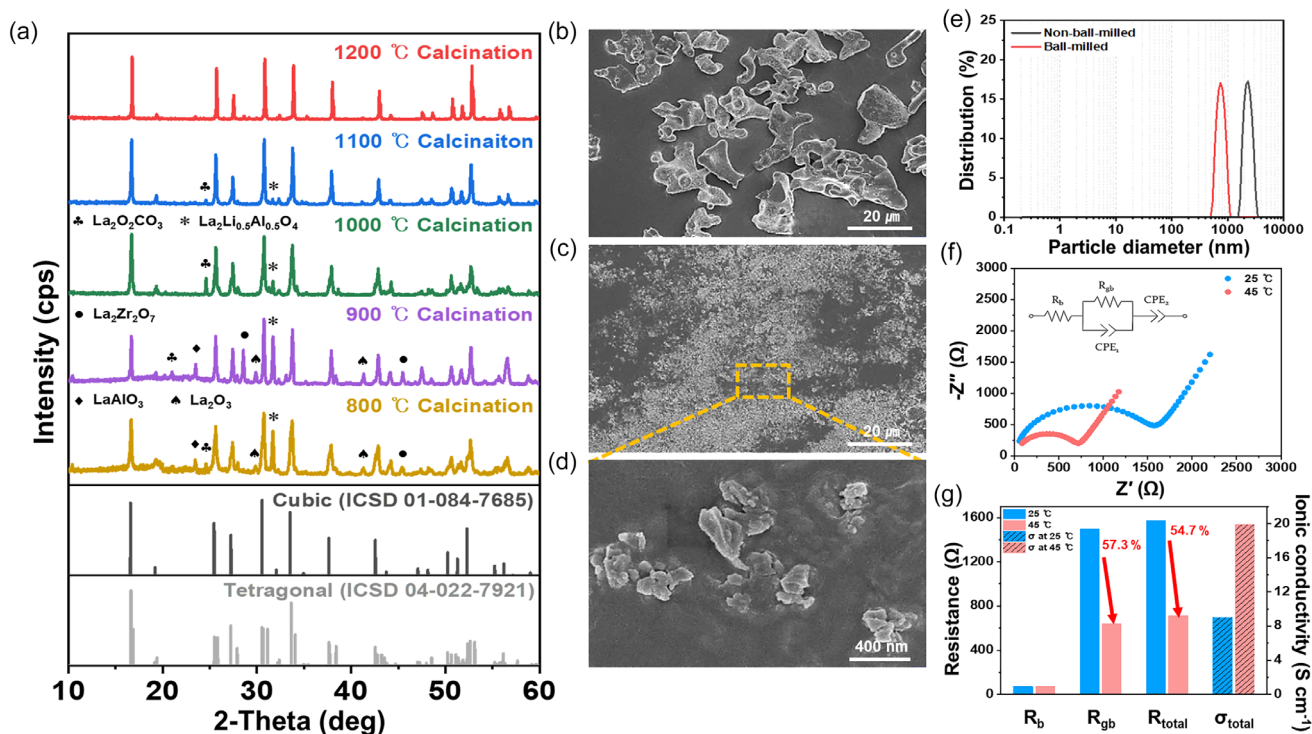


FIGURE 1 | (a) X-ray diffraction (XRD) patterns of calcined Al-doped LLZO powder as a function of calcination temperature (800–1200 °C). SEM images of calcined Al-doped LLZO powder (b) before ball milling and (c,d) after ball milling. (e) Particle size distribution of the as-prepared and ball-milled Al-doped LLZO powder. (f) Nyquist plots of Ag||Al-doped LLZO pellet||Ag symmetric cell type at 25 °C and 45 °C. (g) Extracted bulk resistance (R_b), grain boundary resistance (R_{gb}), total resistance (R_{total}), and total ionic conductivity (σ_{total}) of the Al-doped LLZO pellet at 25 °C and 45 °C.

diffraction patterns were dominated by tetragonal LLZO (t-LLZO, ICSD 04-022-7921) [47–51], accompanied by intermediate phases such as La_2O_3 , $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$, and LaAlO_3 . These intermediate phases were commonly observed during LLZO formation and serves as precursors to cubic LLZO (c-LLZO, ICSD 01-084-7685) at higher temperatures [52, 53]. Specifically, La_2O_3 is typically generated via dehydration of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ below 600 °C, $\text{La}_2\text{Zr}_2\text{O}_7$ formed through La-Zr interactions near 650 °C, and LaAlO_3 reacted with excess Li to yield $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ at approximately 800 °C. $\text{La}_2\text{O}_2\text{CO}_3$, an impurity phase commonly formed from adventitious carbonate incorporating during low-temperature processing, was detected but disappeared with increasing temperatures. At 1000 °C, broad diffraction peaks indicated the onset of t-LLZO to c-LLZO transformation. The peaks sharpened progressively with increasing temperature, and by 1200 °C, the XRD patterns exhibited well-defined peaks corresponding to phase-pure c-LLZO formation, free from detectable intermediate or impurities. Overall, the nitrate-assisted precursor chemistry promoted rapid garnet phase formation while minimizing persistent carbonate residues, supporting scalable Al-LLZO synthesis.

Morphological analysis using scanning electron microscopy (SEM) (Figure 1b–d) revealed that the as-synthesized Al-LLZO powders exhibited large agglomerates with ligament-like structures and a particle size of 20–40 μm (Figure 1b). After 24 h of high-energy ball milling, the particle size markedly reduced to 200–400 nm (Figure 1c,d), primarily owing to mechanical fragmentation and impact-driven pulverization, characteristic of ceramic powder processing [54, 55]. Dynamic light scattering (DLS) analysis (Figure 1e) further confirmed the improved dispersion stability of the milled powder, yielding an average hydrodynamic diameter of approximately 760 nm in ethanol. Comparatively, the non-ball-milled powders exhibited severe agglomeration with an average size of 2.3 μm , indicating that ball milling effectively disrupted particle clustering. The discrepancy between the SEM and DLS particle size measurements was attributed to electrostatic interactions and the formation of electrical double layers during dispersion in ethanol, which influenced the hydrodynamic diameter observed in DLS. The sonication experiments (Figure S1) further elucidated the observed behavior. While non-milled Al-LLZO exhibited localized fragmentation and non-uniform dispersion owing to weak interparticle binding (Figure S1a–S1c), BM Al-LLZO maintained a consistent morphology and particle distribution (Figure S1d–S1f). The results confirmed that ball milling not only reduced the particle size but also enhanced the colloidal stability and dispersion uniformity, both of which are critical for reproducible processing and performance in composite or hybrid solid electrolyte systems.

Electrochemical impedance spectroscopy (EIS) was performed to evaluate the ionic conductivity of the BM Al-LLZO pellets (Figure 1f,g). At 25 °C, the total resistance was measured to be 1570 Ω , primarily arising from grain boundary resistance ($R_{\text{gb}} = 1500 \Omega$) with a minor contribution from the bulk resistance component ($R_{\text{b}} = 70 \Omega$). Such a high grain boundary resistance is typical of polycrystalline solid electrolytes, where grain boundaries and microstructural heterogeneity impede Li^+ migration by introducing localized energy barriers. Upon increasing the temperature to 45 °C, R_{gb} significantly decreased to 640 Ω (approximately 57.3 % lower than at 25 °C), while the bulk

resistance remained constant. This thermal activation of ion transport resulted in a substantial reduction in total resistance from 1570 Ω to 710 Ω , corresponding to a 54.7 % decrease. The enhancement in conductivity from $9.02 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C to $1.99 \times 10^{-4} \text{ S cm}^{-1}$ at 45 °C emphasized the effectiveness of the synthesis process and ball milling approach. The relatively stable R_{b} indicated a well-ordered bulk crystal structure that supported efficient Li^+ conduction within the grains, whereas the temperature-sensitive grain boundary resistance underscored the role of thermal energy in overcoming interfacial barriers. Collectively, nitrate-assisted sol–gel-derived synthesis followed by high-energy ball milling produced phase-pure, nanostructured c-LLZO with suppressed carbonate impurities and improved dispersibility. These attributes are particularly beneficial for its role as a ceramic filler in both hybrid solid electrolytes and composite electrodes, where homogeneous dispersion and percolated Li^+ pathways—rather than dense-pellet transport alone—govern cell-level ionic conduction and interfacial stability.

2.2 | Hybrid Solid Electrolytes Incorporating BM Al-LLZO

Following the synthesis of phase-pure, nanostructured BM Al-LLZO, we investigated its function as a ceramic filler in HSEs. Building upon the promising ionic conductivity of BM Al-LLZO, SPE and HSE were prepared via thermal in situ polymerization, incorporating varying concentrations (1–10 wt%) of BM Al-LLZO, as shown in Figure 2a. It was confirmed that these films can have excellent mechanical strength, which is essential for the stable operation of solid-state batteries through previous studies [23, 56]. The ionic conductivity of the electrolytes was evaluated over a wide temperature range (0–100 °C, Figure S2 and Table S1), with representative values at 45 °C shown in Figure 2b. Notably, the incorporation of 3 wt% BM Al-LLZO enhanced the ionic conductivity from $8.52 \times 10^{-4} \text{ S cm}^{-1}$ (pure SPE) to $1.04 \times 10^{-3} \text{ S cm}^{-1}$. This improvement is attributable to (i) uniform dispersion of BM Al-LLZO particles within the polymer matrix and (ii) enhanced interfacial Li^+ transport at polymer-ceramic boundaries that has been widely reported for ceramic-filled polymer. Interfacial interactions between LLZO surface species and polymer segments can modulate local chain packing and promote Li-salt dissociation/transport, thereby lowering the effective barrier for Li^+ migration [3, 23, 57]. However, when the BM Al-LLZO content exceeded 3 wt%, a decline in conductivity was observed. At higher loadings, the particle–particle interfaces were highly dominant, increasing the tortuosity of the transport pathways and restricting the segmental motion of the polymer chains. This disruption of the polymer network hindered ion mobility and diminished the benefits of the ceramic inclusions. Accordingly, 3 wt% of BM Al-LLZO was identified as the optimal concentration, providing a balance between ionic conductivity enhancement and mechanical stability.

Furthermore, to comprehensively elucidate how the segmental motion of the polymer chains governs Li^+ transport and ionic conductivity, we systematically analyzed the Arrhenius plots of temperature-dependent ionic conductivity and the FT-IR spectra of the cured SPE and the HSE. Because ethylene-oxide-based polymer electrolytes can exhibit non-Arrhenius behavior associated with polymer segmental dynamics, the values obtained from

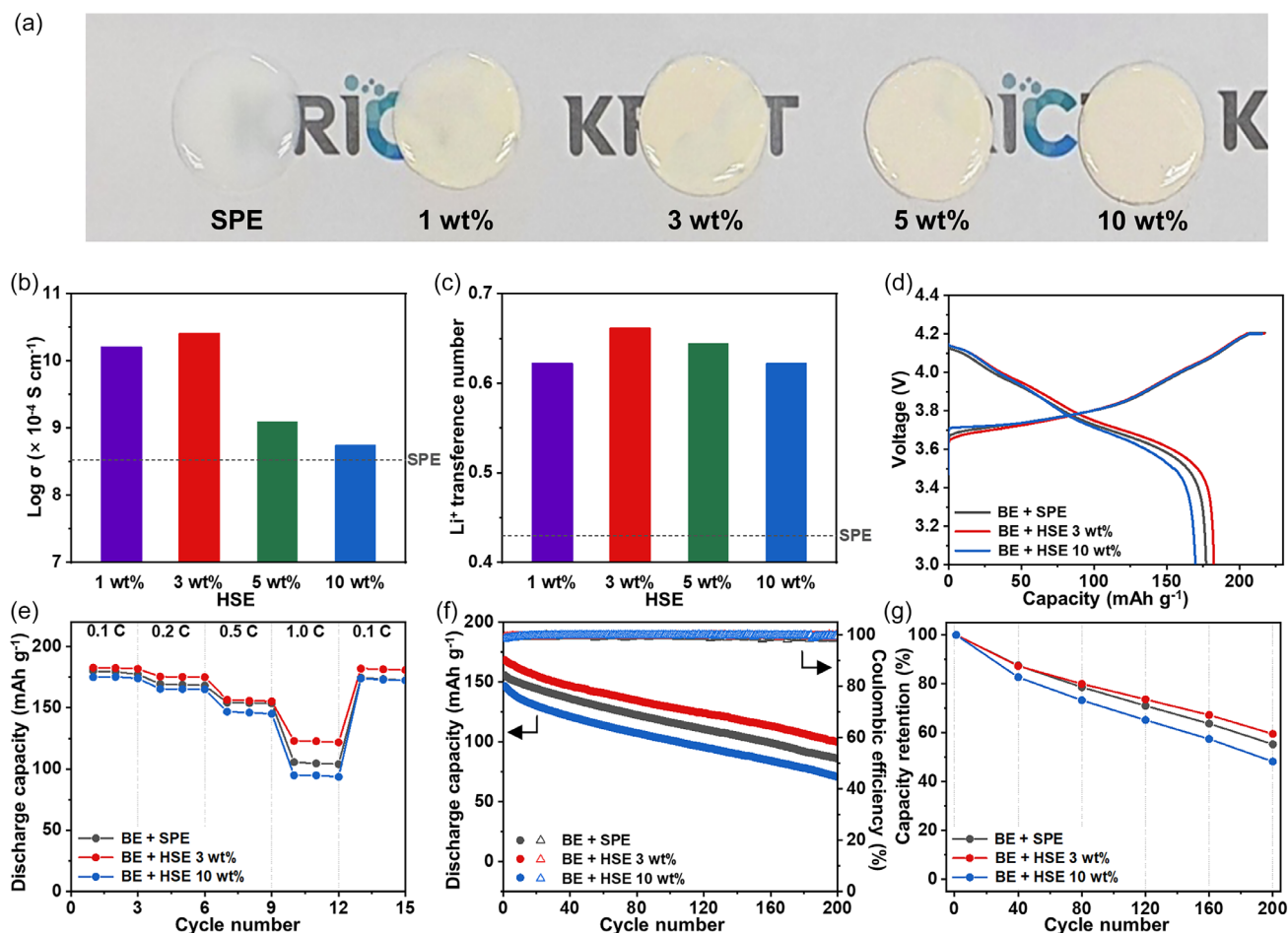


FIGURE 2 | (a) Optical images of the free-standing SPE and HSE films containing 1, 3, 5, and 10 wt% BM Al-LLZO. (b) Ionic conductivities and (c) Li^+ transference numbers as a function of BM Al-LLZO content, measured at 45 °C. Electrochemical performance of BE||SPE||Li, BE||HSE (3 wt%) || Li and BE||HSE (10 wt%) ||Li cells at 45 °C. (d) Initial voltage profiles of three different electrolytes. (e) Rate performance of three different electrolytes, (f) cycling performance and Coulombic efficiency, and (g) discharge capacity retention of the three electrolytes.

linear fitting are described here as apparent activation energies, which are used for comparative interpretation rather than as exact single-pathway migration barriers. The apparent activation energies for the SPE and HSEs containing 1, 3, 5, and 10 wt% BM Al-LLZO are 11.30, 10.15, 10.12, 11.70, and 12.90 kJ mol^{-1} , respectively (Figure S3). The 3 wt% HSE exhibited the highest ionic conductivity alongside a comparably low activation energy. This result indicates that the conductivity improvement simultaneously reflects the complex interplay of apparent activation energy, pathway connectivity, and microstructural dispersion. The enhanced performance of the 3 wt% HSE arises from an optimal balance between efficient polymer-ceramic interfacial transport and robust filler dispersion, where the appropriate BM Al-LLZO loading provides highly advantageous Li^+ transport pathways. In contrast, excessive filler loading can increase interfacial crowding and pathway tortuosity, thereby offsetting the transport benefit. Consequently, the boosted ionic conductivity is driven by a synergistic combination of ceramic bulk conduction, interfacial Li^+ migration, and the optimized microstructural state of the HSE. To further investigate the local microenvironment, FT-IR spectra of SPE and HSE 3 wt% (Figure S4) were analyzed. The C-O-C stretching bands shifted from 1100 and 1058 cm^{-1} in the SPE to 1093 and 1056 cm^{-1} in the HSE 3 wt%, reflecting modified Li^+ coordination and polymer-ceramic

interactions. Additionally, a broader CH_2 twisting region in the HSE indicates perturbed chain packing and decreased crystallinity. These spectral shifts serve as direct structural evidence of enhanced chain flexibility and an expanded amorphous phase, which are fundamental prerequisites for improved segmental mobility. Taken together, the apparent activation energy analysis and FT-IR results support that BM Al-LLZO improves ionic conductivity not only by introducing interfacial Li^+ transport pathways but also by modifying the local polymer environment in a manner consistent with enhanced ion transport. Furthermore, Li^+ transference number (t_+) measurements (Figure 2c, Table S2) confirmed the beneficial role of BM Al-LLZO. Using 3 wt% HSE yielded a t_+ value of 0.661, which was significantly higher than that of pure SPE. This enhancement was attributed to partial anion immobilization/adsorption at LLZO surfaces, which selectively facilitated Li^+ migration by suppressing anion movement [58, 59]. This effect mitigated concentration polarization and contributed to a more efficient electrochemical operation. The electrochemical stability of the electrolytes was assessed through linear sweep voltammetry (LSV) (Figure S5). All compositions of SPE and HSE containing 1, 3, 5, and 10 wt% BM Al-LLZO exhibited stability up to approximately 5.3 V versus Li/Li⁺, indicating compatibility with high-voltage cathode materials such as NCM811. Here, the improved oxidative stability

is attributed to the ceramic filler reinforcing the polymer matrix and mitigating localized decomposition, as commonly observed in ceramic-polymer hybrid electrolytes.

To further validate the practical applicability of the developed electrolytes, BE (bare electrode)||SPE/HSE||Li cells were assembled and tested at 45 °C in the voltage range of 3.0 V–4.2 V (Figure 2d–g). Among the HSEs, the 3 wt% formulation demonstrated the best performance, delivering a discharge capacity of 182.46 mAh g⁻¹ with an overpotential of 3.64 V, surpassing both the pure SPE (3.66 V, 177.02 mAh g⁻¹) and the 10 wt% HSE (3.70 V, 169.68 mAh g⁻¹) (Figure 2d). Consistent with the improved film transport properties, the 3 wt% HSE also exhibited reduced polarization in the voltage profiles, indicating facilitated Li⁺ transport while preserving the elasticity of the polymer network. Conversely, the 10 wt% HSE degraded owing to the increased interfacial resistance and matrix rigidity caused by the excessive filler content. The rate performance results (Figure 2e) further emphasized the superiority of the 3 wt% HSE. Across current rates ranging from 0.1C to 1C, the 3 wt% HSE consistently outperformed both the SPE and 10 wt% HSE formulation. At 1C, the 3 wt% HSE maintained a discharge capacity of 122.72 mAh g⁻¹, outperforming the SPE by 18.15 mAh g⁻¹ and the 10 wt% HSE by 27.88 mAh g⁻¹. This performance enhancement was attributed to the formation of continuous Li⁺ conduction networks and preservation of polymer segmental mobility at the optimal filler level. Conversely, 10 wt% HSE exhibited hindered high-rate performance owing to excessive filler-induced interfacial resistance and restricted chain dynamics.

The long-term cycling stability at 0.5C (Figure 2f,g) further demonstrated the advantages of the 3 wt% HSE, which delivered an initial capacity of 168.29 mAh g⁻¹. The capacity was retained by 59.44 % after 200 cycles, outperforming both the SPE (55.25 %) and the 10 wt% HSE (48.15 %). This superior cycling performance was attributed to the well-preserved Li⁺ transport network and stable electrode–electrolyte interfaces, enabled by the balanced filler content. Conversely, 10 wt% HSE accelerated capacity fading owing to particle agglomeration, interfacial degradation, and mechanical brittleness. Coulombic efficiencies consistently exceeded 99 % across all configurations, confirming the excellent electrochemical reversibility and minimal parasitic reactions. Overall, optimizing the BM Al-LLZO fraction (3 wt%) enabled a favorable balance of ionic conductivity, t_+ enhancement, mechanical resilience, and cycling durability in HSE-based cells. Nevertheless, when polymer electrolytes are introduced into thick/high-loading cathodes, ensuring uniform ion-conducting pathways throughout the cathode depth can remain challenging, motivating the composite electrode strategy.

2.3 | Composite Electrode (CE) Design and Electrochemical Evaluation

Although HSEs significantly enhance the electrochemical performance of ASSBs, achieving uniform ionic access throughout thick/high-loading cathodes remains challenging, because electrolyte-driven infiltration and ceramic-filler redistribution during processing can be insufficient to establish continuous through-plane Li⁺ pathways across the cathode depth. To overcome this challenge, a CE architecture was designed by directly

incorporating BM Al-LLZO into the cathode slurry. By placing the ion-conductive ceramic phase inside the cathode, this strategy is intended to construct a through-thickness Li⁺ percolation network that is less dependent on electrolyte infiltration from the external interface. This approach aimed to achieve a uniform filler distribution and reduce the formation of tortuous ion-transport pathways within the electrode microstructure. The structural and compositional effects of the design were analyzed via cross-sectional SEM and EDS mapping (Figure 3a–l). In the BE + 3 wt% HSE configurations (Figure 3i), the La atom signals originating from the BM Al-LLZO were more uniformly distributed compared with those in the BE + 10 wt% HSE configurations (Figure 3j). In the latter case, pronounced surface enrichment of BM Al-LLZO resulted in a clear compositional gradient, suggesting limited penetration/redistribution of ceramic fillers into the cathode interior under high-filler conditions. This compositional heterogeneity increased the density of the filler-rich regions and expanded the filler-polymer interfacial area, which can increase tortuosity and locally elevate ionic impedance rather than forming a continuous lower-resistance pathway. While modest improvements in conductivity can arise from polymer-ceramic interfacial transport, non-uniform filler placement limits the formation of continuous through-plane conduction pathways across the full electrode thickness, thereby restricting efficient conduction in thick cathodes.

In contrast, the CE configuration achieved by integrating BM Al-LLZO directly into the electrode slurry resulted in a substantially more uniform BM Al-LLZO distribution, as confirmed by cross-sectional EDS mapping (Figure 3k,l). The 3 wt% CE demonstrated minimal compositional gradients and reduced particle aggregation compared to the 10 wt% CE. Additionally, when compared with BE combined with 3 wt% HSE, the CE electrodes demonstrated improved filler distribution and aggregation throughout the entire electrode thickness. To further confirm the structural improvements, SEM analyses of the BE and CE samples were conducted (Figure S6). On the NCM811 surface, 3 wt% CE exhibited less aggregation and a more uniformly distributed LLZO morphology than the 10 wt% CE. Thus, the enhanced filler dispersion not only promoted better mechanical cohesion within the electrode but also facilitated the formation of more continuous Li⁺ transport networks, minimizing the interfacial resistance and supporting the superior electrochemical performance observed in the CE-based cells.

To quantitatively assess ion transport behavior, symmetric cells (BE||SPE||BE and CE||SPE||CE) were assembled to decouple the effective ionic resistance within the cathode layer (R_{ion}) from the bulk electrolyte contribution (R_b) and tested under non-Faradaic conditions at 45 °C in a pristine (0 % state of charge, SOC) state (Figure 3m,n). The bulk electrolyte resistance (R_b) was consistent at approximately 1.48 Ω across all cell configurations, confirming that variations in total resistance originated from electrode structure rather than the electrolyte. The 3 wt% CE exhibited the lowest ionic resistance (R_{ion}) at 4.26 Ω, representing a 31.4 % reduction compared to the BE (6.21 Ω). This reduction indicates improved through-thickness ionic percolation enabled by the homogeneous distribution of BM Al-LLZO within the cathode. Conversely, the 10 wt% CE demonstrated a slightly higher R_{ion} of 5.28 Ω, attributed to excessive filler content introducing a greater number of interfaces and increased pathway

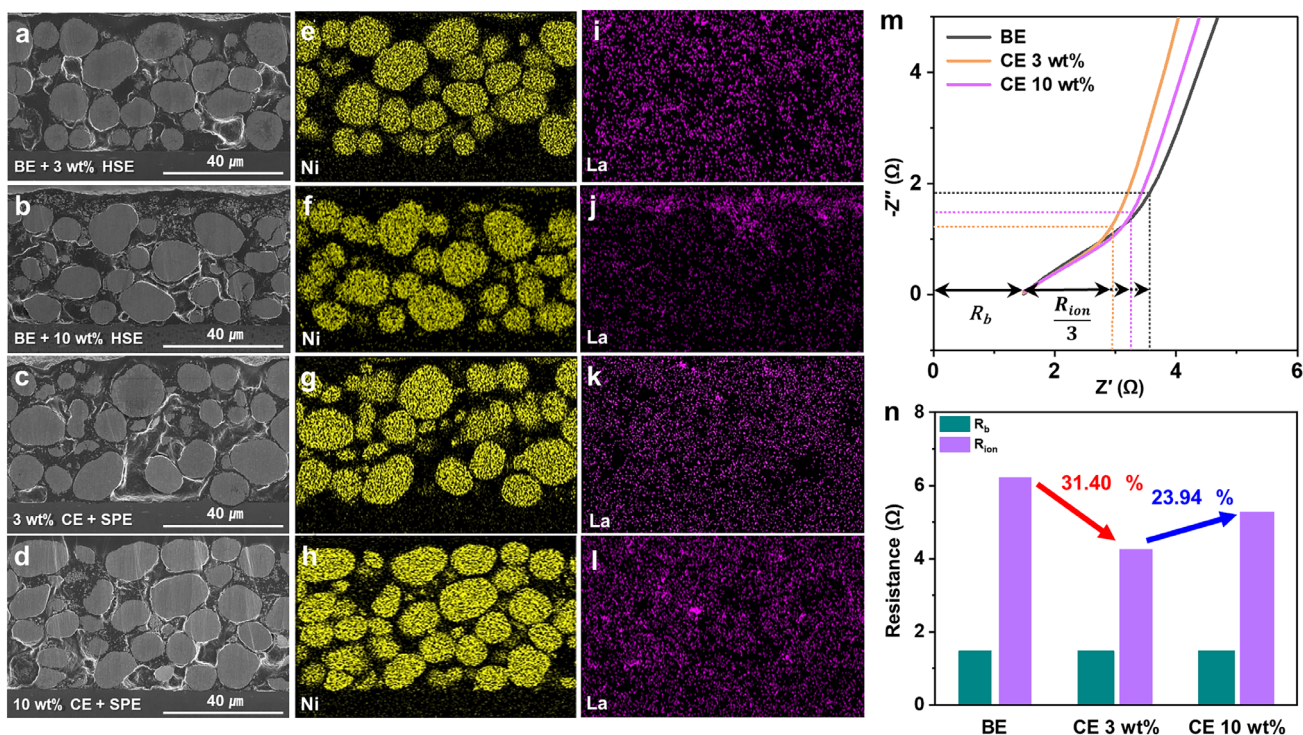


FIGURE 3 | Cross-sectional SEM images of (a) BE + 3 wt% HSE, (b) BE + 10 wt% HSE, (c) 3wt% CE + SPE, and (d) 10 wt% CE + SPE. (e–h) EDS elemental maps of Ni (NCM811) and (i–l) EDS elemental maps of La (BM Al-LLZO). Panels (e,i), (f,j), (g,k), and (h,l) correspond to (a), (b), (c), and (d), respectively. (m) Nyquist plots used to obtain cathode ionic resistance (R_{ion}) for symmetric cells BE||SPE||BE and CE||SPE||CEs cells at 45 °C. (n) Fitted bulk resistance (R_b) and cathode-layer ionic resistance (R_{ion}) for BE||SPE||BE and CE||SPE||CEs cells at 45 °C.

complexity/tortuosity for Li^+ migration. However, the 10 wt% CE outperformed the BE, indicating that BM Al-LLZO incorporation, even at non-optimal levels, yielded noticeable improvements in electrode ionic transport. Collectively, these findings emphasized the critical role of uniform BM Al-LLZO integration in composite cathodes. The 3 wt% CE design achieved optimized particle distribution, minimized interfacial resistance, and improved Li^+ conductivity, providing a promising strategy for high-performance cathode architectures in next-generation solid-state LIBs. Building upon these insights, the subsequent evaluation phase focused on directly comparing the electrochemical behaviors of the BE and CE cathodes by assembling BE/CE||SPE||Li cells, with a detailed analysis of the charge/discharge profiles and rate performances across a range of current densities.

2.4 | Electrochemical Performance of Composite Electrodes

To assess the impact of BM Al-LLZO distribution on electrochemical behavior, BE||SPE||Li and CE||SPE||Li cells were assembled and tested at 45 °C within a voltage range of 3.0 V to 4.2 V. The initial charge–discharge profiles at 0.1C (Figure 4a) demonstrated that both 3 wt% CE and 10 wt% CE cells exhibited nearly identical voltage profiles with comparable average discharge voltages (~ 3.63 V), with discharge capacities of 185.36 mAh g^{-1} and 183.86 mAh g^{-1} , respectively. Furthermore, the 5 wt% CE exhibited an overpotential of ~ 3.65 V and delivered a discharge capacity of 184.35 mAh g^{-1} (Figure S7a). This similarity indicates BM Al-LLZO incorporation into the cathode provides effective ionic access at low rate for both loadings,

consistent with the coulombic efficiency concept of forming an internal Li^+ transport network. Compared with the BE (~ 3.66 V, 177.02 mAh g^{-1}), the 3 wt% CE demonstrated significantly enhanced capacity, highlighting the role of homogeneous LLZO dispersion in improving ionic conductivity and active material utilization. Notably, this trend is consistent with the reduced cathode ionic resistance (R_{ion}) observed for the 3 wt% CE in Section 2.3, suggesting improved through-plane Li^+ percolation within the composite cathode. The rate capability test (Figure 4b, S7b) further demonstrated the kinetic superiority of the 3 wt% CE architecture. Discharge capacities were evaluated from 0.1C to 1C, revealing that 3 wt% CE retained a discharge capacity of 139.15 mAh g^{-1} at 1C, outperforming BE by 34.58 mAh g^{-1} , 5 wt% CE by 6.3 mAh g^{-1} and 10 wt% CE by 11.14 mAh g^{-1} . This significant improvement in the high rate was attributed to the well-connected ion-conducting networks formed by the optimally dispersed BM Al-LLZO, which reduced ionic resistance and supported rapid Li^+ migration. Conversely, the 10 wt% CE exhibited diminished performance at high current densities. Although its performance at low current densities remained comparable, excessive filler content led to increased filler-polymer interfacial area and higher pathway tortuosity, which can hinder efficient Li^+ transport and reduce rate capability. These results highlighted that beyond an optimal concentration, additional BM Al-LLZO content can negatively affect transport continuity and electrode microstructural effectiveness. To evaluate electrochemical resilience, all cells were subjected to three high-rate cycles at 1C followed by a return to 0.1C. All configurations exhibited nearly complete recovery of discharge capacities, indicating minimal irreversible degradation and structural failure. Notably, 3 wt% CE demonstrated the most

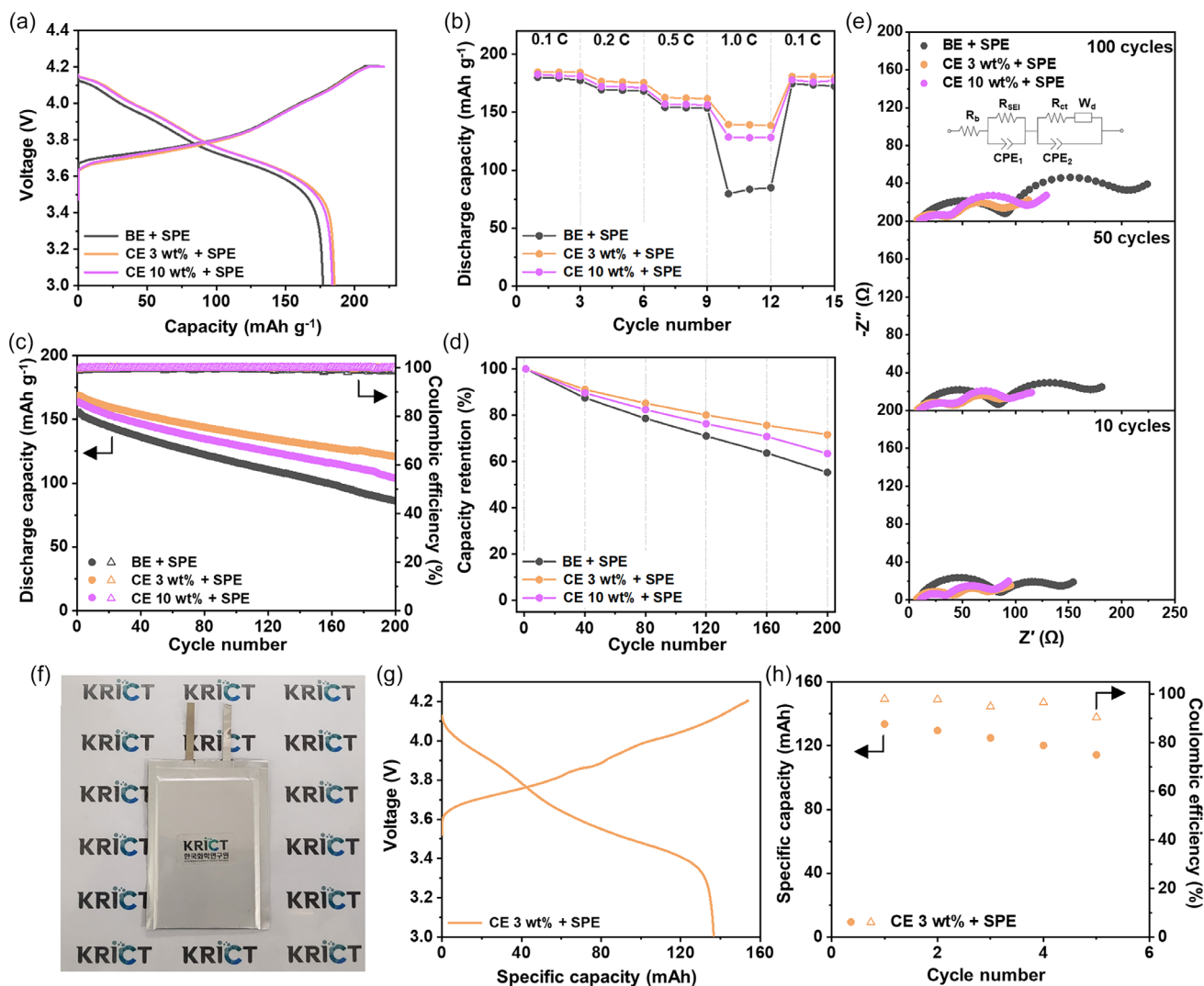


FIGURE 4 | Electrochemical performance of BE||SPE||Li, CE (3 wt%)||SPE||Li and CE (10 wt%)||SPE||Li cells at 45 °C. (a) Initial voltage profiles of three different electrodes. (b) Rate performance of three different electrodes, (c) cycling performance and Coulombic efficiency, and (d) discharge capacity retention of three electrodes. (e) EIS spectra of the three electrodes collected after different cycling numbers (10th, 50th, and 100th cycles) at 45 °C. (f) Optical image of the 4769-type pouch cell. Electrochemical performance of the CE (3 wt%)||SPE||Li pouch cell at 45 °C. (g) Initial voltage profiles and (h) cycling performance and Coulombic efficiency of the CE (3 wt%)||SPE||Li pouch cell.

consistent capacity restoration, reflecting its robust interface stability and durable ionic conduction network.

Long-term cycling stability was evaluated at 0.5C over 200 cycles (Figure 4c, S7C). In the first cycle, the 3 wt% CE achieved the highest discharge capacity of 168.95 mAh g⁻¹, followed by 5 wt% CE (167.61 mAh g⁻¹), 10 wt% CE (163.67 mAh g⁻¹) and BE (155.72 mAh g⁻¹). After 200 cycles, the 3 wt% CE retained 120.90 mAh g⁻¹, significantly outperforming 5 wt% CE (103.87 mAh g⁻¹), 10 wt% CE (103.77 mAh g⁻¹) and BE (86.04 mAh g⁻¹). This performance underscored the role of the optimized BM Al-LLZO content in maintaining stable ion transport and mitigating interfacial resistance build-up over prolonged cycling. The excessive filler content in the 5 and 10 wt% CEs likely contributed to the increased resistance and gradual capacity loss, whereas the lack of a conductive ceramic phase in the BE resulted in limited ionic connectivity. Corresponding discharge capacity retention trends (Figure 4d, S7d) further validated this observation; 3 wt% CE retained

71.55 % of its initial capacity, outperforming 5 wt% CE (61.97 %), 10 wt% CE (63.40 %) and BE (55.25 %). To further elucidate the origins of the superior electrochemical performance in the CE 3 wt%||SPE||Li cell, the interfacial stability between the CE 3 wt% and the SPE was systematically analyzed. This was achieved by monitoring the cross-sectional morphological evolution in its before cycling and after 10 and 200 cycles. Before cycling (Figure S8a), the CE 3 wt%||SPE interface exhibits intimate and conformal contact without noticeable voids, indicating excellent initial interfacial integration. After 10 cycles (Figure S8b), the CE 3 wt%||SPE interface remains well maintained, with no obvious interfacial gaps or delamination. After 200 cycles (Figure S8c), the CE 3 wt%||SPE interface is still largely preserved, demonstrating highly stable cathode/electrolyte contact during prolonged cycling. These results confirmed that the 3 wt% CE configurations offered a favorable balance between structural integrity and electrochemical stability, enabling reliable long-term operation in solid-state battery environments. Moreover, when compared with representative composite cathode reports (Table S3), the 3 wt% CE shows competitive cycling retention

under comparable high-loading conditions. As complementary low-temperature evidence, we additionally compared the electrochemical performance of BE||SPE||Li and CE 3 wt%||SPE||Li cells at 25 °C (Figure S9). In the initial charge-discharge profiles (Figure S9a), the CE 3 wt% cell delivered a higher discharge capacity of 160.30 mAh g⁻¹ than the BE cell (155.20 mAh g⁻¹) and exhibited lower polarization in the voltage profile. The rate capability results (Figure S9b) further showed that the CE 3 wt% cell maintained higher capacities than the BE cell over the evaluated current-density range, delivering 89.11 mAh g⁻¹ at 0.5C. In cycling at 0.2C (Figure S9c, S9d), the CE 3 wt% cell retained 86.74 % of its initial capacity after 60 cycles, whereas the BE retained 77.94 %. These results support that the CE architecture remains beneficial under more transport-limited conditions at 25 °C, although the overall capacities and rate capability are reduced relative to those at 45 °C.

EIS was employed to assess the resistance evolution during cycling for BE and CE configurations at the 10th, 50th, and 100th cycles under 0.5C at 45 °C (Figure 4e, Table S4). The equivalent circuit model incorporates constant-phase elements (CPEs) to capture non-ideal interfacial behavior, and R_{SEI} here represents an effective interphase resistance including contributions from interfacial films formed during cycling [60, 61]. The Nyquist plots exhibit depressed semicircles, indicative of heterogeneous interfacial characteristics at the SPE||BE/CE boundaries, which complicates the distinction between the bulk resistance (R_b), SEI resistance (R_{SEI}), and charge transfer resistance (R_{ct}). After 10 cycles, total resistance (R_{total}) was measured as 142.92 Ω for BE, 75.26 Ω for 3 wt% CE, and 79.16 Ω for 10 wt% CE. As cycling progressed, R_{total} increased across all samples; at the 100th cycle, the BE reached 204.56 Ω (R_{total}), whereas 3 wt% CE maintained the lowest R_{total} (91.30 Ω) and exhibited a comparatively suppressed growth in charge-transfer resistance (R_{ct} = 56.15 Ω). In contrast, 10 wt% CE showed a larger impedance increase by the 100th cycle (R_{total} = 110.98 Ω), consistent with the less favorable transport/structural effects at excessive ceramic loading. Overall, the EIS trends corroborate that optimized BM Al-LLZO dispersion in the CE mitigates impedance build-up and sustains interfacial kinetics during prolonged cycling.

To demonstrate the scalability, a 4769-type pouch cell with high-loading cathode (24.38 mg cm⁻²) and 3 wt% CE formulation was fabricated and tested (Figure 4f). During the initial cycle at 0.05C (3.0 V–4.2 V, 45 °C), the cell exhibited an overvoltage of ~3.62 V and delivered 172.80 mAh g⁻¹ (Figure 4g). After five cycles, the pouch cell retained a discharge capacity of 144.60 mAh g⁻¹ and maintained a coulombic efficiency of 90.40 % (Figure 4h). Although further cycle validation is needed, these results provide a proof-of-concept demonstration that the 3 wt% CE design can be translated to a high-loading pouch format, confirming the viability of 3 wt% CE for high-energy-density ASSBs systems.

3 | Conclusions

High-loading solid-state batteries are often constrained by the coupled challenge of interfacial instability and insufficient through-plane Li⁺ transport in thick cathodes, which polymer-based hybrid electrolytes can alleviate at the interface but often

fail to resolve across the full cathode depth. Here, we demonstrate a dual-domain co-design that aligns the ion-conducting phase across the electrolyte and electrode by employing ball-milled Al-doped LLZO (BM Al-LLZO) as a shared ceramic conductor. BM Al-LLZO, synthesized via a nitrate-assisted sol-gel-derived route and subsequently ball-milled, enabled robust dispersion and phase purity suitable for both HSEs and CEs. With an optimized 3 wt% loading, the HSE achieved the high ionic conductivity of 1.04×10^{-3} S cm⁻¹ (45 °C), a high Li⁺ transference number (0.661), and stability up to 5.3 V versus Li/Li⁺, translating to 59.44 % capacity retention after 200 cycles at 0.5C in HSE-based cells. To directly address cathode-depth transport, embedding BM Al-LLZO into the cathode slurry formed a more homogeneous ceramic distribution across the electrode thickness and reduced the effective cathode ionic resistance by 31.4 %. As a result, 3 wt% CE||SPE||Li cell delivered 168.95 mAh g⁻¹ initially and retained 71.55 % after 200 cycles, outperforming the standard electrode configuration. Finally, 4769-type high-loading pouch cell using the 3 wt% CE provided a proof-of-concept scale demonstration, delivering 172.80 mAh g⁻¹ and 90.40 % Coulombic efficiency over five cycles. Overall, this work establishes materials continuity, realized by a shared BM Al-LLZO phase spanning the electrolyte and cathode, as a scalable design rule that couples interfacial stabilization with through-plane Li⁺ percolation in high-loading solid-state batteries.

4 | Experimental Section

4.1 | Materials

Anhydrous lithium nitrate (LiNO₃) (Alfa Aesar, 99 %), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) (Junsei Chemical Co., Ltd., 98 %), lanthanum(III) nitrate hexahydrate (La(NO₃)₃·6H₂O) (Sigma-Aldrich, 99.99 %), zirconium(IV) n-propoxide solution (Zr(O(CH₂)₂CH₃)₄) in n-propanol (Sigma-Aldrich, 70 wt%), ethyl alcohol (C₂H₅OH) (DUKSAN, 99.9 %), and acetic acid (CH₃COOH) (Sigma-Aldrich, ≥99 %) were purchased and used as received unless otherwise stated. Lithium bis(trifluoromethane)sulfonamide (LiTFSI, Sigma-Aldrich, 99.95 %) was dried in a vacuum oven at 120 °C for 24 h prior to use. Poly(ethylene glycol) dimethyl ether (PEGDME, AMG-450, Mn ≈ 450) and ethoxylated bisphenol A diacrylate (Bis-A, KOREMUL-BP-082S, Mn ≈ 688) were purchased from Hannong Chemical Co., Ltd. Hygroscopic materials were handled under dry conditions, and moisture was minimized (below 50 ppm) using molecular sieves and vacuum drying. Tert-butyl peroxyphthalate (t-BPP, Seki Arkema Co., Ltd.) was purchased, vacuum-packed, and stored at low temperature. Fluoroethylene carbonate (FEC; FOOSUNG Co., Ltd.) was handled under dry conditions. LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811, POSCO Chemical Co., Ltd.) and conductive carbon (Ketjen black, EC-600JD, AkzoNobel Co., Ltd.) were purchased and dried in a vacuum oven at 120 °C for 24 h. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Kynar 2801, Arkema Co., Ltd.), N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich), Al current collector foil (Sam-A Aluminum, 20 μ m), and separator (PAN/PVDF = 1:1, AMO Greentech, 35 μ m) were purchased and used as received. Li metal foil (Honjo Metal, 300 μ m) was purchased and handled under dry atmosphere.

4.2 | Synthesis of Al-Doped LLZO

$\text{Li}_{6.28}\text{Al}_{0.24}\text{La}_3\text{Zr}_2\text{O}_{11.98}$ (Al-LLZO) was synthesized using a modified nitrate-assisted sol-gel method adapted from the procedure reported by Wachsmann et al. [62]. As shown in Figure S10, to synthesize 0.005 mol of the target compound, 2.31 g of LiNO_3 , 0.48 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 6.94 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 5.0 g of $\text{Zr}(\text{O}(\text{CH}_2)_2\text{CH}_3)_4$ were dissolved in 30 mL of ethanol (DUKSAN, 99.9 %). To promote homogeneous mixing and controlled hydrolysis, 15 vol% of acetic acid (CH_3COOH , Sigma-Aldrich, $\geq 99\%$) was added to the precursor solution. An additional 15 wt% of LiNO_3 was introduced to compensate for Li evaporation during high-temperature processing. The resulting solution was magnetically stirred, followed by drying at 100 °C for 24 h to remove the solvent. The dried gel was ground using a mortar and pestle to obtain Al-LLZO precursor powder. The powder was transferred to an alumina crucible and preheated at 500 °C for 4 h (heating rate: 2 °C min^{-1}) in a box-type muffle furnace (3–550, VULCAN) to decompose residual organics. Subsequently, calcination was conducted at 1200 °C for 4 h (2 °C min^{-1}) in a high-temperature box muffle furnace (MSMF1800, Myungsung Engineering Co., Ltd.) to achieve the cubic garnet phase. The calcined powder was initially ground and then ball-milled in ethanol using a planetary mill (GLBM-G, Global Lab Co., Ltd.) for 24 h at 300 rpm with 2 mm and 3 mm zirconia (ZrO_2) balls in a 1:1 ratio. After milling, the slurry was centrifuged (Combi 514R, Hanil Science Co., Ltd.) at 7000 rpm for 10 min at room temperature to separate the solid fraction, followed by vacuum drying at 50 °C for 24 h. The final BM Al-LLZO powder was stored in an Ar-filled container to prevent moisture uptake.

4.3 | Preparation of BM Al-LLZO Pellet

For ionic conductivity measurements of BM Al-LLZO pellets, the powder was uniaxially pressed into pellets using a stainless-steel die (13 mm diameter) at 13 MPa for 5 min with a hydraulic press (181–1110, PIKE Technologies). Cold isostatic pressing (CIP, Ilshin Autoclave Co., Ltd.) was then applied at 200 MPa for 15 min to increase pellet density. The pellets were sintered at 1200 °C for 5 h (heating rate: 1 °C min^{-1}) in an alumina crucible covered with mother powder to minimize Li loss. Finally, the pellet surfaces were polished using a Tegramin-25 polishing machine (Struers) at 40 rpm to ensure a smooth and uniform electrode-electrolyte interface.

4.4 | Preparation of SPE and HSE

The SPE was prepared by dissolving 0.2699 g of LiTFSI in 0.8 g of PEGDME under magnetic stirring at room temperature for 1 hr. The molar ratio of ethylene oxide units to Li ions ($[\text{EO}]/[\text{Li}^+]$) was maintained at 20 to optimize ionic conductivity, in accordance with previous literature [63]. To fabricate the HSEs, BM Al-LLZO was added to the SPE precursor at concentrations ranging from 1 to 10 wt% and stirred continuously for 24 h to ensure a homogeneous dispersion. Subsequently, 0.2 g of Bis-A was introduced as a crosslinking monomer and stirred for an additional 1 h. To improve interfacial stability and suppress side reactions, 5 wt% FEC was introduced as an additive. For thermal initiation of the in situ curing process, 0.25 μL of t-BPP was added to the

formulation. The resulting SPE or HSE solution was injected into the cell assembly and cured by heat treatment at 90 °C for 30 min in a convection oven to form a mechanically stable, in situ polymerized electrolyte membrane. Additionally, FT-IR spectroscopy and thermogravimetric analysis (TGA) were performed on the cured electrolyte to verify whether the electrolyte incorporating the 5 wt% FEC additive successfully achieved a complete solid-state. To confirm the curing behavior of the FEC-containing electrolyte, FT-IR spectra were investigated before and after thermal treatment (Figure S11a, S11b). Before curing, the SPE exhibited distinct C=C vibrational peaks of Bis-A at 1636 cm^{-1} and 1408 cm^{-1} (Figure S11c). Following thermal curing (90 °C, 30 min), these bands were largely suppressed, confirming successful in-situ polymerization and the formation of a robust 3D polymer network [64]. In contrast, characteristic FEC C-F vibrational bands (1240 to 1150 cm^{-1} , Figure S11d) remained detectable post-curing, suggesting FEC is retained in the matrix rather than consumed during crosslinking [65, 66]. Thermogravimetric analysis further verified this retention (Figure S12). The pure FEC decomposes between 61.35 °C and 174.52 °C (Figure S12a), the cured SPE showed a corresponding mass-loss in approximately 60 °C – 175 °C linked to FEC evaporation (Figure S12b). This can be known through derivative weight curve. Although this mass loss partially overlaps with the initial thermal degradation of the polymer matrix, preventing a perfectly isolated quantification, the TGA results confirm that FEC remains stably incorporated within the crosslinked membrane. Additionally, optical imaging (Figure 2a) demonstrates the cured SPE forms a mechanically robust, free-standing solid film rather than a flowable liquid.

4.5 | Characterization

The crystal structure of the synthesized Al-LLZO was analyzed by X-ray diffraction (XRD, D/MAX-2200/PC, RIGAKU) using a Cu K α radiation source ($\lambda = 1.54059 \text{ \AA}$) operated at 40 kV and 40 mA. Diffraction patterns were recorded over the 2θ range of 10°–80° at a scan rate of 2° min^{-1} . The morphology of the Al-LLZO powders and the cross-sectional features of the electrodes and electrolytes were examined using field-emission scanning electron microscopy (FE-SEM, MIRA3 LMU, TESCAN Korea). Prior to imaging, a platinum coating was applied at 10 mA for 120 s, and images were acquired at an acceleration voltage of 5 kV. The elemental distribution and composition were analyzed by energy-dispersive X-ray spectroscopy (EDS, Quantax 200, BRUKER) for elemental mapping and compositional analysis, operating with an energy resolution of <126 eV and capable of detecting elements ranging from Be ($z = 4$) to Ce ($z = 98$).

4.6 | Electrochemical Measurement

To evaluate the ionic conductivity of the BM Al-LLZO pellets, Ag paste was applied to both pellet surfaces, followed by the attachment of Al current collectors. An AC impedance analyzer (Zennium XC, ZAHNER) was used with an amplitude of 5 mV over a frequency range of 5 MHz to 10 kHz at 25 °C and 45 °C. To measure the ionic conductivity of the electrolyte, stainless steel||electrolyte|| stainless steel (SUS||electrolyte||SUS) cells were assembled using SPE or HSE and analyzed from 0 °C to 100 °C

within the frequency range of 10 kHz–2 MHz. For evaluation of the ionic resistance within the cathodes, symmetric pouch cells (cathode (BE/CE)||electrolytes (SPE/HSE)||cathode (BE/CE)) were assembled and tested at 45 °C using a Bio-Logic SAS VPM3 system over a frequency range of 2 kHz to 200 mHz with an AC amplitude of 5 mV. Half cells (cathode (BE/CE)|| electrolyte (SPE/HSE)||Li) were tested using the same system over a frequency range of 1 MHz–10 mHz. The Li^+ transference number (t^+) was determined using Li||SPE/HSE||Li cells. AC impedance was measured within the frequency range of 500 mHz to 500 kHz, with DC polarization applied at 20 mV relative to the open-circuit voltage (OCV). The current was recorded for more than 1 h to ensure steady-state conditions. To evaluate the electrochemical performance, BE cathodes were fabricated by mixing NCM811, conductive carbon, and PVDF-HFP in a weight ratio of 96.5:1.5:2. The CE cathodes were prepared by adjusting the weight ratio of the cathode active material according to the BM Al-LLZO content (1–10 wt%) while keeping the conductive carbon and binder contents constant (e.g., for CE 10 wt%, the formulation is NCM811: conductive carbon : binder : BM Al-LLZO = 86.5 : 1.5 : 2 : 10), and the slurry viscosity was adjusted by adding NMP. The electrode slurries were homogenized using a Thinky mixer (AR-100, MD PROS). Slurries were cast on 20 μm thick Al foil, dried at 100 °C for 3 h, and roll pressed to achieve an areal loading of 9.5–10.5 mg cm^{-2} (based on NCM811 mass unless otherwise stated) and a density of 2.9 g cm^{-3} . Coin-type (2032) and pouch-type (4769) half cells were assembled using BE or CE cathodes, SPE or HSE electrolytes, a separator, and Li metal foil. Cell assembly was performed in an Ar-filled glove-box (dew point < −70 °C) for coin cells, and pouch cells were assembled and sealed in a dry room. Initial formation cycling of coin cells was conducted at 0.1C in the constant current/constant voltage (CC/CV) mode during charge and in the CC mode during discharge, over a voltage range of 3.0–4.2 V versus Li/Li $^+$ at 45 °C, using a charge/discharge cycler (WonATech Co., Seoul, Korea). After the initial cycle (formation cycle), rate capabilities were evaluated by varying discharge current densities from 0.1C to 1C (CC mode, C/10, C/5, C/2, and 1C) while maintaining a charge current density of 0.1C (CC/CV mode) between 3.0 and 4.2 V versus Li/Li $^+$ at 25 °C and 45 °C. Each rate was applied for three consecutive cycles, after which three additional cycles at 0.1C were performed to assess capability retention. The cycle performance of the cells intended for the formation was evaluated by charging at 0.1C (CC/CV mode) and discharging at 0.2C and 0.5C (CC mode), over a voltage range of 3.0–4.2 V versus Li/Li $^+$ at 25 °C and 45 °C. For the CE 3 wt%||SPE||Li 4769-type pouch cell, formation was conducted under the same conditions, followed by charge and discharge at 0.05C using CC/CV and CC mode, respectively, in the voltage range of 3.0–4.2 V versus Li/Li $^+$ at 45 °C for five cycles.

Author Contributions

Hye Su Hwang: conceptualization, data curation, formal analysis, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft, writing – review and editing. **Jinkyu Park:** conceptualization, data curation, formal analysis, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft, writing – review and editing. **Seungju Choi:** data curation, formal analysis. **Junyoung Choi:** investigation, methodology. **Dong-Won Kim:** project administration,

validation. **Jungdon Suk:** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft, writing – review and editing, supervision.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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