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Solid-State Lithium Metal Rechargeable Batteries With High-Mass-Loading NMC Electrode and Multilayer Hybrid Solid Electrolyte Thin-Film

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ABSTRACT

Solid-state lithium metal batteries, assumed to show improved safety and high energy density, have garnered growing interest. Nevertheless, establishing an effective ionic conduction pathway within the composite positive electrode remains challenging, especially with high-active-materials mass-loading in the electrode. Herein, we develop a high-active-mass loading positive electrode for solid-state Li metal rechargeable batteries, optimized for operation at an elevated temperature of 60°C. The electrode is based on NMC622 as active material, incorporating the ionic liquid Pyr₁₄TFSI and LiTFSI (combined-electrolyte, cE). The positive electrode membranes are successfully prepared by preventing undesired gelation of the slurry solution and seamlessly integrating them with a thin-film multilayer hybrid solid electrolyte. Notably, the NMC622-based electrode with 10 wt% of cE achieves a specific capacity exceeding 160 mAh g⁻¹ at a high mass loading of 40 mg cm⁻². The methodology demonstrated in the present study highlights the potential of incorporating a cE into cathode compositions for high energy density solid-state Li metal batteries.

1 | Introduction

The growing demand for safe, reliable, and cost-effective energy storage devices has driven extensive research and development in battery technology over the past decade. While lithium-ion batteries utilizing organic liquid electrolytes are reaching their physicochemical limits, solid-state batteries (SSBs) have emerged as a promising next-generation energy storage solution [1–3]. By eliminating more flammable liquid organic electrolytes, SSBs are reported to notably enhance safety, while the use of high-capacity anodes, such as lithium (Li) metal, offers the potential for increased energy density [4]. A wide range of solid electrolytes (SIEs) has been explored, including solid polymer electrolytes (SPEs) [5–7], inorganic SIEs [8, 9], and especially hybrid solid electrolytes [10–13]. However, each system presents inherent limitations. SPEs typically suffer from low ionic conductivity due to restricted polymer chain mobility, whereas SIEs often

exhibit poor interfacial contact arising from their rigid nature. To address these challenges, hybridization strategies combining multiple electrolyte components have been widely investigated to achieve synergistic improvements in ionic transport, mechanical properties, and interfacial stability. In particular, multilayer HSE architectures have recently attracted significant attention as an effective strategy to address the distinct requirements at the cathode and anode interfaces. For example, Herbers et al. developed a thin-film multilayer HSE derived from a commercial separator, integrating different functional layers for cathode stability, mechanical strength, and Li metal compatibility [10]. This system exhibited high thermal stability (>250°C), good interfacial compatibility, and long-term cycling performance. However, the demonstrated electrochemical performance was limited to relatively low cathode mass loading (4 mg cm⁻²), which remains insufficient for achieving practical high energy density. Achieving high energy density at the cell level requires optimization of key

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technological parameters. One important approach involves utilizing high-mass-loading positive electrodes to achieve high areal capacity [14–16]. However, constructing an effective ionic conduction network in thick composite cathodes remains a major challenge, as increased electrode thickness leads to sluggish Li^+ transport, poor interfacial contact, and increased polarization. In addition, incorporating ionic liquids into composite cathodes has been explored as a strategy to enhance ionic conductivity and interfacial wetting. Ionic liquids can facilitate Li^+ transport and improve interfacial contact while maintaining thermal stability and safety. Nevertheless, their role within high-mass-loading cathodes, particularly in combination with advanced multilayer electrolyte architectures, has not yet been systematically clarified.

In this work, we combine a thin-film multilayer HSE, previously reported by Herbers et al. with a high-active-mass-loading positive electrode to investigate the physical properties and Li metal battery performance at 60°C within a voltage range of 3.00–4.25 V [10]. The multilayer hybrid electrolyte is engineered to improve mechanical strength, cathode contact, oxidative stability, interfacial compatibility, and overall safety. Furthermore, we introduce a combined-electrolyte (denoted as cE in this study), consisting of Pyr₁₄TFSI ionic liquid and LiTFSI, into the cathode to enhance Li^+ transport and electronic conduction pathways. As a result, we successfully fabricate NMC622-based positive electrodes with high active mass loadings of 30 and 40 mg cm⁻², achieving improved electrochemical performance.

2 | Results and Discussion

In this study, we propose a well-designed NMC622-based positive electrode, featuring an optimized Li^+ transfer and electronic conducting network, to achieve superior high-active-mass-loading positive electrodes. To evaluate the electrochemical performance of cathode materials with variable electrolyte compositions (Pyr₁₄TFSI ionic liquid and LiTFSI) ratios of 2 and 10 wt%, we fabricated NMC622-based electrodes with active mass loading of 30 mg cm⁻² and 40 mg cm⁻². These were compared to NMC622-based electrodes that did not contain cE in cathode slurry. In addition, this study is built upon the thin-film multilayer HSE system previously reported [10]. In the original approach, a sandwich-like multilayer electrolyte was constructed by combining a mechanically reinforced separator with tailored electrode-facing layers. A cathode-facing layer based on LATP and PVDF-HFP provides oxidative stability against high-voltage NMC cathodes, while an anode-facing PEO-based layer ensures

stable contact with Li metal. These layers are interconnected by the ionic liquid Pyr₁₄TFSI and LiTFSI, which enhance ionic conductivity and interfacial contact across the multiphase electrolyte system. Building on this established electrolyte chemistry (PVDF-HFP/Pyr₁₄TFSI/LiTFSI), the present work introduces a key modification by incorporating these electrolyte components directly into the cathode composite. In addition to the active material (NMC622) and conductive carbon, the cathode contains PVDF-HFP, Pyr₁₄TFSI, and LiTFSI as a combined electrolyte (cE), forming a percolating ionic conduction network within the electrode. This design is particularly beneficial for high-mass-loading electrodes, where conventional solid-state configurations often suffer from limited ionic accessibility and increased polarization. Within the cathode, the roles of these components differ from those in the bulk electrolyte. PVDF-HFP functions not only as a binder but also as a polymer matrix that accommodates the ionic liquid and lithium salt. Although PVDF-HFP lacks strong coordinating groups for Li^+ transport compared to PEO, its relatively high dielectric constant supports partial dissociation of LiTFSI, especially in the presence of fluorinated anions such as TFSI⁻. Meanwhile, Pyr₁₄TFSI facilitates phase connectivity and enhances ionic mobility; however, Li^+ transport is strongly influenced by the Pyr₁₄TFSI/LiTFSI ratio due to the formation of $[\text{Li}(\text{TFSI})_n]^{(n-1)-}$ complexes. Therefore, optimizing the composition of the combined electrolyte is essential to balance ionic conductivity and electrochemical performance. Table 1 presents the fabrication details and physical properties of the electrode membrane, including density, thickness, and calculated porosity values. Figure 1a illustrates the fabrication procedure for high-active-mass-loading cathode membranes. The cathode membranes were fabricated by mixing the active material, carbon powder, polymeric binder, cross-linking agent, and cE. In the coating process, a well-mixed slurry was prepared by dispersion on the carbon-coated alumina foil by using a doctor blade. Subsequently, the cathode membranes were cross-linked via UV curing and dried under vacuum conditions at 80°C for 48 h. The detailed membrane preparation process is described in the Experimental section. The resulting electrode membranes exhibited thickness ranging from 130–150 μm for 30 mg cm⁻² loading and 160–170 μm for 40 mg cm⁻² loading. As the active mass loading increased, the electrode thickness also expanded. Additionally, an increase in electrolyte ratio corresponded to higher density values and lower calculated porosity due to the increased electrolyte content within the composite.

To further investigate the morphology of the electrodes, a Cross Section Polisher (CSP) was used to treat the positive electrode foil, and the cross-sectional SEM images are displayed in Figure 2a–c,

TABLE 1 | Physical properties of high-active-mass-loading positive electrode membranes, including density, active mass loading, thickness, and calculated porosity.

Run	Density (g cm ⁻³)	Active mass loading (mg cm ⁻²)	Thickness (μm)	Calculated porosity (%)
NMC622	2.45 ± 0.09	30	126.7 ± 6.8	44.15 ± 2.11
NMC622	2.51 ± 0.05	40	164.0 ± 3.0	42.99 ± 1.19
NMC622 + 2 wt% cE	2.56 ± 0.07	30	146.7 ± 2.6	39.55 ± 1.68
NMC622 + 2 wt% cE	2.45 ± 0.05	40	171.7 ± 1.0	42.27 ± 1.13
NMC622 + 10 wt% cE	2.62 ± 0.20	30	149.2 ± 3.3	27.55 ± 5.53
NMC622 + 10 wt% cE	2.76 ± 0.06	40	167.7 ± 6.2	23.58 ± 1.74

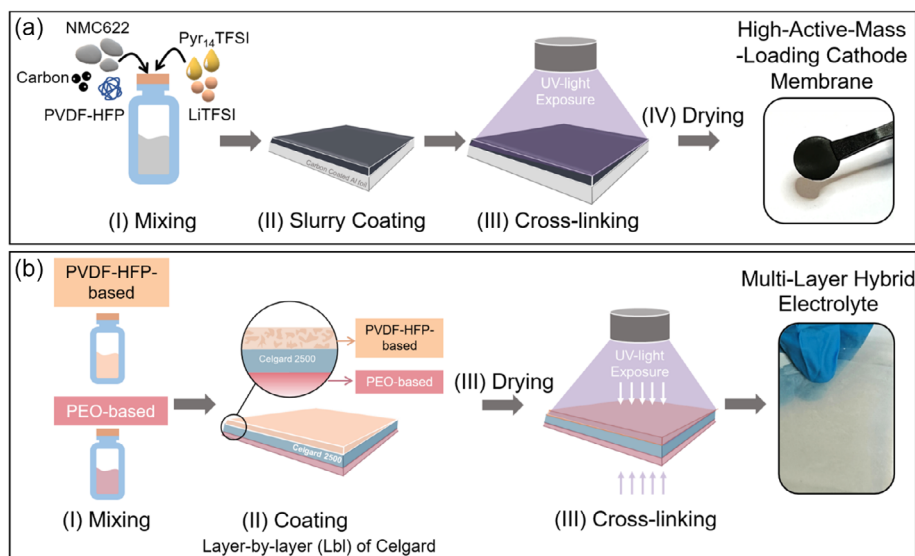


FIGURE 1 | Schematic illustration of the fabrication procedure for (a) high-active-mass-loading cathode membrane and (b) multilayer HSE thin-film.

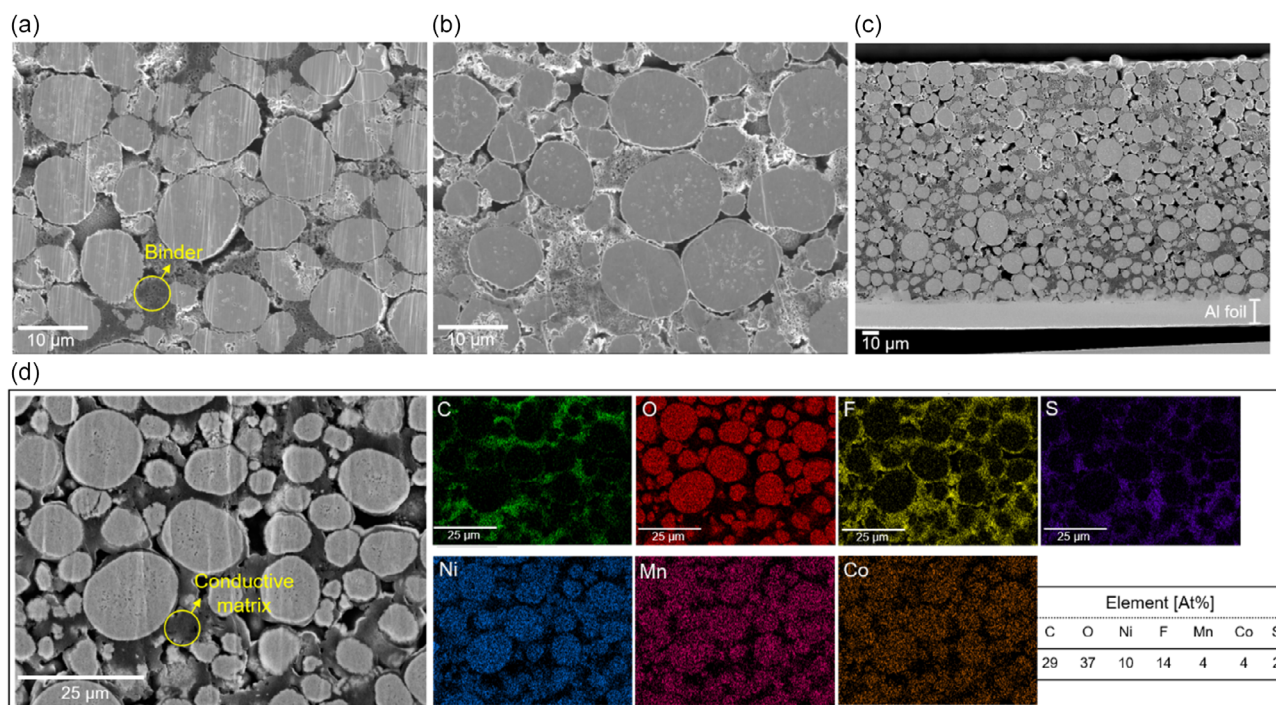


FIGURE 2 | Cross-sectional SEM images of positive electrode membranes: (a) NMC622, (b) NMC622 + 2wt% cE, and (c) NMC622 + 10wt% cE, each with active mass loading of 40 mg cm^{-2} . (d) SEM and EDS mapping analysis of the NMC622 + 10wt% cE (40 mg cm^{-2}) positive electrode membrane, including a table of atomic percentages (%).

Figure S2, and Figure S3, Supporting Information. All electrode types predominantly consist of spherical-shaped NMC particles with diameters ranging from 9 to $20 \mu\text{m}$. The cross-sectional SEM confirmed a homogeneous distribution of NMC622 particles for all electrode types throughout the entire electrode depth (Figure 2c and Figure S2). A porous structure for the binder (represented for the binder without cE) and binder-conductive matrix (represented for the binder with cE) are detected. Furthermore, cross-sectional SEM images and corresponding EDS elemental maps for the electrodes are presented in Figure 2d, Figure S4, and Figure S5, Supporting Information. SEM and EDX analyses of NMC622 + 2 wt% cE and NMC622 + 10 wt% cE electrode

membranes revealed a homogeneous distribution of oxygen (O), nickel (Ni), manganese (Mn), and cobalt (Co) throughout the NMC particles. Carbon (C), fluoride (F), and sulfur (S) elements were primarily located around the NMC622 particles, indicating their association with the binder-conductive electrolyte matrix. Especially, sulfur was found in the cE containing Pyr₁₄TFSI ionic liquid and LiTFSI, with its atomic percentage (At%) increasing in correlation with the electrolyte content, as shown in Table S1. In contrast, sulfur was absent in the NMC622 electrode without cE additive.

Figure 3a exhibits the experimental results of the peel test, which evaluated the adhesion strength between the electrode surface

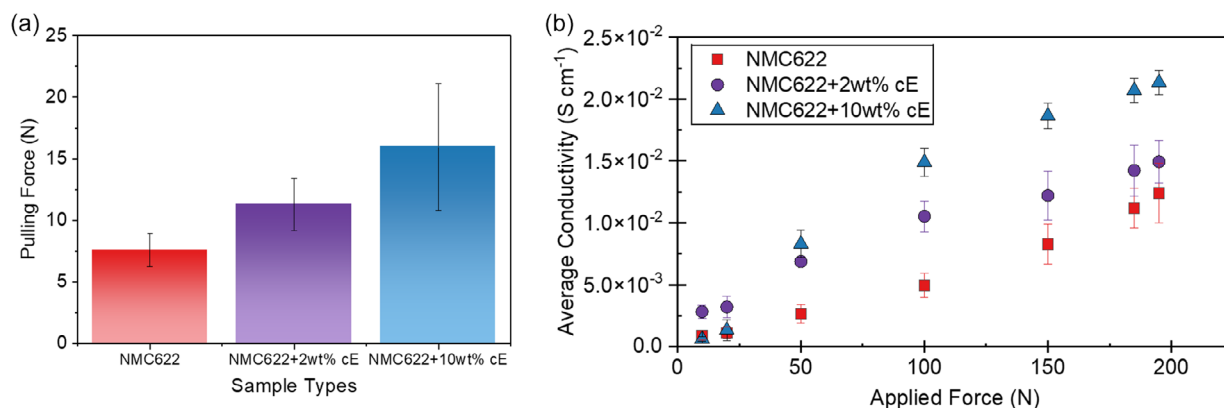


FIGURE 3 | (a) Average pulling force measured for three electrodes. (b) Relationship between average conductivity and applied force for high-active-mass-loading positive electrode membranes.

and adhesive tape. As a result, the average pulling force of the electrode incorporating cE (NMC622 + 2 wt% cE and NMC622 + 10 wt% cE) was higher than that of NMC622 electrode without electrolyte. The average pulling force of the NMC622 + 10 wt% cE exhibited the highest value. Specifically, the average pulling force increased with the addition of cE from 7.59 ± 1.34 N for NMC622 to 11.31 ± 2.12 N for NMC622 + 2 wt% cE and reached its maximum at 15.98 ± 5.15 N for NMC622 + 10 wt% cE. This enhancement in adhesion strength is attributed to the cross-linked binder, which improves bonding properties within the binder-conductive matrix as the cE content increases. The variation of average conductivity depending on the applied force is shown in Figure 3b for positive electrode sheets. The conductivity values correspond to the electronic conductivity of the calendared electrode sheets. These values were calculated from the measured absolute resistance, sample thickness, and electrode area. The measurements were conducted at room temperature using a Zwicki universal testing machine under applied force. It can be observed a positive linear correlation between average conductivity and applied force for all cathode membranes. The correlative coefficient (r) values between conductivity and applied force of all samples are between 0.98–1 which indicates a strong to perfect linear correlation between parameters. Under low applied forces, the average conductivity values of all electrodes were not significantly different. On the other hand, the average conductivity of NMC622 + 10 wt% cE exhibited higher than that of other samples at the large applied force with 50, 100, 150, 185, and 195 N. The increase in conductivity ($S\ cm^{-1}$) with enhancing applied force (N) can be attributed to two key factors: (1) a reduction in contact resistance when materials compress, leading to better contact between the conductivity pathway from the binder-conductive matrix in the electrode membranes with cE additives [17, 18]; (2) an improved percolation pathway facilitated by the binder-conductive matrix [19]. Consequently, the integration of Pyr₁₄TFSI ionic liquid and LiTFSI within the cathode composite improves conductivity while reducing interfacial resistance.

To assess battery cell performance, electrochemical cells were assembled using NMC622, NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE electrodes with active mass loading of $30\ mg\ cm^{-2}$ and $40\ mg\ cm^{-2}$. To quantify evaluate the performance of the positive electrode, a thin-film multilayer HSE was employed, coated onto a commercial Celgard separator, as illustrated in Figure 1b.

The practical solid electrolyte was provided by coating two specific different cathode and anode pastes on both sides of the Celgard2500 ($\leq 50\ \mu m$) and a relatively thick $150\ \mu m$ lithium foil as the negative electrode. This electrolyte system was adapted from a previous study by Herbers et al. [10]. For the multilayer hybrid electrolyte, the Cg-coated displayed a high mechanical strength to prevent short-circuits, a cathode-facing electrolyte layer (PVDF-HFP-based) provided a high oxidative stability ($>4.5\ V$) by lithium aluminum titanium phosphate (LATP), and an anode-facing electrolyte layer (PEO-based) offered to stable cycling of the Li metal battery. Furthermore, Pyr₁₄TFSI and LiTFSI were incorporated across all electrolyte layers to enhance ionic conductivity, interfacial contact, and safety. A schematic representation of the coin-type cell (CR2032) configuration is shown in Figure S1. We investigated three types of positive electrode (NMC622, NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE) and two different loading levels of NMC622 material, specifically $30\ mg\ cm^{-2}$ and $40\ mg\ cm^{-2}$, at $60^\circ C$ with a current density of $0.1\ mA\ cm^{-2}$ and cut-off voltages ranging from 3.00 to 4.25 V. Figure 4 presents the charge/discharge profiles for the 1st, 5th, and 10th cycles of NMC622||Li, NMC622 + 2 wt% cE||Li, and NMC622 + 10 wt% cE||Li cells at active mass loading of $30\ mg\ cm^{-2}$ (Figure 4a–c) and $40\ mg\ cm^{-2}$ (Figure 4d–f). During the first charging process, the voltage of the NMC622 + 10 wt% cE||Li metal cell (Figure 4a) gradually increased from 3.50 to 3.83 V before reaching the cut-off voltage of 4.25 V with a capacity of $179\ mAh\ g^{-1}$. Upon switching to discharge, the voltage initially remained around 4.2 V before gradually decreasing to 3.50 V, reaching the cut-off voltage of 3.0 V with a capacity of $157\ mAh\ g^{-1}$. Additionally, the voltage curves of cell charging equipped with NMC622 + 2 wt% cE shifted to higher voltages, causing the cut-off voltage to be reached at a lower stage of charge within the set voltage range. Moreover, the average cell voltage declined, as indicated by a shift to the lower voltage of discharging. However, the capacities at the first cycle of the NMC622 + 2 wt% cE did not show a significant difference compared to NMC622 + 10 wt% cE. On the other hand, the first cycle of cell equipped with NMC622 exhibited a notably lower specific capacity. For the NMC622 + 10 wt% cE||Li metal cell ($30\ mg\ cm^{-2}$), the specific capacities remained stable from the 1st cycle to the 5th cycle, with a capacity retention of 89%. The specific capacities of the electrodes incorporating cE in composite cathodes remained high even through the 10th cycle, as illustrated in Figure 4c, and Figure 4f. At a higher active mass loading of $40\ mg\ cm^{-2}$, the specific discharge capacities of NMC622 + 10 wt% cE||Li metal cell at the

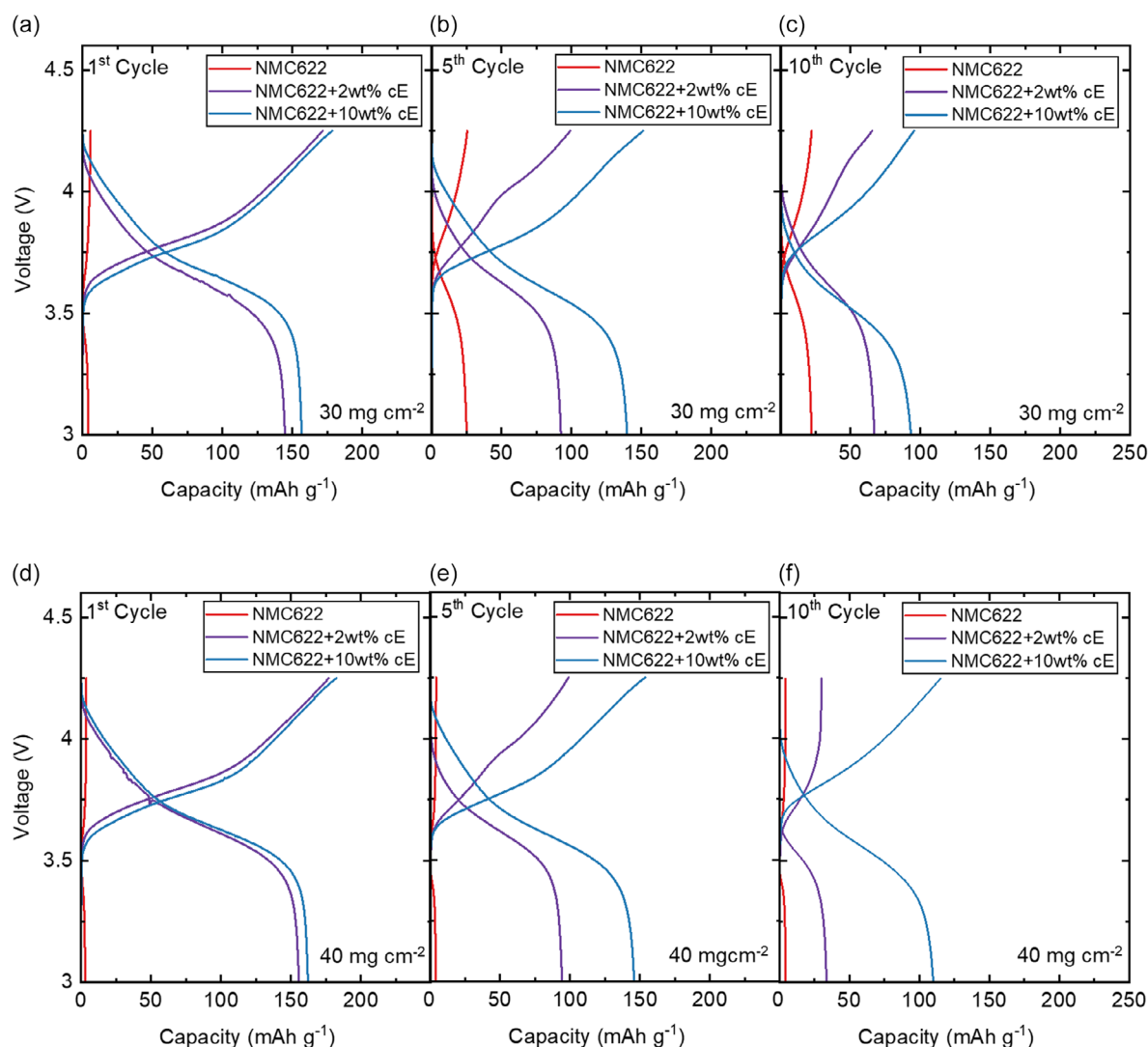


FIGURE 4 | Charge/discharge profiles of the 1st, 5th, and 10th cycles for electrochemical cells equipped with (a–c) 30 mg cm^{-2} and (d–f) 40 mg cm^{-2} active mass loading of NMC622, NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE as the positive electrode at 60°C with 0.1 mA cm^{-2} and cut-off voltages from 3.00–4.25 V.

1st, 5th, and 10th cycles are 162, 146, and 110 mAh g^{-1} , respectively. Moreover, the specific charge capacities of NMC622 + 10 wt% cE cell (40 mg cm^{-2}) at the 1st, 5th, and 10th cycles are 183, 154, and 115 mAh g^{-1} , respectively. These values were slightly higher than those observed for the lower active mass loading, with a capacity retention of 90% at the 5th cycle and 68% at the 10th cycle. In addition, the specific discharge capacities of NMC622 + 10 wt% cE||Li metal cell with 30 mg cm^{-2} were 157, 140, and 93 mAh g^{-1} for the 1st, 5th, and 10th cycles, respectively.

Interestingly, the specific capacity of the sample with the cE substantially increased compared to the active material without the cE in the cathode composite. This enhancement is attributed to improved ionic contact and favorable ionic percolation. We investigated two different loading levels, ranging from 30 mg cm^{-2} to 40 mg cm^{-2} . Figure 5a exhibits the average discharge capacities at the first cycle for various loading levels, revealing that the specific capacity of the cell equipped with NMC622 + 10 wt% cE remained nearly unchanged across both active mass loadings. Intriguingly, the specific capacities increased approximately 42–55 times in NMC622+cE||Li meal cell compared to

NMC622 without cE at 40 mg cm^{-2} active mass loading. The specific energies resulting from the material calculation (calculated based on the total mass of active material, binder, conductive additive, and cE) are shown in Figure 5b. At 60°C , the specific energies for NMC622, NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE cells are 12, 494, and 496 Wh kg^{-1} , respectively, for the 30 mg cm^{-2} , and 9, 532, and 511 Wh kg^{-1} , respectively, for the 40 mg cm^{-2} mass loading. The specific energies were directly related to the active mass loading level, which agrees with the previous report that an increase in mass loading from 10 to 30 mg cm^{-2} resulted in energy densities exceeding 500 Wh kg^{-1} [14]. The cycling performance of NMC622, NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE electrodes based on the 30 mg cm^{-2} , and 40 mg cm^{-2} active mass loading was given in Figure 5c, and Figure 5d, respectively. Cells equipped with NMC622+cE cells exhibited stable cycling performance and high specific capacity from the 1st cycle to the 10th cycle, with a high Coulombic efficiency of over 85% compared to the NMC622 cell, particularly for NMC622 + 10 wt% cE at a current density of 0.1 mA cm^{-2} , indicating the high ionic conductivity of the NMC622 matrix electrode. Interestingly, the effect of electrode

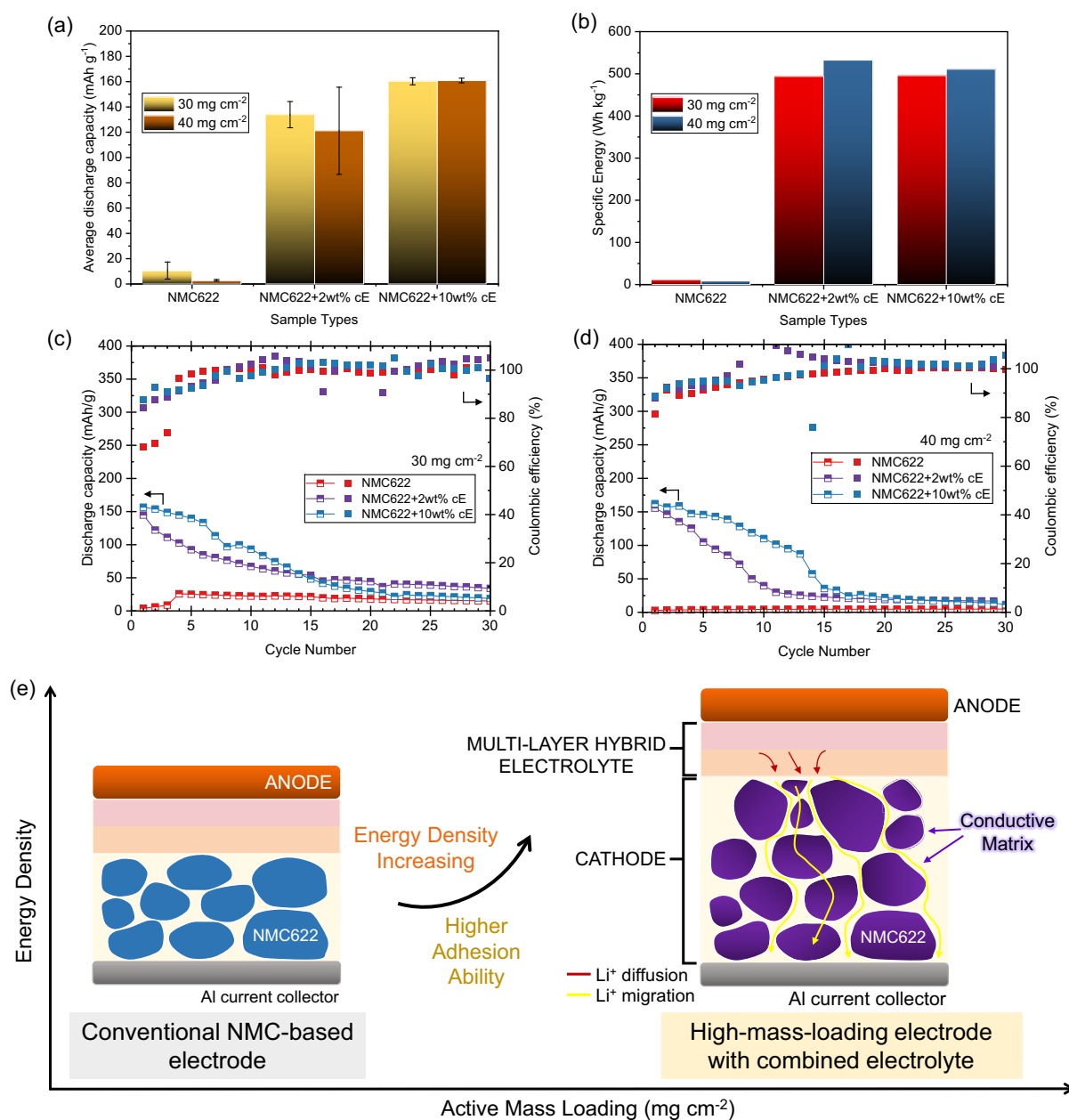


FIGURE 5 | (a) Average discharge capacities and (b) specific energies and average energies of high-active-mass-loading electrodes at various loading levels at 60°C with 0.1 mA cm⁻² and cut-off voltages from 3.00–4.25 V. Discharge capacity and Coulombic efficiency over cycling for high-active-mass-loading positive electrode with (c) 30 mg cm⁻² and (d) 40 mg cm⁻² active mass loading. (e) Schematic illustration of the structural design of high-active-mass-loading electrode with a multilayer hybrid electrolyte.

mass loading on cycling performance strongly depends on the content of the combined electrolyte (cE). At a mass loading of 30 mg cm⁻², the capacity retention shows a moderate improvement with increasing cE content (46% for 2 wt% cE and 60% for 10 wt% cE). In contrast, at 40 mg cm⁻², the impact of cE becomes significantly more pronounced, with capacity retention increasing from 26% (2 wt% cE) to 68% (10 wt% cE). This trend suggests that the role of cE becomes increasingly important as the electrode thickness increases. At lower mass loading, ionic transport pathways are relatively less limiting, and the contribution of cE is therefore less significant. However, at higher mass loading, where ionic transport limitations are more severe, the incorporation of cE facilitates the formation of effective Li⁺ conduction pathways and improves interfacial contact within the composite

cathode [20–23]. As a result, the cE effectively mitigates polarization and enhances cycling stability under high-mass-loading conditions. Therefore, the observed cycling behavior reflects not only the effect of electrode thickness but also the synergistic contribution of cE in overcoming transport limitations in thick electrodes. Figure 5e illustrates a schematic representation of the structural design of the high-active-mass-loading electrodes (NMC622 + 2 wt% cE, and NMC622 + 10 wt% cE) combined with a multilayer hybrid electrolyte. The high-active-mass-loading electrodes often suffer from lacking electronic conductivity; therefore, the cE additives were incorporated with the assistance of a binder. The conductive electrolyte matrix facilitated strong particle adhesion and excellent attachment to the current collector, forming a percolation pathway for efficient charge transport.

Moreover, the incorporation of the cE into the cathode slurry facilitates the formation of effective ionic conduction pathways between active material particles and reduces interfacial resistance at the cathode–hybrid electrolyte interface. On one hand, the presence of the ionic liquid (Pyr₁₄TFSI) and LiTFSI enhances Li⁺ mobility within the composite electrode by establishing a percolating ionic conduction network. On the other hand, the cE improves interfacial contact between active material particles and the multilayer HSE, thereby lowering interfacial resistance and stabilizing the electrode/electrolyte interface. As the cE is distributed throughout the cathode matrix, bulk ionic transport and interfacial effects are intrinsically coupled. Therefore, the improved electrochemical performance is attributed to the synergistic combination of enhanced Li⁺ transport within the electrode and improved interfacial stability. As a result, NMC622+cE||Li metal cells demonstrated a superior electrochemical performance compared to conventional NMC622||Li metal cell, particularly under high mass loading levels and elevated temperature conditions.

3 | Conclusion

In this study, we fabricated NMC622-based positive electrodes incorporating cE with a variable electrolyte composition ratio of 2 wt% (NMC622 + 2 wt% cE) and 10 wt% (NMC622 + 10 wt% cE) for application in solid-state Li metal rechargeable batteries. High-active-mass-loading electrodes (30 and 40 mg cm⁻²) were successfully prepared by suppressing undesired gelation of the slurry solution by integrating them with a thin-film multilayer HSE. The binder-conductive matrix in the cathode possesses an effective ionic percolation pathway between the electrode particles and improved interfacial contact with the electrolyte layer. Notably, the NMC622+cE||Li metal cells exhibited superior battery performance in comparison to the conventional NMC622||Li metal cell. The specific energies were directly correlated with the active mass loading level. Under a high mass loading, NMC622+cE||Li cells delivered a specific capacity exceeding 150 mAh g⁻¹ when operated at 60°C within cut-off voltages from 3.00 V to 4.25 V. In terms of cycling stability, cell equipped with NMC622 + 10 wt% cE demonstrated better capacity retention (68% after 10 cycles) than other samples. The methodology demonstrated in the present study highlight the potential of incorporating cE into cathode compositions for high energy density solid-state Li metal batteries.

4 | Experimental Section

Preparation of NMC622-based high-active-mass-loading positive electrode: A slurry of NMC622 powder (LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂, ShanShan Tech Co.; d_{50} = 10.22 μm, d_{90} = 14.09 μm; 85–94 wt%), carbon black (Super C65; Imerys Graphite & Carbon; 3 wt%), polyvinylidene fluoride (PVDF-HFP; Sigma–Aldrich; 3 wt%) binder, Benzophenone (BP, Merck, 99%), Pyr₁₄TFSI (Solvionic, 99.9%), and LiTFSI (TCI, >98%) dissolved in *N*-methyl-2-pyrrolidone (NMP, Thermo Fisher Scientific, 99.5%, AcroSeal, over molecular sieve) was coated onto a carbon-coated aluminum (Al) current collector (a thickness of 20 μm). The slurry film was cross-linked by UV curing (UVACUBE 100, 100 W lamp, Dr. Hönle AG) for 40 min. Then,

the NMP solvent was removed by heating at 80°C under reduced pressure for 48 h, and the electrode sheets were obtained. The loading amount of the active materials was about 30 and 40 mg cm⁻². Chemicals were dried at 100°C under reduced pressure $\leq 10^{-3}$ mbar for 48 hours. For the NMC622 sample, the mixing process was conducted without the cE of Pyr₁₄TFSI and LiTFSI.

Electrode characterization: Field-emission scanning electron microscopy (S-4800, Hitachi) was used to characterize the morphology of the samples. Adhesion and conductivity measurements were conducted on the calendared electrode sheets using a Zwicki universal testing machine (ZwickRoell GmbH and Co. KG). Both measurements were carried out at room temperature. Prior to testing, the electrode sheets were calendared under an applied force of ~9.8 kN to ensure uniform thickness and mechanical integrity. For conductivity measurements, the applied force was varied from 10 to 195 N, and each measurement was repeated three times to ensure reproducibility. For the peeling test, the electrode sheets were affixed to the top and bottom of two splints of double-sided 3 M tape. The splints were initially pressed together with a force of 2000 N for 60 s, after which they were gradually pulled apart under increasing traction to determine the maximum adhesion force and each measurement was repeated three times.

Preparation of the multilayer HSE thin-film: Two electrolyte pastes were prepared for coating both sides of the Celgard2500 (Cg2500, Celgard), as illustrated in Figure 1b. For the anode paste, PEO (Dow Chemical, molecular weight 4,000,000) was dissolved in ACN (Carl Roth, $\geq 99.9\%$, ROTIDRY, ≤ 10 ppm H₂O; 333 mg per 15 mL) by stirring at 60°C. Pyr₁₄TFSI, LiTFSI, and BP (5 wt% of PEO content) were then added and mixed until a homogeneous mixture was obtained. This paste was applied to one side of the Cg using a doctor blade, with the slit size adjusted to achieve a 12.5 μm thick PEO-based layer after drying for 30 min at room temperature in a dry room. For the cathode paste, PVDF-HFP (Sigma–Aldrich, molecular weight 400,000) was dissolved in NMP (500 mg per 5 mL) at 60°C, then mixed with Pyr₁₄TFSI, LiTFSI, and LATP (MSE PRO Solid Electrolyte, 300 nm; 325 mg). This PVDF-HFP-based paste was applied to the opposite side of the Cg using a doctor blade, forming a 12.5 μm thick layer after drying. The coated films were then dried at 60°C under reduced pressure for 48 h to remove ACN and NMP, followed by UV cross-linking for 10 min.

Electrochemical measurements: All CR2032 two-electrode coin cells were assembled in a dry room, utilizing 12 mm diameter round electrodes and 15 mm diameter electrolyte films, as illustrated in Figure S1. The separator (Cg2500) was coated on both sides with PEO-based and PVDH-HFP-based electrolyte pastes, following the preparation of the thin-film multilayer HSE part. A relatively thick 150 μm lithium foil was used as negative electrode. Electrochemical characterization was performed on a MACCOR Series 4000 battery tester (MACCOR, Inc.) at 60°C. All the cells were cycled at a constant current density of 0.1 mA cm⁻² within a voltage range of 3.00–4.25 V.

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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

Additional supporting information can be found online in the Supporting Information section.