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RESEARCH ARTICLE

Polymer-Assisted Supercooled Lithium Salts: Nonflammable Single-Ion Conducting Liquid Electrolytes for Next-Generation Batteries

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ABSTRACT

Electrolytes that exhibit both high ionic conductivity and a near-unity Li⁺ transference number (t_{Li}) are essential for next-generation rechargeable batteries. Here, we present solvent-free liquid electrolytes based on polymer-assisted supercooled lithium salts that realize single-ion conduction under ambient conditions. A trace amount of poly(methyl methacrylate) suppresses crystallization, stabilizing low-melting Li salts in a deeply supercooled liquid state while retaining $t_{\text{Li}} \approx 1$. To further enhance ion transport, we employ a dual-salt strategy, which lowers the glass transition temperature and increases ionic conductivity without compromising the near-unity t_{Li} . Despite moderate conductivity compared with conventional electrolytes, these supercooled salts suppress concentration overpotentials and support stable cycling in Li/LiCoO₂ cells. The intrinsic adhesive properties of the electrolytes enable the fabrication of binder-free thick cathodes with high areal capacities, providing a scalable route to high-energy-density batteries. Furthermore, the solvent-free nature of these electrolytes ensures intrinsic nonflammability and promotes the formation of robust inorganic-rich interphases, indicating their potential applicability to lithium-metal batteries. This work establishes polymer-assisted supercooled lithium salts as a new class of nonflammable single-ion conducting liquid electrolytes, bridging the gap between solid-state and conventional liquid systems.

1 | Introduction

The demand for Li-ion batteries (LIBs), particularly in the electric transport sector, has experienced significant growth driven by the increasing popularity of electric vehicles, which is accelerating the global transition toward sustainable transportation. However,

the charge/discharge rate of LIBs is insufficient to meet consumer expectations for automotive applications. LIBs capable of fast charging require electrolytes with both high ionic conductivity (σ) and a high Li⁺ transference number (t_{Li}) [1, 2]. At high charge/discharge rates, the concentration polarization of electrolytes with lower t_{Li} values is enhanced, even for electrolytes

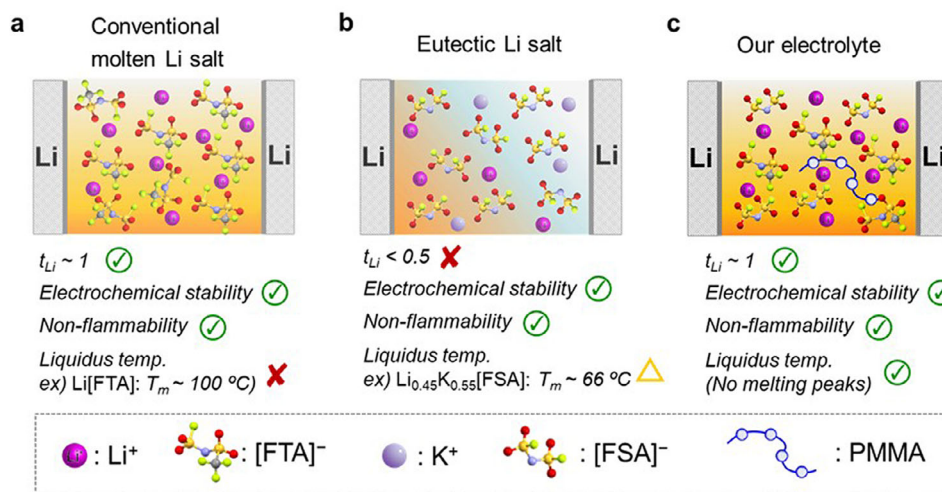


FIGURE 1 | Schematic salt concentration profiles in three molten salt-based electrolytes under applied voltage. (a) Conventional molten salts exhibit $t_{\text{Li}} \approx 1$ because no concentration gradient forms, but their T_{m} is high. (b) Eutectic mixtures with other alkali metal salts reduce T_{m} but lower the t_{Li} value. (c) Polymer-assisted supercooled lithium salts remain liquid at ambient temperature while retaining $t_{\text{Li}} \approx 1$.

with comparable ionic conductivity [3, 4]. Because the prevailing design principle for conventional liquid electrolytes prioritizes ionic conductivity, recent development of LIBs has focused on highly polar solvents and dissociative lithium salts with weak Lewis bases as their anions [5, 6]. The concentration of the lithium salt (c_{Li}) is usually chosen to be close to 1 mol dm⁻³ to maximize the ionic conductivity. However, the t_{Li} values of these electrolyte formulations are typically low (0.1–0.4). Numerous efforts to improve t_{Li} for fast Li⁺-conducting liquid electrolytes, including the use of polyanion-type lithium salts, weakly coordinating solvents, and salt enrichment strategies, have been reported [7–10]. Nevertheless, the presence of solvent molecules can form a salt concentration gradient in the electrolyte within the battery. Highly ion-conductive inorganic solid-state electrolytes with $t_{\text{Li}} = 1$ have been extensively investigated for all-solid-state batteries because they offer the potential for rapid charging. However, all-solid-state batteries present significant challenges in terms of their interface stability, manufacturing complexity, and scalability [11].

Against this background, we focus on molten Li salts, which are capable of achieving $t_{\text{Li}} \approx 1$ in the liquid form [12, 13]. In solvent-free molten salts, the salt concentration and density remain constant. Remarkably, the Li salt does not form a concentration gradient, even when current passes through the electrode–electrolyte interface under anion-blocking conditions [14]. Furthermore, molten Li salts are promising liquid electrolytes for Li-metal batteries owing to their high thermal and electrochemical stabilities [15]. Ultimately, the high salt concentration and inorganic-anion content of these systems promote the formation of a robust, inorganic-rich solid–electrolyte interphase (SEI) through preferential anion decomposition, a feature often observed in highly concentrated electrolytes [16]. However, the high melting points (T_{m}) and crystallinity of conventional molten Li salts have restricted their potential for battery applications at ambient temperature (Figure 1a) [17, 18]. Previous studies have shown that the melting point can be lowered to a certain extent by using eutectic systems of Li salts and the salts of other alkali metals, such as Na, K, and Cs [15, 19, 20]. Although these inor-

ganic salt mixtures preserve high thermal and electrochemical stabilities, while expanding the liquidus temperature range, the increase in the proportion of non-Li cationic species comes at the cost of a lowered t_{Li} value of the molten Li salt (Figure 1b).

Stabilizing the metastable supercooled liquid state can be considered another effective strategy for expanding the liquidus temperature range of molten Li salts. Polymer additives are frequently employed to preserve biological cells at low temperatures, owing to their ability to vitrify water, i.e., to prevent ice crystallization during deep supercooling [21, 22]. The addition of polymers can also allow the amorphization of crystalline pharmaceuticals [23]. This phenomenon can be attributed to the ability of polymers to exert substantial influence on the kinetics of crystal growth in molecular liquids and glasses, i.e., to act as an obstacle to crystal growth [23]. Motivated by these observations, we developed a novel strategy to design solvent-free “liquid” electrolytes by adding a polymer to the Li salts to suppress crystallization. This approach stabilizes the molten salt in a supercooled liquid state while retaining its desired properties, such as a Li⁺ transference number close to unity ($t_{\text{Li}} \approx 1$), and high thermal and electrochemical stabilities (Figure 1c). This contrasts with well-established salt-in-polymer or polymer-in-salt electrolytes [24, 25], which aim to primarily improve the ionic conductivity of “solid-state” polymer electrolytes [26–28]. In those systems, polymers served as a solid medium for Li salts, whereas in our approach they act as additives that impede Li salt crystallization.

In this study, we substantially suppressed the crystallization of Li salts even at ambient temperatures by incorporating a trace amount of polymer into the salt. In particular, Li salts with asymmetric anions or dual Li salt systems with different anions were used, and the ion transport and electrochemical properties of these polymer-assisted supercooled Li salts were characterized. Our findings demonstrated the potential of polymer-assisted supercooled Li salts as a promising class of single Li-ion conducting liquid electrolytes that can suppress the concentration overpotentials and improve the rate capability of lithium

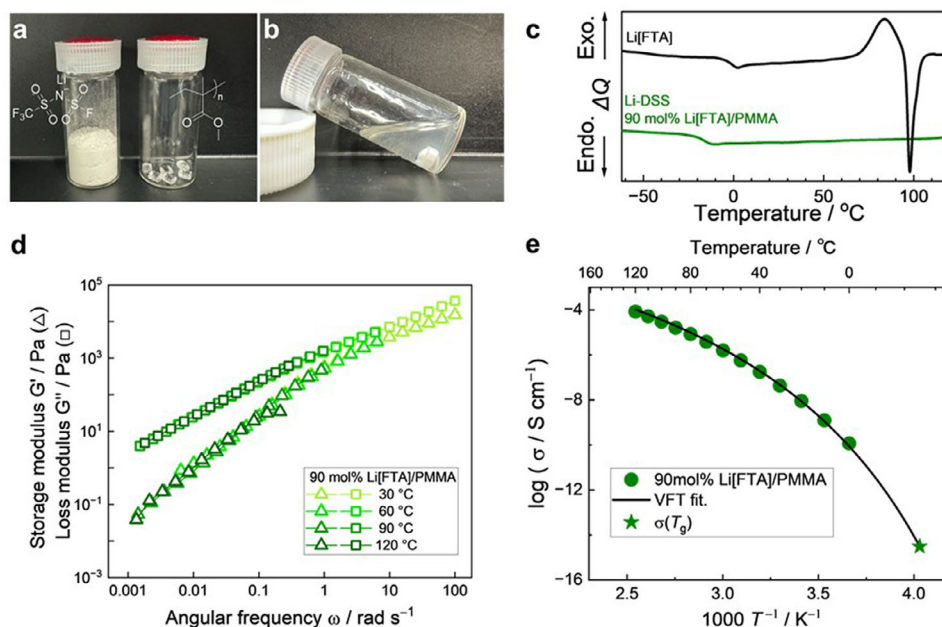


FIGURE 2 | Fundamental properties and ionic conductivity of Li-DSS. (a) Photographs of Li[FTA] salts and PMMA before mixing, and (b) the resulting Li-DSS (90 mol% Li[FTA] and 10 mol% PMMA, monomer-unit basis) showing a homogeneous liquid at ambient temperature. (c) DSC thermograms of Li[FTA] and Li-DSS at a heating rate of 5 °C min⁻¹. (d) Master curve of viscoelastic moduli G' (storage) and G'' (loss) constructed by time-temperature superposition. (e) Temperature dependence of ionic conductivity (σ) in Arrhenius form with VFT fitting and extrapolation to $\sigma(T_g)$.

batteries. Furthermore, a simple process to fabricate thick electrodes was successfully established using our electrolytes comprising deeply supercooled Li salts. Such thick electrodes represent a key trend toward achieving high-energy-density batteries.

2 | Results and Discussion

2.1 | Polymer-Assisted Stabilization of Supercooled Lithium Salts

Figure 2a shows photographs of lithium (fluorosulfonyl) (trifluoromethanesulfonyl)amide (Li[FTA]), which has a relatively low melting point ($T_m \approx 100$ °C) [17, 18] in conjunction with poly(methyl methacrylate) (PMMA), which is compatible with amide-type ionic liquids [29, 30]. Upon mixing Li[FTA] and PMMA in a molar ratio of 9:1 (monomer-unit of PMMA) in a co-solvent, followed by evaporation of the latter under high vacuum, a macroscopically homogeneous liquid-state mixture was produced at ambient temperatures (Figure 2b). The absence of residual co-solvent (acetonitrile) was confirmed via Fourier-transform infrared spectroscopy (FT-IR; Figure S1a, Supporting Information) [31]. Based on prior observations that polymers above the overlap concentration (c^*) can delay the first nucleation event via geometric crowding, we targeted a semi-dilute PMMA concentration regime ($c^* < c < c_e$) that hinders nucleation without forming an elastic network in the entangled regime (c_e) [23]. In our system, the 90 mol% Li[FTA] / 10 mol% PMMA formulation at the processing temperature falls within this semi-dilute regime and is therefore used as the standard composition in this study. The thermal properties of Li[FTA]

with/without PMMA were examined by differential scanning calorimetry (DSC) measurements (Figure 2c). The DSC curve of neat Li[FTA] shows a crystallization peak at 83.8 °C and a subsequent melting peak at 97.9 °C. In contrast, neither of these peaks was discernible for the Li[FTA]/PMMA mixture, indicating that the crystallization of Li[FTA] is significantly suppressed in the presence of PMMA. Additionally, the observed decrease in the glass transition temperature (T_g) from -5 °C to -25 °C indicated that the trace amount of PMMA functions as a plasticizer. Despite the extremely high concentration of lithium salt (95.5 wt%), the supercooled liquid state of the mixture persisted at ambient temperature for at least two months. We examined the potential use of this mixture, designated the “Li-deeply supercooled salt” (Li-DSS), as a liquid electrolyte for LIBs.

The viscoelastic behavior of Li-DSS under practical conditions was studied using oscillatory shear measurements at different temperatures, and time-temperature superposition was applied to construct a master curve at 30 °C (Figure 2d). The resulting master curve demonstrated that the storage modulus (G') remained consistently lower than the loss modulus (G'') across the entire angular frequency range, indicating a dominant liquid-like response. This finding indicates that a substantial elastic network does not form in the system, a property that is inconsistent with the definition of solid polymer electrolytes.

Understanding ionic conduction, particularly the coupling or decoupling of ionic conductivity from structural relaxation, has been the focus of numerous studies on polymer-based electrolytes. The temperature dependence of the ionic conductivity (σ) of Li-DSS (90 mol% Li[FTA]/PMMA) (Figure 2e) reveals that Li-DSS exhibits ion-conducting behavior without crystallization

in the tested temperature range of 0–120 °C. The effects of the polymer additive on the ionic conduction were verified by analyzing the temperature dependence of the ionic conductivity using the Vogel–Fulcher–Tammann (VFT) equation, which accounts for the non-Arrhenius temperature dependence typically observed in glassy or amorphous materials. The VFT model expresses conductivity as a function of temperature via Equation (1):

$$\sigma(T) = AT^{-1/2} \exp[-B/(T - T_0)] \quad (1)$$

where A is a pre-exponential factor proportional to the number of carrier ions, B is the pseudo-activation energy for ionic conduction, and T_0 is the ideal glass transition temperature. All fitting parameters are reported in Table S1 (Supporting Information). The Arrhenius plots of σ for Li-DSS were fitted using the VFT equation, and this enabled the ionic conductivity at T_g , $\sigma(T_g)$, to be estimated [32–34]. In turn, the decoupling index (R_τ), defined as the ratio of the conductivity relaxation time to the structural relaxation time, could be estimated from the $\sigma(T_g)$ value by using the following relationship [35, 36]:

$$\log R_\tau \approx 14.3 + \log \sigma(T_g) \quad (2)$$

The estimated value of $\log R_\tau$ for Li-DSS was 0.2, indicating that the ionic motion of Li-DSS is strongly coupled to the structural relaxation. This suggests that the polymer component contributes negligibly to the ion transport dynamics, and that the Li salt serves as the primary mobile species. As a result, the overall relaxation dynamics are predominantly governed by the motion of the salt, which constitutes the majority of the system.

2.2 | Ion Transport and Structural Dynamics

Although the addition of a minimal quantity of polymer enables the lithium salts to maintain the supercooled liquid state, even at ambient temperature, the pronounced coupling between the structure and dynamics (indicated by R_τ) and the relatively high glass transition temperature (T_g , -25°C) resulted in low conductivity. To further lower the T_g of Li-DSS, we employed a dual-salt strategy [37] using lithium bis(fluorosulfonyl)amide (Li[FSA]), which has a lower T_g than Li[FTA] (Figure S2, Supporting Information), as the second salt. Mixing two lithium salts can depress T_m and T_g and suppress crystallization [38, 39]. These effects widen the liquidus window and modestly improve transport properties below T_m . Although mixing Li salts with other alkali-metal salts also lowers T_m and T_g , we did not explore such mixed alkali-metal salt systems as they can reduce t_{Li} [15]. The T_g values of the binary salts of Li[FTA] $_x$ [FSA] $_{1-x}$ ($0 \leq x \leq 1$) and the corresponding DSC curves are presented in Figure 3a and Figure S2 (Supporting Information), respectively. The T_g of the binary salt decreases monotonically with increasing Li[FSA] content. As a result, the T_g of the dual-salt Li-DSS (90 mol% Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$] in PMMA by repeating unit) was significantly lower by 21.1°C compared to that of the single-salt Li-DSS (90 mol% Li[FTA]/PMMA). The supercooled state persisted at room temperature for more than eight months (Figure 3b; Figures S3 and S4, Supporting Information). However, a further increase in the Li[FSA] content ($x \geq 0.7$) of the binary salt resulted

in the crystallization of Li[FSA], which hinders the preparation of long-term stable Li-DSS (Figure 3b).

As shown in Figure 3c, the dual-salt Li-DSS outperformed the single-salt Li-DSS in ionic conductivity across a broad temperature range (0–120 °C). This enhancement of the ionic conductivity with the dual-salt is more pronounced especially at lower temperatures (e.g., at 30°C , $\sigma_{\text{dual}} = 1.5 \times 10^{-6} \text{ S cm}^{-1}$ and $\sigma_{\text{single}} = 7.5 \times 10^{-8} \text{ S cm}^{-1}$), which reflects the lower T_g value of dual Li-DSS. To elucidate the factors contributing to the improved ionic conductivity, the self-diffusion coefficients (D) of the ionic species in Li-DSS were measured using pulsed-field-gradient (PFG)-NMR (Figure 3d; Table S2, Supporting Information). Remarkably, over the studied temperature range, Li^+ diffusion in the dual-salt system is nearly twice as fast as in the single-salt system, even though the [FTA] $^-$ anion exhibits comparable diffusion coefficients in both cases. An analogous trend was observed for molten lithium salts without the polymer (Figure S5, Supporting Information) [40]. Notably, the self-diffusion coefficient of [FSA] $^-$ in the dual Li-DSS is greater than that of [FTA] $^-$, in line with previous reports that ions with higher conformational flexibility reduce viscosity and enhance ionic diffusivity in ionic liquids [41, 42]. Density functional theory calculations of [FSA] $^-$ and [FTA] $^-$ revealed that the internal rotational barrier of the N–S bond of the N–SO $_2$ –F group is lower than that of N–SO $_2$ –CF $_3$ (Figure S6, Supporting Information) [43]. The higher diffusivity of [FSA] $^-$ is therefore attributable to the more flexible conformational change. In addition, the enhanced self-diffusion of ionic species in the dual Li-DSS increases the overall ionic conductivity. The partial substitution of [FTA] $^-$ with the smaller [FSA] $^-$ anion further raises the charge carrier density, thereby enhancing conductivity.

To examine the influence of polymer incorporation on ion transport dynamics, we conducted atomistic MD simulations (Table S3, Supporting Information). The systems studied were 90 mol% Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$]/10 mol% PMMA (4-mer) and the corresponding polymer-free dual-salt melt, both at 140°C . The snapshot in Figure 3e shows that PMMA occupies only a minor fraction of the volume, whereas the dual-salt matrix forms the continuous phase. MD snapshots of Li^+ -solvation microenvironments, radial distribution functions and cumulative coordination numbers reveal clear Li^+ –O $_{\text{carbonyl}}$ (PMMA) contacts, indicating that the carbonyl groups of PMMA participate in coordination (Figures S7–S9, Supporting Information). On a repeating unit basis, the number of Li^+ ions is approximately nine times higher than the number of PMMA carbonyl oxygens. This imbalance ensures that the dominant first-shell donors around Li^+ remain the anion oxygens of [FTA] $^-$ and [FSA] $^-$ (Figure S10a, Supporting Information). Consequently, the local solvation structure in the polymer-containing system closely resembles that of the polymer-free molten salt (Figure S10b, Supporting Information). Consistent with this structural snapshot, mean-square-deviation analysis (Figure 3f) revealed that the essential transport characteristics of the molten salt are maintained upon polymer addition: Li^+ diffuses faster than the anion in both systems (Figure S11, Supporting Information). In other words, ~ 10 mol% PMMA introduces only weak coordination and minor local perturbations, leaving the dual-salt matrix as the primary determinant of ion transport. Ab initio calculations show that the interaction between Li^+ –[FTA] $^-$ and [FSA] $^-$ is significantly

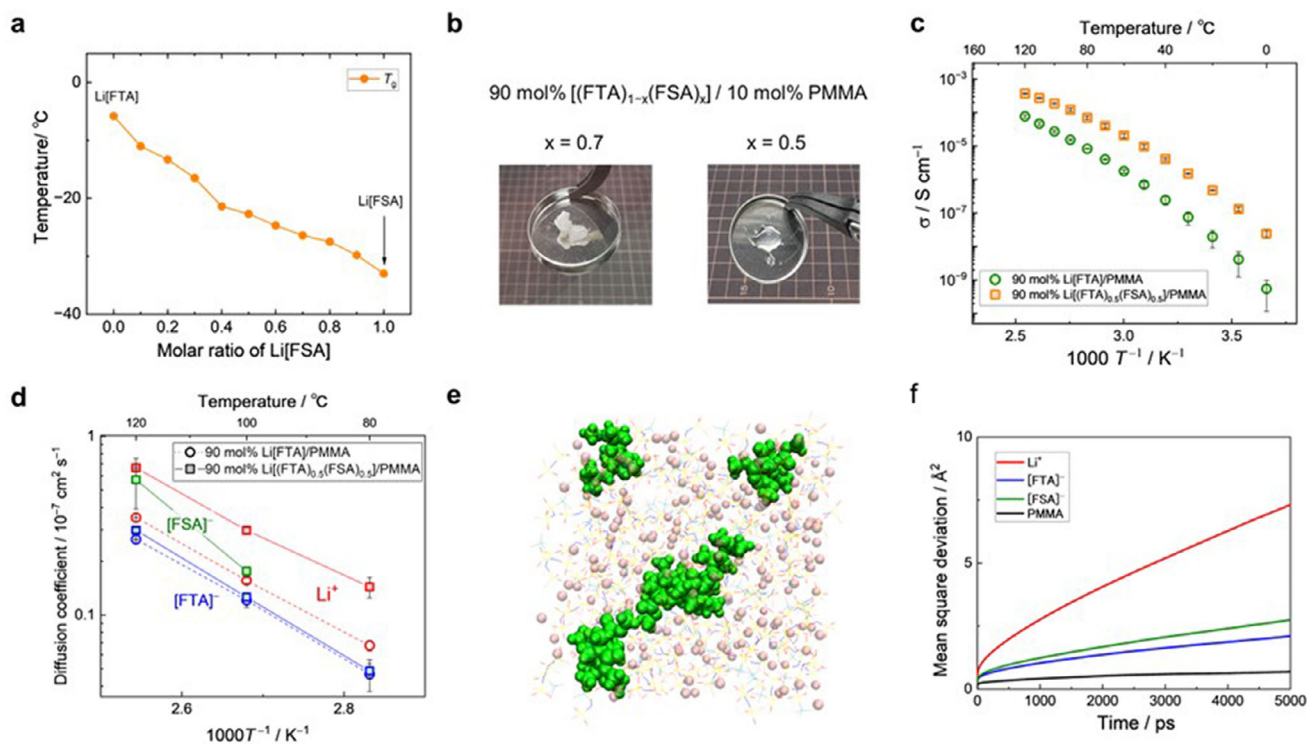


FIGURE 3 | Enhanced ion transport in dual-salt Li-DSS electrolytes. (a) T_g of binary salts Li[(FTA) $_x$ (FSA) $_{1-x}$] ($0 \leq x \leq 1$). (b) Photographs of 90 mol% Li[(FTA) $_{0.3}$ (FSA) $_{0.7}$]/PMMA and 90 mol% Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$]/PMMA after preparation. (c) Temperature dependence of ionic conductivity for single-salt Li-DSS (90 mol% Li[FTA]/PMMA, green) and dual-salt Li-DSS (90 mol% Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$]/PMMA, orange). (d) Comparison of ion diffusivities (Li $^+$: red, [FTA] $^-$: blue, [FSA] $^-$: green) between single- and dual-salt Li-DSS. (e) MD snapshot of 90 mol% Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$]/PMMA (4-mer) at 140°C, showing salt-rich domains (Li $^+$: pink spheres; anions: sticks) and PMMA segments (green). (f) Mean-square displacement (MSD) profiles of ions and PMMA at 140°C (Li $^+$: red, [FTA] $^-$: blue, [FSA] $^-$: green, PMMA: black).

stronger than that between Li $^+$ –PMMA (Figures S12–S14, Supporting Information). Together with the experimental results, the simulations demonstrate that the dual-salt Li-DSS maintains its molten-salt dynamics even with this polymer content, ensuring a Li $^+$ transference number (t_{Li}) close to unity.

2.3 | Li $^+$ Transference Number and Electrochemical Stability

The t_{Li} value of the dual Li-DSS was evaluated using the potentiostatic polarization method with a Li/Li symmetric cell under anion-blocking conditions [44–46]. Figure 4a shows the potentiostatic polarization curve and Nyquist plots measured at 30°C. Notably, the absence of current decay during polarization indicated that the formation of a salt concentration gradient was negligible. The Nyquist plot based on electrochemical impedance measurements on the same symmetric cell showed evident semicircles, confirming the absence of short-circuiting in the cell. The estimated Li $^+$ transference number under the anion-blocking condition (t_{Li}^{abc}) of the dual Li-DSS is almost unity (0.99), representing a liquid electrolyte that approaches single-ion (Li $^+$) conduction at ambient temperature. The parameters required for the calculations are summarized in Table S4 (Supporting Information).

The extremely high t_{Li}^{abc} value in the dual Li-DSS can be validated by estimating the Li $^+$ transference number in different frames

of reference (FoRs) [47–50]. Here, the FoR refers to the choice of a dynamic baseline against which ion motion is described; for example, whether the anion is considered stationary or mobile. This distinction is particularly important to accurately interpret transference numbers. Moreover, the combination of multiple FoRs can offer complementary perspectives on ion dynamics and transport behavior. For instance, in the case of an anion-fixed FoR, such as under anion-blocking conditions, the velocity of the anion is assumed to be zero. Consequently, the transference number of the cation becomes unity in molten-salt electrolytes, where no other molecular species contribute to charge transfer [47]. Additionally, in a solvent-free molten salt (C $^+$ A $^-$) that cannot form a salt concentration gradient, the transference number of the cation (t_c) can be expressed as $t_c^M = M_A/(M_C + M_A)$ in a mass-fixed FoR, and $t_c^V = V_A/(V_C + V_A)$ in a volume-fixed FoR, where M_C , M_A and V_C , V_A are the masses and volumes of the cations and anions, respectively [47, 51]. On the basis of the mass-based description, t_c^M is estimated to be 0.97 for Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$] (see Supporting Information for detailed calculations). In the volume-based description, the Li $^+$ transference number for Li[(FTA) $_{0.5}$ (FSA) $_{0.5}$] is 0.99, calculated using the Conductor-like Screening Model (COSMO)-based protocol proposed by Zhu et al. (Figure S15 and Table S5, Supporting Information) [52]. Remarkably, these theoretical values are highly comparable to the experimental value of t_{Li}^{abc} (= 0.99) for the dual-salt Li-DSS even in the presence of the polymer additive. Recent electrophoretic NMR studies of ionic liquids demonstrated that local molar volume conservation governs ion transport in

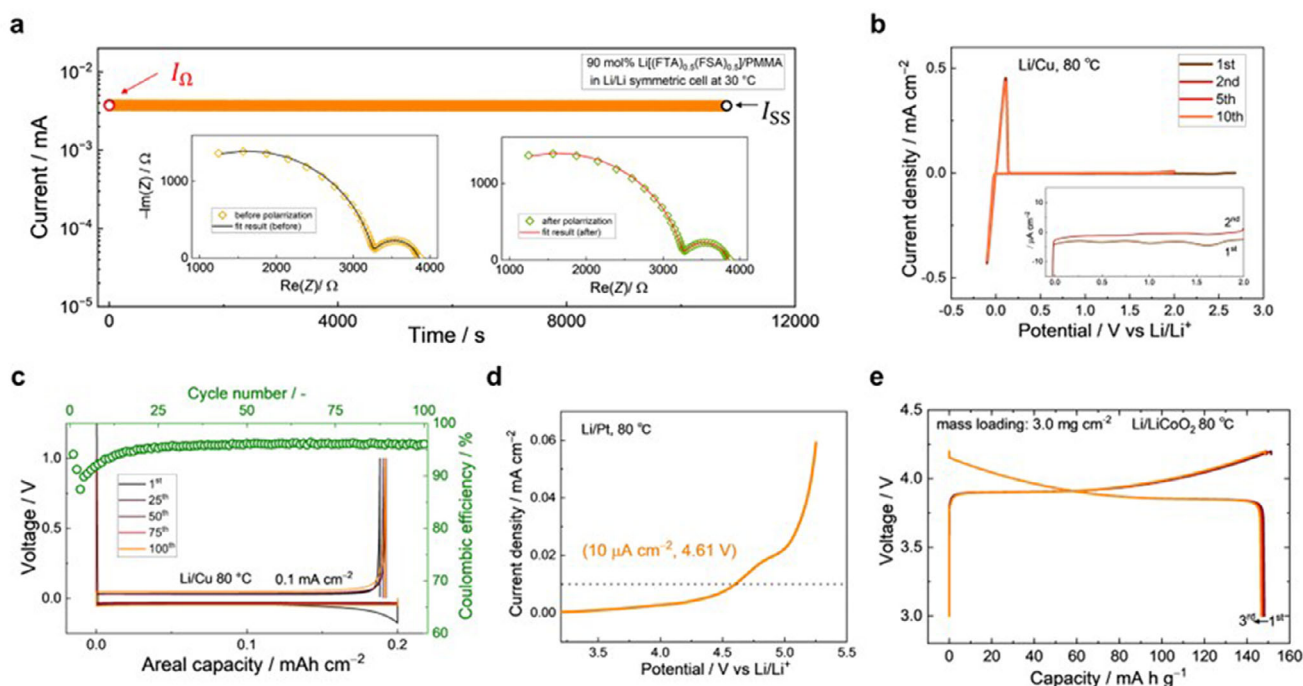


FIGURE 4 | Li⁺ transference number, electrochemical stability, and battery performance of dual-salt Li-DSS. (a) Potentiostatic polarization curves and Nyquist plots of a Li/Li symmetric cell with dual-salt Li-DSS at 30 °C. (b) Cyclic voltammograms of Li/Cu cells. (c) Li deposition/dissolution profiles and Coulombic efficiency of Li/Cu cells. (d) Linear sweep voltammograms of Li/Pt cells. (e) Charge/discharge profiles of Li/LiCoO₂ cells with dual-salt Li-DSS at 0.1 mA cm⁻² and 80 °C.

concentrated electrolyte systems [50, 51], supporting the notion that the ion transport in Li-DSS is similarly controlled by the volume conservation effects. Given its low concentration, the polymer additive appears to minimally influence the t_{Li} value in the electrochemical cell. Consequently, PMMA functions as an anti-crystallizing agent, suppressing nucleation and growth while preserving the near-unity t_{Li} of molten Li salts. This capability enables practical battery applications at lower temperatures.

The applicability of dual-salt Li-DSS to Li secondary batteries was demonstrated by electrochemical tests probing interfacial stability and Li plating/stripping reversibility. To overcome the inherent wettability issue of standard porous polyolefin separators toward highly viscous Li-DSS, an aramid-coated polyolefin membrane was used as a separator in the electrochemical tests [53, 54]. Although all subsequent measurements were conducted at 80 °C because the ionic conductivity is insufficient for battery application at 30 °C, this temperature is significantly lower than those typically employed for molten Li salt electrolytes, which often require 100 °C or higher [12, 14]. Notably, the test was performed at temperatures below the melting point of Li[FTA] and Li[FSA], which highlights the feasibility of low-temperature operation compared to conventional systems.

The reductive stability of the dual-salt Li-DSS (90 mol% Li[(FTA)_{0.5}(FSA)_{0.5}]/10 mol% PMMA) electrolyte was evaluated in Li/Cu cells using cyclic voltammetry (CV) (Figure 4b). In the initial CV cycle (inset of Figure 4b), the reductive current observed at approximately 1.0–1.7 V is attributable to the reductive decomposition of the electrolyte [55, 56]. This reductive current

was not observed in any of the subsequent cycles, indicating reversible plating and stripping of the Li metal over the tested cycles. The dual-salt Li-DSS electrolyte exhibited stable Li plating/stripping over 10 cycles, suggesting its reductive stability. Chronopotentiometry in Li/Cu cells (Figure 4c) further validated this stability during Li deposition/dissolution. As in the CV measurements, an increase in overpotential was observed during the initial cycle, likely due to interfacial formation processes. However, reversible Li deposition/dissolution profiles were subsequently obtained during extended cycling. Although the average Coulombic efficiency (CE) was moderate (~96%), no short-circuiting occurred over 100 cycles, indicating adequate interfacial stability and compatibility with Li metal even at 80 °C. To investigate the relatively low CE, a pseudo-Tafel analysis based on CV measurements was performed in accordance with a previous report [57]. The results reveal a small decrease in the apparent exchange current density upon cycling (Figure S16, Supporting Information). This suggests progressive SEI growth that limits CE to ~96%; replacing CF₃-bearing FTA anion is expected to promote the formation of a LiF-rich SEI and thereby achieve higher CE. The oxidative stability of the dual-salt Li-DSS was evaluated by linear sweep voltammetry (LSV) in Li/Pt cells (Figure 4d). A measurable oxidative current exceeding 0.01 mA cm⁻² was only observed beyond 4.6 V vs. Li/Li⁺, indicating that the dual-salt Li-DSS is compatible with 4-V-class lithium batteries. To validate the compatibility of the dual Li-DSS with 4-V-class cathodes, galvanostatic charge/discharge tests were conducted on a Li/LiCoO₂ cell (Figure 4e). The cell demonstrated reversible charge/discharge behavior with high Coulombic efficiencies (>99%) and exhibited reversible capacities close to the theoretical capacity of LiCoO₂ (136 mA h g⁻¹).

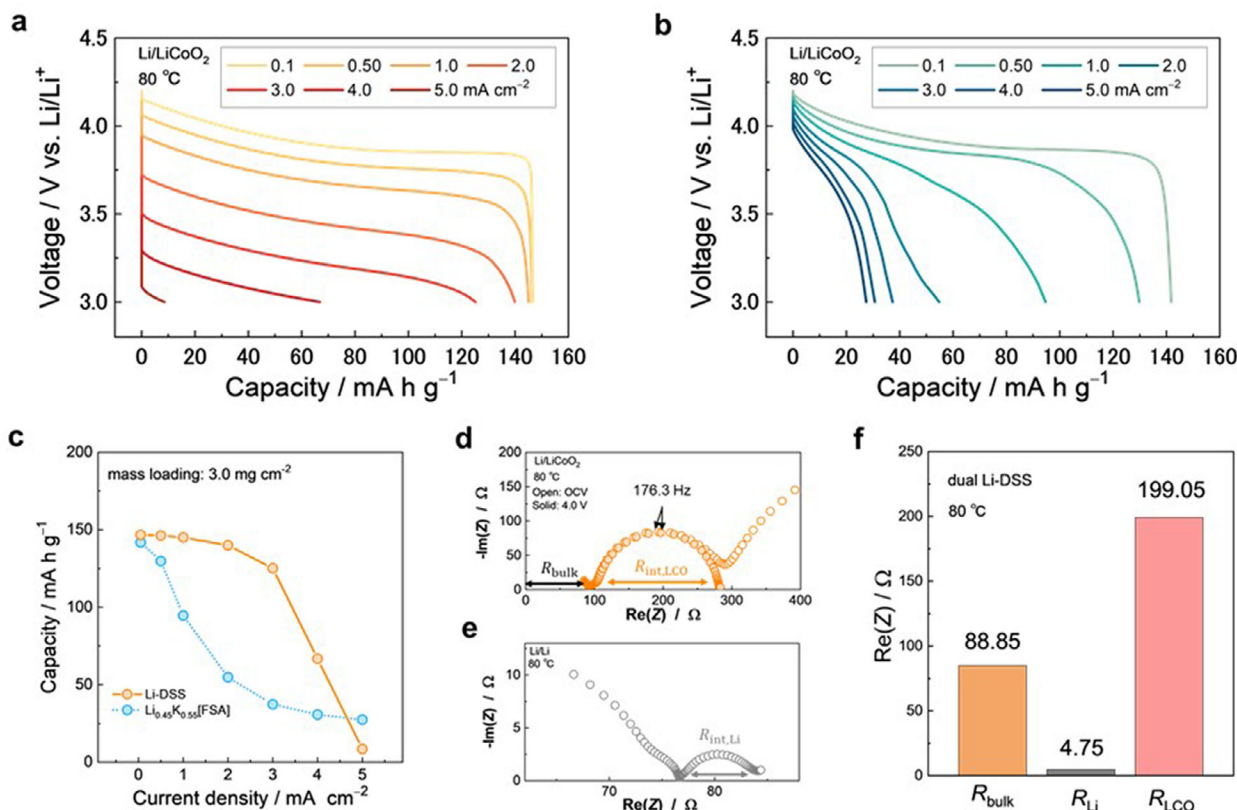


FIGURE 5 | Rate performance and impedance analysis of Li/LiCoO₂ cells with dual-salt Li-DSS at 80°C. (a) Discharge curves of Li/LiCoO₂ cells with dual-salt Li-DSS (90 mol% Li[(FTA)_{0.5}(FSA)_{0.5}]/PMMA) and (b) Li_{0.45}K_{0.55}[FSA] at various current densities (0.1–5.0 mA cm⁻²). (c) Comparison of discharge capacities between the two electrolytes. Nyquist plots of (d) Li/LiCoO₂ and (e) Li/Li symmetric cells measured at open-circuit voltage (OCV, open symbols) and at 4.0 V (solid symbols) at 80°C. (f) Deconvolution of total cell resistance into bulk resistance (R_{bulk}), interfacial resistance at the Li electrode (R_{Li}), and at the LiCoO₂ electrode (R_{LCO}).

2.4 | Rate Capability and Impedance Behavior of Li/LiCoO₂ Cells

The advantageous effect of the high $t_{\text{Li}}^{\text{abc}}$ in the Li-DSS on the battery performance was demonstrated by conducting rate capability tests using Li/LiCoO₂ cells (Figure 5a–c). Particular attention was paid to the shape of the discharge profiles, as they provide insight into the occurrence of concentration polarization at high current densities. For comparison, the rate capability of the cell with a typical eutectic molten salt, Li_{0.45}K_{0.55}[FSA], was also evaluated [15, 19]. At a low current density of 0.1 mA cm⁻², the discharge capacities of both cells were comparable at approximately 140 mA h g⁻¹. However, pronounced differences emerged at higher current densities. The discharge capacity of the Li_{0.45}K_{0.55}[FSA] cell decreased sharply to 37.3 mA h g⁻¹ at 3 mA cm⁻², accompanied by a sloped discharge profile indicative of severe concentration overpotential. In contrast, the cell with Li-DSS retained a high discharge capacity of 125.1 mA h g⁻¹ under the same conditions, with minimal profile distortion. Despite the noticeable initial iR drop, the slope of the discharge profile remained nearly unchanged across the current range, suggesting that the concentration overpotential was negligible even at high current densities. This notable performance of dual-salt Li-DSS is associated with its lithium-ion transference number ($t_{\text{Li}}^{\text{abc}}$) that is close to unity. The high transference number intrinsically suppresses the concentration polarization of the Li salt within

the cell, thereby preventing the system from reaching a diffusion-limited condition even at high discharge rates [14]. Conversely, the Li_{0.45}K_{0.55}[FSA] system has a much lower $t_{\text{Li}}^{\text{abc}}$ value (0.45) as shown in Figure S17 (Supporting Information). As a result, despite the fivefold higher ionic conductivity of Li_{0.45}K_{0.55}[FSA] (0.72 mS cm⁻¹) compared to that of dual-salt Li-DSS (0.16 mS cm⁻¹) at 80°C, its rate capability was markedly inferior. This comparison makes clear that the Li⁺ transference number plays a more decisive role than the total ionic conductivity in ensuring high-rate performance. This interpretation is further supported by the discharge profiles corrected for iR drop (Figure S18, Supporting Information). After eliminating the initial ohmic contribution, the Li-DSS cell exhibited nearly overlapping curves across all current densities, whereas the profiles for the Li_{0.45}K_{0.55}[FSA] cell diverged significantly. This comparison illustrates the difference in the concentration polarization behavior between the two systems, further highlighting the advantage of a high $t_{\text{Li}}^{\text{abc}}$ value in mitigating ion accumulation at high discharge rates.

Despite the suppression of concentration polarization, the Li-DSS cell still showed pronounced initial voltage drops at high current densities. To identify the source of the pronounced iR drop at high current densities, we performed electrochemical impedance spectroscopy (EIS) at both the open-circuit voltage (OCV) and the LiCoO₂ redox potential (4.0 V) (Figure 5d). Interestingly, the Nyquist plots under these two conditions

nearly overlap, suggesting that the charge-transfer resistance at the LiCoO_2 /electrolyte interface contributes negligibly to the iR drop in the discharge profile. The impedance spectrum of the Li/Li symmetric cell (Figure S5e) revealed significantly lower overall resistance, indicating minimal resistance at the Li metal interface. Instead, the dominant impedance likely arises from Li ion transport within the porous LiCoO_2 electrode structure. These observations are quantitatively summarized in Figure 5f: the extracted bulk resistance (R_{bulk}), Li interfacial resistance (R_{Li}), and LiCoO_2 -side interfacial resistance (R_{LiCo}) are 88.95, 4.75, and 199.05 Ω , respectively. The moderate bulk resistance reflects the intrinsically low ionic conductivity of the dual-salt Li-DSS, whereas the relatively high resistance on the LiCoO_2 side indicates that Li ion transport within the porous electrode structure also contributes substantially to the observed iR drop at high current densities. This increased resistance on the LiCoO_2 side is likely associated with the limited infiltration of the porous electrode structure by the highly viscous Li-DSS with a viscosity of $\sim 2 \times 10^5$ mPa s at 80°C (Figure S19, Supporting Information). Although thin LiCoO_2 electrodes were used here to minimize these effects, practical batteries will require thicker electrodes with higher active-material loadings. We therefore explored strategies to improve electrolyte penetration and alleviate ion-transport limitations in such porous structures.

2.5 | Binder-Free Thick Electrode Fabrication and Performance

The high viscosity of the dual-salt Li-DSS presents challenges in terms of the post-impregnation of porous electrodes, potentially limiting uniform electrolyte distribution and performance consistency (Figure 6a). To address this conundrum, we explored an alternative fabrication strategy in which the Li-DSS electrolyte is directly incorporated into the electrode during preparation (Figure 6b). This approach, in which the electrolyte is pre-mixed with the electrode materials prior to electrode fabrication, not only offers a scalable path to high-mass-loading cathodes but also eliminates the need for using the environmentally harmful *N*-methyl-2-pyrrolidone (NMP) solvent when manufacturing the cathode. In addition, given the confirmed adhesion of Li-DSS to metal surfaces (Figure S20, Supporting Information), the electrode was fabricated without a binder, inspired by previous reports on poly(ionic liquids) or polysalts serving as ion-conducting binders in composite electrodes [58–60]. This approach allowed the preparation of thick, high-mass-loading cathodes due to the strong adhesive and cohesive properties of the dual-salt Li-DSS. Importantly, this binder-free architecture eliminates the need for polymeric binders—commonly used to maintain the structural integrity of thick electrodes but often increasing internal resistance—while still ensuring mechanical stability and continuous ion-conduction pathways [61].

The binder-free cathode was prepared by blending the active material (LiCoO_2), conductive carbon (acetylene black), and dual-salt Li-DSS in a mass ratio of 66.7:8.3:25 to form a clay-like paste. This mixture was then molded into electrode sheets directly onto aluminum foil using a hot-pressing process. The resulting binder-less electrode exhibited excellent adhesion, with no delamination of the active material or conductive carbon from the current collector (Figure 6c). The elemental mapping

images acquired via SEM-EDX analysis (Figure 6d; Figure S21, Supporting Information) demonstrate the uniform spatial distribution of all electrode components. All three of these elements are homogeneously distributed throughout the composite while interconnecting with each other. This confirms that the three components had been successfully and uniformly mixed during electrode fabrication to create ion and electron conduction paths within the composite electrode.

In an additional evaluation of the utility of the binder-free electrode approach, we compared two types of electrodes: a conventional electrode (~ 1.5 mAh cm^{-2}) that contains a polymeric binder, and a thick, high-mass-loading electrode (~ 3.8 mAh cm^{-2}) that was fabricated using the binder-free method. As shown in Figure 6e, both the conventional composite cathode (mass loading 10 mg cm^{-2} , red) and the binder-free, high-loading cathode (28 mg cm^{-2} , orange) display reversible charge–discharge profiles at 80°C . Their initial discharge capacities, 1.33 and 3.37 mAh cm^{-2} , respectively, correspond to 88.6% and 87.9% of the theoretical value for each of these electrodes, demonstrating that the binder-free fabrication preserves active-material utilization even at three-fold higher mass loading. The remaining (approx. 12%) difference is ascribed to sub-optimal phase connectivity and electrolyte distribution; further optimization of the LiCoO_2 :AB:Li-DSS ratio and improved dispersion techniques are expected to narrow this discrepancy.

Notably, as shown in the inset of Figure 6e, the initial iR drop (~ 125 mV) of the binder-free electrode is comparable with that of the conventional electrode (~ 145 mV), despite the substantially greater mass loading of the former electrode. These results demonstrate that integrating the pre-mixed electrolyte with the electrode ensures continuous ionic pathways throughout the electrode structure, even at a considerable thickness of 140 μm . The solvent- and binder-free approach eliminates NMP and drying steps, providing a straightforward and scalable route to electrode fabrication.

3 | Conclusion

In summary, we demonstrated a new class of liquid electrolytes with near-unity Li^+ transference numbers, achieved by suppressing Li-salt crystallization using a small polymer additive. These polymer-assisted supercooled Li salts remain stable in the liquid state even at room temperature. Employing dual Li salts further enhanced both the stability of the supercooled state and the ionic conductivity of Li-DSS. Dual-salt Li-DSS, composed of 90 mol% $\text{Li}[(\text{FTA})_{0.5}(\text{FSA})_{0.5}]$ and 10 mol% PMMA, exhibits a Li^+ transference number of almost unity under anion-blocking conditions. Li/LiCoO₂ cells with dual-salt Li-DSS demonstrate high rate capability with suppressed concentration overpotentials. As a further enhancement of the practicality, we demonstrated the integration of dual-salt Li-DSS into binder-free, thick electrodes with high areal capacity. Although improvement of the bulk ionic conductivity remains a future challenge, this work provides a design principle for nonflammable liquid electrolytes that enable near single Li-ion conduction and the formation of a facile electrode/electrolyte interface for future battery technologies. Future developments of Li-DSS should focus on enhancing room-temperature ion transport by adjusting Li-salt compositions and

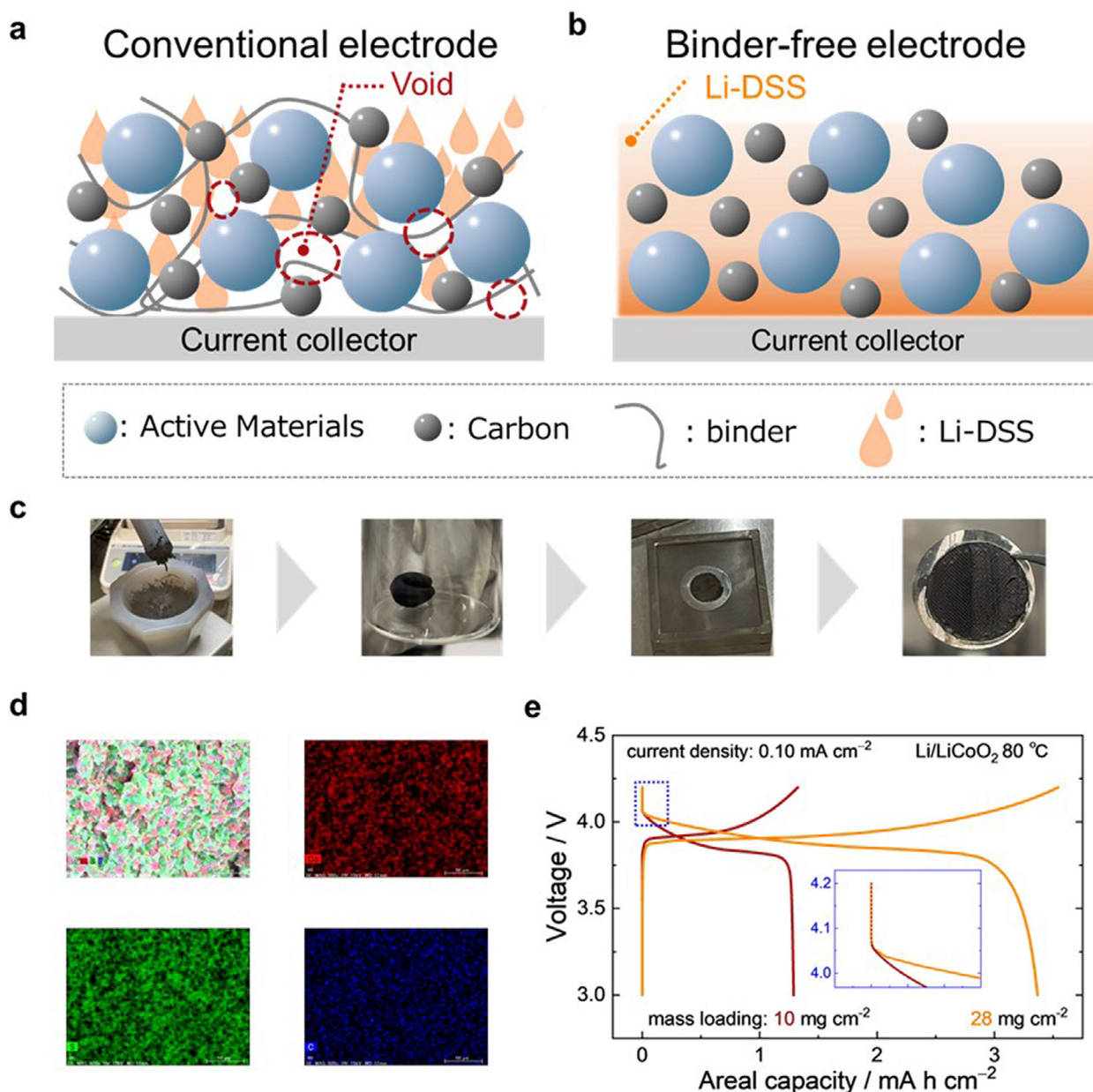


FIGURE 6 | Fabrication and performance of a high-mass-loading binder-free cathode with dual-salt Li-DSS. (a) Conceptual illustration of poor electrolyte infiltration and void formation when high-viscosity Li-DSS is drop-cast onto a conventional thin electrode, and (b) a binder-free composite electrode where dual-salt Li-DSS is directly incorporated. (c) Step-by-step photographs of the fabrication process. (d) SEM-EDX composite image of the binder-free cathode showing distributions of active material (Co, red), Li-DSS (S, green), and carbon (C, blue). (e) Charge/discharge profiles of Li/LiCoO₂ cells at 80°C using a conventional composite electrode (10 mg cm^{-2} , red) and a high-mass-loading binder-free cathode (28 mg cm^{-2} , orange). The inset magnifies the initial iR drops for each electrode.

through rational design of low-melting Li salts and coordinating polymers. Such approaches are expected to improve diffusivity and conductivity while preserving the supercooled state and achieving a near-unity t_{Li} .

4 | Experimental Section

4.1 | Materials

Lithium(fluorosulfonyl)(trifluoromethanesulfonyl)amide (Li[FTA], 98.0–103.0%), poly(methyl methacrylate) (PMMA,

$M_w \approx 48\,000$), and super-dehydrated acetonitrile were purchased from FUJIFILM Wako Pure Chemical Co. (Japan). Lithium bis(fluorosulfonyl)amide (Li[FSA], battery grade; water content <100 ppm) was obtained from Kishida Chemical Co., Ltd. (Japan), and potassium bis(fluorosulfonyl)amide (K[FSA], >95%) from Tokyo Chemical Industry Co., Ltd. (Japan). Li[FTA], Li[FSA], K[FSA], and acetonitrile were used as received. PMMA was dried under vacuum at 65°C overnight before use. All mixing procedures were conducted in an argon-filled glovebox with H₂O levels below 0.5 ppm. The Li salt/PMMA mixtures were prepared at the desired molar ratios in acetonitrile and stirred overnight.

Binary salts of $\text{Li}[\text{FTA}]_x[\text{FSA}]_{1-x}$ ($0 \leq x \leq 1$) and $\text{Li}_{0.45}\text{K}_{0.55}[\text{FSA}]$ were prepared by mortar grinding, followed by melting at 140°C without any co-solvent. $\text{Li}[\text{FTA}]/\text{PMMA}$ mixtures were dried at 65°C for 24 h, with the temperature gradually increased from 45°C to 65°C to prevent thermal stress. Acetonitrile was then removed by vacuum drying at 105°C for 2 h. Mixtures containing $\text{Li}[\text{FSA}]$ were dried using an oil rotary pump at 65°C for 24 h, also by slowly ramping the temperature from 45°C . Subsequently, acetonitrile was removed under high vacuum using a turbomolecular pump at room temperature for 20 h. The absence of residual acetonitrile in all samples was confirmed by FT-IR spectroscopy (Figure S1a, Supporting Information).

4.2 | Thermal Properties

The thermal properties of Li-DSS were analyzed using differential scanning calorimetry (DSC; DSC7020, Hitachi High-Tech Science). Samples were hermetically sealed in aluminum pans inside an argon-filled glovebox ($[\text{H}_2\text{O}] < 0.5$ ppm). To eliminate thermal hysteresis, each sample was first heated to 100°C , cooled to -150°C , and then reheated to 150°C at a rate of 5°C min^{-1} . The thermograms presented correspond to this final heating process. The melting point (T_m) was determined as the peak of the endothermic transition, while the glass transition temperature (T_g) was identified from the onset of the change in heat capacity. To confirm the nonflammability of Li-DSS, flammability tests were performed using a glass-fiber separator (≈ 200 μm) saturated with the electrolyte and exposed to a butane microtorch flame for 5 s. After the flame was removed, the samples were observed for self-extinguishing behavior (Figure S22, Supporting Information). The same protocol was applied to 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 v/v) obtained from Kishida Chemical Co., Ltd. (Japan) for comparison.

4.3 | Rheological Properties

Rheological measurements were conducted using a rotational rheometer (MCR 102, Anton Paar, Austria) equipped with a temperature-controlled chamber (20 – 120°C). A cone-plate geometry with a diameter of 12.5 mm and a gap of ~ 0.2 mm was used. The storage modulus (G') and loss modulus (G'') were recorded over an angular frequency range of 0.1 – 100 rad s^{-1} at constant strain amplitude of 1%. Shear-rate-dependent viscosity was evaluated from 0.01 to 1000 s^{-1} . All measurements were performed under anhydrous conditions to avoid hydrolysis of the samples during heating.

4.4 | Ionic Conductivity

The ionic conductivity of Li-DSS was evaluated using the complex impedance method over a frequency range of 0.1 Hz to 1 MHz with an AC amplitude of 10 mV (Modulab XM ECS, Solartron Analytical). Measurements were conducted using a sealed two-electrode cell equipped with stainless steel blocking electrodes (diameter: 13 mm), assembled in an argon-filled glovebox ($[\text{H}_2\text{O}] < 0.5$ ppm). The temperature-dependent conductivity was assessed from 0°C to 120°C . The cell constant was calibrated using a 0.01 mol dm^{-3} aqueous KCl solution at 25°C . The temperature

dependence of the conductivity of Li-DSS was analyzed by fitting the data to the Vogel–Fulcher–Tammann (VFT) equation to evaluate the ion transport dynamics in the supercooled state. All fitting parameters are summarized in Table S1 (Supporting Information).

4.5 | Diffusivity of Ions

The self-diffusion coefficients of Li^+ (D_{Li}), FTA^- (D_{FTA}), and FSA^- (D_{FSA}) were determined using pulse-field-gradient nuclear magnetic resonance (PFG-NMR) spectroscopy, following established protocols [62]. Measurements were conducted on a JEOL ECX-400 NMR spectrometer equipped with a 9.4 T narrow-bore superconducting magnet and a PFG probe. Calibration of the gradient strength (g) was performed using deuterated water (D_2O). Diffusion measurements were performed via ^7Li and ^{19}F NMR spectroscopy for lithium cations and fluorinated anions, respectively.

4.6 | Li^+ Transference Number

The Li^+ transference number under the anion-blocking condition ($t_{\text{Li}}^{\text{abc}}$) was determined using potentiostatic polarization combined with electrochemical impedance spectroscopy [44–46]. All measurements were performed in symmetric Li/Li cells (electrode diameter: 8.4 mm; electrolyte gap: ~ 0.2 mm), prepared by compressing lithium foil (Honjo Metal) onto stainless steel substrates and assembled in an argon-filled glovebox ($[\text{H}_2\text{O}] < 0.5$ ppm). To ensure stabilization of the Li/electrolyte interface, impedance measurements were conducted every 2 h (frequency range: from 0.1 Hz to 1 MHz; AC amplitude: 10 mV) using a Modulab XM ECS system (Solartron Analytical). After confirming that the interfacial resistance had stabilized, constant DC voltage (10 mV) was applied until the current reached a steady state, at which point a polarization curve was recorded. Following polarization, the impedance spectrum was acquired again under a bias of 10 mV to assess the steady-state interfacial resistance. The transference number $t_{\text{Li}}^{\text{abc}}$ was calculated using the following Equation (3) [44–46]:

$$t_{\text{Li}}^{\text{abc}} = \frac{I_{\text{SS}}(V_{\text{DC}} - I_{\text{Ohm}}R_{\text{interface}, 0})}{I_{\text{Ohm}}(V_{\text{DC}} - I_{\text{SS}}R_{\text{interface}, \text{SS}})} \quad (3)$$

where I_{Ohm} and I_{SS} are the initial and steady-state currents, respectively; V_{DC} is the constant applied voltage during polarization; $R_{i,0}$ and $R_{i,\text{SS}}$ are the initial and steady-state interfacial resistances, including R_{SEI} and R_{ct} , respectively; and I_{Ohm} is calculated using the following Equation (4) [46]:

$$I_{\text{Ohm}} = \frac{V_{\text{DC}}}{(R_{\text{bulk}} + R_{\text{interface}, 0})} \quad (4)$$

4.7 | Computational Methods

The density functional theory (DFT) calculations were executed with the Gaussian 09 software at the B3LYP/6-31G* level to evaluate the torsional potentials and volumes of ions. The S–N–S–F and S–N–S–C(CF_3) dihedral angles in $[\text{FTA}]^-$ and the Li– $[\text{FTA}]$

complex were varied while calculating the torsional potentials [43], the torsion angles were fixed, and other internal geometrical parameters were optimized.

The MD simulations were performed with MPDYNPEF in the isothermal–isobaric (NPT) ensemble. To validate the polarizable force field, we benchmarked the calculated interaction energy potentials using the polarizable force field against those obtained by quantum-chemical calculations (Figure S23 and Table S3, Supporting Information). Balancing tractability with local solvation, PMMA was represented by a 4-mer oligomer. The periodic boundary conditions were the target temperature (e.g., 140°C) and 1 bar; other details of MD simulations and comparison with quantum chemical calculations are provided in Computational Methods in Supporting Information.

In the calculations of the van der Waals volumes using the application MoloVol, the following parameters were used [52]. V_{vdw} , V_{void} , and V_{mol} are all given directly in the report file. V_{vdw} and V_{void} are the van der Waals volume, defined by its van der Waals radius, and the probe exclude volume obtained from a spherical probe, respectively. V_{mol} is the molecular volume and calculated as $V_{\text{vdw}} + V_{\text{void}}$. The calculated volumes for each ion are summarized in Table S2 (Supporting Information).

4.8 | Electrochemical Measurements

All electrochemical measurements were conducted at 80°C using a multichannel potentiostat/galvanostat system (VSP, BioLogic Science Instruments). The cell was assembled in an argon-filled glovebox ($[\text{H}_2\text{O}] < 0.5$ ppm). Cyclic voltammetry (CV) and chronopotentiometry (CP) measurements were carried out using Li/Cu cells. The electrodes consisted of Li foil (diameter: 16 mm) and Cu foil (diameter: 19 mm), encapsulated in 2032-type coin cells with one or two sheets of aramid-coated polyolefin separators (Teijin Ltd.). CV was performed at a scan rate of 1.0 mV s^{−1}. Using these data, a pseudo-Tafel analysis was performed. The overpotential was defined as $\eta = E - E_{\text{eq}}$ with $E_{\text{eq}} \approx 0$ V vs Li/Li⁺. Plating ($\eta < 0$ V) and stripping ($\eta > 0$ V) branches were treated separately; data within a low-overpotential window (typically $|\eta| = 50$ –110 mV) were fitted to extract the apparent exchange current density. For CP, Li deposition/dissolution was conducted at 0.1 mA cm^{−2} for 2 h per cycle at 80°C. This approach enabled assessment of the interfacial stability and reversibility of the lithium deposition/dissolution processes. Linear sweep voltammetry (LSV) was performed using Li/Pt two-electrode cells (diameter: 8.4 mm, electrolyte gap ~0.2 mm) at a scan rate of 1.0 mV s^{−1}.

Galvanostatic charge/discharge tests were conducted using Li/LiCoO₂ cells. The positive electrodes were prepared by mixing LiCoO₂ (Kanto Kagaku), acetylene black (Denka), and poly(vinylidene fluoride) (PVdF; KF1100, Kureha) in a mass ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP; FUJIFILM Wako), following which the slurry was cast onto aluminum foil and dried at 80°C. The resulting electrodes had a mass loading of ~3.0 mg cm^{−2} and a thickness of ~20 μm. Coin cells were assembled with a LiCoO₂ electrode (diameter: 10 mm), Li metal counter electrode (diameter: 16 mm), and one separator sheet. Charge/discharge tests were performed in the voltage range of

3.0–4.2 V in constant current mode of 0.1 mA cm^{−2} for charging and by varying the discharging current (0.1–5.0 mA cm^{−2}). Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range from 1 MHz to 100 mHz with a sinusoidal amplitude of 10 mV to determine the bulk resistance (R_{bulk}), interfacial resistance of the Li electrode (R_{Li}), and LiCoO₂ electrode (R_{LiCoO_2}). Li/Li symmetric cells and Li/LiCoO₂ cells (identical to those used in galvanostatic testing) were used for these measurements. To evaluate R_{LiCoO_2} , impedance spectra were collected at both open-circuit voltage (OCV) and at 4.0 V, the redox potential of LiCoO₂. The overlapping semicircles in the Nyquist plots were analyzed, and R_{LiCoO_2} was calculated by subtracting R_{Li} from the total interfacial resistance ($R_{\text{Li/LiCoO}_2}$) obtained from the Li/LiCoO₂ cell.

4.9 | Binder-Free Thick Electrode

The binder-free composite electrodes consisted of LiCoO₂ (Kanto Kagaku), acetylene black (AB; Denka Co. Ltd.), and dual-salt Li-DSS. These materials were mixed in a mass ratio of LiCoO₂:AB:Li-DSS = 66.7:8.3:25.0 using a mortar to form a homogeneous clay-like mixture. The uniform distribution of each component was confirmed via scanning electron microscopy (SEM) (Figure S21, Supporting Information) and energy-dispersive X-ray spectroscopy (EDX). The resulting mixture was then shaped into 16 mm-diameter electrodes by hot-pressing onto aluminum current collectors using a mold at 80°C and 500 MPa (Figure S14, Supporting Information). The fabricated binder-free electrodes had a high mass loading of 33.4 mg cm^{−2} and a thickness of approximately 170 μm. For comparison, a commercially available medium-thickness composite electrode with a capacity of ~1.5 mAh cm^{−2} and a mass loading of 10 mg cm^{−2} (Piotrek Co., Ltd.) was also tested. The electrode (diameter: 16 mm) was punched from a larger sheet and used without further modification. Charge/discharge tests for both types of electrodes were conducted in 2032-type coin cells, which were assembled with Li metal anode (diameter: 16 mm) and a single separator sheet as described previously. The applied current density was 0.1 mA cm^{−2}, and all other electrochemical conditions were identical to those outlined earlier.

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Conflicts of Interest

The authors declare a competing financial interest: an international patent application covering the materials described in this manuscript has been filed.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

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

Supporting file: aenm70476-sup-0001-SuppMat.docx