

Article

Sustained Lithium Nitrate Release in Gel Polymer Electrolytes Enabled by Bulk Reservoir

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Abstract: In ester-based gel polymer electrolytes (GPEs), lithium nitrate (LiNO_3) is limited by low solubility and fast depletion. As a result, stable interfacial protection on lithium metal anodes cannot be maintained for long. In this work, a conventional PVDF-based GPE with bulk LiNO_3 incorporation (C- LiNO_3 GPE) is proposed. A surface-loaded system (S- LiNO_3 GPE) is also constructed for comparison. The effect of the LiNO_3 location on its release behavior and interfacial evolution is then examined. According to ion chromatography (IC), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and theoretical calculations, different behaviors are observed. For the surface-loaded system, LiNO_3 mainly works at the early stage of cycling. The improvement is not sustained. In contrast, when LiNO_3 is distributed in the bulk, NO_3^- is released continuously. This is attributed to the ion-dipole interaction and van der Waals forces between LiNO_3 and the poly(vinylidene fluoride) (PVDF) chains. A more uniform solid electrolyte interphase (SEI) is thus formed. It is rich in LiN_xO_y and Li_3N . Because of this, battery reversibility is improved. Cycling stability is also enhanced. At 30 °C, the C- LiNO_3 GPE shows an ionic conductivity of $1.11 \times 10^{-3} \text{ S cm}^{-1}$. The Li^+ transference number (T_{Li^+}) reaches 0.62. For the NCM811 full cell, a discharge capacity of 154.72 mAh g^{-1} is still retained after 450 cycles at 1 C. These results confirm that building a bulk LiNO_3 reservoir in ester-based GPEs is an effective strategy. It enables sustained interfacial protection and improves long-term cycling stability.

Keywords: lithium metal batteries; gel polymer electrolyte; PVDF-HFP; LiNO_3 slow release; N-rich SEI

1. Introduction

With the increasing demand for high-energy-density storage systems, conventional lithium-ion batteries are approaching their performance limits [1]. Lithium metal anodes are considered an ideal option for next-generation batteries. This is due to their ultrahigh theoretical capacity and very low potential [2,3]. However, the interface between lithium metal and liquid electrolytes is unstable. The solid electrolyte interphase (SEI) can repeatedly break during cycling. This leads to continuous consumption of active lithium and dendrite growth. Serious safety risks are therefore introduced [4,5]. For this reason, an interfacial protection layer with both high ionic conductivity and good mechanical stability is required. This is a key step toward practical lithium metal batteries [6,7].

Gel polymer electrolytes (GPEs) offer a possible solution. They can balance ion transport and structural stability [8]. Compared with liquid electrolytes, the polymer framework in GPEs provides higher mechanical strength. Dendrite penetration can be suppressed. Direct contact between lithium metal and the electrolyte can also



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be reduced to some extent [9]. Among various polymer matrices, poly(vinylidene fluoride) (PVDF) and its derivatives, such as PVDF-HFP, are widely used. This is mainly due to their good overall properties [10]. In recent years, research has moved beyond simple filler addition [11]. More attention has been given to pore construction [12], framework regulation [13], and interfacial chemistry design [14]. As a result, PVDF-based GPEs are gradually shifting from simple physical composites to more functional structures.

Although pore design and framework modification have improved transport and mechanical properties, some problems remain. Continuous lithium loss and interfacial side reactions are still difficult to suppress [15]. Lithium nitrate (LiNO_3) is widely used as an additive. It can induce the formation of lithium nitride (Li_3N), which has high ionic conductivity. It is therefore considered effective in suppressing dendrite growth at the chemical level [16]. Previous studies provide further insight. Zhang et al. [17] analyzed how LiNO_3 regulates the solvation structure. It was shown that a nitrogen-containing SEI plays a key role in suppressing side reactions and dead lithium formation. Cui et al. [18] reported that even in carbonate electrolytes with very low solubility, a small amount of LiNO_3 can change lithium nucleation behavior. The morphology shifts from dendritic to spherical. Despite these advances, challenges still exist. In GPE systems, it is difficult to introduce LiNO_3 effectively and maintain a stable supply. Some strategies have been reported. For example, separator enrichment was proposed by Winter et al. [19]. An electrospun reservoir method was developed by Sumboja et al. [20]. These methods can load LiNO_3 to some extent. However, the fabrication processes are often complex. In addition, a clear comparison of LiNO_3 release behavior is still lacking.

In this work, the problem of unstable LiNO_3 incorporation in ester-based GPEs is addressed. Two systems are designed. One is based on surface loading, and the other is based on bulk incorporation (Figure 1a,b). Their differences in storage mode, release behavior, and interfacial effects are compared. It is found that LiNO_3 in S- LiNO_3 GPEs mainly participates in interfacial film formation at the early stage. The initial interfacial resistance can be reduced. However, the effect does not last long. In contrast, in C- LiNO_3 GPE, LiNO_3 interacts with PVDF through ion-dipole interaction and van der Waals forces. A slower release process is achieved. More stable interfacial regulation is obtained. As a result, C- LiNO_3 GPE shows an ionic conductivity of $1.11 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C . The Li^+ transference number (T_{Li^+}) reaches 0.62. Better reversibility and more stable long-term cycling performance are observed in different battery systems. These findings indicate that the position of LiNO_3 in the gel electrolyte is critical. It directly affects the release process, interfacial evolution, and electrochemical performance. This work provides a useful idea for designing slow-release additives in lithium metal batteries.

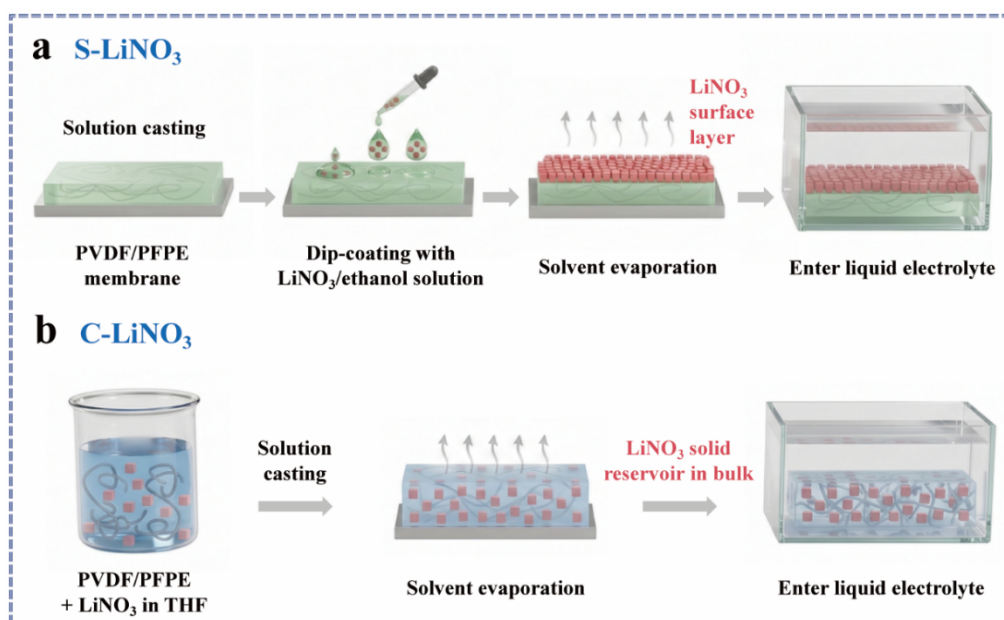


Figure 1. Fabrication process of S- LiNO_3 and C- LiNO_3 GPEs: (a) Construction of LiNO_3 surface-enriched layer; (b) Incorporation of LiNO_3 into bulk phase.

2. Experimental Methods

2.1. Materials and Chemicals

PH (manganese = $455,000 \text{ g mol}^{-1}$) was purchased from Aldrich Co., Ltd. (Taoyuan City, Taiwan). Anhydrous ethanol, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and N-methyl-2-pyrrolidone (NMP)

were supplied by Aladdin Co., Ltd. (Fukuoka, Japan). Lithium iron phosphate (LiFePO_4), LiNO_3 , and lithium nickel cobalt manganese oxide ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) were obtained from Macklin Co., Ltd. (Shanghai, China). Perfluoropolyether methyl methacrylate (PFPE-MAA) was purchased from Suzhou Cangmu New Materials Co., Ltd. (Suzhou, China). The commercial liquid electrolyte consisted of 1 M LiPF_6 in diethyl carbonate/dimethyl carbonate/ethylene carbonate (DEC/DMC/EC, 1:1:1 by volume) with 10 vol% fluoroethylene carbonate (FEC). It was supplied by Suzhou Duoduo Chemical Technology Co., Ltd. (Suzhou, China). Except for anhydrous ethanol, all chemicals and reagents were stored in an argon-filled glovebox. The contents of oxygen and water were both kept below 0.1 ppm. All solid materials were vacuum-dried before use.

2.2. Cathode Preparation

LiFePO_4 or NCM811 was used as the cathode active material. It was mixed with conductive carbon black (Super P) and a binder at a mass ratio of 8:1:1. An appropriate amount of NMP was then added to adjust the viscosity of the slurry. The mixture was stirred until uniform. The LiFePO_4 slurry was stirred for 8 h. The NCM811 slurry was stirred for 24 h. The slurry was coated onto aluminum foil using a coating applicator. It was then dried in a vacuum oven at 80 °C for 720 min. After drying, the electrodes were punched into circular disks with a diameter of 12 mm. The disks were further pressed before use. The areal loadings of LiFePO_4 and NCM811 were approximately 12.34 and 2.13 mg cm^{-2} , respectively.

2.3. Preparation of GPEs

The GPEs were prepared by a solution casting method. The LiNO_3 -free membrane was denoted as Bare GPE. Firstly, 1.0 g of PH was added to 10 mL of THF. The mixture was stirred at 65 °C until complete dissolution. It was then cooled to room temperature. Following that, 0.25 g of PFPE-MAA was added. Stirring was continued until a uniform solution was obtained. The precursor solution was cast into a polytetrafluoroethylene mold. It was left in a glovebox for 24 h to form a membrane. The membrane was then immersed in the electrolyte for 10 h to complete the preparation.

According to different LiNO_3 introduction methods, two types of membranes were obtained. The surface-loaded membrane was denoted as S- LiNO_3 GPE. The bulk-incorporated membrane was denoted as C- LiNO_3 GPE. For S- LiNO_3 GPE, 0.34 g of LiNO_3 was dissolved in 4 mL of anhydrous ethanol. The solution was stirred at 40 °C until it became clear. The concentration was 1.23 M. The Bare membrane was then immersed in this solution. After vacuum drying, it was soaked in the electrolyte to complete liquid uptake. For C- LiNO_3 GPE, the procedure was similar to Bare GPE. The difference is that 0.1 g of LiNO_3 was added together with PFPE-MAA. After sufficient stirring, the solution was cast to form a membrane. By adjusting the soaking concentration and electrolyte uptake, the LiNO_3 loading in S- LiNO_3 GPE was controlled to be close to that in C- LiNO_3 GPE.

2.4. Materials Characterization

The surface and cross-sectional morphologies of the electrolyte membranes were observed by scanning electron microscopy (SEM, SU8000, Hitachi, Japan). Elemental distribution was analyzed by energy-dispersive spectroscopy (EDS). Fourier-transform infrared spectroscopy (FTIR, Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA) and Raman spectroscopy (LabRAM HR Evolution, Horiba, Kyoto, Japan) were used to analyze functional groups and local structures. Crystal structures were examined by X-ray diffraction (XRD, X'Pert PRO, PANalytical, Almelo, The Netherlands). The chemical states of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, Waltham, MA, USA). The ion distribution in the SEI was studied by time-of-flight secondary ion mass spectrometry (TOF-SIMS 5, IONTOF, Münster, Germany). Ion chromatography (IC, Aquion, Thermo Scientific, Waltham, MA, USA) was used to monitor the release of LiNO_3 and evaluate its slow-release behavior.

2.5. Electrochemical Characterization

All coin cells were assembled in an argon-filled glovebox (MBRAUN, LABstar, Selb, Germany). The ionic conductivity, T_{Li}^+ , and electrochemical window (linear sweep voltammetry (LSV)) were measured using CHI660 and CHI760E electrochemical workstations. Rate and cycling performances were tested using a Neware system.

The ionic conductivity was measured using SS|GPE|SS symmetric cells. Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range from 0.1 Hz to 1 MHz. The AC amplitude was 5 mV. The temperature ranged from 30 to 70 °C, with intervals of 10 °C. The ionic conductivity was calculated from the fitted resistance using Equation (1):

$$\sigma = \frac{d}{R_b S} \quad (1)$$

where σ , d , R_b , and S represent the ionic conductivity, thickness of the gel electrolyte membrane, bulk resistance, and contact surface area, respectively. The thickness of the prepared electrolyte membranes was measured multiple times using a micrometer, and the average value was used. It was maintained at $80 \pm 5 \mu\text{m}$.

The electrochemical stability window of the electrolyte was evaluated using Li|GPE|SS cells by LSV. The voltage range was set from 2 to 6 V. The scan rate was 0.5 mV s^{-1} . The T_{Li^+} was measured using Li|GPE|Li symmetric cells. A polarization voltage of 0.01 V was applied. Chronoamperometry and EIS were combined for the analysis. The T_{Li^+} was determined according to Equation (2):

$$T_{\text{Li}^+} = \frac{I_{\text{ss}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{ss}} R_{\text{ss}})} \quad (2)$$

where R_0 and R_{ss} represent the impedance values before and after polarization, respectively; I_0 and I_{ss} represent the initial and steady-state currents, respectively; and ΔV represents the applied polarization voltage.

Li|GPE|Li symmetric cells were cycled at a current density of 0.5 mA cm^{-2} . The voltage profiles were recorded. Li|GPE|Cu coin cells were tested under the same current density. Charge-discharge measurements were performed. The Coulombic efficiency was obtained. For anode-free cells, LFP was used as the cathode, and copper foil was used as the anode. The areal loading of LFP was about 1.98 mg cm^{-2} . Full cells were assembled using LFP or NCM811 as the cathode and lithium metal as the anode. Tests were carried out at 25°C . The voltage ranges were 2.5–3.9 and 2.5–4.3 V, respectively. The corresponding areal loadings were 12.34 and 2.13 mg cm^{-2} . In the coin cells, each GPE membrane absorbed about $16 \mu\text{L}$ of liquid electrolyte. The thickness of the lithium foil was fixed at 0.25 mm.

2.6. Theoretical Calculations

Classical molecular dynamics simulations were carried out to investigate the diffusion behavior of NO_3^- in GPE. The simulation system was composed of PVDF-HFP, PFPE-MAA, EC, DEC, DMC, FEC, Li^+ , PF_6^- , LiNO_3 , and other components. The initial structure was generated using PACKMOL. Intermolecular interactions were described by the GAFF force field. Long-range electrostatic interactions were treated using the particle mesh Ewald (PME) method [21]. After energy minimization, NPT equilibration was performed. Subsequently, an NVT simulation was carried out at 298 K for 40 ns. All calculations were performed using GROMACS 2022.5 [22].

Density functional theory (DFT) calculations were performed using Gaussian 16 (Revision C.01) at the PBE0-D3(BJ) level [23], with geometry optimizations and frequency analyses conducted using the 6-31+G(d,p) basis set, followed by single-point energy calculations with the 6-311+G(d,p) basis set [24]. The binding energy was calculated as $E_{\text{bind}} = E_{\text{complexAB}} - (E_{\text{partA}} + E_{\text{partB}})$.

3. Results and Discussion

To examine how different LiNO_3 incorporation strategies affect the microstructure and spatial distribution of GPE membranes, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were carried out. The results are illustrated in Figures 2a–e and S3. Bare GPE shows a loose layered structure. For S- LiNO_3 GPE, clear micron-sized particles are observed on the surface. Some regions appear discontinuous. This suggests that LiNO_3 is locally enriched and crystallized at the surface. The EDS mapping shows that the nitrogen element is unevenly distributed. In contrast, no obvious crystalline aggregation is observed in C- LiNO_3 GPE. Both the surface and the cross-section appear uniform. The nitrogen element is distributed more evenly. This indicates that LiNO_3 is incorporated into the polymer network during membrane formation.

To further analyze the functional groups and internal chemical environment, Fourier-transform infrared spectroscopy (FTIR) and Raman spectra measurements were performed for Bare GPE, S- LiNO_3 , and C- LiNO_3 samples. The results are depicted in Figure 2f,g. The FTIR spectra show that the characteristic peaks of the PH/PFPE matrix are preserved in all samples. After the introduction of LiNO_3 , new absorption peaks appear at 837 and 1352 cm^{-1} . These peaks correspond to NO_3^- [25]. For the C- LiNO_3 sample, changes in peak shape and intensity are observed in the polymer signals [26]. This implies stronger interactions between LiNO_3 and the polymer chains in the bulk system. The Raman results also confirm the presence of LiNO_3 . In addition, the PH in C- LiNO_3 shows a more pronounced β -phase feature [27]. This suggests that LiNO_3 participates in chain rearrangement during membrane formation. The local polarity is also affected.

As shown in Figure S4, C- LiNO_3 GPE exhibits a lower melting temperature and reduced melting enthalpy compared with Bare GPE and S- LiNO_3 GPE, indicating decreased crystallinity of the PVDF-HFP matrix. The

resulting increase in amorphous regions facilitates polymer segmental motion and Li^+ transport [28]. X-ray diffraction (XRD) analysis was performed to study the crystallization behavior of LiNO_3 and the phase structure of PH (Figure 2h). Diffraction peaks are observed at $2\theta = 17.4, 18.3, 26.6, 19.9$, and 38.9° . These peaks correspond to the α phase ((020), (110), (021)), the β phase ((200)/(110)) [27], and the γ phase (211) [29] of PH. After adding LiNO_3 , new diffraction peaks appear in both S- LiNO_3 and C- LiNO_3 samples. These peaks match the standard pattern of LiNO_3 . For S- LiNO_3 GPE, the LiNO_3 peaks are more pronounced. This suggests that LiNO_3 tends to crystallize on the membrane surface after soaking treatment. A relatively independent crystalline phase is formed. For C- LiNO_3 GPE, a stronger effect on the polymer matrix is observed. Bulk incorporation induces a dehydrofluorination process in PH. The γ phase gradually transforms into the β phase. The β phase has higher polarity and electroactivity. As a result, electrolyte uptake is improved. Ion transport is also promoted [30].

Although SEM, FTIR, Raman, and XRD results confirm that LiNO_3 is successfully introduced, the distribution difference is still not fully clear. Therefore, X-ray photoelectron spectroscopy (XPS) analysis was performed (Figure 2i–k). No nitrogen signal is detected in Bare GPE. In S- LiNO_3 GPE, a clear NO_3^- signal is observed only at the surface [31]. It quickly disappears during sputtering. This indicates that LiNO_3 is mainly located at the surface. In contrast, stable nitrogen signals are observed in C- LiNO_3 GPE at different sputtering times. This confirms that LiNO_3 is distributed more deeply and more uniformly within the membrane.

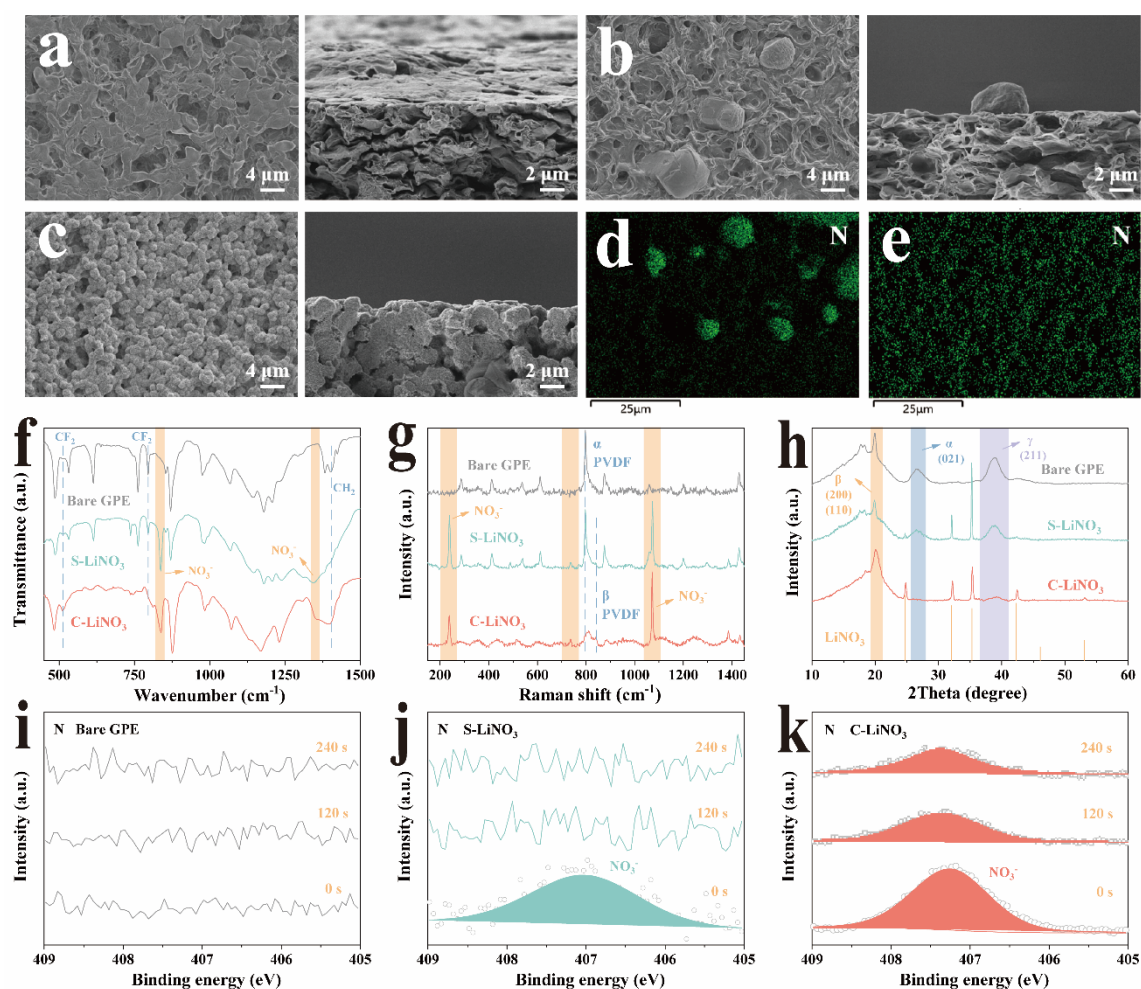


Figure 2. Planar and cross-sectional SEM images of (a) Bare, (b) S- LiNO_3 , and (c) C- LiNO_3 GPEs; Nitrogen element EDS mapping of (d) S- LiNO_3 and (e) C- LiNO_3 GPEs; (f) FTIR spectra and (g) Raman spectra of three PH-based electrolyte membranes; (h) XRD patterns of three PH-based electrolyte membranes and standard card for LiNO_3 ; N 1s XPS spectra of (i) Bare, (j) S- LiNO_3 , and (k) C- LiNO_3 GPEs collected at 0, 120, and 240 s sputtering times.

The contact angle results are presented in Figure 3a–c. The values for Bare, S- LiNO_3 , and C- LiNO_3 GPEs are $31.99, 26.57$, and 24.70° , respectively. A decrease in contact angle is observed after introducing LiNO_3 . This indicates that the wettability of the electrolyte membrane is improved. A lower contact angle allows better electrolyte uptake. Faster filling of the polymer matrix can be achieved. The interfacial contact is therefore

improved. Ion transport becomes more uniform [32]. Among the three samples, C-LiNO₃ GPE shows the smallest contact angle. This suggests that bulk distribution of LiNO₃ enhances the liquid absorption ability. This observation is consistent with the structural results discussed above.

The T_{Li^+} reflects the contribution of Li⁺ to total ionic transport. It was measured at room temperature (Figure 3d–f). The T_{Li^+} for Bare, S-LiNO₃, and C-LiNO₃ GPEs are 0.31, 0.56, and 0.62, respectively. After introducing LiNO₃ on the surface, the ion transport environment is improved. The contribution of Li⁺ becomes higher. C-LiNO₃ GPE shows the highest T_{Li^+} . This indicates that bulk incorporation is more favorable for forming continuous ion transport pathways. The migration of anions is suppressed. Concentration polarization is also reduced [8].

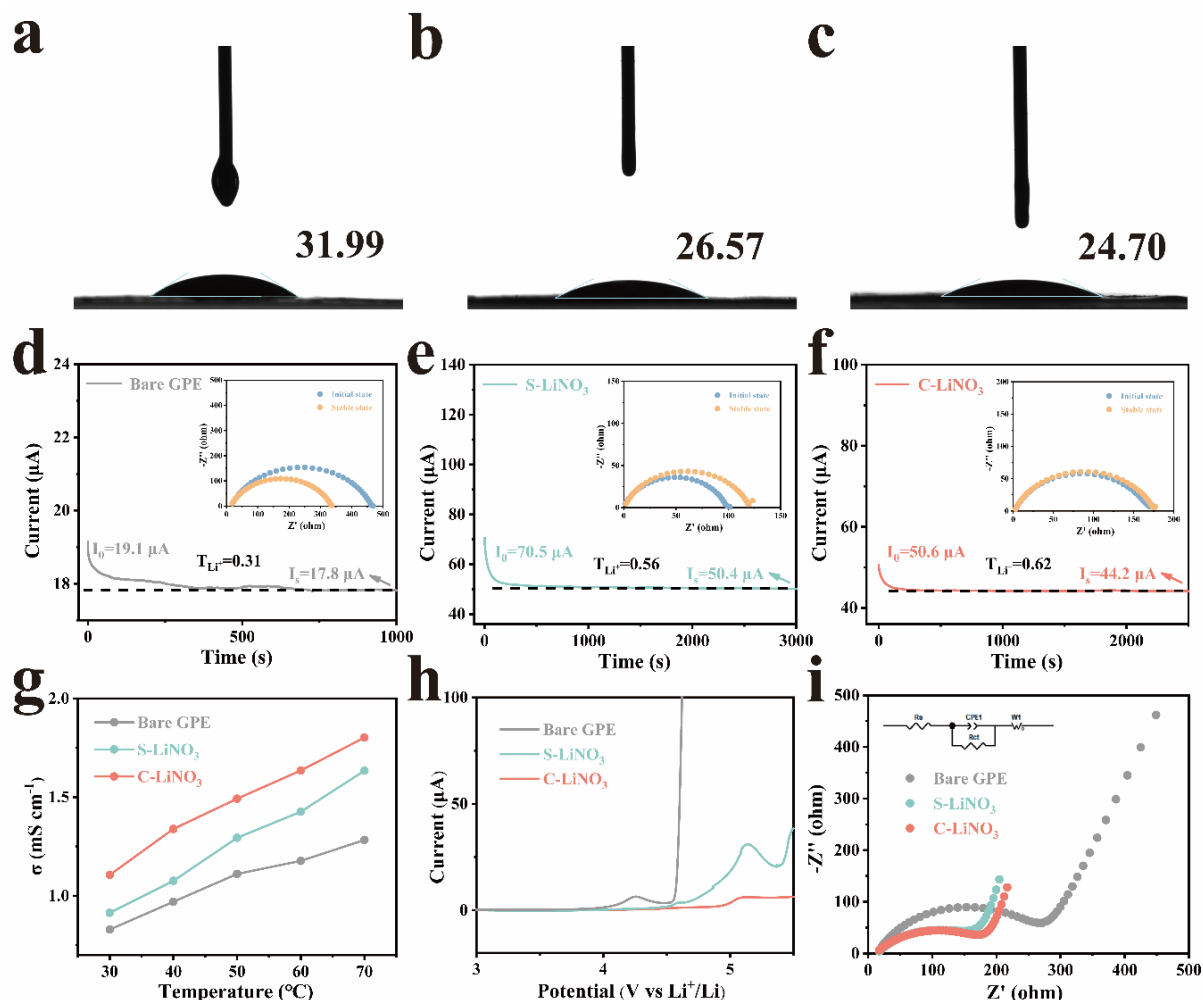


Figure 3. Static contact angle tests of (a) Bare, (b) S-LiNO₃, and (c) C-LiNO₃ GPEs at 0.1 s; Polarization curve and impedance spectrum of (d) Bare, (e) S-LiNO₃, and (f) C-LiNO₃ GPEs; (g) Temperature-dependent ionic conductivity of three PH-based electrolyte membranes; (h) LSV curves of three PH-based electrolyte membranes; (i) Initial AC impedance of three PH-based cells.

The ionic conductivity was measured from 30 to 70 °C (Figure 3g). With increasing temperature, the ionic conductivity gradually increases. This is related to enhanced polymer chain mobility and faster ion transport [33]. Among the samples, C-LiNO₃ GPE shows the highest conductivity. The value reaches $1.11 \times 10^{-3} \text{ S cm}^{-1}$ at 30 °C and $1.80 \times 10^{-3} \text{ S cm}^{-1}$ at 70 °C. This suggests that LiNO₃ reduces the crystallinity of PH and increases electrolyte uptake. As a result, the overall ionic transport is improved [10]. Temperature-dependent Electrochemical impedance spectroscopy (EIS) measurements gave activation energies of 9.56, 12.46, and 10.06 kJ mol⁻¹ for the Bare, S-LiNO₃, and C-LiNO₃ GPEs, respectively, consistent with the reported balance among salt dissociation, anion immobilization, and Li⁺ migration [34]. The comparable activation energies of Bare and C-LiNO₃ suggest that bulk LiNO₃ incorporation does not markedly increase the ion-transport barrier, whereas the higher value of S-LiNO₃ may be associated with its localized LiNO₃ distribution [18].

The electrochemical stability at high voltage is also important. It determines the applicability in high-voltage cathode systems [14]. The results are illustrated in Figure 3h. The stability windows for Bare, S-LiNO₃, and C-LiNO₃ GPEs are 3.94, 4.45, and 4.62 V, respectively. A wider window is observed after introducing LiNO₃. This implies that a more stable chemical environment is formed inside the membrane. Electrolyte decomposition at high voltage is suppressed [35]. As shown in Figure S5, the tensile strength of C-LiNO₃ GPE increases to approximately 4.7 MPa, compared with 2.7 MPa for Bare GPE and 4.4 MPa for S-LiNO₃ GPE. Moreover, C-LiNO₃ GPE exhibits a higher elongation at break, demonstrating its improved mechanical strength and toughness, which are beneficial for maintaining interfacial integrity and resisting dendrite penetration [36,37].

EIS measurements were performed to examine the initial interfacial state (Figure 3i). Compared with Bare GPE, both S-LiNO₃ and C-LiNO₃ GPEs show lower initial impedance. The S-LiNO₃ cell exhibits the smallest semicircle. This suggests that surface-loaded LiNO₃ can quickly participate in interfacial reactions during cell assembly. The interfacial contact is improved [38].

In summary, the introduction method of LiNO₃ strongly affects its distribution in the membrane. Compared with surface loading, bulk incorporation leads to a more uniform distribution. Stronger interaction with polymer chains is also achieved. As a result, ion transport behavior and electrochemical stability are both improved. It can be further inferred that both strategies act as LiNO₃ reservoirs in ester-based systems. However, due to different distribution states, their release behaviors are expected to be different.

Ion chromatography (IC) results are depicted in Figure 4a. Both S-LiNO₃ and C-LiNO₃ GPEs release NO₃[−] into the ester-based electrolyte. This confirms that LiNO₃ remains electrochemically active. It acts as a nitrate source rather than an inert filler. However, the release behaviors are different. In S-LiNO₃ GPE, the NO₃[−] concentration reaches the highest value during the first soaking. It then decreases quickly. This suggests that LiNO₃ is mainly located near the surface. It dissolves rapidly once it contacts the electrolyte. As a result, a continuous supply cannot be maintained. For C-LiNO₃ GPE, the situation is different. Even after repeated soaking, the NO₃[−] concentration remains relatively high. A more stable release behavior is observed. This indicates that LiNO₃ can be supplied continuously in the electrolyte. This provides a basis for sustained interfacial regulation.

To understand the origin of this difference, molecular dynamics analysis was carried out. The migration of NO₃[−] and its interaction with the polymer matrix were examined (Figures 4b–d, S7 and S8). The diffusion coefficients of NO₃[−] are $1.30 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for S-LiNO₃ and $0.64 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for C-LiNO₃. Similarly, the diffusion coefficient of Li decreases from $1.32 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in S-LiNO₃ to $0.66 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in C-LiNO₃, further indicating the restricted motion of LiNO₃-related species in the bulk system. This restricted mobility is related to the slow-release behavior. Interaction energy analysis shows stronger interactions in the bulk system. Both ion-dipole interaction and van der Waals forces are enhanced. These interactions occur between LiNO₃ and the polar sites of the polymer chains. The radial distribution function (RDF) results provide additional information. A first coordination peak appears at 0.20 nm for Li⁺(LiNO₃)-F(PVDF) pairs. The peak intensity is higher in C-LiNO₃. This suggests a higher probability of Li⁺ accumulation near PVDF polar sites [39]. Also, Density functional theory (DFT) calculations were performed to investigate the interactions of PVDF with the Li⁺-NO₃[−] contact ion pair, Li⁺, and NO₃[−] (Figure S9). The binding energy of the PVDF-LiNO₃ system was calculated to be $-25.11 \text{ kcal mol}^{-1}$, indicating an energetically favorable local interaction between them [40].

The SEI formed after 50 cycles was further analyzed by XPS and Time-of-flight secondary ion mass spectrometry (TOF-SIMS) (Figures 4e–h and S12–S15). In addition, the SEI formed after 500 cycles was examined by XPS (Figures S10 and S11). In the S-LiNO₃ system, relatively weak signals of Li_xN_yO_z and Li₃N are detected after sputtering [41]. This suggests that nitrogen-containing species are limited. In contrast, stronger nitrogen-related signals are observed in the C-LiNO₃ system. This indicates that more nitrogen-containing components are formed. The SEI is also more continuous along the depth direction. The TOF-SIMS results show a similar trend. Stronger signals of NO₃[−], Li₃N, NO₂[−], and NO[−] are observed in C-LiNO₃. Their spatial distribution is also more uniform in both 2D and 3D views. This suggests that NO₃[−] continuously participates in interfacial reactions during cycling. In summary, in the bulk incorporation strategy, LiNO₃ is embedded in the polymer network. This is achieved through stronger interactions with the polymer chains. Its diffusion and loss are therefore suppressed. As a result, a sustained supply of NO₃[−] is maintained in the electrolyte. A more uniform SEI enriched with Li₃N and Li_xN_yO_z is formed. The interfacial stability and electrochemical performance are both improved.

Li|GPE|Li symmetric cells were assembled and tested under constant current conditions (Figure 5a). For the S-LiNO₃ cell, large fluctuations in overpotential are observed at the early stage. Failure occurs after approximately 110 h. This behavior is likely related to dendrite growth, which may cause soft short circuits [42]. In comparison, the C-LiNO₃ cell shows stable cycling for more than 600 h at 0.5 mA cm^{-2} . This suggests that a more uniform and reversible lithium deposition/stripping process is maintained [43]. As shown in Figure S16, C-LiNO₃ GPE maintains stable Li plating/stripping up to 1.0 mA cm^{-2} , whereas S-LiNO₃ GPE exhibits pronounced voltage

fluctuations at this current density. The higher CCD of C-LiNO₃ GPE demonstrates its enhanced interfacial stability and tolerance to high-current operation [44]. The morphology of lithium after 50 cycles (Figure 5b–d) and 500 cycles (Figure S17) was further examined by SEM. In the Bare system, the lithium surface appears loose and porous. Many flake-like and dendritic structures are observed. In the S-LiNO₃ sample, layered structures and local protrusions are present. For C-LiNO₃, the lithium surface is more compact and smoother. Only fine and uniform particles are observed. This suggests a more uniform Li⁺ flux and a stable deposition process. The observation is consistent with the cycling results.

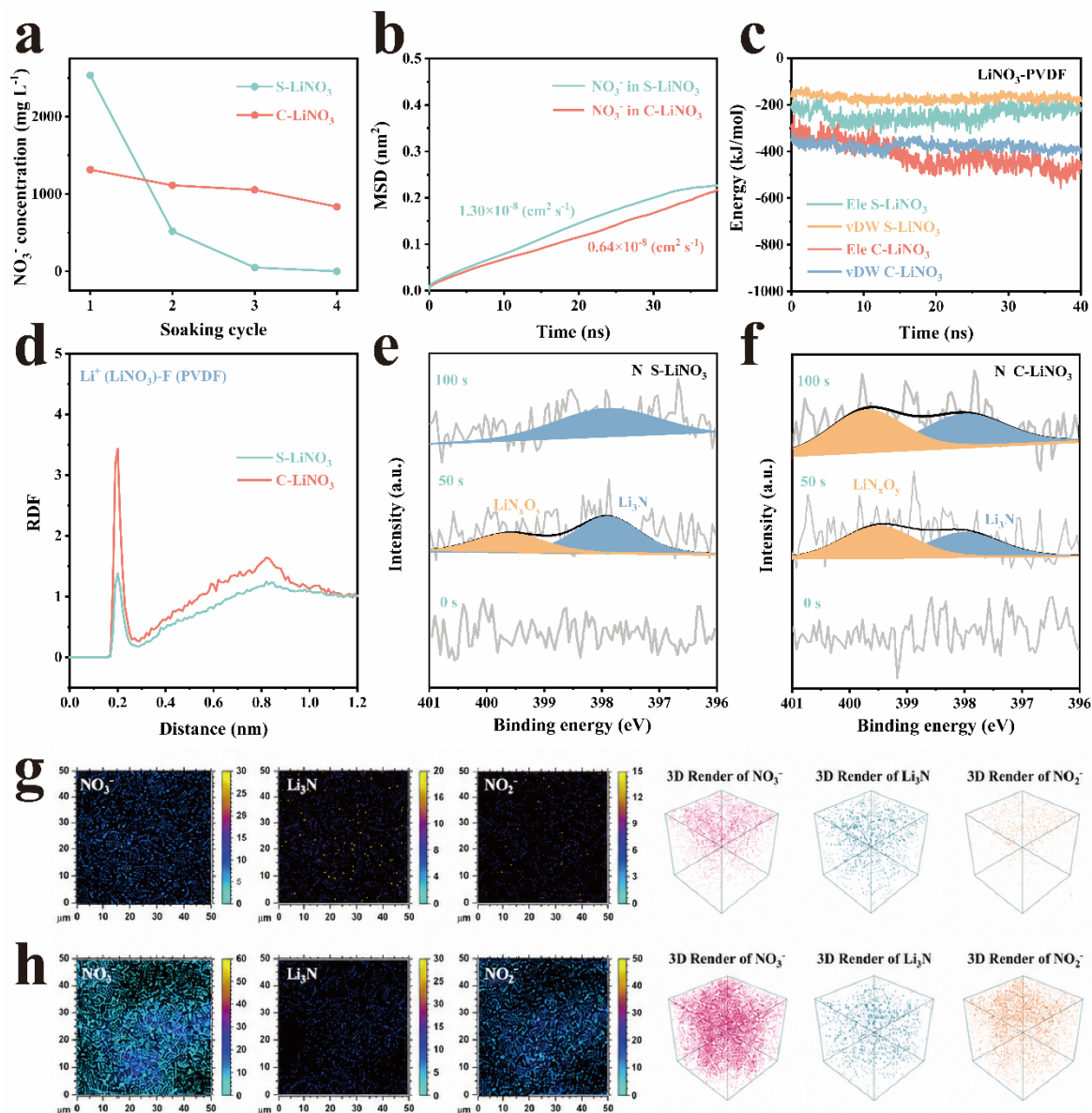


Figure 4. Release behavior of LiNO₃ in different GPEs and its microscopic mechanisms: (a) NO₃[−] concentration changes in ester-based electrolyte after repeated soaking (6 h each) for S-LiNO₃ and C-LiNO₃ GPEs; (b) Mean square displacement (MSD) curves of NO₃[−] in S-LiNO₃ and C-LiNO₃ GPEs with corresponding diffusion coefficients; (c) Variation of electrostatic interaction energy and Van der Waals interaction energy between LiNO₃ and PVDF with time; (d) RDF of Li⁺(LiNO₃)-F(PVDF) atomic pairs; N 1s XPS depth profiling spectra of lithium anode SEI after 50 cycles in (e) S-LiNO₃ and (f) C-LiNO₃; (g) TOF-SIMS 2D distribution and 3D reconstruction of NO₃[−], Li₃N, and NO₂[−] in lithium anode SEI after 50 cycles in S-LiNO₃ and (h) C-LiNO₃.

To further evaluate interfacial evolution, EIS was measured at different cycle numbers (Figure 5e–g). At the initial stage, S-LiNO₃ shows the lowest interfacial resistance. This indicates that surface-loaded LiNO₃ can quickly participate in interfacial reactions. However, with continued cycling, the resistance in C-LiNO₃ increases more slowly. At later stages, it becomes the lowest among the three systems. This suggests better long-term interfacial stability [45]. This difference reflects two distinct behaviors. Surface-loaded LiNO₃ mainly acts at the early stage.

It reduces initial resistance but cannot sustain the effect. In contrast, bulk incorporation provides a continuous source of LiNO_3 within the GPE. This leads to improved electrochemical performance over long cycles.

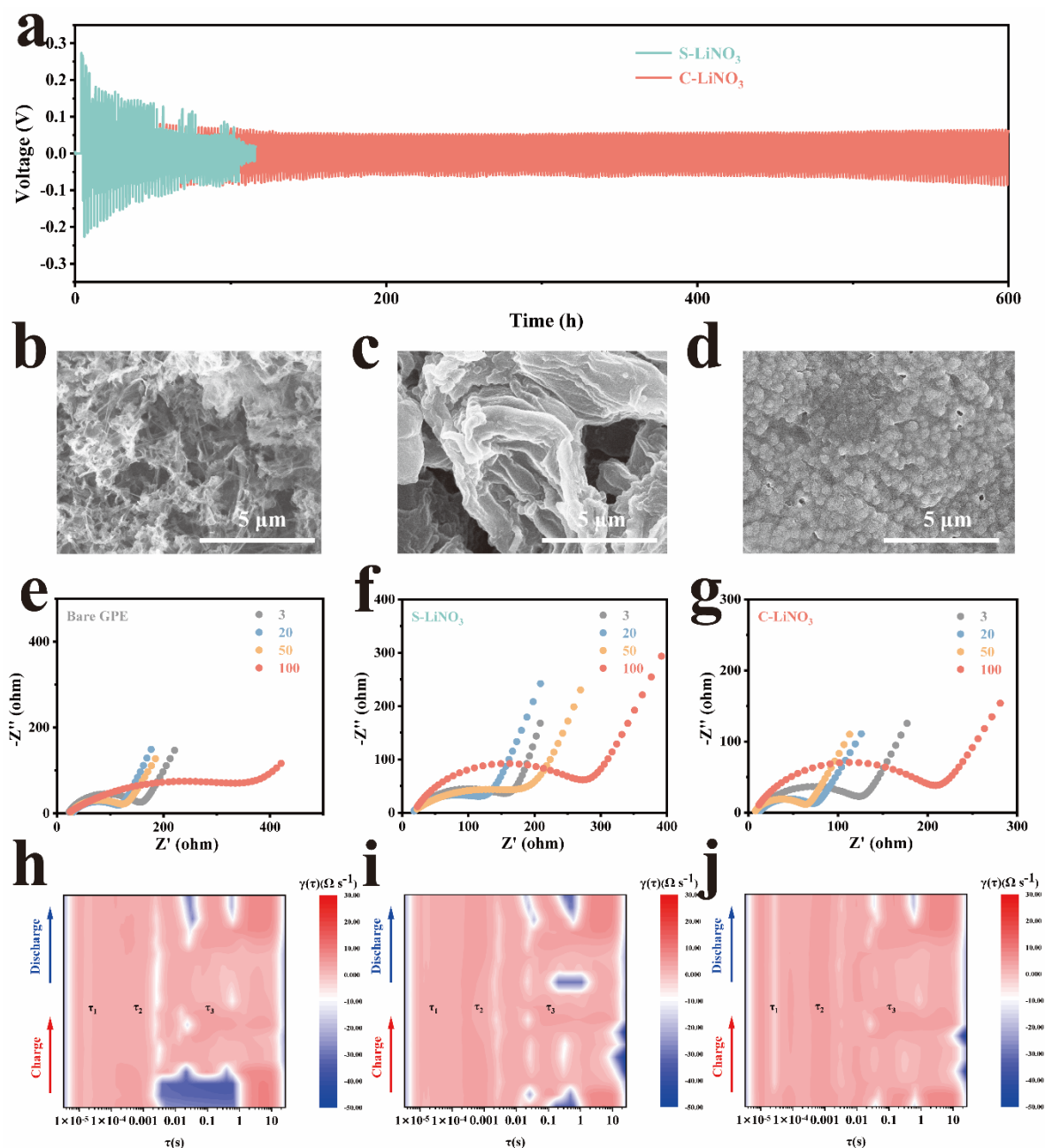


Figure 5. Effect of different GPEs on interface stability of lithium anode interface: (a) Long-cycle voltage profiles of lithium symmetric cells; SEM images of lithium anode surface after 50 cycles for (b) Bare, (c) S-LiNO₃, and (d) C-LiNO₃ GPEs; EIS at different cycle numbers for (e) Bare, (f) S-LiNO₃, and (g) C-LiNO₃ GPEs; *In-situ* DRT contour maps of LFP||Li cells using (h) Bare GPE, (i) S-LiNO₃ GPE, and (j) C-LiNO₃ GPE during charge/discharge.

Further insight into the dynamic evolution of interfacial impedance was obtained by combining *in situ* EIS with distribution of relaxation times (DRT) analysis during the charge/discharge process (Figure 5h–j). Compared with Bare GPE and S-LiNO₃ GPE, C-LiNO₃ GPE exhibits a smoother DRT response, particularly in the charge-transfer and diffusion regions, indicating more stable interfacial kinetics and Li^+ transport [46,47].

Based on the analysis of LiNO_3 storage, release behavior, and interfacial effects, several cell configurations were further tested. These include Li|GPE|Cu cells, LFP|GPE|Cu anode-free cells, NCM811|GPE|Li full cells, and LFP|GPE|Li full cells. The electrochemical performance was evaluated. In Figure 6a, the Coulombic efficiency of the S-LiNO₃ system is improved compared with Bare GPE. However, it decays quickly. In contrast, the C-LiNO₃ system maintains a Coulombic efficiency of 96.39% after 185 cycles. Both cycle life and efficiency are improved. A similar

trend is observed in anode-free cells (Figure 6b). The Bare system shows the fastest capacity decay. Its cycle life is the shortest. At the early stage, the S-LiNO₃ system shows a Coulombic efficiency close to 99%. This value is higher than C-LiNO₃. This suggests that surface-loaded LiNO₃ participates first in interfacial reactions on the Cu collector. Lithium nucleation is also affected. Initial side reactions and irreversible lithium loss are reduced [48]. The C-LiNO₃ system shows the longest reversible cycling life. After 115 cycles, the discharge capacity reaches 151.16 mAh g⁻¹. The Coulombic efficiency remains at 96.03%.

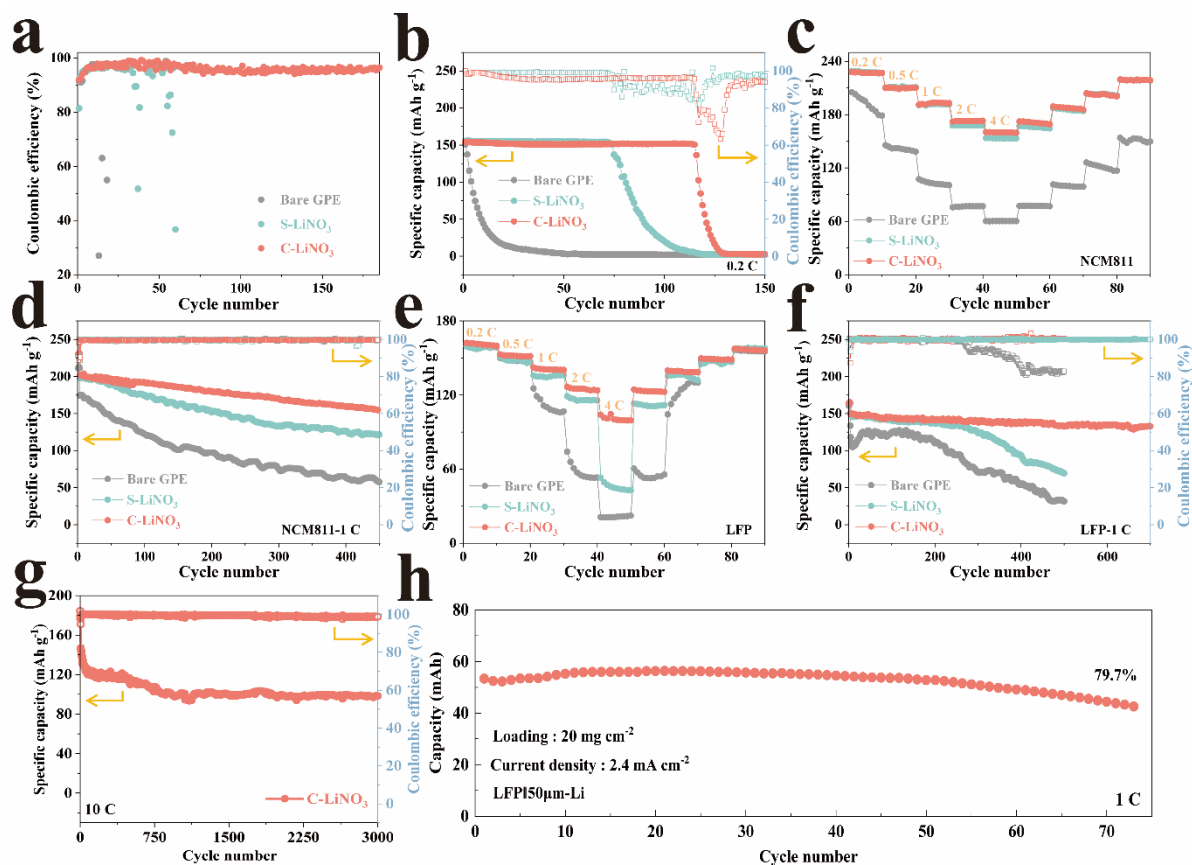


Figure 6. Electrochemical performance of different GPEs: (a) Coulombic efficiency stability test of Li|Cu cells; (b) Cycling performance test of LFP anode-free cells at 0.2 C; Rate performance test of (c) NCM811 full cell (0.2~4 C) and (e) LFP full cell (0.2~4 C); Cycling performance test of (d) NCM811 full cell at 1 C and (f) LFP full cells at 1 C; (g) Cycling performance test of LFP full cells at 10 C; (h) Cycling performance of the C-LiNO₃ GPE-based LFP||Li pouch cell with a high LFP loading of 20 mg cm⁻² and a 50 μm Li anode at 1 C.

The rate performance of NCM811 cells is presented in Figure 6c. At different rates from 0.2 to 4 C, the capacities of C-LiNO₃ and S-LiNO₃ are similar. The Bare system shows the lowest values. Long-term cycling results are illustrated in Figure 6d. After 450 cycles at 1 C, the discharge capacity of C-LiNO₃ remains at 154.72 mAh g⁻¹. This value is much higher than S-LiNO₃ (121.46 mAh g⁻¹) and Bare GPEs (57.41 mAh g⁻¹). Similar behavior is observed in the LFP system (Figure 6e,f). As the rate increases, the capacities of all systems decrease. However, C-LiNO₃ maintains the highest capacity across the entire range. When the rate returns to a lower value, better capacity recovery is observed. Under high loading conditions, the C-LiNO₃ system still delivers 132.81 mAh g⁻¹ after 700 cycles. The capacity retention reaches 88.68%. These values are significantly higher than those of S-LiNO₃ and Bare systems. In addition, the C-LiNO₃-based cell maintains a discharge capacity of 99.01 mAh g⁻¹ after 3000 cycles at 10 C, corresponding to a capacity retention of 71.75%. Overall, surface-loaded LiNO₃ shows some advantages at the early stage. However, this effect is not maintained during long-term cycling. In contrast, C-LiNO₃ provides better reversibility, improved rate capability, and more stable long-term performance across different cathode systems. To further evaluate its practical applicability, a single-layer pouch cell employing a high-loading LFP cathode (20 mg cm⁻²) and a 50 μm Li anode was assembled. As shown in Figure 6h, the C-LiNO₃ GPE-based pouch cell delivered 79.7% capacity retention after 73 cycles at 1 C, demonstrating its feasibility under more practical cell conditions.

A comparison with previously reported sustained LiNO₃ release strategies is provided in Table S4. Unlike external reservoir designs based on separators, interlayers, coatings, or nanocarriers [20,49–51], the C-LiNO₃ GPE

incorporates the LiNO_3 reservoir directly into the bulk ion-conducting membrane and was validated in multiple cell configurations. This comparison further indicates that the storage location of LiNO_3 plays an important role in its release behavior and long-term interfacial regulation.

4. Conclusions

In this work, the limited solubility and poor effectiveness of LiNO_3 in ester-based systems are addressed. A slow-release strategy based on bulk storage is proposed. Surface loading and bulk incorporation methods are compared. The storage state, release behavior, and interfacial effects of LiNO_3 are systematically analyzed. It is found that surface-loaded LiNO_3 mainly participates in interfacial film formation at the early stage of cycling. The initial interface can be improved. However, the effect cannot be maintained for long. In contrast, in the bulk incorporation system, LiNO_3 is anchored within the GPE. This is achieved through ion-dipole interaction and van der Waals forces between LiNO_3 and PVDF chains. A continuous supply of NO_3^- is therefore realized. As a result, C- LiNO_3 GPE induces the formation of a more uniform and stable SEI. This SEI is rich in LiN_xO_y and Li_3N . Improved reversibility is observed. Better rate capability is also obtained. Long-term cycling stability is further enhanced in different battery systems. These findings suggest that the incorporation position of LiNO_3 plays an important role. It affects both the release process and interfacial evolution. This work provides a useful approach for the design of slow-release GPEs.

Supplementary Materials

The additional data and information can be downloaded at: <https://media.sciltp.com/articles/others/2609021644510921/eChem-26040240-SM-Final.docx>. Refs [52,53] are cited in the supplementary materials.

Author Contributions

X.Z.: Conceptualization, Data Curation, Formal Analysis, Writing—original draft; Y.Z. (Yu Zhao): Investigation, Data Curation, Formal Analysis; K.M.: Investigation; J.H.: Methodology; N.W.: Conceptualization, supervision, Methodology, Funding Acquisition, Writing—Review & Editing; Y.Z. (Yaohui Zhang): Methodology, Funding Acquisition, Conceptualization, supervision, Writing—Review & Editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

The data supporting the findings of this study are available within the article and its Supporting Information. Additional data are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used ChatGPT (OpenAI) for language translation and polishing, as well as for assisting in the generation of some schematic graphical elements in Figure 1. After using this tool, the authors carefully reviewed and edited the content as needed and take full responsibility for the content of the published article.

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