

RESEARCH ARTICLE

Bifunctional Electrospun Polymer–Inorganic Interlayer for Stable and High-Energy-Density Anode-Free Lithium Metal Batteries

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ABSTRACT

Lithium metal batteries have a high energy density but suffer from severe volume changes and non-uniform Li deposition, which hinder their long-term cycling stability. Herein, we present an innovative strategy employing an electrospun nitrile-butadiene rubber (NBR)/polyacrylonitrile (PAN) membrane embedded with Li–SiO₂ nanoparticles as an interlayer for the Li anode. The elastic NBR matrix accommodates the volume deformation induced by Li plating and stripping, while the nitrile groups in PAN guide uniform Li⁺ ion flux through coordination interactions. Simultaneously, Li–SiO₂ assists in regulating interfacial Li⁺ distribution and mechanically reinforces the fibrous network. This synergistic combination improves mechanical resilience, interfacial stability, and Li⁺ ion transport. As a result, pouch-type anode-free LMBs (AFLMBs) incorporating the interlayer and LiNi_{0.88}Co_{0.10}Al_{0.02}O₂ (active mass: 22.67 mg cm^{−2}) cathode achieve a capacity retention of 76.9% after 250 cycles at 45°C and 1.0 C, outperforming cells without the interlayer. Moreover, the thickness increase of the pouch cell incorporating the LS-NP interlayer was limited to 16.6%, nearly half that observed for the cell without the interlayer. Our findings demonstrate that the cooperative functionality of the polymer matrix and Li–SiO₂ nanoparticles establishes a robust and stable interface, highlighting the promise of the bifunctional interlayer for high-energy-density AFLMBs.

1 | Introduction

Lithium (Li) metal anodes (LMAs) possess an exceptionally high theoretical specific capacity of 3 860 mAh g^{−1}, nearly ten times that of conventional graphite (372 mAh g^{−1}), making them one of the most promising anode candidates for next-generation electric vehicles and large-scale energy storage systems [1, 2]. In particular, anode-free Li metal batteries (AFLMBs) further amplify this advantage by eliminating the need for excess Li on the anode side [3, 4]. Instead, Li is deposited in situ onto

a bare current collector during the initial charging process. This anode-free configuration simplifies the cell architecture and streamlines manufacturing, offering significant benefits in terms of cost, energy density, and structural efficiency. Despite these advantages, the practical realization of AFLMBs remains severely constrained by the interfacial instability of the LMA. During repeated Li plating and stripping, substantial volume changes (>100%) and the formation of dendritic Li lead to mechanical degradation, continuous electrolyte decomposition, and the evolution of an unstable solid electrolyte interphase (SEI)

[5, 6]. These degradation processes lower the Coulombic efficiency and increase the risk of internal short-circuiting, particularly under high current density and high areal capacity conditions. Therefore, stabilizing the Li–electrolyte interface is imperative for achieving durable and reliable AFLMB operation.

Several strategies have been explored to address these challenges, including the construction of artificial SEIs [7, 8], lithiophilic surface modification [9, 10], and the design of three-dimensional (3D) structured current collectors [11, 12]. Although artificial SEIs and surface treatments can enhance interfacial chemistry and initial stability, their effectiveness often diminishes during long-term cycling due to severe volumetric changes of the Li metal. Furthermore, 3D host or scaffold-based configurations generally require pre-lithiated structures or additional Li reservoirs, which contradict the host-free concept of AFLMBs and add complexity to the system [13]. Recently, polymer-based interlayers have emerged as a promising and scalable strategy to address these challenges by directly regulating Li⁺ ion flux and accommodating electrode deformation [14, 15]. Among them, electrospun interlayers offer distinct advantages such as high porosity, interconnected channels, structural tunability, and mechanical flexibility, making them highly adaptable for various LMB configurations [16, 17]. However, most reported designs exhibit limited functionality, as they primarily focus on either enhancing ionic transport or improving mechanical robustness. Consequently, they often fail to sustain interfacial stability and suppress degradation under practical, long-term cycling conditions [18].

In this study, we introduce a multifunctional electrospun interlayer (denoted as LS-NP) composed of Li–modified SiO₂ (Li–SiO₂) nanoparticles, nitrile-butadiene rubber (NBR), and polyacrylonitrile (PAN). The elastic NBR/PAN fibers accommodate the volumetric deformation associated with Li plating and stripping during cycling, while the nitrile groups in the polymer chains help regulate local Li⁺ transport through coordination interactions. Meanwhile, Li–SiO₂ assists in regulating the local Li⁺ distribution at the interface and reinforces the fibrous network with inorganic rigidity. This synergistic architecture simultaneously enhances mechanical resilience, interfacial wettability, and ionic transport, thereby stabilizing the electrode–electrolyte interface and promoting uniform Li deposition. When implemented in pouch-type AFLMBs with a high-loading LiNi_{0.88}Co_{0.10}Al_{0.02}O₂ (NCA, active mass loading: 22.67 mg cm^{−2}) cathode, the LS-NP interlayer effectively mitigates internal pressure buildup and electrode swelling, leading to outstanding cycling stability. After 250 cycles at 45°C and 1.0 C, the cell incorporating LS-NP retained 76.9% of its initial capacity, which is significantly higher than the 56.8% retention of the cell without the interlayer. Moreover, its thickness increase was reduced by nearly 50%, confirming the effective suppression of volume change during the repeated cycling. These results demonstrate that the cooperative effects of the polymer matrix and Li–SiO₂ nanoparticles establish a robust and reversible interface, offering a practical pathway toward durable, high-energy-density AFLMBs.

2 | Results and Discussion

AFLMBs face critical challenges including dendritic Li growth and drastic volume changes at the anode interface, which cause

rapid interfacial degradation and severe capacity fading. To mitigate these issues, we developed a multifunctional electrospun interlayer (denoted as LS-NP) capable of simultaneously regulating Li⁺ transport and buffering mechanical stress at the anode interface. Figure 1 illustrates the design concept and schematic working mechanism of the interlayer. In the absence of an interlayer (Figure 1b), Li deposits unevenly on the bare Cu surface, leading to incomplete stripping and accumulation of dead Li, which accelerates interfacial degradation during cycling. In contrast, as shown in Figure 1c, the fibrous LS-NP interlayer forms a mechanically compliant and ion-regulating network that homogenizes Li⁺ ion flux, suppresses dendrite formation, and accommodates volume expansion and contraction during Li plating/stripping. This synergistic effect effectively relieves interfacial stress and enables stable, long-term Li deposition behavior.

The composition of the polymer matrix was optimized by examining the morphologies of electrospun membranes with varying NBR: PAN ratios. As shown in Figure S1, the membranes with a high NBR content exhibited poor fiber formation due to limited spinnability, whereas those with a high PAN content, although well-formed, were brittle and lacked elasticity. Consequently, a 1:1 weight ratio yielded a uniform and continuous fibrous membrane with well-balanced mechanical compliance and was selected for the fabrication of the LS-NP interlayer. This composition was therefore adopted as the optimal formulation for subsequent investigations.

The optimized NBR: PAN composition was integrated with Li–SiO₂ nanoparticles to fabricate the LS-NP interlayer. The obtained LS-NP interlayer was placed between the Cu current collector and the separator, as illustrated in Figure S2. The morphology of the LS-NP interlayer was examined using scanning electron microscopy (SEM). As shown in Figure 2a, the membrane displayed a uniform network of interconnected nanofibers with an average diameter of approximately 0.38 μm, which is favorable for electrolyte infiltration. Its energy-dispersive spectroscopy (EDS) mapping (Figure 2b) confirmed the homogeneous distribution of Si and O elements throughout the fibrous membrane, verifying the successful incorporation of Li–SiO₂ nanoparticles. The uniform dispersion of Li–SiO₂ within the fibrous network is further confirmed by higher-magnification SEM and EDS mapping images (Figure S3). Fourier transform infrared (FT-IR) spectroscopy was also employed to investigate the chemical structure of various samples. Characteristic peaks corresponding to PAN (C≡N stretching at ~2243 cm^{−1}) and NBR (–CH=CH– stretching at 967 cm^{−1}) were observed, while Li–SiO₂ exhibited Si–O–Si (~1100 cm^{−1}) and Si–OH (~960 cm^{−1}) vibrations (Figure S4a) [19, 20]. Notably, only the LS-NP sample showed a small Si–O–Si band in Figure S4b, confirming the successful incorporation of Li–SiO₂ within the fibrous polymer membrane. The mechanical strength and electrolyte wettability of the interlayers were examined to assess their interfacial compatibility. As shown in Figure 2c, the polyethylene (PE) separator exhibited the highest tensile strength (21 MPa), however, it lacked elasticity, which limits its ability to accommodate mechanical stress. In contrast, the NP interlayer showed the lowest tensile strength (5.5 MPa) but the largest strain at break (42%), reflecting the elastic nature of the polymer matrix. Incorporating Li–SiO₂ nanoparticles into NP improved the mechanical balance. As a result, LS-NP achieved a

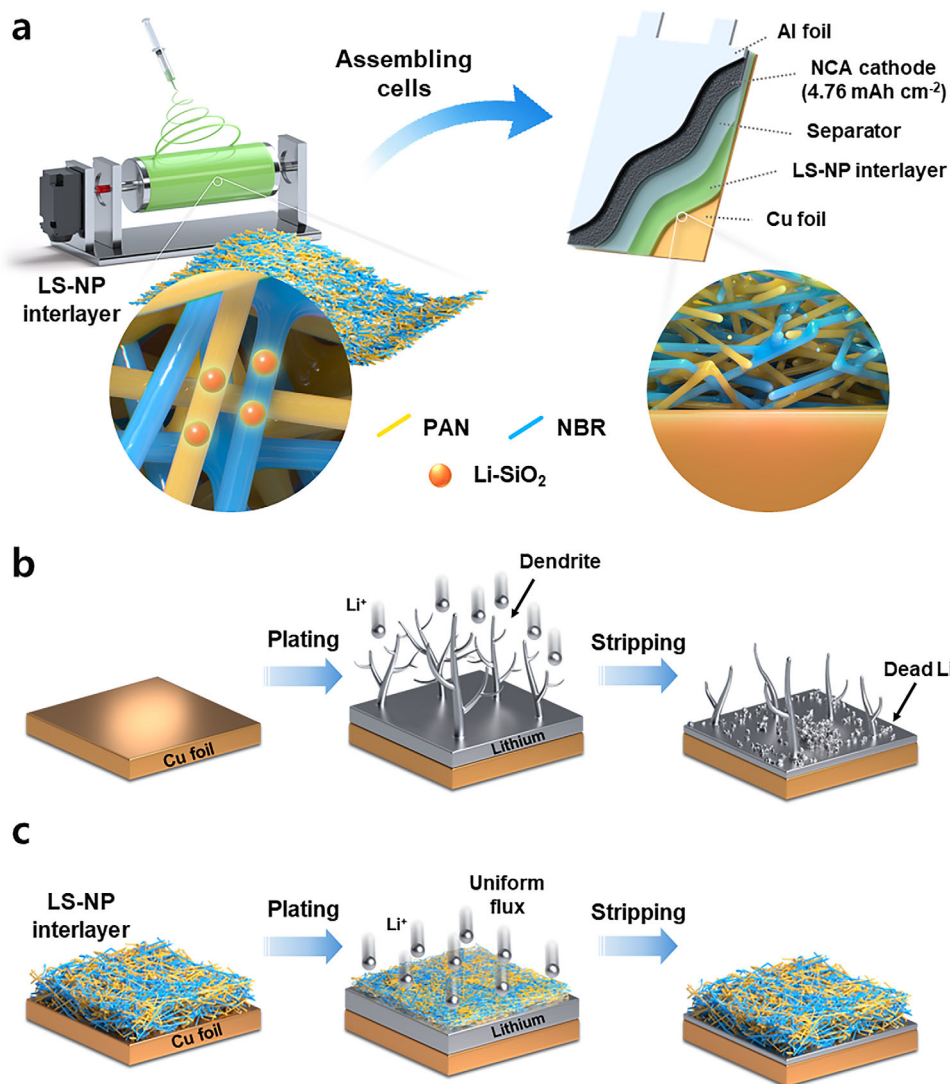


FIGURE 1 | Schematic illustration of the working mechanism during Li plating and stripping in AFLMBs. (a) Fabrication process of the LS-NP interlayer and pouch-cell assembly. Li plating and stripping behavior (b) without an interlayer and (c) with the LS-NP interlayer.

tensile strength of 7.5 MPa with 32% elongation, providing both robustness and elasticity. To further probe the local mechanical properties, nanoindentation measurements were conducted (Figure 2d). As summarized in Table S1, the elastic modulus (E_{IT}) and hardness (H_{IT}) followed the order: separator (6.83 and 0.22 GPa) > NP (3.02 and 0.08 GPa) > LS-NP (1.33 and 0.03 GPa). Unlike tensile testing, nanoindentation evaluates localized regions, making it highly sensitive to variations in porosity and microstructure [21, 22]. The polyolefin separator exhibited the highest modulus and hardness, indicating strong local rigidity but limited stress accommodation. Conversely, LS-NP displayed the lowest values owing to its finer fiber diameter and Li-SiO₂-induced structural heterogeneity. This local compliance allows for effective stress relaxation, which helps mitigate interfacial damage during cycling, while the moderate bulk tensile strength ensures overall structural integrity.

The electrolyte wettability of the interlayers was evaluated through contact angle measurements (Figure 2e–g). The electrolyte consisted of 0.6 M LiBF₄ and 0.6 M LiDFOB dissolved in a mixed solvent of fluoroethylene carbonate (FEC), diethyl

carbonate (DEC), and butyronitrile (BN). BN was introduced as a co-solvent to enhance oxidative stability under high-voltage conditions [23]. This effect was confirmed by the linear sweep voltammetry results shown in Figure S5, where the BN-containing electrolyte exhibited a delayed onset of oxidation and a lower current response at elevated voltages. In addition, the incorporation of BN contributes to a reduction in viscosity, which improves interfacial contact and ion transport. Based on the contact angle measurements, it was confirmed that the PE separator exhibited the highest contact angle (26.9°), indicating poor electrolyte affinity. In contrast, the NP interlayer showed an improved wettability with a smaller contact angle of 22.5°, attributed to its porous structure and the presence of polar nitrile groups. Upon addition of Li-SiO₂ nanoparticles, the LS-NP interlayer further reduced the contact angle to 19.0°, owing to the increased surface polarity introduced by Li-SiO₂ [24]. This enhanced wettability is expected to facilitate uniform Li⁺ transport and maintain stable interfacial contact during cycling.

The effect of the interlayer on local Li⁺ coordination and transport behavior was investigated through Raman spectroscopy,

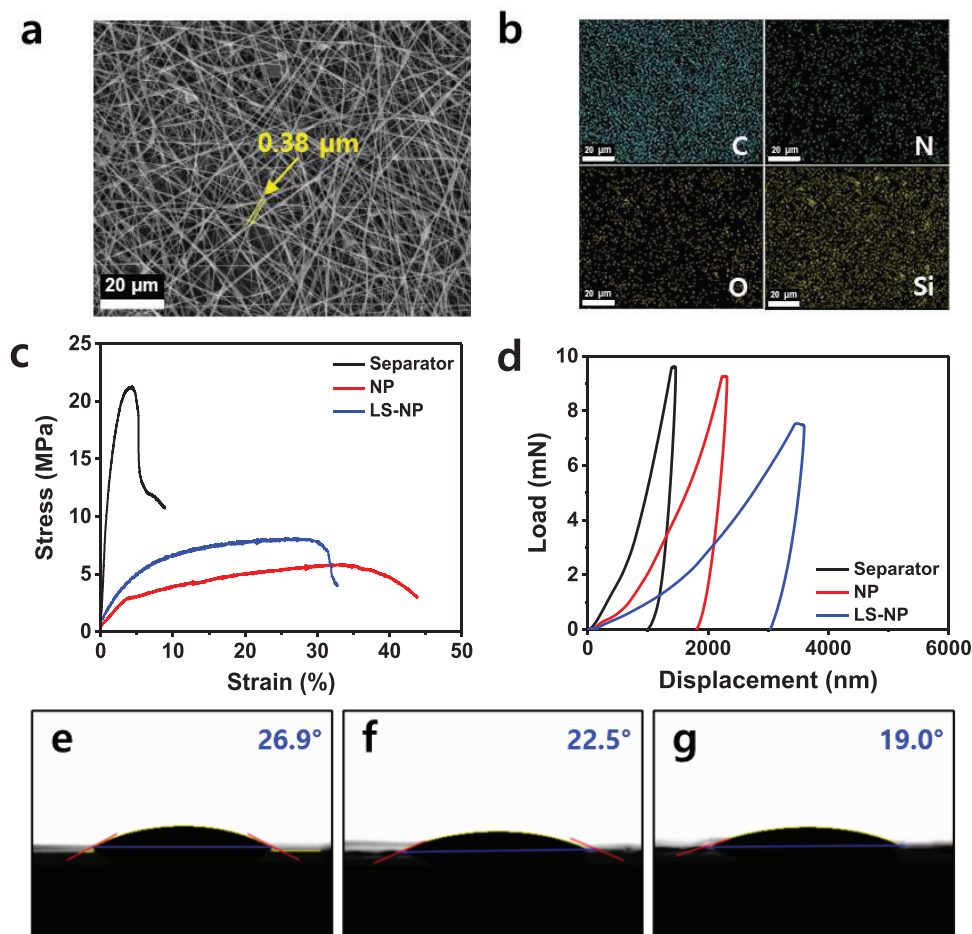


FIGURE 2 | Structural and physicochemical properties of interlayers. (a) SEM image and (b) EDS elemental maps of LS-NP. (c) Stress–strain and (d) nanoindentation curves of separator, NP, and LS-NP. Contact angle of electrolyte droplets on (e) separator, (f) NP, and (g) LS-NP.

density functional theory (DFT) calculations, and electrochemical analyses. Here, LE denotes the BN-containing electrolyte used for cell evaluation unless otherwise specified. Figure 3a shows the Raman spectra of LS-NP in the $C\equiv N$ stretching region ($2220\text{--}2260\text{ cm}^{-1}$). The dry LS-NP interlayer exhibited a nitrile band at 2238 cm^{-1} , corresponding to free $C\equiv N$ groups. Upon electrolyte uptake, an additional band appeared at a higher wavenumber, which can be assigned to Li^+ -nitrile coordination, indicating ion–dipole interactions between Li^+ and the nitrile-containing polymer components. Because the BN-containing LE also contains nitrile groups, additional Raman measurements were performed using a BN-free electrolyte to exclude the contribution of butyronitrile (Figure S6). The LS-NP soaked with BN-free electrolyte shows a similar coordinated nitrile feature, confirming that the nitrile groups in the interlayer participate in local Li^+ coordination. The FEC-based electrolyte was also used as a feasible single-solvent reference condition because sufficient dual-salt solubility was obtained at the same salt concentration (Figure S7). In the $C\equiv N$ stretching region, the LS-NP soaked with FEC-based electrolyte also exhibits a coordinated nitrile feature (Figure S7a), further supporting local Li^+ -nitrile coordination within the interlayer. For comparison, Raman spectra of NP soaked with the BN-free electrolyte are provided in Figure S8. The coordinated nitrile feature observed in Figure S8a indicates that the nitrile-containing polymer matrix can also

participate in Li^+ -nitrile coordination [25]. Raman spectra in the $700\text{--}750\text{ cm}^{-1}$ region (Figure 3b) further reveal changes in the solvation structures associated with $DFOB^-$ and fluoroethylene carbonate (FEC) coordination [26, 27]. In the BN-containing LE, strong contact-ion pair (CIP) and aggregate (AGG) signals dominated, with CIP/AGG species accounting for 86.4% of the total solvated species. Under these conditions, 20.6% of FEC was coordinated to Li^+ and 79.4% remained free. In the presence of LS-NP, the CIP/AGG bands were moderately suppressed and the CIP/AGG fraction decreased to 70.2%. At the same time, the fraction of FEC coordinated to Li^+ decreased to 12.4%, while the proportion of free FEC increased to 87.6%. These trends were further supported by the BN-free electrolyte measurement (Figure S6b), in which the coordinated FEC fraction decreased from 27.2% to 15.4% after soaking with LS-NP, while the free FEC fraction increased from 72.8% to 84.6%. The CIP/AGG contribution associated with $DFOB^-$ was also reduced under the BN-free condition, confirming that the observed solvation modulation does not originate from butyronitrile. In the FEC-based electrolyte (Figure S7b), the coordinated FEC fraction similarly decreased from 12.6% to 7.5%, accompanied by an increase in the free FEC fraction from 87.4% to 92.5%. Because the $DFOB^-$ -related bands were weak and poorly resolved under this single-solvent condition, quantitative deconvolution into $DFOB^-$ -associated species could not be performed. For NP soaked

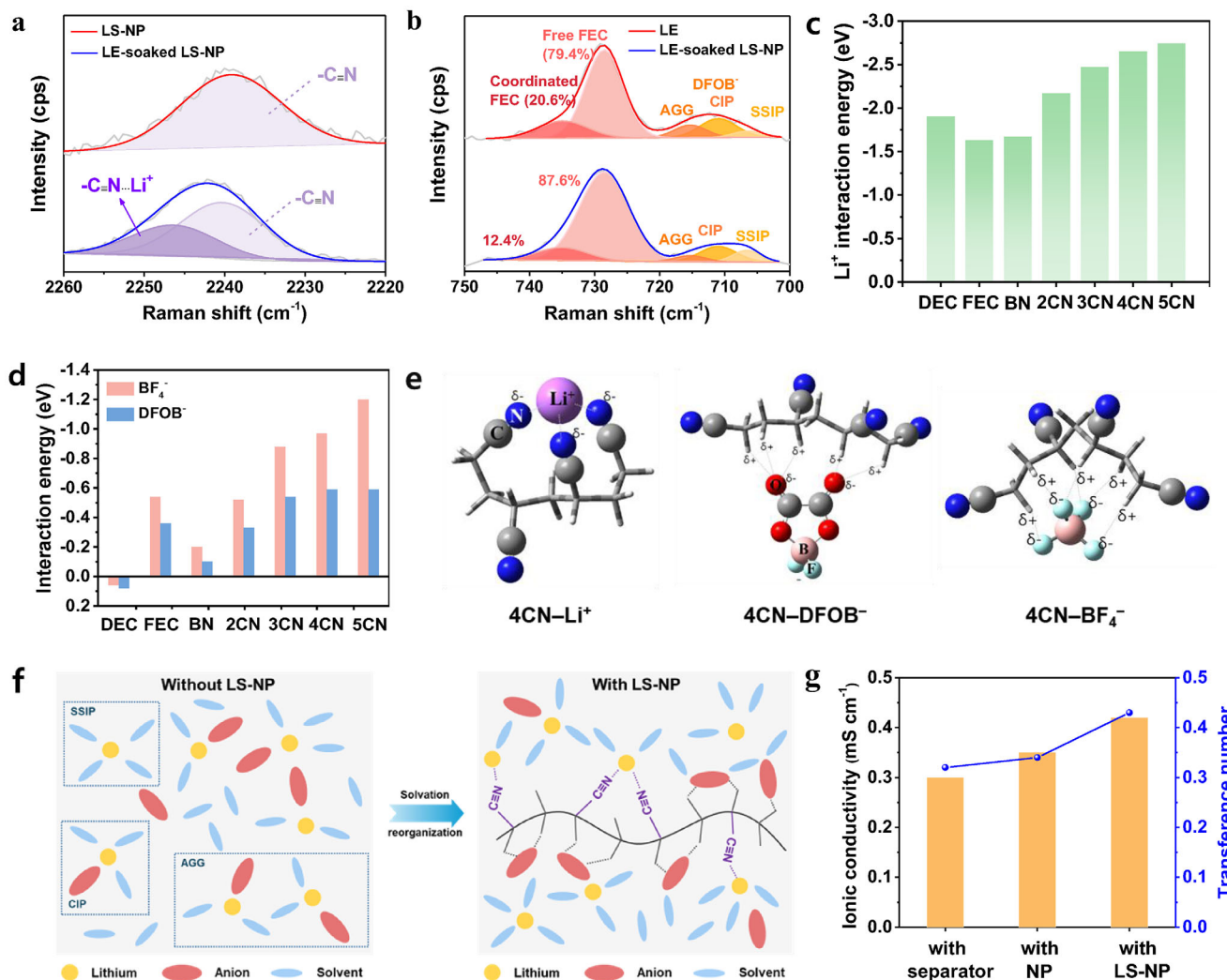


FIGURE 3 | (a) Raman spectra in the C≡N stretching region (2220–2260 cm⁻¹) of LS-NP and BN-containing electrolyte-soaked LS-NP. (b) Raman spectra in the 700–750 cm⁻¹ region corresponding to DFOB⁻ coordination and FEC solvent vibrations for BN-containing LE and BN-containing LE-soaked LS-NP. (c) Calculated interaction energies of Li⁺ with solvent molecules and polymer nitrile groups. (d) Calculated interaction energies of anions with solvent molecules and polymer nitrile groups. (e) Optimized configurations of Li⁺ and anions interacting with polymer nitrile groups. (f) Schematic illustration of local Li⁺ solvation structure in the presence of the interlayer. (g) Ionic conductivity and Li⁺ transference numbers of LE with separator, NP, and LS-NP interlayers.

with the BN-free electrolyte (Figure S8b), 19.8% of FEC was coordinated to Li⁺ and 80.2% remained free, showing that the nitrile-containing polymer matrix can also influence the local coordination environment. These results suggest that the nitrile-functionalized interlayer modulates the local solvation structure within the electrolyte-filled porous interlayer. In particular, it alleviates excessive Li⁺-anion aggregation and partially shifts the population from strongly associated CIP/AGG environments toward less associated states, rather than eliminating Li⁺-anion association. Notably, CIP/AGG still constitute the majority (> 2/3 of the solvated species) even with the interlayer, implying that the electrolyte remains anion-rich and can still provide sufficient anion-derived components for SEI formation at the Li metal surface. Such local solvation reorganization increases the proportion of free FEC molecules and creates a low-aggregation environment within the electrolyte-wetted interlayer, which is expected to facilitate more homogeneous Li⁺ transport at the anode interface. To gain molecular-level insights, DFT calculations were per-

formed using PAN oligomers containing two to five nitrile groups (Figure 3c–e and Figure S9). The calculated interaction energies (Figure 3c) reveal that Li⁺ interacts more strongly with nitrile nitrogen atoms than with carbonate solvents, confirming the high affinity of multidentate nitrile coordination. Bulky anions such as DFOB⁻ and BF₄⁻ exhibited relatively weaker interactions with the PAN backbone (Figure 3d), though their non-negligible values indicate partial association. The optimized configuration in Figure 3e visually confirms that Li⁺ preferentially coordinates to nitrile sites, whereas anions are weakly associated with methylene protons through weak electrostatic interactions rather than direct nitrile binding. While DFOB⁻ showed minimal change in interaction strength with increasing nitrile content, BF₄⁻ exhibited a moderate increase, though still significantly weaker than Li⁺ coordination. These results highlight that nitrile functionalities primarily stabilize Li⁺ ions, while anion interactions remain secondary. Together, they contribute to the stabilization of less aggregated solvation environments in the interlayer region.

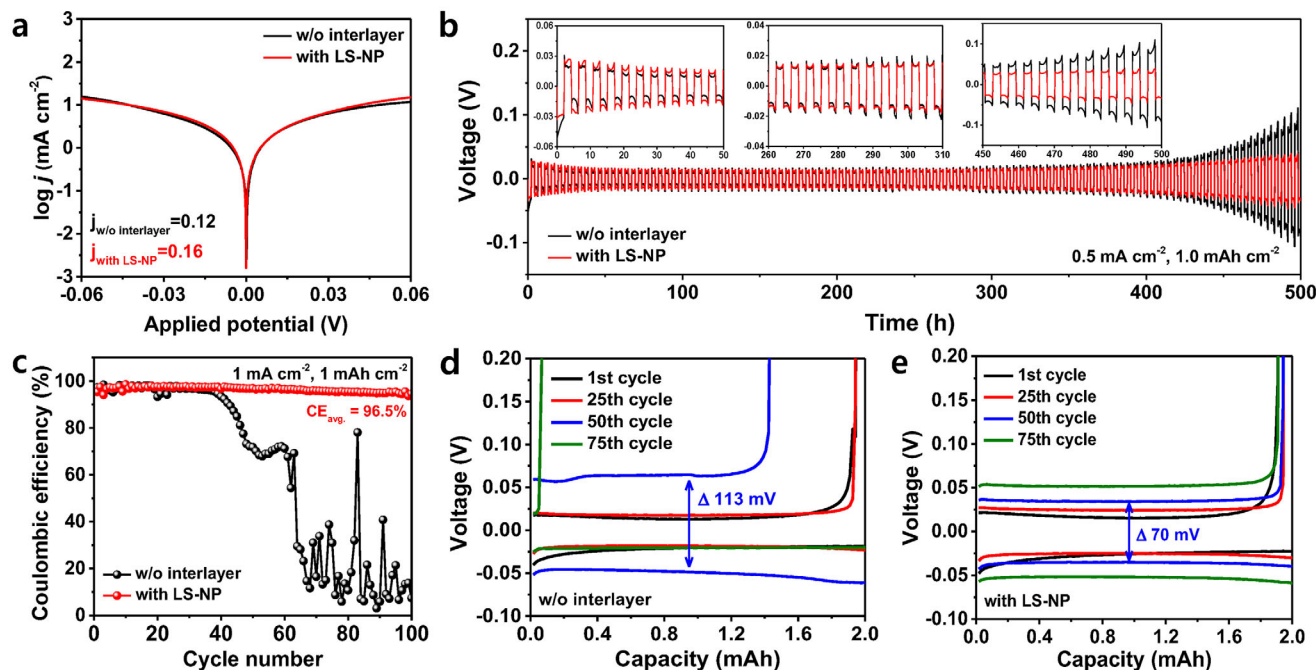


FIGURE 4 | Electrochemical performance in symmetric and asymmetric cells with and without the LS-NP interlayer. (a) Tafel plots of symmetric Li/Li cells. (b) Galvanostatic cycling profiles of symmetric Li/Li cells. (c) Coulombic efficiency of Li/Cu cells, and corresponding voltage profiles of (d) the cell without the interlayer and (e) the cell with the LS-NP interlayer.

Raman spectroscopy and DFT calculations collectively indicate that the nitrile-functionalized interlayers reorganize the solvation structure by selectively stabilizing Li^+ and weakly associating with anions. As a result, strong Li^+ -anion association within the electrolyte-wetted interlayer region is attenuated rather than completely prevented. This dual effect moderately reduces the population of strongly associated CIP/AGG species within the interlayer region, consistent with the experimentally observed increase in the fraction of free FEC molecules. Based on these findings, a mechanistic illustration is proposed in Figure 3f. In the absence of an interlayer, Li^+ predominantly exists in CIP/AGG environments. In contrast, with the NP or LS-NP interlayer, Li^+ coordinates not only with carbonate solvents but also with nitrile groups, which loosens the strongly aggregated environments and leads to more weakly associated, less aggregated solvation structures. In this case, CIP/AGG still remain the majority species, while anions interact only weakly with the polymer backbone. This local solvation reorganization promotes more homogeneous Li^+ transport within the interlayer. Near the Li metal surface, however, Li^+ desolvation and interfacial reduction of FEC and anions still proceed, which is consistent with the formation of an anion-rich, LiF-containing SEI discussed later. The LS-NP interlayer is designed as a thin and porous structure that is fully wetted by the electrolyte. The Li^+ ion transport properties of electrolyte-soaked PE separators without and with interlayers were evaluated (Figure 3g). AC impedance spectra for the conductivity measurement are presented in Figure S10. The ionic conductivity was slightly increased in the presence of the porous interlayers, indicating that the interlayers do not hinder ion transport. This result can be attributed to improved electrolyte infiltration within the electrospun porous structure compared to the conventional separator [28]. The Li^+ transference number (t_{Li^+}) increased from 0.32 for the separator to 0.34 for NP

and 0.43 for LS-NP, and the corresponding impedance spectra used for the transference number analysis are shown in Figure S11. The increase is attributed to nitrile-assisted Li^+ dissociation and the presence of Li-SiO₂, which promote Li^+ transport at the interface. To examine the dissolution behavior of Li^+ from Li-SiO₂, the LS-NP interlayer was soaked in the electrolyte, and the resulting solution was analyzed by ICP-OES, as summarized in Table S2. Si was not detected in the electrolyte after soaking, indicating that the SiO₂ framework remains intact without measurable dissolution. By contrast, the Li concentration increased slightly from 0.89 to 0.91%, which can be attributed to the partial dissociation of Li^+ ions from the sulfonate groups, since Li-SiO₂ is composed of sulfonate groups ($-\text{SO}_3\text{Li}$) tethered to the SiO₂ framework. These results suggest that only a limited amount of Li^+ is released into the electrolyte, while the inorganic framework remains structurally stable.

The electrochemical kinetics and interfacial stability imparted by the LS-NP interlayer were evaluated using symmetric and asymmetric cell configurations. Figure 4a presents the Tafel plots of symmetric Li/Li cells. The cell incorporating LS-NP exhibited a higher exchange current density (0.16 mA cm^{-2}) compared to the cell without the interlayer (0.12 mA cm^{-2}), indicating that the interlayer facilitates charge transfer reaction at the Li interface [29]. Galvanostatic cycling (Figure 4b) further revealed distinct differences in long-term cycling stability. Although both cells operated for 500 h without short-circuiting, they showed markedly different polarization behaviors. The cell without an interlayer exhibited a gradual increase in overpotential, reflecting the progressive buildup of interfacial resistance. On the other hand, the LS-NP-containing cell maintained a relatively stable voltage profile throughout cycling. After 500 h, the overpotential of the cell without the interlayer was nearly twice that of the

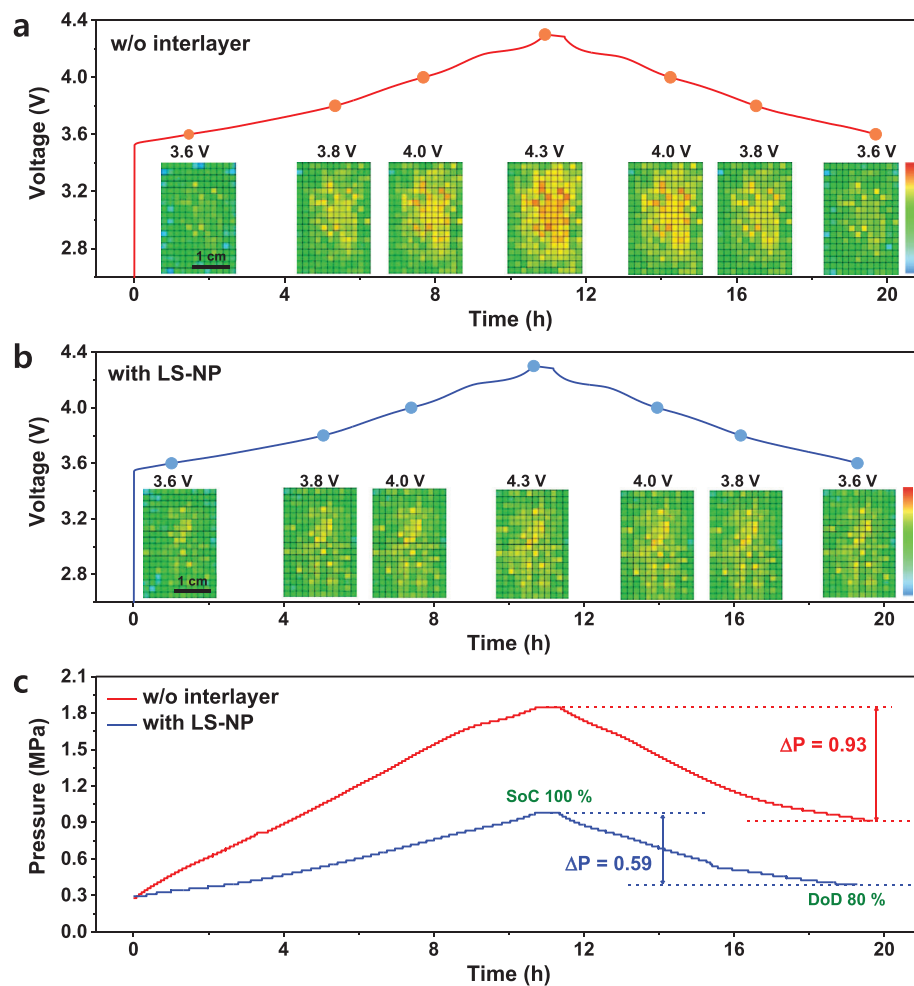


FIGURE 5 | Operando spatial pressure analysis during the initial cycling of AFLMB pouch cells (0.1 C, stack pressure = 0.3 MPa). Voltage profiles and corresponding pressure mapping images for cells (a) without and (b) with the LS-NP interlayer. (c) Temporal evolution of mean internal pressure, where ΔP is defined as the pressure difference between 100% SoC and 80% DoD.

LS-NP cell, confirming that the interlayer effectively suppresses polarization by homogenizing Li^+ flux and accommodating electrode volume changes. Figure S12 presents the galvanostatic intermittent titration technique (GITT) profiles of symmetric Li/Li cells used to evaluate the influence of the interlayer on Li^+ transport kinetics and concentration polarization [30]. Across the entire current density range, the cell incorporating the LS-NP interlayer consistently exhibited lower overpotentials and faster relaxation behavior, indicating enhanced Li^+ transport kinetics and reduced concentration polarization during repeated cycling. The asymmetric Li/Cu cell configuration further demonstrated the stabilizing effect of the interlayer. As shown in Figure 4c, the cell without an interlayer exhibited unstable cycling accompanied by a rapid decline in Coulombic efficiency (CE), whereas the cell with LS-NP maintained a high and stable CE, averaging 96.5% over 100 cycles. The corresponding voltage profiles clearly highlight the differences in overpotential (Figure 4d,e). At the 50th cycle, the cell without an interlayer displayed an overpotential of 113 mV, compared to 70 mV for the LS-NP cell. These results confirm that the LS-NP interlayer promotes highly reversible Li plating/stripping by homogenizing Li^+ flux, suppressing dead Li formation, and mitigating dendrite-induced polarization.

Operando spatial pressure mapping was conducted to investigate the influence of the LS-NP interlayer on the mechanical stability of AFLMB pouch cells. The cells were cycled under a limited depth-of-discharge (DoD) condition, as described in the experimental section. As shown in Figure S13, a customized fixture equipped with a load cell maintained a constant stack pressure of 0.3 MPa, while a pressure sensor monitored the real-time pressure distribution beneath a pouch cell (cell size: $2 \times 3 \text{ cm}^2$). Figure 5a,b display the voltage profiles and corresponding pressure maps during the pre-conditioning cycle at 0.1 C. For the cell without an interlayer, the pressure distribution became highly heterogeneous upon charging, with pronounced high-stress regions emerging at 100% SoC, indicative of localized volume expansion [31]. During discharge, the pressure could not fully recover, evidencing irreversible deformation and non-uniform stripping. In contrast, the LS-NP integrated cell maintained a homogeneous pressure distribution throughout cycling, exhibiting minimal formation of localized stress regions, which suggests improved interfacial compliance and reversible electrode breathing behavior. The temporal evolution of the mean internal pressure is compared in Figure 5c. The pressure variation (ΔP), defined as the pressure difference between the fully charged (100% SoC) and

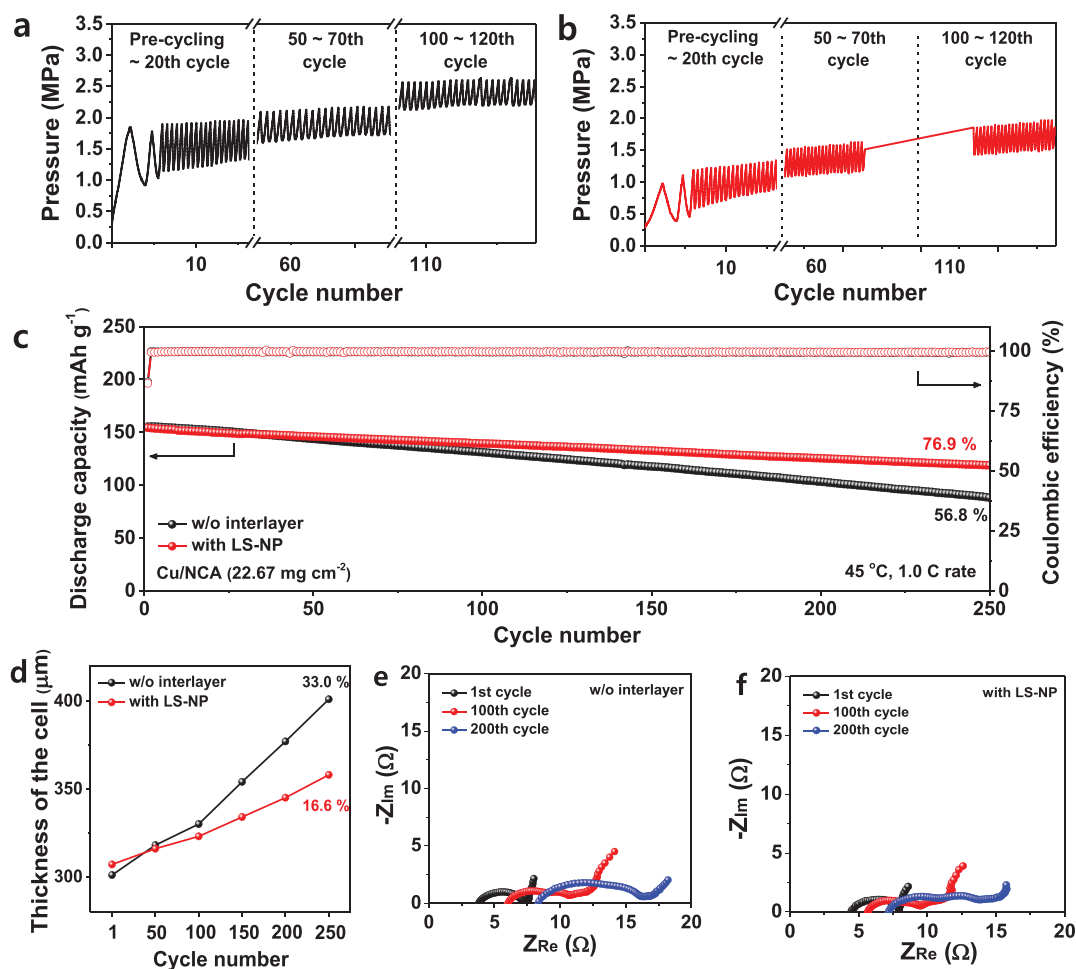


FIGURE 6 | Electrochemical and mechanical performance of AFLMB pouch cells. Internal pressure profiles of cells (a) without and (b) with the LS-NP interlayer. (c) Cycling performance of AFLMB pouch cells. (d) Thickness evolution during cycling. AC impedance spectra of cells (e) without and (f) with the LS-NP interlayer during cycling.

80% discharged (80% DoD) states, reached 0.93 MPa for the cell without an interlayer but was reduced to 0.59 MPa for the LS-NP cell. This significant suppression highlights the dual functionality of the LS-NP interlayer: the elastic fibrous framework buffers volumetric fluctuations, while its ion-regulating capability ensures uniform Li⁺ flux, collectively mitigating stress accumulation and stabilizing the Li metal interface.

The effect of the LS-NP interlayer on the long-term cycling performance was investigated using AFLMB pouch cells assembled with high-loading NCA cathodes (active mass loading: 22.67 mg cm⁻²). Operando pressure monitoring (Figure 6a,b) revealed a continuous increase in internal pressure for the cell without an interlayer, consistent with inhomogeneous Li deposition and irreversible volume buildup [32]. The LS-NP integrated cell also exhibited a gradual pressure increase, but the overall profile was much more stable, and the magnitude of pressure rise was significantly smaller, indicating improved interfacial reversibility and suppression of localized stress accumulation. The voltage profiles of the cells further underscore this difference. As shown in Figure S14, the LS-NP cell displayed reversible charge-discharge curves with lower polarization over 250 cycles, whereas the cell without an interlayer exhibited progressive polarization and capacity fading, indicative of continuous inter-

facial degradation. Consequently, the LS-NP cell retained 76.9% of its initial capacity after 250 cycles, compared to 56.8% for the cell without an interlayer (Figure 6c). We additionally evaluated the cell performance under full DoD conditions (2.8–4.3 V). As shown in Figure S15, the cell cycled under full DoD exhibits significantly faster capacity decay compared to that under limited DoD conditions. This result confirms that complete Li stripping leads to more rapid capacity decay due to aggravated Li loss and interfacial degradation. Mechanical reversibility was further supported by thickness evolution data (Figure 6d). The cell without the interlayer underwent continuous swelling, reaching a 33.0% increase after 250 cycles, evidence of dendrite-induced volume accumulation and parasitic reactions. In contrast, the LS-NP cell showed markedly reduced swelling, limited to 16.6% after 250 cycles, nearly half that of the cell without the interlayer, confirming the interlayer's effectiveness in suppressing irreversible expansion and maintaining structural integrity. In addition, we prepared a thinner LS-NP interlayer (3 μm) and evaluated its performance in combination with PE separator, in comparison with the thicker LS-NP interlayer (10 μm) + PE separator configuration. As shown in Figure S16, the thinner interlayer exhibited a slightly higher initial discharge capacity, likely due to reduced ionic resistance. However, its cycling stability was inferior to that of the thicker interlayer. Further structural analysis using

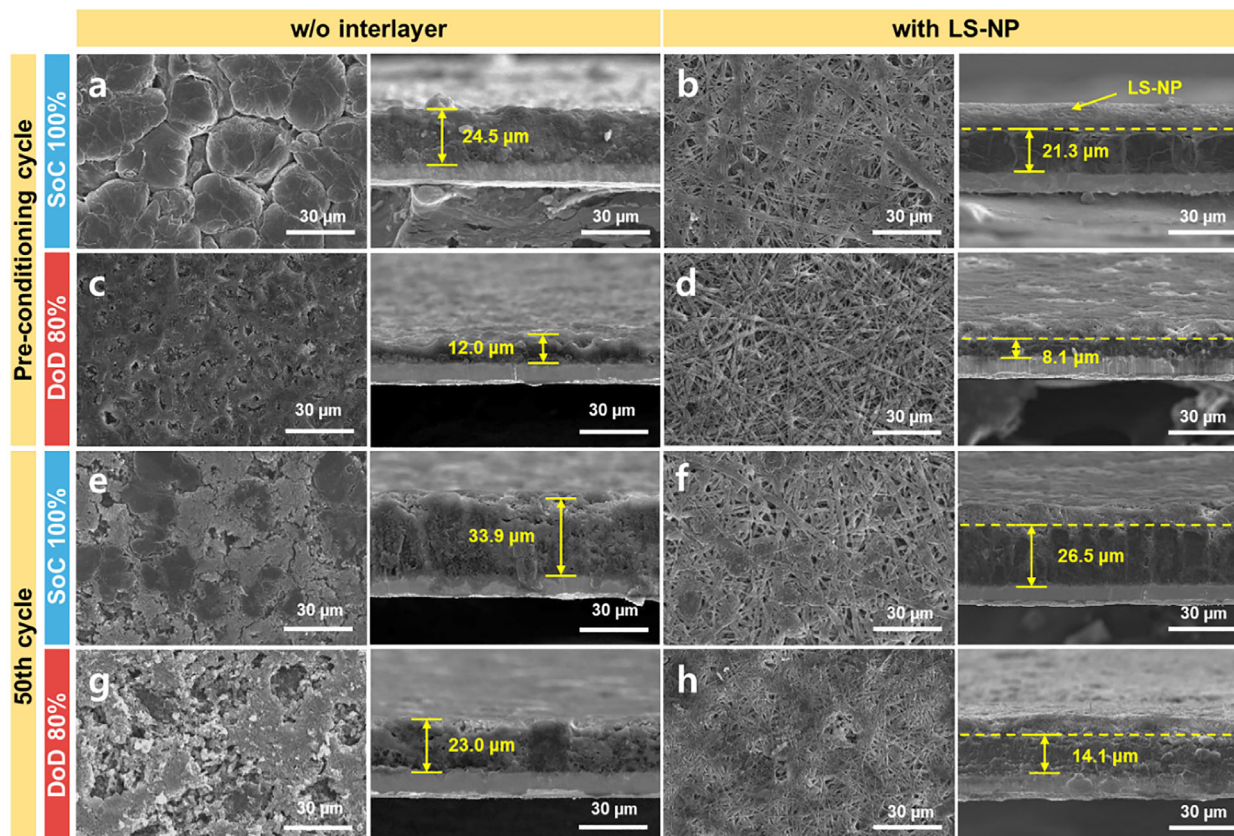


FIGURE 7 | SEM images of Li anodes from AFLMB pouch cells with and without the LS-NP interlayer. (a,b) Charged state after the pre-conditioning cycle. (c,d) Discharged state after the pre-conditioning cycle. (e,f) Charged state after the 50th cycle. (g,h) Discharged state after the 50th cycle.

SEM (Figure S17) revealed that the thinner interlayer did not maintain a uniform fibrous morphology or sufficient interfacial coverage. This led to inhomogeneous Li deposition and reduced structural integrity during cycling. These observations indicate that insufficient interlayer thickness limits both mechanical robustness and effective interfacial regulation. Electrochemical impedance spectroscopy (Figure 6e,f) revealed a consistent trend. The cell without an interlayer exhibited a pronounced increase in interfacial resistance during cycling, attributed to continuous SEI growth, electrolyte decomposition, and dead Li accumulation [33]. In contrast, the LS-NP integrated cell maintained a stable impedance response with only a slight increase in charge-transfer resistance, indicating that the interlayer preserves efficient ion-transport pathways and mitigates interfacial degradation. To further demonstrate the practicality and scalability of the interlayer design, nine-stack double-sided pouch cells were fabricated using the same electrolyte composition (Figure S18). As shown in Figure S19, the pouch cell incorporating the LS-NP interlayer delivered a discharge capacity of 2.2 Ah and retained 85.1% of its initial capacity after 100 cycles, confirming stable cycling behavior even under high-loading and multi-stacked configurations. The calculated gravimetric and volumetric energy densities reached 390.8 Wh kg⁻¹ and 900.8 Wh L⁻¹, respectively (based on the total cell mass and volume, Table S3), highlighting that the interlayer design enables high energy density AFLMBs under practical multi-stacked architectures. Collectively, these results demonstrate that the LS-NP interlayer effectively suppresses dendrite formation, alleviates internal pressure buildup, and stabilizes the Li–electrolyte interface, thereby ensuring

lasting long-term cycling stability in anode-free lithium metal batteries.

The morphological evolution of Li anodes was examined after pre-conditioning and 50 cycles in AFLMB pouch cells (Figure 7). In the absence of the interlayer, the deposited Li layer thickened from 24.5 μm (charged state) and 12.0 μm (discharged state) after the pre-conditioning cycle to 33.9 and 23.0 μm after 50 cycles. This irreversible thickening is attributed to the progressive accumulation of electrically isolated dead Li and parasitic byproducts, which contribute to inactive volume buildup at the interface [34]. In contrast, the anodes with the LS-NP interlayer exhibited much smaller thickness variations while retaining their fibrous morphology in both top view and cross-sectional observations. The Li layer increased from 21.3 to 26.5 μm in the charged state and from 8.1 to 14.1 μm in the discharged state, indicating suppressed dead Li accumulation and improved reversibility. Notably, the LS-NP interlayer remained clearly discernible after extended cycling, confirming its role as a mechanically compliant network that guides Li⁺ flux and accommodates interfacial stress. This morphological preservation is consistent with the operando pressure analysis discussed earlier. The concurrent suppression of both thickness growth and pressure buildup validates the dual functionality of the LS-NP interlayer in mitigating dead Li formation and relieving localized mechanical stress, thereby stabilizing the Li electrode–electrolyte interface during prolonged cycling.

To elucidate the interfacial chemistry governing morphological stability, XPS analyses were performed on Li anodes after 50

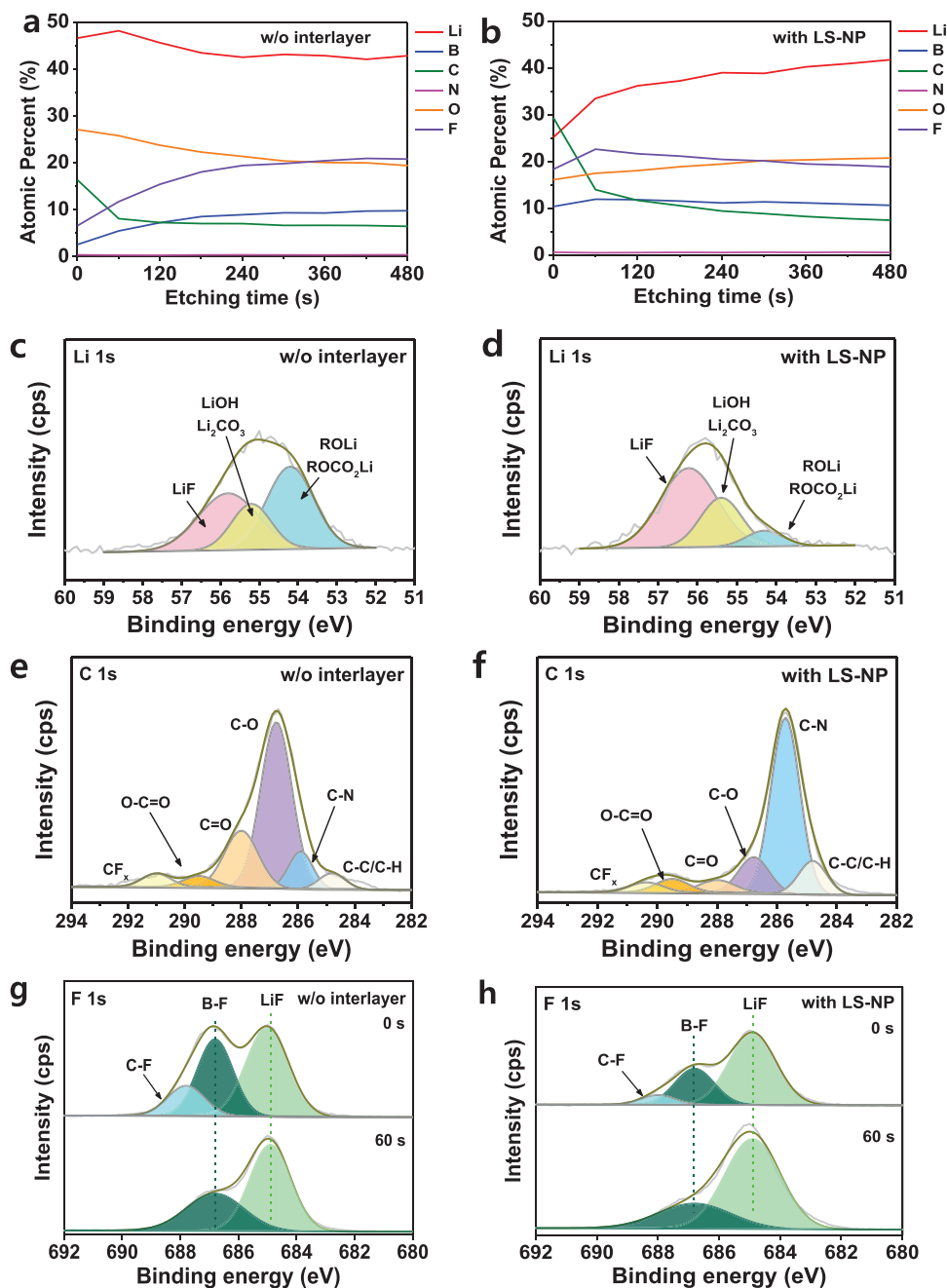


FIGURE 8 | XPS spectra of Li metal anodes after 50 cycles without and with the LS-NP interlayer. (a,b) Depth-dependent elemental profiles. (c–h) Li 1s, C 1s, and F 1s spectra of Li anodes without and with the LS-NP interlayer. The F 1s spectra were collected at the surface (0 s) and after 60 s of sputtering.

cycles. Additional Li 1s spectra collected after the first preconditioning charge (Figure S20) show that both cells, with and without the LS-NP interlayer, initially form an anion-rich, LiF-dominant SEI on the Li deposits, indicating that the interlayer does not suppress anion-derived SEI formation at the early stage. This is consistent with the Raman analysis (Figure 3), where CIP/AGG species still constitute the majority of the solvated species even in the presence of the interlayer, indicating that the initial SEI formation remains anion-rich regardless of the interlayer. Figure 8a,b show the depth-dependent elemental profiles of Li anodes after cycling. For the Li anode without an interlayer, the C and O signals gradually decreased while the F and B intensities

increased with sputtering, suggesting continuous decomposition of carbonate solvents and LiDFOB, leading to the build-up of organic- and borate-rich components on top of the initially formed LiF-containing SEI. In contrast, the anode with the LS-NP interlayer exhibited a sharp decrease in carbon and a nearly constant fluorine content throughout the etched depth, accompanied by a pronounced suppression of B species. These compositional features indicate that the LS-NP interlayer effectively mitigates additional organic and borate-derived decomposition, limiting the growth of thick decomposition products and helping to preserve a LiF-enriched SEI [35]. The Li 1s spectra (Figure 8c,d) further highlight the distinct interfacial chemistries. The Li anode

without an interlayer exhibits broad and asymmetric features with pronounced contributions from Li_2CO_3 and ROCO_2Li , whereas the anode with the LS-NP interlayer shows a stronger and sharper LiF peak, indicating preferential preservation of LiF and suppression of electrolyte-derived species. The C 1s spectra (Figure 8e,f) reveal that the anode without an interlayer contains prominent O=C=O and C=O peaks associated with carbonate decomposition products, while the LS-NP cell displays reduced carbonate intensity and a relatively enhanced C–N contribution. The more pronounced C–N contribution observed in Figure 8f can be interpreted as a relative increase in the C 1s spectrum, primarily resulting from the suppression of other carbonate-derived species (e.g., Li_2CO_3 and ROCO_2Li). To further clarify this behavior, the C 1s spectra after the pre-conditioning cycle are provided in Figure S21. At this stage, only minor differences in the C–N contribution are observed between the two systems, while the overall spectral features remain comparable, indicating that the initial interphase compositions are largely similar. The N 1s spectra in Figure S22 show a weak signal near 400 eV corresponding to C–N bonding, corroborating the presence of nitrogen-containing fragments observed in the C 1s spectra. The F 1s spectra (Figure 8g,h) further support these findings. The LS-NP anode maintains a LiF-dominated signal both at the surface and after 60 s of sputtering, whereas the anode without an interlayer exhibits multiple components attributed to C–F and B–F bonds. The persistent LiF signature and uniform F distribution across the depth confirm that the interlayer helps retain a LiF-rich inorganic SEI by mitigating parasitic decomposition reactions at the interface. Collectively, the XPS and morphological analyses demonstrate that the LS-NP interlayer regulates the evolution of the initially formed anion-rich, LiF-containing SEI, suppresses the accumulation of organic- and borate-rich species, and maintains a LiF-enriched SEI that alleviates interfacial stress and thereby extends the cycle life of AFLMBs.

3 | Conclusion

In this work, a fibrous interlayer composed of NBR, PAN, and Li– SiO_2 was developed to mitigate the severe volume changes of Li metal and stabilize the electrode interface in AFLMBs. The elastic polymer matrix effectively accommodated the deformation induced by Li plating and stripping, while the polar functional groups regulated Li^+ flux to promote uniform deposition. When applied to Cu/NCA anode-free pouch cells with a high active mass loading of 22.67 mg cm^{-2} and operated at 3.6 – 4.3 V (0.33 C charge and 1.0 C discharge), the LS-NP interlayer enabled stable cycling for over 250 cycles with a capacity retention of 76.9%. Moreover, the overall cell thickness increased by only 16.6%, approximately half that of the cell without an interlayer, confirming the effective suppression of irreversible swelling. Collectively, these results demonstrate that the structurally and chemically engineered fibrous interlayer suppresses dendrite formation, alleviates internal mechanical stress, and stabilizes the Li–electrolyte interface. This bifunctional interfacial design provides a robust and scalable strategy for realizing high energy density AFLMBs and offers valuable insights into the rational design of polymer-based interlayers for next-generation lithium metal batteries.

4 | Experimental Section

4.1 | Materials

Polyacrylonitrile (PAN, $M_w = 150\,000$) and Li– SiO_2 nanoparticles (average diameter: 200 nm) were purchased from Sigma–Aldrich. The Li– SiO_2 nanoparticles consist of sulfonate-functionalized silica ($\text{SiO}_2\text{--O}(\text{CH}_2)_3\text{SO}_3^-\text{Li}^+$), where Li^+ is associated with fixed anionic sites on the SiO_2 surface. Nitrile-butadiene rubber (NBR, $M_w = 350\,000$) was kindly supplied by Kumho Petrochemical Co., Ltd. *N,N*-Dimethylacetamide (DMAc, anhydrous, 99.8%, Sigma–Aldrich) was used as the solvent without further purification. Lithium foil (thickness: 20 μm , Honjo Metal) and copper foil (thickness: 8 μm , Iljin Materials) were used as received. A polyethylene (PE) separator (thickness: 9 μm , Senior) was vacuum-dried at 60°C for 12 h prior to use. The electrolyte was prepared by dissolving 0.6 M LiBF_4 and 0.6 M LiDFOB in a mixed solvent of fluoroethylene carbonate (FEC), diethyl carbonate (DEC), and butyronitrile (BN) at a volume ratio of 31:55:14.

4.2 | Preparation of the Interlayer

Figure 1a schematically illustrates the fabrication process of the interlayer and the corresponding cell configuration. The NP interlayer was fabricated via electrospinning of a mixed polymer solution containing 10 wt.% PAN and 10 wt.% NBR dissolved in DMAc. The solution was loaded into a syringe and electrospun under an applied voltage of 10 kV at a flow rate of 1 mL h^{-1} . The resulting nanofibers were collected on a grounded aluminum drum positioned 15 cm from the nozzle under ambient conditions, followed by vacuum drying at 60°C overnight to remove residual solvent. The as-prepared membrane exhibited a uniform thickness of approximately 10 μm . The LS-NP interlayer was produced using the same procedure, except that 5 wt.% Li– SiO_2 nanoparticles were incorporated into the polymer solution prior to electrospinning.

4.3 | Electrode Preparation and Cell Assembly

The $\text{LiNi}_{0.88}\text{Co}_{0.10}\text{Al}_{0.02}\text{O}_2$ (NCA) cathode was prepared by casting a slurry containing 97.7 wt.% active material onto aluminum foil using *N*-methyl-2-pyrrolidone (NMP) as the solvent. The resulting cathode exhibited an active mass loading of 22.67 mg cm^{-2} . Anode-free pouch cells were assembled in a double-sided cathode configuration, where an NCA cathode coated on both sides of Al foil was paired with two bare Cu foils serving as anode current collectors. The dimensions of the cathode and anode were 2.0 cm $\times$ 3.0 cm and 2.2 cm $\times$ 3.2 cm, respectively. A PE separator was employed together with the LS-NP interlayer, which was inserted as a freestanding layer between the separator and each Cu foil. All cell components were stacked and vacuum-sealed within aluminum-laminated pouches. The electrolyte was added at an electrolyte-to-capacity ratio of 3.0 g Ah^{-1} . All pouch cells were assembled in a controlled dry-room environment.

4.4 | Electrochemical Measurements

The ionic conductivity was measured using stainless steel symmetric cells, in which a separator with or without an interlayer was soaked in electrolyte. AC impedance spectroscopy was performed using a ZIVE MP1 (WonATech) over a frequency range of 10 Hz to 1 MHz with an amplitude of 10 mV at 25°C. Li/Li symmetric cells were assembled in CR2032-type coin cells using Li foil and a separator. The NP or LS-NP interlayer was inserted between the separator and both Li electrodes. The Li^+ transference number (t_{Li^+}) of the interlayer was determined by combining DC polarization and AC impedance measurements at 25°C [36]. Galvanostatic cycling was carried out at a current density of 0.5 mA cm^{-2} with a capacity of 1.0 mAh cm^{-2} . Tafel analysis was conducted using Li/Li symmetric cells by applying low-voltage polarization ($\pm 250 \text{ mV}$ vs. OCV) at a scan rate of 0.1 mV s^{-1} to evaluate the exchange-current density and interfacial charge transfer kinetics [37]. The galvanostatic intermittent titration technique (GITT) was performed using Li/Li symmetric cells to examine Li^+ diffusion behavior. A current pulse of 0.1 mA cm^{-2} for 10 min was applied, followed by a 2 h open-circuit rest, and the process was repeated over multiple cycles [38]. The Coulombic efficiency (CE) of Li plating/stripping was evaluated in Li/Cu cells at 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} . Galvanostatic charge-discharge tests of pouch-type anode-free cells were conducted within a voltage range of 3.6–4.3 V using a WBCS 3000 cyler (WonATech). The cells were cycled under a limited depth-of-discharge (DoD) condition to avoid complete Li stripping, as commonly adopted in anode-free battery systems to improve cycling stability [39]. The first cycle was performed at 0.1 C for pre-conditioning, followed by 0.33 C charging and 1.0 C discharging. In situ pressure evolution was monitored using a custom-built fixture equipped with an inline load cell. The pouch cell stack was compressed between two stainless steel plates under an applied pressure of 0.3 MPa, and pressure variations were recorded during cycling. Cell thickness was measured every 50 cycles using a micrometer, and AC impedance spectra of the cycled cells were collected every 100 cycles using the ZIVE MP1 analyzer.

4.5 | Characterization

Fourier-transform infrared (FT-IR) spectroscopy (Nicolet iS50, Thermo Fisher Scientific) was performed to identify the functional groups present in the interlayer. Raman spectroscopy was conducted using a DXR3xi Raman Imaging Microscope (Thermo Fisher Scientific) equipped with a 785 nm laser to investigate the coordination interactions between Li^+ ions and nitrile groups within the interlayer. For the Raman characterization, the LS-NP interlayer was soaked with the BN-containing electrolyte used for electrochemical cell evaluation. Additional measurements were performed using LS-NP soaked with BN-free electrolyte ($0.6 \text{ M LiBF}_4 + 0.6 \text{ M LiDFOB}$ in DEC/FEC (2/1, v/v)) and FEC-based electrolyte ($0.6 \text{ M LiBF}_4 + 0.6 \text{ M LiDFOB}$ in FEC). For comparison, an NP soaked with the BN-free electrolyte was also examined. The surface morphology of the Li metal and the microstructure of the interlayer were examined by field-emission scanning electron microscopy (FE-SEM, Verios G4UC, Thermo Fisher Scientific). x-ray photoelectron spectroscopy (XPS, K-Alpha⁺, Thermo Fisher Scientific) was employed to analyze the

chemical composition and bonding states at the anode interface. The mechanical properties of the interlayer were evaluated using a universal testing machine (UTM, Instron 345C-1) under ambient conditions. Uniaxial tensile tests were performed to compare the elasticity and tensile strength of the different interlayers, while nanoindentation tests were conducted to determine their local mechanical modulus. Contact angle measurements were also carried out to assess the wettability of the interlayer toward the liquid electrolyte.

4.6 | Computational Details

Ab initio calculations were performed using the Gaussian software package [40]. Structural isomers for the initial geometries of a single molecule (A) were generated with the Balloon program through Monte Carlo sampling [41]. The obtained structures were first optimized using semi-empirical PM6 calculations [42]. Subsequently, several low-energy geometries identified at the PM6 level were re-optimized using density functional theory (DFT) with the M06-2X functional and the 6-311+G* basis set, followed by refinement at the 6-311+G** level [43, 44]. Frequency calculations were carried out at the M06-2X/6-311+G** level to confirm that the final lowest-energy structures corresponded to true minima on the potential energy surface. The initial geometries of the AR complexes ($\text{R} = \text{Li}^+, \text{BF}_4^-, \text{DFOB}^-$) were constructed using the Packmol program, based on the optimized local-minimum structures of A [45]. Depending on the degrees of freedom of A, hundreds to thousands of structural isomers were generated. All geometries were optimized at the M06-2X/6-311+G** level. Gibbs free energies at 298 K (including zero-point energy corrections) were calculated using the equation $G^R = G(\text{AR}) - G(\text{A}) - G(\text{R})$.

Author Contributions

Hyun-Woo An: methodology, investigation, validation. **Dong Yong Kim:** formal analysis, validation. **Hyeonsu Kim:** formal analysis, validation. **Sung-Min Koo:** methodology, formal analysis, investigation. **A-Hyeon Ban:** conceptualization, methodology, investigation, writing – original draft. **Dong-Won Kim:** conceptualization, investigation, funding acquisition, project administration, writing – review and editing, supervision. **Seung Woo Lee:** validation, formal analysis, writing – review and editing. **Woo Jin Bae:** validation, formal analysis. **Jong-Seok Moon:** formal analysis, validation. **Donggi Hong:** validation, data curation, formal analysis, writing – original draft.

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