



Ion-conductive protective layer–integrated lithium metal anodes via high-current electrodeposition under ambient pressure

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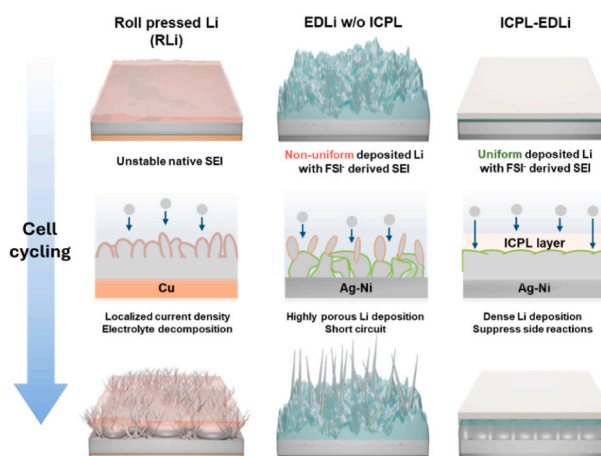
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HIGHLIGHTS

- ICPL enables uniform lithium electro-deposition at 6 mA cm^{-2} under ambient pressure.
- ICPL-integrated lithium shows stable cycling over 400 h and CCD of 17 mA cm^{-2} .
- Li/NCM cell with $20 \mu\text{m}$ ICPL-lithium anodes retains 82.9% capacity after 200 cycles.
- The strategy offers a scalable route to high-performance lithium metal anodes.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium metal is a highly attractive anode for next-generation high-energy-density batteries, however, the practical fabrication of thin lithium anodes via electrodeposition is severely constrained, since it is typically conducted at low current densities and under high external pressures to suppress dendritic growth. Here, we report an ion-conductive protective layer (ICPL)-assisted electrodeposition strategy that enables uniform, dendrite-free lithium deposition at high current densities under ambient pressure. The ICPL, composed of Li^+ -conductive $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ particles and an elastomeric dual-polymer binders, provides high ionic conductivity, a high Li^+ transference number, and mechanical resilience. This combination allows stable lithium electrodeposition at 6 mA cm^{-2} without external pressure, forming a dense lithium anode integrated with the protective layer. The ICPL-integrated anode shows stable cycling for over 400 h and a critical current density of 17 mA cm^{-2} . In Li/LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cells with an active cathode loading of 15 mg cm^{-2} , a $20 \mu\text{m}$ ICPL-

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integrated lithium anode retains 82.9% of its initial capacity after 200 cycles at 45 °C, outperforming cells using commercial rolled lithium metal. This work presents a scalable route for fabricating thin, high-performance lithium metal anodes under practical conditions.

1. Introduction

The ever-growing demand for high-energy-density batteries has spurred extensive interest in lithium (Li) metal anodes owing to their high theoretical specific capacity (3860 mAh g⁻¹) and the lowest redox potential (−3.04 V vs. SHE) [1–3]. However, the practical implementation of Li metal in rechargeable lithium batteries is severely hindered by its high reactivity, which leads to the formation of a non-uniform, resistive, and mechanically unstable solid electrolyte interphase (SEI). Such a defective SEI fails to effectively regulate Li⁺ transport, resulting in localized current density hotspots that promote dendritic lithium growth and continuous electrolyte decomposition. These detrimental processes accelerate the irreversible consumption of lithium and electrolyte, ultimately limiting the cycling stability and safety of lithium metal batteries [4–6].

Electrodeposition of lithium has recently emerged as a promising strategy to address these challenges. The Li electrodeposition facilitates the in-situ formation of a more homogeneous and stable SEI on the surface, which regulates Li⁺ flux and effectively suppresses dendritic growth during cycling, thereby mitigating parasitic side reactions and improving long-term cycling stability [7]. In addition, the electrodeposited lithium offers superior interfacial uniformity and morphology control compared to conventionally rolled lithium metal, enabling the formation of a conformal and thin lithium layer directly on the current collector [8–11]. Furthermore, the electrodeposition allows scalable fabrication of ultrathin and wide lithium metal with precisely controlled thickness, which is difficult to reliably achieve using conventional mechanical rolling processes. However, uniform lithium electrodeposition is typically achievable only at low current densities and under high external pressures, which practically limits the scalability of this technique for large-area or high-throughput lithium deposition processes [12–14]. Under practical lithium metal manufacturing conditions required for the mass production of thin lithium foils, such as atmospheric-pressure operation combined with high current densities, achieving smooth and dendrite-free lithium deposits remains a critical challenge [15]. To address this issue, artificial protective layers have been extensively investigated for stabilizing lithium metal anodes [16–18]. These protective layers physically suppress dendritic lithium growth while simultaneously shielding the lithium surface from parasitic side reactions. Building on this concept, coating a protective layer onto the current collector prior to lithium electrodeposition, followed by lithium deposition beneath the layer, represents a rational and promising solution. This configuration preserves intimate interfacial contact between lithium and the current collector, enables regulated lithium-ion transport during electrodeposition, and imposes minimal constraints on electrolyte composition or solvent selection [19–21].

In this study, we develop an ion-conductive protective layer (ICPL) integrated with a lithiophilic Ag-coated Ni substrate (Ag-Ni) to enable uniform lithium metal electrodeposition under high current density and ambient-pressure conditions. The ICPL is composed of ion-conductive Li_{6.4}La_{3.0}Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) particles and dual-binder consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and nitrile butadiene rubber (NBR). The resulting protective layer exhibits high ionic conductivity, a high Li⁺ transference number, excellent electrochemical stability, and mechanical robustness. In addition, it retains notable elastic resilience even in the electrolyte-swollen state, allowing it to accommodate the volume changes of lithium during the electrodeposition process. Using the ICPL integrated Ag-Ni (ICPL@Ag-Ni) and an ether-based electrolyte, lithium metal was uniformly electrodeposited beneath the ICPL at high current density and under

ambient pressure. The electrodeposited lithium, intrinsically integrated with the ICPL@Ag-Ni, maintains structural integrity during repeated plating and stripping cycles while effectively suppressing dendritic lithium growth. The electrodeposited thin lithium anode with a thickness of 20 μm was further evaluated in the Li/LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM) cells. Notably, the Li/NCM cells (cathode active mass loading: 15 mg cm⁻²) assembled with the electrodeposited lithium anode exhibited markedly improved cycling performance compared to the cells employing the commercial rolled lithium metal anodes.

2. Experimental section

2.1. Materials

Li_{6.4}La_{3.0}Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO, d₅₀ = 400 nm) was purchased from MTI Korea Co., Ltd. Nitrile butadiene rubber (NBR) with a nitrile content of 35 wt% was kindly supplied by Kumho Petrochemical Co., Ltd., and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Solef 21510) was obtained from Solvay. All organic solvents used in this study were purchased from Sigma-Aldrich. The liquid electrolyte used for lithium electrodeposition consisted of dimethoxyethane (DME), lithium bis(fluorosulfonyl)imide (LiFSI), lithium nitrate (LiNO₃), and fluoroethylene carbonate (FEC) with a mass ratio of 71.2:27.6:0.6:0.6. For the cycling tests of Li/NCM cells, a liquid electrolyte composed of 0.6 M lithium tetrafluoroborate (LiBF₄) and 0.6 M lithium difluoro(oxalato)borate (LiDFOB) dissolved in a mixed solvent of diethyl carbonate (DEC) and FEC (2:1, v/v) was used. Both electrolytes were kindly provided by Dongwha Electrolyte Co., Ltd. A polyethylene (PE) separator (Asahi ND420) was vacuum-dried at 80 °C for 12 h prior to use. The rolled lithium metal with a thickness of 20 μm, laminated onto a copper current collector, was purchased from Honjo Metal Co., Ltd.

2.2. Fabrication of ion-conductive protective layer

Ag-coated nickel foil (Ag-Ni) was employed as the current collector to facilitate uniform lithium deposition. The Ag layer, with a thickness of approximately 1 μm, was uniformly deposited onto a 10 μm-thick Ni foil via electrodeposition. The ion-conductive protective layer (ICPL) was fabricated on the Ag-Ni substrate using a simple solution-casting method. The casting solution consisted of LLZTO, PVdF-HFP, and NBR dissolved in a mixed solvent of tetrahydrofuran (THF) and dimethylacetamide (DMAc). The solution was homogenized using a planetary centrifugal mixer (Thinky ARE-310). The detailed compositions of the casting solutions used for preparing the protective layers are summarized in Table 1. The prepared solution was cast onto the Ag-Ni substrate using a doctor blade and subsequently dried under vacuum at 45 °C for 6 h. The total thickness of the resulting ICPL-coated Ag-Ni was measured to be 24 μm (Fig. S1), corresponding to an ICPL thickness of approximately 13 μm.

Table 1

Composition of the casting solutions used for the preparation of ion-conductive protective layers.

Ion-conductive protective layer	LLZTO (g)	PVdF-HFP (g)	NBR (g)	THF (g)	DMAc (g)
ICPL-1	90	10	0	250	0
ICPL-2	90	10	0	200	50
ICPL-3	90	5	5	200	50

2.3. Li electrodeposition and cell assembly

For lithium electrodeposition under ambient conditions, a self-designed Teflon-based electrodeposition cell (ED-cell) was employed (Fig. S2). The electrochemical cell was assembled using lithium metal foil as the lithium reservoir, an ether-based liquid electrolyte, and an Ag-Ni current collector. Lithium was electrodeposited galvanostatically at a current density of 6.0 mA cm^{-2} to a target areal capacity of 4.0 mAh cm^{-2} , which corresponds to an estimated deposited lithium thickness of $\sim 20 \text{ }\mu\text{m}$. The resulting electrode, denoted as electrodeposited lithium beneath the ICPL (ICPL-EDLi), was gently roll-pressed to ensure a uniform surface. As a control lithium metal anode, commercially rolled lithium metal (thickness: $20 \text{ }\mu\text{m}$) laminated onto a copper foil was used. The NCM cathode was fabricated by casting an *N*-methyl-2-pyrrolidone (NMP)-based slurry composed of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM, L&F), conductive carbon (Super P, TIMCAL), and poly(vinylidene fluoride) (PVdF, Solef 5130, Solvay) at a weight ratio of 95:3:2 onto an aluminum current collector. The active material mass loading of the cathode was 15 mg cm^{-2} . Coin-type Li/NCM cells were assembled using the above-mentioned lithium anodes and NCM cathode, with a polyethylene (PE) separator sandwiched between the electrodes. The calculated N/P ratio in the Li/NCM cells was approximately 1.29. The liquid electrolyte, corresponding to approximately 3.0 g Ah^{-1} , was then injected into the cell.

2.4. Characterization and measurements

The morphology of the ICPL@Ag-Ni before and after lithium electrodeposition was examined using field-emission scanning electron microscopy (FE-SEM; Verios G4), and the elemental distribution was analyzed by energy-dispersive X-ray spectroscopy (EDS). Fourier-transform infrared (FT-IR) spectroscopy was performed in the range of $400 - 4000 \text{ cm}^{-1}$ to confirm the chemical structure of the ICPL (Nicolet iS50 spectrometer). The crystal structures of LLZTO and the ICPL were investigated by X-ray diffraction (XRD; D8 Advance, Bruker) over a 2θ range of $10 - 80^\circ$. The mechanical properties of the ICPLs were evaluated by nanoindentation tests using a NanoTest NTX system (Micro Materials) under a maximum load of 5 mN . The chemical composition of the SEI formed on the lithium surface was analyzed by X-ray photoelectron spectroscopy (XPS; K-Alpha+, Thermo Fisher Scientific) using Al $K\alpha$ radiation as the X-ray source. All XPS spectra were calibrated with respect to the LiF peak at a binding energy of 684.5 eV . The lithium-ion transference number (t_{Li}^+) was determined using a combination of DC polarization and AC impedance measurements with a CHI660d electrochemical workstation (CH Instruments, Inc.). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were performed at a scan rate of 1 mV s^{-1} using a cell configured with an Ag-

Ni electrode as the working electrode and lithium metal serving simultaneously as the counter and reference electrodes. The Li/NCM cells were galvanostatically cycled within a voltage range of 3.0 to 4.3 V at 45°C using a battery testing system.

3. Results and discussion

Fig. 1a presents a schematic illustration of the fabrication process for the ICPL-coated Ag-Ni, while the detailed preparation procedure and ICPL compositions are provided in the Experimental Section. The Ag-Ni current collector was selected based on the high electrochemical and chemical stability of Ni, combined with the lithiophilic nature of the Ag that promotes uniform lithium nucleation and deposition [20,22,23]. The primary component of the ICPL is LLZTO, which imparts high lithium-ion conductivity, excellent electrochemical and mechanical stability to the protective layer [24–26]. As polymeric binders, PVdF-HFP and NBR were employed to synergistically enhance both electrochemical and mechanical properties. PVdF-HFP offers outstanding electrochemical stability and resistance to oxidative and reductive degradation, thereby ensuring long-term cycling durability. The amorphous HFP segments in PVdF-HFP facilitate electrolyte uptake, enabling efficient electrolyte infiltration and enhanced ionic transport within the ICPL [27]. In contrast, NBR contributes superior elasticity and strong adhesion, while its polar nitrile groups improve interfacial interactions with inorganic LLZTO and polymer matrix. These characteristics, together with its compatibility with fluorinated binders such as PVdF-HFP, allow NBR to effectively alleviate mechanical stress arising from lithium deposition and stripping [28]. Fig. 1b and c display the optical images of the ICPL integrated onto the Ag-Ni substrate. The resulting protective layer exhibits excellent mechanical flexibility without delamination from Ag-Ni, maintaining a smooth, crack-free surface even after being rolled around a cylindrical rod with a diameter of 10 mm .

Fig. 2a–c present the surface and cross-sectional SEM images of a representative ICPL (ICPL-3), along with the corresponding EDS elemental mappings. The ICPL-3 exhibits a uniform surface morphology with a thickness of approximately $13 \text{ }\mu\text{m}$. The elemental mapping images in Fig. 2c reveal that nitrogen (N) and fluorine (F) originating from the polymer binders (NBR and PVdF-HFP), as well as lanthanum (La) from the LLZTO particles, are homogeneously distributed throughout the protective layer, indicating uniform dispersion of both polymeric and inorganic components. The crystalline structures of LLZTO and the various protective layers were further investigated by X-ray diffraction (XRD) analysis. Fig. S3a shows the XRD patterns of PVdF-HFP and NBR, confirming the semi-crystalline nature of PVdF-HFP and the amorphous structure of NBR. As shown in Fig. 2d, the ion-conductive protective layers do not exhibit the characteristic crystalline peaks of PVdF-HFP.

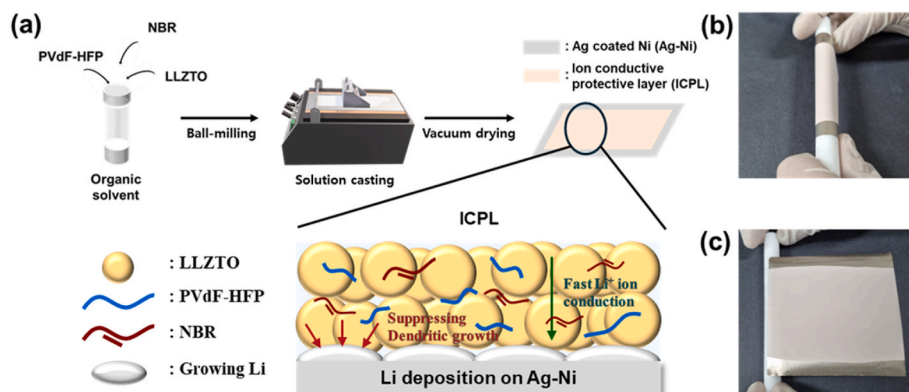


Fig. 1. (a) Schematic illustration of the fabrication process for the ICPL-coated Ag-Ni. (b) Photograph of the ICPL-coated Ag-Ni rolled around a cylindrical rod with a diameter of 10 mm . (c) Photograph of the same sample after being unrolled and placed on a flat substrate.

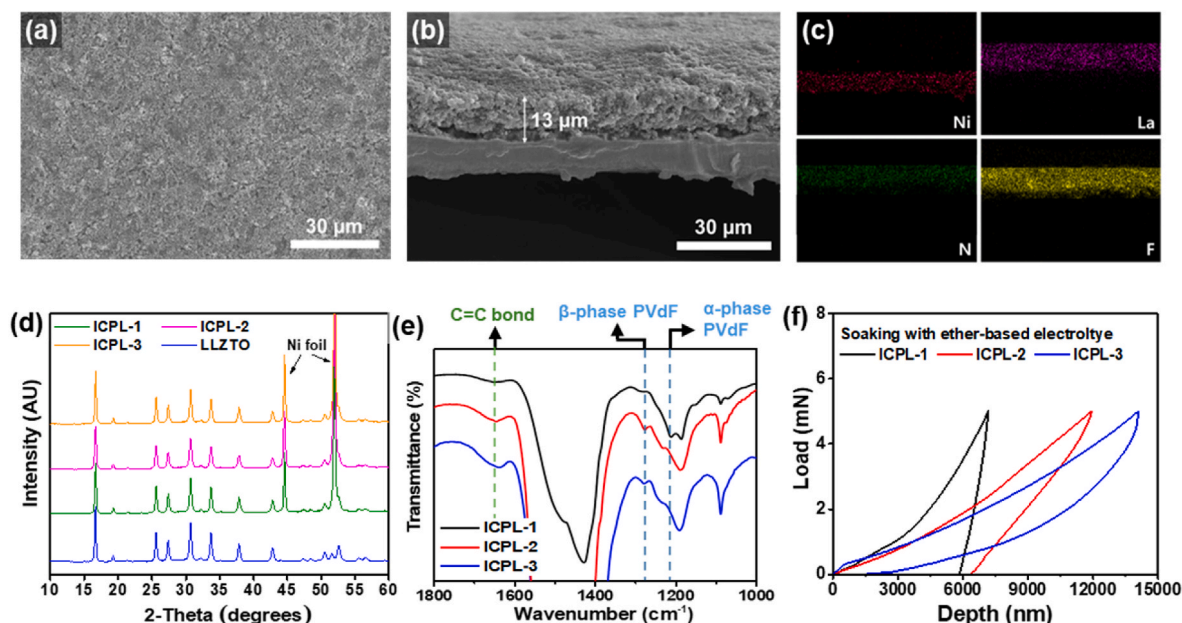


Fig. 2. (a) Surface and (b) cross-sectional SEM images of ICPL-3 and (c) the corresponding EDS elemental maps. (d) XRD patterns of LLZTO, ICPL-1, ICPL-2, and ICPL-3. (e) FT-IR spectra of the various ion-conductive protective layers. (f) Nanoindentation load-displacement curves of the protective layers after soaking in liquid electrolyte.

This observation suggests that the presence of LLZTO effectively suppresses the crystallinity of PVdF-HFP through a filler-induced effect, which is expected to enhance lithium-ion mobility within the polymer matrix [29]. Meanwhile, no noticeable changes are observed in the diffraction peaks associated with LLZTO, indicating that its crystal structure remains intact after the fabrication process. It should be noted that the diffraction peaks appearing at approximately 45° and 53° originate from the underlying Ni current collector as shown in Fig. S3b. Fig. 2e presents the FT-IR spectra of the various protective layers in the wavenumber range of $1000 - 1800 \text{ cm}^{-1}$. A weak absorption band observed at approximately 1650 cm^{-1} is attributed to the C=C stretching vibrations of the polymer binders, while the bands between 1400 and 1000 cm^{-1} correspond to characteristic C-F vibrations of PVdF-HFP, including the antisymmetric CF_2 stretching mode (1179 cm^{-1}), the α -phase band (1210 cm^{-1}), and the β -phase band (1275 cm^{-1}) [30,31]. With the introduction of a small amount of DMAc into the casting solution (ICPL-2 and ICPL-3 in Table 1), the intensity of the C=C peak increases, whereas the α -phase peak of PVdF-HFP noticeably decreases. These spectral changes can be attributed to the dehydrofluorination of PVdF-HFP induced under alkaline conditions generated by the interaction between LLZTO and DMAc [29]. Because the α -phase of PVdF-HFP is more susceptible to dehydrofluorination, its preferential consumption leads to the formation of C=C bonds and a concomitant reduction in the α -phase content [32]. As a consequence, the relative fraction of the β -phase PVdF-HFP increases with addition of DMAc. The β -phase is known to be more favorable for lithium-ion transport due to its chain conformation, which facilitates ionic conduction and promotes uniform lithium deposition [33]. Nanoindentation tests were performed to evaluate the mechanical properties of the protective layers under a maximum load of 5 mN . As the applied load increased, the indenter tip penetrated deeper into the layers, indicating that a larger penetration depth corresponds to lower stiffness. The extent of displacement recovery during unloading was used as an indicator of the elastic recovery behavior of the protective layers. As shown in Fig. S4, the three types of protective layers exhibit comparable mechanical responses under dry conditions. This similarity is mainly attributed to the high LLZTO content, which dominantly governs the mechanical characteristics of the protective layers. To further assess the mechanical behavior under conditions relevant to practical lithium electrodeposition, additional

nanoindentation tests were conducted after soaking the protective layers in liquid electrolyte. Electrolyte uptake led to swelling of the polymeric components and resulted in pronounced changes in mechanical properties of ICPLs. As shown in Fig. 2f, the penetration depths of ICPL-2 and ICPL-3 increased markedly compared to that of ICPL-1. This behavior is attributed to dehydrofluorination-induced structural rearrangements in PVdF-HFP, which weaken the cohesive strength of the polymer binder in the swollen state. Notably, ICPL-3 exhibits a substantially larger penetration depth than ICPL-1 and ICPL-2, primarily due to the intrinsically lower elastic modulus of NBR relative to PVdF-HFP. ICPL-3 shows significant recovery after unloading of the indenter tip, whereas ICPL-1 and ICPL-2 display limited elastic recovery. The high recovery ratio of ICPL-3 is ascribed to the elastomeric nature of NBR, which enhances the flexibility and resilience of the protective layer. This unique mechanical response is expected to effectively mitigate mechanical deformation of the protective layer arising from large volume changes during lithium deposition and stripping processes [34–36].

Lithium electrodeposition was performed using the ED-cell (Fig. S2) at current density of 6.0 mA cm^{-2} and total areal capacity of 4 mAh cm^{-2} under ambient pressure with various ICPLs. As shown in Fig. S5a, when ICPL-1 was applied, lithium was not deposited beneath the protective layer; instead, lithium penetration through the protective layer was observed. This behavior indicates insufficient mechanical compliance of ICPL-1 to accommodate lithium deposition. In the case of ICPL-2 (Fig. S5b), the protective layer fractured during electrodeposition, which is attributed to its inadequate elastomeric properties. In contrast, ICPL-3 enabled uniform lithium electrodeposition beneath the protective layer while maintaining its structural integrity without any visible cracks throughout the electrodeposition process (Fig. S5c). This improved mechanical stability is attributed to both the high mechanical strength of LLZTO and the elastomeric nature of the NBR binder, which effectively accommodates deformation induced by lithium growth. Based on these lithium deposition behaviors, ICPL-3 was selected for further in-depth investigation and is hereafter denoted simply as ICPL. Furthermore, the electrolyte wettability of the selected ICPL was evaluated and compared with that of the PE separator and the Ag-Ni current collector (Fig. S6). The ICPL exhibited the smallest contact angle (14.60°), which is significantly lower than those of Ag-Ni (23.49°) and the PE separator (50.32°). These results demonstrate the superior

wettability of the ICPL, which enhances interfacial compatibility and facilitates Li^+ ion transport through the ICPL.

The morphology of lithium electrodeposited beneath ICPL (denoted as ICPL-EDLi) was compared with that of electrodeposited lithium without any protective layer (EDLi) after roll pressing (Fig. 3a–3f). The surface of EDLi remained highly uneven and rough, with a thickness of $51.6\ \mu\text{m}$, owing to the presence of large dendritic structures that could not be fully flattened during the pressing process (Fig. 3c). In contrast, ICPL-EDLi exhibited a smooth and uniform surface after pressing, without any visible physical damage to the ICPL (Fig. 3d). As presented in Fig. 3f, the roll-pressed ICPL-EDLi displays a dense and compact cross-sectional morphology with a reduced thickness of approximately $23\ \mu\text{m}$. Cross-sectional EDS elemental mapping of ICPL-EDLi (Fig. S7) further confirms that lithium was homogeneously deposited between the Ag-Ni current collector and the ICPL, indicating effective confinement and densification of lithium beneath the protective layer. Additionally, large-area lithium electrodeposition was performed on the ICPL-coated Ag-Ni current collector, as shown in Fig. S8. A uniform lithium layer was successfully deposited beneath the ICPL over an area of $5\ \text{cm} \times 10\ \text{cm}$ ($50\ \text{cm}^2$) without any visible damage to the protective layer. Fig. 3g shows the voltage profiles during lithium deposition in the ED-cell at a current density of $6\ \text{mA cm}^{-2}$, with and without the ICPL. In the absence of the protective layer, the deposition overpotential continuously increases, which is attributed to the formation of non-uniform lithium deposits. Such inhomogeneous lithium growth increases electrode tortuosity, leading to pronounced lithium-ion concentration gradients and consequently higher internal resistance [37]. By contrast, lithium electrodeposition on ICPL@Ag-Ni proceeds with a more stable potential response and results in a reduced overpotential at the completion of

deposition relative to the pristine Ag-Ni electrode. Fig. 3h presents the voltage profiles during lithium stripping for EDLi and ICPL-EDLi operated at a current density of $0.4\ \text{mA cm}^{-2}$. The coulombic efficiency, defined as the ratio of reversibly stripped lithium to the deposited lithium, reaches 85.3% for the ICPL-EDLi, which is significantly higher than that of the bare EDLi without the ICPL. It should be noted that the relatively low coulombic efficiency during electrodeposition is primarily attributed to the irreversible consumption of lithium associated with SEI layer formation. Overall, ICPL@Ag-Ni demonstrates both reduced lithium deposition overpotential and markedly improved lithium stripping efficiency, as summarized in Fig. 3i. These results clearly indicate that the ICPL effectively suppresses the formation of dendritic and electrically isolated lithium, thereby enhancing the reversibility and electrochemical stability of the lithium metal electrode. After the stripping tests, the morphologies of the Li anodes were examined, as shown in Fig. S9. In the case of the Ag-Ni electrode, a significant amount of mossy and porous Li remained on the surface after stripping. In contrast, the ICPL@Ag-Ni electrode maintained its structural integrity after the stripping test, and most of the deposited Li was removed, as shown in Fig. S10.

The temperature-dependent ionic conductivities of the PE separator and ICPL soaked with an ether-based liquid electrolyte were measured, and the results are presented in Fig. 4a. Notably, the ionic conductivity of the ICPL is significantly higher than that of the PE separator over the measured temperature range, indicating a substantially lower ionic resistance in the ICPL compared with the conventional PE separator. The Li^+ transference numbers of the PE separator and the ICPL, both impregnated with a same electrolyte, were determined in symmetric Li/Li cells using the Bruce-Vincent method [38]. As shown in Fig. 4b and c,

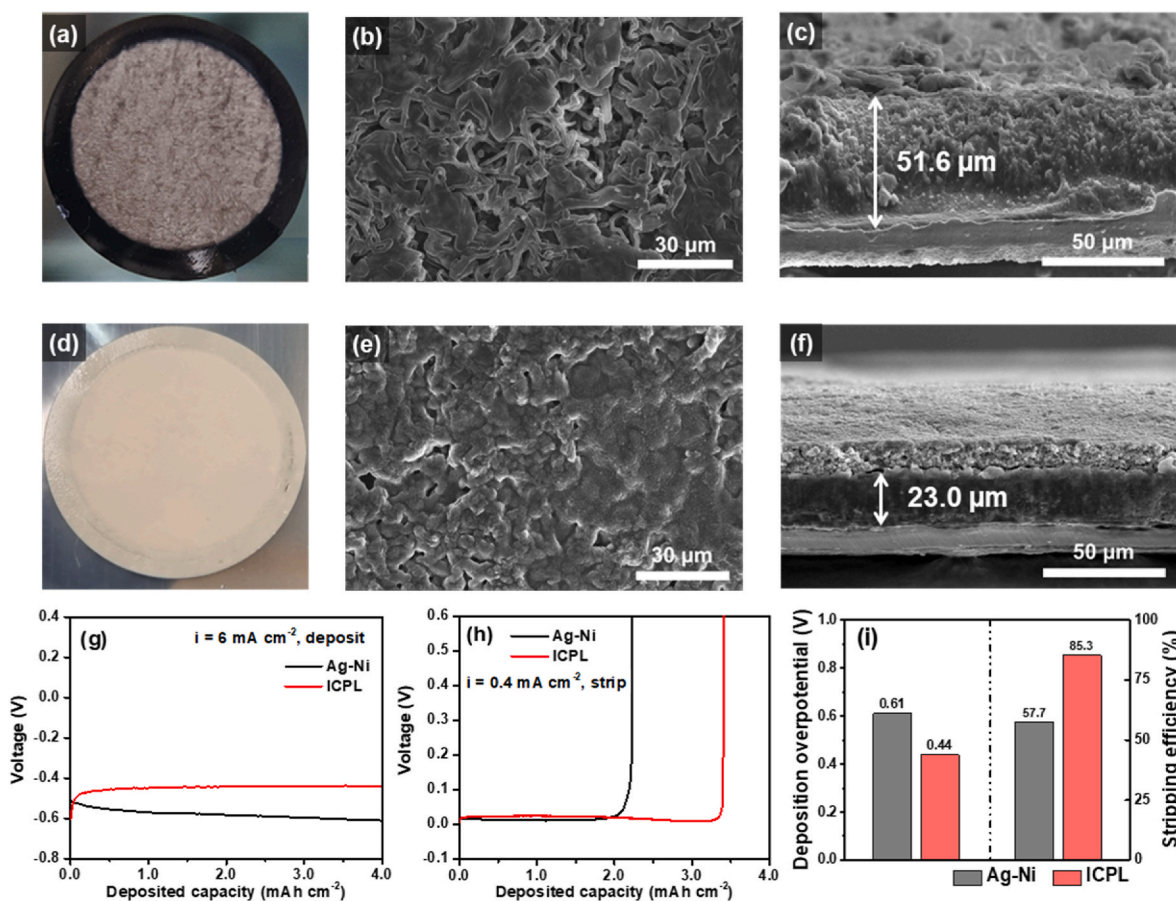


Fig. 3. Optical images, and surface and cross-sectional SEM images of roll-pressed lithium metal electrodeposited on Ag-Ni (a–c) without and (d–f) with the ICPL. (g) Voltage profiles during lithium electrodeposition with and without the ICPL. (h) Voltage profiles during lithium stripping for roll-pressed EDLi and ICPL-EDLi electrodes at a current density of $0.4\ \text{mA cm}^{-2}$. (i) Comparison of the deposition overpotential and stripping efficiency of EDLi and ICPL-EDLi electrodes.

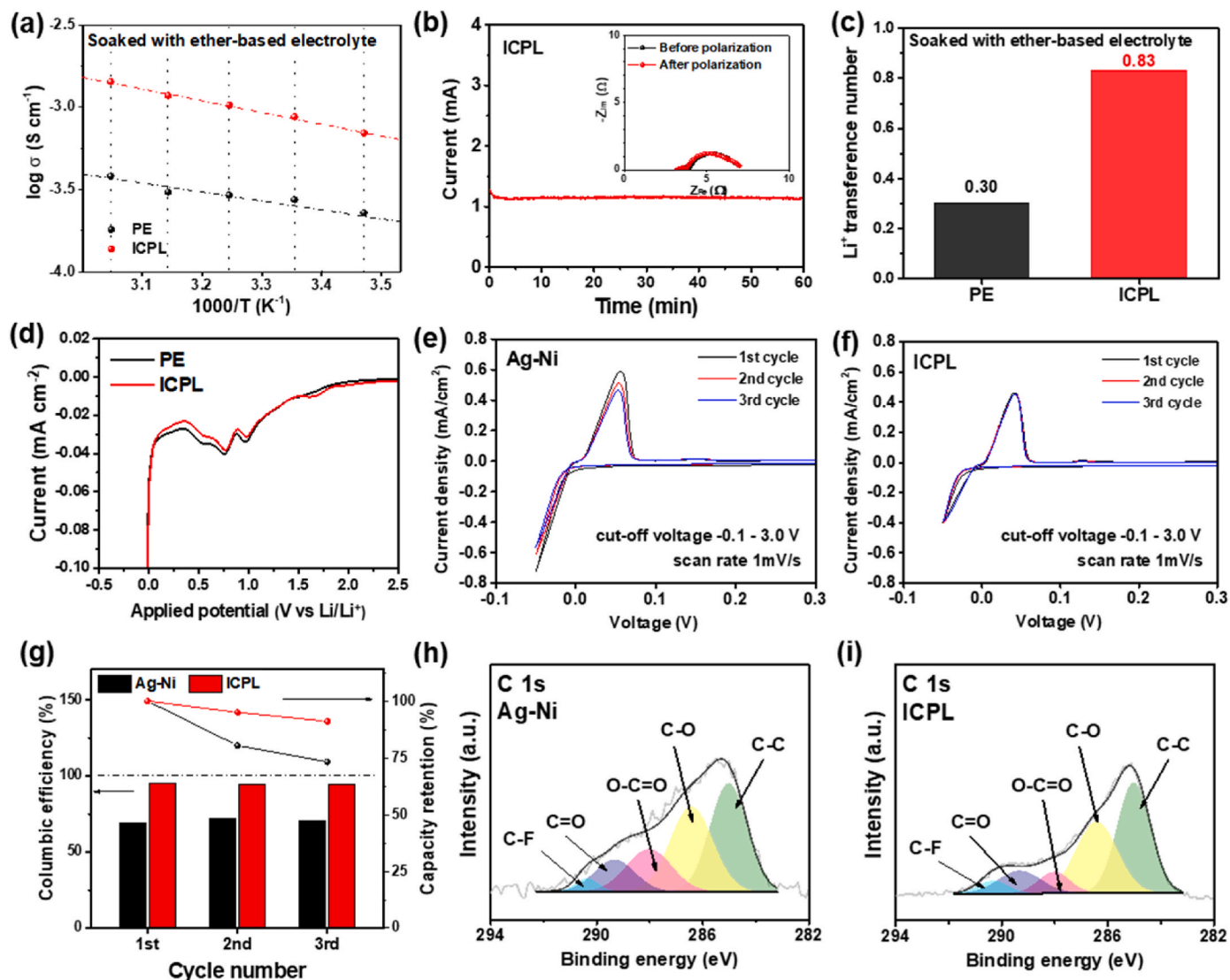


Fig. 4. (a) Ionic conductivities of liquid electrolyte-impregnated PE and ICPL. (b) DC polarization and AC impedance responses used for determining the Li^+ transference number. (c) Calculated Li^+ transference numbers of PE and ICPL after electrolyte impregnation. (d) Linear sweep voltammetry results of PE and ICPL containing liquid electrolyte. Cyclic voltammograms of Ag-Ni (e) without and (f) with ICPL. (g) Comparison of coulombic efficiency and capacity retention obtained from cyclic voltammetry. C 1s XPS spectra of (h) EDLi and (i) ICPL-EDLi.

the Li^+ transference number of ICPL reaches 0.83, whereas that of the PE separator is limited to 0.30. The simultaneously enhanced ionic conductivity and Li^+ transference number of the electrolyte-soaked ICPL are attributed to the high content of Li^+ -conductive LLZTO within the ICPL. The embedded LLZTO particles likely provide continuous fast-ion conduction pathways and promote efficient interfacial Li^+ ion transport within the gelled PVdF-HFP-based electrolyte [26]. To further evaluate the compatibility between the ICPL and the Ag-Ni current collector, we fabricated symmetric cells without Li deposition using a PE separator and electrolyte. The AC impedance spectra of symmetric cells with Ag-Ni/PE/Ag-Ni and ICPL@Ag-Ni/PE/ICPL@Ag-Ni configurations are shown in Fig. S11. When ICPL was coated on the Ag-Ni current collector, the bulk resistance of electrolyte was slightly increased. This feature can be attributed to the ionic resistance of the ICPL. Importantly, the increase in bulk resistance resulting from the introduction of the ICPL is minimal. These results indicate that the ICPL exhibits good compatibility with the Ag-Ni. The electrochemical stability of the ICPL soaked with liquid electrolyte was evaluated by linear sweep voltammetry (LSV), as shown in Fig. 4d. Regardless of the presence of the ICPL, identical reductive peaks were observed at approximately 1.65, 1.3, and

0.6 V. These peaks are attributed to the formation of the SEI arising from the reductive decomposition of LiNO_3 , FEC, and LiFSI, respectively [39, 40]. Importantly, no additional reductive peaks appeared in the presence of the ICPL, indicating that its constituent components (LLZTO, PVdF-HFP, and NBR) are electrochemically stable and compatible under lithium deposition conditions. To further investigate the electrochemical behavior during repeated lithium deposition and stripping, cyclic voltammetry (CV) measurements were performed in the voltage range of -0.05 to 3.0 V. The CV profiles focusing on the lithium deposition and stripping region (-0.1 to 0.3 V) are presented in Fig. 4e and f. In the absence of the ICPL, the peak currents progressively decreased with cycling, indicating deteriorated reversibility and interfacial instability. In contrast, when the ICPL was employed, the peak currents remained stable over repeated cycles, demonstrating enhanced electrochemical reversibility. The magnified CV curves shown in Fig. S12 confirm that the Ag alloying and dealloying processes proceeded without hindrance and that no significant parasitic reactions occurred during subsequent cycling. To quantitatively assess lithium reversibility, the capacities of lithium deposition and stripping were calculated by integrating the current over time, as shown in Fig. 4g. With the ICPL, the

coulombic efficiency associated with Li deposition and stripping consistently exceeded 96% throughout cycling, and a capacity retention of 92.1% was achieved after three cycles. By contrast, in the absence of the ICPL, the coulombic efficiency was limited to approximately 70%, and the capacity retention after three cycles was only 73.3%. These results clearly demonstrate that the ICPL effectively facilitates reversible lithium deposition and stripping, not only during the initial cycle but also over subsequent cycles, by stabilizing the electrode-electrolyte interface and suppressing parasitic side reactions. The chemical composition of the SEI formed on lithium metal during electrodeposition was investigated for EDLi and ICPL-EDLi using XPS. In good agreement

with the LSV and CV results, no additional chemical species or unexpected peaks were detected for ICPL-EDLi, confirming that the ICPL does not induce parasitic interfacial reactions during lithium deposition. As shown in Fig. 4h and i, the C 1s spectra were deconvoluted into five characteristic components corresponding to C–C (285.0 eV), C–O (286.4 eV), O–C=O (288.1 eV), C=O (289.8 eV) and C–F (290.2 eV). The deconvoluted O 1s and F 1s spectra, together with their corresponding peak assignments, are presented in Fig. S13 [41,42]. Notably, the intensity of peaks associated with solvent decomposition products, such as O–C=O peak corresponding to the Li_2CO_3 in C 1s spectra and C=O in O 1s spectra, is lower for ICPL-EDLi than for EDLi. The peak area ratio of

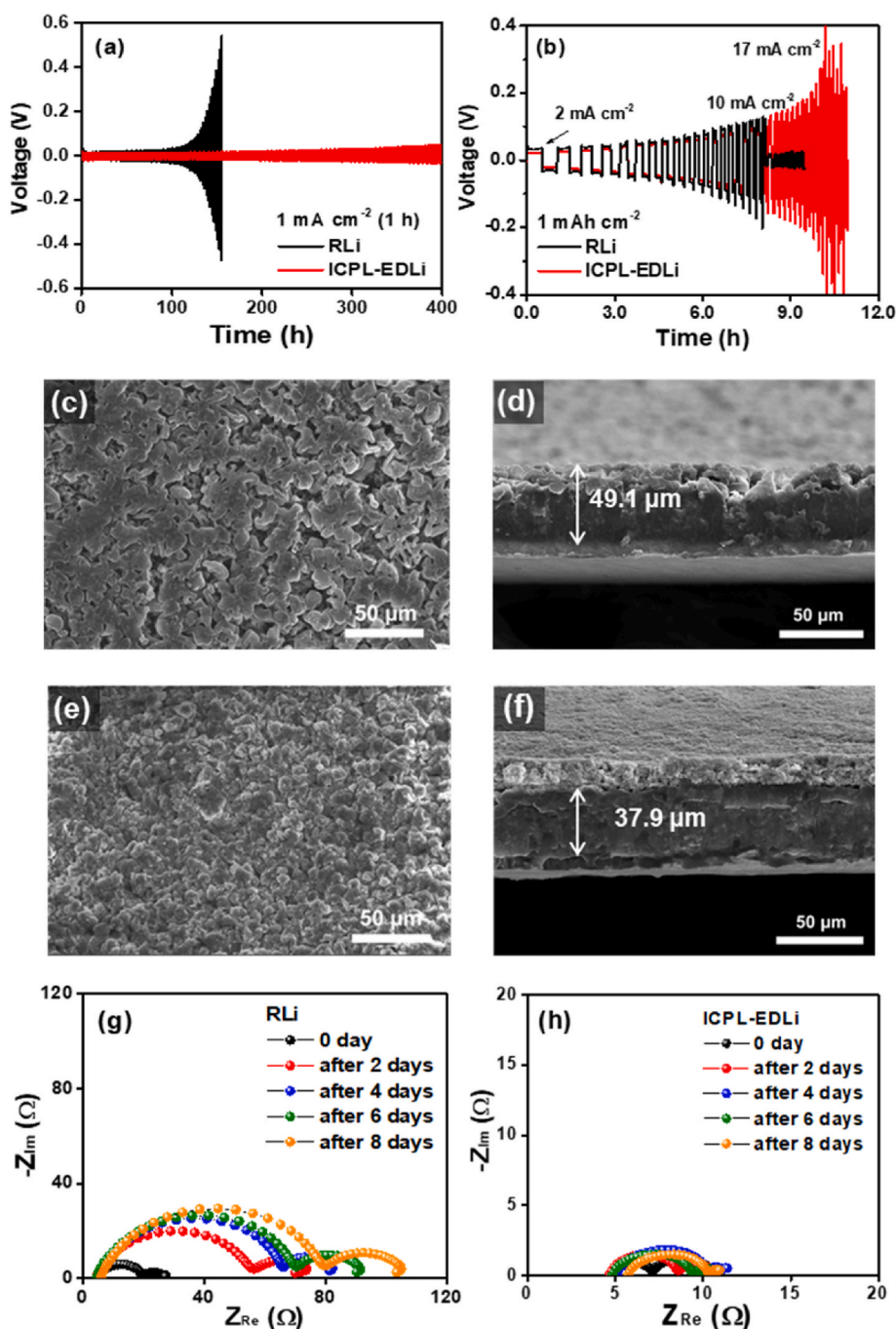


Fig. 5. (a) Galvanostatic cycling voltage profiles of symmetric Li cells employing RLi and ICPL-EDLi in carbonate-based electrolyte. (b) Voltage profiles of symmetric Li cells used to determine the CCD. (c) Surface and (d) cross-sectional SEM images of the Li electrode in the RLi cell after 50 cycles. (e) Surface and (f) cross-sectional SEM images of the Li electrode in the ICPL-EDLi cell after 50 cycles. AC impedance spectra of symmetric Li cells assembled with (g) RLi and (h) ICPL-EDLi measured as a function of storage time at 45 °C.

XPS spectra are summarized in Table S1. The results demonstrate that the ICPL facilitates the formation of a more inorganic-rich SEI compared to the bare Ag-Ni system. This observation indicates that the presence of the ICPL effectively suppresses solvent decomposition during lithium electrodeposition [43]. The mitigated solvent decomposition can be attributed to the synergistic roles of the polymeric binder and the LLZTO within the ICPL. Specifically, the polymeric binder hinders solvent migration toward the lithium surface, thereby limiting direct solvent reduction. Meanwhile, LLZTO serves as an efficient Li^+ -conductive pathway, facilitating preferential Li^+ transport while reducing the amount of solvent molecules co-transported with migrating Li^+ ions [44]. As a result, the ICPL promotes the formation of chemically stable and less solvent-derived SEI layer, which is consistent with the enhanced lithium reversibility observed in the electrochemical measurements.

To validate the electrochemical performance of ICPL-EDLi as an anode for lithium metal batteries, its electrochemical properties were compared with those of a commercial rolled lithium (denoted by RLi, 20 μm thick) laminated on Cu current collector. Because ether-based electrolytes are unsuitable for high-voltage Li/NCM cells due to their limited oxidative stability, a carbonate-based electrolyte composed of 0.6 M LiBF_4 and 0.6 M LiDFOB dissolved in DEC/FEC was employed for the cycling tests [45,46]. The fundamental electrochemical characteristics of the ICPL soaked with the carbonate-based electrolyte, including ionic conductivity, electrochemical stability evaluated by LSV, and the Li^+ transference number, are summarized in Fig. S14. These properties are comparable to those obtained using the ether-based electrolyte discussed earlier, indicating that the ICPL maintains consistent ion-transport characteristics and electrochemical stability regardless of electrolyte type. These results reveal the robustness of the ICPL and support its applicability as a practical lithium metal anode under high-voltage operating conditions. To evaluate the cycling stability of ICPL-EDLi under continuous lithium deposition and stripping, galvanostatic cycling tests were performed using symmetrical lithium cells. The symmetrical cells were assembled with commercial rolled lithium (RLi) and electrodeposited lithium with ICPL (ICPL-EDLi) electrodes, respectively. All cells were cycled at a current density of 1 mA cm^{-2} with a deposition and stripping time of 1 h per half-cycle (cut-off capacity: 1 mAh cm^{-2}). As shown in Fig. 5a, the RLi-based cell exhibited a rapid increase in overpotential after approximately 120 h, reaching 0.5 V at 155 h, which indicates severe interfacial degradation and unstable lithium cycling. In contrast, the ICPL-EDLi-based cell demonstrated remarkably stable cycling for over 400 h with a low and steady overpotential, highlighting its superior interfacial stability. The enlarged voltage profiles presented in Fig. S15 further reveal that the ICPL-EDLi cell exhibits a slightly lower overpotential than the RLi cell throughout initial cycling. Additionally, the exchange current densities of RLi and ICPL-EDLi electrodes were determined from the Tafel plot using Li symmetrical cells, as presented in Fig. S16 [47]. As shown in the figure, the ICPL-EDLi electrode exhibits a much higher exchange current density compared to that of RLi. This improvement can be attributed to the facile Li^+ transport within the ICPL layer as well as the formation of a robust and stable SEI during the electrodeposition process. The critical current density (CCD) was evaluated using the same symmetrical cell configuration, and the corresponding voltage profiles are shown in Fig. 5b. The current density was stepwise increased from 2 to 20 mA cm^{-2} , while the total areal capacity was fixed at 1 mAh cm^{-2} for each step to ensure consistent lithium utilization [48]. The cell employing commercial rolled lithium (RLi) exhibited a short circuit at a current density of 10 mA cm^{-2} , indicating its limited tolerance to high current rate lithium deposition and stripping. In contrast, the ICPL-EDLi-based cell remained electrochemically stable up to 17 mA cm^{-2} and became unstable beyond this point due to short-circuit. The substantially higher CCD of the ICPL-EDLi cell clearly demonstrates its superior compatibility with continuous lithium deposition and stripping under high current density conditions. This enhanced performance can be attributed to the synergistic effects of a stable SEI layer formed during

electrodeposition and the mechanically robust protective layer, which together suppress dendritic lithium growth and mitigate interfacial instability. Consequently, the ICPL-EDLi enables reliable lithium cycling at significantly higher current densities compared to conventional rolled lithium. To examine the microstructural evolution of lithium electrodes after cycling, symmetrical Li cells were disassembled after 50 cycles and analyzed by SEM. For ICPL-EDLi, the ICPL was carefully removed prior to SEM observation to directly examine the underlying lithium surface. As shown in Fig. 5c and d, the surface and cross-sectional SEM images of the RLi electrode reveal a highly porous and rough morphology after cycling, indicating severe structural degradation and non-uniform lithium stripping/deposition. In contrast, the ICPL-EDLi electrode exhibits a dense and relatively uniform morphology, as observed in Fig. 5e and f. Fig. S17 presents the optical and SEM image of ICPL-EDLi prior to detaching the ICPL, showing no visible cracks or mechanical damage in the protective layer even after repeated cycling. These observations demonstrate that the ICPL effectively suppresses dendritic lithium growth and mitigates parasitic reactions with the liquid electrolyte by regulating lithium deposition and preserving interfacial integrity during cycling. AC impedance spectra of symmetric Li/Li cells assembled with RLi and ICPL-EDLi were measured as a function of storage time at 45°C , and the corresponding results are shown in Fig. 5g and h. All spectra consist of two distinguishable semicircles, which are attributed to the film resistance (R_f) associated with the SEI layer and the charge transfer resistance (R_{ct}) at the lithium-electrolyte interface, respectively [49]. For the cell employing RLi, the total interfacial resistance ($R_f + R_{ct}$) gradually increased with storage time. This continuous increase can be ascribed to side reactions between the electrolyte and the highly reactive Li, leading to progressive SEI growth and interfacial degradation. In contrast, the ICPL-EDLi cell exhibited a relatively stable interfacial resistance throughout the storage time. This stability originates from the formation of a stable SEI layer during the electrodeposition process using an ether-based electrolyte, together with the presence of an ion-conductive protective layer on the electrodeposited Li metal, which effectively suppresses further parasitic reactions during storage.

Li/NCM cells were assembled using RLi or ICPL-EDLi as the anode and an NCM cathode with a carbonate-based electrolyte. Prior to long-term cycling, the cells were pre-cycled for two cycles to activate the cells at 0.1C rate and 45°C , followed by galvanostatic cycling at a charge rate of 0.2C and a discharge rate of 0.5C within a voltage range of 3.0–4.3 V. Fig. 6a presents representative voltage profiles of the Li/NCM cell employing the ICPL-EDLi anode after two pre-cycling, and the voltage profiles for the cell with RLi are shown in Fig. S18. The Li/NCM cell with ICPL-EDLi delivered an initial discharge capacity of 204.2 mAh g^{-1} , corresponding to an areal capacity of 3.1 mAh cm^{-2} . A comparison of the cycling performance of cells with different lithium anodes is shown in Fig. 6b. Notably, the cell employing ICPL-EDLi exhibited superior cycling stability, retaining 82.9% of its initial capacity after 200 cycles. In contrast, the cell with RLi showed more rapid capacity decay, reaching a capacity retention of 32.0% at 200 cycle. The enhanced cycling performance of the ICPL-EDLi cell can be attributed to the effective suppression of dendritic lithium growth by the ICPL, together with the pre-formed, stable, and robust SEI generated during the electrodeposition process. These features collectively mitigate continuous lithium consumption and electrolyte depletion arising from parasitic side reactions. AC impedance spectra of the Li/NCM cells were measured at the fully charged state during cycling, as shown in Fig. 6c and d, and the corresponding equivalent circuit is presented in Fig. S19 [50]. Owing to the incorporation of the ICPL, the cell employing ICPL-EDLi exhibits a slightly higher electrolyte resistance (R_e), as indicated by the X-axis intercept in the Nyquist plots. Despite this increase, both the film resistance (R_f) and charge transfer resistance (R_{ct}) of the cell with ICPL-EDLi are markedly lower than those of the cell employing RLi. This behavior can be attributed to the presence of a stable, pre-constructed SEI layer and the suppressed dendritic lithium growth enabled by the ICPL, as discussed earlier. In contrast, the Li/NCM cell with RLi shows a

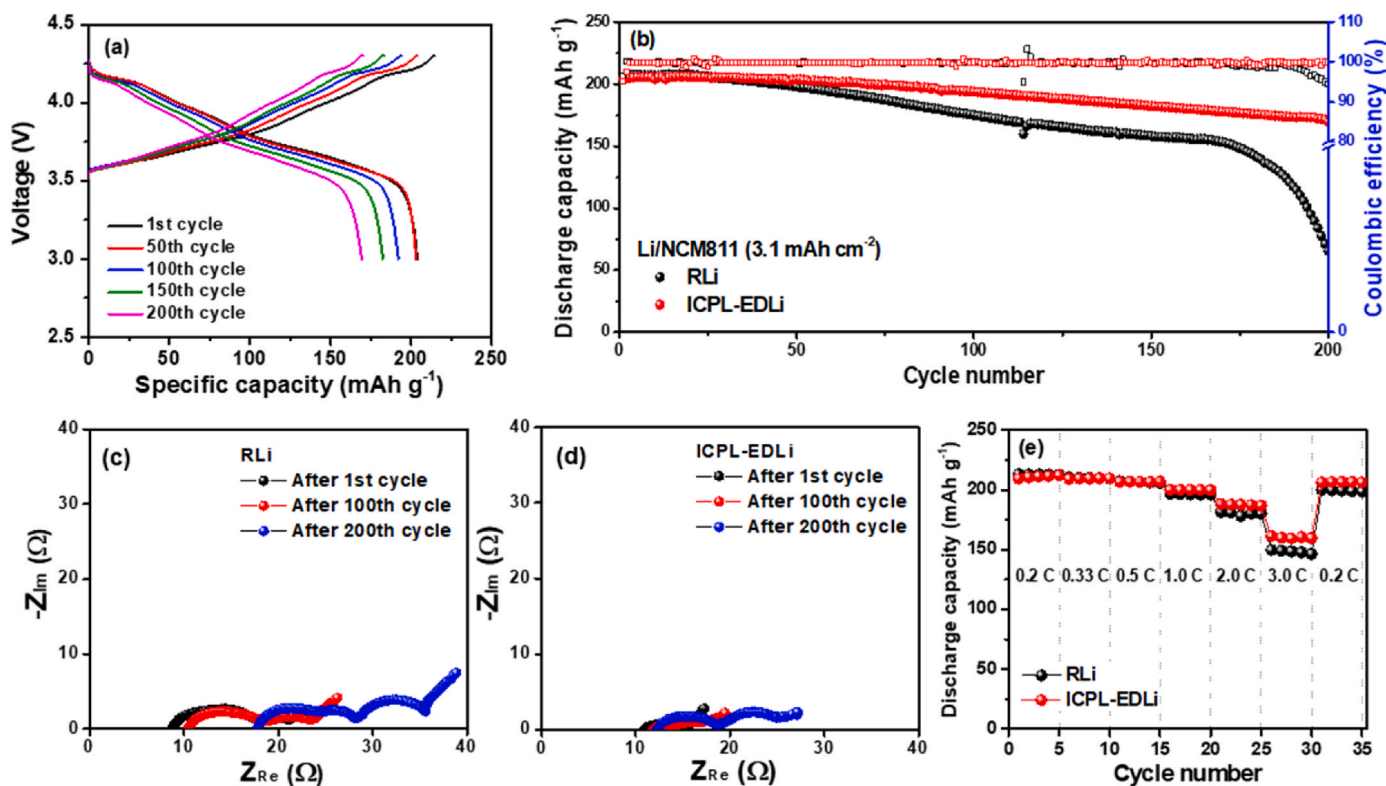


Fig. 6. (a) Voltage profiles of the Li/NCM cell employing the ICPL-EDLi anode at a charge rate of 0.2C and a discharge rate of 0.5C within a voltage range of 3.0–4.3 V at 45 °C. (b) Discharge capacity and coulombic efficiency of Li/NCM cells employing RLi and ICPL-EDLi anodes. AC impedance spectra of Li/NCM cells assembled with (c) RLi anode and (d) ICPL-EDLi anode, measured at the fully charged state after different cycle numbers. (e) Discharge rate capability of Li/NCM cells with different lithium anodes evaluated at 45 °C.

pronounced increase in interfacial resistance after 200 cycles. This resistance growth is associated with severe dendritic lithium growth, which accelerates electrolyte depletion and promotes the formation of a continuously evolving and unstable SEI. Conversely, the cell employing ICPL-EDLi exhibits only a minor increase in resistance even after 200 cycles, underscoring its superior interfacial stability during prolonged cycling. Fig. S20 shows the nanoindentation results of the ICPL before and after cycling. The ICPL maintains excellent mechanical resilience even after extended cycling, as evidenced by the high recovery ratio during the unloading process. Interestingly, the maximum penetration depth slightly decreases after cycling, suggesting a degree of structural densification within the ICPL. This behavior can be attributed to the physical compaction of the composite structure induced by the stack pressure applied during full-cell operation. These findings further confirm the robust mechanical stability of the ICPL under practical operating conditions. Fig. S21 presents the FE-SEM images of RLi and ICPL-EDLi anodes retrieved from Li/NCM cells after 100 cycles. All images were acquired at the fully charged state. For the ICPL-EDLi sample, the ICPL was carefully removed prior to SEM analysis to observe the underlying lithium surface. As evident from the images, the ICPL-EDLi anode exhibits a more uniform and dense morphology compared to the RLi anode, indicating more homogeneous lithium deposition and reduced structural degradation during cycling. The rate capability was evaluated at various charge and discharge rates. Fig. S22 and Fig. 6e compare the discharge capacities of Li/NCM cells employing different lithium anodes under different charge and discharge rates, respectively. The corresponding voltage profiles during the rate capability tests are presented in Fig. S23. To evaluate the charge rate capability, the cells were charged under only constant current mode, while the discharge rate was fixed at 0.2C. For the discharge rate capability test, the charge rate was maintained at 0.2C. In both cases, the ICPL-EDLi system consistently exhibited superior performance

compared to the RLi system. Notably, when the current rate was reverted to 0.2C, the ICPL-EDLi cell recovered a higher discharge capacity than RLi cell. These results clearly demonstrate the superior cycling stability and enhanced rate capability of the Li/NCM cell with ICPL-EDLi, which can be attributed to its stable interfacial characteristics and uniform lithium morphology, in contrast to the cell employing conventional rolled lithium metal.

To confirm the effect of the ICPL on the SEI composition, XPS analysis was conducted on the Li metal anodes after 100 cycles (Fig. S24). The ICPL-EDLi was initially formed in an ether-based electrolyte and subsequently cycled in a carbonate-based electrolyte, which leads to differences in the XPS spectra before and after cycling. For example, newly emerged peaks such as B–F species are observed, which can be attributed to the decomposition of the carbonate-based electrolyte. Importantly, compared to the RLi electrode, the ICPL-EDLi electrode clearly exhibits S–F species and nitrogen-containing components in the F 1s and N 1s spectra, respectively. These features indicate that the robust SEI initially formed during the electrodeposition process is largely preserved, while an additional SEI layer is formed during subsequent cycling in the carbonate electrolyte. Taken together, these results suggest that the ICPL enables the formation of a stable and durable interphase that remains effective even under electrolyte transition conditions. To highlight the uniqueness and superiority of the ICPL system, a comparison table is provided in Table S2. This table summarizes the modification strategies, electrodeposition conditions, and electrochemical performance of recently reported studies on current collector modifications. Through this comparison, the advantages of the ICPL system are more clearly contextualized relative to prior work.

Based on the experimental results, the lithium electrodeposition and cycling behaviors on RLi, EDLi, and ICPL-EDLi are schematically illustrated in Fig. 7. In the presence of the ICPL, lithium is uniformly deposited under ambient pressure, even at a high current density of 6

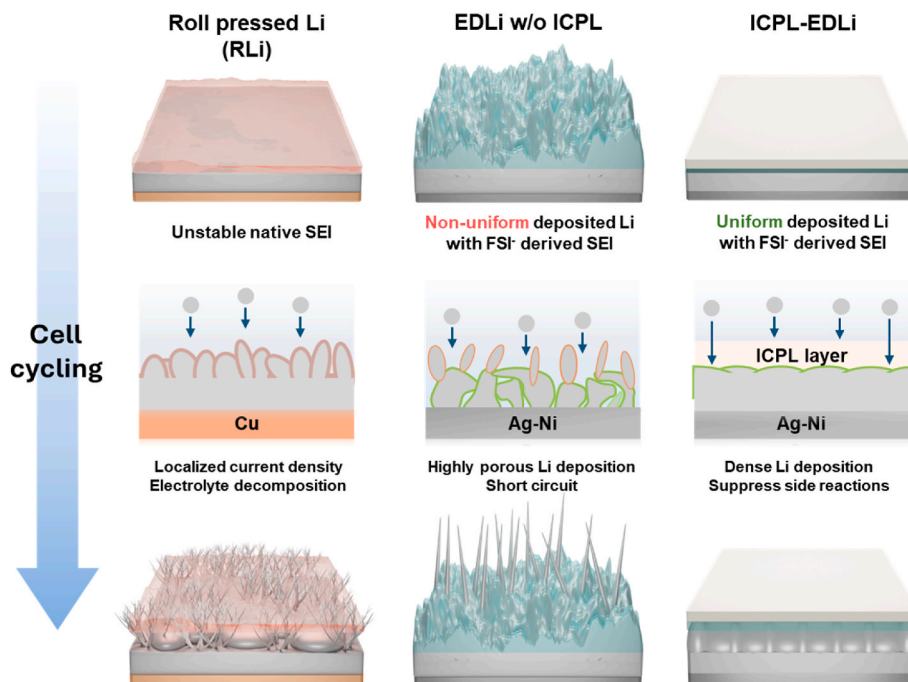


Fig. 7. Schematic illustration of the lithium deposition and cycling behavior on RLi, EDLi, and ICPL-EDLi.

mA cm^{-2} , accompanied by the formation of a stable SEI. During subsequent cycling, this protective layer effectively suppresses dendritic lithium growth and alleviates irreversible electrolyte decomposition at the anode side. Consequently, a dense lithium morphology and enhanced interfacial stability are maintained throughout cycling. As a result, the Li/NCM cell employing ICPL-EDLi exhibits markedly improved cycling performance compared with cells using electrodeposited lithium without the ICPL or commercial rolled lithium metal. These findings clearly demonstrate the effectiveness of integrating an ion-conductive protective layer with electrodeposited lithium as a viable strategy for improving the cycling performance and durability of lithium metal batteries.

4. Conclusion

In this work, we present a practical and effective strategy for fabricating thin, dendrite-free lithium metal anodes by integrating an ion-conductive protective layer (ICPL) with lithium electrodeposition under ambient-pressure conditions. The ICPL, consisting of Li^+ -conductive LLZTO particles and a dual-polymer binder (PVdF-HFP/NBR), simultaneously provides high ionic conductivity, high Li^+ transference number, and excellent mechanical resilience in the electrolyte-swollen state. These synergistic properties enable uniform lithium-ion transport and effective accommodation of volume changes during lithium deposition and stripping. When pre-coated onto an Ag-Ni current collector, the ICPL enables uniform and compact lithium electrodeposition beneath the protective layer at 6 mA cm^{-2} without external pressure. As a result, the ICPL-EDLi anode exhibits a dense lithium morphology, reduced overpotential, and improved stripping efficiency compared to bare electrodeposited lithium. Furthermore, the ICPL promotes the formation of a stable, less solvent-derived SEI, effectively suppressing parasitic side reactions and dendritic lithium growth during cycling. Symmetric cell tests demonstrate exceptional cycling stability and a high critical current density of 17 mA cm^{-2} . Consequently, the Li/NCM cells assembled with ICPL-EDLi show significantly enhanced cycling stability and rate capability, retaining 82.9% of their initial capacity after 200 cycles. The proposed ICPL-assisted electrodeposition strategy is well suited for scalable manufacturing processes, providing a

promising pathway toward the practical realization of thin, high-performance lithium metal anodes for next-generation lithium metal batteries.

CRediT authorship contribution statement

Ji-Wan Kim: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jusung Song:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Heesu Kim:** Methodology, Investigation, Formal analysis, Data curation. **Jin-Hong Kim:** Validation, Project administration, Methodology, Investigation, Formal analysis. **Sun-Min Park:** Validation, Investigation, Data curation, Conceptualization. **Dong-Won Kim:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2026.240061>.

Data availability

Data will be made available on request.

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