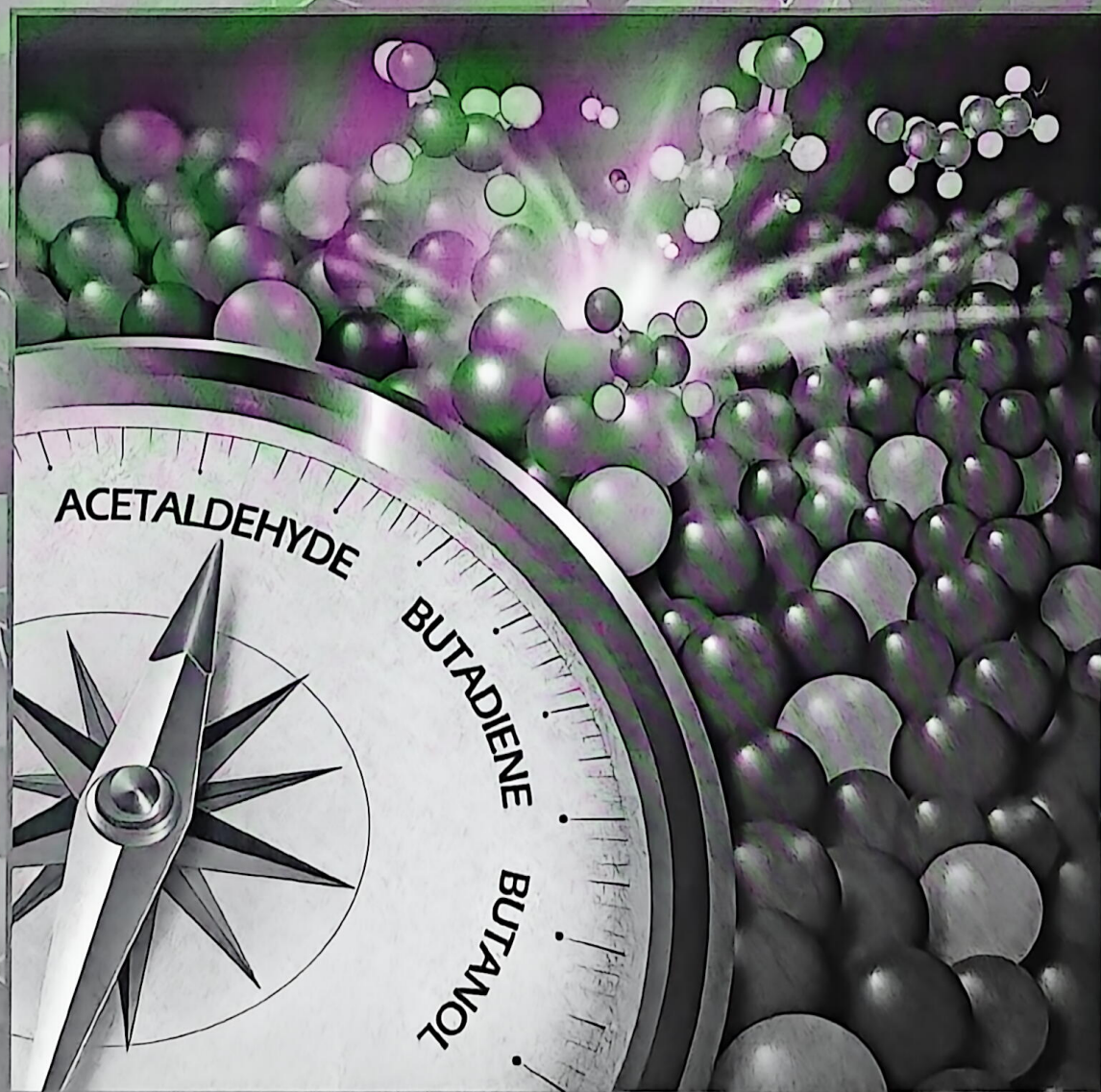


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Electrophoretic Interfacial Engineering Enables Self-Healing Ionomer Interphase for Anode-Free Lithium Metal Batteries

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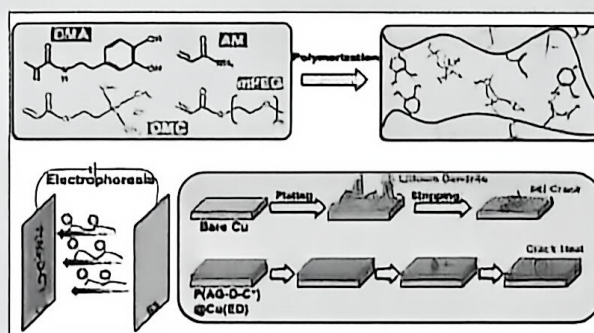
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Supporting Information

ABSTRACT: Anode-free lithium metal batteries (AFLMBs) are considered promising candidates for next-generation high-energy-density batteries. However, AFLMBs suffer from the continuous depletion of active lithium stemming from an unstable solid electrolyte interphase (SEI), as well as the structural instability of the anode caused by severe volume changes during charge–discharge cycles. Herein, a self-healing ionomer interphase [P(AG-D-C⁺)@Cu(ED)] is fabricated on a copper current collector via electrophoretic deposition of a cationic copolymer [P(AG-D-C⁺)]. Owing to the incorporation of functional monomers such as 3-methacrylamido dopamine (DMA) and poly(ethylene glycol) methyl ether methacrylate (mPEG), the interphase of the P(AG-D-C⁺) ionomer demonstrates outstanding self-healing capability, strong adhesion, and high Li⁺ transport efficiency. As a result, the as-assembled Li||P(AG-D-C⁺)@Cu(ED) half-cell delivers excellent cycling stability, maintaining a Coulombic efficiency (CE) of 99.2% over 200 cycles. This work provides a novel strategy for high-performance AFLMBs.

KEYWORDS: self-healing ionomer, cationic copolymer, electrophoretic deposition, interfacial engineering, anode-free lithium metal batteries



INTRODUCTION

The ever-growing reliance of electric vehicles, drones, and other electric mobility devices on advanced energy-storage systems has made it imperative to develop high-energy-density batteries to meet market requirements.^{1–3} Among various candidate technologies, lithium metal batteries are regarded as the “ultimate solution” for high-energy-density storage systems.^{4–6} To reduce manufacturing costs and further enhance practical energy density, anode-free lithium metal batteries (AFLMBs) have garnered considerable attention recently.^{7–10} However, AFLMBs suffer from the continuous depletion of active lithium stemming from an unstable solid electrolyte interphase (SEI), as well as the structural instability of the anode caused by severe volume changes during charge–discharge cycles, leading to low Coulombic efficiency and poor-cycling lifespan.¹¹ Therefore, improving the cycle life of AFLMBs has become a critical challenge.

Considerable strategies have been proposed to address anode-related challenges in AFLMBs, with current research primarily focusing on electrolyte optimization,^{12–16} current collector design,^{17–20} and interfacial engineering.^{21–24} Among these, constructing an artificial interphase on the current collector presents an effective and practical approach.²⁵ The cycle life of AFLMBs depends critically on the efficiency of lithium deposition/stripping on copper collectors. However, naturally formed SEI is heterogeneous and unstable, resulting in uneven lithium

deposition, dendrite formation, and the generation of “dead lithium”, which rapidly depletes both active lithium and electrolyte.²⁶ As such, an artificial interphase offers a targeted solution.^{27,28} Artificial interphases are generally categorized as inorganic, organic, or hybrid materials. Among them, organic polymer interphases have attracted widespread research interest due to their excellent structural tunability, ideal interfacial contact, and ease of large-scale fabrication.^{29,30}

However, the artificial interphases remain prone to cracking during long-term cycling due to the mechanical stress caused by repeated changes in lithium thickness. Consequently, several studies have proposed strategies for self-healing polymer interphases.^{31–34} For example, Chiu et al.³¹ copolymerized brittle PAMPS, which possesses hydrogen-bonding self-healing capability and sulfonate-based lithium-ion pathways, with flexible PBA that provides mechanical adaptability, thereby designing a PAMPS-co-PBA copolymer artificial interface featuring both self-healing and single-ion conduction. Despite the notable

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effectiveness of the self-healing interphase strategy, those studies merely employed a simple coating method to construct the interphase on the current collector surface. The interphase may detach during cycling due to uneven coating or poor adhesion to the current collector, thereby compromising the battery's cycle life. Therefore, selecting a controllable, efficient, and readily scalable approach for interphase construction is also crucial for improving the cycle life of anode-free lithium metal batteries.

Herein, inspired by mussel bioadhesives, we designed a cationic copolymer [(P(AG-D-C⁺))] cross-linkable through multiple hydrogen bonds. A uniform, dense, self-healing ionomer interphase was then constructed on a copper current collector via electrophoretic deposition (ED). The incorporation of 3-methacrylamido dopamine (DMA) into the P(AG-D-C⁺) ionomer introduces catechol groups that coordinate effectively with copper species during the electrophoretic deposition process, thereby enhancing the adhesion between the interphase and the copper current collector. Simultaneously, the phenolic hydroxyl groups can form a robust hydrogen-bonding network with polar groups such as amides, carboxyl, and ether oxygens. The synergistic effect between this hydrogen-bonding interaction and the dynamic reconstruction of polymer segments driven by van der Waals forces endows the polymer with excellent self-healing capability, which effectively alleviates the structural damage to the anode caused by severe volume changes during charge–discharge cycles. Furthermore, the incorporation of the poly(ethylene glycol) methyl ether methacrylate (mPEG), which enables uniform Li⁺ transport channels, synergized with the electrostatic anion confinement by cationic groups. This improves the lithium-ion transference number ($t_{\text{Li}^+} = 0.78$) of the P(AG-D-C⁺) ionomer. As a result, the Li||P(AG-D-C⁺)@Cu(ED) half-cell exhibits excellent cycling stability, maintaining a Coulombic efficiency of 99.2% over 200 cycles. The assembled (NCM811 + Li₂NiO₂)||P(AG-D-C⁺)@Cu(ED) AFLMB demonstrates a high initial discharge capacity of 213 mAh g^{−1} at 0.05 C with only 0.47% capacity decay per cycle. Notably, the AFLMB with a NCM811 loading of 25 mg cm^{−2} has a high specific capacity of up to 164 mAh g^{−1} at 0.1 C.

EXPERIMENTAL SECTION

Synthesis of 3-Methacrylamido Dopamine Self-Healing Monomer

A mixture of Na₂B₄O₇ (10 g, Sinopharm) and NaHCO₃ (8 g, Sinopharm) was dissolved in deoxygenated water. Under an argon atmosphere, dopamine hydrochloride (10 g, Guangzhou Jiankuo Technology Co., Ltd.) was added, and the mixture was stirred for 15 min, after which the pH was adjusted to ≥9.8. At −15 °C, methacryloyl chloride (5.2 mL, Shanghai Ge'er Chemical Reagent Co., Ltd.) was added dropwise, and the reaction proceeded for 30 min before warming to room temperature and stirring for an additional 6 h. After filtration, the pH of the mixture was adjusted to <2 and extracted repeatedly with ethyl acetate. The combined organic extracts were dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure using a rotary evaporation to obtain the crude product. The crude product was then dissolved in 50 mL of n-hexane and recrystallized at −20 °C. The resulting grayish-white powder was collected by filtration to give the self-healing monomer 3-methacrylamido dopamine (DMA).

Synthesis of Self-Healing Ionomer

0.08 g of DMA, 4.50 g of poly(ethylene glycol) methyl ether methacrylate (mPEG, Titan Scientific), and 3.4 g of methacryloethyl

trimethyl ammonium chloride (DMC, Shanghai Datan Fine Chemicals Co., Ltd.) were dissolved in deoxygenated water, followed by the addition of an aqueous NaHSO₃ reducing agent solution. Separately, 1.01 g of acrylamide (AM, Sinopharm) and ammonium persulfate (APS, Shanghai Lingfeng Chemical Reagent Co., Ltd.) was each dissolved in deoxygenated water. Under an argon atmosphere, the mixture was heated to 50 °C. The APS solution and AM solution were then added dropwise sequentially, and the reaction was continued with stirring for 5 h. Subsequently, the temperature was raised to 60 °C for 1 h of reaction. After completion, the product was purified by dialysis to remove unreacted monomers and oligomers, yielding the purified P(AG-D-C⁺) self-healing ionomer. For comparison, the P(AG-C⁺) ionomer was synthesized following the similar procedure without the addition of the DMA self-healing monomer.

Construction of Self-Healing Ionomer Interphase

The synthesized P(AG-D-C⁺) self-healing ionomer was diluted with deionized water and ethanol to a solid content of 6 wt %. Electrophoretic deposition (ED) was employed to deposit the ionomer onto a bare copper current collector. In this process, the copper substrate served as the cathode and a stainless-steel plate as the anode, with a voltage of 1.2 V applied for 60 s. The coated substrate was then dried at 60 °C for 3 h, followed by further drying in a vacuum oven at 120 °C for 2 h, yielding the self-healing ionomer interphase-modified copper current collector, denoted as P(AG-D-C⁺)@Cu(ED).

For comparison, the same self-healing ionomer (also diluted to 6 wt %) was applied onto a bare copper current collector using a 10 μm doctor blade. The coated sample was dried at 60 °C for 3 h and then in a vacuum oven at 120 °C for 2 h, yielding the counterpart denoted as P(AG-D-C⁺)@Cu(Coated). A bare copper current collector without any treatment was used as the control and designated as Cu(Bare).

Characterization

Fourier transform infrared (FTIR) spectroscopy was conducted on a Thermo Fisher Scientific Nicolet 6700 spectrometer. Nuclear magnetic resonance (¹H NMR) spectra were acquired using a Bruker ASCEND 400 MHz spectrometer with deuterated dimethyl sulfoxide as the solvent. Sample morphology was characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, ZEISS Sigma 560), three-dimensional confocal laser scanning microscopy (Keyence VK-X200K), focused ion beam scanning electron microscopy (FIB-SEM, Thermo Scientific Helios 6 HD), and optical microscopy (Dangdangli DDLMI). The chemical composition of the current collector surface after adhesive tape removal of the interlayer was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha). Mechanical properties and puncture tests were evaluated using a Mark-10 ESM303 universal testing machine. Ionomer stability was assessed with a Malvern Zetasizer Nano S nanoparticle analyzer. Ionic conductivity and lithium-ion diffusion coefficients were measured using a CHI760E electrochemical workstation (Chenhua Instruments, Shanghai).

RESULTS AND DISCUSSION

3-Methacrylamido dopamine (DMA), inspired by the chemical structure of mussel adhesive proteins, exhibits excellent self-healing ability. It was synthesized through the amidation reaction between dopamine hydrochloride and methacryloyl chloride (Figure S1). Its chemical structure was verified by Fourier transform infrared (FTIR) and ¹H nuclear magnetic resonance (NMR) spectroscopy (Figure S2).³⁵ The self-healing P(AG-D-C⁺) ionomer was subsequently synthesized by using solution radical copolymerization using four monomers: acrylamide (AM), poly(ethylene glycol) methyl ether methacrylate (mPEG), methacryloethyl trimethyl ammonium chloride (DMC), and DMA. The synthesis process is schematically illustrated in Figure 1a. Among them, each monomer served a

specific function: AM enhanced the molecular weight of the ionomer; DMC offered cationic groups for electrophoretic deposition; *m*PEG provided homogeneous channels for Li^+ migration, thereby increasing ionic conductivity; and DMA enabled superior self-healing and interfacial adhesion through the synergistic effect of hydrogen bonding and dynamic chain rearrangement. Based on comparative tests of mechanical properties, electrolyte resistance, ionic conductivity, and lithium transference number, the optimal ionomer composition was determined as follows: 0.8 wt % DMA; *m*PEG/AM = 2.23; DMC/AM = 1.68 (Figures S3–S10).

Figure 1b presents the FTIR spectra of $\text{P(AG-C}^+)$ and $\text{P(AG-D-C}^+)$. Both polymers exhibit characteristic peaks at 3500–3100, ~1665, 1114, and 952 cm^{-1} , corresponding to the N–H/O–H stretching of AM and DMA, the C=O stretching of the amide group in AM, the C–O–C of *m*PEG, and the quaternary ammonium salt of DMC, respectively. These results confirm successful copolymerization of AM, *m*PEG, and DMC.^{36,37} Compared with $\text{P(AG-C}^+)$, the C=O stretching vibration in $\text{P(AG-D-C}^+)$ exhibits a redshift from 1674 to 1661 cm^{-1} (~13 cm^{-1}). Furthermore, it can be found that the hydrogen-bonded N–H/O–H stretching peak at 3191 cm^{-1} broadened in the $\text{P(AG-D-C}^+)$. However, the degree of hydrogen bond in the $\text{P(AG-D-C}^+)$ increases compared to the $\text{P(AG-C}^+)$. These features not only confirm the successful incorporation of DMA,³⁸ but also indicate the formation of an extensive intermolecular hydrogen-bonding network, which contributes to the self-healing capability of the $\text{P(AG-D-C}^+)$ ionomer.

Figure 1c illustrates a schematic diagram of the electrophoretic deposition of $\text{P(AG-D-C}^+)$ ionomer on the copper current collector. With copper foil serving as the cathode and a stainless-steel sheet as the anode, the cationic ionomer migrates

directionally toward the cathode under an applied electric field, enabling its deposition onto the copper foil surface to form a uniform and dense interphase. The amide groups in acrylamide and the catechol groups in the dopamine moiety undergo dynamic bonding with copper species. This chemical interaction is considerably stronger than physical adsorption, which significantly improves the adhesion between $\text{P(AG-D-C}^+)$ interphase and the copper substrate. Consequently, it may effectively suppress the delamination and peeling of the $\text{P(AG-D-C}^+)$ interphase during charge–discharge cycles. Moreover, the catechol groups in DMA have strong coordination ability toward Li^+ ions, forming dynamic reversible O–Li–O multidentate coordination structures. This dynamic coordination mechanism may not only facilitate the interfacial transport kinetics of Li^+ but also mitigate local Li^+ concentration fluctuations and reduce the desolvation energy barrier of Li^+ . Therefore, it is supposed to significantly reduce the dendrite growth induced by the “tip effect”. Additionally, the synergistic effect between the formed SEI layer and the dynamic catechol– Li^+ coordination may further suppress the propagation of lithium dendrite tips driven by localized high-electric fields.

More importantly, the phenolic hydroxyl groups in DMA can form a dynamic hydrogen-bonding network with other polar functional groups, such as amides, carboxyl groups, and ether oxygens. This network endows the interphase with excellent self-healing capability, which enables rapid structural reconstruction of integrity after mechanical failure. Cross-sectional scanning electron microscopy (SEM) image of the $\text{P(AG-D-C}^+)$ -modified copper current collector [$\text{P(AG-D-C}^+)$ @Cu(ED)] clearly shows that the interphase is in close contact with the copper substrate, exhibiting uniform deposition and an ultrathin thickness of ~1.3 μm (Figure 1d). Combined with the elemental mapping (Figure 1e),

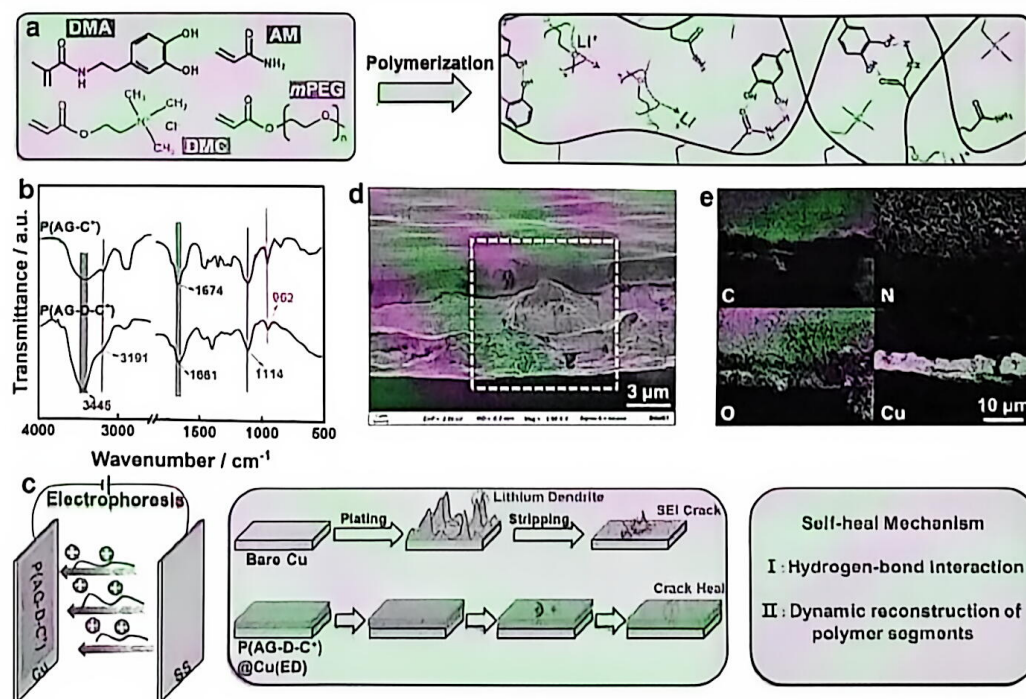


Figure 1. (a) Schematic diagram of the synthesis process and action mechanism of the $\text{P(AG-D-C}^+)$ ionomer. (b) FTIR spectra of $\text{P(AG-D-C}^+)$ and $\text{P(AG-C}^+)$ ionomers. (c) Schematic diagram of the construction of $\text{P(AG-D-C}^+)$ @Cu(ED) by electrophoretic deposition and self-heal mechanism. (d) Cross-sectional FE-SEM image and (e) EDS mappings of C, N, O, and Cu elements of $\text{P(AG-D-C}^+)$ @Cu(ED).

it can be observed that the C, N, and O elements are uniformly distributed over the copper surface. This confirms that the electrophoretic deposition can successfully construct a high-quality interphase.

To evaluate the effect of DMA incorporation on the comprehensive properties of the ionomer, a series of tests were conducted on the ionomer membranes. First, the self-healing efficiencies of the P(AG-D-C⁺) and P(AG-C⁺) membranes were compared under thermal induction. Specifically, strips of the two polymers were cut, aligned, and placed in intimate contact, followed by standing at 60 °C for 3 h. The tensile test results presented in Figure 2a indicate that the P(AG-D-C⁺) and P(AG-C⁺) membranes possess tensile strengths of 11.5 and 5.2 MPa, respectively, while their corresponding elongations at break are 458 and 493% (Figure 2b). After 3 h of self-healing following fracture, the P(AG-D-C⁺) membrane recovered a tensile strength of 11.2 MPa, corresponding to a self-healing efficiency of 97.4%. In contrast, the healed P(AG-C⁺) membrane showed a significantly reduced tensile strength of only 1.02 MPa, with a healing efficiency of 19.6%. These results demonstrate that the introduction of the DMA substantially improves both the self-healing capability and the mechanical strength of the ionomer membrane.

To further evaluate the self-healing capability imparted by the DMA, the P(AG-D-C⁺) membrane was cut in half along its diameter. The two semicircular pieces were then aligned along the cut interface and heated at 60 °C for 3 h. Even under forceful tearing, the healed film exhibited significant deformation without rupture, maintaining its overall structural integrity (inset in Figure 2a). The scratch-healing process of the P(AG-D-C⁺) membrane was observed using SEM (Figure 2c). After 1 h of healing, partial closure of the scratch was observed. After 3 h, the scratch was nearly eliminated without visible defects. Optical microscopy further confirmed that the originally separated red and black film segments merged into an integrated structure after 3 h of healing (Figure S11).

Puncture tests on P(AG-D-C⁺) and P(AG-C⁺) modified current collector show that the critical puncture stress of P(AG-C⁺) is only 0.97 MPa, while that of P(AG-D-C⁺) reaches 2.13 MPa (Figure 2d). This indicates that the incorporation of DMA leads to the cross-linking of ionomer through multiple hydrogen bonds, which significantly enhances the critical puncture stress of the P(AG-D-C⁺) membrane.

The electrolyte resistance of the ionomer membranes was further investigated by immersing 1.2 cm diameter discs of P(AG-D-C⁺) and P(AG-C⁺) in electrolyte at 60 °C for 24 h. As shown in Figure S12a, after 24 h of immersion, the P(AG-D-C⁺) membrane maintained its overall structural integrity without cracking or fragmentation. However, the membrane exhibited swelling, with its diameter increasing from 1.2 to 1.7 cm. In contrast, the P(AG-C⁺) membrane underwent noticeable dissolution under the same conditions, resulting in fragmentation and a loss of structural integrity (Figure S12b). These results demonstrate that DMA incorporation not only provides excellent self-healing capability and mechanical strength but also significantly improves its electrolyte resistance.

Considering the actual operating environment of the battery, we designed experiments to simulate the self-healing behavior of the interphase in an electrolyte-wet environment at 25 °C. Artificially cut strips of P(AG-D-C⁺) were prepared and then wetted with the electrolyte. The fractured surfaces were then aligned and brought into contact, and the strips were allowed to stand at 25 °C for different durations, after which digital photographs were taken. The results show that within the first 2 h, the crack region gradually healed, and after 3 h, the crack had completely disappeared (Figure S13). Tensile tests were also conducted on the P(AG-D-C⁺) strips with different healing times. As seen in Figure 2e,f, with increasing self-healing time, the tensile strength and elongation at break of the P(AG-D-C⁺) strips gradually recovered. After standing for 5 h, the self-healing efficiency reached 92%, confirming that this material possesses excellent self-healing capability under actual operating

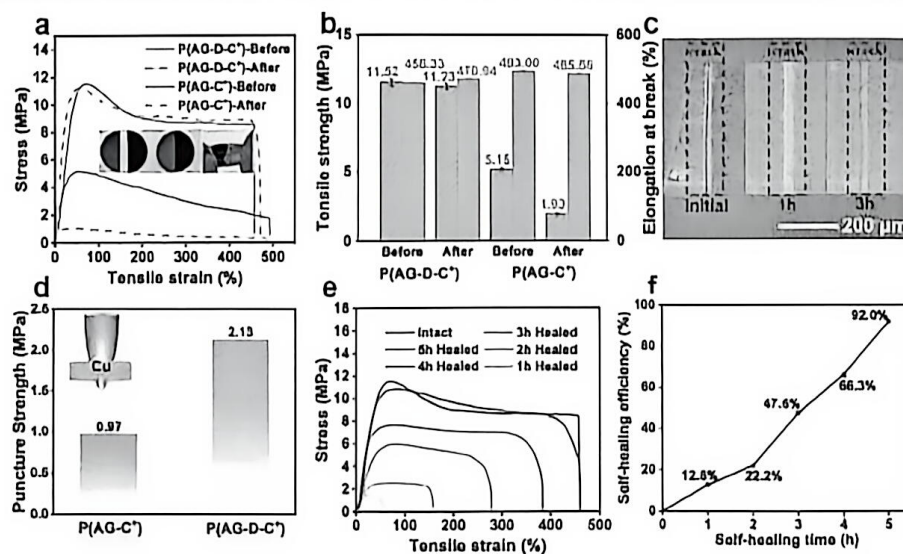


Figure 2. (a) Stress–strain curve (inset: digital photos of the P(AG-D-C⁺) membranes showing fracture, self-healing, and stretching) and (b) tensile strength and elongation of P(AG-D-C⁺) and P(AG-C⁺) membranes before and after thermally induced self-healing. (c) FE-SEM images during the thermally induced healing process of the scratch on the P(AG-D-C⁺) membrane. (d) Puncture strength of P(AG-D-C⁺) and P(AG-C⁺) membranes. (e) Stress–strain curves and (f) self-healing efficiency of the P(AG-D-C⁺) after different wet induced self-healing durations.

temperature and working environment (in the presence of electrolyte).

As a key parameter for evaluating ionic transport in interphase, the lithium-ion transference number (t_{Li^+}) directly reflects the charge carrier transport efficiency. Accordingly, the t_{Li^+} of P(AG-D-C⁺) membrane was then determined by electrochemical impedance spectroscopy (EIS). The Li||P(AG-D-C⁺)||Li symmetric cell with the P(AG-D-C⁺) membrane was assembled for polarization test and EIS measurement before and after polarization. The Bruce-Vincent equation yielded a t_{Li^+} of 0.78 for the interphase (Figure S14a). This is considerably higher than that of conventional PEO-based polymers (0.37, Figure S14b),^{39,40} which can be attributed to the coordination of Li⁺ with the amide groups in AM and DMA molecules, as well as with the ester groups in DMC and mPEG. Moreover, the cationic ionomer anchors the mobile anions in the electrolyte through electrostatic interaction. Furthermore, the P(AG-D-C⁺) membrane swollen with the electrolyte was assembled SS||P(AG-D-C⁺)||SS symmetric cell for EIS testing. As shown in Figure S14c, the corresponding ionic conductivity reached $1.39 \times 10^{-3} \text{ S cm}^{-1}$.

The P(AG-D-C⁺)@Cu(coated) and P(AG-D-C⁺)@Cu(ED) interphases were constructed via coating and electrophoretic deposition, respectively, and their surface roughness was characterized by three-dimensional confocal microscopy. As can be seen

from Figure S15a,b, the P(AG-D-C⁺)@Cu(ED) interphase exhibits superior flatness with a surface roughness of 0.273 μm . In contrast, the P(AG-D-C⁺)@Cu(Coated) interphase exhibits poorer surface flatness with a surface roughness of 0.695 μm . This indicates that the electric field force can more effectively homogenize the deposition of the ionomer, resulting in a dense and continuous film coverage. Cross-sectional FE-SEM images (Figure 1d and Figure S15c) further confirm that the electrophoretic approach produces a homogeneous and tightly integrated interphase on the copper current collector.

And to verify the effect of the interphase constructed via electrophoretic deposition on the adhesion between P(AG-D-C⁺) and the copper current collector, peeling tests were conducted on two anodes respectively. As shown in Figure 3a, the peeling strength of the P(AG-D-C⁺)@Cu(ED) is as high as 275 N m^{-1} , whereas that of the P(AG-D-C⁺)@Cu(Coated) sample is only 168 N m^{-1} . This result indicates that the electrophoretic deposition process significantly enhances the interfacial adhesion between the interphase and the copper sheet. Furthermore, after immersing the two types of anode samples in the electrolyte at 25 $^{\circ}\text{C}$ for 24 h, it was observed that the P(AG-D-C⁺)@Cu(Coated) interphase underwent partial delamination, whereas the P(AG-D-C⁺)@Cu(ED) interphase remained structurally intact and maintained close contact with the copper foil (Figure S16). Meanwhile, the swelling of

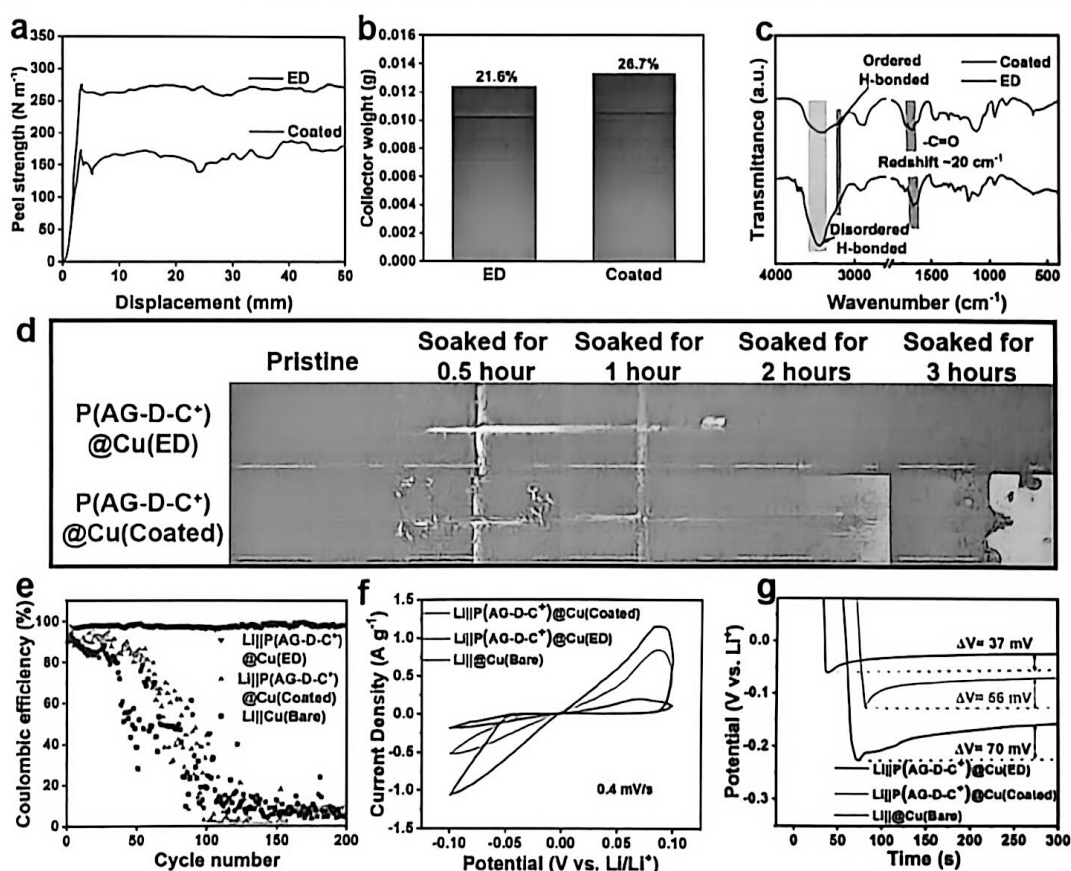


Figure 3. (a) Peeling strength-displacement curves, (b) swelling ratios after soaking in electrolyte at 25 $^{\circ}\text{C}$ for 24 h, and (c) FTIR spectra of the P(AG-D-C⁺)@Cu(Coated) and P(AG-D-C⁺)@Cu(ED) interfacial phases. (d) Comparative SEM images of scratch self-healing on P(AG-D-C⁺)@Cu(Coated) and P(AG-D-C⁺)@Cu(ED) surfaces. (e) Coulombic efficiency of Li deposition/stripping, (f) CV curves, (g) overpotential comparison for Li||Cu(Bare), Li||P(AG-D-C⁺)@Cu(Coated), and Li||P(AG-D-C⁺)@Cu(ED) half cells.

P(AG-D-C⁺)@coated is 26.7%, which is also larger than P(AG-D-C⁺)@Cu(ED) (21.6%, Figure 3b). These immersion results further corroborate the significant advantage of the electrophoretic deposition strategy in constructing an interphase with high adhesion.

To probe the mechanism of adhesion enhancement of the interphase by electrophoretic deposition, the P(AG-D-C⁺)@coated and P(AG-D-C⁺)@Cu(ED) interphases were separately peeled off from the current collectors and characterized by FTIR spectroscopy (Figure 3c). The FTIR spectra clearly show that due to enhanced coordination between the ionomer and copper species, the lone pair electrons of the carbonyl oxygen are transferred to the metal center, leading to a decrease in the force constant of the C=O bond and a shift of its stretching vibration frequency to lower wavenumbers by $\sim 20\text{ cm}^{-1}$.^{41,42} Meanwhile, although some ordered H-bonds become free, the total H-bond content in P(AG-D-C⁺)@Cu(ED) is much higher than that in P(AG-D-C⁺)@coated.

The P(AG-D-C⁺)@Cu(ED) anode was then characterized by FIB-SEM and EDS elemental mapping for Cu, C, and O. As can be seen from Figure S17, distinct Cu signal is distributed within the P(AG-D-C⁺)@Cu(ED) interphase, with a stronger Cu signal near the copper foil side. This further demonstrates that the interphase constructed by electrophoretic deposition can coordinate with copper species, which facilitates intimate contact between the interphase and the current collector. This coordination promotes a conformal, robust interphase that suppresses side reactions between Li and electrolyte. Moreover, the tighter adhesion indirectly improves the self-healing of the P(AG-D-C⁺)@Cu(ED) interphase.

To further assess the impact of electrophoretic deposition on interphase self-healing, we created cross-scratches with a width of $\sim 60\text{ }\mu\text{m}$ on both P(AG-D-C⁺)@coated and P(AG-D-C⁺)@Cu(ED) anodes, immersed them in electrolyte at 25 °C for set times, and then recorded digital photos and SEM images. As shown in Figure S18 and Figure 3d, the scratches on both types of interphases gradually healed within 2 h, and after 3 h of immersion, the cross-scratches had completely disappeared. This indicates that P(AG-D-C⁺)@Cu(ED) interphase exhibits excellent self-healing capability under the actual operating conditions of the battery, capable of continuously mitigating the short-circuit risk caused by the continuous growth of lithium dendrites. Furthermore, comparison of the SEM images taken after 2 and 3 h of immersion also demonstrates that the P(AG-D-C⁺)@Cu(ED) interphase remains intact without detaching from the current collector after immersion.

Li||Cu(bare), Li||P(AG-D-C⁺)@Cu(coated), and Li||P(AG-D-C⁺)@Cu(ED) half-cells were assembled separately for electrochemical tests. As shown in Figure 3e, under a current density of 1 mA cm^{-2} and areal capacity of 1 mAh cm^{-2} , both the Li||Cu(bare) and Li||P(AG-D-C⁺)@Cu(coated) systems exhibited low Coulombic efficiency (CE) with rapid decay after only a few cycles. In contrast, the Li||P(AG-D-C⁺)@Cu(ED) system demonstrated exceptional cycling stability, maintaining a high CE of 99.2% over 200 cycles. Compared to the bare copper electrode, the P(AG-D-C⁺)-modified electrode stabilizes the electrode–electrolyte interface during charge/discharge cycling, preventing unnecessary electrolyte consumption caused by the repeated breakdown and repair of the SEI. Furthermore, relative to Li||P(AG-D-C⁺)@Cu(coated), the interphase in the P(AG-D-C⁺)@Cu(ED) electrode adheres tightly to the copper current collector, which can fully isolate the electrolyte from

lithium metal and reduce the occurrence of side reactions. Additionally, the uniform interphase can guide the homogeneous deposition of lithium, significantly suppressing the growth of mossy lithium dendrites and effectively minimizing lithium loss.

Cyclic voltammetry (CV) was employed to investigate the redox behavior and interfacial stability of cells fabricated with different anode current collectors. As shown in Figure 3f, the peak current of Li||Cu(Bare) cell is an order of magnitude lower than that of the Li||P(AG-D-C⁺)@Cu(ED) cell. Furthermore, the poor reversibility of lithium deposition/stripping on bare copper resulted in slower electrochemical kinetics, manifesting as weak and poorly defined redox peaks compared to the Li||P(AG-D-C⁺)@Cu(ED) and Li||P(AG-D-C⁺)@Cu(coated) systems. Figure 3g compares the nucleation overpotentials of lithium metal on the three current collectors. The Li||P(AG-D-C⁺)@Cu(ED) cell exhibited a nucleation overpotential of only 37 mV, which represents reductions of 19 and 33 mV compared to Li||P(AG-D-C⁺)@Cu(coated) and Li||Cu(bare) cells, respectively. This demonstrates that the P(AG-D-C⁺)@Cu(ED) interphase effectively reduces the lithium nucleation barrier, promoting uniform lithium nucleation and deposition. Such low-overpotential nucleation not only enhances the controllability of lithium metal deposition but also mitigates the formation of localized high-electric-field regions at the interface.

Figure S19 shows that the Li||P(AG-D-C⁺)@Cu(ED) cell exhibits stable voltage plateaus with an initial polarization of 66.9 mV, which is lower than the 73.4 mV of the Li||P(AG-D-C⁺)@Cu(Coated) cell. After 200 cycles, the polarization voltage of Li||P(AG-D-C⁺)@Cu(ED) remained stable at 56.4 mV. This improvement can be attributed to the P(AG-D-C⁺)@Cu(ED) interphase reducing the lithium nucleation overpotential, promoting uniform Li⁺ deposition, and ultimately enhancing the reversibility of lithium plating/stripping. Figure S20 presents the Nyquist plot EIS results corresponding to equivalent circuit simulation for half-cells with three anode current collectors, measured before and after 200 cycles at 0.5 C. The Li||P(AG-D-C⁺)@Cu(ED) battery exhibits the smallest impedance both before and after cycling, which was attributed to the uniform and dense interphase that reduces interfacial resistance and enhances Li⁺ transport.

The FE-SEM images in Figure 4a–c show lithium metal deposited at 1 mA cm^{-2} and 3 mAh cm^{-2} on P(AG-D-C⁺)@Cu(ED), P(AG-D-C⁺)@Cu(coated), and bare Cu for assembled half-cells, respectively. On the surface of P(AG-D-C⁺)@Cu(ED) (Figure 4a), the lithium metal is deposited beneath the interphase, forming uniformly distributed “mushroom-like” protrusions with a size of approximately $20\text{ }\mu\text{m}$. This indicates that the interphase effectively regulates lithium nucleation, which promotes uniform deposition of lithium beneath the interphase. Moreover, the interphase constrains lithium growth, suppressing the uncontrolled formation of lithium dendrites. Lithium metal on the surface of P(AG-D-C⁺)@Cu(coated) also demonstrates the nucleation regulation. However, the uniformity of deposition is significantly reduced, and the size distribution of the protrusions is inhomogeneous (Figure 4b). In contrast, severe dendrite formation and porous deposition are observed on bare copper (Figure 4c). This can be attributed to the lack of an effective interphase on the bare copper surface, which fails to regulate lithium nucleation. Consequently, lithium cannot distribute uniformly during the initial nucleation stage, resulting in localized overpotential that drives disordered deposition and dendrite growth.

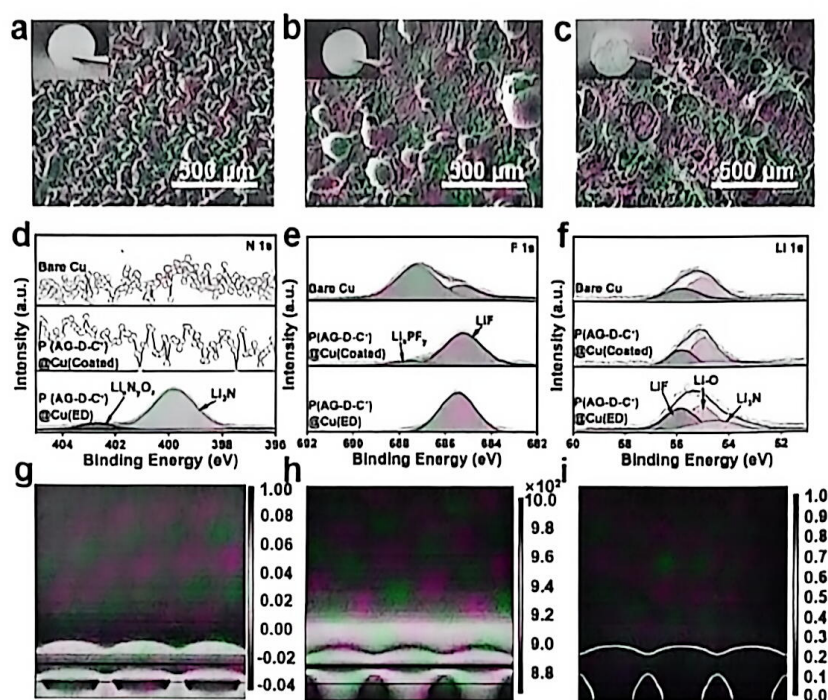


Figure 4. (a–c) Superficial FE-SEM images of Li||P(AG-D-C⁺)@Cu(ED), Li||P(AG-D-C⁺)@Cu(coated), and Li||Cu(bare) half-cells after lithium metal deposition at a current density of 1 mA cm^{−2} with a capacity of 3 mAh cm^{−2} (inset: digital photos of Li deposition). (d) N 1s, (e) F 1s, and (f) Li 1s XPS spectra of on the anode surface after 200 cycles for Li||Cu(bare), Li||P(AG-D-C⁺)@Cu(coated), and Li||P(AG-D-C⁺)@Cu(ED) half-cells. (g) Electric field distribution, (h) Li⁺ concentration distribution, (i) evolution process of lithium dendrites in P(AG-D-C⁺)@Cu(ED).

Optical microscopy further confirms uniform and continuous lithium deposition on the P(AG-D-C⁺)@Cu(ED) surface (inset in Figure 4a), indicating effective regulation of Li⁺ nucleation and deposition. By comparison, lithium deposition on P(AG-D-C⁺)@Cu(coated) shows noticeable inhomogeneity with localized bare areas (inset in Figure 4b), reflecting its diminished ability to guide uniform Li⁺ nucleation. In contrast, bare copper exhibits even more severe exposure (inset in Figure 4c), which demonstrates a high nucleation overpotential that promotes localized lithium nucleation, leading to the formation of dendrite and “dead” lithium, thereby severely deteriorating the cycling stability of the cell. Figure S21 compares the lithium-stripping behavior on three Cu current collectors. When stripped to a cutoff voltage of 2 V, the P(AG-D-C⁺)@Cu(ED) surface returns almost completely to its initial state, appearing smooth and clean with minimal residual lithium. In contrast, both P(AG-D-C⁺)@Cu(coated) and bare copper show dark residues, indicating the presence of dead lithium and side products from electrolyte decomposition. These results demonstrate that P(AG-D-C⁺)@Cu(ED) effectively promotes uniform lithium deposition/stripping and significantly suppresses side reactions.

After 200 cycles, the Li||P(AG-D-C⁺)@Cu(ED), Li||P(AG-D-C⁺)@Cu(coated), and Li||Cu(bare) half-cells were disassembled, and X-ray photoelectron spectroscopy (XPS) was employed to analyze the chemical composition of the interface on the copper current collectors (Figure 4d–f). Compared to Cu(bare) and P(AG-D-C⁺)@Cu(coated), the N 1s spectrum of P(AG-D-C⁺)@Cu(ED) clearly shows characteristic peaks at 402.7 and 399.8 eV, corresponding to Li_xN_yO_z and Li₃N, respectively. In the F 1s spectrum, the LiF peak at 685.2 eV is most intense in P(AG-D-C⁺)@Cu(ED), while the peak at

687.3 eV corresponding to the electrolyte decomposition product Li_xPF_y, shows the lowest intensity. The Li 1s spectrum exhibits three characteristic peaks at 55.8 (LiF), 55.0 (Li-O), and 54.4 eV (Li₃N). Compared to the other two systems, P(AG-D-C⁺)@Cu(ED) shows significantly stronger LiF and Li₃N peaks. This enhancement is attributed to the abundant amide groups in P(AG-D-C⁺), which coordinate with lithium ions and effectively promote the formation of Li₃N. Furthermore, the tight adhesion between the P(AG-D-C⁺) and the copper substrate in the P(AG-D-C⁺)@Cu(ED) electrode restricts electrolyte penetration between the interphase and the lithium plating layer, thereby minimizing solvent-related side reactions. This facilitates the formation of beneficial secondary SEI components such as LiF and Li₃N, which improves the interfacial stability and the uniformity of lithium deposition.

Multiphysics simulations were conducted to elucidate the regulatory mechanism of the P(AG-D-C⁺)@Cu(ED) self-healing interphase on lithium deposition behavior. As observed in Figure S22a, the electric field distribution at the interface of bare copper is highly inhomogeneous, with localized “sawtooth-like” field enhancement peaks indicating significant field distortion. In contrast, the electric field isosurface of P(AG-D-C⁺)@Cu(ED) is flatter (Figure 4g), indicating that this interphase establishes a smooth and stable electric field environment, which facilitates uniform Li deposition. For the bare copper, Li⁺ preferentially deposits at high-field tips. This spatial inhomogeneity is continuously amplified in subsequent cycles, leading to sustained dendrite growth (Figure S22b). In contrast, the interphase in the P(AG-D-C⁺)@Cu(ED) effectively shields against local electric field distortion. This enables a uniform distribution of Li⁺ and promotes isotropic

deposition, which significantly suppresses the probability of dendrite formation (Figure 4h). A phase-field model was further employed to simulate the growth behavior of lithium dendrites. As shown in Figure S22c, lithium dendrites on bare copper exhibit typical disordered, branch-like morphology, which reflects uncontrolled deposition due to the lack of interfacial regulation. In contrast, benefiting from the lithiophilicity of the interphase and its electric-field-homogenizing effect, the probability of lithium dendrite formation is greatly reduced, resulting in continuous, uniform, and smooth lithium deposition on the P(AG-D-C⁺)@Cu(ED) interphase (Figure 4i). This is consistent with the SEM images of lithium deposited on the interphase (Figure 4a).

To investigate the effect of the self-healing interphase on the electrochemical performance of AFLMBs, we fabricated the cathode sheets by using NCM811 as the active cathode material and Li₂NiO₂ as the lithium supplement agent (The mass is 25% of the NCM811). The electrolyte consisted of 1.0 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio 1:1). The cathodes were then assembled with Cu(bare), P(AG-D-C⁺)@Cu(coated), and P(AG-D-C⁺)@Cu(ED) to fabricate AFLMBs. The effect of incorporating Li₂NiO₂ as a lithium supplement on the electrochemical performance of the cathode was evaluated (Figure S23). The results indicate that the addition of Li₂NiO₂ significantly enhances the specific capacity and rate capability of the cathode while reducing the charge transfer resistance both before and after cycling. These improvements suggest that Li₂NiO₂ effectively stabilizes the electrode interface and enhances electrochemical kinetics, improving the cycling stability and rate performance of the battery. Therefore, the incorporation of Li₂NiO₂ is considered essential.

Figure 5a presents the CV curves of the three AFLMBs at a scan rate of 0.4 mV s⁻¹. The results show that the redox peaks

are indistinct in the AFLMB with bare copper; those AFLMBs with P(AG-D-C⁺)@Cu(coated) and P(AG-D-C⁺)@Cu(ED) exhibit distinct redox peaks. This difference is ascribed to the high-nucleation overpotential and sluggish kinetics on bare copper, which obscure the redox activity in the bare copper system. Figure 5b displays the initial charge/discharge profiles of the three AFLMBs at 0.05 C. The results show that the P(AG-D-C⁺)@Cu(ED) AFLMB delivers a high-discharge-specific capacity of 213 mAh g⁻¹ (E/C ratio of 4.15 μ L mAh⁻¹), outperforming those with P(AG-D-C⁺)@Cu(coated) (200 mAh g⁻¹) and Cu(bare) (187 mAh g⁻¹).

Figure 5c shows the rate performance of the three AFLMBs. The NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(ED) AFLMB consistently delivered the highest specific discharge capacity across various current densities. Notably, it achieves superior capacity of 86 mAh g⁻¹ at 2 C. In contrast, the discharge capacity of the NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(coated) AFLMB reaches only about 34 mAh g⁻¹ at 2 C, while that of the NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(bare) AFLMB shows almost negligible capacity (close to 0 mAh g⁻¹) at the same rate. Cycling performance results (Figure 5d) demonstrate that the NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(ED) AFLMB maintains a high Coulombic efficiency of 98% and a capacity retention of 53% after 100 cycles. Conversely, the NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(coated) and NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(bare) AFLMBs exhibit capacity fading to near zero after 100 and 39 cycles, respectively. These results indicate that the P(AG-D-C⁺)@Cu(ED) interphase significantly improves the cycling performance of AFLMBs. EIS measurements revealed the Li⁺ diffusion kinetics in the different AFLMBs (Figure S24). The three AFLMBs showed similar series resistances (*R*_s) before cycling. After 100 cycles, the NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(ED) AFLMB displays the lowest impedance values, with *R*_s = 2.7 Ω and *R*_{ct} = 96.9 Ω . These values

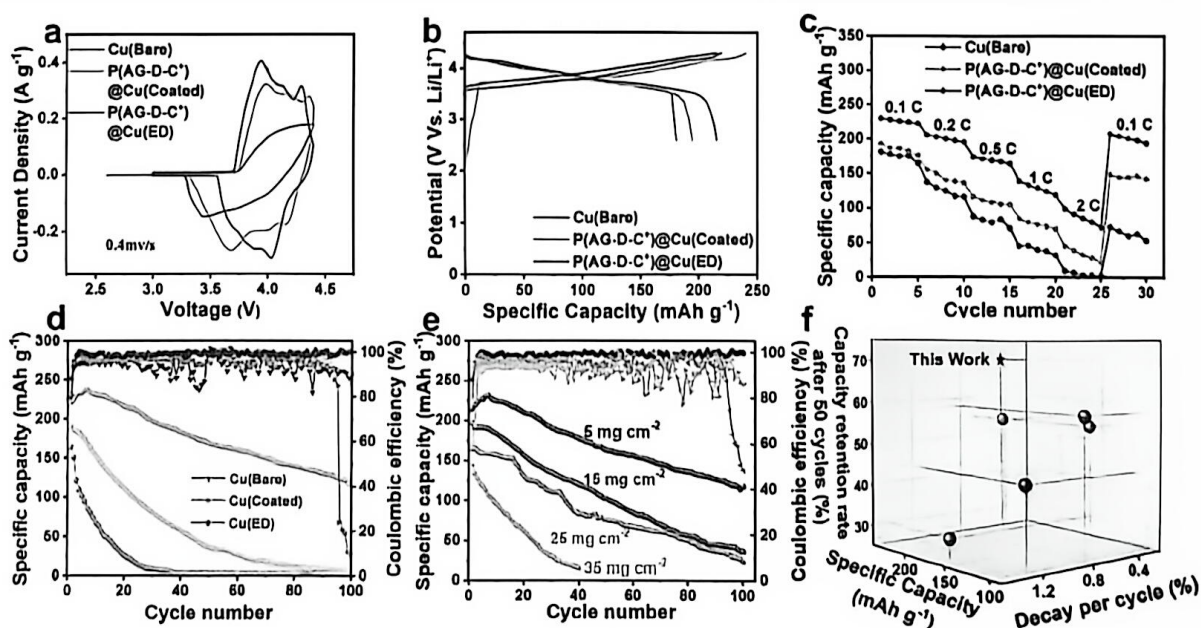


Figure 5. (a) CV curves at a scan rate of 0.4 mV s⁻¹; (b) 1st charge–discharge curves at 0.05C; (c) rate performance, (d) cycling performance and Coulombic efficiency of NCM811 + Li₂NiO₂||Cu(Bare), NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(Coated), NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(ED) AFLMBs. (e) Cycling performance of NCM811 + Li₂NiO₂||P(AG-D-C⁺)@Cu(ED) AFLMBs with different cathode loadings. (f) Electrochemical performance comparisons between this work and other reports on AFLMBs.

are considerably lower than the those of NCM811 + $\text{Li}_2\text{NiO}_2\|\text{P(AG-D-C}^+)\text{@Cu(coated)}$ ($R_s = 7.4 \Omega$, $R_{ct} = 163.9 \Omega$) and the NCM811 + $\text{Li}_2\text{NiO}_2\|\text{Cu(bare)}$ AFLMBs ($R_s = 7.7 \Omega$, $R_{ct} = 297.2 \Omega$). This indicates that the electrophoretically modified $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ possesses enhanced reaction kinetics.

To further explore the application potential of $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ in AFLMBs, its electrochemical performance was evaluated with cathodes of different loadings (Figure S25 and Figure 5e). With cathode mass loadings of 5, 15, 25, and 35 mg cm^{-2} , the AFLMBs delivered initial discharge-specific capacities of 214, 196, 164, and 143 mAh g^{-1} at 0.1 C, all demonstrating high initial capacity. Figure 5e shows the cycling performance under different cathode loadings. Even at 25 mg cm^{-2} , the AFLMB maintains high Coulombic efficiency. This indicates that the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ electrode possesses excellent interfacial stability in the AFLMB configuration. This performance supports its potential application in high-energy-density battery systems.

Figure 5f presents a comprehensive performance comparison between the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ self-healing artificial interphase and previously reported advanced systems.^{29,31,43,44} Our design demonstrates exceptional overall performance, achieving the highest specific capacity of 213 mAh g^{-1} among all compared systems. Furthermore, it exhibits outstanding cycling stability with a low-capacity decay rate of 0.47% per cycle and maintains 76% capacity retention after 50 cycles. These results confirm that the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ interphase successfully balances high capacity, superior energy density, and prolonged cycle life, positioning it as a highly competitive candidate for practical applications.

CONCLUSIONS

In summary, we propose the construction of a $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ ionomer interphase on a copper current collector by using electrophoretic deposition, which combines efficient Li^+ conduction and self-healing capability. FTIR, SEM, and mechanical tests confirm that the incorporation of DMA promotes the formation of a multiple hydrogen-bonding network, thereby endowing the interphase with excellent self-healing performance. The incorporation of mPEG creates homogeneous Li^+ transport channels, synergized with the electrostatic anion confinement by cationic groups, which significantly enhances the Li^+ transference number ($t_{\text{Li}^+} = 0.78$). Benefiting from these features, the $\text{Li}\|\text{P(AG-D-C}^+)\text{@Cu(ED)}$ half-cell exhibits a high Coulombic efficiency of 99.2% over 200 cycles. When paired with a commercial NCM811 cathode and Li_2NiO_2 lithium supplement, the assembled AFLMB delivers an initial discharge capacity of 213 mAh g^{-1} at 0.05 C, with an average cycle capacity decay rate of only 0.47%. Moreover, under a high cathode loading of 25 mg cm^{-2} , the full cell achieves a specific capacity of 164 mAh g^{-1} at 0.1 C, highlighting its exceptional performance under practical conditions. This work provides a feasible solution for advanced SEI engineering to stabilize AFLMBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.6c04733>.

Device assembly; electrochemical measurements; simulation details; schematic illustration of the synthesis of DMA; FTIR spectrum, and ^1H NMR spectrum of DMA; ionomer component optimization; optical photos of the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ membrane before and after scratch healing (thermally induced); swelling behavior test of $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ and $\text{P(AG-C}^+)\text{@Cu(ED)}$ membranes; self-healing process of the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ strip; t_{Li^+} of $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ and PEO-based polymer and ionic conductivity of $\text{P(AG-D-C}^+)\text{@Cu(ED)}$; 3D confocal images and electrolyte resistance test of interphases; cross-sectional FIB-SEM image of the $\text{P(AG-D-C}^+)\text{@Cu(ED)}$ interphase and corresponding EDS; self-healing process of interphases; voltage-capacity profiles, EIS spectra, equivalent circuit diagrams, and digital photos of Li stripping of $\text{Li}\|\text{Cu(Bare)}$, $\text{Li}\|\text{P(AG-D-C}^+)\text{@Cu(coated)}$, and $\text{Li}\|\text{P(AG-D-C}^+)\text{@Cu(ED)}$ half-cells; COMSOL simulations of Cu(bare) ; comparison of the electrochemical performance of NCM811 $\|\text{Li}$ and NCM811 + $\text{Li}_2\text{NiO}_2\|\text{Li}$ half-cells; EIS spectra, equivalent circuit diagrams of AFLMBs; first-cycle charge–discharge curves of AFLMBs; comparison of comprehensive performance with other works (DOCX)

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Notes

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