Energy & Environmental Science





Cite this: Energy Environ. Sci., 2024, 17, 4519

Received 25th January 2024, Accepted 20th May 2024

DOI: 10.1039/d4ee00399c

rsc.li/ees

Broader context

Achieving stable lithium metal anodes *via* the synergy of electrostatic shielding and the high Li⁺ flux inorganic interphase[†]

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Uncontrolled dendrite growth and slow Li⁺ transport kinetics at the anode/electrolyte interface severely hamper the practical applications of lithium metal batteries (LMBs). Herein, a high-charge density cationic polymer, poly(octaallyltetraazacyclo-decane nitrate) (POTA-NO₃), was developed as an anodic protective layer to moderate Li⁺ deposition and enhance Li⁺ transport efficiency. According to Li⁺ deposition characteristics and simulation, POTA-NO₃ with multiple positive charge sites provided excellent electrostatic shielding and enhance Li⁺ desolvation process to the anodes. Meanwhile, anions generated a robust and high Li⁺ flux inorganic SEI to inhibit the polymer cationic layer and electrolyte decomposition. With the POTA-NO₃ protective layer, Li||Li symmetric batteries achieved a stable cycling of 6300 h at a high current density of 5 mA cm⁻² with a capacity of 5 mA h cm⁻². Furthermore, the POTA-NO₃-protected Li||LiCOO₂ batteries exhibited a capacity retention of over 80% after 1400 long-term cycles at 1C. This work opens up the possibility for the development of stable lithium anodes.

Unfavorable dendrite growth and continuous electrolyte decomposition at the lithium anode/electrolyte interface have severely limited the development of lithium-metal batteries (LMBs), despite their high energy densities. Understanding the Li⁺ plating/stripping mechanism on lithium metal electrodes is essential to control the Li⁺ uniform deposition. The rough lithium anode surface and negative potential can create a localized electric field concentration on the protrusion to cause Li⁺ preferential deposition, leading to the growth of lithium dendrites. Therefore, modulating the prominent electric field on the surface of the lithium anode and fabricating a stable, robust, and intervening SEI with high Li⁺ conductivity are essential for the practical applications of LMBs. Inert organic cationic polymers with high charge density are applied to the surface of lithium anodes to neutralize localized protruding electric fields and homogenize Li⁺ deposition. Meanwhile, anions generated a robust and high Li⁺ flux inorganic SEI to inhibit the polymer cationic layer and electrolyte decomposition. This work provides an effective way for constructing stable lithium metal electrodes based on molecular structural design, which has the potential to facilitate the practical use of LMBs.

Introduction

The dramatic progress of smart electrical devices, electric vehicles, and other industries has intensified the urgent need

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for battery systems with higher energy densities.^{1–3} Among the proven anode materials, Li metal is considered the "golden" anode owing to its high theoretical specific capacity of 3860 mA h g⁻¹ and favourable negative equilibrium electrode potential of -3.04 V *versus* standard hydrogen electrode (SHE).^{4–6} However, several inherent defects hinder the practical applications of Li anodes, such as high reactivity resulting in electrolyte decomposition, uncontrolled dendrite growth with thermal runaway safety issues, and poor reversibility.^{7–10} The original solid electrolyte interphase (SEI), formed by parasitic reactions between the electrolyte and Li metal, contains a complex composition with uneven distribution, low Li⁺ flux, and restricted availability, resulting in uneven Li⁺ deposition, high Li⁺ transfer energy barrier, and continuous SEI cracking with the decomposition of the electrolyte.^{11,12} Moreover, the

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[†] Electronic supplementary information (ESI) available: Additional analysis details, Fig. S1–S49, Tables S1 and S2 as described in the main text. See DOI: https://doi.org/10.1039/d4ee00399c



Fig. 1 Schematic illustration of the Li^+ plating modulation by the POTA-NO₃ protective layer. (a) Li^+ plating behaviour in the electrolyte-derived original SEI. (b) Mechanism of the POTA-NO₃ protective layer to inhibit tip deposition and improve Li^+ transport kinetics.

rough anode surface will create a localized electric field concentration on the protrusion to cause Li⁺ preferential deposition, leading to the growth of lithium dendrites (Fig. 1a).^{13–15} These issues are responsible for the low Coulombic efficiency (CE), poor cycling stability, and safety issues of LMBs, particularly at high current densities.^{16,17} Therefore, modulating the prominent electric field on the surface of the lithium anode and fabricating the stable, robust, and intervening SEI with high Li⁺ conductivity are essential for the practical applications of LMBs.

To date, many works had attempted to ameliorate the drawbacks of the original SEI, such as the formulation and molecular manipulation optimization of electrolytes/additives,18-21 regulation of Li⁺ solvated structures,^{22,23} architectural engineering of electrodes,^{24,25} and constructing artificial SEIs.²⁶⁻²⁸ In particular, using electrochemically inert cations as an artificial SEI to modulate electric field distribution is a radically creative strategy.^{29–32} The inactive cations can shield deposition hotspots due to locally high electric fields and inhibit Li⁺ deposition at electrode protrusions by Coulombic forces with Li⁺, thus fundamentally altering the Li⁺ deposition pathway. In this strategy, cations such as Cs⁺,³³ Rb⁺ and pyrrolidinium (Py⁺) have been explored for charge shielding layers since they showed lower reduction potentials than Li⁺.16 According to the Coulombic law, $F = (q_1 q_2)/(4\pi \epsilon d^2)$ and the Coulombic force is proportional to the magnitude of ion charge. The stronger the positive charge of the cation, the better the regulation of the electric field on the electrode surface. Building more cationic sites in molecules to elevate charge density can more effectively neutralize the local high electric field at the electrode surface, resulting in uniform lithium nucleation and regular deposition

at the anode tip. Meanwhile, cationic polymers in the electrolyte system can interact with solvent molecules (EC, DMC, *etc.*) or anions (PF_6^- and $TFSI^-$) *via* ion-dipole and Coulombic forces, creating Li⁺ transport sites and reducing Li⁺ transport resistance.^{34,35} Beyond cationic protective layers, the selection of anions in artificial SEI is also crucial.^{36,37} Suitable anions can effectively participate in the formation of the inorganic SEI, which significantly contribute to inhibiting electrolyte decomposition, enhancing the reduction resistance of the cationic shielding layer and achieving rapid Li⁺ transfer kinetics.³⁸⁻⁴¹ Because of the structural tunability and polymeric properties, the cationic polymer can achieve effective synergies of cation shielding and high-Li⁺ flux inorganic SEI by a rational choice of anions and cations, thereby resulting in dendrite-free and stable Li metal anodes.

In this work, we developed a high-charge density cationic polymer (POTA–NO₃) consisting of cations with multiple positive charge sites (OTA⁴⁺) and anions (nitrate, NO₃⁻) as an anodic protective layer to reduce Li⁺ deposition (Fig. 1b). The OTA⁴⁺ cations with high charge density provided strong electrostatic shielding and promoted the desolvation of Li⁺ by interacting with solvent molecules, leading to the preferential formation of uniform lithium nucleation. Meanwhile, the anion (NO₃⁻) can preferentially decompose to generate a robust and high–Li⁺ flux inorganic SEI, enhancing the Li⁺ transport kinetics into SEI. As a result, the POTA–NO₃-protected Li||Li symmetric cells showed 6600 h cycling stability at 2 mA cm⁻² and 2 mA h cm⁻². The protected Li||LiCOO₂ batteries cycled stably for 1400 cycles with more than 80% capacity retention. Moreover, the POTA@Li||LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cells displayed

more than 99% Coulombic efficiency during 1000 cycles. This work offers additional horizons for the fabrication of stable lithium metal electrodes and the practical application of LMBs.

Results and discussion

To obtain the POTA-NO₃ protective layer, the ionic monomer, OTA-NO₃, was synthesized via a bromination reaction and anion exchange (Fig. S1, ESI⁺). The structural information of obtained OTA-NO3 was confirmed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectra (Fig. S2 and S3, ESI†). The peak at 124.11 m/z can be attributed to the OTA⁴⁺ cation in LC-QTOFMS (Fig. S4, ESI⁺). Fourier transform infrared (FTIR) spectroscopy revealed the structural information of OTA-NO₃ (Fig. S5, ESI[†]). After the substitution of allyl bromide, the vibration of the N-H bond (stretching and deforming vibrations at 3284 cm⁻¹ and at 1554 cm⁻¹) disappeared in OTA-NO₃ and POTA-NO₃. The disappearance of the C=C bond peak in POTA-NO₃ indicated the complete polymerization reaction of OTA-NO₃ monomers. The XPS results also confirmed the structural information of OTA-NO3 and the complete polymerization reaction (Fig. S6, ESI[†]). Meanwhile, the gel fraction was used to assess the polymer's cross-linking degree (Table S1, ESI[†]). The results indicated that POTA-NO₃ polymers demonstrated high cross-linking properties due to the abundance of C=C bonds in the OTA-NO3 monomer. Thermogravimetric analysis (TGA) displayed good thermal stability of the POTA-NO₃ polymer (Fig. S7a, ESI⁺). Differential scanning calorimetry (DSC) results indicated that POTA-NO₃ polymers had a glass transition temperature of 62.3 °C (Fig. S7b, ESI⁺). The POTA-NO₃ polymer was immersed in an LB-003 electrolyte to characterize whether there was the mutual reaction and dissolution between the polymer and electrolyte. No new substances appeared in the ¹H NMR and FTIR spectra, indicating the stability of the POTA-NO₃ in the electrolyte (Fig. S8, ESI[†]). Then, the POTA-NO₃ protective layer was fabricated via dropping, and the precursor solution was polymerized on the surface of Li metal (named POTA@Li) or copper (named POTA@Cu) (Fig. S9, ESI[†]). Scanning electron microscopy (SEM) images revealed that less amounts of precursor solution (5 μ L) resulted incomplete covering of the surface electrode by the polymer protective layer and more amounts of precursor solution (10 µL and 20 µL) completely covered the electrode (Fig. S10, ESI[†]). The crosssectional SEM images showed that the thicknesses of the POTA-NO₃ protective layer on the lithium metal surface were approximately 5 µm and 10 µm (Fig. S11, ESI†). The 5 µm polymer protective layer was chosen for fabricating the electrodes. Bare Li||Li and POTA@Li||POTA@Li symmetric cells were assembled to evaluate the chemical stability of the POTA-NO₃ polymer layer against lithium metal electrodes. The low change in impedance illustrated the thermodynamic stability the of POTA-NO₃ protective layer and Li anode in POTA@Li||POTA@Li cells (Fig. S12, ESI[†]). Furthermore, the electrochemical stability of the OTA⁴⁺ groups was measured by linear sweep voltammetry (LSV). The lower reduction potential of OTA^{4+} than that of Li^+ was a precondition to neutralize the Li anode surface local electric field. The LSV results indicated that OTA^{4+} cations (-3.39 V vs. SHE) remained stable at a Li⁺ plating/stripping potential of -3.04 V vs. SHE (Fig. S13, ESI⁺). The CV curves of Li||Cu cells can be utilized to investigate the redox behaviour occurring at the electrodes. The obvious reductive peak (1-1.4 V) of Li||POTA@Cu was attributed to the reductive decomposition of NO₃⁻ anions (Fig. S14, ESI⁺).¹¹

LillLi symmetric cells were assembled to characterize the Li⁺ transfer kinetics through the SEI. Arrhenius points displayed that the POTA@Li||POTA@Li cells had a lower ion transfer active energy (E_a) (49.72 kJ mol⁻¹) compared to the bare Li||Li cells (61.77 kJ mol⁻¹), suggesting that the POTA@Li anode enhanced the Li⁺ transport kinetic process (Fig. 2a and Fig. S15, ESI[†]). The Tafel results demonstrated a higher exchange current density (6.75 mA cm⁻²) of POTA@Li||POTA@Li cells than that of bare Li||Li cells (2.95 mA cm⁻²), which illustrated the faster Li⁺ plating/stripping process on the POTA@Li electrode surface (Fig. 2b). POTA@Li||POTA@Li with thick polymer layers (10 μ m) exhibited high E_a (-62.31 kJ mol⁻¹) and low exchange current density (0.43 mA cm^{-2}), suggesting that the polymer layer should be of a suitable thickness, and that thicker polymer layers are detrimental to Li⁺ transport (Fig. S16, ESI[†]). Meanwhile, the cyclic voltammetry (CV) test showed that the POTA@Li|| POTA@Li batteries had a higher peak current than that of the bare LillLi battery, corresponding to the highly redox rate of the POTA@Li electrode (Fig. S17, ESI[†]). The Li⁺ transfer number (t_{Li}^{+}) represented Li⁺ transport properties in batteries. POTA@Li||POTA@Li batteries exhibited a higher t_{Li}^{+} value (0.76) than that of bare Li||Li cells (0.22) because the ionic-dipole interaction of OTA4+ with solvent molecules can detach Li⁺ from the solvated structure (Fig. 2c and Fig. S18, ESI⁺). The high t_{Li}^+ value can attenuate electrochemical and concentration polarization, thereby enhancing the cycling stability of LMBs. The improvement in the electrochemical performance of POTA@Li electrodes illustrated that the POTA-NO₃ protective layer promoted the Li⁺ transport kinetics at the electrolyte/electrode interface.

Furthermore, grand canonical Monte Carlo (GCMC) simulations were utilized to investigate how the mechanism of POTA- NO_3 polymers promoted the Li⁺ desolvation process. The molecular dynamics (MD) simulation system constructed in this work was focused on the POTA-NO₃ protective layer and its inner electrolyte rather than the whole electrolyte system. The binding state and the molecule configuration in the electrolyte system can be recognized from the snapshots of the simulation box in the LB-003 electrolyte and LB-003 with POTA-NO3 (Fig. 2d and e). In the LB-003 electrolyte system, Li⁺ was surrounded by carbonate solvent molecules (EC, DMC, and DEC) and PF₆⁻ anions due to ionic dipole and Coulombic forces. Li⁺ need to separate from the solvent molecules and anions (desolvation process) before Li⁺ deposition on the Li anode. Compared to Li⁺, OTA⁴⁺ had stronger ionic-dipole interactions with solvent molecules and Coulombic force with anions (Fig. S19, ESI[†]). As a result, the combining energy of Li⁺ with solvent molecules and anions was significantly reduced in the LB-003 system since the competition of OTA4+ and Li+ to



Fig. 2 POTA–NO₃ protective layer promoted the Li⁺ desolvation process. (a) Arrhenius plots of bare Li||Li and POTA@Li||POTA@Li cells. (b) Tafel curves of bare Li||Li and POTA@Li||POTA@Li cells. (c) Li⁺ transfer numbers of bare Li||Li and POTA@Li||POTA@Li cells. GCMC simulation model snapshots of (d) the LB-003 electrolyte and (e) LB-003 electrolyte with POTA–NO₃. (f) Radial distribution function of Li⁺ in the LB-003 electrolyte. (g) Combining energy of Li⁺ with carbonate molecules and PF_6^- anions in the LB-003 electrolyte and LB-003 electrolyte with POTA–NO₃. (h) Radial distribution function of Li⁺ in the LB-003 electrolyte with POTA–NO₃.

bind solvent molecules and anions, which facilitated that Li⁺ detached from the solvated shell (Fig. 2g). Radial distribution function (r(Å)) responds to the distance between molecules. In the LB-003 electrolyte, r(Å) between Li⁺ and PF₆⁻, EC, DMC and EMC was 1.91 Å, 1.93 Å, 1.94 Å, and 1.97 Å, respectively (Fig. 2f). Under the effect of the POTA-NO₃, r(Å) between Li⁺ and PF₆⁻, EC, DMC and EMC increased to 1.93 Å, 1.97 Å, 1.95 Å, and 1.98 Å, respectively (Fig. 2h). The increased r(Å) value also demonstrated the Li⁺ release from the solvated structure. The FTIR results of LB-003 with POTA-NO3 showed a shift to higher wavenumbers for the C=O bonds than the LB-003 electrolyte. This shift can be attributed to the competitive interaction between OTA⁴⁺ cations and Li⁺ in the carbonate solvent. This interaction demonstrates the impact of POTA-NO3 polymers on the solvated structure of Li⁺ and its role in promoting their desolvation process (Fig. S20, ESI[†]). GCMC simulations and FTIR results illustrated that POTA-NO₃ polymer cations with multiple cationic sites can competitively bind solvent molecules and anions around Li⁺ to promote the detachment of Li⁺ from the solvated shell, which can improve Li⁺ transport kinetics at the electrolyte/electrode interface.

Li||Cu cells were also assembled to explore the influence of the POTA-NO₃ protective layer on the Li⁺ deposition behaviour on the anodes. Meanwhile, the absence of the reduction peak in subsequent cycling indicated that the inorganic SEI generated by the reduction of NO₃⁻ inhibited the continued decomposition of the NO₃⁻ and electrolyte. Moreover, the CV at -0.2 to 0.3 V showed the Li⁺ lower plating overpotential (65 mV) and greater redox current (0.14 mA cm⁻²) at the POTA@Cu electrode than the bare Cu electrode (72 mV, 0.074 mA cm⁻²), suggesting the rapid Li⁺ reaction kinetics on POTA@Cu electrodes (Fig. S21, ESI[†]). The Li⁺ nucleation overpotential (μ_{nuc}) and mass transfer stabilization plateau potential (μ_{pla}) related to the Li⁺ deposition kinetics and stability can be identified from the constant current-voltage curves of Li⁺ deposition on the bare Cu and POTA@Cu electrodes (Fig. S22, ESI[†]).²⁶ Benefiting from the low ion transport resistance and the rapid charge transfer of the POTA-NO₃ protective layer, nucleation overpotential and plateau potentials on POTA@Cu electrodes showed lower values (μ_{nuc} = 49 mV, μ_{pla} = 33 mV) compared to bare Cu electrodes (μ_{nuc} = 59 mV, μ_{pla} = 45 mV). Meanwhile, the CE of Li||Cu cells under a deposition condition of 1 mA cm⁻²



Fig. 3 Electrochemical properties of POTA@Cu and POTA@Li electrodes. (a) Coulombic efficiency of Li||bare Cu and Li||POTA@Cu cells. (b) Voltagetime profiles of bare Li||Li, POTA-PF₆-protected Li||Li, POTA-TFSI-protected Li||Li and POTA-NO₃-protected Li||Li cells under a cycling condition of 1 mA cm⁻², 1 mA h cm⁻². Voltage-time profiles of bare Li||Li and POTA@Li||POTA@Li cells under cycling conditions of (c) 2 mA cm⁻², 2 mA h cm⁻² and (d) 5 mA cm⁻², 5 mA h cm⁻². (e) Comparison of the cycling stability of POTA@Li||POTA@Li cells with those previously reported in the published literature. Li 1s XPS in-depth spectra of (f) bare Li and (g) POTA@Li electrodes with bare Li||Li and POTA@Li||POTA@Li cells after 20 cycles in bare Li||Li and POTA@Li||POTA@Li cells at 1 mA cm⁻² and 1 mA h cm⁻².

and 1 mA h cm⁻² was characterized to examine the reversibility of Li⁺ plating/stripping on the POTA@Cu electrode. The Li||PO-TA@Cu cell was stably cycled for 120 cycles with an average CE of over 98%. However, the stability and the CE of the Li||bare Cu cell decreased rapidly after 43 cycles. The voltage–capacity curves showed that the Li||POTA@Cu cell displayed a stable lithium plating/stripping voltage plateau during cycling (Fig. S23, ESI†). The CE of Li||bare Cu and Li||POTA@Cu cells was evaluated using Aurbach's measurement strategy (Fig. 3a).⁴² The results showed that the Li||POTA@Cu cells exhibited significantly enhanced CE (98.81%) compared to the Li||bare Cu cell (90.64%). The high CE of Li||POTA@Cu batteries derived from the stable electrolyte/electrode interface and highly reversible redox behaviour of the POTA@Cu electrode were comparable to that of Li||Cu cells previously stabilized by other strategies (Fig. S24, ESI†).⁴³⁻⁵⁰ These results demonstrated the ability of

the POTA-NO₃ protective layer to stabilize the Li^+ plating/ stripping behaviour, which is beneficial for achieving highperformance LMBs.

In addition, the LillLi batteries were also used to investigate the stability of Li⁺ plating/stripping on POTA@Li electrodes. The galvanostatic polarization curves of LillLi cells at different current densities were constructed to measure the cycling stability of Li⁺ plating/stripping on POTA@Li electrodes. To highlight the individual role of OTA⁴⁺ in regulating the plating/stripping of Li⁺ on lithium metal electrodes, we prepared polymer protective layers with different anions (PF_6^- , TFSI⁻, and NO₃⁻). In the LB-003 electrolyte, the polarization voltage of bare LillLi increased continuously during operation after 130 h at 1 mA cm⁻² and 1 mA h cm⁻². However, the POTA-PF₆-protected LillLi cell exhibited increased cycling stability with more than 500 h of stable cycling compared to bare Li||Li cells. Since the TFSI⁻ can induce the generation of a LiF-rich inorganic SEI on the lithium metal surface, the POTA-TFSI protected Li||Li cell stably cycled 650 h. Notably, the POTA-NO₃ protected Li||Li cells exhibited the best cycling stability even at higher current densities (Fig. 3b and Fig. S25, ESI⁺). To evaluate the ability of the POTA-NO₃ protective layer on lithium metal for a long time, the LS-002 electrolyte, which is more compatible with lithium metal, was chosen for LillLi cell testing. The polarization voltage of bare Li||Li increased continuously (from 40 mV to 1700 mV) during operation and short-circuits after 308 h at 1 mA cm⁻² and 1 mA h cm⁻². However, the POTA@Li electrode exhibited superior cycling stability (6250 h) at 1 mA cm⁻² and 1 mA h cm⁻² (Fig. S26a, ESI[†]). The local enlarged plots of the voltage-time curves at 298-303 h and 4991-4995 h showed that the POTA@Li electrode exhibited a stable and flat plating/stripping plateau (Fig. S26b-d, ESI⁺). High current density provided increased challenges for Li⁺ plating/stripping on electrodes. The POTA@Li electrode still exhibited stable cycling of 6600 h and low polarization voltage (75 mV) at 2 mA cm⁻² and 2 mA h cm⁻² (Fig. 3c). The bare Li||Li cell developed short-circuit after 390 h at 5 mA cm⁻² and 5 mA h cm⁻². Significantly, the POTA-NO₃ protected Li||Li cell still showed cycling stability (6300 h) and a low voltage plateau (Fig. 3d). The stable lithium anodes achieved by POTA-NO₃ had significant advantages over the artificial SEI constructed by other previous strategies (Fig. 3e and Table S2, ESI⁺), such as inorganic SEI, alloy anodes, organic-inorganic SEI, cationic shield, and NO₃⁻ derived SEI.^{12,16,17,37,43,51-64}

The surface images of the POTA@Li electrode and bare Li electrode after 50 cycles were observed by SEM. The surface of the bare Li electrode appeared to be severely cracked with large amounts of lithium dendrites. The Li⁺ deposition on the POTA@Li electrode surface was relatively flat and tended to be in the form of large spherical deposits rather than dendrites (Fig. S27, ESI⁺). To investigate the mechanism of POTA–NO₃ to stabilize the Li anodes, X-ray photoelectron spectroscopy (XPS) was performed to analyse the composition of the SEI on the bare Li and POTA@Li surfaces. After POTA@Li ||POTA@Li and bare Li||Li batteries cycled 40 h at 1 mA cm⁻², 1 mA h cm⁻², the compositional change from the surface to the deeper layers

of the SEI was analysed. The C 1s spectra revealed the composition and the associated content of the organic matter in the SEI (Fig. S28, ESI†). On the bare Li electrode, C-H/C-C (284.8 eV), C-O (286.6 eV), C=O (289.7 eV), and $-CO_3-$ (292.6 eV) were derived from the decomposition of electrolyte solvents and electrolyte salts. The presence of organic species was detrimental to the mechanical strength and Li⁺ conduction of the SEI. The content of the organic component (C-O, C=O, and C-C) decreased dramatically and the decomposition product, $-CO_3-/$ ROCOLi, disappeared from the surface to the deeper layers on the POTA@Li anode, suggesting the stabilization of POTA–NO₃ with the lithium anode and the inhibitory effect on the electrolyte decomposition.

Due to the presence of 1% LiNO₃ in the electrolyte, Li_xN_y , Li_3N , and LiN_xO_y were recognized in the N 1s spectra of the POTA@Li and bare Li electrodes (Fig. S29, ESI⁺). As the etching time increased, the composition of SEI changed to inorganic components such as Li_3N and LiN_xO_y . After 240 s of sputtering, the SEI was mainly composed of pure Li₃N. Since Li₃N is a lithium superionic conductor, the large amount of Li₃N in the SEI achieved fast and uniform Li⁺ conduction, which was undoubtedly beneficial for the stable cycling of LMBs. Meanwhile, the results of O 1s spectra showed that Li₂O on the POTA@Li anode increased dramatically with the deepening of the etching compared to bare Li, and the by-products such as Li₂CO₃ (531.21 eV) and C-O (532.6 eV), contained even less because the NO3- anion in POTA-NO3 contributed to the generation of crystalline Li₂O (Fig. S30, ESI[†]). LiF derived from anions is widely recognized as a positive SEI component with suitable ionic conductivity and mechanical strength. A certain amount of LiF was detected on bare Li and POTA@Li electrodes (Fig. S31, ESI[†]). From Li 1s spectroscopy (Fig. 3f and 3g), large amounts of by-products such as Li2CO3/ROCOLi were still detected in the deep SEI on the bare Li electrode. On the POTA@Li electrode, the main components of SEI were Li₃N/ LiN_xO_v and Li₂O at sputtering times of 120 s and 240 s (inner layer of SEI), which were beneficial for Li⁺ conduction. The above-mentioned results showed that the SEI on the surface of the POTA@Li electrode consisted mainly of an upper layer of an OTA⁴⁺ polycationic backbone and a deeper layer of Li_3N , LiN_rO_{ν} , and Li_2O derived from NO_3^- . Among them, the polycation layer can shield the concentrated electric field at the anode surface protrusion, regulating the Li⁺ deposition path and promoting the Li⁺ desolvation process; the anionderived inorganic SEI component can enhance the Li⁺ transport kinetics.

To confirm the effect of the POTA-NO₃ protective layer on the Li⁺ deposition process, POTA@Cu, bare Cu and POTA@Li, bare Li electrodes were deposited with different amounts of lithium at a current density of 0.5 mA cm⁻². The deposition morphology of the electrode surface was investigated by SEM. After the deposition of 2 mA h cm⁻² lithium on the POTA@Cu and bare Cu electrodes, the bare Cu electrode showed loose lithium deposition and a large amount of lithium dendrites. The thickness of the deposited lithium on the bare Cu electrode was about 11.56 µm (Fig. S32a and c, ESI†). On the POTA@Cu

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Fig. 4 Li^+ plating/stripping behavior on Li and Cu anodes. SEM images of (a) and (c) bare Cu and (b) and (d) POTA@Cu electrodes after deposition of 4 mA h cm⁻² and 8 mA h cm⁻² lithium at a current density of 0.5 mA cm⁻². Microscopic morphology of (e) and (g) bare Li and (f) and (h) POTA@Li electrodes after 4 mA h cm⁻² and 8 mA h cm⁻² lithium deposition at a current density of 0.5 mA cm⁻². Li⁺ flux during the Li⁺ deposition on (i) bare Li and (j) POTA@Li and mechanistic chart of the POTA=NO₃ protective layer ability to uniformly deposit Li⁺.

electrode, Li⁺ was deposited in bulky round spherical shapes. The thickness of the deposited lithium layer was about 8 μ m, suggesting that POTA–NO₃ can enable more homogeneous Li⁺ deposition on the electrode, thus avoiding the appearance of lithium dendrites (Fig. S32b and d, ESI†). Moreover, when the lithium deposition on the Cu electrode was increased to 4 mA h cm⁻², the morphology of the bare Cu electrode was looser and the lithium dendrites were still present (Fig. 4a). The thickness of the deposited lithium layer was increased to 32 μ m (Fig. S33a, ESI†). However, the POTA@Cu electrode was flat and the spherical lithium deposition morphology became more frequent (Fig. 4b). The POTA@Cu electrode exhibited a deposition thickness of only 20 μ m (Fig. S33b, ESI†). In particular, the amount of lithium plated on the bare Cu and POTA@Cu

electrodes was further increased to 8 mA h cm⁻², and Li⁺ was more loosely deposited onto the bare Cu electrode and exhibited smaller dispersed particles with a deposition thickness of 42 μ m (Fig. 4c and Fig. S34a, ESI⁺). It was noteworthy that the Li⁺ deposition on the POTA@Cu electrodes was relatively flat with large massive dense deposition even at the large surface capacity, and the deposition thickness was much smaller than that on the bare Cu electrodes (Fig. 4d and Fig. S34b, ESI⁺).

Meanwhile, the evolution of the Li^+ deposition morphology at different stages of plating/stripping on the Cu electrodes was observed at a current density of 1 mA cm⁻² (Fig. S35, ESI†). When lithium was deposited onto the bare Cu electrode for 2 mA h cm⁻², lithium dendrites were observed.

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By increasing the lithium deposition to 4 mA h cm^{-2} , the surface of the bare Cu electrode was still rough and appeared to contain a large number of streak deposits. The plated lithium was then stripped back to the Li electrode for 2 mA h cm⁻², and the lithium on the bare Cu electrode was partially dissolved with the remaining lithium appearing as filaments. After the plated lithium was completely stripped, a significant amount of "dead lithium" remained on the bare Cu electrode, which was the main reason for the low CE of the Lillbare Cu cells. However, in the plating stage (Stage I and Stage II), POTA@Cu electrodes showed flat lithium deposition. In the stripping stage, lithium dissolution was more evenly distributed without obvious filamentary lithium. After the complete stripping of lithium, the surface of the POTA@Cu electrode was relatively flat without obvious dead lithium. The plating and stripping experiments indicated that the POTA-NO₃ protective layer was capable to restrain Li⁺ for uniform and dense deposition, which was related to the charge dispersion effect of the high-charge density organic cations and the inorganic layer derived from anions in the POTA-NO₃ protective layer.

Furthermore, the micro-nano morphology of lithium deposited on bare Li electrodes and POTA@Li electrodes with different capacities was observed (Fig. 4e-h). The SEM results showed that the surface of bare Li is not fully covered with the deposition at a capacity of 4 mA h cm^{-2} . More seriously, obvious lithium dendrites were observed, which was unfavourable for the stability and safety of the battery. After gradually increasing the lithium deposition capacity to 8 mA h cm^{-2} , the lithium deposition state on the surface of the bare Li electrode was not improved. Owing to the regulation of Li⁺ deposition by the POTA-NO₃ protective layer, the POTA@Li electrodes exhibited dense and flat lithium deposition at 4 mA h cm⁻² and 8 mA h cm $^{-2}$, which was essential for the stable cycling and high safety of LMBs. The morphological results of Li⁺ deposition on Cu and Li electrodes indicated that the POTA-NO3 protective layer can homogenize the electric field distribution on the electrode surface, and regulate the Li⁺ nucleation sites and deposition pathways, thereby achieving stable lithium metal electrodes.

COMSOL multiphysics field simulation was used to investigate the distribution of current density on the electrode surface during the Li⁺ deposition on bare Li and POTA@Li electrodes (Fig. 4i, j).¹⁷ Due to the tip effect and the low electrode potential, a large concentrated negative charge field was generated above the protrusions. On bare Li electrodes, Li⁺ preferentially migrated and deposited at the tip due to the concentrated negative charge field and the concentrated charge effect was naturally self-amplifying, resulting in the continuous growth of lithium dendrites. Uniquely, because of the presence of POTA-NO₃ cationic polymers, the concentrated negative electric field at the protrusions was shielded, thus the Li⁺ deposition at the tip was suppressed and tended to be deposited away from the protuberances on POTA@Li electrodes. Meanwhile, the high ionic conductor SEI layer derived from the NO₃⁻ anions facilitated Li⁺ transportation. Stable lithium anodes were achieved by the synergistic interaction of OTA^{4+} cations and NO_3^- anions in the POTA-NO₃ protective layer (Fig. 4k and l).

Li||LiCoO2 and Li||NCM811 batteries were assembled to characterize the utility and feasibility of the POTA-NO₃ protective layer in practical battery operation. The Li⁺ diffusion coefficient was determined by galvanostatic intermittent titration technique (GITT) to investigate the Li⁺ migration capacity in POTA@Li and bare Li electrodes (Fig. 5a). As a result, compared to bare Li||LCO batteries, the higher Li⁺ diffusion coefficients of POTA@Li||LCO batteries proved the higher Li⁺ conductivity of the POTA-NO3 layer, which originated from the strong co-desolvation ability of the OTA⁴⁺ cations and the formation of the rapid Li⁺ conductor inorganic layer by the NO₃⁻ decomposed (Fig. 5b). The redox kinetics of POTA@ Li||LCO and bare Li||LCO cells were characterized by CV tests at different scan rates. The high redox current of POTA@Li ||LCO revealed the high Li⁺ diffusion capacity and redox stability of the POTA@Li electrode (Fig. S36, ESI⁺). Moreover, the capacity performance of POTA@Li||LCO and bare Li||LCO full batteries at different charge/discharge rates (0.1C, 0.2C, 0.3C, 0.5C, 1C, 2C, and 3C) were characterized (Fig. 5c). The specific capacities of POTA@Li||LCO batteries were higher than those of the bare Li||LCO batteries from 0.1C to 3C (186.2 to 154.2 mA h g^{-1}). The voltage-capacity curves of the Li||LCO cells at different rates showed that the cells with the POTA-NO₃ protective layer exhibited lower polarization voltage (Fig. S37, ESI†). Long-cycle battery tests of POTA@Li||LCO and bare LillLCO full cells at 1C were performed (Fig. 5d). Notably, the POTA@Li||LCO cells demonstrated more than 80% capacity retention after 1400 cycles with CE exceeding 98%. In contrast, the bare LillLCO cells showed a capacity retention of 12% after 220 cycles. The corresponding voltage-capacity curves also revealed the increasing polarization of the bare LillLCO cells (Fig. S38, ESI[†]). Moreover, POTA-PF₆ and POTA-TFSI-protected Li||LCO batteries exhibited stable cycling over 500 and 600 cycles, respectively, which illustrated the active role of OTA⁴⁺ cations in regulating Li⁺ plating/stripping (Fig. S39 and S40, ESI[†]). The SEM images of Li||LCO cells after 50 cycles at 1C showed that the surface of the POTA@Li electrode displayed a flatter lithium deposition topography than that of the bare Li electrode (Fig. S41, ESI⁺). Li||LCO batteries were measured under low N/P ratio (4.28) conditions to demonstrate the outstanding stabilization of the lithium anode by the POTA-NO3 protective layer (Fig. S42, ESI†). Compared to the bare Li||LCO batteries, POTA@Li||LCO batteries displayed good cycling stability (capacity retention 96% vs. 51%) after 100 cycles at 0.5C. Furthermore, at an N/P ratio of 2.49, the POTA@Li||LCO cells still showed better cycling stability than bare Li||LCO cells (Fig. 5e and S43, ESI†). In addition, POTA@ Li||NCM811 cells still maintained a higher specific capacity and lower polarization than bare Li||NCM811 at different charge/discharge rates (Fig. S44, ESI[†]). In the long-cycle tests of Li||NCM811 cells, the bare Li||NCM811 cells showed capacity degradation after 150 cycles. However, POTA@Li||NCM811 cells still showed 110 mA h g^{-1} (capacity retention over 70%) and more than 99% Coulombic efficiency after 1000 cycles

Paper

(a)

(d)



Fig. 5 Electrochemical performance of Li||LCO and Li||NCM811 cells. (a) Voltage–capacity curves and (b) corresponding Li⁺ diffusion coefficients for POTA@Li||LCO and bare Li||LCO cells in GITT tests. (c) Rate capabilities of POTA@Li||LCO and bare Li||LCO cells. (d) Cycling performance of the POTA@Li||LCO and bare Li||LCO cells. (e) Cycling performance of Li||LCO cells with the bare Li and POTA@Li| and bare Li||LCO cells. (e) Cycling performance of Li||LCO cells with the bare Li and POTA@Li| and bare Li||LCO cells. (e) Cycling performance of Li||LCO cells with the bare Li and POTA@Li||NCM811 and bare Li||NCM811 cells. ElS resistance of (g) bare Li||NCM811 and (h) POTA@Li||NCM811 cells at different cycles. R_{s} , R_{sEI} , and R_{CT} represent the ohmic resistance, SEI resistance, and charge transfer resistance, respectively.

(Fig. 5f and S45, ESI[†]). To verify the electrode/electrolyte interface stability of POTA@Li and bare Li electrodes during operation, the EIS results of bare Li||NCM811 and POTA@Li|| NCM811 cells were tested and fitted under different cycles (Fig. S46, ESI[†]). The bare Li||NCM811 cells displayed dramatic variations in $R_{\rm SEI}$ (from 34.31 Ω to 70.35 Ω) and $R_{\rm CT}$ (from 51.82 Ω to 146.05 Ω) during battery operation, which originated from the fragile electrolyte/electrode interface and the unstable original SEI layer (Fig. 5g). In contrast, the POTA@Li||NCM811 cell exhibited slight changes in impedance ($R_{\rm SEI}$ from 9.77 Ω to 17.21 Ω and $R_{\rm CT}$ from 29.72 Ω to 49.55 Ω), which was attributed to the electrostatic shielding effect of the cations in the POTA–NO₃ polymer protective layer and the stable electrolyte–electrode interface created by the anion-derived robust inorganic SEI layer (Fig. 5h).

The components of the POTA@Li and bare Li anode surface SEI were analysed by in-depth XPS after bare Li||LCO and POTA@Li||LCO cells cycled for 20 cycles at 1C. For the C 1s spectrum, the bare Li electrode contained higher organic species content, originating from electrolyte decomposition compared to POTA@Li (Fig. S47, ESI†). Since there was no N-containing component in the LB-003 electrolyte, no elemental N signal was detected on the bare Li anode (Fig. 6a). However, large amounts of N-containing compounds such as Li₃N, LiN_xO_y, and LiNO₂ from the NO₃⁻ anion decomposition and

C-N from the POTA-NO₃ polymer were detected on POTA@Li. Meanwhile, the main component was Li₃N with high mechanical strength and ionic conductivity in the deep SEI (Fig. 6b). Due to the decomposition of NO_3^- anions in POTA-NO₃, the POTA-NO₃ SEI contained more Li₂O components, particularly in the deeper layers (rapidly becoming larger with increasing depth) than those of the bare Li anode in the O 1s spectra (Fig. S48, ESI^{\dagger}). Moreover, the lower Li₂CO₃ content on POTA@Li than bare Li indicated that the POTA-NO₃ protective layer can suppress electrolyte decomposition. High contents of Li₃N, LiN_xO_y and Li₂O in the protective layer of the POTA@Li resulted in good mechanical strength and high Li⁺ flux. The LiF, which is favourable for the Li⁺ transfer, was mainly derived from the decomposition of the PF_6^- anion, and thus LiF and $Li_x PO_y F_z$ products were detected at both the POTA@Li and bare Li anodes (Fig. S49, ESI[†]).

Furthermore, the Li 1s spectra can identify variations in lithium salt content with the depth of SEI layers. On the bare Li anode, ROCOLi/Li₂CO₃ was the main component with poor mechanical strength and low Li⁺ conductivity. On the POTA@Li electrolyte, the content of ROCOLi/Li₂CO₃ was low and decreased significantly with increasing sputtering depth (Fig. 6c). Meanwhile, Li₃N and Li₂O occupied the main components in the deep SEI of the POTA@Li anode (Fig. 6d). The atomic ratios of different elements in the SEI layer on the bare



Fig. 6 Composition of SEI on lithium anode surfaces. Bare Li||LCO and POTA@Li||LCO cells analysed for SEI components after 20 cycles at 1C. N 1s XPS in-depth spectra of (a) the bare Li and (b) POTA@Li anode with different etching times. Li 1s XPS in-depth spectra of (c) bare Li||LCO and (d) POTA@Li||LCO with different etching times. Atomic mixing distribution ratio of (e) the bare Li and (f) POTA@Li anode at different etching depths. (g) Schematic structure of the SEI layer derived from the POTA-NO₃ protective layer on the surface of the POTA@Li anode.

Li and POTA@Li anode surfaces were identified from the XPS results (Fig. 6e and f). As the etching depth increased, the SEI still consisted of a high content of organic species. In contrast, the content of elemental C in the inner layer on the POTA@Li electrode was significantly reduced. Moreover, the increasing N content with sputtering depth was instructive for a growing content of species such as Li₃N and LiN_xO_y. The XPS results on the electrode surface showed that the POTA-NO₃ protective layer was an organic-inorganic bilayer component, and the surface layer of the artificial SEI was mainly an organic OTA⁴⁺ cationic skeleton, while the main internal components were inorganic compounds such as Li₂O, Li₃N, LiN_xO_y, and LiF (Fig. 6g). The structure and composition of the POTA-NO₃ protective layer determined the ability to balance the nonuniform electric field on the rough Li anode surface and the rapid Li⁺ transfer kinetics, which was vital to achieve stable battery operation. The POTA-NO₃ protective layer sufficiently improved the instability of the lithium anode/electrolyte

interface, which provided an effective way to realize the nextgeneration high-energy density LMBs.

Conclusion

In summary, we have developed an artificial SEI layer with the ability to tune the electric field on rough electrode surfaces and improve the ion transport kinetics by the structural design of anions and cations in monomers for dendrite-free and high-stability lithium metal electrodes. In POTA-NO₃ artificial SEI, the OTA⁴⁺ cationic polymer back-bone "shielded" the concentrated electric field on the electrode protrusions, regulated the Li⁺ deposition path, and promoted the Li⁺ desolvation process; the NO₃⁻ anion generated a high-Li⁺ flux and robust inorganic SEI with Li₃N, LiN_xO_y, and Li₂O before electrolyte decomposition. Li anodes with high stability and Li⁺ conductivity were realized by the synergistic action of NO₃⁻ anions and OTA⁴⁺

cations. With the POTA–NO₃ protective layer, Li||Cu cells exhibited a Coulombic efficiency of 98.8% and POTA@Li||PO-TA@Li batteries demonstrated more than 6600 h stable cycling at 2 mA cm⁻² and 2 mA h cm⁻². POTA@Li||POTA@Li cells still exhibited good cycling stability (6300 h) at a high current density of 5 mA cm⁻² and a capacity of 5 mA h cm⁻². Moreover, POTA@Li||LCO batteries exhibited ultra-long cycling stability (over 80% capacity retention after 1400 cycles) at 1C. Similarly, the POTA@Li||NCM811 battery still revealed 70% initial capacity after 1000 cycles. This work provides an effective way for constructing stable lithium metal electrodes based on the molecular structural design, which is hopeful to facilitate the practical use of LMBs.

Author contributions

J. Y. and F. Y. initiated the project and supervised this research. J. Y. and X. M. performed the experiments and analysed the data. J. Y. and Y. H. assisted the experiments and participated in the material structural characterizations. X. M., J. Y., M. Y., and S. S. discussed the battery performances. X. Z. assisted performed an MD simulation. S. S., J. Y., and F. Y. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (52333002), the Jiangsu Province Science Foundation for Carbon Emissions Peak and Carbon Neutrality Science and Technology Innovation (BK20220007), Collaborative Innovation Center of Suzhou Nano Science and Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions. Thanks to Prof. Chenglung Chen from National Sun Yat-sen University for his guidance on the simulation part of this paper. The authors are grateful for the technical support for Nano-X from Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences (SINANO).

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