Highly efficient lithium utilization in lithium metal full-cell by simulated missile guidance and confinement systems

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ABSTRACT The efficient utilization of metallic lithium (Li) is the key to enable application of Li metal full-cell with low amount of excess Li, contributing to higher safety and energy density. Herein, we report an extraordinary Li metal full-cell with only 20% excess Li, which demonstrated significantly improved reversibility and high Coulombic efficiency. Ingenious simulated missile guidance and confinement system (SMGCS) was designed to guide and confine Li deposition through constructing compatible silver lithiophilic sites and nitrate layer. Silver sites act as effective Li nuclei to attract Li ions and direct the initial nucleation. The generated nitrate layer affords an interfacial environment favorable for confined and uniform deep Li deposition, which is theoretically verified by molecular dynamics (MD) simulations. The two combined merits offer a robust and dendrite-free Li deposition, enabling the application of Li metal full-cell with slight excess Li. They also result in an outperformed Li cycling efficiency of ca. 99% for over 300 cycles along with deep cycling at a high capacity of 10 mA h cm⁻² in carbonate electrolytes. The unprecedented high degree of Li utilization opens a new avenue for the future development of highly efficient Li metal full-cells.

Keywords: lithium utilization, lithium metal, full-cell, Li nucleation, Li deposition

INTRODUCTION

Metallic Li, the ultimate anode for Li-based and perhaps all next-generation rechargeable batteries with the highest specific capacity (3860 mA h g⁻¹) and lowest redox potential (−3.040 V vs. the standard hydrogen electrode) of

all possible alternatives [1–3], is encountering significant obstacles: the low degree of Li utilization, poor reversibility, and dendrite formation during cycling, which is responsible for low Coulombic efficiency (CE), large voltage polarization, poor capacity retention and short-circuiting [4–7]. The major issue of fast Li loss exists during Li metal full-cell operation, thus more than 200% excess Li is demanded to avoid capacity degradation. Moreover, excess Li exacerbates safety problems and decreases the energy density [8]. These issues hinder the large-scale applications of Li metal anodes. Therefore, the challenge towards the practical applications of Li metal batteries (LMBs) is to achieve excellent stability with Li loading as low as possible (i.e., higher degree of Li utilization) to obtain higher safety level and energy density. It has been known that ether-based electrolytes have significant impact on the uniform deposition of Li, offering high CE [9]. However, the high flammability and low oxidation decomposition potential (<4 V vs. Li⁺/Li) of ether solvents does not satisfy the required safety indexes in widely-used high-voltage cathodes, hindering their widespread application [9]. High-salt-concentration ether electrolytes have been recently proposed, but their economic effectiveness need to be evaluated for large-scale commercial applications [9–12]. Conversely, low-cost carbonate-based electrolytes such as 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 volumetric ratio) exhibit lower flammability and higher voltage tolerance; thus, they could be applied in almost all commercial Li-ion batteries (LIBs). Nevertheless, carbonate electrolytes are highly corrosive to Li metal, resulting

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in catastrophic growth of Li dendrite and poor cycling efficiency [9,13]. Therefore, these severe problems for LMBs with carbonate-based electrolytes urgently need to be solved. Extensive efforts have been devoted to improving the efficiency and cycle life of Li metal electrodes in carbonate-based electrolytes [9,13–17], such as carefully designed solid-electrolyte interfaces (SEI) based on different additives including nitrogenous and fluorinated compounds [13–15], protective coatings [16–18], nanostructured electrodes [19–21], and separator modification [22]. However, so far, the cycling efficiency in carbonate-based electrolytes is barely satisfactory accompanied by a low degree of Li utilization. In the present work, our target is to achieve excellent cycling efficiency at high capacity in commonly employed carbonate-based liquid electrolytes and to realize high Li utilization in Li metal full-cells.

It is well-known that the initial nucleating behavior of Li could largely determine the final deposition morphology. Substrates with ‘lithiophilic’ sites with great affinity of metallic Li could reduce Li nucleation barrier. Therefore, it is highly desirable to introduce lithiophilic nucleation sites, which could serve as nucleation seeds towards directing Li nucleation and growth at the initial process of Li plating. Nearly zero nucleation overpotential is needed to nucleate Li in some types of metals, including Au and Ag, which exhibit a specific Li solubility [21]. Furthermore, during the long-term and deep cycling, an interfacial environment favorable for attracting Li ions towards a homogeneous Li ion flux distribution and uniform Li deposition is of crucial importance for electrochemical cycling of metallic Li. LiNO_3 is usually used for SEI formation in ethers for Li-sulfur batteries due to the preferential reduction of nitrate anions (NO_3^-) instead of other electrolyte components. In particular, LiNO_3 could substantially alter the interfacial chemistry *via* the formation of nitrogen-containing species, such as Li_3N and lithium oxynitrides (LiN_xO_y), which have been long considered to possess the highest ionic conductivity rendering dendrite-free, reversible, and highly dense metallic Li deposition [9,23–25]. However, LiNO_3 remains less explored in carbonate-based electrolytes due to its severe solubility limitation thereby leading to unsustainable decomposition and weak SEI.

Herein, we simulated missile guidance and confinement systems (SMGCS) to realize pronounced stability and unprecedentedly high degree of Li utilization (merely 20% excess anodic capacity in Li metal full-cell) by simultaneously inducing and confining Li deposition from the perspective of both initial nucleation stage and the

following deep-cycling stage. Silver lithiophilic sites and an *in-situ* formed nitrate layer are achieved on the surface of Li metal anode through a facile displacement reaction between the deposited Li and introduced AgNO_3 membranes due to the large electronegativity difference between alkali metals and metallic Ag [26–28]. The lithiophilic Ag could play the role of nucleation sites to reduce Li nucleation overpotential and guide the Li-ions in the initial nucleation process. Furthermore, the nitrate-rich layer provides favorable interfacial environment with narrow and smooth ionic transportation channels to confine and homogenize Li deposition, which was further verified by the MD simulations. The missile guidance and confinement systems synergistically act to enable uniform Li deposition with high reversibility in commonly used carbonate-based electrolytes without compromising the ionic conductivity, viscosity, and cost of the electrolytes. Moreover, an extraordinarily high utilization of Li metal anode can be achieved (merely 20% excess Li, i.e., Li utilization of 83.3%), which is expected to favor the safe use of Li metal anode, opening a new avenue for the future development of Li metal full-cells.

EXPERIMENTAL SECTION

Preparation of the SMGCS

AgNO_3 was purchased from Alfa Aesar and mechanically ball-milled for five hours. The Cu substrates were cleaned by ethanol and water before use. Pre-calculated amount of AgNO_3 powder was homogeneously dispersed in 1,2-dimethoxyethane *via* ultrasonication by ultrasonic cell grinder. Droplet-coating technique was employed in the fabrication to prepare AgNO_3 membrane on Cu under darkness at room temperature. After slow evaporation of the solvent, the substrate was rolled by electric rolling machine.

Material characterization

The *in-situ* X-ray diffraction (XRD) measurements were performed on the X-ray diffractometer (D8 ADVANCE, Bruker AXS GmbH Co., Ltd). Argon ion etching was conducted on an X-ray photoelectron spectroscope (XPS) in an ultra-high vacuum ESCALAB 250 set-up equipped with a monochromatic Al K α X-ray source (1486.6 eV; anode operating at 15 kV and 20 mA). The *in-situ* observation for the Li deposition was performed on a metallurgical microscope (Caikon Optical Instrument DMM-330C). Morphologies were observed by scanning electron microscopy (SEM, SU8010, Japan) and transmission electron microscopy (TEM, Titan Themis Cubed

G2 300).

Electrochemical characterization

A commercial electrolyte based on 1 mol L⁻¹ LiPF₆ in EC/DEC (1:1 volumetric ratio) was used. The assembly of the Li||Cu cell was conducted in an Ar-filled glovebox. The amount of electrolyte used in the Li||Cu cells was 20 μL. The CE of a cell was defined by dividing the stripped capacity to the plated capacity at each charging-discharging cycle. Tests with excess Li were also performed: Li with a certain amount was plated (in accordance with the amount of excess Li), followed by some Li stripping/plating cycles. Finally, the cell was charged to 1 V. Then we could obtain the average CE as the ratio of the total stripped Li to that of the plated Li. The long term stability of Li metal with a certain amount of excess Li was also conducted. Cu or SMGCS electrodes were pre-deposited with certain amounts of Li as anodes and then they were paired with cathodes to constitute Li metal full-cells. The “lithium utilization” is the ratio of cathode capacity to anode capacity in the lithium metal full-cell. The mass loading of LiCoO₂ (LCO) cathode (purchased from company of HF-kejing) was about 18.5 mg cm⁻². The amount of electrolyte used in the Li||LCO cells was 50 μL and the electrolyte-to-capacity ratio was ~18 μL mA⁻¹ h⁻¹. The current density of the Li||LCO was 2 mA cm⁻², and the voltage range was 4.45–3 V vs. Li/Li⁺. The voltage range of Li||LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) was 4.3–2.7 V vs. Li/Li⁺. The battery performances were tested by using a battery testing system (LAND CT 2001A, Wuhan, China). The EIS measurements were conducted on a CHI 660E (Chenhua Shanghai, China) electrochemical workstation.

MD simulations

MD simulations were carried out with the open source software package Gromacs, version 5.0.5. The initial configurations were constructed by dispersing certain amounts of LiNO₃ molecules (0, 16, 1600) into the interface environments (480 EC + 256 DEC + 64 LiPF₆ molecules). EC and DEC were simulated by the OPLS-AA force field. NO₃⁻ and PF₆⁻ ions were parameterized according to the literatures [29,30]. For Li⁺ ions in LiNO₃ and LiPF₆, the parameters were obtained from a document [31]. Intermolecular van der Waals interactions were represented by the Lennard Jones (LJ) potential with the geometric combination rules. LJ interactions as well as the short-range electrostatic interactions were truncated at 1.2 nm, while the long-range electrostatic interactions were calculated by the particle mesh Ewald

algorithm with a Fourier spacing of 0.12 nm in the reciprocal space. For all simulation systems, energy minimization was first performed with the steepest descent algorithm, followed by isothermal-isobaric equilibration at 298.15 K/1 bar for 50 ps. Then, production runs were carried out under NPT ensemble for 20 ns, with system temperature and pressure controlled by the Nose-Hoover thermostat and Parrinello-Rahman barostat, respectively. The periodic boundary conditions were applied in all directions. Leap-frog algorithm with a time-step of 1 fs was used to integrate the motion equations during simulations.

RESULTS AND DISCUSSION

According to the Li-Ag phase diagram (Fig. S1), Ag has an appreciable solubility in Li and can generate a solid solution buffer layer before Li metal formation. Therefore, it could improve the lithiophilic nature and lower the deposition interface energy between current collectors and Li metal. As schematically illustrated in Fig. S2a, when lithiophobic Cu was employed as the substrate, the nucleation overpotential of Li metal onto the pristine Cu is much higher and the isolated initial nucleation sites are randomly distributed on the heterogeneous and rough Cu surface, which leads to random Li deposition underneath [32]. Consequently, the surface of deposited Li metal is not uniform and the large number of protuberances would enhance the local electric field and attract Li ions, leading to a dendritic morphology [33]. Thereby, we need to introduce lithiophilic nucleation sites serving as nucleation seeds to attract and guide Li ions due to their low surface diffusion energy barrier [19]. Nearly zero nucleation overpotential is needed to nucleate Li metal on Ag, which could act as an effective Li nuclei, facilitating Li nucleation and growth (Fig. S2b). However, upon continuous Li plating, the nucleation sites are progressively covered by the Li layer. Thus, it is of particular importance to synergistically combine the lithiophilic nucleation sites with an efficient ionic conductive interface film together, which is beneficial for a homogeneous Li ion flux distribution. As a result, we proceed to SMGCS novel system to combine the lithiophilic Ag nucleation sites with LiNO₃-rich layer through the facile displacement reaction between the deposited Li and introduced AgNO₃ membrane on the current collector. This specific approach can lead to uniform Li nucleation and dendrite-free growth during the initial nucleation and subsequent plating process (Fig. S2c). The SEM and energy dispersive spectrometer (EDS) characterizations for AgNO₃ layer on the Cu substrate were conducted (Figs S3 and S4). Ob-

viously, the AgNO_3 layer was smoothly and homogeneously distributed on the substrate, which is helpful for the uniform Li deposition. The influences of the thickness and roughness of AgNO_3 layer on battery performances were also estimated. Clearly, the thickness of 200 nm was enough for the excellent battery performance (Fig. S5). More AgNO_3 would worsen the energy density of batteries. Smoothly and homogeneously distributed AgNO_3 layer on the substrate was helpful for the uniform Li deposition (Fig. S6).

MD simulations were conducted to explore the different interfacial environments in different Li/electrolyte systems. Schematic for interfacial environments of ordinary interface in pristine EC/DEC (Fig. 1a), interface with little LiNO_3 (Fig. 1b), LiNO_3 -rich layer (Fig. 1c) and their corresponding MD simulation boxes (Fig. 1d–f) are

illustrated. Distinctly, the molecules EC/DEC are the major components for the ordinary interface. According to the integral radial distribution functions (RDF) for $\text{Li-O}_{\text{EC/DEC}}$ in Fig. 1g, four oxygen atoms from the electrolyte solvents EC/DEC can randomly interact with a Li ion in the ordinary interface. In addition, the introduction of a low amount of LiNO_3 in the interfacial environment can decrease the $\text{Li-O}_{\text{EC/DEC}}$ number, indicating less interaction between $\text{O}_{\text{EC/DEC}}$ and Li ions (Fig. 1g). The appearance of new $\text{Li-O}_{\text{NO}_3^-}$ entities (Fig. 1h) also proves the participation of nitrate traces in the interaction between Li ions. More importantly, the LiNO_3 -rich layer exhibits a profound impact on the Li surface chemistry. A sharp drop of $\text{Li-O}_{\text{EC/DEC}}$ (Fig. 1g) along with a sharp increase of $\text{Li-O}_{\text{NO}_3^-}$ number is taking place and about 3.5 oxygen atoms from NO_3^- interact

Figure 1 Illustrations and MD simulation results for different interfacial environments. Schematic illustrations and MD simulation boxes of (a, d) ordinary interface in pristine EC/DEC, (b, e) interface with little LiNO_3 , (c, f) LiNO_3 -rich layer. Li: green; O: red; C: teal; H: grey; N: blue; F: pink; P: tan. (g) Integral RDF for $\text{Li-O}_{\text{EC/DEC}}$. (h) Integral RDF for $\text{Li-O}_{\text{NO}_3^-}$.

with Li ion (Fig. 1h). The strong interaction of NO_3^- with Li ions within the LiNO_3 -rich layer provides narrow and smooth ionic transportation channels to induce and confine Li-ion flux, which is just like that a missile is precisely guided and confined to the destination controlled by MGCS. Besides, the favorable interfacial environment in the LiNO_3 -rich layer results in a small probability of EC/DEC decomposition, which would be beneficial for the avoidance of the formation of fragile and unstable SEI.

To further unveil the origin of superiority of the designed SMGCS Li metal anode, *in-situ* galvanostatic cycling XRD characterization was used to monitor the Li plating behavior and to estimate the phase composition and changes in real time during the plating process (Fig. 2a). The initial XRD patterns demonstrate characteristic diffraction peaks of the starting phase (AgNO_3) at 21.50° , 24.35° , 29.72° , 31.97° , 32.86° , 35.58° , 38.99° , 39.18° , 40.18° , 41.73° , 42.78° and 43.55° . Along with slow Li deposition, it is clear that these peaks for AgNO_3 progressively weaken and finally vanish. Then two new featured peaks of metallic Ag appear at 38.23° and 44.3° ,

and peaks for LiNO_3 could also be observed at 32.1° , 35.4° and 42.5° , indicating the gradual consumption of AgNO_3 and the generation of Ag and LiNO_3 [34]. Furthermore, XPS analysis was carried out on electrodeposited Li nuclei with step-by-step sputtering to exactly analyze the depth-dependent chemical composition distribution of the AgNO_3 -derived interface film. Fig. 2b depicts the depth-dependent Ag 3d and N 1s XPS spectra. The peaks at 367.5 and 373.5 eV on the surface are assigned to Ag 3d_{5/2} and Ag 3d_{3/2} of Ag^+ , respectively, in the original AgNO_3 . The peaks shift upwards to 368.5 and 374.5 eV indexed the featured peaks of Ag and the peak intensities increase with the sputtering thickness, indicating the formation of Ag lithiophilic nucleation sites at the bottom. In addition, the surface nitrogen species exhibit higher oxidation states (LiNO_3 and LiNO_2), and Li_3N and LiN_xO_y can be detected downward. The abundant NO_3^- reveals a profound influence on the Li surface chemistry, towards the formation of Li_3N and LiN_xO_y species *via* the preferential reduction of NO_3^- . These species have long been acknowledged to possess superior Li-ion conductivity and low Li-ion transfer resistance. Consequently, it is appar-

Figure 2 Investigations for the origin of superiority of the SMGCS. (a) *In-situ* galvanostatic cycling XRD characterization during initial Li plating process. (b) Depth-dependent Ag 3d and N 1s XPS spectra on the electrodeposited Li nuclei. Cross-sectional SEM images of the Li layer plated on the Cu current collector in the 20th cycle under 2 mA cm^{-2} & 2 mA h cm^{-2} for Li||Cu cells: (c) pristine Cu, and (d) SMGCS. The scale bar is $6 \mu\text{m}$. *In-situ* optical microscopy for the deposition of Li for (e) pristine Cu foil and (f) SMGCS.

ent that the introduction of AgNO_3 membrane enables the SMGCS *via* the construction of compatible silver lithiophilic sites and nitrate layer. Ag sites with almost no nucleation barrier could act as effective Li nuclei to attract Li ions and direct the initial nucleation. On the other hand, the generated nitrate-rich layer can provide a favorable interfacial environment, which offers the required ionic transportation channels to induce and confine Li deposition. These particular SMGCS features synergistically contribute to an outperformed Li cycling efficiency and stability in commercial carbonate electrolytes. Intuitive visual perception was also acquired to verify its outstanding performance. SEM and TEM were conducted to monitor the morphology of Li deposits after 20th cycle (Fig. 2c, d and Figs S7 and S8). The Li deposits on pristine Cu electrode are dendritic and mossy with a loosely packed structure (Fig. 2c and Fig. S7). In stark contrast, a smooth, uniform and sturdy morphology without any traces of dendrites is displayed for the SMGCS Li deposits

and the interface structure remains stable upon the increase of Li loading (Fig. 2d and Fig. S8). Furthermore, *in-situ* optical microscopy was conducted to intuitively observe the depositing behavior of Li. Dendrites grow fast and the pristine Cu foil is almost totally covered (Fig. 2e). In complete contrast, dense and uniform Li plating for SMGCS could be apparently observed (Fig. 2f), confirming the key role of SMGCS in controlling the dendrite-free morphology.

Li||Cu cells with a commercial carbonate electrolyte, $1 \text{ mol L}^{-1} \text{ LiPF}_6$ in EC/DEC (1:1 volumetric ratio), were assembled to investigate the electrochemical Li plating/stripping processes. The nucleation overpotential at the beginning of deposition, defined as the difference between the bottom of the voltage dip and the flat part of the voltage plateau [21,32], was employed to quantitatively assess the resistance of Li plating at the electrode surface (Fig. 3a). Regarding pristine Cu, high overpotential of $\sim 62 \text{ mV}$ is needed to overcome the hetero-

Figure 3 Electrochemical performance for Li||Cu cells. (a) The nucleation overpotentials for Li metal. (b) CEs of Li||Cu cells cycled under 1 mA cm^{-2} & 1 mA h cm^{-2} . (c) The corresponding EIS spectra taken at the full Li-plated state (1 mA h cm^{-2} of Li plated on the Cu foil) after various numbers of cycles. (d) CEs of Li||Cu cells cycled under 2 mA cm^{-2} & 2 mA h cm^{-2} . (e, f) The corresponding discharge-charge curves of the Li||Cu in (d). (g) CEs of Li||Cu cells cycled under 5 mA cm^{-2} & 5 mA h cm^{-2} and 5 mA cm^{-2} & 10 mA h cm^{-2} .

geneous nucleation barrier, due to the large thermodynamic mismatch between Li and Cu. In addition, a relatively high overpotential of ~ 50 mV with little LiNO_3 is also observed in the initial stage of Li nucleation, indicating the significance of nucleation seeds. Significantly, almost zero nucleation potential at the onset is observed for SMGCS. It can be attributed to the fact that almost no nucleation barrier exists for Li metal nucleating on Ag [21]. The CE of the cell, defined as the ratio of the amount of the stripped Li to that of the plated Li at each charging-discharging cycle, is frequently adopted as a performance index to evaluate the cyclability of the Li metal electrode. At the current density of 1 mA cm^{-2} with capacity depth of 1 mA h cm^{-2} , the cell of pristine Cu exhibits remarkably inferior cycling performance with an average CE of 80% only for 50 cycles. The CE performance for the cell with little LiNO_3 is slightly improved. In complete contrast, the cell of SMGCS can be stably cycled for over 300 cycles, delivering a high CE of $\sim 99\%$ (Fig. 3b). Li ion transfer resistances for the Li||Cu cells upon cycling were also investigated to uncover the kinetic features of the electrode interfacial film (Fig. 3c and Fig. S9). The Nyquist plots of the cells of pristine Cu and with little LiNO_3 additive exhibit large and changed interfacial resistance (including SEI layer resistance and charge transfer resistance) due to the crack and repair of fragile SEI film, which aggravates the deterioration for the battery performances. In contrast, the cell of SMGCS shows exceptionally small and stable resistance, indicating fast charge transfer rate, low diffusion impedance of Li ions and steady interfacial environment (Tables S1 and S2). Under harsher conditions of 2 mA cm^{-2} and 2 mA h cm^{-2} , the CE for SMGCS cell could reach 98% and remains stable for 100 cycles. The cell of pristine Cu fails after 30 cycles, exhibiting a CE as low as 78% (Fig. 3d). The corresponding Li plating/stripping behavior is probed by the charging-discharging voltage profiles, as plotted in Fig. 3e and f. The charging voltage profiles of pristine Cu are apparently shorter than the discharging ones in the time scale, implying the large irreversible capacity loss. On the contrary, the Li loss of SMGCS cell is negligible because of its high CE. Moreover, the long-term voltage hysteresis between charging and discharging voltage plateau can be observed. The cell of SMGCS realizes a much smaller and quite stable hysteresis, while the polarization of pristine Cu is dramatically increased. A sharp and steep increase of hysteresis is observed in the 30th cycle, in complete agreement with the failure of Li anodes with the drastic increase in Li-ion diffusion resistance [35]. The promoted SMGCS Li metal

anode contributes largely to small polarization, high Li utilization and stable cycling. Furthermore, in order to achieve much higher capacities (i.e., can be much more deeply cycled), we analyzed the Li||Cu cells at high capacities of 5 and 10 mA h cm^{-2} (Fig. 3g). The cell of pristine Cu is not even cyclable, whereas stable CE ($\sim 97.8\%$) could still be obtained for SMGCS, further indicating its superior capability to render deeply cyclable Li metal anodes.

Usually, excess Li is required for practical use of LMBs to avoid fast capacity degradation. In this regard, we evaluated the CE of Li metal anodes with different amounts of excess Li (Fig. 4a). Notably, when 200% excess Li is used, the average CE of SMGCS Li metal anode could reach a high value of 98.51%. The average CE gradually decreases when the amount of excess Li is reduced. Significantly, a high average CE of 98.15% still can be obtained when only 50% excess Li is applied. Under the same conditions, sharp peak occurs at charging process for pristine Cu and with little LiNO_3 because active Li metal on Cu is quickly exhausted and the remaining Li could not be removed. Further estimations for the reversibility and stability of Li metal anode with 50% excess Li were also conducted. With 1.5 mA h cm^{-2} Li deposited, the electrode was then stripped/deposited with capacity of 1.0 mA h cm^{-2} until the excess Li was entirely consumed (Fig. 4b and Fig. S10). The charge plateau remains stable for over 100 Li stripping/plating cycles (or 200 h), which is a satisfactory result when only 50% excess Li is applied. The terminal charge potential in each cycle is also demonstrated in Fig. 4c, which remains stable after more than 100 cycles. These results highlight the excellent stability of SMGCS Li metal and the possibility to realize application of Li metal full-cell with excellent cycling performance, high energy density and security. To further demonstrate the feasibility of such a structure in practical applications, predeposited Li anodes with slight excess Li were used to construct full cells (Fig. 4d). Because of its proven high operation voltage window (4.45 V), high practical capacity (150 mA h g^{-1}) and compatibility with carbonate electrolytes, we select commercial LiCoO_2 (LCO) as the cathode with a high mass loading $\sim 18.5 \text{ mg cm}^{-2}$. The full cells paired with predeposited Li metal on pristine Cu exhibit a dramatic capacity fading and rather low CEs. In sharp contrast, the full cells of LCO||50% excess Li and even LCO||20% excess Li for SMGCS Li anode both deliver excellent cycling stability and significantly improved CEs, which are extraordinary results for Li-metal full cells (Fig. 4e, f and Figs S11 and S12). Furthermore, the full cells of LCO||20% excess Li

Figure 4 Highly reversible LMB with slight excess Li. (a) The CEs of Li anodes with different amounts of excess Li. (b) The long-term cycling performance of Li metal anode with 50% excess Li. (c) The terminal charge voltage in each cycle of (b). (d) The schematic structure of Li metal full-cell. Cu or SMGCS electrodes were pre-deposited with certain amounts of Li as anodes and were paired with LCO cathodes to constitute Li metal full-cells. The cycle lives and CEs of the Li metal full-cells of (e) LCO||50% excess Li and (f) LCO||20% excess Li. The mass loading of LCO cathode was about 18.5 mg cm^{-2} .

(SMGCS) delivered much better stability than the full cell of LCO||200% excess Li (pristine Cu), further indicating the superiority of SMGCS for safer large-scale practical application of Li metal anodes (Fig. S13). Moreover, coupled with the high average discharging voltage of 4 V, the full cell of LCO||20% excess Li could afford a high specific energy of 572 W h kg^{-1} based on the total mass of electrode active materials. In addition, electrochemical performances of Li||NCM with pristine Li and AgNO_3 -modified Li with cathode areal loading of 20 mg cm^{-2} were also investigated. The AgNO_3 -modified Li demonstrated much better battery performance (Fig. S14). Therefore, the performance of SMGCS anode is superior to recently reported Li-metal anodes in terms of achieved

area capacities and current densities. In addition, the high degree of Li utilization in full-cells demonstrates their potential for practical implementation in high safety-level and energy-density Li batteries (Table S3).

CONCLUSIONS

In summary, highly efficient utilization of SMGCS Li metal (merely 20% excess anodic capacity in Li metal full-cell) in carbonate electrolytes was realized by introducing AgNO_3 membranes. Through a facile displacement reaction between AgNO_3 and Li during Li plating, *in-situ* silver lithiophilic sites and nitrate-rich layers can be obtained on the surface of Li metal anode. The as-proposed design could act as an SMGCS towards guiding and

confining Li deposition: Ag acts as lithiophilic nucleation sites to reduce Li nucleation overpotential and guide the Li initial nucleation; the nitrate-rich layer is helpful to confine and homogenize Li-ion flux, thus rendering reversible and dendrite-free Li metal deposition. Consequently, high CE of ~99% was achieved for over 300 cycles and Li metal can be deeply cycled at high capacity of 10 mA h cm⁻². More importantly, the Li metal full-cell with merely 20% excess Li (i.e., Li utilization of 83.3%) demonstrated significantly improved reversibility and CEs with almost all of the cathode capacity delivered. The present study realized the goals of excellent cycling efficiency in commercial carbonate-based liquid electrolytes and highly efficient Li utilization in Li metal full-cell. This is expected to favor the safe practical use of Li metal anodes, opening a new horizon towards the future development of Li metal full-cells.

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Supplementary information Supporting data are available in the online version of the paper.

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模拟导弹制导约束系统实现锂全电池中锂金属的高效利用

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摘要 金属锂的有效利用是实现锂金属全电池高安全性和高能量密度应用的关键。本文中, 我们报道了一种仅含20%过量锂且可逆性和库仑效率显著提高的锂金属全电池。我们通过设计巧妙的模拟导弹制导约束系统(SMGCS), 构建兼容的亲锂银位点和硝酸盐层来引导和限制锂的沉积。银位点充当有效的锂沉积位点, 吸引锂离子, 引导锂的初始成核。生成的硝酸盐层提供了有利于均匀受限且高容量锂沉积的界面环境, 这在理论上已通过分子动力学(MD)模拟得到了验证。这两种优点相结合, 实现了坚固且无枝晶的锂沉积以及含有极少量过量锂的锂金属全电池的应用。并且该锂金属在碳酸酯电解液中表现出优异的循环效率(300次以上的循环中库伦效率约99%), 还可以在 10 mA h cm^{-2} 的高容量下进行深度循环。本文中锂金属前所未有的高利用率为未来高效锂金属全电池的发展开辟了一条新的道路。