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Uniform lithium plating within 3D Cu foam enabled by Ag nanoparticles



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ABSTRACT

Lithium metal is recognized as the "Holy Grail" of anode materials for high-energy-density batteries. However, the application of the lithium anode is seriously hindered due to its instability especially during the large-capacity lithium stripping/plating process. In this study, a dimensionally stable Li composite electrode is fabricated by electrodepositing lithium on Ag-modified Cu foam. The Li-Ag alloy formed during the initial plating shows micro-structural affinity to lithium and promotes the subsequent uniform Li stripping/plating on the Cu skeleton. The symmetric cell with Li/Ag-modified Cu composite electrode shows much-improved stability as compared to both the Li/3D Cu composite and Li plate electrodes. By investigating the electrochemical performance of the full cells with Li₄Ti₅O₁₂ cathode, we find the interface stability of the Li composite electrode is deteriorated because of the increase of specific surface area. This work indicates that both dimensional and interface stabilities of lithium anodes are important for fabricating practical secondary lithium batteries.

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1. Introduction

Metallic lithium, with ultrahigh specific capacity (3860 mAh g^{-1}) and extremely low electrochemical potential (-3.04 V vs. SHE), is recognized as an ideal anode material for the nextgeneration rechargeable batteries [1–3]. Continuous efforts are conducting to apply lithium metal anodes to the high energy density batteries, such as lithium-sulfur and lithium-air batteries [4,5]. However, the practical utilization of metallic lithium as the anodes is severely hindered by several problems. These obstacles can be roughly classified in the following aspects. First, the uncontrollable growth of lithium dendrites is a crucial problem, because the lithium dendrites formed at the electrode/electrolyte interface are easy to puncture the separator and give rise to short-circuit, causing the potential safety hazard [6-8]. Second, the continuous formation of unstable solid electrolyte interphase (SEI) film consumes the electrolyte gradually during cycling. In other words, the fragile property of SEI film leads to the electrolyte's continuous reaction when fresh lithium metal is exposed to the electrolyte, resulting in the low coulombic efficiency (CE) of the battery [9]. Third, the stripping/plating mechanism of the Li anode causes the huge volume fluctuation during charge-discharge process. This huge dimensional change of anode leads to an unstable interface

and poor CE [10-12]. Besides, the above problems are interrelated, making the instability of Li anode complex.

Tremendous efforts have been made to address the above problems in decades, such as using electrolyte additives [13-17], fabricating artificial SEI [18-21], and utilizing solid-state electrolytes [22-24]. However, these solutions mainly stress improving interface stability and have a limited effect on the dimensional stability of the Li electrode. In recent years, an effective strategy for improving dimensional stability is to fabricate porous host materials with three-dimension (3D) structures for lithium plating [1]. The 3D structured hosts feature porosity and large specific surface area, which is a favor to reduce the local current density. More important, the porous structure can provide sufficient space to accommodate the volume variation of lithium anode during cycling [25]. Some lithium alloys can form 3D skeleton after Li stripping, which can stabilize the electrode structure in the bulk state. Recently, Kong et al. found Li-poor Li-Mg alloy formed after lithium stripping can be used as a mixed electron/Li-ion conducting matrix for the subsequent plating process [2]. Similarly, Yang et al. reported Li-B alloys with loofah flesh structure as a composite Li anode [26,27]. The well-designed 3D hosts of carbon materials have been extensively studied. Jin et al. prolonged the cycling life of lithium batteries by using a composite lithium anode based on a carbon nanotubes host [28]. Ji et al. suppressed lithium dendrite by introducing SiO₂ layer on carbon nanofibers host [29]. Also, metal foams have been widely investigated for lithium loading [30]. The above efforts are effective in stabilizing Li anodes in terms of volume

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fluctuation. For lithium loading within these hosts, metallic Li can be embedded by roll pressing [31], melting [32], or electroplating [33] to form composite electrodes. However, due to the relatively weak affinity between host materials and lithium, it is difficult to realize the uniform plating of Li within the porous structure. To reduce the nucleation barrier on the 3D hosts and facilitate the uniform plating of Li, the surface modification of the 3D skeleton have been conducted in some ways, such as loading lithiophilic materials by electroplating [34], in-situ growth [35], or electric joule heating [36] on the skeleton surface. Besides, some lithiophilic materials including Au [37], N-doped graphene [38], and Zn [39] have been demonstrated effective for uniform Li plating. However, how to achieve uniform Li plating within the skeleton's structure other than on the outer surface remains a great challenge especially in the large-capacity redox process. Moreover, due to the large specific surface area of the composite lithium electrode during cycling, the interface stability of this kind of Li anode should attract more attention.

Copper (Cu) is a promising current collector and host material for metallic Li loading because of its high conductivity and remarkable mechanical character. The porous structure of Cu can be fabricated by stacking Cu nanowires to form nano-scale pores [40] or be provided by Cu foam with micron-scale pores. The Cu foam has attracted increasing attention due to its low cost and availability. Also, the Cu foam with a micropore structure can provide rich space for lithium storage, which is effective for designing lithium metal batteries with a high reversible areal capacity [41]. Meanwhile, the excellent electrical conductivity of the 3D skeleton is in favor of reducing the large resistance during battery cycling. Compared with the carbon skeleton, Cu foam has higher mechanical strength, which can accommodate more structural deformation [42]. According to the explanation of Sand's law, the time of lithium dendrite nucleation is inversely proportional to the square of current density on the electrode surface [43]. Hence, 3D Cu foam is believed to have the ability to inhibit the growth of lithium dendrites via adjusting the distribution of the electric field [44]. However, metallic Cu, either in foam or in foil state, is not a lithiophilic substrate for uniform deposition [45]. Previous studies on optimizing 3D structures, such as constructing secondary pore structure [46] and designing the hierarchical structure of Cu [47], have limited effects on Li plating in the inner space of the 3D structure. Note that, when the site of the host materials have large curvature, it would generate charge concentration, and lithium is more likely to deposit on the top surface of electrodes rather than within the pores [48]. To improve lithium affinity of Cu foam, recent studies conducted surface modification with materials that can react with metallic lithium [49–52]. However, the long-term affinity to lithium of the host is insufficient. Therefore, choosing a long-term lithiophilic material to modify the Cu foam is necessary. Since silver (Ag) can react with Li to form Li-Ag alloy, Ag is regarded as a lithiophilic materials [53]. Moreover, the surface of Li-rich Li alloys are thermodynamically stable because lithium has the least surface energy [54], providing the possibility of nucleating Li on the Li alloys surface. Recent computational study indicates that Li alloys have ideal characteristics for lithium nucleation and growth, thus can be used as promising current collectors [55]. The theoretical investigation also shows that Li-Ag alloy can achieve lower Li nucleation overpotential and has good lithiophilicity [56]. So it is possible to regulate Li deposition within 3D Cu foam by modifying Ag on 3D Cu.

In this work, a silver-modified 3D Cu foam, denoted as Cu@Ag foam, is fabricated via a facile electroless plating method. A composite Li electrode is obtained by using the Cu@Ag foam as Li plating host. As the schematic (Fig. 1) illustrates, the 3D skeleton of Cu foam can support the bulk structure of the composite electrode. Due to the weak Li affinity of bare Cu foam, Li tends to deposit on



Fig. 1. Schematic illustration of the Li plating processes on Cu and Cu@Ag foams.

the top surface. After modifying with Ag, the Cu foam shows a low electrochemical nucleation barrier, facilitating Li plating within the inner space, because the initial alloying process between Li and Ag can guide the following plating. The dealloying potential of Li-Ag alloy is higher than the dissolution potential of Li, so the dealloying reaction of Li-Ag does not occur during the Li stripping process. Actually, the formed Li-Ag alloy is stable and plays an important role in maintaining microstructural stability. The design integrates the bulk-structurally stable Cu foam and microstructurally lithiophilic Li-Ag alloy, realizing the greatly improved dimensional stability of the composite electrode. With this architecture, the Li composite electrode can maintain remarkable bulk stability at a large capacity of 15 mAh cm⁻² during stripping/plating process for 3000 h. However, the interface stability needs to be improved as demonstrated by investigating the electrochemical performance of the full cells with $\mathrm{Li}_4\mathrm{Ti}_5\mathrm{O}_{12}$ cathode. The results of this work raise a new concern for fabricating stable practical Li anodes.

2. Experimental

2.1. Preparation of 3D Cu@Ag 3D foam host

The silver-plated Cu samples (Cu@Ag foam) were prepared by electroless plating method [57]. First, Cu foams were cleaned with acetone and anhydrous ethanol to remove surface stains, then dried in a vacuum at 50 °C for 10 h. The reducing solution was obtained by diluting anhydrous alcohol solution (12.5 mL) containing glucose (5.62 g) and tartaric acid (0.5 g) to 125 mL with deionized water. Next, the plating solution is formulated as follows. Aqueous ammonia (2 wt%) was added to the silver nitrate solution (10 mL, 6.9 mol/L) drop by drop until the solution turns clear. And then, sodium hydroxide solution (10 mL, 12.5 mol/L) was poured into the above solution to make it cloudy. After that, dilute ammonia was added for a second time to make the turbid solution transparent, then the plating solution was formulated. Finally, the reducing solution and plating solution were mixed evenly with a volume ratio of 1:1, and Cu foam was inserted vertically immediately into this solution for 1.5 min, followed by rinsing with deionized water and ethanol, respectively. The obtained Cu@Ag foam was cut into wafers with a diameter of 14 mm after vacuum drying at 60 °C for 12 h.

2.2. Fabrication of the Li-Cu@Ag foam and Li-Cu foam composite electrodes

The composite electrodes were fabricated by an electroplating method. Specifically, the coin cells were assembled in an Ar filled glove box ($O_2 \le 0.1$ ppm, $H_2O \le 0.1$ ppm), whereas lithium metal was used as the counter electrode and Cu@Ag or Cu foam as the working electrode. The electrolyte was consisted of 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in 1,2-dimethoxyethane

(DME) and 1,3-dioxolane (DOL) (1:1 by volume). The working electrodes after depositing lithium at a current density of 0.5 mA cm⁻² were disassembled to obtained the composited electrodes.

2.3. Materials characterizations

X-ray diffractometer (XRD, Rigaku mini Flex II) was employed to test the phase composition of the samples with Cu K α 1 radiation ($\lambda = 0.15405$ nm). The morphologies of Cu foams and composite electrodes were characterized by using a scanning electron microscope (SEM, Supra 55VP, Zeiss). The X-ray photoelectron spectra (XPS, Thermo Scientific ESCALAB 250Xi) was used to analyze the surface composition of the Cu foams. The distribution of elements in the composite electrodes of Li-Cu foam and Li-Cu@Ag foam was analyzed by laser-induced breakdown spectroscopy (LIBS, ASI J200) within an area of 4.5 mm \times 4.5 mm. Lithium dendrite growth, as well as gas evolution, was monitored in a transparent optical cell under optical microscopy (Nikon SMZ800N).

2.4. Electrochemical characterizations

Coin-type cells (2032) were assembled to study the electrochemical performance. The Li/Cu foam or Li/Cu@Ag foam halfcells, the symmetric cells and full cells were assembled with Clegard 2300 as the separator and 40 µL electrolyte for each cell. To fabricate the full batteries, the cathode is composed of Li₄Ti₅O₁₂ (LTO, Shenzen Kejing Star Co.), Super P and a binder of polycinylidene fluoride with the mass ratio of 8:1:1. The full cells of Li/LTO and Li-Cu@Ag/LTO were assembled and tested under 1 C rate (160 mA g^{-1}). The cutoff potentials for discharge and charge were 1.0 V and 2.2 V, respectively. All discharge/charge tests were carried out with LAND-CT2001A instruments (Wuhan Jinnuo, China). The electrochemical impedance spectra (EIS) were measured with a VERTEX.C.EIS electrochemical workstation with an amplitude of 5 mV and the frequency range from 10 mHz to 100 kHz.

3. Results and discussion

To fabricate the Cu@Ag foam, the electroless plating method is employed. This method ensures even the plating of metals, so it is more suitable than other methods for plating on complex porous materials [58]. The mechanism of electroless plating Ag in this work is a silver mirror reaction that can proceed at room temperature, which greatly improves the operability of the process [59]. After Ag plating, the surface color of the Cu foam has changed significantly, from the initial pinkish-orange to a bright silver. Because the color difference indicates that the phase composition has changed, XRD is used to test the phase composition of Cu foam before and after Ag plating. XRD patterns (Fig. S1) show that the weak characteristic peaks of Ag appear after electroless plating, indicating the formation of a low quantity of Ag due to the short plating time. Fig. 2 shows SEM images of Cu foam and Cu@Ag foam. The bare Cu foam has a macroporous cross-linking skeleton structure, and the scaffold has a diameter of 50-70 µm (Fig. 2a). Moreover, the skeleton surface is smooth and flat at the micron scale as shown in Fig. 2b. By contrast, the Cu@Ag foam has nano-sized Ag grains on the Cu foam surface (Fig. 2c and 2d). Nanoparticles can provide a large surface area, which is effective to reduce local current density and promote uniform deposition of lithium on the matrix. Furthermore, spherical nanoparticles with small curvature lack sharp edges and corners on their surfaces, so this structure can effectively avoid the tip effect caused by concentrated charge. Under this condition, the concentration gradient of lithium ions is uniform, and the dendrite growth is not easy to occur [60]. To explore the existing state of Ag on the surface of Cu foam, an XPS test is conducted and the results are shown in Fig. S2.



Fig. 2. SEM images of the surface morphologies of (a, b) Cu foam and (c, d) Cu@Ag foam.

The spectra peaks at 374.23 and 368.22 eV correspond to Ag $3d_{3/2}$ and Ag $3d_{5/2}$, respectively. This result suggests that Ag on the surface of Cu exists as the metallic state rather than an oxidized state. After Ag plating on the Cu foam, the Cu 2p peak shifts to the low binding energy with only 0.18 eV, which also indicates that Ag is adsorbed to the surface of Cu.

To evaluate how the Ag modification affects the lithium deposition, the morphologies of lithium deposition on Cu 3D foams with and without Ag modification are observed. Performed in Li/Cu foam and Li/Cu@Ag foam half-cells at the current density of 0.5 mA cm⁻², lithium with the capacity of 20 mAh cm⁻² is electrodeposited on the 3D structures, and the resulting digital and SEM images of composite electrode surface are shown in Fig. S3. Compared with the method of melting infusion, the electrodeposition method is more facile to load lithium with controlled areal capacity. When the capacity of lithium deposition reaches 20 mAh cm⁻², the two Li composite electrodes show a similar appearance from the digital pictures. However, from the SEM pictures, the Li-Cu@Ag composite electrode shows a flatter surface and has fewer cracks as compared to the Li-Cu electrode. The cross-sections of composite electrodes are shown in Fig. 3a and 3d, Cu foam and Cu@Ag foam have the same thickness before Li electroplating. After Li electroplating with the same capacity of 20 mAh cm⁻², there is an obvious difference in the thickness between the two electrodes, 279 µm for Li-Cu and 214 µm for Li-Cu@Ag electrodes. This observation suggests that Li prefers to deposit within the Cu@Ag foam, whereas metallic lithium tends to deposit on the surface of Cu foam. Note that, more cracks can be observed on the cross-section of Li-Cu@Ag foam. These cracks are believed to result from the cutting process for SEM test, during which the integrity of Li-Cu@Ag foam is destroyed, so the lithium metal in the interspace loses the skeleton support and is easier to peel off. The distribution of elements in the bulk composites is investigated by LIBS as shown in Fig. 3. For the LIBS images, the gradient from red to purple reflects the gradual decrease in the element content. For the Li-Cu electrode, the distributions of Li element and Cu element are inconsistent, and a large amount of lithium grow on the outer surface of Cu foam, while less lithium deposits on the middle and bottom of the bulk Cu foam. For the Li-Cu@Ag electrode, the distribution of Li is quite uniform along with the macropores within the Cu@Ag foam as shown in Fig. 3e, 3f and S4, and there is no excessive Li on the electrode surface. Note that the distribution of Li has a high consistency with that of Ag. This



Fig. 3. SEM pictures of a cross-section of (a) Li-Cu foam and (d) Li-Cu@Ag foam; LIBS images showing the distributions of (b) Li and (c) Cu in the Li-Cu foam electrode, and (e) Li and (f) Ag in the Li-Cu@Ag foam electrode, within an area of 4.5 mm \times 4.5 mm.



Fig. 4. (a) Nucleation overpotentials of lithium on Cu foam and Cu@Ag foam; (b) Nyquist plots and fitting lines of the Li/Cu foam and Li/Cu@Ag foam half-cells before cycling.

result is direct evidence that Ag particles on the Cu surface play a role in guiding the Li uniform plating behavior.

The overpotential during Li plating process includes nucleation overpotential and the mass transfer overpotential, these overpotentials can be roughly obtained from i-E curves. The nucleation overpotential is the difference from the lowest voltage to the discharge platform, and the mass transfer overpotential is the discharge voltage plateau [61,62]. When lithium-ion deposits on the two substrates, the nucleation overpotentials show an obvious difference (Fig. 4a). The nucleation overpotential for Li on Cu foam is high of 163 mV, this observation has also been reported elsewhere [63,64]. Because of this high nucleation barrier from heterogeneous nucleation behavior, lithium tends to deposit on the electrode surface where the diffusion of Li ions is easy, and the subsequent depositing can be guided by the formed metallic lithium. As deposited on the Cu@Ag foam, the nucleation overpotential of lithium is not obvious, confirming the nucleation barrier for Li on Cu@Ag foam is eliminated to a great extent. The amount of Ag on Cu foam is small, so the potential platform is not observed. But from careful observation, there is a small slope above 0 V (vs Li/Li+) during the initial depositing (inset of Fig. 4a), indicating the forming process of Li-Ag alloy [8,65]. The formation of Li alloys is thermodynamic preferred than Li deposition during the cathodic process. More important, it was reported that underpotential deposition (UPD) for lithium can occur on the Li-Ag alloy surface [66], which endows Li-Ag alloy a strong lithiophilic characteristic. Also, the lithium-ion diffusion barrier on Li-Ag alloy is low [55]. These characteristics induce the uniform Li deposition on the Cu surface decorated with Li-Ag alloy. The Nyquist plots (Fig. 4b) and resistance of charge transfer (R_{ct} , Table S1) of the Li/Cu foam and Li/Cu@Ag foam half-cells before cycling also support this view. The Cu@Ag foam has a smaller charge-transfer resistance (R_{ct}), indicating this electrode has a facile electrochemical reaction as compared to Cu foam during the initial Li plating process.

The role of Ag on Cu can be described as follows: Ag nanoparticles are similar to artificially introduced nucleating agents in the metallurgical industry. The nanoscale lithiophilic Li-Ag alloy formed during lithium depositing can homogenize the charges by increasing the specific surface area [67–69]. During Li plating process, the microstructure of the anode is tuned by Li-Ag alloy via the lithiophilic surface. The uniform deposition of Li is achieved by integrating the Li-Ag alloy nanoparticles and conducting a robust Cu skeleton. Thus, a dimensionally stable Li composite electrode is obtained.

The rate performance of Li/Cu foam and Li/Cu@Ag foam halfcells is tested with the lithium deposition capacity of 2 mAh cm⁻² at various current densities (Fig. 5a). Generally speaking, a higher current causes higher polarization, but the rate tests did not show obvious potential variation with the current density. This observation is because 3D Cu and Cu@Ag foams have a large specific



Fig. 5. (a) Voltage profiles of Li/Cu foam and Li/Cu@Ag foam half-cells at various current densities; (b) Coulombic efficiency of the Cu foam and Cu@Ag foam with a capacity of 2 mAh cm⁻² at 0.5 mA cm⁻²; Nyquist plots of the (c) Li/Cu foam and (d) Li/Cu@Ag foam half-cells in different cycles.

surface area, which can reduce polarization both in charge transfer and mass diffusion. However, Li/Cu@Ag foam half-cell shows lower overpotential and less variation of potential at different current densities as compared with Li/Cu foam half-cell because of the introduction of Ag nanoparticles (inset of Fig. 5a). Under multiple changes in current density, the plating potential of Li/Cu@Ag foam half-cell keeps stable. Especially, when the current density is returned to 0.5 mA cm⁻², the potential change can be neglected. On the contrary, the nucleation overpotential of Li/Cu foam increases at 5 mA cm⁻², and the voltage hysteresis is accompanied by the sudden change of current density during this process. Interestingly, the nucleation overpotential is still very small even eliminated after rate testing, and mass transfer overpotential decreases as compared to Li/Cu foam half-cell. The above results reveal that the Cu@Ag foam still maintains a good Li-ion diffusion channel to ensure low ion transport resistance under the gradient change of current, thus reducing the lithium dendrites growth caused by the mass diffusion-controlled process. CE is the ratio of the amount of lithium of stripping to that in the plating process, and it can be used as a guiding parameter to evaluate the reversibility of an electrode [70]. As shown in Fig. 5b, the CE of Li/Cu foam half-cell shows obvious fluctuation after 32 cycles with the discharge capacity of 2 mAh cm⁻² at the current density of 0.5 mA cm⁻². As a contrast, Li/Cu@Ag foam half-cell can keep stable for 70 cycles, together with the results of rate test, demonstrating the improved reversibility of Cu@Ag foam 3D host for Li plating/stripping. The high CE and stable cycling also can be supported by EIS (Fig. 5c and 5d). The R_{ct} on Li/Cu@Ag foam is smaller than that on Li/Cu foam during the cycling process, and this resistance keeps stable (Table S1). For the Li/Cu foam, the resistance increases gradually upon cycling. Obviously, the volume and interface fluctuation effects caused by lithium plating and stripping on Cu@Ag foam are weakened by introducing Ag nanoparticles.

To verify the unique advantage of Li-Cu@Ag foam composite electrode in term of uniform lithium plating, the cycling performance of the symmetric cell is compared with that of Li-Cu foam



Fig. 6. (a) Voltage profiles of the Li-Cu foam and Li-Cu@Ag foam symmetric cells at 5 mA cm⁻² for 15 mAh cm⁻²; SEM images and elemental mapping signals of (b) Li-Cu foam and (c) Li-Cu@Ag electrodes retrieved from the symmetric cells after 500 cycles.

with a capacity of 15 mAh cm⁻² at 5 mA cm⁻². As shown in Fig. 6a, Li-Cu@Ag foam composite electrode can maintain a low potential and stable cycling for 3000 h under such a high capacity. But for the Li-Cu foam electrode, the polarization is much high, indicating the fluctuating lithium surface is unstable. The crosssections of the two electrodes after 500 cycles are significantly different as shown in Fig. 6b and 6c. For the Li-Cu foam electrode, an obvious delamination phenomenon appears between Cu foam and deposited Li, indicating that the Li prefers to plate on the outer surface of Cu foam especially in the long-term plating/stripping process. As for the Li-Cu@Ag foam electrode, the observation of



Fig. 7. (a) Cycling performance of Li plate and Li-Cu@Ag foam symmetric cells with 2 mAh cm^{-2} at 2 mA cm^{-2} ; (b, c) SEM images of Li plate and Li-Cu@Ag foam electrodes disassembled from the symmetric cells with 2 mAh cm^{-2} after 50 cycles at 2 mA cm^{-2} .

more cracks agrees with the results of Fig. 3, indicating the integrity structure before cutting with a knife. Moreover, the elemental mapping signals reveal that Ag anchored on Cu foam in the bulk electrode keep uniform and stable during long cycling, which induces the Li plating within the Cu foam. The above results demonstrate the active role of well-distributed Ag nanoparticles on fabricating a dimensionally stable Li composite electrode.

Compared with plate structures, a robust 3D Cu foam host provides rich Li storage space and endures the volume change during Li stripping/plating process. In other words, Li composite electrode with the Cu skeleton has better structural and mechanical stability than Li plate electrode. The performance of the symmetric cells is compared between Li plate electrode and Li-Cu@Ag foam composite electrode as shown in Fig. 7. Li-Cu@Ag foam electrode can be stably operated under the discharge capacity of 2 mAh cm⁻² at various current densities. At the current density of 0.5 mA cm⁻² (Fig. 7a), there is no obvious potential fluctuation during the long cycling of the Li-Cu@Ag foam electrode, and the potential maintains a low-value level. As for the Li plate electrode, the remarkable potential fluctuation indicates the instability of the interface due to the bulk volume change. Also, the overpotential of the Li-Cu@Ag foam symmetrical cell is only 6.5 mV, which is much smaller than that of the Li plate electrode (26 mV). As reported in previous studies, the importance of initial lithium deposition morphology for the subsequent deposition process was emphasized [61,71]. After the initial cycling, lithium dendrites on the electrode surface cannot be removed in the following cycle, and the pits on the stripped side cannot be filled in time, leading to a huge difference in the shape of the electrode surface. This difference results in unstable voltage as well as polarization. The polarization can be aggravated along with cycling due to the accumulation of destroyed SEI at high current density. In contrast, the symmetric cell of Li-Cu@Ag foam electrode shows much-improved stability after the initial activation that indicates the formation of SEI film. The good voltage symmetry and the stable voltage during long cycling confirm that Li stripping/plating process occurs within the composite electrode even at a high current density. In addition to the host structure, improved stability is believed to result from the intrinsic character of the Li alloy skeleton [72]. Importantly, the permanent lithiophilic characteristic is key for the long-term stability of a composite Li anode.

SEM pictures in Fig. 7b and 7c compare the surface morphologies of Li plate and Li-Cu@Ag foam composite electrodes after 50 cycles with a capacity of 2 mAh cm⁻² at 2 mA cm⁻². The Li plate electrode shows a mossy morphology, whereas the Li-Cu@Ag foam composite electrode still has a flat and smooth surface. The mossy "dead lithium" or broken SEI stacks and forms a loose surface layer, building the tortuous Li-ion transport channels, which have negative effects on lithium transport, nucleation and even growth. Even at a low current density of 0.5 mA cm⁻², the Li plate electrode still shows a remarkable voltage fluctuation because of the uneven and unstable interface (Fig. S5). In contrast, the Li-Cu@Ag foam symmetrical cell performs stable Li stripping/plating process for at least 1000 h.

To evaluate the practicality of the Li-Cu@Ag foam electrode, the full cells of Li/Li₄Ti₅O₁₂ and Li-Cu@Ag/Li₄Ti₅O₁₂ were assembled. Different from the half-cells and symmetric cells, the full cell with Li-Cu@Ag foam anode shows inferior cycling stability as compared with the full cell with Li plate anode. As shown in Fig. 8a, after cycling at 1 C rate (160 mA g^{-1}) for 150 cycles, the cell of Li-Cu@Ag/Li₄Ti₅O₁₂ delivers a capacity of 96.4 mAh g^{-1} , whereas the cell of Li/Li₄Ti₅O₁₂ can remain 118.4 mAh g^{-1} . Since Li₄Ti₅O₁₂ is a stable electrode material, and the designed capacity of Li anode or Li-Cu@Ag anode is much higher than that of the cathode, the obvious capacity decay for the cell of Li-Cu@Ag/Li₄Ti₅O₁₂ is believed to relate to the depletion of electrolyte. To verify this hypothesis, electrochemical Li stripping and plating on Li and Li-Cu@Ag electrodes were performed in a transparent cell under optical microscopy. As shown in Fig. 8b, when the Cu@Ag electrode immersed in the electrolyte, small bubbles began to form due to the loose bulk Li composite that is yielded by the electroplating method, whereas Li plate can remain stable at this stage. After lithium stripping for



Fig. 8. (a) Cycling performance of Li/LTO and Li-Cu@Ag/LTO full batteries. (b) In-situ observation of Li stripping and platting process at 10 mA cm⁻² for Li/Li and Li/Li-Cu@Ag cells.

60 min (10 mAh cm⁻²), gas evolution is more severe on the Cu@Ag electrode than on the Li plate electrode because the larger surface of Li induces more side reactions of electrolyte. Followed by Li plating for 60 min (10 mAh cm⁻²), the surface of Cu@Ag electrode keeps flat though a large bubble has formed. As for the Li plate electrode, a large amount of mossy Li has accumulated on the Li surface and becomes "dead lithium". The above results demonstrate the advantage of Li composite in dimensional stability, especially during the large capacity stripping/plating process. However, the interface stability gets worsen because of the increased inner surface in the 3D structure.

Li composite electrode with conducting skeleton is a promising solution in addressing the dimensional instability of the Li plate electrode. Three-dimensional metal foams, such as Cu and Ni foams, can be used as mechanical supports and current collectors. However, the microstructure should be lithiophilic for uniform plating within the internal interface. Copper is an ideal current collector but has a low affinity toward metallic lithium, so the plating of Li on the surface of the pristine 3D Cu foam is difficult to prohibit especially at high current density or high charge/discharge capacity. In this study, Ag nanoparticles as lithiophilic materials anchored on Cu foam can form Li-Ag alloy, which is driven by thermodynamic. More importantly, the resulting Li-Ag alloy endows the underpotential deposition of lithium, thus guiding the Li nucleation process. The nucleation process is a key factor for following lithium crystal growth. Actually, the Ag nanoparticles function as a stabilizer for the microstructure of a composite electrode. This study also raises a new concern on the interface stability of Li composite electrode, which should be attracted more attention in the future study.

Conclusions

In this work, Ag nanoparticles are successfully deposited on the skeleton surface of Cu foam by using electroless plating. The welldistributed Ag can react with lithium to form Li-Ag alloy, which guides uniform Li plating within Cu foam via underpotential deposition. The dimensionally stable Li composite electrodes with an areal capacity of 20 mAh cm⁻² are fabricated by electrochemical depositing metallic lithium within the Ag-modified Cu foam. The structural stability of this composite electrode is realized by combining the conducting Cu foam and lithiophilic Li-Ag alloy microstructure. The symmetric cell with Li-Cu@Ag foam electrode shows excellent cycling performance in terms of low and stable voltage hysteresis. Even with a high stripping/plating capacity of 15 mAh cm⁻², the symmetric cell can maintain remarkable bulk stability for 3000 h. However, the full cell with Li-Cu@Ag foam anode shows faster capacity decay because of the exacerbated sidereactions between Li and electrolyte, thus the interface stability of the Li composite anodes should be stressed in future studies. The strategy of combing bulk stability and micro-structural affinity to lithium in this study provides a feasible strategy for constructing stable Li composite electrodes for high-energy-density lithium metal secondary batteries.

Declaration of Competing Interest

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

Credit authorship contribution statement

Zi-Wei Zhu: Methodology, Writing – original draft, Data curtion. **Zhen-Yu Wang:** Methodology. **Sheng Liu:** Conceptualization, Writing – review & editing. **Guo-Ran Li:** Formal analysis. **Xue-Ping Gao:** Supervision, Writing – review & editing.

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Supplementary materials

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