

Silver Copper Oxide Nanowires by Electrodeposition for Stable Lithium Metal Anode in Carbonate-Based Electrolytes

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behavior, infinite volume expansion, and dendrite formation, Li metal anodes have seriously restricted the practical application of lithium metal batteries (LMBs). In this study, a three-dimensional (3D) Li metal anode host composed of a copper oxide nanowires (CuO NWs) as the substrate with silver nanoparticles (Ag NPs) as the induced deposition sites was prepared (Ag@CuO NWs) by electrochemical machining technology. On the one hand, CuO NWs with a specific 3D structure obtained through an anodic oxidation process can provide enough space for Li deposition and thus would hinder the downside of volume change. On the other hand, Ag NPs, which are evenly distributed on the substrate by electrodeposition method can significantly reduce the nucleation



overpotential and induce uniform Li deposition in this whole 3D structure. As a result, Ag@CuO NWs could maintain a capacity retention of 85.6% for 200 cycles at a 1 C rate in carbonate-based electrolytes. This work proposes a strategy that can effectively regulate the Li metal deposition behavior by means of anodic oxidation and electrodeposition.

KEYWORDS: Li metal anode, Anodic oxidation, Electrodeposition, Ag nanoparticles, CuO nanowires, Uniform Li deposition

INTRODUCTION

In the past few decades, lithium-ion batteries (LIBs) have been widely applied to many aspects due to their high energy density and long cycle lifespan.¹ However, with the rapid development of new energy industries, people have put forward higher requirements for the energy densities of batteries.² The capacity of LIBs is limited by the amount of Li ions (Li⁺) that can be removed from the cathode, which greatly restricts its energy density. Li metal has an ultrahigh theoretical specific capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (-3.040 V compared with a standard)hydrogen electrode).^{3,4} Furthermore, Li metal anodes could match some high capacity lithium-free cathodes such as sulfur⁵ and oxygen^o to have a chance to develop much higher energy density batteries systems.⁷ As a result, Li metal batteries (LMBs) using Li metal anodes have increasingly been extensively studied by researchers.^{8,9}

Unfortunately, there are still severe challenges in getting Li metal into practical applications. Different from the host–guest electrochemical reaction of LIBs, the deposition and stripping of Li metal is a hostless process, which could be regarded as an infinite volume change during cycling.¹⁰ It means that the solid electrolyte interphase (SEI) layer will rupture and regenerate repeatedly, leading to the uncontrollable Li deposition as well as continuous reaction between fresh Li metal and an electrolyte. The final results are a decrease in the Coulombic

efficiency and formation of dendrites, which is not beneficial for the acceptable cycle performance and safety of LMBs. Therefore, how to carry out an effective strategy to regulate the deposition behavior of a Li metal anode is very essential for LMBs to improve the electrochemical performance.

In order to achieve effective regulation of Li metal deposition, it is necessary to understand the nucleation and growth process of Li metal. In classical understanding, Li⁺ ions obtain electrons in the initial stage and deposit on the current collector, which can be seen as a heterogeneous nucleation step.¹¹ Many results of studies pointed out that the initial nucleation process will have an important effect on the final metal Li deposition morphology. The nucleus formed during the initial nuclear suppression process is thermodynamically unstable and has the tendency to dissolve again, so that a certain overpotential is required to provide a driving force for the nucleation of Li metal. Previous studies have also indicated that the morphology of the crystal nuclei is related to the size of the nucleation overpotential.¹² The presence of an

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excessively high nucleation overpotential can promote the formation of a local charge field at the nucleation site and an uneven distribution of Li⁺ ions, which leads to uneven Li deposition and dendrites formation. Therefore, reducing or eliminating nucleation overpotential is of great significance for achieving uniform deposition behavior of a Li metal anode. Cui and his colleagues found that there are no nucleation barriers for some metals with a certain solubility in Li metal, while an obvious nucleation barrier exists for those without solubility by studying the phase diagram of Li with kinds of metals.¹³ By comparing Li deposition behavior on such different types of metals, it is found that a homogeneous alloying reaction occurs when Li is deposited on the surfaces of Au, Ag, Zn, and Mg with a greatly decreased overpotential of Li nucleation. It can be concluded that Li tends to prioritize nucleation and grow on these mostly lithiophilic materials and taking full advantage of such lithiophilic metals may be a solution for uniform deposition of Li metal.

Another question that should be further considered is the volume change of Li metal once it is working as a rechargeable anode. Due to the hostless mechanism of the ion plating/ stripping process, a Li metal anode could obtain its theoretical capacity by compromising with cycle reversibility. The success of LIBs by introducing a host structure should be a meaningful reference. As the supporting material of the active material, the structure and composition of the current collector can be directly acted on by the Li deposition behavior.¹⁴ However, the traditional 2D current collector has a limited surface area and little space to accommodate a huge volume change during the Li plating/stripping process. Therefore, the construction of a 3D porous conductive network with a higher surface area and larger volume as the substrate for deposition of Li metal is a preferential choice.^{15–20} It can reduce the current density of Li deposition and accelerate uniform Li deposition, as well as provide a stable substrate for accommodating Li deposition and inhibiting dendrite formation. Additionally, the surface composition or active site of the current collector also can be directly acted on by the Li deposition behavior.¹⁴ Combined with the above research points, Zhao et al. constructed a polyvinylidene fluoride (PVDF) framework decorated by an Ag concentration gradient as the 3D host for a Li metal anode.²¹ Yang et al. also have devised a 3D conductive network with a lithiophilic interface by coating Ag NPs on carbon nanotubes.²² Thus, the production of dead Li and the consumption of active substances would decrease, which can improve the Coulombic efficiencies and cycle lifespans of LMBs.

Anodic oxidation and electrodeposition, the simple and welldefined structure regulations for surface machining of materials, provide a reference for the construction of 3D lithiophilic interface current collectors. Anode oxidation is where the metal is connected to a positive electrode and treated by a suitable current for a certain time. The pore size and thickness of the oxide film can be controlled, so it can be widely used as a good template material in the synthesis of ordered nanostructures.^{23,24} For example, the thickness of an alumina template can be controlled under a stable current density. Due to the characteristics of the metal itself and the action of the current, the flat metal will be transformed into a 3D porous structure after oxidation. Electrodeposition can realize precise control of an electrochemical reaction by adjusting the current and electrification time. During the electrodeposition process, the reaction in the region with a

certain current density is nonselective, so both a metal particle of a specific size or a uniform surface can be obtained.²⁵ However, it is difficult for an ordinary chemical deposition method to achieve this goal. Li metal deposition on the anode is also substantially an electrodeposition process. The conventional electrodeposition can obtain a uniform and dense coating layer on the substrate surface, which is the most desired morphology in Li deposition. Therefore, the combination of them may find a new way to solve the problem of Li deposition regulation.

Herein, anodic oxidation and electrodeposition methods were used to synthesize a kind of Ag@CuO NWs as a 3D current collector to help LMBs achieve an improved electrochemical performances in carbonate-based electrolytes (Figure 1(a)). As is shown in Figure 1(b), Cu mesh was first



Figure 1. (a) Schematic diagram for obtaining Ag@CuO NWs current collector. Schematic diagram of (b) anodic oxidation and (c) electrodeposition.

anodized in a 2 M KOH solution to form copper hydroxide nanowires $(Cu(OH)_2 \text{ NWs})$. Then, $Cu(OH)_2 \text{ NWs}$ were calcined to obtain the CuO NWs substrate. Ag NPs were introduced on CuO NWs by the electrodeposition process (Figure 1(c)). On the one hand, a CuO NWs array could provide sufficient space and reduce the current density for Li deposition to promote uniform deposition. On the other hand, Li nucleation on the anode is more uniform due to the induction of Ag NPs. This combination results in a more controllable behavior of Li plating and stripping, which can effectively overcome the volume change of a Li metal anode and provide a stable base for the construction of SEI. The construction of this substrate system provides a feasible strategy for the future application of Li metal anodes.

EXPERIMENTAL SECTION

Preparation of CuO Nanowires. Cu mesh (150 mesh, 2 cm \times 3 cm) was immersed in hydrochloric acid (HCl, 1 M) for 5 s to remove the oxide film on the surface. After being cleaned with deionized water and dried in an oven at 80 °C, Cu mesh was placed in a 2 M KOH solution at room temperature and treated with a current of 20 mA cm⁻² for 2 min. Then, copper hydroxide nanowires (Cu(OH)₂ NWs) were obtained by this anodic oxidation process with Cu mesh and a platinum (Pt) plate used as the working and counter electrodes, respectively. The obtained Cu(OH)₂ NWs were washed with deionized water and dried in an oven at 80 °C for 2 h. Finally, CuO NWs were obtained by calcination at 200 °C in argon (Ar) for 1 h at a heating rate of 2 °C min⁻¹.

Synthesis of Ag@CuO Nanowires. Ag@CuO NWs were synthesized by pulsed electrodeposition in a silver ammonia solution (3 mM) in an electrolytic cell. The parameters of pulse deposition

were set to power on for 0.1 s and off for 0.3 s for 75 cycles. A twoelectrode system was used, with a CuO NWs substrate as the working electrode and a Pt plate as the counter electrode. The silver ammonia solution was obtained by dissolving 0.025 g of $AgNO_3$ (Xilong Chemical Company, China) in a beaker in a certain amount of deionized water and then adding ammonia solution (0.55 M) into it. Add ammonia to the $AgNO_3$ solution so it begins to precipitate, and then, continue to add ammonia until the precipitation disappears. Finally, the volume of the resulting solution was fixed to 50 mL.

Materials Characterization. XRD patterns were measured employing an X-ray diffractometer (Rigaku, Miniflex 600, Cu K α , λ = 0.154 nm). Scanning electron microscopy (SEM, Zeiss Gemini SEM 500), energy dispersive spectrometry (EDX, Ultim extreme, Oxford), and transmission electron microscopy (TEM, Tecnai F30 TWIN, FEI) were used to analyze the morphologies, elemental analyses, and microstructures of the samples. The elemental valence states of the materials were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, Escalab Xi+)). The affinity of the collector to electrolytes was shown through a contact goniometer (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co., Ltd.).

Electrochemical Performance Characterization. In order to test the Coulombic efficiency, impedance value, and whole battery performance in the electrochemical process, coin cells were assembled. The electrolyte used for the battery assembly was ethylene carbonate (EC) and diethyl carbonate (DEC) as the solvents (1:1 in volume), lithium hexafluorophosphate (LiPF₆, 1 M) as the solute, and vinylidene carbonate (VC, 5 wt %) as the electrolyte additive. A Celgard 2500 microporous membrane was used as the separator. Here, a 75 µL electrolyte was added to each cell. Cu mesh, CuO NWs, and Ag@CuO NWs were made into electrode pieces with a diameter of 12 mm. A CR2032 battery was assembled with Li metal to test its cycle performance and impedance before and after cycling. During the cycle, the current was controlled at 1 mA cm⁻², and the deposition capacity was 2 mAh cm⁻². The sample was also equipped with with LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) as the cathode to test the full cell performance. NCM523, acetylene black, PVDF were mixed in N-methyl pyrrolidone (NMP) at a mass of 8:1:1, respectively. The resulting slurry is evenly coated on aluminum foil, dried, and cut into a round disk with a diameter of 12 mm. Cu mesh, CuO NWs, and Ag@CuO NWs all (12 mm in diameter) were predeposited on 5 mAh cm⁻² of Li to be matched with NCM523 as a CR2032. The electrolyte used was the same as the above half-cells, and the dosage was 75 μ L. The separator was also the Celgard 2500 microporous membrane (18 mm in diameter). All cell assemblies were carried out in an argon glovebox, and tests were carried out by a Xinwei battery tester at 25 C. The electrochemical impedance spectroscopy (EIS) measurements were saved from 10 mHz to 100 kHz on Solartron 1287/1260.

RESULTS AND DISCUSSION

Because $Cu(OH)_2$ and CuO NWs have small diameters and are only thin layers, it could be seen that there are no other corresponding characteristic peaks except for the main peaks of Cu in the XRD diffraction spectrum (Figure S1(a)). Furthermore, the TEM image confirms the CuO NWs with needle-shaped morphologies (Figure 2(a)). The lattice stripes of CuO NWs are shown in the HRTEM image (Figure 2(b)). The spacing of them was measured at 0.23 nm, corresponding to the (111) crystal plane on the standard spectrum of CuO. At the same time, the amount of Ag deposited on the surface is very small, and the particle size is between 100-200 nm, which means that the diffraction peak of Ag is easily covered by strong copper peaks. Therefore, it is difficult to find Ag diffraction peaks on the XRD diffraction spectrum.²⁶ Also, the difference can be seen from the apparent morphologies of them. As shown in Figure S1(b), $Cu(OH)_2$ is blue in color, while calcined CuO appears black due to the presence of many



Figure 2. TEM image (a) and HRTEM image (b) of CuO NWs. SEM image (c) and elemental mappings (d, e, f) of Ag@CuO NWs.

nanowires on the surface. By analyzing the element mapping image of the Ag@CuO NWs, the Ag element (Figure 2(d)) is evenly distributed between Cu (Figure 2(e)) and O (Figure 2(f)), which also shows that the 3D substrate with lithophilic interface is successfully constructed by electrochemical treatment. The nonselectivity of electrodeposition allows Ag NPs to be evenly distributed on CuO NWs at substantially the same size. Under the induction of Ag NPs, the overpotential of Li nucleation will be basically eliminated, and Li metal tends to grow rapidly with the existence of Ag NPs. Since Ag NPs are evenly distributed, the nucleation of Li metal on the substrate will also be more uniform.

XPS characterization is used to study the chemical composition and valence of Ag@CuO NWs materials. In the full spectrum, the obvious peaks of Ag, Cu, and O are obvious. For Ag elements, the peaks at 368.8 and 374.8 eV corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, confirm the formation of Ag (Figure 3(a)).²⁷ For Cu 2p, there are two distinct peaks at 933.8 and 953.2 eV (Figure 3(b)), characterized by Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. The substance corresponding to these binding energy peaks is CuO.²⁸ The remaining weaker peaks at 932.6 (Cu $2p_{3/2}$) and 953.2 eV (Cu $2p_{1/2}$) indicate that a small amount of Cu₂O is still present.²⁹ This may be due to insufficient oxidation during anodizing or the disproportionation of Cu and CuO during high-temperature calcination. However, the substrate is still mainly in the form of CuO, which will not have a significant impact on its basic performance. Without introduction of carbon throughout the process, there are no peaks in the carbon spectrum other than the standard peaks (Figure 3(d)).

The SEM images show that Cu mesh is flat on the surface, and the diameter of the mesh is over 50 μ m. Thus, the specific surface area is limited (Figure 4(a) and (d)). However, after anodizing treatment, a large number of needle-shaped CuO nanowires (CuO NWs) arrays are formed on the surface (Figure 4(b), (e), (g), and (h)). The obtained nanowires are



Figure 3. Ag@CuO NWs XPS spectra of (a) Ag 3d, (b) Cu 2p, (c) O 1s, and (d) C 1s.



Figure 4. Different magnifications of SEM images of (a, d) Cu mesh, (b, e, g, h) CuO NWs, and (c, f, i) Ag@CuO NWs substrates.

4–6 μ m in length, and the diameter of the top needle is between 300 and 500 nm. It is found that the CuO NWs are obtained by sintering Cu(OH)₂ NWs clusters (Figure S2). These nanowires not only increase the specific surface area but also further increase the internal space of the material. The results are that there is more space for accommodation with later Li deposition, as well as having a chance to provide effective and uniformly dispersed sites for Ag NPs on the substrate. Finally, after electrodeposition, Ag⁺ ions are more likely to have electrons at the tip owing to the tip discharge effect during the deposition process (Figure 4(c), (f), and (i)). Once the tip positions were completely occupied, the Ag NPs began to deposit around the nanowires, slowly covering all the surfaces of the nanowires. The average particle size of the Ag NPs is between 100 and 200 nm. Meanwhile, due to Ag^+ ions being reduced to individual Ag NPs on the CuO NWs rather than the Ag layer, individual distributed Ag NPs have more contact area between the ordinary Ag layer. There is a large



Figure 5. (a) Galvanostatic discharge voltage profiles of different anodes during the initial Li deposition at 1 mA cm⁻². Nyquist plots (b) before cycling and (c) after 10 cycles of different current collectors. Coulombic efficiencies of Ag@CuO NWs, CuO NWs, and Cu mesh current collectors at (d) 1 mA cm⁻² for 2 mAh cm⁻² and (e) 0.5 mA cm⁻² for 5 mAh cm⁻².

binding force during the electrochemical reactions, which means that Ag NPs can be tightly bound to the CuO NWs substrate. Further, the Li metal plating/stripping at the substrate interface is the process of obtaining and losing electrons, and the excellent conductivity of Ag can play a role as a bridge to help electron transmission in the cycle. Therefore, Ag NPs and the substrate can maintain stability during Li metal plating/stripping. These particles densely exist at the tip and around the CuO NWs forming a lithiophilic interface, which could allow the Li metal to nucleate and grow evenly on the substrate.

During the process of anodic oxidation, Cu mesh begins to oxidize from the surface to the interior to form Cu(OH)₂ NWs.³⁰ The degree of the reaction is related to the current density and power-on time. A typical anodic oxidation process is where the metal anode is first dissolved, and the metal ions then react with the electrolyte to form the corresponding metal hydroxide or oxide film on the surface of the electrode. Therefore, the current density plays a decisive role in the dissolution reaction of the metal. This work mainly regulated the structures of CuO NWs by regulating current densities from 10 to 30 mA cm⁻² for 2 min. As is shown in Figure S3(a), once the current density is as low as 10 mA cm⁻², the CuO NWs are too short and thick to provide good deposition sites for Ag NPs and achieve Li metal deposition regulation. Meanwhile due to the fast reaction rate during oxidation at 30 mA cm⁻², the obtained CuO NWs present irregular loose porous morphologies (Figure S3(c)). They do not have stable specific structures and simply do not provide stable conductive substrates for Li metal deposition. However, a substrate with a higher specific surface area and a relatively stable structure has been obtained at 20 mA cm⁻² (Figure S3(b)). It is shown that the lengths and diameters of CuO NWs formed in this anodic oxidation process could be easily tuned by changing the operation current density. Thus, this method also gives a

chance to obtain various structures of the substrate with different specific surface areas and porous volumes, further providing a possibility to achieve a tunable Li metal deposition process and morphology. Similarly, Ag^+ ions are highly oxidized in the solution, and it is easy to have electrons be reduced into Ag. Therefore, a certain amount of ammonia is added to the electrolyte to complex with Ag^+ ions, and they are protected to inhibit disorderly deposition. Meanwhile, pulse electrodeposition is used to reduce the electrochemical polarization of Ag particles; thus, they have enough time to reach the negative interface for reactions, and then be in control of the particle sizes of Ag^+ ions.

Ag@CuO NWs were used as working electrodes, and Li foil was used as the reference electrode and counter electrode to carry out the coin cell test. At the same time, Cu mesh and a CuO NWs substrate were used as working electrodes for a comparative test. Except for the different working electrodes, other assembly and testing conditions were consistent. The batteries were tested for cycles at a current of 1 mA cm⁻² and a discharge capacity of 2 mAh cm⁻². The nucleation overpotential of the Li metal of the first cycle is defined as the difference between the bottom of the voltage dip and the flat part of the voltage plateau in the initial cycle discharge curve.¹³ Li metal exhibits a significant nucleation overpotential of about 40 mV on Cu mesh (Figure 5(a)). The overpotential of Li metal nucleation on the CuO NWs is about 18 mV because it has a slightly higher specific surface area than Cu mesh. The Ag@CuO NWs substrate shows no significant overpotential for nucleation of Li deposition. Owing to the limited specific surface area of Cu mesh, the polarization of Li deposition on it will be considerable. In addition, there is no two-phase region where Li and Cu can form an alloy; thus, the Li nucleation on the Cu mesh is a heterogeneous nucleation process. CuO NWs can reduce the current density of the anodic electrochemical reaction and the polarization of Li metal nucleation for its



Figure 6. Li deposition SEM images of the (a, c) Cu mesh and (b, d) Ag@CuO NWs with deposition capacity of 5 mAh cm⁻².

higher specific surface area; thus, it shows a lower nucleation overpotential than Cu mesh. The presence of Ag NPs and a CuO NWs substrate have an inducing effect on uniform nucleation and Li deposition. Thus, the Li nucleation on the Ag@CuO NWs become easier. It could effectively control the nucleation of Li metal and make full use of the expanded volume on the substrate. On this basis, it can inhibit Li dendrite growth while maintaining the stability of SEI. Also, it has a positive effect on the uniform Li deposition metal and electrochemical performances of LMBs.

The EIS curves of different batteries in the initial state and after 10 cycles were tested. Before cycling, the resistance values of Ag@CuO NWs and CuO NWs were only 105.1 and 150.2 Ω , respectively (Figure 5(b)). However, Cu mesh showed a little higher impedance value, which reached 203.6 Ω . This indicates that Ag@CuO NWs exhibits an outstanding interface reaction ability with an anode and Li⁺ ion transport performance compared with Cu mesh before cycling. After 10 cycles, it was found that the impedance value of each substrate had increased (Figure 5(c)) by various extents. The values of Ag@CuO NWs reached 137.4 Ω , which showed a slight increase. CuO NWs and Cu mesh had experienced a high growth rate. CuO NWs had grown from 150.2 to 253.7 Ω , which was about 1.86 times the value before cycling. Cu mesh had grown from 203.6 to 431.7 Ω , which was about 2.12 times the original value. This shows that under the action of Ag@CuO NWs the interface impedance value could be maintained at a lower level, and the interface reaction of the Li metal is more stable. The SEI layer formed on the Ag@CuO NWs substrate was more uniform than that of CuO NWs and Cu mesh. It also explained that Li⁺ ions have a lower interface transport impedance on Ag@CuO NWs during the cycle, which makes them easier to pass through SEI for deposition. This reduces the surface concentration polarization, which is conducive to nucleation and Li uniform deposition on the anode.

The half-cells were assembled on the basis of a carbonate electrolyte for electrochemical performance tests. The current was controlled at 1 mA cm⁻², and the discharge capacity was 2 mAh cm⁻². Through the testing result, it is found that Ag(@) CuO NWs could perform 100 cycles stably under this condition and maintain a high Coulombic efficiency of

95.3% (Figure 5(d)). But CuO NWs and Cu mesh had steadily cycled about 60 and 40 cycles, respectively, and their highest Coulombic efficiency was only about 90.2%. On the basis of its low specific surface area and volume, there is not enough volume to hold Li metal for Cu mesh in the deposition process. Thus, Li tends to start to nucleate and grow uncontrollably. In this case, the huge volume change produced by Li deposition causes SEI to repeatedly generate and rupture. This further aggravates the uneven composition and spatial distribution of SEI, making Li⁺ ions unable to uniformly obtain electrons to achieve even deposition and thus produce Li dendrites. This step-by-step response is the rapid consumption of active substances, which greatly reduces the cycle lifespan and Coulombic efficiency of the battery in the Cu mesh. Although CuO NWs improve the surface area and volume of the substrate, they reduce the current density of Li deposition while holding more deposited Li. Li still has a large nucleation overpotential on the CuO NWs. CuO NWs also contain a little amount of Cu₂O, and the study has shown that Cu₂O on a substrate surface would react irreversibly with deposited Li to produce Cu and Li₂O.²⁹ In Figure S4, this can be demonstrated by cyclic voltammetry (CV) curves of four substrates and Li at the same scanning rate. In the Ag@CuO NWs and CuO NWs curves, a new reduction peak is generated around 2.2 V during the negative scanning process (Figure S4(b)). Owing to the low content of Cu_2O_2 , the peak intensity is also low. It will still allow active Li to be consumed to reduce the Coulombic efficiency of the battery. For Ag@CuO NWs, the uniformly distributed Ag NPs obtained by electrodeposition provide a lithiophilic interface, which can make the Li nucleation more uniform. The even Li⁺ ion flow can also be reduced in the anode through the SEI layer, which effectively avoids the growth of Li dendrites; thus, the reversibility of the electrode reaction has been enhanced. Therefore, the cycle lifespan and Coulombic efficiency have been significantly improved in LMBs due to the introduction of Ag@CuO NWs.

Simultaneously, the electrochemical performance was tested at 0.5 mA cm⁻² with a discharge capacity of 5 mAh cm⁻² (Figure 5(e) and Figure S5). It showed that Ag@CuO NWs could maintain the Coulombic efficiency of 90.3% after 80 cycles, while CuO NWs and Cu mesh could only cycle for only



Figure 7. Full-cell electrochemical performance with NCM523 cathode. The cycling performance of the Cu mesh, CuO NWs, and Ag@CuO NWs at rates of (a) 1 C and (d) 2 C. The voltage profiles of (b) Cu mesh and (c) Ag@CuO NWs at the rate of 1 C at different cycles. The voltage profiles of (e) Cu mesh and (f) Ag@CuO NWs at the rate of 2 C at different cycles.

50 and 20 cycles, respectively. This further illustrates that there is not enough volume on the Cu mesh to accommodate such a high-capacity Li metal, and Li cannot be reversibly deposited and stripped on the Cu mesh. It also shows that even if the pristine CuO NWs substrates have large specific surface areas and volumes, the nucleation and growth of Li metal on the surfaces are not uniform. It is difficult to withstand the repeated high-capacity Li metal stripping/deposition process. Li deposition on CuO NWs only occurs on the surfaces, and it is impossible to fully utilize the spaces inside the nanowires. For Ag@CuO NWs, due to the induction of uniformly distributed Ag NPs, Li is able to preferentially grow in the local shaped nuclei. Li metal uniformly nucleates on these Ag NPs, which can promote its even deposition, hinder the reaction between Li metal and the electrolyte, and finally, prolong the lifespan of the battery. Further, the homogeneous nucleation and growth of Li metal on Ag@CuO NWs can make full use of increased volume through anodic oxidation on CuO NWs. High capacity and long cycle lifespan are the pursuit of all secondary battery systems, and high energy density in LMBs is easy to achieve. However, it is difficult to achieve long cycle lifespan at the same time. This work therefore provides some ideas for the design of high-capacity and long cycle lifespan LMBs.

The microstructures of Ag@CuO NWs and Cu mesh after deposition with 5 mAh cm⁻² of Li were observed by SEM. Li deposition on the Cu mesh was uneven, showing a typical dendritic morphology (Figure 6(a)). Furthermore, it could be found that the Li deposition on the Cu mesh was heterogeneous (Figure 6(c)). As for Ag@CuO NWs, it showed no dendrite formation, and Li metal filled the whole porous structure of the CuO NWs evenly (Figure 6(b) and (d)). Cu mesh has a limited specific surface area, and the current density for Li deposition on the Cu mesh is quite higher, resulting in an obvious polarization. As a result, Li metal cannot achieve uniform nucleation around the Cu mesh. The subsequent growth of Li metal also gathers on these uneven nuclei. Thus, the higher the deposition capacity is, the more obvious the deposition inhomogeneity is. From the perspective of nucleation, because the Li deposition on the Cu mesh belongs to a heterogeneous reaction, there is a huge barrier for Li nucleation. It means that when some uneven nuclei are formed on the Cu mesh, the remaining Li will tend to be deposited directly on the existing nuclei rather than to form a new nucleus. This will further exacerbate the uneven Li deposition. But for the Ag@CuO NWs substrate, Ag NPs are evenly distributed on the CuO NWs substrate, which means that a large number of lithiophilic sites are existing on this substrate. Then, there will be a number of Li nuclei formations on the Ag NPs. In this way, the remaining Li will tend to grow on these stable nuclei, which in turn inhibits the uneven Li deposition. Meanwhile, the CuO NWs substrates can also provide more space for Li deposition than Cu mesh. Thus, the Ag@CuO NWs substrate can significantly improve the Li deposition behavior. Such deposition behavior would inevitably lead to low Coulombic efficiency and being unable to maintain a long cycle stability. In contrary, the 3D structures combined with Ag NPs introduced on CuO NWs have higher specific surface areas, bigger volumes, and lithiophilic interfaces. The Ag NPs on the CuO NWs can induce Li nucleation easily, so Li metal tends to nucleate and grow inside the CuO NWs and then deposit. This deposition behavior can maximize the use of the 3D structure formed by the CuO NWs substrate, effectively alleviating the volume change during the Li metal deposition and ultimately providing the battery with a high Coulombic efficiency. It also showed that the structural stabilities of CuO NWs during Li plating and stripping can provide a stable substrate for a long battery lifespan. These different deposition behaviors vividly explained the core thought of this work. It is to predesign a 3D structure substrate and then introduce a lithiophilic interface into the substrate. Through the induction effect of this interface on Li metal deposition, it will make full use of the volume of the 3D structure and finally realize the effective regulation of Li metal deposition. Then, an even Li metal deposition layer would make a SEI layer be more stable during the cycle. In turn, this

will cause a uniform stream of Li⁺ ions to pass through the SEI layer and continue to nucleate and grow uniformly, forming a virtuous cycle. Through these means, the Coulombic efficiency and lifespan of the battery could be improved. The contact angle tests are to compare the wettability of the electrolyte to Ag@CuO NWs and Cu mesh. There was a contact angle of 23.7 °C between the Cu mesh and electrolyte (Figure S6(a)). However, Ag@CuO NWs could be completely infiltrated with the electrolyte (Figure S6(b)). The complete infiltration of the electrolyte also allows Li⁺ ions to better enter the 3D structure, which could allow Li⁺ ions to more easily get electrons to deposit inside the nanowires to inhibit the volume change of Li deposition and drive uniform Li deposition.

Finally, the performance of full batteries with different current collectors were tested. The capacities of 5 mAh cm⁻² Li were predeposited on different substrates, which were assembled with NCM523 for testing (Figure 7(a)). To pair with a limited Li anode, the mass loading of NCM523 in the test is 3.06 mg cm^{-2} . To further investigate the utilization of Li by Cu mesh, CuO NWs, and Ag@CuO NWs, the long-term cycle performances of the full-cell were tested at 1 and 2 C, respectively. It was found that Ag@CuO NWs still had a capacity retention of 85.6% after 200 cycles at 1 C. In contrast, the CuO NWs substrate and Cu mesh began to decay rapidly after 100 and 60 cycles, respectively. A further comparison of the cycle curves between Ag@CuO NWs and Cu mesh in a single cycle showed that Ag@CuO NWs could achieve a stable operation from the first to 200th cycle, and the discharge specific capacity was kept at a high level (Figure 7(b)). But the discharge specific capacity of the Cu mesh began to decline rapidly after the 70th cycle (Figure 7(c)). Meanwhile, the capacity retention of Ag@CuO NWs was 89.2% after 100 cycles at 2 C (Figure 7(d)). However, CuO NWs and Cu mesh only maintained a lifespan of 45 and 30 cycles, respectively. For the charge-discharge curve, the discharge specific capacity of Cu mesh had begun to decrease rapidly after 25 cycles (Figure 7(e)). For Ag@CuO NWs, there is a stable discharge specific capacity from the first to 100th cycle, indicating that Li could be steadily stripped from the anode (Figure 7(f)). The reason could be analyzed from the point of the deposition morphologies. It could be seen that the capacities of the CuO NWs and Cu mesh after a certain cycle began to decline rapidly, rather than decaying as slowly as ordinary batteries. The reason can be also found in the electrochemical performance of the half-cell. CuO NWs and Cu mesh, because their structures for Li deposition are not effectively regulated, result in low Coulombic efficiencies during the cycle, which produce a large amount of dead Li and constantly consume the electrolyte. Bring this behavior into the full battery, the three substrates are added with the same volumes of electrolyte. Because of the production of dead Li in the CuO NWs and Cu mesh, the electrolyte is quickly consumed, eventually leading to a rapid dive in battery capacity. Therefore, under the condition that all three substrates are added with the same volumes of electrolyte, CuO NWs and Cu mesh make the electrolyte quickly deplete due to the production of dead Li, which eventually leads to sharp attenuation of capacity. The detailed morphologies of 5 mAh cm⁻² Li deposited in different substrates are shown in Figure S7. It could be intuitively seen that Li completely covered the whole Ag@CuO NWs substrate evenly (Figure S7(a)), which provided a uniform and flat surface for the battery and was conducive to Li plating and stripping. Li deposition on CuO NWs (Figure S7(b)) and Cu

mesh (Figure S7(c)) could be clearly identified with uneven morphologies, which would lead to uncontrollable Li plating and stripping on the substrate and accelerate the generation of Li dendrites. Thus, it could be found that Ag@CuO NWs have greater advantages over the other two substrates. It is proved that Ag@CuO NWs are extremely compatible with highvoltage cathodes and conducive to the high-capacity properties of Li metal anodes. However, Ag@CuO NWs exhibit high Coulombic efficiency in half batteries, resulting in longer stable cycle life in full batteries.

CONCLUSIONS

In general, a kind of Ag@CuO NWs substrate as a 3D current collector was synthesized by two simple and well-defined electrochemical machining methods. While a CuO NWs substrate is matched to provide a deposition host for Li metal, Ag NPs can induce uniform Li deposition. The uniform deposition behavior can maintain the stability of substrate, which enhances the protection of SEI and reduces the consumption of the reaction between Li and the electrolyte. The outstanding conductivities of Ag NPs and large specific surface areas of CuO NWs can reduce the current density of Li deposition and inhibit the generation of Li dendrites. On this basis, Ag@CuO NWs could maintain a capacity retention of 85.6% for 200 cycles at 1 C in carbonate-based electrolytes. Under the combined action of Ag NPs and CuO NWs substrates, the plating and stripping Li metal could be controlled. The design of this work provides a new way for the realization of LMBs with high energy densities.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c01846.

XRD patterns, SEM images, CV curves, CE plots, contact angle test images, and photographs (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Chazalviel, J. Electrochemical aspects of the generation of ramified metallic electrodeposits. *Phys. Rev. A* **1990**, 42 (12), 7355–7367.

(2) Borchardt, L.; Oschatz, M.; Kaskel, S. Carbon Materials for Lithium Sulfur Batteries-Ten Critical Questions. *Chem.* **2016**, 22 (22), 7324–51.

(3) Shi, P.; Li, T.; Zhang, R.; Shen, X.; Cheng, X. B.; Xu, R.; Huang, J. Q.; Chen, X. R.; Liu, H.; Zhang, Q. Lithiophilic LiC6 Layers on Carbon Hosts Enabling Stable Li Metal Anode in Working Batteries. *Adv. Mater.* **2019**, *31* (8), No. 1807131.

(4) Xu, A.; Cui, J.; Liu, Y.; Zhang, S.; Jin, B.; Shao, M. LiCoO2 Ultrathin Layer for Uniform Lithium Deposition toward a Highly Stable Lithium Metal Anode. *ACS Sustainable Chem. Eng.* **2021**, 9 (44), 14663–14669.

(5) Chen, J. J.; Dong, Q. F. Research Progress of Key Components in Lithium-Sulfur Batteries. J. Electrochem. **2020**, 26 (5), 648–662.

(6) Wang, D.; Xiao, J.; Xu, W.; Zhang, J.-G. High Capacity Pouch-Type Li-Air Batteries. J. Electrochem. Soc. 2010, 157 (7), A760–A764.

(7) Chen, X. R.; Zhao, B. C.; Yan, C.; Zhang, Q. Review on Li Deposition in Working Batteries: From Nucleation to Early Growth. *Adv. Mater.* **2021**, 33 (8), e2004128.

(8) Zhang, Y.; Han, Z.; Huang, Z.; Zhang, C.; Luo, C.; Zhou, G.; Lv, W.; Yang, Q.-H. Dendrite-Free Non-Newtonian Semisolid Lithium Metal Anode. *ACS Energy Lett.* **2021**, *6* (11), 3761–3768.

(9) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117* (15), 10403–10473.

(10) Wang, H.; Hu, P.; Liu, X.; Shen, Y.; Yuan, L.; Li, Z.; Huang, Y. Sowing Silver Seeds within Patterned Ditches for Dendrite-Free Lithium Metal Batteries. *Adv. Sci.* (*Weinheim*) **2021**, 8 (14), No. e2100684.

(11) Liu, J.; Ma, H.; Wen, Z.; Li, H.; Yang, J.; Pei, N.; Zhang, P.; Zhao, J. Layered Ag-graphene films synthesized by Gamma ray irradiation for stable lithium metal anodes in carbonate-based electrolytes. *J. Energy Chem.* **2022**, *64*, 354–363.

(12) Pei, A.; Zheng, G.; Shi, F.; Li, Y.; Cui, Y. Nanoscale Nucleation and Growth of Electrodeposited Lithium Metal. *Nano Lett.* **2017**, *17* (2), 1132–1139.

(13) Yan, K.; Lu, Z.; Lee, H.-W.; Xiong, F.; Hsu, P.-C.; Li, Y.; Zhao, J.; Chu, S.; Cui, Y. Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. *Nat. Energy* **2016**, *1* (3), 16010.

(14) Jin, S.; Jiang, Y.; Ji, H.; Yu, Y. Advanced 3D Current Collectors for Lithium-Based Batteries. *Adv. Mater.* **2018**, 30 (48), No. 1802014.

(15) Chi, S.-S.; Liu, Y.; Song, W.-L.; Fan, L.-Z.; Zhang, Q. Prestoring Lithium into Stable 3D Nickel Foam Host as Dendrite-Free Lithium Metal Anode. *Adv. Funct. Mater.* **2017**, *27* (24), 1700348.

(16) Yun, Q.; He, Y. B.; Lv, W.; Zhao, Y.; Li, B.; Kang, F.; Yang, Q. H. Chemical Dealloying Derived 3D Porous Current Collector for Li Metal Anodes. *Adv. Mater.* **2016**, *28* (32), 6932–9.

(17) Shen, X.; Cheng, X.; Shi, P.; Huang, J.; Zhang, X.; Yan, C.; Li, T.; Zhang, Q. Lithium-matrix composite anode protected by a solid electrolyte layer for stable lithium metal batteries. *J. . Energy Chem.* **2019**, *37*, 29–34.

(18) Liu, W.; Cheng, P.; Yan, X.; Gou, H.; Zhang, S.; Shi, S. Facile One-Step Solution-Phase Route to Synthesize Hollow Nanoporous CuxO Microcages on 3D Copper Foam for Superior Li Storage. *ACS Sustainable Chem. Eng.* **2021**, 9 (12), 4363–4370.

(19) Pinson, M. B.; Bazant, M. Z. Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction. J. Electrochem. Soc. **2013**, 160 (2), A243–A250. (20) Yao, W.; He, S.; Xu, J.; Wang, J.; He, M.; Zhang, Q.; Li, Y.; Xiao, X. Polypyrrole Nanotube Sponge Host for Stable Lithium-Metal Batteries under Lean Electrolyte Conditions. ACS Sustainable Chem. Eng. **2021**, 9 (6), 2543–2551.

(21) Zhao, Y.; Wang, L.; Zou, J.; Ran, Q.; Li, L.; Chen, P.; Yu, H.; Gao, J.; Niu, X. Bottom-up lithium growth guided by Ag concentration gradient in 3D PVDF framework towards stable lithium metal anode. *J. Energy Chem.* **2022**, *65*, 666–673.

(22) Yang, C.; Yao, Y.; He, S.; Xie, H.; Hitz, E.; Hu, L. Ultrafine Silver Nanoparticles for Seeded Lithium Deposition toward Stable Lithium Metal Anode. *Adv. Mater.* **2017**, *29* (38), 1702714.

(23) Wan, Y. Study on Anodic Oxidation and Sealing of Aluminum Alloy. Int. J. Electrochem. Sci. 2018, 2175–2185.

(24) Li, L.; Zhang, Y.; Lei, J.; He, J.; Lv, R.; Li, N.; Pan, F. Wateronly hydrothermal method: a generalized route for environmentallybenign and cost-effective construction of superhydrophilic surfaces with biomimetic micronanostructures on metals and alloys. *Chem. Commun.* (*Camb.*) **2014**, *50* (56), 7416–9.

(25) Li, S.; Chen, H.; Liu, J.; Deng, Y.; Han, X.; Hu, W.; Zhong, C. Size- and Density-Controllable Fabrication of the Platinum Nanoparticle/ITO Electrode by Pulse Potential Electrodeposition for Ammonia Oxidation. ACS Appl. Mater. Interfaces **2017**, *9* (33), 27765–27772.

(26) Lian, Z.; Wang, W.; Xiao, S.; Li, X.; Cui, Y.; Zhang, D.; Li, G.; Li, H. Plasmonic silver quantum dots coupled with hierarchical TiO2 nanotube arrays photoelectrodes for efficient visible-light photoelectrocatalytic hydrogen evolution. *Sci. Rep.* **2015**, *5*, 10461.

(27) Zhang, T.; Zhou, T.; He, L.; Xu, D.; Bai, L. Oxidative degradation of Rhodamine B by Ag@CuO nanocomposite activated persulfate. *Synth. Met.* **2020**, *267*, 116479.

(28) D'Oliveira, M. R.; Rabelo, J.; Veiga, A. G.; Chagas, C. A.; Schmal, M. In Situ DRIFTS Investigation of Ethylene Oxidation on Ag and Ag/Cu on Reduced Graphene Oxide. *Cataly. Lett.* **2020**, *150* (10), 3036–3048.

(29) Parvathiraja, C.; Shailajha, S. Bioproduction of CuO and Ag/ CuO heterogeneous photocatalysis-photocatalytic dye degradation and biological activities. *Appl. Nanosci.* **2021**, *11* (4), 1411–1425.

(30) Huang, J.; Xiong, Y.; Peng, Z.; Chen, L.; Wang, L.; Xu, Y.; Tan, L.; Yuan, K.; Chen, Y. A General Electrodeposition Strategy for Fabricating Ultrathin Nickel Cobalt Phosphate Nanosheets with Ultrahigh Capacity and Rate Performance. *ACS Nano* **2020**, *14* (10), 14201–14211.