Li_xCu alloy nanowires nested in Ni foam for highly stable Li metal composite anode

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ABSTRACT Porous metal architectures are widely adopted as three-dimensional conducting scaffolds for constructing Li metal composite anodes, whereas their macropores hinder their practical application due to limited surface area and large pore size of few hundred micrometers. In this work, a network of Li_xCu solid solution alloy nanowires is *in situ* formed *via* infiltrating molten Li-Cu alloy into Ni foam and subsequent cooling treatment, whereby a three-component composite anode consisting of Li metal, Li_xCu alloy, and Ni foam is fabricated. The Li_xCu nanowires nested as secondary frame split the macropores into micropores, enlarging the active surface area and inducing uniform Li deposition significantly. The lithiophilicity of the alloy wires and the shrunken void size built by the hierarchical architecture can further tune the nucleation and growth behavior of Li. The multiscale synergetic effect between the primary and secondary scaffold guarantees the composite anode sheet with extraordinarily long-term cycling stability even under high current rates.

Keywords: Li metal anode, Li dendrite, nickel foam, Li-Cu alloy

INTRODUCTION

Lithium (Li) metal anode is regarded as an ideal choice for next-generation secondary batteries because of its high theoretical specific capacity (3860 mA h g⁻¹) and low redox potential (−3.04 V vs. the standard hydrogen electrode) [1]. However, Li metal reacts with the organic liquid electrolyte to form a solid electrolyte interface (SEI) between the anode and the electrolyte, which is accompanied by continuous consumption of active Li atoms and the electrolyte, lowering the battery's energy density. Moreover, the “hostless” nature of Li metal anode induces “infinite” volume change during the Li plating/stripping process, which easily destroys dimensional integrity of the SEI layer and exposes the surface of fresh Li metal in the liquid electrolyte, giving rise to low coulombic efficiency. Consequently, the uneven deposition of Li metal occurs at the sites of the broken SEI, and Li dendrite growth is frequently observed. In a extreme case, the microscale dendrites can pierce the separator to cause safety problems. Currently, these problems are hindering the

development of Li metal battery [2–4].

Many methods have been developed to enhance the quality of SEI film *via* adopting electrolyte additives to stabilize it [5–9] or constructing artificial SEI film on the surface of Li metal to inhibit the growth of Li dendrites and realize uniform deposition of Li metal [10–14]. Frankly speaking, the modified SEI cannot guarantee a perfect cycling performance, because the huge volume fluctuation of the Li anode in the process of charging/discharging has not been solved [15].

Recently, Li metal composite electrode with a three-dimensional (3D) architecture as the porous skeleton has been intensively investigated since the 3D porous structure can provide void space for Li deposition and inhibit the volume change of the Li anode [16,17]. Furthermore, the enlarged specific surface area of the porous conducting host can effectively reduce the local current density to suppress Li dendrite growth [18,19]. As we know, copper (Cu) sheet is the most commonly used current collector in commercial Li-ion batteries in terms of its electrochemical inertness, low price, and mechanical strength. Therefore, a variety of 3D porous Cu current collectors have been designed [20,21]. Yang *et al.* [20] synthesized Cu nanowire arrays on planar Cu foil as a 3D framework to guide uniform deposition of metallic Li within the porous structure, resulting in greatly improved cycle performance. Following this pioneer work, commercially available and home-made Cu foams have been widely explored as 3D hosts [22–24]. In addition, nickel (Ni) foam was also proposed as the porous host for pre-storing Li metal *via* thermal infiltration, resulting in the formation of the composite Li anode with a stable framework and enhanced electrochemical performance [25]. Recently, Zhang and co-workers [26] used carbon fibers as matrix materials to fabricate Li-matrix anode, which was then protected by a solid electrolyte layer. The upper solid electrolyte layer possessed high mechanical strength and uniform Li ion diffusion capability and the bottom matrix showed a robust structure, providing accessible electron paths and large interspace for Li deposition. Under the synergetic function of the two constituents, Li dendrites and volume expansion are well controlled.

It is well known that metallic Cu and Ni do not show strong lithiophilicity since large nucleation overpotentials are recorded for Li deposition relative to that of lithiophilic Au and Ag [27].

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Hence, uneven Li nucleation may occur occasionally, and then the reduced Li atoms prefer to deposit on the nucleation sites, leading to quick appearance of Li dendrites [28]. Therefore, it is necessary to modify the native metal foam for advanced performance. To reduce the Li nucleation overpotential, the idea of decorating metallic foam with lithiophilic surface has been applied including the coating of oxide, sulfide, and Li alloy [29–35]. Taking the widely applied ZnO layer as an example, ZnO reacts with Li to form LiZn alloy and Li₂O [31], leading to the significantly improved wettability of Cu foam toward Li *via* the alloy sites. Herein, the well dispersed LiZn nanoparticles on the foam surface can lower the nucleation overpotential and induce uniform Li growth *via* superior lithiophilicity of Zn/LiZn. Moreover, Huang and co-workers [36] developed a one-step method by simple vulcanization of Cu foil to *in situ* form a modified layer of Cu₂S nanoparticles, where the nucleation overpotential of Li was significantly lowered with the assistance of the Cu₂S lithiophilic layer. Very recently, 1D/2D substances have been anchored on the 3D hosts [37–45]. Sun *et al.* [39] introduced tightly arranged ZnO nanorods on Ni foam, where the high aspect ratio of these nanorods offered a large electrode surface area, leading to further reduced local current density and efficient suppression of Li dendrites. Moreover, the nanorod arrays confine Li deposition within the matrix without any discernible anode volume change during cycling. Accordingly, Tao's group [43] prepared a 3D Cu@Sn nanocone current collector which was synthesized using a simple electrodeposition approach to grow Sn-modified Cu nanocone array on a planar Cu foil. The Cu@Sn nanocones can facilitate uniform electric field and the dispersion of current density to inhibit Li dendrites. Huang *et al.* [44] prepared lithiophilic Co₃O₄ nanosheet arrays-decorated Ni foam. The Co₃O₄ nanosheets provide a perfect wettability toward Li and achieve uniform Li stripping/plating. Besides, Lu and co-workers [45] demonstrated a facile strategy for coating uniform aluminum-zinc oxides (AZO) layers on Cu foams, which improved the lithiophilic property of Cu foams and achieved uniform Li deposition. It should be noted that the size of these lithiophilic species is no more than 1000 nm, which may collapse due to the repeated alloying/de-alloying reaction in the process of Li plating/stripping [35]. Additionally, these lithiophilic composites consisting of Li alloy and oxide are poor conductors, which inevitably increase the internal resistance [3].

Up to now, the surface modification of the 3D porous host has been intensively investigated. Unfortunately, the role of the porous structure itself has not been discussed deeply. As we know, the areal capacity of commercial Li-ion battery is around 3 mA h cm⁻², which is nearly equal to 15 μm in thickness of Li metal film. Apparently, the surface effect of the substrate is negligible while the deposited Li layer is thicker than 1000 nm [46]. Generally, the lithiophilic species anchored on the porous architecture is no more than few micrometers in length. It means that the upper part of the deposited Li may growth uncontrollably even inside the modified porous host. Moreover, the pore size of these conventional porous materials is larger than 100 μm. That is to say, the local environment at the spots far from the framework should be very similar to that of the conventional plane Li metal, which might be the reason responsible for the failure of Li composite anode after limited cycles [21,47,48]. Apparently, it is urgent to decrease the pore size of 3D host and perfect the functions of the scaffold while designing the advanced composite Li anode. Following this idea,

to build a secondary network structure nested in the macropores of the 3D host is a facile but feasible approach [49].

In our group, a series of dual-phase Li-rich alloy composites including Li-Ca [50], Li-Zn [51], and Li-Cu [52] have been prepared *via* a thermal infusion method, where the phase-segregation process leads to a Li alloy phase as a 3D scaffold dispersed in the matrix of Li metal phase. Recently, Li-rich alloys such as Li-B [53], Li-Si [54], Li-Ag [55], Li-Mg [56], and Li-Sn [57] have also been reported by other groups, showing highly improved electrochemical performance. Taking the Li-Cu dual-phase alloy composite as an example, the Li_xCu alloy nanowires with a diameter of about 100 nm and a length approaching centimeter scale can self-assemble into a randomly aligned network that is subsequently used as the 3D skeleton to alleviate the volume change and regulate Li stripping/plating behaviors. However, this built-in alloy framework is not robust enough to guarantee successful fabrication of self-standing composite anode films since the diameter of these nanowires is quite small.

Herein, the merits of both metallic porous foam and Li-Cu dual-phase alloy are tightly combined, leading to the production of a novel composite Li anode, in which a Li_xCu solid solution alloy nanowire network is nested in commercial Ni foam *via* a simple thermal infiltration treatment. After the molten Li-Cu alloy is accommodated in the Ni foam, the Li_xCu alloy nanowires are *in situ* generated *via* phase segregation in the cooling process, which act as a secondary network to split the macropores into smaller micropores (Fig. 1). At the same time, the phase segregation process leads to the appearance of Li metal phase, resulting in the formation of a three-component composite self-standing sheet consisting of Li metal, Li_xCu alloy frame, and Ni porous host (noted as Li-Cu@Ni) with the weight ratio of 48.85%, 7.4% and 43.75%, respectively. Different from the pristine Ni foam, the lithiophilic Li_xCu nanowire framework provides a larger surface area for Li nucleation and lower local current density to effectively inhibit Li dendrite growth. Furthermore, the coupling of microscale alloy framework and macroscale Ni host leads to the formation of a multi-scale scaffold, where the synergistic effect ensures a stable performance of the Li plating/stripping. As a result, the Li-Cu@Ni composite anode sheet shows better performance in comparison with the Li-Cu alloy anode and Li@Ni composite anode. Under the condition of carbonate-based electrolyte, the Li-Cu@Ni electrode is cycled up to 1200 h at a current density of 1 mA cm⁻² and an area capacity of 1 mA h cm⁻² in a Li/Li symmetric cell. Even at a higher current density of 3 and 5 mA cm⁻², the cyclic lifetime is more than 500 and 300 h, respectively. The capacity can retain about 95% after 1000 cycles in a Li₄Ti₅O₁₂ (LTO)-based full cell at a current rate of 5 C.

EXPERIMENTAL SECTION

Preparation of Li-Cu@Ni

Ni foam was punched into disks with a diameter of 15 mm. Then these Ni disks were cleaned by performing consecutive ultrasonication in ethanol for 10 min and dried at 60°C. The fabrication of Li-Cu alloy was carried out in an argon-filled glove box (Mikrouna) with less than 0.01 ppm oxygen and 0.01 ppm H₂O. At first, the mixture of Cu foil and Li foil was heated up to 400°C on a stainless steel (SS) foil with an atomic ratio of 1:60. Then the Cu foil was slowly dissolved in the liquid Li, resulting in the formation of the molten Li-Cu alloy. Following that, the Ni foam

Figure 1 Schematic of the behavior of Li plating on the (a) Ni foam and (b) Cu@Ni foam.

disk was quickly infiltrated into the liquid alloy while contacting the disk with the molten liquid. Finally, the Li-Cu@Ni composite anode was produced *via* a quick cooling treatment.

Characterization

X-ray diffraction (XRD) patterns were recorded using Cu K α ($\lambda = 0.154056$ nm) radiation at a scanning rate of 5° min^{-1} over the 2θ range from 20° to 80° . The anode morphology was obtained on a field emission scanning electron microscope (FE-SEM, Hitachi, S3400N) at 20 kV.

Electrochemical measurements

Battery testing was carried out with a CT2001A cell test instrument (LAND Electronic Co. Ltd.) at constant temperature (25°C). Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Parastat 2263) in the frequency range of 1 MHz to 100 mHz. To estimate the electrochemical behavior of the Li-Cu@Ni anode, the symmetrical cells were assembled in a CR2032 coin cell, where two identical Li-Cu@Ni electrodes or Li@Ni composite electrodes were used. The electrolyte was 1.0 mol L^{-1} Li hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v) with 5 vol% fluoroethylene carbonates (FEC). The amount of the electrolyte in each cell was fixed at 100 μL , and Celgard 2325 was used as the separator sheet.

For the full cell test, the LTO, LiFePO₄ (LFP) or LiCoO₂ (LCO) cathode was paired with Li@Ni or Li-Cu@Ni composite anode which was loaded 27.6 mg cm^{-2} of Li with a diameter of 12 mm. The active material powders with super P and polyvinylidene fluoride (PVDF, binder) (8:1:1, wt/wt) were mixed in *N*-methyl-2-pyrrolidone (NMP) to form uniform slurry, which was pasted on an aluminum (Al) foil and further dried at 110°C under vacuum for 12 h. The Celgard 2325 was used as the separator sheet with a diameter of 19 mm. The areal loading of LTO was about 2 mg cm^{-2} ($0.35 \text{ mA h cm}^{-2}$). The areal loadings of LFP and LCO were about 17.2 mg cm^{-2} ($2.45 \text{ mA h cm}^{-2}$) and 11.9 mg cm^{-2} (1.7 mA h cm^{-2}), respectively. The LTO, LFP and LCO cathode sheets were punched into disks with a diameter of

10 mm. The amount of electrolyte used was fixed at 100 μL . The full cells were cycled between 1.0–3.0 V for LTO cells, 2.2–3.85 V for LFP cells and 3–4.2 V for LCO cells.

RESULTS AND DISCUSSION

The top-view and side-view SEM images of the desired states were recorded and illustrated in Fig. 2a–h. A continuous 3D scaffold structure of the bare Ni foam is clearly displayed in the SEM images (Fig. 2a, e), where the pore size is as large as $\sim 300 \mu\text{m}$ and the neighboring void spaces are well connected. After the Li-rich dual-phase Li-Cu alloy was filled in the macropores, the as-obtained Li-Cu@Ni composite anode became dark, which was different from the silver color of the Ni foam according to the optical photos (the insets of Fig. 2a, b). The Ni framework is still visible either on the surface or in the bulk of the composite (Fig. 2b, f), indicating the molten Li-Cu alloy does not destroy the structure of Ni foam. Fig. S1 shows the XRD pattern of the Li-Cu@Ni composite. The diffraction peaks of Li_xCu are obviously down-shifted relative to those of the standard Cu peaks (Fig. S1b–d), indicating the formation of the Li_xCu solid solution alloy with expanded interplanar distance [52]. As a reference, the peak position belonging to the Ni foam is fixed, confirming that the Ni skeleton remains intact and no alloy phase is formed. Moreover, Li metal phase is also dominant in the XRD pattern. Conclusively, the Li-Cu@Ni composite consists of Li metal phase, Li_xCu alloy phase and Ni foam.

In order to reveal the morphology of the Li_xCu alloy phase, the Li-Cu@Ni composite was immersed in deionized water so as to selectively dissolve all of Li metal phase. As shown in Fig. 2c, the large pores of Ni foam are fully filled with the randomly arranged nanowires. The cross-sectional SEM image in Fig. 2g illustrates that these Li_xCu alloy nanowires are uniformly dispersed from the top surface to the bottom of the electrode. That is to say, the Li_xCu nanowires are assembled into a stable and conductive network, and the pore size of Ni foam is reduced to a few micrometers or even nanometer scale. The macroscopic Ni foam and microscopic Li_xCu network are successfully integrated as the multiscale and multifunctional scaffold, in which the

Figure 2 (a) The top-view and (e) side-view SEM images of the Ni foam and (b, f) Li-Cu@Ni, where the insert images are the corresponding optical photographs. (c) The top-view and (g) side-view SEM images after removing all of Li from Li-Cu@Ni. (d) The top-view and (h) side-view SEM images of the state after plating 5 mA h cm^{-2} of Li back. The inset is the corresponding high-magnification SEM image.

robust Ni foam offers dimensional stability of the electrode, and the secondary scaffold of the Li_xCu nanowire network enlarges the electrochemical active area and effectively suppresses the formation of Li dendrites. Remarkably, this sub-scaffold is *in situ* formed in the process of preparing the composite. Despite the two sets of inactive scaffolds, the Li-Cu@Ni composite anode still has very high specific capacity. As shown in Fig. S2, Li-Cu@Ni can still provide a specific capacity of about 1690 mA h g^{-1} after being delithiated at -2 V , which is very close to the theoretical specific capacity of 1886 mA h g^{-1} (Table S1).

Fig. 2d is the top-view SEM image after plating 5 mA h cm^{-2} Li back in the fully delithiated Li-Cu@Ni composite anode at 1 mA cm^{-2} . The deposited Li changes the surface morphology of the electrode completely. Although there are a lot of micropores on the surface, the Li-Cu@Ni composite anode is relatively flat without forming Li dendrites. The pore size is greatly reduced, and each of the alloy nanowires is well covered with the deposited Li metal. Fig. 2h is the corresponding side-view SEM image, revealing that the reduced Li prefers to be deposited on the alloy nanowires scaffold because of the lithiophilicity of Li_xCu nanowire network. The electroplated metallic Li exhibits a uniform and compact deposition on the top surface and the bottom of the anode. On the contrary, the electroplated Li on the bare Ni foam (Fig. S3) shows different behaviors. A large amount of dendritic and mossy Li appears on the Ni framework, which is loose and uneven because of the large nucleation overpotential of Li on the Ni foam. These dendrites grow quickly and eventually pierce the separator after limited cycles, causing safety issues. Moreover, the Li stripping/plating behavior of Li-Cu@Ni was also investigated (Fig. S4). After stripping 10 mA h cm^{-2} of Li, the Li_xCu alloy network is clearly exposed, dividing the Ni foam into interpenetrated microporous structures. When the deposition areal capacity is 5 mA h cm^{-2} , the reduced Li atoms preferentially fill these micropores, resulting in the uniform and dense morphology within the Ni foam. As the Li deposition capacity further increases to 10 mA h cm^{-2} , the Li_xCu nanowires are completely covered. The deposited Li on the surface of the skeleton is very smooth and no Li dendrites are observed. The morphology evolution on the surface and in the

bulk of the composite anode demonstrates that the secondary scaffold of the lithiophilic nanowire network nested in the Ni foam is able to induce conformal deposition of Li metal, providing a dendrite-free morphology.

Galvanostatic charge/discharge measurements at different current densities with a total capacity of 1 mA h cm^{-2} were conducted to evaluate the electrochemical performance of the symmetric cell, which was assembled with two identical Li-Cu@Ni composite electrodes. In order to highlight the role of the Li_xCu nanowire secondary network, Li@Ni anode was prepared for comparison. The voltage-time profile was utilized to monitor any instability during the cycling, in which the voltage hysteresis referred to the sum of overpotentials for the Li plating/stripping process. As shown in Fig. 3a, the Li-Cu@Ni anode shows a lower stripping/plating overpotential of $\sim 35 \text{ mV}$ for 800 h at 1 mA cm^{-2} , then the voltage hysteresis gradually increases and finally the Li-Cu@Ni anode can cycle up to 1200 h. In contrast, the Li@Ni anode exhibits an overpotential of $\sim 60 \text{ mV}$ in the initial stage, which is almost twice that of the Li-Cu@Ni anode. Furthermore, the voltage hysteresis is larger than 500 mV at 750 h, which should be ascribed to the formation of “dead Li” layer, and then an abrupt voltage drop is recorded, indicating the short circuit of the cell induced by the Li dendrites. When the current density increases to 3 mA cm^{-2} or even 5 mA cm^{-2} , the Li@Ni anode exhibits larger overpotential beyond 500 mV at 200 and 120 h, respectively. Then the voltage fluctuation is observed at 220 and 180 h, respectively, suggesting the short circuit is formed in a short period. This phenomenon is attributed to the fact that the high current density exacerbates the uneven deposition behavior of Li on Ni foam, resulting in quick growth of Li dendrites. In sharp contrast, the Li-Cu@Ni anode not only has a relatively low overpotential of ~ 100 and $\sim 140 \text{ mV}$ at 200 and 120 h, respectively, but also exhibits a more stable stripping/plating process for a long term (500 h at 3 mA cm^{-2} and 300 h at 5 mA cm^{-2}). Even when the current density is increased to a harsh condition (10 mA cm^{-2} , 1 mA h cm^{-2}), the Li-Cu@Ni anode still exhibits a smaller voltage hysteresis for a prolonged cycling lifetime ($\sim 190 \text{ mV}$ at 80 h). Unfortunately, the Li@Ni symmetric cell displays an extremely

Figure 3 Electrochemical characterization of the symmetric cells. (a) Voltage hysteresis of the Li-Cu@Ni anode (red) and Li@Ni anode (black) with 1 mA h cm^{-2} at 1, 3, and 5 mA cm^{-2} , respectively. Nyquist plots of Li@Ni and Li-Cu@Ni symmetric cells (b) before and (c) after 50 cycles with 1 mA h cm^{-2} at 3 mA cm^{-2} .

unstable voltage profile with large hysteresis (Fig. S5a). To further test the cycling stability of the symmetrical cells under larger areal capacity, the capacity was increased to 3 mA h cm^{-2} and the current density to 3 mA cm^{-2} . The Li-Cu@Ni symmetrical cell could maintain a long-term cycling stability for 250 h. However, the Li@Ni symmetric cell shows a voltage fluctuation at 170 h, which means the Li dendrites pierce the separator and cause a short circuit (Fig. S5b). Further increasing the current density to 5 mA cm^{-2} and the areal capacity to 5 mA h cm^{-2} (Fig. S5c), the Li-Cu@Ni cell still shows much improved cycling stability for 180 h, which is one of the significantly effective result in carbonate electrolytes. Obviously, the Li-Cu@Ni symmetric cell has smaller voltage hysteresis and more stable stripping/plating platform for longer lifetime, demonstrating the better quality of SEI layer during the repeated plating/stripping. Compared with the published results (Table S2), the Li-Cu@Ni electrode in symmetric cell shows the best cycling performance even at higher current densities in the carbonate-based electrolyte. The possible reason is that the uniform Li deposition/dissolution in the Li-Cu@Ni structure contributes to superior electrode interface stability and eliminates Li dendrites and “dead” Li significantly. In other words, the Li-Cu@Ni anode possesses larger surface area and better affinity to Li, thereby improving the cycle reversibility and stability of the cell.

The Nyquist plots of the impedance spectra were used to evaluate the interface property for the Li@Ni and Li-Cu@Ni symmetric cells. Fig. 3b shows the impedance plots of Li@Ni and Li-Cu@Ni symmetrical cells before cycling. The radius of the

semicircle in the high frequency region reflects the charge transfer resistance (R_{ct}). Before cycling, the R_{ct} of the Li-Cu@Ni symmetric cell is $\sim 200 \Omega$, slightly lower than $\sim 225 \Omega$ of Li@Ni symmetric cell. Benefiting from the Li_xCu alloy nanowire network, a more stable electrode/electrolyte interface is formed on the Li-Cu@Ni electrode. After 50 cycles at 3 mA cm^{-2} (Fig. 3c), the R_{ct} of Li@Ni is $\sim 32 \Omega$, while that of Li-Cu@Ni is only 13Ω . The smaller interfacial impedance of the cycled Li-Cu@Ni electrode reflects that the Li_xCu nanowire scaffold can optimize the Li deposition process and enhance the quality of SEI layer.

In order to reveal the morphology evolution of the cycled electrodes, the SEM images of Li@Ni and Li-Cu@Ni electrodes were collected after 50 cycles at 3 mA cm^{-2} with the areal capacity of 1 mA h cm^{-2} . As shown in Fig. S6a, the surface of the pristine Li@Ni anode is flat and smooth, and the Li metal is completely perfused inside the large pores of Ni foam (Fig. S6b). After 50 cycles (Fig. 4a), many cracks appear on the surface of Li@Ni electrode since the stripping/plating reaction prefers to occur near the Ni skeleton due to its high electronic conductivity and small reaction impedance. The deposited Li layer is loose and as thick as about $20 \mu\text{m}$, displaying a rough surface with many Li dendrite clusters and mossy Li (Fig. 4b, c). As for the Li-Cu@Ni anode, although the metallic Li prefers to appear on the surface (Fig. 4d) after 50 cycles, the surface of the Li-Cu@Ni anode is relatively smooth without any cracks and Li dendrites. As shown in Fig. 4e, f, the cross-section of the cycled Li-Cu@Ni anode has a dendrite-free morphology without significant change in the thickness. Because of the electrochemical inertness

of Li_xCu alloy nanowires, the Li_xCu skeleton can keep excellent mechanical stability with no structure evolution observed during repeated plating/stripping. This result can be attributed to the lithiophilicity of the Li_xCu nanowire network, which leads to a uniform Li deposition. Consequently, the stability of the Li-Cu@Ni anode has been greatly improved since the potential safety problem caused by Li metal is greatly alleviated.

The role of Li_xCu nanowire network was further highlighted *via* assembling full cell, which was fabricated by pairing Li@Ni or Li-Cu@Ni anode with LTO cathode. The typical discharge/charge curves at 1 and 5 C are illustrated in Fig. 5a, b. Obviously, the difference in the specific capacity is mainly determined by the voltage gap between the charge and discharge plateaus. The voltage hysteresis is 14 mV for Li-Cu@Ni at 1 C, which is smaller than 20 mV for Li@Ni. This tendency is further confirmed at the highest current rate of 5 C, in which the voltage hysteresis of Li-

Cu@Ni cell is 20 mV, much smaller than 70 mV of the Li@Ni cell. The smaller voltage hysteresis leads to the larger specific capacities. As shown in Fig. 5c, the rate performances were compared. The cell with Li-Cu@Ni anode shows specific capacities of 167, 160, and 155 mA h g^{-1} at 0.5, 1, and 2 C, respectively, which are higher than 155, 144, and 131 mA h g^{-1} of the Li@Ni cell. Especially at 5 C, the capacity with Li-Cu@Ni anode is 140 mA h g^{-1} . On the contrary, the capacity quickly declines to 50 mA h g^{-1} for the cell with Li@Ni anode. Apparently, the Li_xCu nanowire network in Li-Cu@Ni is helpful to maintain the electrochemical condition of the cell even under high current rates. This tendency is further proved by the long-term cycling test at 5 C as exhibited in Fig. 5d. The Li-Cu@Ni cell shows an initial capacity of 143 mA h g^{-1} , which remains 135 mA h g^{-1} even after 1000 cycles with high capacity retention rate of ~95%. By contrast, the Li@Ni cell only exhibits a low initial capacity of

Figure 4 The top-view SEM images of (a) Li@Ni and (d) Li-Cu@Ni after 50 cycles, side-view SEM images of (b, c) Li@Ni and (e, f) Li-Cu@Ni after 50 cycles. All electrodes were obtained from symmetric cells cycled at a current density of 3 mA cm^{-2} with the capacity of 1 mA h cm^{-2} .

Figure 5 Electrochemical performance of the Li-Cu@Ni/LTO cell and the Li@Ni/LTO cell (voltage profiles) at (a) 1 and (b) 5 C; (c) rate performance from 1 to 5 C; (d) long-term cycling performance at 5 C.

130 mA h g⁻¹, which rapidly declines to 83 mA h g⁻¹ after 200 cycles with the capacity retention rate of ~64%. As for the high-area capacity (Fig. S7), the Li-Cu@Ni/LFP full cell still can provide a long-term stability of up to 200 cycles at the rate of 1 C with a capacity retention of 83.2%, whereas the capacity retention of the Li@Ni/LFP cell drops to 56% in less than 100 cycles. Moreover, the Li-Cu@Ni/LCO cell can exhibit a capacity retention of 77.2% after 150 cycles at a rate of 0.5 C. By contrast, the capacity of the Li@Ni/LCO cell quickly decays from 98.5 to 35.8 mA h g⁻¹ within 130 cycles demonstrating a poor capacity retention of 30.6% (Fig. S8).

The experimental results clearly depict that the Li-Cu@Ni anode has superb electrochemical performance in terms of higher specific capacity, prolonged cycling lifetime, reduced voltage hysteresis and smaller interfacial impedance. Obviously, these improved electrochemical parameters originate from the Li_xCu nanowire network. This secondary network can not only enlarge the specific surface area of the scaffold to effectively inhibit the growth of Li dendrites, but also divide the macropores of Ni foam into micropores, restricting the plating/stripping behavior of Li in a limited space and rendering a uniform deposition of Li metal inside the Ni foam. The excellent performance of Li-Cu@Ni composite electrode in the configuration of both symmetric and full cells demonstrates the importance of constructing multifunctional sub-network in the porous framework, which paves a way for the practical application of Li metal anode in the visible future.

CONCLUSIONS

In this work, the Li_xCu alloy nanowires were self-assembled in the Ni foam as the secondary scaffold network, and meanwhile the Li-Cu@Ni composite anode was synthesized by infusing molten Li_xCu alloy inside Ni foam and cooling down to room temperature. The nanowire network splits the macropore of Ni foam into numerous micropores, greatly limiting the size of the deposited Li metal. Besides, the Li_xCu alloy nanowires act as the lithiophilic sites to induce uniform deposition of Li and offer large surface area efficiently suppressing the growth of Li dendrites. The synergetic effect between the primary Ni foam framework and the secondary scaffold of Li_xCu nanowire nest can perfect the cyclic stability even under extreme operation conditions. The symmetric cells can run for 500 h at 3 mA cm⁻² and 300 h at 5 mA cm⁻², and the LTO-based full cell exhibits excellent long-term cycling performance even after 1000 cycles at 5 C, which is much better than that of Li@Ni composite electrode. Nesting the primary porous skeleton with the secondary network is one of the possible ways to develop advanced Li metal composite anode. Particularly, further reducing the thickness of the porous metal skeleton and lowering the Li content in the anode are the key issues to design high-energy-density Li metal batteries for practical applications.

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Conflict of interest The authors declare no conflict of interest.

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

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Li_xCu 合金纳米线嵌套在泡沫镍中实现高度稳定的Li金属复合负极

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摘要 多孔金属骨架已经被广泛应用于制备Li金属复合负极的三维集流体,但其孔径通常达到几百微米,表面积有限,阻碍了其实际应用.在本工作中,我们通过将熔融的锂铜合金热灌入到泡沫镍中再进行冷却,原位形成了 Li_xCu 合金网络,整个体系由Li金属、 Li_xCu 合金和泡沫镍组成. Li_xCu 纳米线嵌套在泡沫镍内部,组成了次级网络,将泡沫镍的大孔结构分割成了微孔,增大了表面积,并显著诱导Li均匀沉积. Li_xCu 合金纳米线良好的亲锂性和次级网络减小的孔尺寸,可以进一步调控Li的成核和生长行为.泡沫镍和次级合金网络之间的多尺度协同效应使得复合负极即使在高电流密度下仍表现出超长循环稳定性.