Improving Li Plating Behaviors Through Cu–Sn Alloy-Coated Current Collector for Dendrite-Free Lithium Metal Anodes

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Abstract

Alloy anode with good reversibility of lithium plating/stripping and long cycling stability is considered as promising anode materials. Here, Cu–Sn alloy is used as the substrate for Li deposition to induce the most densely packed arrangement of Li atoms, thus presenting high lithiophilicity and improving Li plating behaviors. The LiFePO₄-based full cell with the as-prepared dendrite-free Li metal anode retained at 85 mAh g^{−1} with a high coulombic efficiency of 99.5% after 300 cycles, presenting a capacity retention of 79.4%. This strategy provides a new perspective to structure dendrite-free Li anode for the next-generation high-energy density batteries.

Keywords Li metal anodes · Dendrite-free · Composite electrode · Lithiophilic surface

1 Introduction

Metallic lithium electrode has been regarded as one of the most promising anode materials for high-energy batteries due to its high specific capacity (3860 mAh g^{−1}) and lowest potential (−3.04 V vs SHE) [1, 2]. However, Li metal anode suffers from several serious issues, including severe growth of dendritic or mossy Li caused by non-uniform Li deposition, which results in internal short circuit and safe accidents [3]; instable solid electrolyte interphase (SEI) promotes electrolyte consumption and electrode pulverization due to the high reactivity of Li metal, which leads to reduced coulombic efficiency (CE) and fast capacity decay upon cycling [4]. To date, considerable efforts have been devoted to solving these issues, including development of protective layers to reduce parasitic side reactions [5], adding electrolyte additives to produce stable SEI [6], employing solid electrolyte

to improve safety [7], constructing three-dimensional (3D) current collectors to reduce the effective current density during charge/discharge process [8, 9], modifying lithiophilic phases to decrease Li nucleation overpotential [10], and designing composite lithium electrodes based on Li melt infusion to alleviate electrode volume change during Li plating/stripping [11]. Among these approaches, using alloy anodes is a hopeful strategy for stabilizing Li metal anodes (LMAs) owing to the following advantages: (1) enhanced stability of metal-containing SEI and a smooth Li deposition morphology [12, 13]; (2) Li-poor alloy with high electronic/ionic conductivity can act as an excellent current collector and then host for Li plating [14]. Notably, Nazar and co-workers designed a Li-X alloy (X = In, Zn and Bi) SEI layer to guide uniform Li nucleation and deposition [14]. Luo's group reported the use of Cu–Zn alloy as artificial defects to lower the deposition interface energy for stable LMAs [15]. However, its high cost, sophisticated process and poor structure stability hinder its large-scale application and further development.

In this work, we report a facile approach to construct the lithiophilic nature of substrate to depress Li dendrites growth for safe and high-performance LMAs. This process is simply done by electrodeposition of Cu–Sn alloy on Cu foam. In addition, the lattice orientation of Sn is investigated, and it is found that it could enhance affinity between current collector and Li metal, achieving dendrite-free Li

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deposition. The as-prepared LMAs show high CE and long cycling life in LiFePO₄-based full cells.

2 Experimental

The synthesis of Cu–Sn-decorated Cu foam combined preparation of polystyrene (PS) template, Cu–Sn alloy electroplating, and a thermal annealing treatment. The clean Cu foam (CF) substrates were immersed in PS solution at 70 °C for 2 h. After drying, the PS template/CF was prepared and used as the working electrode for electroplating of Cu–Sn alloy. The electrolyte composition consisted of 33 mM Cu₂P₂O₇, 12 mM Sn₂P₂O₇, 0.33 M K₄O₇P₂, and 0.20 M K₂HPO₄. The electroplated electrodes were thoroughly rinsed with dichloromethane to remove the template. Finally, the electrodes were annealed at 260 °C for 2 h.

Electrochemical performances of the as-prepared electrodes were evaluated by CR2032-type coin cells using Celgard as separator and Li foil or LiFePO₄ cathodes as counter

electrode. The LiFePO₄ cathodes were composed of 80% LiFePO₄, 10% Super-P, and 10% PVDF binder. The electrolyte was 1 M LiTFSI in dioxolane (DOL) and dimethoxyethane (1:1, v/v) with 1 wt% LiNO₃. The CE of cells was characterized by discharging 1 mAh cm^{−2} and then charging to 1 V at a current density of 1.5 mA cm^{−2}. Galvanostatic cycling was carried out between 2.4 V and 4.2 V at 5 C.

3 Results and Discussion

Figure 1a shows the morphology of Cu foam, which is composed of a network of 3D interconnected ligaments, and demonstrates a rough surface of ligament consisted of irregularly shaped micro-size granules (inset in Fig. 1a). After electrodeposition of alloy on Cu foam, the Cu–Sn alloy with quasi-ordered pores was successfully coated on Cu foam surface, and Sn particles were uniformly grown on the substrate (Fig. 1b). TEM and the corresponding energy-dispersive X-ray spectroscopy element mapping results show

Fig. 1 SEM images of **a** Cu foam **b** Cu–Sn-decorated Cu foam (inset showing the morphology of Cu foam at high magnification and the digital photograph of Cu–Sn-decorated Cu foam). **c** TEM image and the corresponding **d** Cu, **e** Sn, **f** overlapping element mapping images. **g** XRD patterns of Cu foam and Cu–Sn-decorated Cu foam

that the distribution of Sn is around the surface layer while the distribution of Cu is around the central cores (Fig. 1c–f), which illustrated that metallic Sn was grown on Cu–Sn alloy substrate. XRD patterns of as-prepared electrodes show new diffraction peak of Sn (the {101} family of planes) and Cu–Sn alloy compared to Cu foam electrode (Fig. 1g), which is consistent with the above results.

The morphologies that Li electrodeposits form during the earliest stages of electrodeposition are known to play a critical role in the recharge of Li metal battery. The initial morphology evolution of Li deposition on different current collectors was investigated through SEM. It could be seen that Li deposition was guided by uniform Sn particles from Fig. 2a–c, forming a smooth Li coating layer on the substrate. While Li clusters grown on bare Cu foam, then clusters transformed into dendrites (Fig. 2d–f). Reducing the Li nucleation barrier could result in smooth Li deposition, so that Li dendrites were inhibited and electrochemical performance of Li anode was improved [16, 17]. Bulk Li deposited along the most stable (110) direction, which presented lowest nucleation barrier due to the {110} family of planes, had the most densely packed arrangement of atoms [18]. Electrodeposition on a heterogeneous substrate was preceded by under-potential deposition that affected by lattice mismatch between the substrate and the Li metal. Sn component in as-prepared electrode alloyed with lithium to form Li–Sn alloy layer, which alleviated lattice mismatch between the substrate and subsequent Li deposition. Moreover, the Sn (101) face could serve as appropriate orientation

for enhancing lattice coincidence with the Li (110) plane, enhancing affinity between current collector and Li metal, achieving dendrite-free Li deposition.

Electrochemical performance of Cu–Sn-decorated Cu foam and Cu foam electrode is demonstrated in Fig. 3. The Cu–Sn-decorated electrode maintained a high CE of 97% over 100 cycles, whereas that of the Cu foam electrode decreased sharply to below 3% after 75 cycles (Fig. 3a). Moreover, impedance spectra of Cu–Sn-decorated electrode revealed smaller interfacial resistance than Cu foam electrode after 120 cycles (Fig. 3b). The dendrite-free Li deposition induced stable SEI, improving the cycling performance of LMAs. Furthermore, the LiFePO_4 -based full cell with Cu–Sn-decorated electrode also exhibited enhanced cycling performance compared to that using the Cu foam electrode (Fig. 3c). The capacity of full cell with Cu–Sn-decorated electrode was retained at 85 mAh g^{-1} with a high CE of 99.5% after 300 cycles, presenting a capacity retention of 79.4% while the capacity of full cell with Cu foam electrode dropped to 20 mAh g^{-1} with a CE of 98.3%. In comparison with full cell with Cu foam electrode, the voltage profile of full cell with Cu–Sn-decorated electrode also shows lower voltage polarization. According to SEM images in Fig. 4, after 300 cycles, the surface of Cu–Sn-decorated Cu foam electrode was smoother than Cu foam electrode, and no obvious dendritic and mossy Li could be observed. In terms of the above results, the electrochemical performance of as-prepared 3D skeletons significantly is better than one of recently reported alloy modified skeletons [15, 19].

Fig. 2 SEM images of Li deposition on the Cu–Sn-decorated Cu foam substrate after **a** 0.5 mAh cm^{-2} , **b** 1.5 mAh cm^{-2} , **c** 3 mAh cm^{-2} of Li plating. SEM images of Li deposition on the Cu foam substrate after **d** 0.5 mAh cm^{-2} , **e** 1.5 mAh cm^{-2} , **f** 3 mAh cm^{-2} of Li plating

Fig. 3 **a** Coulombic efficiency (CE) of Cu foam and Cu–Sn-decorated Cu foam. **b** Impedance spectra of Cu foam and Cu–Sn-decorated Cu foam at 1.5 mA cm⁻² after 120 cycles. **c** Electrochemical performance of full cell with LiFePO₄ cathodes using Cu foam and Cu–Sn-decorated Cu foam as current collector at 5 C, **d** their voltage profiles for the 300th cycle

Fig. 4 SEM morphologies of **a** Cu foam/Li anode **b** Cu–Sn-decorated Cu foam from a full cell with LiFePO₄ cathode after 300 cycles

Metallic Sn has definite solubility in lithium metal so that it could generate a solid solution buffer layer before Li metal formation [20], and the Sn (101) face serves as appropriate orientation for enhancing lattice coincidence with the Li (110) plane, improving affinity between substrate and lithium, inducing uniform and dendrite-free Li deposition [21, 22]. Cu–Sn alloy-coated electrode with

high surface area is able to decrease local current density and suppress continued propagation of Li dendrite [23]. Alloy-induced dendrite-free Li plating improves the interfacial stability between Li and electrolyte and alleviates the formation of inactive Li, enhancing safe and long-life performance for Li metal batteries [24].

4 Conclusion

In this work, A Cu–Sn alloy-coated current collector was prepared through co-deposition technology for inhibiting Li dendrites. Sn component of Cu–Sn alloy shows high lithiophilicity with Li and is utilized as heterogeneous medium for Li deposition. Moreover, highly porous Cu–Sn alloy architecture with an increased surface area is designed to reduce local current density during Li plating/stripping. As a result, Cu–Sn alloy-coated electrodes exhibit uniform lithium deposition without dendritic formation, high CE, low interfacial resistance, and long cycling life. The LiFePO₄-based full cell with the as-prepared Li anode retained at 85 mAh g^{−1} with a high CE of 99.5% after 300 cycles. Surface engineering on current collector offers a promising strategy to structure dendrite-free Li anode and facilitate the practical application of Li metal batteries.

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