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High-performance CuO/Cu composite current collectors with array-pattern porous structures for lithium-ion batteries

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ABSTRACT

The surface structure and material composition of current collectors significantly affect the electrochemical performances of lithium-ion batteries. This study forms array-pattern blind holes and creates a layer of copper oxide (CuO) on the surface of thin copper plates using the chemical etching method. This copper plate is made into a CuO/Cu composite current collector with array-pattern porous structures for lithium-ion batteries. Using mesocarbon microbead graphite powders as the anode material, this new composite current collector is assembled into CR2032 coin half-cells for electrochemical tests. Batteries with this porous current collector exhibit high reversible discharge capacities of 383.9 $mAh\,g^{-1}$ at 0.5 mA and 374 $mAh\,g^{-1}$ even after 0.2C and 0.5C rate cycles, whereas batteries with a complanate current collector deliver only 309.6 $mAh\,g^{-1}$ and 296.7 $mAh\,g^{-1}$. It is believed that the array-pattern blind holes coupled with the morphological effects of the oatmeal-like CuO significantly enhance the electrochemical performances of batteries in terms of reversible capacity, cycling stability, electrical conductivity and coulombic efficiency.

1. Introduction

As one of the most successful applications in the electrochemical field, the lithium-ion battery (LIB) is considered to be a promising versatile power source and has been widely used in various fields because of its advantages, such as its high energy density, electrical potential and stability, low self-discharge, no memory effect, and so on [1–6]. Currently, with the rapid popularization of electric vehicles and portable electronic devices, it is of great urgency to enhance the electrochemical performance of LIBs in terms of reversible capacity, cycling stability, electrical conductivity, and so on [7–10].

However, the anode based on commercial graphitic carbon mostly shows a low theoretical capacity of 372 $mAh\,g^{-1}$, which cannot satisfy the requirement of future energy-storage devices with high power densities and energy densities [11–14]. Therefore, it is essential to explore new high-capacity anode materials for LIBs. In this regard, some researchers focus on the use of transition metal oxides (TMOs) based on a different conversion mechanism from graphite materials. As first reported by Poizot et al. [15], TMOs have been proven to have extremely high reversible capacities. Among all developed transition metal oxides, CuO is considered to be a promising candidate material for the anode of LIBs because of its high theoretical capacity of 674 $mAh\,g^{-1}$ and ease of preparation [16–21]. Zhang et al. [18] prepared a relatively pure CuO as the anode material for LIBs using a hydrothermal synthesis method, and the battery showed good capacity retention during high-rate cycles. However, the pure CuO in their studies inevitably decreases other battery performances because of its poor ion transport kinetics, inferior intrinsic electrical conductivity and large volume variation during the discharge-charge processes. To address this issue, some have proposed various optimization strategies [22–28]. For example, Lamberti and coworkers [22] presented an easy and effective strategy to prepare nanostructured cuprous oxide thin films directly on copper current collectors by a rapid thermal oxidation process. As a result, the batteries with these nanocomposite films exhibited excellent cycling stability and capacity retention due to the high surface area, short diffusion n path and good conduction of the nanocomposite films. Similarly, Wang et al. [27] fabricated porous CuO microspheres with a dandelion-like hollow structure using a hydrothermal synthesis method. Because these CuO microspheres, which have a large surface area and

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Nomenclature

CMC	carboxymethylcellulose
CNT	carbon nanotube
EIS	electrochemical impedance spectroscopy
LIB	lithium-ion battery
MCMB	mesocarbon microbead
PVD	physical vapor deposition
SEI	solid electrolyte interface
TMO	transition metal oxide

porosity, were used as the anode material, the battery exhibited stable capacity retention and high reversible capacities. Xiang et al. [28] reported a simple self-assembled synthesis of hierarchical CuO particles with various morphologies and concluded that the special structural features of CuO particles dramatically improved the discharge capacities and cycling performances of the battery. Obviously, the aforementioned optimization strategy mainly enhanced the electrochemical performance of LIBs by synthesizing CuO with various unique nanostructures and porous morphologies. Another popular method to optimize the anode structure is to fabricate a hybrid nanocomposite with conductive matrixes, e.g. carbon, carbon nanotubes and graphene nanosheets, and so on, to overcome the drawbacks of the inferior intrinsic electrical conductivity of CuO [29–34]. For example, Liu et al. [30] prepared CuO/C microspheres and applied them to the anode of LIBs. They found that this method yielded a better rate capability than pure CuO because of a series of positive effects from the carbon microspheres. Likewise, Ko et al. [34] introduced mesoporous CuO particles that were threaded with CNTs for LIBs and significantly improved the reversible capacity and rate capability of the batteries.

In addition, it is noteworthy that the current collector is considered to be a key component in LIBs, which helps carry electrode materials and collect the current. Therefore, the diverse surface structures of a current collector also play an important role in enhancing the electrochemical performances of LIBs. However, most commercially used current collectors for LIBs are made of electrolytic copper foils at the anode or aluminum foils at the cathode. According to their different morphological properties, copper- and aluminum-based foils either have smooth or rough surfaces on both sides, which significantly limits their application in future LIBs. In this regard, Poetz et al. [35] prepared a new three-dimensional cathode current collector for LIBs by physical vapor deposition (PVD) to increase the contact surface between the cathode material and current collector, which significantly improved the electrical conductivity of the electrode. Zhong et al. [36] and Choi et al. [37] presented a new method to prepare the cathode current collectors with excellent interface features by using carbon nanotubes (CNTs). They claimed that the structure of CNTs and the porous surface of CNT films improved the electrode conductivity. For the anode current collector, copper foams with a high porosity were fabricated by Yue et al. [38] and Li et al. [39], who successfully validated that the special structure of the copper foams effectively restrained the volume change of the anode materials. Moreover, for the higher performance of LIBs, Fan and coworkers [40,41] prepared porous copper plates as the anode current collectors by electrodepositing. Following this method, Jiang et al. [42] developed a valley-ridge copper architecture and systematically evaluated the structural advantages of the special copper framework in restricting severe volume changes of the anode materials.

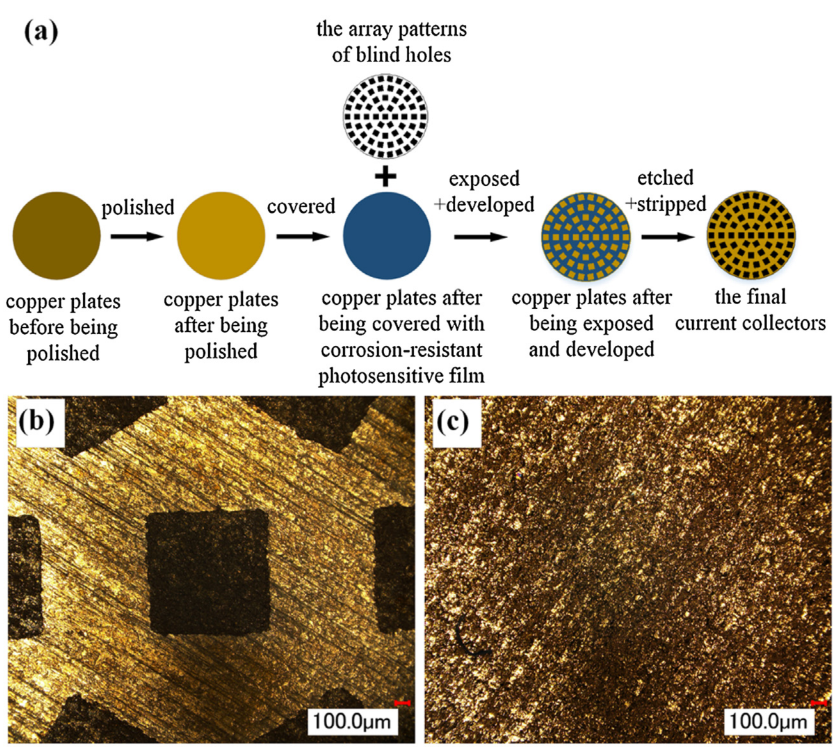

Fig. 1. (a) Procedure to prepare the CuO/Cu composite current collector with array-pattern porous structures; digital microscope images of (b) the porous current collector and (c) complanate current collector.