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# Hierarchical MCMB/CuO/Cu anode with super-hydrophilic substrate and blind-hole structures for lithium-ion batteries

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ABSTRACT

This study presents a hierarchical MCMB/CuO/Cu anode structure with super-hydrophilic CuO substrate and blind-hole structures (BHSs) for lithium-ion battery (LIB) application. The porous hierarchical CuO clusters with controllable morphology and super hydrophilicity are prepared and combined with the BHSs on the surface of copper plates (CPs). Results indicate that the new anode yields a considerable improvement in reversible capacity and robustness under the condition of rate cycles. Compared with the conventional pattern of MCMB/Cu, the MCMB/CuO/Cu anode with BHSs produces reversible initial discharge and charge capacities of 381.5 and 347 mAh $g^{-1}$ at a constant current of 0.5 mA. After 30 cycle times, the battery retains 276.7 and 276.6 mAh $g^{-1}$, which amounts to 5 times as much as that of 0.5 C rate cycles. The energy density of the battery can be also greatly promoted. The larger surface area and porosity of the new anode facilitate formation of contact interface between the active material and current collector (CC). It also helps shorten the diffusion path of Li-ions and alleviate the volume expansion during the insertion and desertion processes of Li-ions.

## 1. Introduction

Materials for harvesting and storing energy have been extensively explored in the last decades. In this field, lithium-ion batteries (LIBs) have been widely investigated because of its advantages such as high energy density, no memory effect, slow self-discharge rate and longer battery lifetime [1–5]. On the anode side, graphite as well as graphitized carbon, such as natural graphite, artificial graphite, mesocarbon microbeads (MCMBs), cokes and so on, is widely used for commercial LIBs. Among these candidate materials, the MCMB is considered as one of the most popular materials with commercial value, which has a better cyclic performance because of its spherical lamellar structure and lower specific surface area [6]. However, with the development of LIBs for portable devices, these materials fail to gain a higher capacity and energy density so as not to meet the increasing demand for a longer battery life, owing to its limited theoretical capacity ($LiC_6$, 372 mAh $g^{-1}$) [7–9] and energy density [4,10].

In order to improve the performance of traditional LIBs, many studies concentrate on modification of either the chemical composition or macroscopic structure of the components [5]. For example, graphene has been used as a novel flexible electrode in LIBs due to its excellent mechanical properties and high electrical conductivity [11,12]. However, the inherent tendency for $\pi$-$\pi$ stacking interactions of graphene nanosheets severely reduces the effective specific surface area, thereby limiting the diffusion of electrolyte ions [13]. To address this issue, some researchers further develop graphene/carbon nanotubes (CNTs) composite with different architectures [14]. The use of CNTs can help prevent restacking of graphene nanosheets, increase the cross-plane conductivity, and also improve the contact between graphene nanosheets [15]. Interestingly, it is effective to adopt carbon-based matrix or carbon coating on metal oxides to enhance the electrochemical performance of LIBs, especially for high-rate cycles. There is already evidence that the carbon component helps to elevate the electrical conductivity of the electrode and ameliorate the aggregation and pulverization of electrochemical active materials, thereby enhancing the cycle life [16,17].

Compared with the commercial carbonates-based anodes, the 3D transition metal oxides (TMOs, where M can be Fe, Co, Ni, and Cu, etc.), firstly reported by Tarscon et al. [18] are regarded as a potential substitute for graphite. However, such materials are likely to induce poor electronic conduction and large volume expansion, which inevitably lead to severe capacity fade and low rate performance due to inertial kinetics [19–21]. These drawbacks greatly

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hinder their practical application. Among the TMOs for possible use, CuO has attracted much attentions due to its high theoretical capacity (670 mAh $g^{-1}$), low-cost, non-toxic, easy preparation and preservation [22]. Like most of the TMOs, CuO also inherits the inferior performances in electric conductivity, ion transport kinetics and volume expansion/contraction during the cyclic processes [23,24]. These features directly lead to crystallinity decrease of CuO due to the conversion reaction mechanism [25], large loss of initial irreversible capacity, poor capacity retention over extended cycles, as well as cycle instability [26]. To overcome these challenges, creating nanostructures of CuO has been proven to be an effective solution [27–29]. Many efforts [30] have been made to fabricate the nanostructured CuO materials in the form of porous [31,32], hollow micro/nano-structures [33,34], hierarchical arrays [35–37], nanoparticles [38], nanorods, nanowires [39], nanoplates [40], and nanotubes [41]. These nanostructures take effect because they are more able to provide shorter transport paths for electrons and Li-ions. Furthermore, such well-defined structures can mitigate uneven volume change and withstand somehow mechanical strain due to their larger surface area and higher surface energy during the insertion and desertion of Li-ions.

Besides, other types of nanostructured hybrid electrode materials with novel architectures have been designed to deal with the aforementioned defects [42,43]. Some studies report on how to make three-dimensional branched heterostructures upon a conductive substrate, successfully validating their advantages including large surface area, efficient electron transfer, fast ion transport, easy electrolyte access to electrode, and good strain accommodation. In this case, the substrates not only serve as a physical support for nanoarrays but also provide the channels for charge transport. This is beneficial to maximize the utilization of electrochemically active materials [44–49]. Specifically, the formation of surficial CuO will lead to the loss of electrical conductivity but enhancement of antioxidation ability of Cu. Meanwhile, the Cu substrate helps improve its electrical conductivity and structure stability of copper oxides between substrate and active materials. As a result, the $Cu_xO$-Cu composite architecture exhibits multifunctional characteristics of Cu and $Cu_xO$, showing potential applications for LIBs [30].

Up to now, it is known that the current open literature focus more on the synthesis of chemical composite materials, macro/micro/nano-structure components, and sometimes double-layer composites as functional anodes for LIBs, breaking through a series of intractable issues from the perspective of functional structures. With the above background, in this study, we intend to optimize the surface properties of prepared current collectors (CCs) in order to enhance the electrochemical performance of LIBs. The core idea is to create substructures with super-hydrophilicity [50] upon the surface of copper plate (CP) via oxidation process so as to improve the adhesive strength between the active material and CC. The CuO clusters are synthesized directly from the raw material of CP in solution with no need for additional materials. Simultaneously, a macrostructure based on blind-hole structures (BHSs) combined with the oxidation is used to increase the contact interface area between the CC and active materials as well as decrease the residual strain of crystal lattice after the electrochemical reactions. Moreover, we prove that the CuO clusters on the surface of the copper plate can boost the energy density of LIBs due to fake-capacity reaction between the CuO and electrolyte. By combining the superior properties of CuO micro/nano-structures with the advantages of blind-hole macrostructures, we successfully realize preparation of a high-capacity anode with excellent energy density for LIBs.

## 2. Experimental

The procedure for preparing the experimental anode electrodes consists of etching the BHSs, forming CuO clusters on the surface of CC with the help of alkali-assisted surface oxidation, preparing slurry, coating, drying in a vacuum atmosphere and so forth. It should be noted that some steps described above may not be implemented in the individual experiments.

In this study, we chose MCMBs (Shenzhen Kejingstar Technology Co., Ltd) as the active material of working electrodes. The particle size distribution of the MCMBs (specific surface area is 1.0–2.0 $m^2$ $g^{-1}$) is ranged from 5 to 20 μm with a crystallization degree of 97.61%, as shown in Fig. 1c–d. Other auxiliary materials are prescribed as follows: carboxymethylcellulose sodium, styrene-butadiene rubber and carbon black (i.e. Super P) with a ratio of 2:2:3 wt %. These four materials were mixed evenly and treated in a stirring machine for 12 h. Then, the as-prepared slurry was pasted uniformly on the surface of treated CC in a coating machine (Shenzhen Kejingstar Technology Co., Ltd), followed by a drying process at 60 °C for 24 h under a vacuum infrared condition. Unless otherwise stated, all the involved chemicals were of analytical grade and as received without further purification.

### 2.1. Electrochemical test

To explore the performance of the working electrodes more accurately, electrochemical tests of the batteries were carried out using a coin cell (CR2032), as shown in Fig. 1a. The as-prepared electrode was used as the working electrode, and a lithium foil (Shenzhen Kejingstar Technology Co., Ltd, lithium content ≧99.9%) as both the counter and reference electrodes. The coin cells were assembled in an argon-filled glove box, using Celgard 2325 as the separator, and 1 M $LiPF_6$ (dissolved in ethylene carbonate, dimethyl carbonate and diethyl carbonate, with a 1:1:1 vol ratio) as the electrolyte.

After a period of 12 h for inner electrochemical equilibration within the cells, the galvano-static charge and discharge tests were carried out in the range of 0.002 and 3 V at different current densities on a commercial battery testing system (LAND CT2001A, Wuhan LAND electronics Co., Ltd). The cyclic voltammetry (CV) measurements were conducted on an electrochemical work station (CHI650D, Shanghai Chen Hua Instrument Co., Ltd) at a rate of 0.2 mV $s^{-1}$ over the potential range of 0.002–2 V. The tests of electrochemical impedance spectroscopy (EIS) were implemented with the sinusoidal excitation voltage (5 mV) applied to the batteries. The frequency was from 100 kHz to 10 mHz.

Since the equivalent circuit for the batteries with two-layer active material has been rarely proposed, we proposed an evolving solution based on the previous studies [51–55]. A self-developed equivalent circuit model suitable for fitting and analysis of the tested battery is shown in Fig. 1b. Here, the intercept at the $Z_{real}$ axis in high frequency of $R_s$ is the ohmic resistance including the electrolyte, and $R_{SEI}$ denotes the resistance for Li-ion conduction in the solid electrolyte interphase (SEI) film, and $C_{SEI}$ describes the space charge capacitance of the film [51]. The values of $C_{dl}$ and $R_{ct}$ represent the double layer capacitance and the charge-transfer resistance, respectively. Specifically, the constant phase element $Q_{dl}$ instead of pure capacitance is used for CuO material due to the non-ideal nature of the electrode [19]. $Z_w$ is the Warburg impedance arising from semi-infinite diffusion of Li-ion in the active materials [54]. $R_b$ and $C_b$ are the resistance and capacity characterizing the structure-change of the active material particles. Based on the combination of $R_b$ and $C_b$ with $C_{int}$, the accumulation and consumption of Li-ion during the solid-state diffusion process can be illustrated. The above three parameters, i.e. $C_b$, $R_b$, and $C_{int}$, describes the change of crystalline structures for active materials as well as the generation of new phase [55]. The parameters of