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Synthesis of CuO nanowire arrays as high-performance electrode for lithium ion batteries

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ABSTRACT

CuO nanowire arrays composed of nanoparticles are directly grown on Cu foam by a facile electrodeposition method. Free-standing CuO nanowires grow quasi-vertically on the substrate and show average diameters of ~180 nm as well as a length of ~20 μm. The as-prepared CuO nanowire arrays are tested as anode material of lithium ion. The resultant CuO nanowire arrays exhibit high specific capacity and good cycle stability (687 mAh g^{-1} at 0.2C (0.15 mA cm^{-2}) up to 120 cycles), as well as enhanced high-rate capability. The improved performance is mainly attributed to the one-dimensional nanowire architecture, which offers good strain accommodation, short electron/lithium ion transport path and excellent electrical contact between active material and current collector.

1. Introduction

Advanced lithium ion batteries (LIBs) with high energy density and high rate capability are critically important for next-generation energy storage systems [1–3]. In the past decades, efforts have been made worldwide to search for high-capacity anode materials that will be considered as alternative options to replace the currently commercialized graphite anode (372 mAh g^{-1}) [4]. Of the explored candidates, copper oxides (CuO) have been widely studied as anode materials for LIBs due to its high theoretical capacity of 674 mAh g^{-1}, low toxicity, low cost, environmental benignity and easy preparation [5,6]. The electrochemical conversion reaction of CuO with Li^+ is shown in the following reaction:

$$CuO + 2Li^{+} + 2e^{-} \leftrightarrow Cu + Li_2O \tag{1}$$

Each unit of CuO can react with two Li^+ to form a composite containing Cu nanoclusters embedded in amorphous Li_2O matrix, which reversibly converts back to CuO in charging process.

However, its poor conductivity and large volume change during the cycling process lead to electrode pulverization and loss of interparticle contact and, consequently, resulting in a large irreversible capacity loss and poor cycling stability [6,7]. In order to deal with these problems, researchers usually alleviate the adverse mechanical effects to improve the overall electrochemical performance of CuO anodes by coupling with a conductive matrix or construction of various nanostructures [8,9]. In particular, one-dimensional nanowire structures arouse considerable research interest due to their rich accessible electro-active sites and fast lithium ion diffusion [10]. To further improve the cycle stability and rate capability, one of the effective approaches is to fabricate CuO nanowire arrays directly on conductive substrates as electrodes, in which no binder and conductive agents are used without introducing undesirable interface.

In this work, we synthesize porous CuO nanowire arrays on Cu foam by a simple anodic electrodeposition method. Impressively, the electrochemical performance of CuO nanowire array is enhanced with high capacity and excellent cycling life. This enhancement is mainly benefited from the nanowire array configuration with high surface area, short ion/electron diffusion path, and direct growth on conductive substrate.

2. Experimental

The CuO nanowire arrays were prepared by a facile anodic electrodeposition method. The electrodeposition was performed in a standard three-electrode glass cell at 25 °C, the copper foam as the working electrode, Hg/HgO electrode as the reference electrode and a Pt foil as the counter electrode. The electrolyte was 1 M KOK. The anodic electrodeposition experiments were carried out at constant anodic current of 10 mA cm^{-2} for 2700 s. Finally, the as-prepared samples were rinsed and then annealed at 450 °C for 2 h in flowing argon.

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The morphology and microstructure of the sample were characterized by a scanning electron microscopy (SEM, Hitachi S-4700 and FESEM, FEI Sirion-100), transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 300 kV) and X-ray power diffraction (XRD, Rigaku D/max 2550 PC, Cu Kα).

The electrochemical tests were carried out using a coin-type half cell (CR 2025) with pure lithium foil as both the counter and the reference electrodes. The CuO nanowire arrays were directly used as the working electrode. Test cells were assembled in an Ar-filled glove box. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DME) (1: 1 in volume), a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator. The galvanostatic charge-discharge tests were conducted on a LAND battery program-control test system at room temperature (25 ± 1 °C). Cyclic voltammetry curves were scanned at 0.1 mV s^{-1} using an electrochemistry system (CHI660E).

3. Results and discussion

XRD (Fig. 1a) is performed to study the phase purity and crystal structure. Except for the peaks of copper foam, the left diffraction peaks of the sample can be identified as pure, well-crystalline, monoclinic symmetry of CuO phase (JCPDS80-1917). No other impurity peaks are detected, indicating the high purity of sample. The morphology and microstructure of the as-prepared CuO nanowire arrays are investigated by means of SEM and TEM. Fig. 1b shows that the skeleton of the Cu foam is uniformly covered by the CuO nanowires. Obviously, the CuO nanowires are homogeneously aligned and separated apart adequately, forming an array with a highly open structure on a large scale. And the average diameter and length are about 180 nm and 20 μm, respectively. From the relatively high-magnification SEM image shown in Fig. 1c, the surface of the nanowire is a little coarse. The detailed structural features of the CuO nanowire array are examined by TEM shown in Fig. 1d. The CuO nanowire is highly porous and composed of nanocrystallites of 20 – 40 nm leaving nanopores of 10 – 20 nm. Thus, all the CuO nanowires are highly accessible to electrolytes for energy storage due to the presence of convenient diffusion channels.

As for the formation mechanism, the involved reactions are simply illustrated as follows:

$$Cu - 2e^{-} \rightarrow Cu^{2+} \tag{2}$$

$$Cu^{2+} + 2OH^{-} \rightarrow Cu(OH)_2 \tag{3}$$

During annealing process:

$$Cu(OH)_2 \rightarrow CuO + H_2O \tag{4}$$

From the SEM and TEM results, it is noticed that the CuO nanowires are composed of interconnected nanoparticles with large-quantity pores, which is due to the successive release and loss of H_2O during the thermal decomposition of $Cu(OH)_2$ precursor.

The cyclic voltammogram (CV) of the obtained CuO nanowire arrays electrode is shown in Fig. 2a. During the first discharge, three cathodic peaks can be observed around 2.2, 1.2 and 0.75 V. It corresponds to the multi-step electrochemical lithium reaction processes related to the formation of $Cu_{1-x}Cu_xO_{1-x/2}$ solid solution, reduction to Cu_2O, further reduction to Cu and Li_2O, and the formation of solid electrolyte interface (SEI) film [11]. And two anodic peaks can be seen near 1.6 and 2.5 V, which are due to the partial decomposition of SEI film and reformation of CuO. Fig. 2b displays the galvanostatic discharge/charge curves of CuO nanowire array electrode measured at 0.2C (0.15 mA cm^{-2}). The plateaus on the voltage profiles coincide well with the cathodic and anodic peaks in the CV curve. And the first discharge and charge capacity of the CuO nanowire is 853.3 and 676.1 mAh g^{-1} respectively, corresponding to an initial columbic efficiency of 79.2%. The initial irreversible capacity

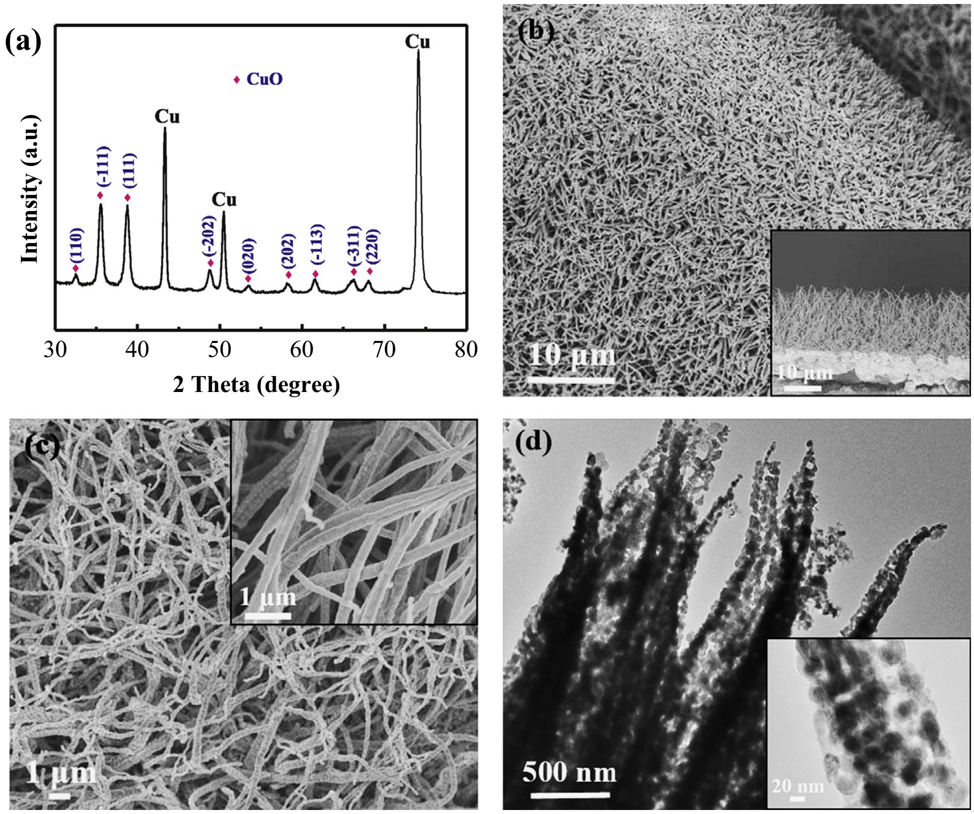

Fig. 1. (a) XRD patterns of CuO nanowire array; (b, c) SEM micrographs of CuO nanowire arrays at different magnification (cross-sectional image and (fine structure in inset); (d) TEM micrograph of CuO nanowire arrays (fine structure in inset).