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Copper oxide nanowire arrays synthesized by in-situ thermal oxidation as an anode material for lithium-ion batteries

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ABSTRACT

Copper oxide nanowires with an average length of 7.4 μm are prepared by in-situ thermal oxidation at 500 °C for 6 h in air, and their lithium storage performances are promoted by a further ammonia treatment. The morphologies, structures and lithium storage properties of copper oxide nanowire arrays are investigated by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy and a series of electrochemical measurements. The results show that after the reprocessing, the CuO nanowire arrays exhibit a higher reversible capacity of 645 mAhg^{-1} after 100 cycles at a current density of 50 mAg^{-1}, excellent cyclability and high-rate capability. The good electrochemical performance and simple preparation process make it a promising anode material for lithium-ion batteries.

1. Introduction

As an important class of one dimension nanostructures, nanowire matierials, under the condition of low-dimensional and confined space [1,2], have been shown many unique characteristics in electronics, optoelectronics, field emission, electrochemistry and some other territories. In particular, the semiconductor nanowires, as an important type, have become a very promising material for nano-devices and very large scale integrated circuits manufacturing [3].

Transition metal oxide CuO, a p-type semiconductor with a high theoretical capacity of 674 mAh g^{-1}, low toxicity, low cost and easy preparation, has been used as electrode materials in lithium batteries for decades [4–6]. However, its poor conductivity and large volume change in the cyclic process results in capacity attenuation [7–9]. In order to deal with these problems, scientists usually employ nanocrystallization and composite process to change the microstructures of the CuO anode materials. Sun et al. [10] directly deposited CuO nanoribbons array on a copper current collector by one-step synthesis route, and found that the CuO nanoribbons, after 275 cycles at a current density of 175 mAh g^{-1}, still exhibited a reversible capacity of 608 mAh g^{-1}. Song et al. [11] prepared an interesting CuO hollow nanoparticles/graphene nanosheets composite with the advantages of graphene and hollow CuO structures by using the Kirkendall effect. The composite exhibits not only excellent high-rate performance but also outstanding cyclability, even after 300 cycles at a current density as high as 500 mA g^{-1}, still remains a capacity of 448 mAh g^{-1}. Although many different kinds of CuO nanostructures and composites [12–14] have been developed, and their electrochemical capacity and cycling performance are improved at some level, the requirement of strict control conditions in the preparation of CuO materials, such as reaction temperature, solution pH, and reactants concentration, has made the synthesis process complicated. And certain raw materials will increase the preparation cost [15].

As an interesting occurrence of the growth of CuO nanowires during the in-situ thermal oxidation of copper in air, there has been many articles to report the study and applications of this phenomenon [16–23]. In our study, in-situ thermal oxidation was adopted to prepare CuO nanowire arrays (NWAs). The CuO nanowires grown on the oxides scale present a high aspect ratio, large-scale and aligned morphology. In this paper, in order to promote the electrochemical performance of NWAs, a simple ammonia treatment was performed to remove the Cu_2O layer. The effects of this retreatment on the morphology, structure and electrochemical performance of copper oxide arrays were investigated in detail.

2. Experimental

2.1. Samples preparation

In a typical synthesis procedure, a copper foil (99.99% purity) with a thickness of 0.2 mm and a size of 20 mm × 15 mm was first dipped into an aqueous solution of 1 mol/L HCl for 10 min to purge

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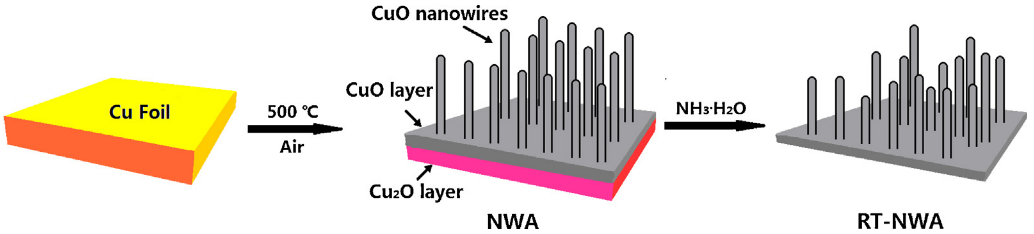

Fig. 1. The fabrication of NWAs and RT-NWAs.

the oxide layers on the surface, and rinsed in deionized water, then cleaned by acetone under an ultrasonic bath for 5 min and dried in N_2 flow afterwards. The copper foil was placed in an alumina boat and loaded into a box furnace, annealed at 500 °C for 6 h in air with a heating rate of ~10 °C/min. After the oxidation process, the sample was cooled down to room temperature by furnace cooling. Finally, the black thin oxide scale i.e., NWAs, comprising both CuO and Cu_2O, was peeled off carefully and set aside. In order to remove the Cu_2O layer, a reprocessing of NWAs was performed based on its easy dissolving in ammonia solution. The NWAs was soaked in an ammonia solution (13 M) for 48 h, then seperated by filtration and washed by deionized water for several times until neutralization, after dried in oven at 60 °C for 12 h we obtained the product recorded as RT-NWAs. The fabrication scheme of NWAs and RT-NWAs is shown in Fig. 1.

2.2. *Characterization*

The morphologies of NWAs and RT-NWAs were characterized by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700). The phases determination was performed by X-ray diffraction (XRD; Rigaku D/max-2500B2+/PCX system with CuKα=1.5406 Å, 2θ=5–90°). The detail of the microstructures was identified by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010F).

2.3. *Electrochemical investigation*

Electrochemical performances of the as-products were measured with two-electrode coin-type cell with lithium foil as counter electrode. The working electrode was prepared by smearing the slurry, formed by dispersing the mixture of 65% active mass, 20% acetylene black and 15% poly(vinylidene difluoride) in N-methyl pyrrolidinone, on nickel foam sheets, and drying the working electrode in a vacuum oven at 80 °C for 4 h and then at 120 °C for 12 h. Assembling procedure of the cells was performed in a re-circulating argon glove box and the electrolyte was a 1 mol/L $LiPF_6$ solution in a mixture of ethylene carbonate/dimethyl carbonate (1:1 v/v). The galvanostatical charge-discharge tests were carried out within the potential range of 0.01-3 V vs. Li/Li^+ at the current densities of 50, 500 and 1000 mA g^{-1}, respectively. Electrochemical impedance spectroscopy(EIS) and cyclic voltammetry (CV) measurements of the working electrode were taken on an electrochemical workstation (CHI 660B). AC impedance spectra were obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz. The cyclic voltammograms were obtained over the potential range of 0.01-3 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1}.

3. Results and discussion

3.1. *Characterization of NWAs and RT-NWAs*

XRD was performed to investigate the phases of as-products with the results shown in Fig. 2. The XRD pattern of NWAs show peaks of both Cu_2O and CuO. The strongest peak at 2θ=36.4° can be indexed to the (111) crystal plane of Cu_2O, and the peaks at 2θ=29.6°, 42.3°, 61.3°, 73.5° and 77.3° are also in good conformability with the diffraction pattern of cubic Cu_2O phase(JCPDS No.77-0199, as shown by blue rhombus in Fig. 2). Although the characteristic peaks of CuO are weaker than those of Cu_2O, on the sides of the most prominent peak are two bands at 2θ=35.5° and 38.7° corresponded to the (-111) and (111) planes of the monoclinic CuO, respectively. The intensity comparison between the respective peaks illustrates that the amount of the Cu_2O layer is greater than the sum of CuO layer and nanowires, while in the XRD pattern of RT-NWAs, all the diffraction peaks can be indexed completely to the standard pattern of monoclinic symmetry CuO (JCPDS No.80-0076,as shown by red box in Fig. 2). The change of the spectra should be attributed to the reprocessing of removing all the Cu_2O phase on NWAs.

Fig. 3 shows the SEM and HRTEM images of NWAs. Fig. 3a illustrates that the CuO nanowires grown in NWAs are very dense and of high aspect ratio. A statistical measurement shows that the average length and diameter of the nanowires are 7.4 μm and 0.3 μm, respectively, and the growth density is ca. 4.38 per μm^2. Fig. 3b shows a cross-sectional view of NWAs, from which we can see that the nanowires are quite aligned and almost perpendicular to the oxide scale surface. Another noticeable phenomenon is that the oxide scale nanowires growing on can be divided into three layers: a top nanowires layer,a thin intermediate layer and a thick bottom layer which is directly in contact with Cu substrate. It is found that the thickness of the intermediate layer is ca. 1.2 μm, and the bottom layer is ca. 7.6 μm. According to the oxidation law of metal copper in air, we could consider that the intermediate layer is CuO

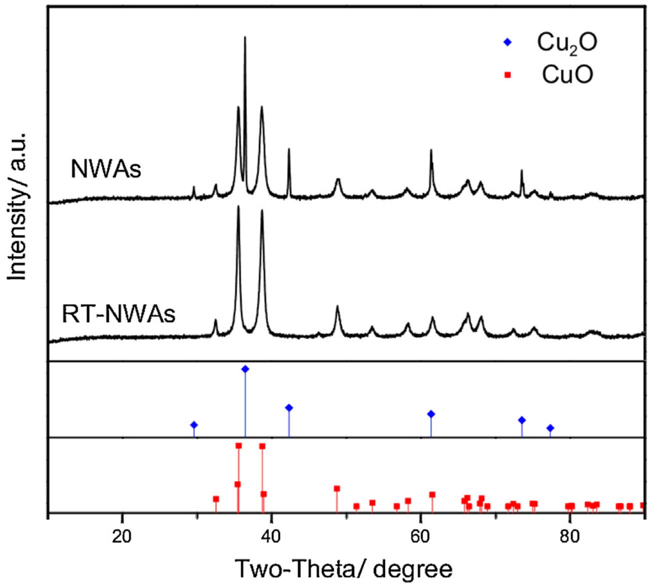

Fig. 2. XRD patterns of NWAs and RT-NWAs. The XRD patterns of standard materials are shown: the blue rhombus for Cu_2O and the red box for CuO.