



In-situ oxidized copper-based hybrid film on carbon cloth as flexible anode for high performance lithium-ion batteries



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ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form 10 July 2016

Accepted 11 July 2016

Available online 12 July 2016

Keywords:

Cupric Oxide

Anode material

Copper interlayer

Flexible

Lithium-ion batteries

ABSTRACT

Large-scale aligned CuO nanosheets on conductive carbon cloth were successfully synthesized by a facile two-step approach include magnetron sputtering and solution immersion. The in-situ growth mechanism for the CuO nanostructures is proposed. When tested as anodes for lithium-ion batteries, the CuO nanosheets delivers an initial capacity of 711.2 mAh g^{-1} at 500 mA g^{-1} and maintained 88% after 100 cycles. Even at 2000 mA g^{-1} , a stable capacity as high as 448.9 mAh g^{-1} could be achieved. The obtained high performance is due to (1) 2D sheet-like structure with short diffusion length, fast electron transfer and efficient accommodation of volume expansion (2) carbon cloth substrate with high flexibility and conductivity (3) intermediate copper layer with enhanced mechanism adhesion (4) 3D hierarchical structure with large contact area between active material and electrolyte. Achieved electrochemical performance by directly growing ordered CuO nanosheets on conductive carbon cloth makes them promising anode for flexible LIB application.

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1. Introduction

Due to the increasing consumption of worldwide energy, the demand for developing advanced power sources in a variety of domains like portable electronics and electric vehicles has become critical [1,2]. Rechargeable lithium-ion batteries (LIBs) have been attracting extensive attention in recent years on account of their relatively high energy density, long life span and environmental benignity [3–6]. In comparison to current commercial graphite anodes, transition metal oxides (MO_x , where M is Cu, Fe, Co, Ni, etc.) offer advantages of higher specific capacity and better rate capability, which make them appealing candidates for next-generation rechargeable LIBs [7–11].

Among various potential anode materials, Copper Oxide (CuO) has been extensively studied due to its high theoretical specific capacity (674 mAh g^{-1}), natural abundance, affordable price and environmental friendly [12]. However, its considerable capacities are generally accompanied by poor conductivity and large volume change during the delithiation-lithiation process, leading to limited electrochemical performance [13,14]. In order to address

these challenges, one feasible approach is to develop CuO nanostructures with stable morphologies [15–17]. So far, different CuO nanostructures such as ribbons [18,19], spheres [20], fibers [21], sheets [22–24] and other composite architectures [25,26] have been fabricated via different approaches. In particular, the sheet-like nanostructures with high porosity and large specific surface area has been considered as promising anode material.

Recently, constructing CuO nanoarchitecture on conductive substrates to maintain the structural integrities and avoid the influence of binder materials have been proposed to improve the energy storage properties. Zhang and co-workers [27] have fabricated CuO nanowires on nickel foam by thermal oxidation and e-beam evaporation, which supplied a reversible capacity over 692 mAh g^{-1} after 50 cycles. Zhang et al. [28] demonstrated that the copper oxide nanobelts directly grown on copper substrate via solvothermal method could deliver a reversible capacity over 600 mAh g^{-1} after 100 cycles at 0.2C rate. Yuan [18] reported a hydrothermal method for growing CuO clusters assembled by sponge-like mesoporous nanocrystal ribbons over Ni foam, releasing a reversible capacity of 430 mAh g^{-1} after 50 cycles. Most of the previous researches were based on the rigid substrate, such as nickel foam [27], copper foil [24,29] and stainless steel [30]. Recently, a few studies about growing CuO nanostructures on flexible substrates for LIB applications have been reported. For

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instance, CuO nanosheets/Graphene oxide composite paper was prepared by vacuum filtration and hydrothermal reduction, delivered a stable capacity of 736.8 mAh g^{-1} after 50 cycles at 67 mA g^{-1} [31]. Huang et al. [32] succeed in synthesis of CuO nanosheets/CNT composite film with the aid of electrostatic interaction in aqueous solution, which provided a discharge specific capacity of 571 mAh g^{-1} after 40 cycles. Very recently, mesoporous CuO/carbon nanofiber paper [33] synthesized by electrophoretic deposition exhibited a good reversible capacity of 400 mAh g^{-1} with a current density of 1000 mA g^{-1} . The above works reveal that CuO is a promising anode material for flexible LIB application. The weak bonding between active material and its heterogeneous substrate is a common issue for limiting the structural stability, an intermediate layer is often indispensable for enhancing the mechanical adhesion [27,34,35]. Besides, the commercially available carbon clothes have been widely applied as flexible substrates in LIB due to its 3D structure, tensile strength, good corrosion resistance, excellent conductivity and high flexibility [34,36–39].

Herein, we have proposed a facile two-step method to directly grown CuO nanosheets on flexible carbon cloth as binder-free anodes for LIBs for the first time. A conventional magnetron sputtering was utilized to simply prepare copper-film-coated carbon cloth for subsequent growth of highly ordered CuO nanosheets. The growth mechanism for the formation of CuO nanosheets on carbon cloth was investigated. The as-fabricated CuO nanosheets/carbon cloth electrode exhibited high capacity, superior cycling stability and good rate capability. Cu intermediate layer plays a pushing role to enhance the morphology stability, hence improving the cycling performance.

2. Experimental

2.1. Synthesis of CuO nanosheets/carbon cloth

All chemical reagent were analytical grade and used as received without further purification. The carbon cloth (WOS 1002 CeTech CO., Ltd., China; 12.5 mg cm^{-2} , 0.32 mm in thickness) was cleaned in acetone, ethanol and water by ultrasonication for 15 min respectively. After being dried, the clean-washed carbon cloth was placed into a conventional magnetron sputtering system. After the vacuum level reached $5 \times 10^{-3} \text{ Pa}$, a layer of copper was deposited on the surface of carbon cloth for 30 min. Subsequently, the as-obtained sample was immersed into 50 ml aqueous solution containing 3 mmol $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 75 mmol NaOH at room temperature and stand for 12 h. Then the sample was taken out, rinsed with ethanol and DI water several times, and dried in a vacuum oven at 60°C for 12 h.

2.2. Characterization

The morphology and structure of the prepared samples were examined with scanning electron microscopy (FEI Nova NanoSEM 450) and transmission electron microscopy (FEI Tecnai G2 S-TWIN). Crystal structure identification was carried out using X-ray diffraction (XRD, PANalytical B.V., Holland) equipped with Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) were performed on VG MultiLab2000 system with a monochromatic Al-K α X-ray source (ThermoVGSscientific). Raman spectroscopy was recorded on a Renishaw inVia plus laser Raman spectrometer (wavelength: 785 nm , power: 3 mW , spot size: $1.2 \mu\text{m}$).

2.3. Electrochemical measurements

Electrochemical tests were conducted using two-electrode coin cells (CR 2032) with Li foil serving as counter electrode and

reference electrode, which were assembled in an argon-filled glove box (Mikrouna, China) with the concentrations of moisture and oxygen below 1 ppm. The as-synthesized product was cut into 12 mm disk and used directly as working electrode. The commercial CuO electrode was prepared by mixing active material, carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1. Celgard 2400 polymer film was utilized as separator, and the electrolyte was 1M LiPF₆ in a 50:50 w/w mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Before measurement, the cell was aged for 12 h to ensure full infiltration. The ambient-temperature half-cell performance was measured using a multi-channel battery measurement system (Land, China) at various current densities and a potential range between 0.01 and 3V. Electrochemical impedance spectra (EIS) test was performed on an Autolab workstation (PGSTAT-302N, Eco Chemie B.V. Company) in the frequency range of 0.01 Hz–100 KHz with an amplitude of 5 mV. The CuO nanosheets mass on CuO nanosheets/carbon cloth could be determined by comparing the weight difference between the samples before and after a hydrochloric acid cleaning treatment. In this work, the loading mass of CuO nanosheets in the electrode was determined to be approximately 0.8 mg cm^{-2} , and the weight ratio of Cu interlayer to CuO nanosheets is about 2:0.8.

3. Results and discussion

The CuO nanosheets on carbon cloth electrode was fabricated via a two-step approach include magnetron sputtering and solution immersion. As a green and facile technique, the magnetron sputtering has been extensively used to deposit purified and stable thin metal films. The non-woven carbon cloth, which consists of interlaced carbon fibers with an average diameter of 10 μm , was used as the conductive substrate. Fig. 1 illustrates the two-step growth process of CuO nanosheets/carbon cloth composite. Firstly, the thin copper layer was deposited on carbon cloth via magnetron sputtering. Secondly, the sample was immersed in the mixed solution of NaOH and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. In the early stage of the reaction, $\text{Cu}(\text{OH})_2$ nanotubes were formed by stacking of $\text{Cu}(\text{OH})_2$ nanosheets. With the increase of immersion time to 12 h, $\text{Cu}(\text{OH})_2$ nanotubes gradually transformed into 2D CuO nanosheets. The photographic images of carbon cloth are also displayed in Fig. S1. During the different stage of reaction, the sample showed different colors of carbon black, yellow, blue and black. Besides, the carbon cloth possess high flexibility, which is shown in Fig. S2, make them promising candidates for flexible LIB applications.

Fig. 2a shows X-ray diffraction (XRD) patterns of the final products of CuO nanosheets/carbon cloth. All the diffraction peaks can be indexed to CuO, Cu and carbon, which CuO shows a monoclinic symmetry (space group C2/c 15, JCPDS 48-1548) with lattice constant $a = 4.688 \text{ \AA}$, $b = 3.423 \text{ \AA}$, $c = 5.132 \text{ \AA}$. Broad peak at 26.3° demonstrate graphitized carbon originating from the carbon cloth. Besides, the peak located on 43.2° can be indicated to orthorhombic-phase Cu (JCPDS 04-0836), which illustrates that the copper layer hasn't been fully oxidized. Hence, the final product is C/Cu/CuO hybrid structure, and untransformed copper layer between carbon cloth and CuO nanosheets could provide good conductivity and firm bonding property. In addition, There is no peak related with $\text{Cu}(\text{OH})_2$ and Cu_2O , showing the sufficient dehydration process. As shown in Fig. 2b, the CuO nanosheets exhibit characteristic Raman peaks centered at about 277 and 618 cm^{-1} [40,41]. Although the strong characteristic peaks of carbon (D band 1341 cm^{-1} and G band 1582 cm^{-1}) exist, the CuO peaks can be easily distinguished, which means that the CuO nanosheets are compactly integrated to the substrate. Fig. 2c and d show the Cu 2p and O 1s core-level spectra of the CuO nanosheets/carbon cloth sample. The Cu 2p spectra exhibits two peaks

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