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A novel electrochemical activation effect induced morphology variation from massif-like Cu_xO to forest-like Cu_2O nanostructure and the excellent electrochemical performance as anode for Li-ion battery

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ABSTRACT

Novel massif-like Cu_xO nanostructure was directly growing on Cu foam via a facile thermal oxidation method in air atmosphere. The massifs are about 5 μm in mean diameter and 4 μm in mean height, which consist of a large number of nanoparticles with mean size about 100 nm. Cu_xO nanowires that evolve from the particles locate at the laps of the massifs. Galvanostatic battery testing shows that the Cu_xO/Cu electrode exhibits excellent cycle stability and rate capability. The charge and discharge capacities are both 1.8 mAh cm^{-2} after 100 cycles under a discharge/charge rate of 0.35 C. After testing at various rates from 0.2 to 12 C over 50 cycles, the 5th-cycle discharge capacity can resume well when lowering the discharge/charge rate to 0.2 C. The performances are testified due to a novel electrochemical activation effect that induces the reconstruction of porous forest-like morphology in cycling.

1. Introduction

Transition metal oxides (TMOS) are promising anode materials for high performance Li-ion batteries owing to their high theoretical capacity (500–1000 mAh g^{-1}) that based on reduction/oxidation reaction mechanism ($2yLi^+ + 2ye^- + Me_xO_y \leftrightarrow xMe + yLi_2O$) [1–3]. Such conversion reactions turn out not to be specific to oxides but can be extended to sulfides, nitrides, phosphides or fluorides [4–10], showing typical representation for one sorts of electrode material of Li-ion batteries. It is always accepted that the electrochemical reactions in Li-ion battery will lead to the formation of nanosized metals in discharge process, which can be called for electrochemical activation. Those nanosized metals with high surface-to-volume ratio will easily aggregate due to their high reaction activity, which can be called for electrochemical sintering [11–15]. As anodes for Li-ion battery, TMOS show poor cycling performance because they have low electrical conductivity and cannot maintain their integrity over several discharge/charge cycles owing to the specific electrochemical sintering effect. Nevertheless, the formation of nanosized metals and further construction of secondary architecture is novel and magic. It is undeniable that keeping structure integrity for electrode over cycling test is a feasible way to gain satisfactory electrochemical performance, whereas the construction of new favorable architecture in cycling, which can be called for electrochemical reconstruction, is also a desirable approach to achieve excellent electrochemical performance. For example, based on similar charge/discharge mechanism, graphene wrapped Fe_3O_4 electrode shows good structure integrity after cycling test [16], whereas Ni_3S_2 nanorods electrode forms a new porous architecture after cycling owing to a novel electrochemical reconstruction effect [17].

Cu_xO are typical TMOS with attractive advantages as inexpensive, non-toxic, easily produced and readily stored, which have been widely studied. However, Cu_xO show typical semiconductor characteristics with low electrical conductivity, which is not beneficial for charge transfer. To improve the electrochemical performance of Cu_xO, much work including fabrication of various morphology of Cu_xO nanostructure and preparation of sorts of Cu_xO–Cu or Cu_xO–C composite materials has been done [18–22].

Cu foam is of 3-dimensional porous architecture, which was widely adopted as conductive collector of active material such as Sn and Si for construction of Li-ion battery electrodes [23–27]. The porous architecture and fine electronical conductivity can enhance the reaction kinetics of active material, and thus lead to improved electrochemical performance. Here in this paper, we report directly growing of novel massif-like Cu_xO ($x = 1, 2$) on Cu foam as anode for Li-ion battery. It is delighted to find an interesting phase transformation from massif-like Cu_xO ($x = 1, 2$) to porous forest-like Cu_2O in cycling due to a novel electrochemical reconstruction effect, which results into excellent electrochemical performance.

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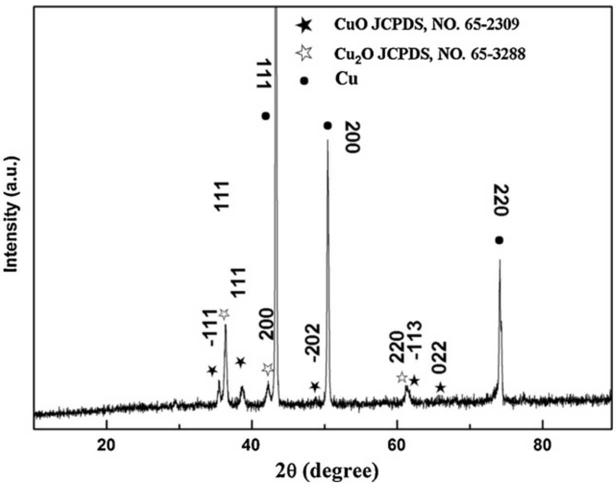

Fig. 1. XRD pattern of the as-synthesized electrode.

2. Experimental

2.1. Fabrication procedure

Massif-like Cu_xO/Cu electrode was fabricated by direct thermal oxidation of Cu foams in air atmosphere. Cu foams (100 PPI pore size, 380 g m^{-2} surface density, 1.5 mm thick, purchased from Changsha Lyrun New Material) were heated at a rate of 3–400 °C min^{-1} and held for 3 h by a tube furnace.

2.2. Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-ray powder diffraction (Rigaku Ultima IV Cu Kα radiation $\lambda = 1.5406$ Å), field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL) equipped with energy disperse spectroscopy (EDS) and transmission electron microscopy (TEM, FEI, Tecnai G2 F30) equipped with selected area electron diffraction (SAED).

2.3. Electrochemical characterization

For fabricating of Li-ion battery, the as-prepared Cu_xO/Cu foams (disc electrode with diameter of 14 mm) were dried (120 °C, 24 h, vacuum). Coin-type cells (2025) of Li/1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/Cu_xO/Cu disc electrode were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, $H_2O < 1.0$ ppm, $O_2 < 1.0$ ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.5 mV s^{-1} between 0 and 3 V.

3. Results and discussion

Typical XRD pattern of the as-prepared electrode is shown in Fig. 1. The diffraction peaks located at 43.3, 50.4 and 74.1° (marked with ●) correspond to (1 1 1), (2 0 0) and (2 2 0) faces of Cu foam (04-0836). Diffraction peaks located at 35.6, 38.8, 48.9, 61.7 and 65.9° (marked by ★) can be indexed as (−1 1 1), (1 1 1), (−2 0 2), (−1 1 3) and (0 2 2) faces of monoclinic CuO with lattice constant $a = 4.662$ Å, $b = 3.416$ Å and $c = 5.118$ Å, which are in good agreement with JCPDS, No. 65-2309. Diffraction peaks located at 36.5, 42.4 and 61.5° (marked by ☆) can be attributed to (1 1 1), (2 0 0) and (2 2 0) faces of cubic Cu_2O with lattice constant $a = 4.260$ Å (JCPDS, No. 65-3288). The XRD results indicate that thermal oxidation leads to the formation of CuO–Cu_2O composite structure on Cu foam.

Fig. 2(a) is a low magnification SEM image of the as-prepared Cu_xO/Cu electrode. As seen, frame work of porous Cu foam is preserved after oxidation (the insert of Fig. 2(a) is a SEM image of Cu foam). The surface of Cu foam after annealing is much different from that before annealing, which indicates the growth of copper oxides on the surface of Cu foam. Fig. 2(b) shows a higher magnification SEM image of the Cu_xO/Cu electrode, which exhibits novel massif-like morphology. The massifs are about 5 μm in mean diameter and 4 μm in mean height, among which a large number of nanowires can be observed. Fig. 2(c) is a high magnification SEM image of the Cu_xO, which indicates the Cu_xO massifs consist of a large number of particles with little size, and these nanowires located at the laps of the massifs. To study the growth mechanism of the nanowires, magnified SEM image of the Cu_xO nanoparticles and nanowires was characterized. As shown in Fig. 2(d), the nanoparticles are of mean size about 100 nm. The nanowires grow directly on the surface of the nanoparticles, showing mean diameter about 100 nm with length ranges from several hundreds of nanometers to several micro-meters.

The composition of the nanoparticles and nanowires were studied. The energy disperse spectroscopy (EDS) patterns of the Cu_xO nanoparticles and nanowires are shown in Fig. 3(a) and (c), in which are the analytical results of weight and atom ratio for the nanoparticles and nanowires. The corresponding locations where the EDS characterization carried out are shown in Fig. 3(b) and (d). As seen, the nanoparticles show O and Cu atom ratio of 47.35:52.65, which is close to the composition of CuO. In addition, the nanowires show O and Cu atom ratio of 35.02:64.98, which is close to the composition of Cu_2O. According to the EDS results, we suggest thermal oxidation leads to the formation of CuO–Cu_2O composite architecture.

Fig. 4(a) shows the representative TEM image of the Cu_xO nanoparticles, which consists of small particles with size tens of nanometers. The insert of Fig. 4(a) is the corresponding selected area electron diffraction (SAED) pattern of the particles, regular diffraction spots suggest the nanoparticles are well crystallized. Fig. 4(b) is a high resolution TEM (HR-TEM) image of the Cu_xO nanoparticles, which shows clear lattice fringes. The interplanar spacing is about 0.251 nm, which corresponds to the (−1 1 1) plane of monoclinic CuO. It can be noticed that the out layer of these nanoparticles is amorphous, which may be formed under low temperature during the temperature increasing process. Fig. 4(c) is the representative TEM image of a single Cu_xO nanowire, which indicates the width of the nanowire is about 60 nm. The insert of Fig. 4(c) shows the SAED pattern of the nanowire, regular diffraction spots suggest the nanowire is well crystallized. Fig. 4(d) is a high resolution TEM (HR-TEM) image of the Cu_xO nanowire, which shows clear lattice fringes. The interplanar spacing is about 0.246 nm, which corresponds to the (111) plane of cubic Cu_2O. The observations are in agreement with the EDS results in Fig. 3, suggesting the Cu_xO film consists of CuO nanoparticles and Cu_2O nanowires.

The formation process of the novel massif-like Cu_xO was also studied via tuning the reaction temperature. Fig. 5 is the SEM images of Cu_xO/Cu electrode obtained at 200 and 300 °C for 3 h. As shown in a low magnification SEM image in Fig. 5(a), the Cu_xO/Cu obtained at 200 °C exhibits clear hierarchical structure, which consists of bottom layer of nanoparticles and upper layer of microspheres. Fig. 5(b) is a high magnification SEM image of the Cu_xO/Cu electrode obtained at 200 °C, which suggests these nanoparticles are of mean size about 30 nm and these microspheres are composed of nanoparticles with mean size about 30 nm. Fig. 5(c)