Electrochimica Acta 109 (2013) 419–425

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Preparation of Cu_2O–Cu anode for high performance Li-ion battery via an electrochemical corrosion method

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ARTICLE INFO

Article history:
Received 21 April 2013
Received in revised form 10 July 2013
Accepted 11 July 2013
Available online 29 July 2013

Keywords:
Copper oxides
Electrochemical corrosion
Li-ion battery

ABSTRACT

Cu_2O was directly grown on Cu foam via a facile electrochemical corrosion method by the aid of H_2O_2. Galvanostatic battery testing shows that the Cu_2O–Cu electrode exhibits excellent cycle stability and rate capability. It delivers charge and discharge capacity about 0.76 mA h cm^{-2} without attenuation over 100 cycles under a charge/discharge rate of 0.15 C. After testing at various rates from 0.2 to 35 C over 60 cycles, the 5th-cycle discharge capacity can resume 98.9% when lowering the charge/discharge rate to 0.2 C. The performances are due to both the fine electric contact between Cu_2O and Cu foam and a possible porous architecture of Cu_2O electrode. The electrochemical reaction kinetic of Cu_2O–Cu electrode was studied by cyclic voltammetry measurement at various scan rate, which indicates the anodic and cathodic peak currents show linear dependence on the square root of scan rate from 0.1 to 3 mV s^{-1}, suggesting a lithium ion diffusion controlled mechanism in the charge/discharge process.

1. Introduction

Copper has been widely used in our lives and industry fields as interior decoration, electrical wire, high temperature electromagnetism heater, ink-jet printing and specific alloys due to its highly conductivity, good thermodynamics stability, fresh metallic luster and low cost than Ag and Au [1]. However, Cu in ambient atmospheric temperature and pressure inevitably has surface oxide layers because the copper oxide phases are thermodynamically more stable than pure Cu, which can be ascribed to a chemical corrosion effect. For Cu, the formation of copper oxide on the surface will lead to the loss of electronical conductivity and metallic luster as well as the enhancement of antioxidation ability of Cu. For copper oxide, the Cu substrate can improve its electrical conductivity and structure stability. As a result, Cu_xO–Cu composite architecture shows multifunctional properties of Cu and Cu_xO, which may have potential applications in some new fields.

During the past few years, copper oxides show potential application in Li-ion batteries base on a novel redox reaction mechanism ($2yLi^+ + 2ye^- + Cu_xO_y \leftrightarrow xCu + yLi_2O$) [2–5]. However, copper oxides show poor cycling performance because they possess low electrical conductivity and cannot maintain their integrity over several charge/discharge cycles. In order to improve the electrochemical performance of copper oxides, efforts have been devoted on combining copper oxides with matrix phase such as carbon material and/or directly growing copper oxides on conductive substrate [6–12]. In our previous study, we prepared Cu_xO–Cu composite electrode via annealing Cu foam in air atmosphere at 400 °C, which exhibits good electrochemical performance as anode for Li-ion batteries [13]. The preparation of Cu_xO–Cu anode via annealing in air is essentially a chemical corrosion, which needs relative high temperature. In addition, the Cu_xO layer is usually uniform and compact because chemical corrosion is always not sensitive to the surface morphology of metal. As we know, electrochemical corrosion is another typical corrosion of metal, which occurs under solution environment and can be easily controlled via tuning the solution environment. Furthermore, the electrochemical corrosion of metal is usually sensitive to the surface morphology of metal, which will probably lead to the formation of porous architecture on metal substrate. Recently, we successfully prepared porous $Ni(OH)_2$ nanowalls on Ni foam via a facile electrochemical corrosion method, which shows excellent electrochemical performance as anode for Li-ion battery [14]. Considering the above research results and the fact that Cu shows worse anticorrosive property than Ni, we are inspired to envision whether the electrochemical corrosion of Cu foam can lead to the formation of novel composite architecture and have potential application in Li-ion battery. Here in this paper, we report the growth of Cu_2O on Cu foam via an electrochemical corrosion method in the presence of H_2O_2 at low temperature, and the electrochemical performance of the Cu_2O–Cu as anode for Li-ion battery was studied by galvanostatic battery testing and cyclic voltammetry (CV) measurement.

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http://dx.doi.org/10.1016/j.electacta.2013.07.088

Table 1
Preparation conditions of the electrodes.

Electrode	H_2O_2 (ml)	Reaction time (h)
a	0.6	12
b	0	12
c	0.6	24

2. Experimental

2.1. Fabrication procedure

Cu_2O–Cu electrode was fabricated by an electrochemical corrosion method. Cu foams (100 PPI pore size, 380 g m^{-2} surface density, 1.5 mm thick, purchased from Changsha Lyrun New Material) were placed in a 50 ml teflonlined autoclave, an appropriate amount of H_2O_2 and distilled water was subsequently added to 80% of its capacity. The autoclave was then sealed and placed in an oven, heated at 90 °C for 12 and/or 24 h. The preparation conditions of the electrodes were shown in Table 1.

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) and field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL).

2.3. Electrochemical characterization

For fabrication of Li-ion battery, the as-prepared Cu_2O–Cu foams (disk electrode with diameter of 14 mm) were dried (120 °C, 24 h, vacuum). Coin-type cells (2025) of Li/1M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/Cu_2O–Cu disk 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 0.2 mV s^{-1} between 0 and 3 V.

3. Results and discussion

Typical XRD pattern of electrode is shown in Fig. 1. The diffraction peaks located at 43.3°, 50.4° and 74.1° (marked with ●) correspond to the (1 1 1), (2 0 0) and (2 2 0) lattice plans of Cu foam (JCPDS, No. 04-0836). Diffraction peaks located at 36.5°, 42.4° and 61.5° (marked by ☆) can be attributed to the (1 1 1), (2 0 0) and (2 2 0) lattice plans of cubic Cu_2O with lattice constant $a = 4.260$ Å (JCPDS, No. 65-3288). The XRD results indicate that the electrochemical corrosion leads to the formation of Cu_2O–Cu composite architecture. The electrochemical and/or chemical reactions during the hydrothermal process are likely to be as follows:

$$2Cu + H_2O_2 \rightarrow 2CuOH \qquad (1)$$

$$2CuOH \rightarrow Cu_2O + H_2O \qquad (2)$$

Fig. 2(a) is a low magnification SEM image of electrode a. As seen, framework of porous Cu foam is preserved after electrochemical corrosion (the insert of Fig. 2(a) is a SEM image of Cu foam). The Cu foam after electrochemical corrosion shows coarse surface, which indicates the growth of copper oxides on the surface of Cu foam. In addition, a large number of holes as well as a small amount of cracks on the surface of Cu foam can be clearly seen, which is due to the unique asymmetric electrochemical corrosion of Cu that relevant to the porous architecture and special morphology of Cu foam. Fig. 2(b) shows a high magnification SEM image of the Cu_2O–Cu electrode, exhibiting a large number of particles with size ranges form 200 nm to 1.5 μm on the surface of a uniform layer. The insert of Fig. 2(b) is a SEM image of Cu foam with the same magnification as Fig. 2(b), which shows clear crystal boundaries on the surface. The surface morphology of Cu foam is much different from that of the uniform layer of Cu_2O–Cu, indicating the formation of Cu_2O film on the surface of Cu. In addition, cracks and holes on the surface of Cu_2O film suggest a possible porous architecture, which is similar to that of Cu_2S–Cu [15].

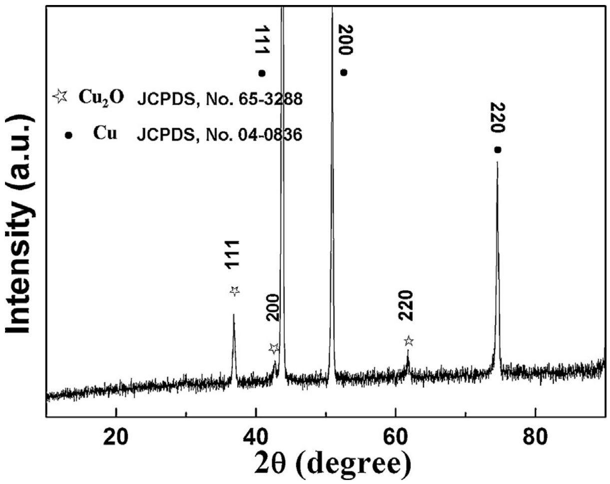

Fig. 1. XRD pattern of electrode a.

Galvanostatic charge/discharge cycling was carried out in the potential window of 0.02–3.0 V versus Li. Fig. 3(a) shows the capacity retention and the initial three charge/discharge voltage profiles of electrode a at a rate of 0.15 C (1 C means accomplishing discharge or charge in an hour). It can be seen that electrode an exhibits a slope potential region from 1.25 to 0.3 V in the initial discharge curve, which is relevant to the formation of SEI and the generation of Cu [16]. The subsequent two discharge curves are much different from the initial one, showing two slope potential regions (1.75–1.0 and 1.0–0.3 V). The difference between the 1st and 2nd discharge curve can be ascribed to the activation of Cu_2O electrode, which is similar to NiO that possesses similar charge/discharge mechanism [17]. The charge curve shows no distinct variation in the initial three cycles, exhibiting a sloping potential range from 1.0 to 2.5 V, which can be ascribed to the decomposition of the SEI and the oxidation of Cu into Cu_2O [18,19]. The initial discharge capacity is about 2.08 mA h cm^{-2}, much higher than the initial charge capacity (0.68 mA h cm^{-2}). This is mainly due to the formation of solid electrolyte interface (SEI) resulting from electrochemically driven electrolyte degradation, which is a phenomenon also observed in other systems operating through conversion reactions [2,20,21]. The subsequent charge and discharge capacity increase slowly along with cycle number in the initial 10 cycles and then gradually reach stable value, being both 0.76 mA h cm^{-2} after 100 cycles. This observation suggests a gradual participation in electrochemical reaction of active Cu_2O along with cycling number, which is similar to that for Cu_xO–Cu electrode [13]. The cyclic voltammetric (CV) curve of the Cu_2O–Cu electrode was tested over a voltage region from 0 to 3.0 V at a scan rate of 0.2 mV s^{-1}. As shown in Fig. 3(b), the profile of the 2nd and 3rd CV curve is similar, whereas an obvious difference between the first and subsequent two is found. In the 1st cathodic scan, a strong reduction peak ranges from 1.25 to 0.3 V was observed, which corresponds to the formation of