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Cobalt nanosheet arrays supported silicon film as anode materials for lithium ion batteries

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ABSTRACT

Cobalt nanosheet arrays supported silicon film is prepared and used as anode materials for lithium ion batteries. The film is fabricated using chemical bath deposition, hydrogen reduction and radio-frequency magnetron sputtering techniques. The microstructure and morphology are characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). In this composite film, the silicon layer is supported by interconnected aligned cobalt nanosheet arrays that act as the three-dimensional current collector and buffering network. The electrochemical performance as anode materials for lithium ion batteries is investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge tests. The results show that the film prepared by sputtering for 1500 s exhibits high capacity, good rate capability and stable cycle ability. It is believed that the cobalt nanosheet arrays play important roles in the electrochemical performance of the silicon layer.

1. Introduction

As a new type anode materials of lithium ion batteries, silicon delivers high theoretical capacity up to 4200 mAh g^{-1}, so it shows promising application in the lithium ion battery field [1,2]. However, for most unmodified silicon materials, the actual capacity and cycling performance is still quite low, especially at high current densities. One reason for this is the poor conductivity of silicon. It increases the electrode polarization, reduces the electrochemical reaction rate, and thus limits the utilization of silicon materials. The other reason is the pulverization of silicon caused by the volume expansion over 300% during the lithiation process. The brittle silicon cannot afford such high stress and becomes pulverized, and loses contact with the current collector. To solve these problems, many approaches have been developed in the last decade, including forming composites with conductive and/or flexible matrix and preparation of nanosized silicon with various structures.

Forming composites is a common method to enhance the electrochemical performance of silicon. Materials with good conductivity and ductility, such as carbon [3–11], metals [12–14] and conductive polymers [15], are often introduced to silicon materials. They act as the matrix to enhance conductivity of silicon and suppress its pulverization. Preparing nanostructures, such as ordered porous [16,17], hollow [18], core-shell [19], yolk-shell [20,21] and low-dimensional [22–24] structures, is also extensively investigated for the purpose of enlarging the specific surface area and shortening the diffusion path.

Apart from above mentioned approaches, binder-free electrodes are often designed for further improvements of electrochemical performance. The binder-free electrodes contain no binder or conductive powder, but compose of active materials that grow directly on the substrates, leading to good electrical contacts. As a result, they often exhibit higher specific capacity, rate capability and cycle stability than those of traditional powder electrode. However, many of these electrodes are just nanosized thin films, in which the mass of active materials is too low to meet the demands of practical applications. Simply increasing the thickness of the film often worsens the cycle stability due to the poorer conductivity and more severe pulverization. Therefore, it is important to design an electrode with increased film thickness for a higher actual electrode capacity, but not at the expense of cycling performance.

In this present work, an arrayed substrate that can act as the three-dimensional current collector is prepared to support the micro-sized silicon film, and the electrochemical performance of this electrode is studied in detail.

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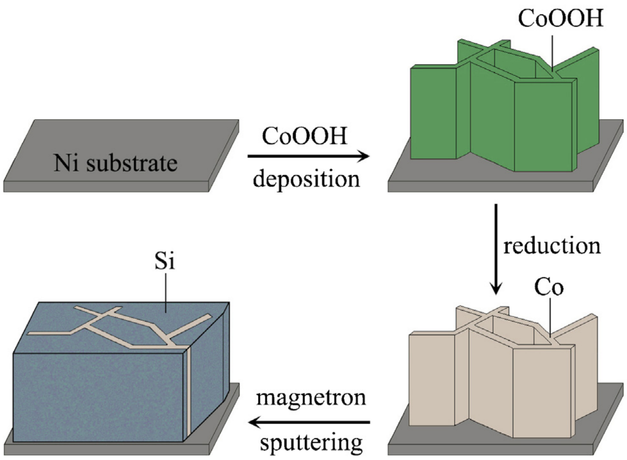

Fig. 1. Schematic diagram of the preparation process of cobalt nanosheet arrays supported silicon film.

2. Experimental

The schematic diagram of preparation process of cobalt nanosheet arrays supported silicon film is illustrated in Fig. 1. The first step is the preparation of CoOOH nanosheet arrays by a chemical bath deposition technique according the method reported in our previous work [25–28]. Briefly, the deposition solution was mixed by 11.24 g cobalt sulfate heptahydrate ($CoSO_4·7H_2O$), 2.03 g potassium persulfate ($K_2S_2O_8$), 90 mL distilled water and 10 mL concentrated ammonia ($NH_3·H_2O$). A flat nickel foil was used as the substrate, and it was suspended vertically in the bath solution. The deposition lasted 60 min at room temperature and CoOOH nanosheet arrays were deposited on the nickel foil. The second step is the reduction of CoOOH nanosheet arrays. The film was transferred to a quartz-tube furnace, and calcined at 400 °C for 2 h under flowing Ar/H_2 gas mixture (5% H_2) to reduce it to metallic cobalt nanosheet arrays. The final step is the silicon deposition by radio-frequency magnetron sputtering. A polysilicon wafer (99.999%) with a diameter of 6 cm was used as the target. The distance between the target and the substrate holder was fixed at 20 cm. Before the deposition, the chamber was pumped to a base pressure of 4.7×10^{-7} Torr, and then pure argon was introduced to the chamber and the working pressure was kept at 8×10^{-3} Torr. At a constant radio-frequency power of 60 W, silicon layer was deposited onto the cobalt nanosheet arrays for 500, 1000, 1500 and 2000 s, respectively. The mass of silicon in the film was weighed by the high-precision balance with the accuracy of 0.1 μg equipped in a simultaneous thermal analyzer (Netzsch, STA 449 F3).

The films were characterized by means of scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20), both of which are equipped with energy dispersive spectrometer (EDS).

CR2025 coin-type cells were assembled to investigate the electrochemical performance of the films. The assembly process was carried out in an argon-filled glove box in which the concentrations of water and oxygen were controlled below 1 ppm. The film working electrode, polypropylene (PP) membrane, and lithium foil counter electrode were stacked together in turn inside the cell. After injecting the electrolyte, that is, 1 M $LiPF_6$ in ethylene carbonate (EC)-diethyl carbonate (DEC) (1:1 in volume), the cell was sealed in the glove box and placed still for 12 h before electrochemical measurements.

Cyclic voltammetry (CV) analysis of the electrode was performed on an electrochemical workstation (Metrohm Autolab PGSTAT302N) in a potential range of 0–1.5 V (vs. Li^+/Li) at a scan rate of 0.1 mV s^{-1}. Galvanostatic charge–discharge tests were carried out on a program-controlled battery analyzer (LAND CT2001A) using different current densities between 0.02 and 1.5 V.

3. Results and discussion

During the chemical bath deposition, CoOOH precursor film is generated and deposited on the nickel foil substrate. The related chemical reactions are listed below.

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \quad (1)$$

$$2Co(OH)_2 + S_2O_8{}^{2-} + 2OH^- \rightarrow 2CoOOH + 2SO_4{}^{2-} + 2H_2O \quad (2)$$

Subsequently, during the calcination process under Ar/H_2 atmosphere, the CoOOH precursor film is converted to metallic Co by the reduction of H_2, as follows.

$$2CoOOH + H_2 \rightarrow 2Co + 2H_2O \quad (3)$$

The typical SEM morphology of the CoOOH precursor film is presented in Fig. 2. As shown in Fig. 2a with low magnification, the film is porous and exhibits a net-like structure. According to the image under high magnification, Fig. 2b, the film is constructed by many interconnected nanosheets. The nanosheets almost stand vertically on the substrate and form an arrayed structure. The nanosheets are about 20 nm in thickness and 100–200 nm in length.

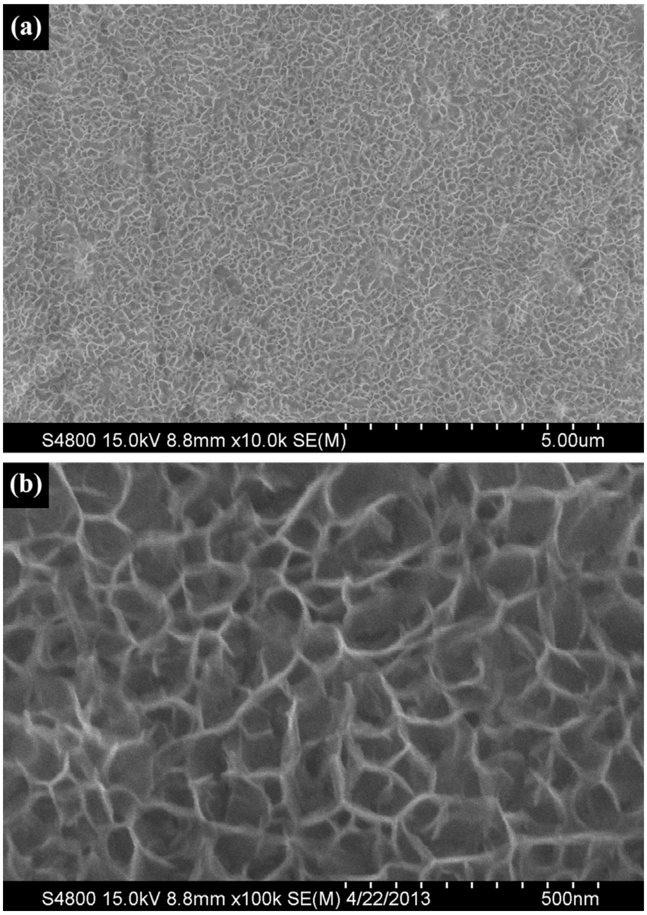

Fig. 2. SEM images of the films prepared by chemical bath deposition under (a) low magnification and (b) high magnification.