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PVD amorphous carbon coated 3D $NiCo_2O_4$ on carbon cloth as flexible electrode for both sodium and lithium storage

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ABSTRACT

With the advent of flexible electronics, flexible secondary rechargeable batteries have attracted considerable attentions as a promising power source in the new generation of flexible electronics such as roll-up displays, smart electronics, and implantable medical devices. In this work, we report the fabrication of 3D $NiCo_2O_4$ arrays on carbon cloth as a binder-free anode for sodium/lithium ion storage. Amorphous carbon layer is used to modify the surface of $NiCo_2O_4$ arrays by physical vapor deposition (PVD). The electrochemical performance measurements demonstrate that the amorphous carbon layer can improve the electrochemical stability of $NiCo_2O_4$. The $NiCo_2O_4$@ C/carbon cloth electrode exhibits a high reversible capacity of 749.9 mAh g^{-1}, stable cycling with more than 535.47 mAh g^{-1} at 500 mA g^{-1} over 100 cycles and impressive rate capability (318 mAh g^{-1} at 5 A g^{-1} over 700 cycles) for SIBs and excellent electrochemical performance for LIBs (reversible capacity of 807.63 mAh g^{-1} were observed for 100 cycles).

1. Introduction

In order to take the advantages of rapidly growing capacity of renewable resources and avoid the curtailment of renewable energy generation without sacrificing grid reliability, two types of electrochemical devices, lithium-ion batteries (LIBs) [1,2] and sodium-ion batteries (SIBs) [3,4] are the key area to modernization. Over the past few years, we have evidenced the LIBs have been widely used in portable intelligent devices with huge success. Owing to its low theoretical lithium storage capacity of 372 mAh g^{-1}, the use of conventional commercial anode material (graphite) restricts improvement of the energy density for LIBs. Currently, SIBs, as the competitive alternatives to LIBs, have received a great deal of research interest particularly for large energy storage devices, due to the relative abundance of sodium and similar electrochemical mechanism to LIBs [4]. However, the exploration of new high-performance electrode materials for SIBs remains a considerable challenge due to the fact that the radius of sodium ion (1.06 Å) is about 40% larger than that of lithium ion (0.76 Å). The fact would result in low capacity utilization, inferior rate capacity and poor cycling stability for electrode materials during charging and discharging process [5]. In order to satisfy the ever-increasing demand for prospective battery technology, both in LIBs and SIBs with high cycling performance, large energy and power densities, footsteps of investigating for optimal anode materials and development of suitable morphology structure have never stopped [6].

To this end, various high-capacity anode materials have been proposed, including carbon-based materials [4,7], alloy-based materials [8], metal oxides [9,10], and transition metal sulfides [11]. Among them, $NiCo_2O_4$, an important member of the binary metal oxides, holds great promise as electrode materials in electric energy storage (EES) devices owing to the coupling of two metal species (Ni and Co), which could render the $NiCo_2O_4$ with rich redox reactions and high theoretical capacities [12,13]. In addition, it exhibits higher electrical conductivity than single metal oxides by generating two active metal species with relatively low activation energy for electron transfer [14,15]. These attractive features make $NiCo_2O_4$ potential as anodes for both SIBs and LIBs. Alcantara et al. first proved that $NiCo_2O_4$ powder has improved theoretical performance, but delivered a poor reversible capacity and cycling performance, especially at high discharge rate [16]. To resolve these problems, various types of $NiCo_2O_4$ nanostructures have been studied as anodes for SIBs or LIBs, such as

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mesoporous nanosheets [17], nanoflakes [18], and $NiCo_2O_4$ nanowalls composed of ultrathin nanosheets [19]. Although enhanced storage performance has been achieved, none of them combines an excellent cycle life, high charge current density and outstanding capacity with a free-standing electrode.

Herein, we report the carbon-coated 3D $NiCo_2O_4$ arrays on flexible carbon cloth by a hydrothermal and subsequent physical vapor deposition process for the first time. As a binder-free anode for SIBs and LIBs, the $NiCo_2O_4$@ C/carbon cloth electrode can not only modify the mechanical strength and flexibility of the electrode, but also improve the specific capacity, cycling stability and rates performance. The design of the $NiCo_2O_4$@C/carbon cloth is based on following principles. First, compared to traditional electrodes, the $NiCo_2O_4$ nanowire arrays grown on the activated carbon cloth have an excellent electronic conductivity, because $NiCo_2O_4$ nanowire arrays attached tightly to the carbon cloth to form stable structure and good electrical contact, reducing the interfacial impedance between active material and current collector. Second, the $NiCo_2O_4$@ C/carbon cloth ensures the loose textures and open spaces between adjacent nanowire arrays, which provide ideal conditions for accommodating the volume change of the electrode during electrochemical reactions. Third, the process of physical vapor deposition is a novel approach to make high-quality amorphous carbon layer on the surface of $NiCo_2O_4$ nanowires, which result in materials with higher conductivity as well as structural stability.

2. Experimental section

2.1. Materials and preparation of $NiCo_2O_4$@ C/carbon cloth composite

All reagents were of analytical grade and used directly without further purification. $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, NH_4F and $CO(NH_2)_2$ were purchased from Aladdin Chemistry Co., Ltd. Carbon cloth (0.35 mm of thickness) and C target was obtained from Shanghai Lishuo composite materials Co, Ltd, and Yipin Chuancheng (Beijing) Technology Co, Ltd, respectively.

$NiCo_2O_4$@ C/carbon cloth composite was prepared by a hydrothermal method combined with subsequent magnetron sputtering deposition process. First, 2 mmol $Ni(NO_3)_2\cdot 6H_2O$, 4 mmol $Co(NO_3)_2\cdot 6H_2O$, 12 mmol NH_4F and 30 mmol $CO(NH_2)_2$ were dissolved in 75 ml of distilled water. The solution was stirred for 30 min, after then, putting a piece of cleaned carbon cloth (2 cm × 4 cm) and transferred into a 100 mL Teflon-lined stainless at 100 °C for 10 h. After being restored at room temperature, the resulting carbon cloth were washed with deionized water for three times, and then dried in a vacuum at 60 °C for 12 h. Finally, samples were put in an electric furnace and calcined at 250 °C for 6 h with a ramping rate of 3 °C/min in air atmosphere to get the $NiCo_2O_4$/carbon cloth composite. Second, magnetron sputtering deposition was performed on the ultrahigh vacuum magnetron sputtering equipment (TRP-450, SKY Technology Development Co., Ltd. Chinese Academy of Sciences). Amorphous carbon was deposited onto the $NiCo_2O_4$/carbon cloth by radio-frequency magnetron sputtering with pure C targets (purity 99.99%) at room temperature. The base pressure before deposition was smaller than 10^{-4} Pa and the deposition was carried out under Ar atmosphere (purity 99.99%). To clean the surfaces, the C target was pre-sputtered at 100 W for 15 min before deposition. The sputtering pressure was 1.0 Pa, power 200 W and sputtering time 90 min. The $NiCo_2O_4$@C/carbon cloth composite was obtained after the carbon deposition process being accomplished.

2.2. Characterization

The morphology and microstructure of the as-prepared samples were observed by scanning electron microscopy (FE-SEM, SuPRA 55, German ZEISS) and high resolution transmission electron microscopy (HRTEM, Philips Tecnai-12). The crystal structure of the prepared samples elemental makeup was characterized by X-ray powder diffraction (XRD, Rigaku, model D/max-2500 system). The specific surface area was measured by N_2 adsorption/desorption technique at 77 K (Quantachrome Nova2000e). Thermogravimetric analysis (TGA) was conducted on a TGA Q600 (Thermal Analysis Instruments, Burlington, MA, USA).

Electrochemical measurements were performed by a CR2016-type coin half-cell assembled in argon-filled glove box (German, M. Braun Co., $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The $NiCo_2O_4$@ C/carbon cloth composite was cut into 12 mm in diameter and was directly utilized as the working electrode without adding any binders or conductive agent. The loading quality of the $NiCo_2O_4$@ C active materials was calculated as 2.1–2.3 mg. While the corresponding Na metal foils or Li metal were utilized as both the counter and reference electrode for SIBs or LIBs, respectively. As the electrolyte, 1.0 M of $NaClO_4$ in ethylene carbonate/diethyl carbonate (EC/DEC = 1:1 by volume) was applied for SIBs and 1.0 M of $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/EMC = 1:1:1) was used for LIBs in this study. For the separator, glass fiber was used for SIBs, polypropylene was used for LIBs.

3. Results and discussion

3.1. Phase and microstructures

The strategy for the fabrication of the $NiCo_2O_4$@ C/carbon cloth composite is schematically illustrated in Fig. 1. Firstly, Co^{2+} and Ni^{2+} ions were coordinated with F^- to form $[NiCo_2F_{3x}]^{3(x-2)-}$ in the as prepared homogeneous solution. As the temperature of the solution was raised to above 100 °C, a variety of CO_3^{2-} and OH^- was formed gradually, which generated by urea the hydrolysis. The CO_3^{2-} and OH^- anions could help to release Co^{2+} and Ni^{2+} ions slowly from $[NiCo_2F_{3x}]^{3(x-2)-}$ in the solution. After the concentration of anions (CO_3^{2-}, OH^-) in the as-prepared reactant solution reached a certain value, the precursors of $NiCo_2(OH)_{3y}(CO_3)_{1.5(2-y)}\cdot nH_2O$ was generated. Then the precursor converted into $NiCo_2O_4$ at calcination temperature of 250 °C under air atmosphere. During the first step, the F^- in the solution has played a crucial role throughout the whole preparation process. Without the assistance of the additive NH_4F, pre-literature research reveals the fact that the precursor of $NiCo_2(OH)_{3y}(CO_3)_{1.5(2-y)}\cdot nH_2O$ cannot directly grow on smooth substrates [20]. The reaction mechanism can be referred Eqns. (1)–(5), and calcined process Eqn. (6), Secondly, amorphous carbon layer was deposited onto the $NiCo_2O_4$/carbon cloth by radio-frequency magnetron sputtering and the $NiCo_2O_4$@ C/carbon cloth composite was obtained.

$$Ni^{2+}+2Co^{2+}+3xF^- \rightarrow [NiCo_2F_{3x}]^{3(x-2)-} \quad (1)$$

$$CO(NH_2)_2+H_2O \rightarrow 2NH_3+CO_2 \quad (2)$$

$$CO_2+H_2O \rightarrow CO_3^{2-}+2H^+ \quad (3)$$

$$NH_3.H_2O \rightarrow NH_4^+ + 2OH^- \quad (4)$$

$$[NiCo_2F_{3x}]^{3(x-2)-}+1.5(2-y)CO_3^{2-}+3yOH^-+nH_2O \rightarrow NiCo_2(OH)_{3y}(CO_3)_{1.5(2-y)}\cdot nH_2O+3xF^- \quad (5)$$

$$NiCo_2(OH)_{3y}(CO_3)_{1.5(2-y)}\cdot nH_2O + O_2 \rightarrow 2NiCo_2O_4+(3y+2n)H_2O+3(2-y)CO_2 \quad (6)$$

Fig. 2 shows typical SEM images of the $NiCo_2O_4$/carbon cloth