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# Nickel cobalt sulfide Nanotube Array on Nickel Foam as Anode Material for Advanced Lithium-Ion Batteries

D.J. Yu[a], Y.F. Yuan[a,b,*], D. Zhang[c], S.M. Yin[a], J.X. Lin[a], Z. Rong[a], J.L. Yang[a], Y.B. Chen[a], S.Y. Guo[a,*]

[a] College of Machinery and Automation, Zhejiang Sci-Tech University, Hangzhou 310018, China
[b] State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China
[c] Hang Zhou City of Quality and Technical Supervision and Testing Institute, Hangzhou 310019, China

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ABSTRACT

A facile twice-hydrothermal method is developed for large-scale growth of $NiCo_2S_4$ nanotube array on Ni foam with robust adhesion. As-prepared materials are characterized by SEM, XRD and EDS. It can be observed that $NiCo_2S_4$ nanotubes directly grow on Ni foam with an average inner-diameter of ~55 nm, external-diameter of 100 nm, and length of ~2 μm. When evaluated as a binder-free anode for LIBs, $NiCo_2S_4$ nanotube array exhibits outstanding lithium-storage performance that includes high special capacity, excellent cyclic stability and desirable rate capability. At 0.2 C rate, $NiCo_2S_4$ nanotube array delivers the average discharge capacity of 720 mAh $g^{-1}$ during 50 cycles that slightly surpasses its theoretical capacity of 703 mAh $g^{-1}$. When the current comes back to 0.2 C after rate measurements, $NiCo_2S_4$ nanotubes can still stably deliver the discharging capacity of 652 mAh $g^{-1}$, reaching 92.7% of that at the initial 0.2 C. Cyclic Voltammetry (CV) measurements reveal that $NiCo_2S_4$ nanotube array contains two sets of electrochemical reaction behavior come from Ni and Co. The unique $NiCo_2S_4$ nanotube array exhibits great potential as an anode material for high-performance Lithium-ion batteries.



## 1. Introduction

Lithium-ion batteries (LIBs) as a clean and reliable energy-storage device are very popular in wide applications involving portable electronic devices, electric tools, electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1,2]. Transition metal oxides (TMOs) own high theoretical capacity, natural abundance and environment friendliness, considered as promising anode materials for advanced LIBs, and including NiO [3], ZnO [4,5], $Co_3O_4$ [6], $Fe_3O_4$ [7], $MnO_2$ [8,9], and so on. Nevertheless, electrochemical performances of conventional binary TMOs usually rapidly degrade in the high-rate discharging-charging current because of their poor electron conductivity [10], which limits their practical application. Compared with binary TMOs, the ternary TMOs are better alternative anode materials, and attract intense interest due to their higher electron conductivity and redox activity. For example, It has been reported that spinel-type bimetallic oxide nickel cobaltite ($NiCo_2O_4$) possesses richer redox chemistry (both Ni and Co active species) and much better electronic conductivity (at least two orders of magnitude higher) than corresponding binary nickel or cobalt oxides [11,12]. So far, $NiCo_2O_4$ has been widely used in the fields of LIBs [13,14], electrochemical capacitors (ECs) [15,16], Li-$O_2$ batteries [17], etc. Although the electron conductivity of $NiCo_2O_4$ is much higher than that of binary TMOs, the sulfide of $NiCo_2O_4$ ($NiCo_2S_4$) further possesses 2 orders of magnitude higher electron conductivity than $NiCo_2O_4$ [18,19]. Theoretically, $NiCo_2S_4$ is also a potential advanced electrode material and worth studying deeply. At present, $NiCo_2S_4$ has been extensively investigated in the field of ECs and shows high special area capacitance, desirable rate capability, excellent cyclic stability [20–23]. However, the application of $NiCo_2S_4$ in LIBs has been still seldom reported [24–26].

Another problem of TMOs as anode material of LIBs is their poor cycling performance, and the electrode materials seldom maintain their structure stability over several discharging-charging cycles [27–29]. It has been demonstrated that this problem can be partly solved by constructing nanostructured electrode materials because the nanostructure can better accommodate strain change induced by the repeated insertion-desertion of Li-ion than micrometer-scale materials [30,31]. The binder-free free-standing one-dimensional (1D) nanostructured anode arrays grown on

* Corresponding authors at: College of Machinery and Automation, Zhejiang Sci-Tech University, Hangzhou 310018, China. Tel.: +86 571 8684 3343.
*E-mail addresses:* yuanyf@zstu.edu.cn (Y.F. Yuan), syiguo@163.com (S.Y. Guo).

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current collector is a more effective solution against the volume change problem, because the geometry of 1D materials, e.g. nanowires, nanorods, nanotubes, is not easily pulverized or broken due to facile strain relaxation [32–34]. Especially, compared with nanowires and nanorods, inner and outer surface of nanotubes can provide more electroactive sites for the reaction of electrode materials with the electrolyte.

Combined the aforesaid two aspects, herein, we adopted a cost-effective solution method to directly grow $NiCo_2S_4$ nanotube array on Ni foam substrates. Due to high electrical conductivity of $NiCo_2S_4$ as well as structure characteristics of the nanotube and the binder-free free-standing electrode, $NiCo_2S_4$ nanotube array manifested high specific capacity, excellent cycling stability and high rate capability.

## 2. Experimental

### 2.1. Synthesis of $NiCo_2S_4$ Nanotube Array

All the chemicals used in this work were of analytic grade and directly used without further purification. Firstly, a piece of Ni foam (12 mm in diameter) was cleaned by sonication for 10 min with acetone, ethanol and deionized water, and then soaked into 3 M HCl solution for 10 min. Cleaned by deionized water again, the cleaned Ni foam was dried at 60 °C under vacuum.

Twice-hydrothermal methods were adopted to grow $NiCo_2S_4$ nanotube array on Ni foam. In the first hydrothermal reaction, 0.44 g $Ni(NO_3)_2{\cdot}6H_2O$, 0.72 g $CoCl_2{\cdot}6H_2O$, 2.00 g urea and 0.75 g hexamethylene tetramine (HTMA) were dissolved into 75 ml deionized water, forming a pink solution, transferred into a 100 mL Teflon-lined stainless steel autoclave. The cleaned Ni foams were vertically placed into the autoclave. Then, the autoclave was heated to 120 °C for 6 h. After the autoclave was cooled down to the room temperature naturally, the Ni foams were taken out, cleaned with absolute ethanol and deionized water, respectively. In the second hydrothermal reaction, 0.72 g $Na_2S{\cdot}9H_2O$ was dissolved into 75 ml deionized water, and then the solution was transferred into a 100 ml autoclave. The Ni foams with the precursor were again placed into the autoclave. The autoclave was subsequently heated to 160 °C for 6 h. After the autoclave was cooled down to room temperature, the Ni foam was taken out, washed with deionized water and absolute ethanol, dried at 60 °C.

NiS and $Co_3S_4$ grew onto Ni foam by the above same method for comparison investigation, respectively, but the synthesis of NiS did not use $CoCl_2{\cdot}6H_2O$; the synthesis of $Co_3S_4$ did not use $Ni(NO_3)_2{\cdot}6H_2O$.

### 2.2. Material Characterization

The phase structure of the product was characterized by X-ray Diffraction (XRD, Bruker D8 ADVANCE) with a monochromatized source of Cu Kα radiation (λ = 0.1542 nm). The morphologies were characterized by Field Emission Scanning Electron Microscopy (FESEM, ultra55, Carl Zeiss AG) at 3.0 KV. The Energy Dispersive X-ray spectroscopy (EDS) spectra were acquired on Scan Electron Microscope (SEM, JEOL JSM–5610LV).

### 2.3. Electrochemical Measurements

The CR2025-type coin cells were assembled in an argon-filled homemade glovebox with $NiCo_2S_4$ arrays/Ni foam as the working electrode, metallic lithium foil as the counter electrode, Celgard 2300 film as the separator, and 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) as the electrolyte.

Galvanostatic discharging-charging measurements were performed by the Neware battery tester at ambient temperature. Using Parstat 2273 advanced electrochemical workstation, Cyclic Voltammetry (CV) measurements were conducted in a potential window of 0.005 ~ 3.0 V (vs $Li/Li^+$) at a scan rate of 0.1 mV $s^{-1}$, and Electrochemical Impedance Spectroscopy (EIS) was performed at the amplitude of 5 mV in the frequency range from 0.1 Hz to 100 KHz.

## 3. Results and Discussion

Twice-hydrothermal methods were used to grow $NiCo_2S_4$ nanotube array on Ni foam. After the first hydrothermal reaction, the precursor grows onto the Ni foam; and then Ni foam changes to atrovirens one. After the second hydrothermal reaction, the Ni foam again changes to black one. To determine phase structure and phase purity of the resulting product, the black Ni foam was analyzed by XRD and the result is shown in Fig. 1. Five distinct diffraction peaks are observed at 2θ values of 26.8, 31.3, 38.3, 50.3 and 55.4°, respectively. They can be indexed to (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) crystal planes and assigned to cubic phase $NiCo_2S_4$ (JCPDS Card No.20-0782). The diffraction peaks of $NiCo_2S_4$ shows dwarfed and widen characteristic, meaning that the synthesized $NiCo_2S_4$ could be poor crystalline state and nanoscale size. XRD does not detect the diffraction peaks of other materials except those of Ni substrate ("*" in Fig. 1), suggesting the high purity of the synthesized $NiCo_2S_4$.

The morphologies of the precursor and $NiCo_2S_4$ were examined by FESEM. Fig. 2a is the SEM image of the precursor. After the first hydrothermal reaction, the nanowires with approximately 100 nm in diameter and 2 um in length grow on Ni foam, forming a homogeneous nanowires array. The nanowire surfaces are very smooth. EDS spectrum analysis of these nanowires (the inset of Fig. 2a) indicates that the nanowire precursor is composed of Ni, Co, C, O, H. It can be inferred from the element content that the precursor could be $NiCo_2(CO_3)_{1.8}(OH)_{2.4}$, named usually as NiCo-precursor. After the second hydrothermal reaction, the smooth NiCo-precursor nanowires are changed to the rough $NiCo_2S_4$ array (Fig. 2 b-c). In the low-magnification SEM image (Fig. 2b), the array characteristic shown by $NiCo_2S_4$ is the same as that of the NiCo-precursor nanowire array, without obviously broken and flaked off. In the high-magnification SEM image (Fig. 2c), however, it can be clearly observed that $NiCo_2S_4$ presents the nanotube structure; its tube wall is very rough and thin. The inner diameter of the nanotubes is about 50 nm and the external diameter about 100 nm.

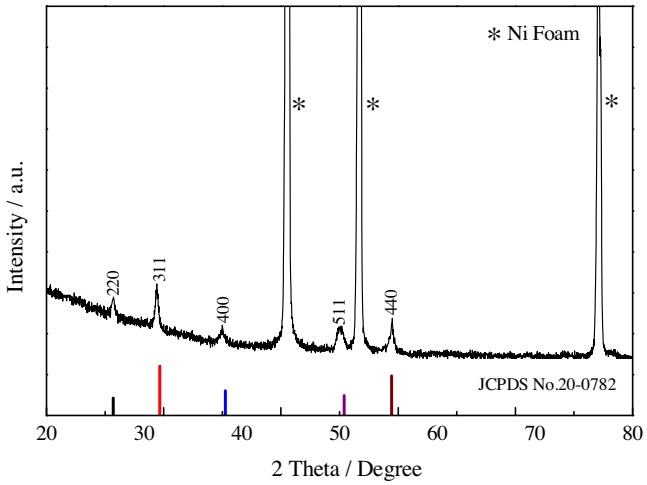


**Fig 1.** XRD pattern of $NiCo_2S_4$ nanotube array growing on Ni foam.