



Design and fabrication of highly open nickel cobalt sulfide nanosheets on Ni foam for asymmetric supercapacitors with high energy density and long cycle-life



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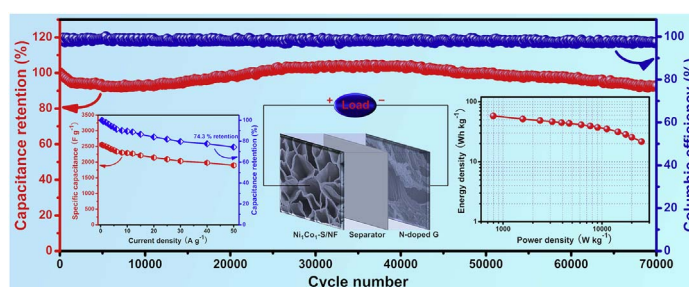
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HIGHLIGHTS

- Highly open nickel cobalt sulfide nanosheets on Ni foam were rationally designed.
- The optimized electrode showed excellent specific capacitance and rate capability.
- The assembled asymmetric supercapacitor delivered a high energy of 58.1 Wh kg⁻¹.
- The device exhibited remarkable long-term cycling durability after 70,000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel cobalt sulfides (NiCo-S) are promising electrode materials for high-performance supercapacitors but normally show poor rate capability and unsatisfactory long-term endurance. To overcome these disadvantages, a properly constructed electrode architecture with abundant electron transport channels, excellent electronic conductivity and robust structural stability is required. Herein, considering that in situ transformation can mostly retain the specific structural advantages of the precursors, a two-step strategy is purposefully developed to construct a binder-free electrode composed of interconnected NiCo-S nanosheets on Ni foam (NiCo-S/NF), in which NiCo-S/NF is synthesized via the in situ sulfuration of networked acetate anion-intercalated nickel cobalt layered double hydroxide nanosheets loaded on Ni foam (A-NiCo-LDH/NF). Noticeably, the optimized Ni₁Co₁-S/NF exhibits an ultrahigh specific capacitance of 2553.9 F g⁻¹ at 0.5 A g⁻¹, excellent rate capability (1898.1 F g⁻¹ at 50 A g⁻¹) and superior cycling stability (nearly 90% capacitance retention after 10,000 cycles). Furthermore, the assembled asymmetric supercapacitor based on Ni₁Co₁-S/NF demonstrates a high energy density of 58.1 Wh kg⁻¹ at a power density of 796 W kg⁻¹ and impressive long-term durability even after a repeated charge/discharge process as long as 70,000 cycles (~92% capacitance retention). The attractive properties endow the Ni₁Co₁-S/NF electrode with significant potential for high-performance energy storage devices.

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1. Introduction

Due to the urgent situations of ever-increasing energy demand and environmental pollution, intense enthusiasm to exploit clean and renewable energy sources as well as the corresponding advanced energy storage devices has been sparked worldwide. Of which, supercapacitors have drawn extensive attention in virtue of their high power output, quick charge/discharge rate, long service life with low maintenance cost and prominent reliability [1–3]. Considering the predominant effect of the electrode material on the overall performance of a supercapacitor, it is imperative to explore advanced electrode materials with prominent advantages, such as high specific capacitance and rate capability, remarkable energy density and power density, inexpensive cost and ultralong lifespan [3–6].

Considering the energy storage mechanism, a rough classification of electrode materials into two types can be achieved. Where conventional carbon-based electrical double layer capacitive (EDLC) materials normally suffer from limited specific capacitance and inferior energy density [7,8], pseudocapacitive materials, which store charge by undergoing reversible redox reactions at (or near) the electrode-electrolyte interface, can deliver distinctly higher specific capacitance and energy density than carbonaceous materials [9,10]. Among various pseudocapacitive materials, transition metal sulfides have been widely explored as high-performance electrode materials for advanced electrochemical energy storage devices [11–13]. In which, bimetallic nickel cobalt sulfides have been widely investigated as promising candidates on account of the obviously higher electrochemical activity and electrical conductivity than their oxides/hydroxides counterparts as well as the better mechanical and thermal stability [13–19]. Furthermore, benefiting from the effective integration of both Ni and Co elements, which have multiple valence states, bimetallic nickel cobalt sulfides normally possess richer redox-active sites than single component sulfides, thus giving rise to improved electrochemical activity and specific capacitance [17–20]. Nevertheless, the intrinsic electrical conductivity of nickel cobalt sulfides alone is still insufficient for high-rate charge transfer, which inevitably causes deteriorated capacitance and unsatisfactory rate capability [21–23]. Moreover, the poor electrochemical stability during long-term charge-discharge processes of nickel cobalt sulfide electrode materials is another problem that needs to be solved [10,16,21].

To this end, ideal high-performance nickel cobalt sulfide electrode materials should have a specific structure with more accessible electroactive sites, faster charge transfer ability, shortened ion diffusion paths and enhanced electrochemical stability [24]. To date, many studies have been carried out to thoroughly overcome these barriers. Among which, the proper hybridization of nickel cobalt sulfides with various carbon materials has been regarded as a feasible solution [19,25–28]. Whereas, when these powdery hybrids are treated with a conventional slurry-coating procedure to prepare working electrodes, the tedious process, including grinding and high-pressure tableting, unavoidably damages the as-constructed structures and restricts charge transport [16]. Besides, the addition of low-capacitance conductive additives and insulative polymer binders also obstructs charge transfer and depresses the electrochemical properties [29–31]. As another route to effectively realizing the supposed performance without sacrificing the intrinsic merits of the electrodes, the rational construction of a binder-free system via directly growing nickel cobalt sulfides onto conductive substrates has also been proven valid and discussed in detail [16,17,22,24,32,33].

Up to now, among the various methods to fabricate high-performance nickel cobalt sulfides, in situ transformation from the corresponding oxide/hydroxide precursors has been proven highly efficient [24,32–35]. During this transformation, the structure and morphology of precursors can be basically reserved, which inspired us to prepare nickel cobalt sulfide-based materials with specific nanostructures by controlling the precursors. Therefore, the selection and investigation of

appropriate precursors with special properties are also of great importance. Recently, we constructed binder-free electrodes composed of highly interconnected acetate anion-intercalated nickel cobalt layered double hydroxide nanosheets on Ni foam (A-NiCo-LDH/NF) through a feasible alkali-free “solvothetical and in situ hydrolysis” strategy [36]. These electrodes showed distinctly enhanced electrochemical properties and cycling stability, which were attributed to the intercalate-induced expanded interlayer spacing and stable architecture with unique morphology. In consideration of retaining the abovementioned structural merits, we attempted to transform the A-NiCo-LDH/NFs into their associated binder-free nickel cobalt sulfide electrodes (NiCo-S/NFs) via an in situ procedure.

Herein, we performed another solvothetical treatment to sulfurize the as-obtained A-NiCo-LDH/NFs into the corresponding NiCo-S/NFs electrodes. As expected, sulfuration was achieved in situ, and the original structural and morphological features of the A-NiCo-LDH/NFs were basically maintained. Benefiting from the special nanostructure and significant synergetic effects among the components, the optimized Ni₁Co₁-S/NF electrode presented extraordinary electrochemical performance, including ultrahigh specific capacitance, excellent rate capability and brilliant long-term endurance. Furthermore, an asymmetric supercapacitor (ASC) device based on Ni₁Co₁-S/NF and nitrogen-doped graphene (NG) was assembled. Notably, the assembled ASC device delivered an impressively high energy density (58.1 Wh kg⁻¹) and power density (25,081.7 W kg⁻¹), as well as a spectacular cycling durability even after a long charge/discharge process repeated for 70,000 cycles.

2. Experimental section

2.1. Chemicals and materials

Prior to the experiments, Ni foam substrates were treated with the procedure given in the [supplementary information](#) to ensure a clean surface. All other analytical reagents were directly used as received. Nickel acetate tetrahydrate (Ni(Ac)₂·4H₂O, 99%), cobalt acetate tetrahydrate (Co(Ac)₂·4H₂O, 99%) and sodium sulfide nonahydrate (Na₂S·9H₂O, 98%) were sourced from Aladdin Industrial Cooperation. Anhydrous methanol was purchased from Sinopharm Chemical Reagent Co., Ltd. All involved aqueous solutions were prepared using deionized water (DW).

2.2. Synthesis of NiCo-S/NF electrodes

All NiCo-S/NF electrodes were prepared through a two-step strategy, as depicted in Fig. 1a. First, A-NiCo-LDH/NFs were obtained via our reported approach [36]. Afterwards, an in situ solvothetical sulfuration was applied using A-NiCo-LDH/NFs as precursors to acquire the desired NiCo-S/NFs. Typically, 15 mL of homogeneous methanol solution containing 0.5 mmol Ni(Ac)₂·4H₂O and 0.5 mmol Co(Ac)₂·4H₂O was added into a 25 mL Teflon-lined autoclave together with three pieces of treated Ni foam (1 × 1 cm). To ensure the complete surface wetting of the Ni foams, the autoclave was sealed for 1 h before heating. Subsequently, the autoclave was heated at 180 °C for 12 h and then naturally cooled. The substrates were collected and repeatedly washed with DW under ultrasonication to obtain A-NiCo-LDH/NFs. Then, these A-NiCo-LDH/NFs were placed into a 25 mL autoclave containing 15 mL of 0.1 M Na₂S aqueous solution and kept at 120 °C for 6 h. After the reaction was complete, the black products were sufficiently washed with DW and ethanol 5 times each and then dried at 60 °C for 24 h. The ultimate product was denoted as Ni₁Co₁-S/NF with an average active mass loading of ~1.4 mg on the projected area of per square centimeter. To clarify the influence of substrate, the individual Ni foams also underwent the same two-step solvothetical procedure, except for the absence of Ni(Ac)₂·4H₂O and Co(Ac)₂·4H₂O in the first-step solvothetical process. Notably, the influence of the substrate can

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