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Effect of the bimetal ratio on the growth of nickel cobalt sulfide on the Ni foam for the battery-like electrode

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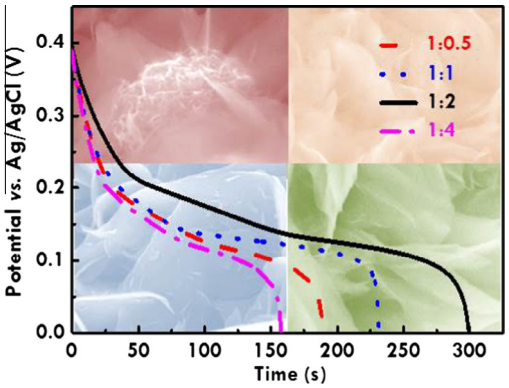
GRAPHICAL ABSTRACT



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ABSTRACT

The nickel cobalt sulfide is one of the most attractive electroactive materials for battery-like electrodes with multiple oxidation states for Faradaic reactions. Novel structures of the nickel cobalt sulfide with large surface areas and high conductivities have been proposed to improve the performance of the battery-like electrodes. The hydrothermal reaction is the most common used method for synthesizing nickel cobalt sulfide nanostructures due to the simple and cost-effective features, but the precursor concentration on the morphology and the resulting electrochemical performance is barely discussed. In this study, various Ni to Co ratios are used in the hydrothermal reaction to make nickel cobalt sulfides on the nickel foam, and the Ni to Co ratio is found to play great roles on the morphology and the electrocapacitive performance for the pertinent battery-like electrodes. The sheet-like structures are successfully obtained with large surface area for charge accumulation, and the optimized sample presents the largest nanosheets among all with several wrinkles on the surface. A high specific capacity of 258.2 mAh/g measured at the current density of 5 A/g and a high-rate charge/discharge capacity are also attended for the optimized battery-like electrodes. The excellent cycling stability of 94.5% retention after 2000 cycles repeated charge/discharge process is also obtained for this system.

1. Introduction

With the increasing demands on the clean energy to solve the serious pollution issues and to achieve a sustainable world, several energy-generating and energy-storing devices were developed

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intensively [1–3]. The supercapacitor (SC) is one of the significant energy-storing devices due to its high energy and power densities as well as the long charge/discharge cycling life [3,4]. There are two sorts of the SC, the electrochemical double layered capacitor (EDLC) and the pseudocapacitor. The EDLCs directly accumulate charges on the surfaces of the electroactive materials, while the Faradic redox reactions only occur on the surfaces of the electroactive materials for the pseudocapacitors. Therefore, the higher cycling stability can be achieved for the EDLC but the larger specific capacitances (C_F) can only be achieved for the pseudocapacitor due to its fast redox kinetics [4].

Bimetallic transition metal sulfides have been greatly studied as the electroactive materials for the pseudocapacitors due to the multiple oxidation states for the Faradaic redox reactions and the high electronic conductivity because of the coupling of bimetallic transition metal species [5–10]. Among the transition metals, cobalt and nickel are two of the most investigated species due to their high redox activities. Chen et al. used a one-step electrochemically co-deposition method to prepare ternary nickel cobalt sulfide nanosheets on the conductive carbon and got a C_F value of 1418 F/g at the current density of 5 A/g for the resulting pseudocapacitor electrode [11]. Xiao et al. developed $NiCo_2S_4$ single crystalline nanotube arrays grown on a flexible carbon fiber paper as the pseudocapacitive material and the resulting pseudocapacitive electrode presented superior electrocapacitive performance as compared with its oxide counterpart [12]. Among the literatures dealing with the pseudocapacitor electrode with nickel cobalt sulfides as the electroactive material, the Ni foam was usually acted as the substrate since nickel existed in both substrate and the electroactive material for this kind of system, among which most of the nickel cobalt sulfide was grown directly on the Ni foam substrate instead of being synthesized as the powder form and then deposited on the Ni foam. Chen et al. synthesized $NiCo_2S_4$ nanotubes on the Ni foam via the hydrothermal and anion-exchange methods to attend a C_F value of 14.39 F/cm^2 at the current density of 5 mA/cm^2 for the pertinent pseudocapacitor electrode [9]. Li et al. obtained nickel cobalt sulfides on the Ni foam using a hydrothermal method to achieve a C_F value of 2415 F/g at the current density of 2.5 mA/cm^2 [10]. Liu et al. fabricated three-dimensional porous $NiCo_2S_4$ nanonetworks on the Ni foam through an anion exchange reaction and obtained a C_F value of 1501 F/g at the current density of 1 A/g and a robust cycling stability for the pertinent pseudocapacitor electrode [13]. However, most of the researchers focused on synthesizing novel structures of the nickel cobalt sulfide with high surface area and high electronic conductivity as the electroactive material for the SC electrode [14–17], but the study for discussing the influence of the nickel to cobalt ratio in the hydrothermal reaction on the structure and the performance of the corresponding device is limited. Tang et al. synthesized cobalt nickel phosphate nanospheres with honeycomb-like mesopores via a facile hydrothermal process combining with low temperature pyrolysis. Different cobalt to nickel ratios were applied to find the best electroactive material for the pseudocapacitor electrode, and the one based on $Co_{0.86}Ni_{2.14}(PO_4)_2$ exhibited the highest C_F value of 1409 F/g at the current density of 0.25 A/g and the highest rate-performance [18]. Lin et al. decorated the binary metal sulfide nanoparticles composed of nickel and cobalt on multi-walled carbon nanotubes via a facile glucose-assisted hydrothermal method and tuned the nickel to cobalt ratio in the composite to find an optimized capacity up to 153 mAh/g, superior rate capability and excellent electrochemical stability [19]. To the best of our knowledge, there is no report focused on tuning the nickel to cobalt ratio in the hydrothermal reaction to synthesize nickel cobalt sulfides with different morphologies as the electroactive material for achieving the enhanced performance for the pseudocapacitor electrode. However, some of the materials are described as "pseudocapacitive" materials despite the fact that their electrochemical signature is analogous to that of a "battery"

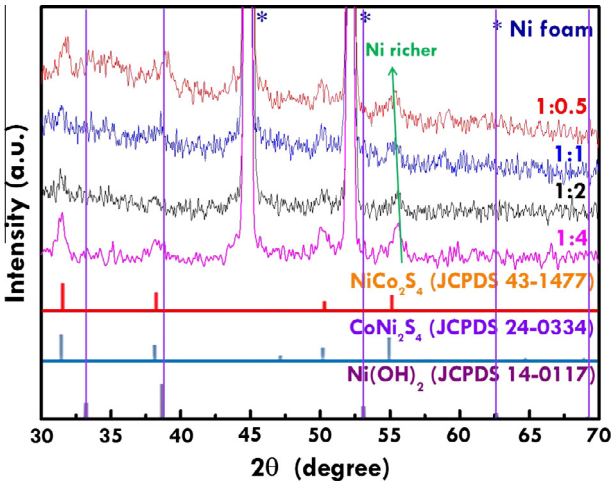

Fig. 2. The XRD patterns for the nickel cobalt sulfide battery-like electrode prepared by using different Ni to Co ratios in the precursor solution.

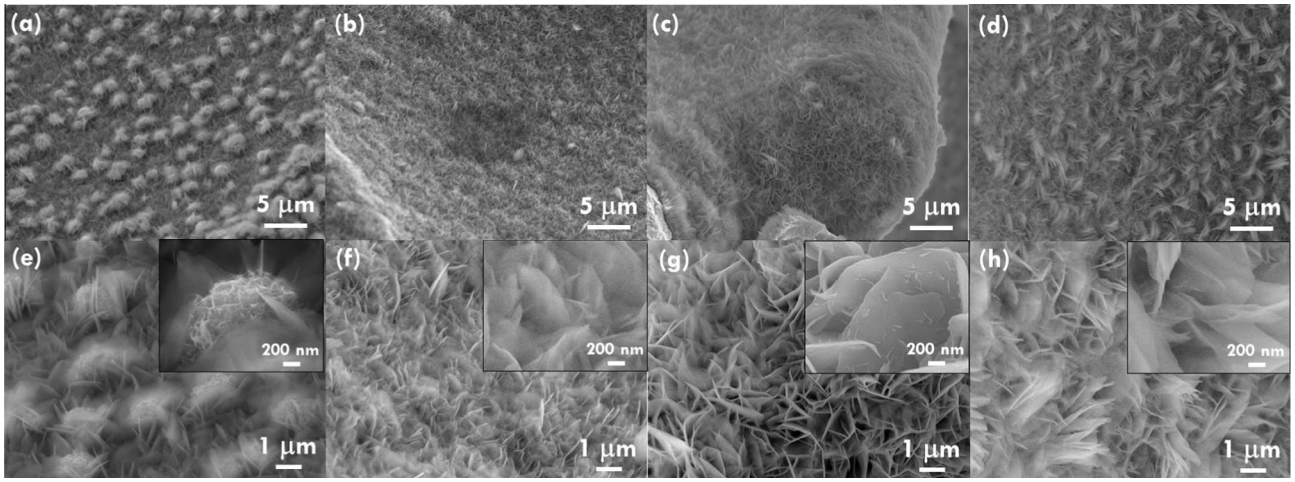

Fig. 1. The SEM images for the nickel cobalt sulfide on the nickel foam with the Ni to Co ratio of (a, e) 1:0.5, (b, f) 1:1, (c, g) 1:2, and (d, h) 1:4.