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3D meso/macroporous Ni_3S_2@Ni composite electrode for high-performance supercapacitor

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ABSTRACT

Ni_3S_2@Ni composite electrode for supercapacitor is synthesized via a one-step solvothermal treatment of Ni foam at 120 °C, exhibiting a 3D meso/macroporous network structure. The structure contains Ni_3S_2 nanosheets with 15–20 nm in thickness and meso/macropores with an average pore size of 24.69 nm, and its formation is regulated through the slow release of S^{2-} ions and the solid/liquid interfacial reactions in absolute ethanol. At a current density of 17.15 A g^{-1}, the composite electrode demonstrates a high specific capacitance of 945.71 F g^{-1}, and at various current densities below 17.15 A g^{-1}, it retains capacitance retention ratios above 100% after 2000 charge/discharge cycles. A two-step oxidation and three-step reverse reduction process occurs during the reversible Faradaic reaction of Ni_3S_2 in KOH aqueous solution, which is due to the valence transitions of Ni^0 in Ni_3S_2 between Ni^0 and Ni^{3+}. The homogeneous cracking in Ni_3S_2 layer is a critical factor for achieving its long-term cycling stability, however, the cycling results in its amorphization. An asymmetric supercapacitor is assembled using Ni_3S_2@Ni composite electrode as the positive electrode and Ni foam as the negative electrode, which delivers an energy density of 55.79 Wh kg^{-1} at the power density of 938.98 W kg^{-1}.

1. Introduction

As rechargeable energy storage devices, supercapacitors (SCs) have a great expectation for their ultra-long cycle life, high security coefficient and fast charge/discharge applications [1–6]. In recent decades, Ni_3S_2, a typical nickel sulfide with a high theoretical capacity of 2412 F g^{-1}, is found to offer fluent charge transfer due to its high electrical conductivity and especially intrinsic metallic property, and these properties have attracted increasingly intensive attention of researchers to develop high-performance SCs using Ni_3S_2 as the electrode materials [1,6–10]. During the fast charge/discharge processes, efficient Faradaic reaction usually proceeds within the near surface region of active materials [6], therefore nano-sized Ni_3S_2 crystals are favorable for achieving the high energy density through their high utilization efficiency in the Faradaic reaction. Pan et al. synthesized Ni_3S_2 nanoparticles of 8–28 nm and reported a specific capacitance of 147.2 F g^{-1} at a scan rate of 5 mV s^{-1} [11]. Li et al. prepared Ni_3S_2 nanoparticles of 100 nm with a specific capacitance of 911 F g^{-1} at a current density of 0.5 A g^{-1} [12]. In fact, those reports all use the binder, conducting agent to prepare the electrodes, however, such additives inevitably impede the contact between active materials and current collector resulting in a slow electron transport [1,10].

In order to take full advantage of the high theoretical capacity and the intrinsic metallic property of Ni_3S_2, it is necessary to reduce the internal resistance of electrodes, thus binder-free approaches to synthesize Ni_3S_2@Ni composite electrodes by growing Ni_3S_2 nanocrystals directly on Ni foam (NF) current collectors are considered favorable for ion and electron transport [1,6]. Usually, Ni oxysalt and S source are both used in hydrothermal synthesis of Ni_3S_2 films on NF substrate, and the active materials prepared by Li et al. and Huo et al. were reported with specific capacitances of 2230 F g^{-1} at 3.6 A g^{-1} and 1370.4 F g^{-1} at 2 A g^{-1}, respectively [13,14]. To alleviate the volumetric strains in Ni_3S_2 active materials produced during the consecutive charge/discharge processes, reduced graphene oxide (rGO) nanosheets with high conductivity are also added into the reaction mixture, and the Ni_3S_2-rGO electrode materials were reported with specific capacitances of 3234.6 F g^{-1} at 3.85 A g^{-1} and 987.8 F g^{-1} at 1.5 A g^{-1}, respectively [15,16]. Moreover, Ni_3S_2@Ni composite electrodes can be directly

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fabricated by sulfuration of NF substrate, and the Ni_3S_2 electrode materials were reported with specific capacitances of 2233.3 F g^{-1} at 3.3 A g^{-1} and 1109.8 F g^{-1} at 1.3 A g^{-1}, respectively [17,18].

As to the preparation of Ni_3S_2@Ni composite electrodes, there is still room for improvement in microstructure tailoring and uniform distribution of Ni_3S_2 due to the following reasons: (1) With the addition of Ni oxysalt, the generation of Ni_3S_2 nuclei can be achieved through either homogeneous nucleation in reaction mixture or heterogeneous nucleation on the surfaces of NF substrate, however, the growth of such Ni_3S_2 nuclei formed in reaction mixture will not proceed on NF substrate. (2) Approaching a critical temperature, S sources such as thioacetamide and thiourea will hydrolyze to release a large amount of H_2S molecules and S^{2-} ions within a short time [19], which is unfavorable for controllable growth and microstructure tailoring of Ni_3S_2 nanocrystals.

In the present work, a 3D meso/macroporous Ni_3S_2@Ni composite electrode is achieved through in-situ sulfuration of NF substrate in absolute ethanol at 120 °C, which exhibits good electrochemical performance and excellent long-term cycling stability contributed by the following factors: (1) Without an extra addition of Ni source, both the heterogeneous nucleation and subsequent growth of Ni_3S_2 nuclei proceed directly on the surface of NF substrate to naturally achieve inter-atomic bonding within the interfacial region, thus forming a well-adhered interface between Ni_3S_2 active materials and NF current collector to be favorable for fluent charge transfer. (2) In absolute ethanol, S^{2-} ions are slowly released with the help of small amount of crystal water thermally decomposed from $Na_2S \cdot 9H_2O$, which is favorable for the microstructure construction of Ni_3S_2 nanocrystals on NF substrate. (3) The meso/macropore sizes and the thickness of Ni_3S_2 nanosheets are in the ranges of 10–100 nm and 15–20 nm, respectively, therefore such porous structures can not only cope adequately with fast ion transfer and exchange [20–22], but also effectively alleviate the volumetric strains in Ni_3S_2 through structural synergy and self-cracking to achieve the long-term cycling stability.

In addition, an asymmetric supercapacitor (ASC) is assembled to assess the potential application using Ni_3S_2@Ni composite electrode as the positive electrode and NF as the negative electrode. More importantly, we systematically discuss the formation mechanism of Ni_3S_2 porous network structure, the mechanism behind the Faradaic reaction of Ni_3S_2 in KOH aqueous solution, and the impact of long-term cycling on the microstructures of Ni_3S_2 active materials. These results offer the valuable ideas for the controllable growth of Ni_3S_2 nanocrystals and the evaluation of their electrochemical performances using as active electrode materials for SCs.

2. Experimental

2.1. Synthesis of Ni_3S_2@Ni composite electrode

All chemicals were of analytical grade and used without purification except for further removal of water from absolute ethanol. In a typical synthesis, 6.25 mmol of $Na_2S \cdot 9H_2O$ was ultrasonically dispersed in 15 mL of absolute ethanol for 30 min under the ultrasonic power of 120 W to prepare a milk-white reaction mixture for later use. A piece of 1 × 3 cm^2 NF treated with hydrochloric acid, about an average weight of 39.6 mg cm^{-2}, was washed with deionized water and absolute ethanol for several times, immersed into the reaction mixture, subjected to ultrasonic vibration for 10 min, and then transferred into a 25 mL of Teflon-lined stainless steel autoclave. After that, the autoclave was sealed, heated at 120 °C for 20 h, and cooled down to room temperature when the reaction was completed. Finally, the Ni_3S_2@Ni composite electrode was taken out, rinsed several times with deionized water and absolute ethanol, and dried in air at 80 °C for 12 h.

For convenience, the Ni_3S_2@Ni composite electrode synthesized at 120 °C was marked as NS-120 electrode. In addition, 10 pieces of 1 × 3 cm^2 NS-120 electrodes were immersed into 100 mL of 10 wt% hydrochloric acid solution and subjected to ultrasonic vibration for 10 min under the ultrasonic power of 120 W, and the weight difference between dried electrodes before and after ultrasonic treatment in hydrochloric acid was carefully measured. The average areal mass loading of active materials and the average weight of NS-120 electrode were determined as 3.5 mg cm^{-2} and 40.3 mg cm^{-2}, respectively.

2.2. Fabrication of Ni_3S_2@Ni//NF ASC

A single Ni_3S_2@Ni//NF ASC was assembled using a piece of 1 × 1 cm^2 NS-120 electrode as the positive electrode and a piece of 2 × 3 cm^2 NF as the negative electrode, and the electrodes were mounted on the opposite sides of an open 3.5 × 3 × 4 cm^3 vessel filled with 30 mL of 6 M KOH aqueous electrolyte. Moreover, three ASCs were connected sequentially with platinum wires to form a unity, denoted as three ASCs in series, for electrochemical measurements.

2.3. Material characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku D/max 2200 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) at a scanning speed of 2° min^{-1}. Field emission scanning electron microscopy (FESEM) images were performed on a FEI Nova NanoSEM 230 field emission scanning electron microscopy with an accelerating voltage of 20 kV. The elemental mapping and energy dispersion spectrum (EDS) were recorded using an Oxford INCA model 7421 energy dispersion spectrometer with an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALab 250Xi spectrometer with an Al Kα radiation.

In order to truly reflect the initial pore structures in active materials, a piece of 1 × 3 cm^2 NS-120 electrode was cut into 6 pieces of 0.5 × 1 cm^2 electrodes, then directly subjected to nitrogen adsorption/desorption at 77 K on a Micromeritics ASAP 2020 sorptometer, and the obtained Brunauer-Emmett-Teller (BET) surface areas and pore volumes measured on the electrode were further converted to those of active materials according to the areal mass loading on NF substrate.

2.4. Electrochemical measurement

The electrochemical response of the individual electrode was performed in a three-electrode cell configuration, in which a piece of 1 × 1 cm^2 NS-120 electrode, a piece of 3 × 3 cm^2 platinum plate, a standard Hg/HgO electrode, and a 6.0 M KOH aqueous solution were used as the working electrode, the counter electrode, the reference electrode, and the electrolyte, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were all carried out on a CHI 660E electrochemical workstation. The EIS measurements were conducted over the frequency range from 0.01 to 10^5 Hz while applying an open-circuit voltage amplitude of 5 mV. As to the ASCs, the electrochemical performances were also investigated on the CHI 660E electrochemical workstation but in a two-electrode cell configuration.

Herein, the areal capacitance (C_A, F cm^{-2}), the specific capacitance (C_S, F g^{-1}), the energy density (E, Wh kg^{-1}) and the power density (P, W kg^{-1}) were respectively calculated using the parameters deduced from the corresponding galvanostatic discharge profiles [7,15,23], according to the following Eqs. (1)–(4):