Materials Letters 181 (2016) 25–28

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Superior electrochemical performance of NiS/Ni obtained via electrochemical corrosion

Jicheng Zhang [a], Shibing Ni [a,b,*], Jun Tang [a], Xuelin Yang [a,b,*]

[a] College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China
[b] Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University, China

ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form
5 May 2016
Accepted 28 May 2016
Available online 30 May 2016

Keywords:
Nickel sulfides
Composite materials
Corrosion
Energy storage and conversion

ABSTRACT

NiS is successfully grown on Ni foam via an in situ electrochemical corrosion method. It is proposed that H_2O_2 can act as cathodic depolarizer that promotes the corrosion of Ni, which is crucial for the formation of NiS. The NiS shows flower-like morphology with mean size about 2 μm, consisting of flocky particles with size range from 500 nm to 1 μm. The as prepared NiS/Ni can be directly used as binder free anode for Li-ion batteries, which shows excellent electrochemical performance. It delivers initial discharge and charge capacities are 836 and 668 mA h g^{-1} at a specific current of 150 mA g^{-1}, respectively. After 70 cycles, the charge capacity can maintain of 589 mA h g^{-1}.

1. Introduction

Nickel sulfides have become promising anode materials for Li-ion batteries owing to their high specific capacity, which are typically multiple times higher than that of graphite [1]. However, the main obstacle of the practical application of nickel sulfides in Li-ion is their inferior cycle stability and rate performance. Tremendous research effort on improving the electrochemical performance of nickel sulfides has been made from three aspects: 1) fabricating nanostructured metal sulfides, which offer the advantages of high surface-to-volume ratio, shortened diffusion ways of lithium ions, and high freedom for the volume variation upon lithiation/delithiation [2–4]; 2) incorporating metal sulfides with conductive matrices, especially as graphene, which can obviously improve the electronic conductivity of nickel sulfides [5–8]; 3) growing metal sulfides on electric substrate, which can distinctly improve their electronic conductivity and structure stability in cycling [9–15]. Among them, the 3rd way has been well recognized because metal sulfides/electric substrate composite architecture obtained from this way can be directly used as binder free electrode for Li-ion batteries, which can effectively avoid the morphology destruction of metal sulfides, resulting in impressive electrochemical performance [16,17]. Despite the improvement of electrochemical performance, the main challenge originates from the low valency state of nickel in nickel sulfides. The lower the valence state of Ni in nickel sulfides is, the lower the specific capacity of nickel sulfides exhibit. Thus, based on growing metal sulfides on electric substrate, improving the valency of Ni in nickel sulfides/Ni becomes a feasible way to improve the specific capacity of nickel sulfides.

Here in this paper, we report the preparation of NiS/Ni via an in situ electrochemical corrosion method using H_2O_2 as cathodic depolarizer, which exhibits good electrochemical performance as binder free electrode for Li-ion batteries.

2. Experimental section

All the chemicals are of analytical grade. Firstly, 5 mmol thiourea was dissolved in 20 ml distilled water, and 1.5 ml hydrogen peroxide was added into the solution drop by drop. Secondly, the homogeneous solution was transferred into a 50 ml teflonlined autoclave, and Ni foam was placed in the autoclave. Thirdly, the autoclave was placed in a vacuum oven, heated at 120 °C for 5 h. At last, the reacted Ni foam was dried in an oven at 60 °C for 24 h. For measuring the weight of active NiS on Ni foam, the as-prepared NiS/Ni was washed by diluted hydrochloric acid (10%vol), and the weight difference before and after washing is estimated to be the weight of the NiS. The structure and morphology of the resulting products were characterized by X-Ray powder diffraction (Rigaku Ultima IV Cu Kα radiation λ = 1.5406 Å), and field-emission scanning electron microscopy

* Corresponding authors at: College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China.
E-mail addresses: shibingni07@126.com (S. Ni), xlyang@ctgu.edu.cn (X. Yang).

http://dx.doi.org/10.1016/j.matlet.2016.05.130
0167-577X/

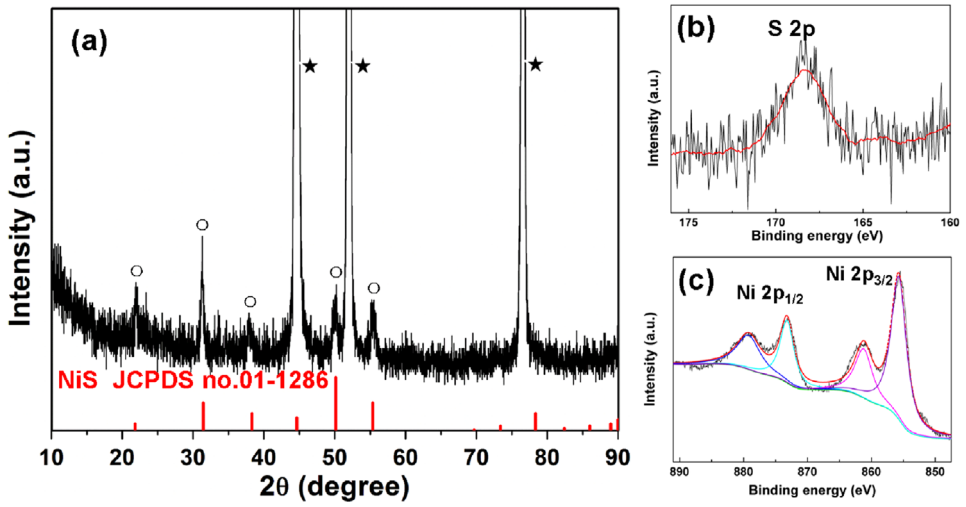

Fig. 1. XRD pattern (a), high resolution XPS spectrum of S 2p (b) and Ni 2p (c) of the as-synthesized electrode. The fitted curves are colorful ones. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

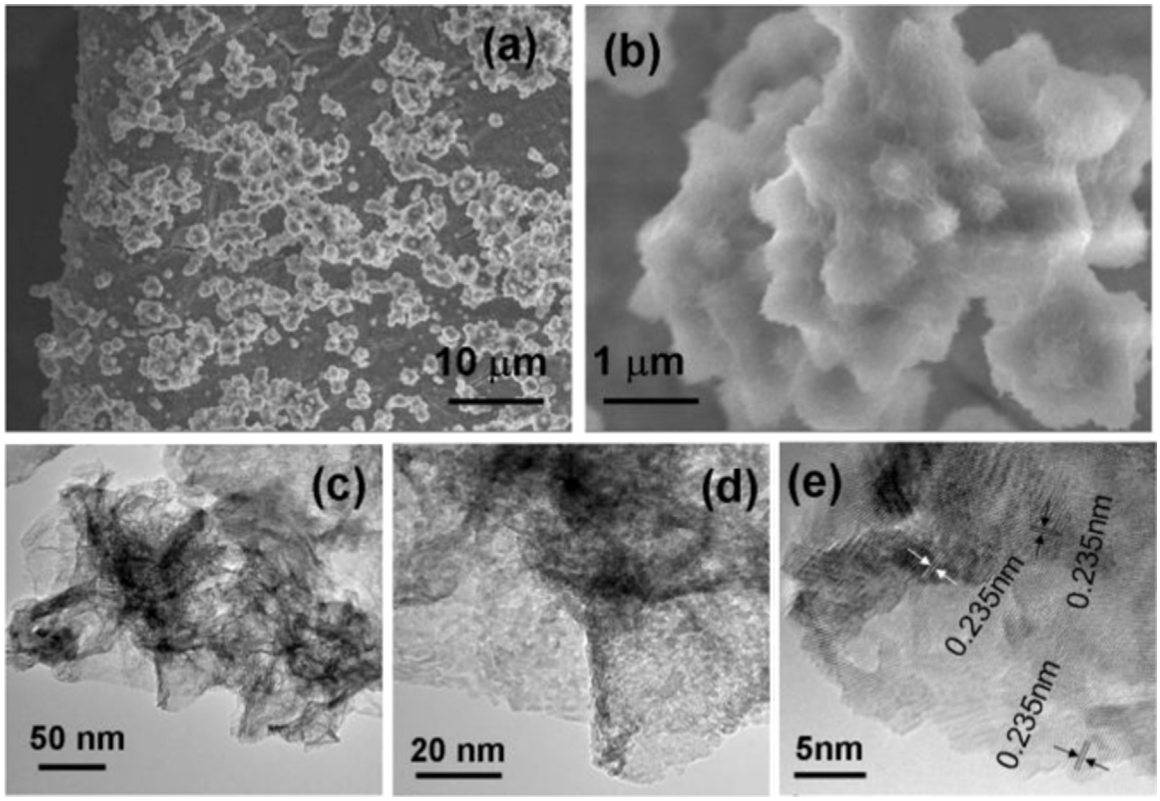

Fig. 2. Low (a) and high (b) magnification SEM images, Low (c) and high (d) magnification TEM images, (e) HRTEM image of the NiS/Ni.

(FE-SEM JSM 7500F, JEOL). For fabricating Li-ion battery, the as-prepared NiS/Ni foams (disc electrode with diameter of 14 mm) were dried in a vacuum oven (120 °C, 24 h). Coin-type cells (2025) of Li/1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1, v/v/v)/NiS/Ni were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, $H_2O < 1.0$ ppm, $O_2 < 1.0$ ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The cyclic voltammetry (CV) curves of the electrodes were measured on an electrochemical workstation (CHI660C).

3. Results and discussion

Typical XRD pattern of the as-prepared electrode is shown in Fig. 1(a). The diffraction peaks located at 44.4°, 51.7° and 76.4° (marked with ★) can be assigned to the (111), (200) and (220) faces of Ni foam (04-0850), respectively. Diffraction peaks other than those of Ni (marked by ○) can be indexed as hexagonal NiS (JCPDS, no. 01-1286). The electrochemical reactions during the corrosion process are likely to be as follows:

$$(NH_2)_2CS + 2H_2O \rightarrow 2NH_4^+ + CO_2 + S^{2-} \quad (1)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (2)$$