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Electrochemical properties of monolithic nickel sulfide electrodes for use in sodium batteries

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ABSTRACT

Monolithic nickel sulfide electrodes were prepared using a facile synthesis method, sulfuration and annealing. As-prepared Ni_3S_2 electrodes were characterized by X-ray diffractometry and field emission scanning electron microscopy. Thermal stability was determined by thermal gravimetric analysis and differential scanning calorimetry. Electrochemical properties were measured by galvanostatic charge and discharge cycling for Na-ion batteries. Three kinds of Ni_3S_2 electrodes were prepared by varying the sulfuration time (5, 15 and 25 min). The electrochemical results indicated that the capacities increased with an increase in sulfuration time and the cycle performance was stable as a result of monolithic integration of nanostructured Ni_3S_2 on Ni plates, leading to low interfacial resistance.

1. Introduction

Fossil fuel consumption has increased greenhouse gas emissions in the atmosphere, causing serious environmental problems such as global warming and pollution. There is an urgent need to develop alternative power sources such as solar and wind powers, which are called green energies. However, the energy supply generated from renewable sources is inconsistent and unpredictable. To secure an alternative energy supply, it is necessary to develop rechargeable batteries that can store and release energy on demand.

Currently available lithium ion batteries that use lithium metal oxide ($LiMO_2$, M = Co, Mn, Ni) and graphite can offer high power, high energy density, cycle life, and high rate capability to small mobile devices [1–3], but are limited when it comes to new emerging applications such as electrical energy storage systems (ESS), electric vehicles (EVs), and hybrid electric vehicles (HEVs), because of cost and safety. Instead, a wide range of metal sulfides has been proposed as candidates for cathode materials that provide high theoretical capacities at low cost [4–6]. Among the metal sulfides, nickel sulfide has the advantages of good electronic conductivity, environment-friendly, low cost, and high energy capacity. Nickel sulfide is a material with a multiphase such as Ni_3S_2, $Ni_{3+x}S_2$, Ni_4S_{3+x}, Ni_6S_5, and Ni_7S_6. Among these phases Ni_3S_2 is electrochemically active, chemically stable, and compatible with organic solvents [4,7].

Traditionally, bulk Ni_3S_2 produced by ball-milling is contaminated and has low crystallinity [8]. A high-purity and nanostructured Ni_3S_2 can be synthesized through a variety of methods such as H_2S gas reacting with nickel nano-particles on graphene or the soft solution chemical route [9,10].

In this study, a facile method was employed to prepare nanostructured Ni_3S_2 on a nickel plate [11]. As some authors have proposed, it is expected that the synthesis of materials with an integrated nanostructure will have high surface areas and good ionic conductivity, as well as the benefits of not having a binder or conductive agent [12–14]. Monolithically integrated Ni_3S_2 on Ni plates was characterized using field emission electron microscopy (FE-SEM) and X-ray diffractometry (XRD). Thermal analysis was conducted to measure weight loss and phase transition temperature. Electrochemical measurements of monolithic Ni_3S_2 electrodes were taken for sodium ion batteries.

2. Experimental

Nickel (Ni) plates were polished to remove oxidation layers before the sulfuration process. For nickel sulfuration, a solution was prepared by adding sulfur (S, Sigma–Aldrich) to ammonium sulfide ($(NH_4)_2S_x$, Kanto Chemical). Ni plates were soaked in the

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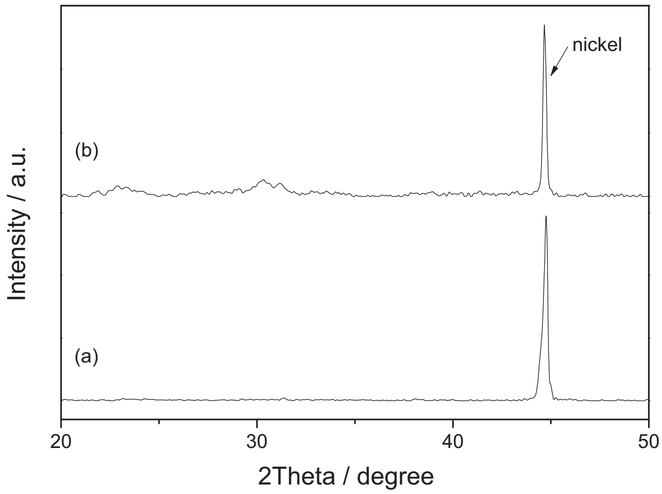

Fig. 1. XRD patterns of (a) a bare nickel plate after being polished; and (b) a nickel plate after undergoing sulfuration for 25 min.

solution, which was heated up to 70 °C. Sulfuration proceeded for durations of 5 min, 15 min, and 25 min. The decolorized nickel plates were removed promptly from the solution, washed with ethanol, and then dried in an oven for 24 h. The sulfurated nickel plates were annealed at 500 °C for 3 h.

The as-prepared nickel sulfide plates were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an Ar atmosphere using a thermal analyzer (Q600).

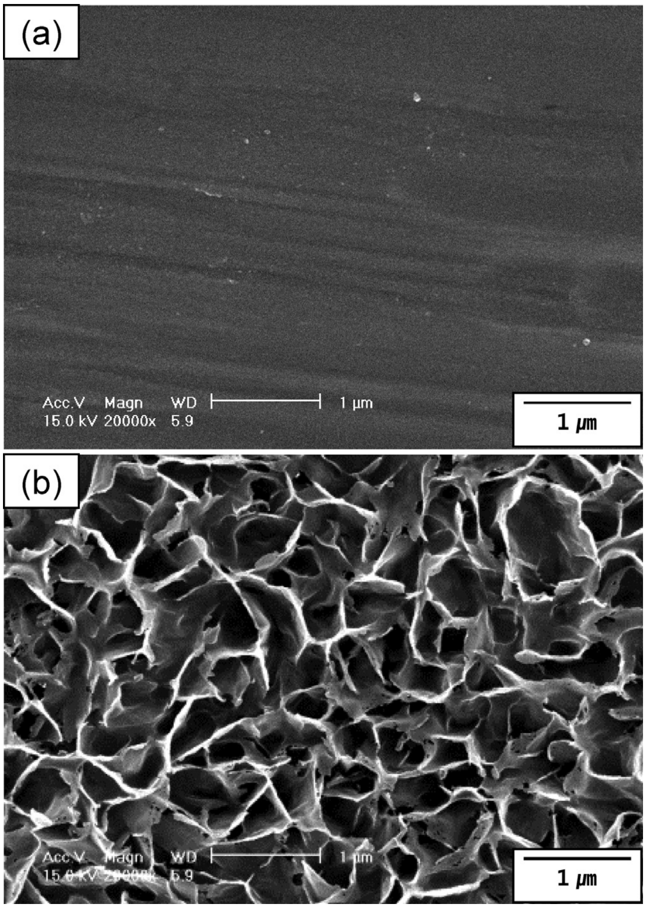

Fig. 2. FE-SEM images of (a) a bare nickel plate after being polished; and (b) a nickel plate after undergoing sulfuration for 25 min.

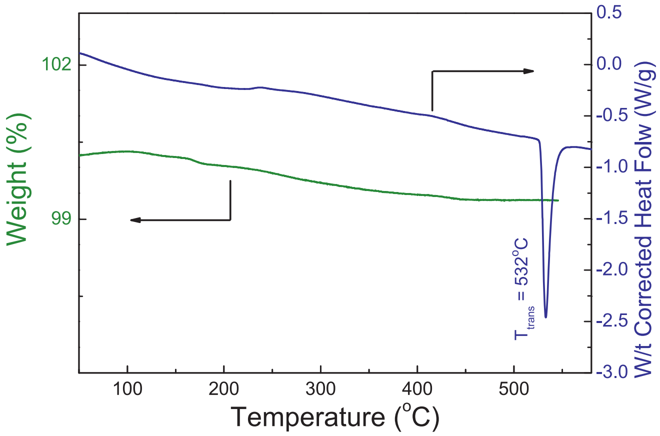

Fig. 3. TGA/DSC curves of an as-prepared nickel plate by sulfuration.

The temperature was ramped at a rate of 10 °C/min up to 550 °C and 600 °C for TGA and DSC, respectively. The crystallographic structure was confirmed by X-ray diffractometry (XRD, D3 Advance, Bruker) with a Cu X-ray tube. XRD patterns were recorded in the range of 20–50° at a scan speed of 1°/min. The morphologies were photographed using a field emission scanning electron microscope (FE-SEM, Philips XL30S FEG) with an acceleration voltage of 30 kV.

Two-electrode Swagelok-type cells were assembled by stacking sliced sodium metal (Na, Aldrich), a separator (Cellgard®-2400) with a liquid electrolyte, and the nickel sulfide electrode. The liquid electrolyte was 1 M sodium tetrafluoroborate salt ($NaBF_4$, Aldrich) dissolved in tetra ethylene glycol dimethyl ether (TEGDME, Aldrich). The whole cell assembly procedure was carried out in a glove box in a sophisticatedly controlled argon atmosphere because Na metal is extremely sensitive to oxygen and moisture. The charge/discharge cycling test was performed in the potential range of 0.5–2.5 V at room temperature using a WBCS 3000 battery tester (WonA Tech).

3. Results and discussion

Fig. 1 presents X-ray diffraction patterns of bare and sulfurated Ni plates. Both patterns show a sharp peak at 44.5°, corresponding

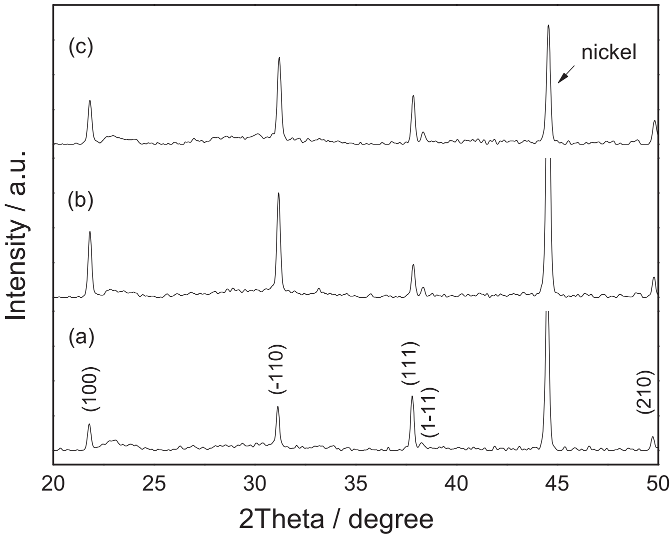

Fig. 4. XRD patterns of as-prepared Ni_3S_2 electrodes by sulfuration of nickel plates after heat treatment at 500 °C for 3 h: (a) for 5 min, (b) for 15 min, (c) for 25 min.