

# Nanostructured nickel sulfide synthesized via a polyol route as a cathode material for the rechargeable lithium battery

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## Abstract

Nanostructured nickel sulfide (NiS) was synthesized via a simple polyol route. The NiS powders were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and electrochemical testing. The results revealed that the cycle life of the annealed NiS sample was improved over that of the as-prepared sample. The electrochemical performance was also tested using 1 M lithium trifluoromethanesulfonimide (LiTFSI) in a solvent of poly(ethylene glycol) dimethyl ether (PEGDME) in order to compare with a sample tested in the conventional electrolyte of 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The results showed that the electrochemical properties were improved by using the 1 M LiTFSI/PEGDME electrolyte. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Nanostructured NiS; Polyol route; Lithium rechargeable batteries

## 1. Introduction

Among the various candidate active materials for secondary lithium batteries, metal sulfides are known to be promising materials because of their high theoretical capacity. A variety of metal sulfides have been considered for cathode materials in lithium batteries [1–8], including sulfides of W, Ni, Mo, Ti, and Jasinski et al. first reported that nickel sulfide could be used as a cathode material for lithium rechargeable batteries because it had an energy density in the range of 388–685 Wh/lb and six stable crystallographically defined sulfides (Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>6</sub>S<sub>5</sub>, Ni<sub>7</sub>S<sub>6</sub>, NiS, Ni<sub>3</sub>S<sub>4</sub>, and NiS<sub>2</sub>). Material utilization was about 35% for NiS in a lithium cell with 1 M LiClO<sub>4</sub> propylene carbonate at a current density of 10 mA/cm<sup>2</sup>. Recently, Lee et al. [4] reported that they used the ex-situ X-ray diffraction

method to determine that the reaction products were Li<sub>2</sub>S and nickel metal. The cathode reaction of nickel sulfide is as follows:



The total charging–discharging reaction of NiS can be presented as follows:



Considerable research on nanosize cathode materials indicates that the nanomaterials improve the capacity compared with electrodes made from larger size particles [9–12]. The direct polyol synthesis of homogeneous particles of NiS has been reported [13]. To the best of our knowledge, nanosize NiS has not been studied as a battery material. In the present investigation, nanostructured NiS powders were synthesized by a simple polyol method as cathode materials for rechargeable lithium batteries. The electrochemical performances were also tested.

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## 2. Experimental

Nanostructured NiS powder was synthesized via a simple polyol route [13]. 0.05 mol  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$  and thiourea were placed in a 100 ml round-bottomed flask. Then the flask was filled with 100 ml glycol solution. After stirring for a few seconds, the solution was heated and refluxed for 2 h. After cooling, the mixture was centrifuged, and the separated black precipitate was washed thoroughly. Finally, the black mass was dried at 100 °C for 4 h under vacuum.

Phase analysis was performed by powder X-ray diffraction using a Phillips 1730 X-ray generator and diffractometer with Cu  $\text{K}\alpha$  radiation. Traces software was used for peak display and peak analysis using Scherrer's formula. The morphology and structure of the NiS powders were investigated at intermediate magnifications by scanning electron microscopy (SEM) using a Leica Model Stereoscan 440 instrument. Transmission electron microscopy (TEM) was performed using a JEOL 2011 200 keV analytical instrument, with samples prepared by dispersion of powders on holey carbon support films.

To fabricate the NiS electrodes, 70 wt.% NiS was mixed with 20 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder, using *N*-methyl-2-pyrrolidinone (NMP) as a dispersant to form a slurry. The slurry was spread on aluminium foil substrates. After drying under vacuum, the electrodes were cut into a  $1 \times 1 \text{ cm}^2$  size. CR2032 coin-type cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). An electrolyte of 1 M lithium trifluoromethanesulfonimide ( $\text{LiTFSI}$ ) in a solvent of poly(ethylene glycol) dimethyl ether 500 (PEGDME 500) was also tested. The cells were galvanostatically charged and discharged in the range of 1.0–3.0 V at a current density of about  $125 \text{ mA g}^{-1}$ . Cyclic voltammetry (CV) measurements were performed using a CHI 660 Electrochemical Workstation at a scanning rate of  $0.1 \text{ mV s}^{-1}$ .

## 3. Results and discussion

In the synthetic process for nickel sulfide, the high solubility of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was used. When the metal salt and thiourea are dissolved in the polyol solvent, the change in the solution color showed that a strong complex reaction between the metal ions and the thiourea had occurred. At a temperature of 300 °C, the stability of the Ni–thiourea complexes decreased, and then they thermally decomposed to form nickel sulfide.

X-ray diffraction patterns obtained from the as-prepared NiS and annealed powders are shown in Fig. 1. The patterns indicate that the NiS powder prepared via the polyol route was amorphous. After annealing the as-prepared NiS powders at 300 °C in flowing argon, the

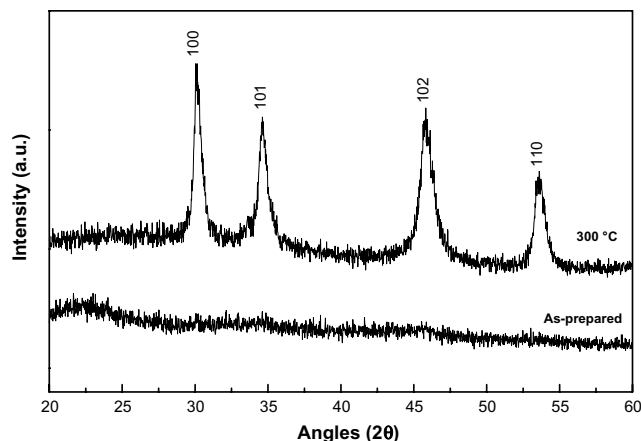


Fig. 1. X-ray diffraction patterns of NiS powders.

NiS, which had a disordered structure, was converted to nanocrystalline NiS. The average crystal size of the nanocrystalline NiS powder, as estimated using the Scherrer Formula, is about 6.89 nm. All diffraction lines are indexed to the hexagonal phase ( $P63/mmc$ ) with lattice parameters  $a = 3.416 \text{ \AA}$ ,  $c = 5.23 \text{ \AA}$ , while the peak positions agree with JCPDS 75-0613. No impurities such as Ni, NiOX, or other nickel sulfides can be detected in the XRD pattern.

SEM images of the as-prepared NiS powder and the annealed powder are shown in Fig. 2. In the as-prepared sample (Fig. 2a), the particles are fairly uniform, with sizes around 200–300 nm. However, after heating to 300 °C, the particles agglomerated to form clusters, many of these more than 1  $\mu\text{m}$  in diameter (Fig. 2b).

Fig. 3 shows TEM results obtained from the as-prepared and annealed NiS. The amorphous structure of the as-prepared sample (Fig. 3a) was confirmed by the diffuse nature of the rings in the selected area electron diffraction (SAED) pattern (inset, Fig. 3a). The dense, nanocrystalline nature of the hexagonal phase produced in the 300 °C annealed product (bright-field image, Fig. 3b) was confirmed by dark field imaging combined with SAED (inset, Fig. 3c). A 3–10 nm crystallite size was revealed using centered dark field imaging (Fig. 3c, obtained using the indicated reflections circled in the SAED inset).

The electrochemical properties of the electrode materials were determined using cyclic voltammetry (CV) and charge/discharge testing. Fig. 4 shows the CV curves for a Li/NiS cell, with the electrode containing powder from the as-prepared sample. The potential sweep rate was  $0.10 \text{ mV s}^{-1}$ , with the voltage ranging between 3.0 and 1.0 V vs.  $\text{Li/Li}^+$ . Two peaks exist at around 1.80 V and 1.30 V during discharging. Also, we can find a large charging current peak at 1.90 V and a small peak at 2.2 V vs.  $\text{Li/Li}^+$ . It is suggested that the Li/NiS cell discharges in a two-step process. The first step could be the transformation of NiS to  $\text{Ni}_3\text{S}_2$  at higher potential (Peak a), and the second step could be the conversion of  $\text{Ni}_3\text{S}_2$  to Ni at lower potential (Peak b). Nickel sulfide is regenerated in the fully charged state [4].

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