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Lithium electrochemistry of $NiSe_2$: A new kind of storage energy material

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Abstract

$NiSe_2$ thin film has been successfully fabricated by reactive pulsed laser deposition and was investigated for its electrochemistry with lithium for the first time. The reversible discharge capacities of $NiSe_2$/Li cells cycled between 1.0 V and 3.0 V were found in the range of 314.9–467.5 mA h g^{-1} during the first 200 cycles. By using *ex situ* X-ray diffraction, transmission electron microscopy, and selected-area electron diffraction measurements, the intermediates of β-NiSe, and Ni_3Se_2 were identified during the reversible conversions of $NiSe_2$ into metal nickel and Li_2Se. Both cation (nickel) and anion (selenium) in $NiSe_2$ provide the redox active centers in its electrochemical reaction with lithium, indicating one of the features of its lithium electrochemistry. The high reversible capacity and good cycle ability of $NiSe_2$ electrode made it become a promising cathode material for future rechargeable lithium batteries.

Keywords: $NiSe_2$; Pulsed laser deposition; Thin film; Cathode; Rechargeable lithium batteries

1. Introduction

As a class of remarkable storage energy materials for rechargeable lithium batteries, much strengths has been paid to developing advanced materials of metal selenides such as $TiSe_2$, $ZrSe_2$, $NbSe_2$, Ta_2Se, Mo_6Se_6, and VSe [1–7]. Most of these metal selenides are Li insertion/deinsertion compounds with layered structures and show a similar single phase or two-phase behavior with lithium intercalation. For example, Tarascon reported a solid-state electrode material of Mo_6Se_6 and found that this material could reversibly take up nine lithium atoms per Mo_6Se_6 without losing its linear chain structure [1]. Due to the low lithium intercalation coefficients, the discharge capacities of these layered metal selenides are low. In order to achieve the highest specific capacity of an electrode material, it is necessary to utilize all the possible oxidation states of a compound during the redox cycle [8]. Recently, we studied the electrochemical reaction of SnSe and Ag_2Se with lithium and found that both SnSe and Ag_2Se could react with lithium reversibly to form metal and Li_2Se [9,10]. These works provided some information on lithium electrochemistry of metal selenides and the possibility using them as storage energy materials for the application and development of rechargeable lithium batteries. Here, an attempt to extend the investigation of electrochemical properties of other metal selenides such as nickel diselenide was made. To our knowledge, there is no available report on the lithium electrochemistry of nickel diselenide.

Nickel diselenide ($NiSe_2$) occurs naturally in two kinds of forms of penroseite and kullerudite. The most common crystal form of penroseite is cubic structure of the pyrite type, space group $Pa\bar{3}(Z = 4)$ and can be considered as a NaCl-like group of metal atoms and chalcogen atom pairs Se_2. The distance in a Se_2 pair is short because of a covalent bond. $NiSe_2$ is a Pauli paramagnetic metal (PM) with the resistivity below $10^{-3}\ \Omega\,\text{cm}$ [11,12]. Such a high electrical conductivity is a quite favorable as storage energy

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materials for rechargeable lithium batteries. In this study, we firstly attempted to prepare $NiSe_2$ thin film by pulsed laser deposition, the electrochemical behavior, structure, composition and morphology of $NiSe_2$ thin films were characterized by galvanostatic cycling, cyclic voltammetry, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). The motivation of this work is to explore the possibility of using nickel diselenide as Li-storage material for rechargeable lithium batteries and to elucidate its electrochemical reaction mechanism with lithium.

2. Experimental

The apparatus used for pulsed laser deposition has been described elsewhere [9,10]. Experimental conditions for depositing thin films are described briefly as follows. A 355 nm laser beam, provided by the third harmonic frequency of a Q-switched Nd:yttrium aluminum garnet (YAG) laser (Quanta-Ray GCR-150), was focused onto the surface of the target. The incident angle between the laser beam and the target surface normal was 45°. The laser energy intensity was about 2 J/cm^2. The repetition rate and pulse width of the laser was 10 Hz and 10 ns, respectively. The targets were made from Ni and Se powders (both pure 99.9%), they were mixed and ground in certain element molar ratios of $Ni:Se = 1:3$, then were pressed to form a 1.3 cm diameter pellet as the ablated target. An excessive Se in a mixture target can compensate Se loss due to its vacuum sublimation during laser ablation. The base pressure of the chamber was 10^{-2} Pa, and the ambient Ar gas pressure during deposition was kept at 5 Pa by a needle valve. The thin films were deposited on stainless steel (SS) substrate, which was kept at 200 °C. The distance between target and substrate was 4 cm. The weight of the thin film was measured to be about 0.20 mg. All the thin films were examined by electrobalance (BP 211D, Sartorius). The precision of the weight is ± 0.01 mg.

XRD patterns and the morphology of the thin films were characterized by a Bruker D8 advance diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) and scanning electron microscopy (SEM) (Philips XL30 microscope), respectively. TEM and SAED measurements were carried out by a 200 kV side entry JEOL 2010 TEM with energy dispersive X-ray (EDX) analyzers.

For the electrochemical measurements, the cells were constructed by using the as-deposited thin film as a working electrode and one lithium sheet as a counter electrode. The electrolyte consisted of 1 M $LiPF_6$ in a nonaqueous solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. The cells were assembled in an Ar-filled glove box. Galvanostatic cycling measurements were carried out at room temperature with a Land CT 2001 A battery test system. The cells were cycled between 1.0 and 3.0 V vs. Li^+/Li at a current density of 5 $\mu A\ cm^{-2}$. Cyclic voltammetry (CV) tests were performed with a scanning rate of 0.1 $mV\ s^{-1}$ between 0.01 V and 2.5 V on a CHI660A electrochemical working station (CHI Instruments, TN).

In order to gain insight into the reaction mechanism of $NiSe_2$ with lithium, *ex situ* SEM, XRD, HRTEM and SAED measurements were carried out to reveal the structure and morphology change of $NiSe_2$ thin film electrodes at selected voltage points during the initial discharge and charge process. The model cells were dismantled in an Ar-filled glove box and the electrodes were rinsed in anhydrous, dimethyl carbonate (DMC) to eliminate residual salts. For TEM and SAED measurements, the active materials were scratched from the SS substrate. The loose powders were then mixed with ethanol to prepare slurry, out of which one drop was taken, and deposited on a copper grid. To avoid exposure to oxygen or water, the grids were rapidly transferred into the chambers for cleanness.

3. Results and discussion

Fig. 1a shows the XRD pattern of the target used in pulsed laser deposition. Several peaks at 23.5°, 29.7°, 41.3°, 43.6°, 44.5°, 45.4°, 51.8°, 55.7° and 56.0° are in good accord with the diffraction peaks of nickel and selenium (JCPDS card no. 04-0850 and 06-0362). After laser ablation of the mixed target, gray-colored thin films were deposited on the SS substrate in our experimental condition, the XRD pattern of the as-deposited thin film was shown in Fig. 1b. Apart from two diffraction peaks appearing at $2\theta = 43.6°$ and 50.8° corresponding to the SS substrate (marked by asterisks), three peaks at 30.0°, 33.6° and 36.9° could be assigned to the (200), (210) and (211) reflection of the $NiSe_2$ (penroseite pattern, JCPDS card no. 88-1711). The average crystallite size calculated by the Scherrer formula is estimated to be 20 nm (using the strongest peak at 33.6°). XRD data suggest that a nanocrystalline $NiSe_2$ thin film could be prepared by pulsed laser ablation of the mixed target of nickel and selenium.

The galvanostatic cycling profiles of the $NiSe_2/Li$ cell cycled between 1.0 V and 3.0 V under a current density

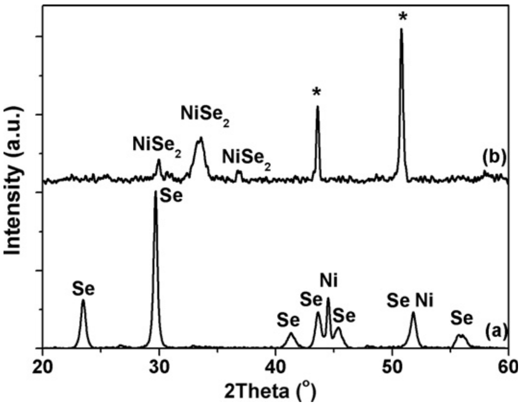

Fig. 1. XRD patterns of (a) the target and (b) as-deposited thin film. The peaks marked with asterisk corresponding to stainless steel substrate.