



Short communication

Conversion and displacement reaction types of transition metal compounds for sodium ion battery



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H I G H L I G H T S

- We have fabricated FeSe and CuWO₄ thin films by R.F. sputtering.
- We have examined the electrochemical behaviors of FeSe and CuWO₄ thin film electrodes with sodium.
- We have proposed the conversion and displacement reaction mechanisms for FeSe/Na and CuWO₄/Na cells.

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Transition metal compounds of FeSe and CuWO₄ thin films have been successfully fabricated by using R.F. sputtering method. Although two kinds of transition metal compounds of FeSe and CuWO₄ thin films can react with sodium electrochemically, they exhibit different electrochemical features. The nanosized metal Fe is highly dispersed into Na₂Se matrix and metal Cu is extruded from Na₂WO₄ mixture after the FeSe/Na and CuWO₄/Na cells are discharged, respectively. The conversion reaction mechanism between FeSe and Na₂Se is proposed for the FeSe/Na cell. While the displacement reaction mechanism for CuWO₄/Na cell is proposed for the first time based on the transmission electron microscopy (TEM) and selected area electron diffraction (SAED) data. These various mechanisms make transition metal compounds interesting materials for rechargeable sodium ion batteries.

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1. Introduction

There has been increasing interest in sodium ion battery (SIB) as a potential alternative power source for lithium ion battery (LIB) due to the cheap price and abundant reserve of sodium. The development and study of new electrode materials and their reaction mechanisms with sodium have become a major topic in the area of rechargeable SIB [1–4]. It seems that the electrode materials in lithium-ion batteries could provide the best library for the selection of advanced materials with higher store densities of sodium for future SIB, and the fundamental studies on the reaction mechanisms of these electrode materials with sodium have revealed various electrochemical processes analogous to those in LIB, such as

intercalation/deintercalation reactions [5–7], alloy/dealloying reactions [8,9] and conversion reactions [10–12]. Among these studies, conversion compounds show a group of promising electrode materials for SIB due to their high specific capacities. Alcatara et al. [10] were the first to propose that the conversion-reaction mechanism also existed in SIB. In their study, the transition metal compound of NiCo₂O₄ was found to reversibly decomposed and formed during discharge and charge processes in SIB which is similar to that in LIB. Subsequently, a vast amount of work demonstrated other conversion compounds such as Sb₂O₄ and Cu₂Se react with sodium in a similar fashion with lithium [11,12]. However, the electrochemistry of most conversion compounds with sodium was different from that of the same materials with lithium. For example, CoO, NiO, and FeO with excellent reactive activity with lithium [13–15] did not exhibit any electrochemical activity with sodium. The investigations about conversion compounds for SIB, however, have not been satisfactorily carried out

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yet. It is a challenge to identify the existence of new conversion compounds for SIB due to the complex chemistry of Na conversion reaction. FeSe has been found to be one of the conversion reaction materials in LIB [16] by our group and Qian et al. prepared carbon-coated FeSe nanoparticles by one-pot reaction method and employed it as an anode material for LIB [17]. However, to our best knowledge, little information is available on the electrochemistry of FeSe with sodium.

In addition, copper extrusion/insertion reaction in LIB involves the intercalation of Li ions accompanied by the extrusion of metallic copper from the electrode materials during discharge process. Upon charge process, metallic copper is re-oxidized into copper ions and injected into the host structure, replacing the Li ions in discharged products. Such type of reactions, which are suggested to be referred as displacement reactions by Tarascon et al. [18], were first found in the electrochemical behavior of intermetallic alloys such as Cu_6Sn_5 [19] by Thackeray's group and then extended to copper vanadates ($\text{Cu}_{2.3}\text{V}_4\text{O}_{11}$ [20] and $\text{Cu}_{1.1}\text{V}_4\text{O}_{11}$ [21]) by Tarascon and co-workers. Because the displacement-type electrode materials involves a two-electron redox reaction $\text{Cu}^{2+} + 2e \leftrightarrow \text{Cu}$ in contrast to most of the classical intercalation-type cathode materials via one-electron redox processes, these materials have larger theoretical specific capacities than intercalation materials, making them potential candidates as cathode materials for LIB. The theoretical gravimetric capacity of CuWO_4 for LIB and SIB is 172.1 mAh g^{-1} . It had been tested as a cathode material for primary lithium batteries in late 1970s with a specific capacity of 160 mAh g^{-1} [22]. Li et al. reported reversible electrochemical behavior of CuWO_4 thin film electrodes versus lithium and identified that the reaction mechanism of CuWO_4 thin film electrode for LIB is displacement reactions with dual center redox pairs [23]. However, it is not clear whether the displacement reaction mechanism exists in an electrode material for SIB, which could provide large specific capacities.

In this work, we present, for the first time, a new conversion reaction compound of FeSe and a displacement reaction compound of CuWO_4 for SIB. Their thin films are prepared by radio frequency sputtering (R.F.) sputtering. Since the electronic resistance of the resulting film electrode-material is reduced remarkably, conductive additives such as carbon black and a polymeric binder are not needed. Therefore, such thin film electrode is a "pure" and "clean" system without any binders or additives, which is ideal to investigate a material's intrinsic characteristics.

2. Experimental

The apparatus used for R.F. magnetron sputtering has been described elsewhere [23]. The sputtering chamber was vacuumed below $7 \times 10^{-4} \text{ Pa}$ with a turbo-molecular pump combining with a mechanical pump. The mixed Fe/Se target made from Fe powder and Se powder with a certain element molar ratios of Fe:Se = 1:1.5 and CuWO_4 target were used for the deposition of thin films as previous work [23]. The thin films were grown on stainless steel substrates. The ambient gas of Ar and O_2/Ar (1:3) were set for growing FeSe and CuWO_4 thin films, respectively. The chamber pressure was maintained at about 1.0 Pa. The R.F. power was fixed at 40 W, and the distance between substrate and target was 5 cm. The substrates were kept at room temperature. The deposition time was fixed in 1 h after pre-sputtering the target for 30 min to remove target contamination. The as-deposited thin films for CuWO_4 were annealed at 500°C in air for 5 h. The thicknesses of all thin films were measured by a Tencor Alpha Step 200 surface profilometer. The weights of FeSe and CuWO_4 thin films were measured by an electrobalance (BP 211D, Sartorius) and were found to be 0.12 nm and 0.16 mg, respectively. The precision of the weight was

$\pm 0.01 \text{ mg}$.

XRD patterns of thin film electrodes were recorded by a Bruker D8 advance diffractometer equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) measurements were carried out in a 200 kV side entry JEOL 2010 TEM. The copper concentration in the electrolyte solutions after discharging or charging is detected on a P-4010 inductively coupled plasma atomic emission (ICP-AES) spectrometer.

For the electrochemical measurements, the cells were constructed using the as-deposited thin films as a working electrode and two sodium sheets as counter and reference electrodes, respectively. All model cell consisted of an H shape glass tube to separate positive and negative electrodes (electrode area: 1 cm^2) as well as two rubber plugs for sealing. The electrolyte consisted of 1 M NaPF_6 (Alfa Aesar) in a nonaqueous solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 (Shanshan Tech). The cells were assembled in an Ar filled glove box. Galvanostatic charge–discharge measurements were carried out at room temperature with a Land CT 2001A battery test system.

3. Result and discussion

In order to identify the structure and composition of these as-deposited thin films, XRD patterns of these thin films were measured and are shown in Fig. 1. As shown in Fig. 1(a), XRD pattern of the as-deposited thin film is totally different from the XRD pattern of the mixed Fe and Se target. This indicates the formation of new products on the substrate. The diffraction peaks at $2\theta = 16.0^\circ$ and $2\theta = 32.4^\circ$ can be assigned to (001) reflection of tetragonal FeSe (JCPDS 85-0735) and (101) reflection of hexagonal FeSe (JCPDS 75-0608). This result suggests that the as-deposited thin film mainly consists of FeSe. XRD pattern of the CuWO_4 thin film is shown in Fig. 1(b). Standard XRD pattern from JCPDS file 73-1823 is also included for reference. It can be observed that most of the peaks in the pattern can be well indexed to the reflection of CuWO_4 with monoclinic structure apart from two peaks marked with asterisk which can be assigned to the diffraction of stainless steel substrate, indicating the formation of a CuWO_4 thin film. This result is in agreement with previous data [23]. XRD data showed that FeSe and CuWO_4 thin films were successfully prepared by using R.F. sputtering method.

Fig. 2 shows SEM image of these FeSe and CuWO_4 thin films. The as-deposited FeSe thin film (Fig. 2(a)) exhibits a well-defined surface texture and is composed of small crystalline grains uniformly distributed with an average size less than 50 nm. Meanwhile, some particle agglomerates can be found. A rough surface with pin holes of annealed CuWO_4 thin film is observed in Fig. 2(b). Particle agglomerates also can be found, which may be caused by the growth of crystalline during the high temperature annealing process.

Reversible Na storage behavior and cyclic performance of FeSe and CuWO_4 thin film electrodes were revealed by galvanostatic cycling measurements. Fig. 3 shows the charge–discharge curves of FeSe/Na and CuWO_4/Na cells at a current density of 60 mA g^{-1} . Their corresponding open circuit voltages are 2.03 V and 2.54 V, respectively. As shown in Fig. 3(a), when FeSe/Na cell is cycled between 1.2 V and 3.0 V, a long discharge plateau at around 1.4 V is observed in the initial discharge cycle with the specific discharge capacity of 336.5 mAh g^{-1} . In the subsequent cycles, the discharge curves are similar to each other with a discharge plateau at around 1.94 V. All the charge curves show two voltage plateaus at 2.0 V and 2.3 V. After 200 cycles, the specific discharge capacity of 253.7 mAh g^{-1} could still be retained as shown in the inset of Fig. 3(a), indicating good cycling performance of FeSe/Na cell. When CuWO_4/Na cell is cycled between 1.7 V and 3.7 V (Fig. 3(b)), one

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