Facile synthesis and electrochemical properties of Fe$_2$SeS for lithium ion batteries

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HIGHLIGHTS

- Pure Fe$_2$SeS is synthesized by facile solid-state reaction.
- Electrochemical properties of Fe$_2$SeS are investigated as an anode material.
- Only one step reaction occurs during both charge and discharge process.
- Fe$_2$SeS has higher capacity and better cycle performance than FeS and FeSe.

ABSTRACT

Fe$_2$SeS is successfully synthesized by facile solid-state reaction and the electrochemical investigation of Fe$_2$SeS as anode for lithium ion batteries is reported for the first time. Fe$_2$SeS deliverers a large initial discharge capacity of 471 mAh g^{-1}. The initial coulombic efficiency (92.56%) is higher than most of double-anion compounds reported previously. It is unexpected to find that Fe reacts simultaneously with Li$_2$S and Li$_2$Se to reform Fe$_2$SeS during charging process, which is different from most double-anion compounds.

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1. Introduction

Double-anion compounds MXY (M = transition metal, X or Y = O, F, N, S, etc.), such as metal oxyfluoride [1–7], oxynitride [8,9] and oxysulfide [10–14] have been extensively investigated and are expected to combine the advantages of two corresponding single anionic compounds, which have already drawn much attention for the electrode materials of lithium ion batteries. The insertion of Li into MXY leads to the formation of LiX, LiY and M nanocomposites, which could be converted back to MX and MY [3,7] while in some cases back to MXY [1,9,14] upon Li extraction. These double-anion compounds usually exhibited better electrochemical performance than their single-anion counterparts. However, most of recent work on double-anion compounds focused on oxy-compounds. Other types of double-anion compounds are barely reported. Therefore, it is interesting to explore new double-anion compound systems for lithium ion batteries.

Recently, ferric sulfide [15–18] and ferric selenide [19–21] have been investigated as storage lithium electrodes because of their high theoretical capacities against commercial graphite. However, the discharge products of Li$_2$S cannot completely react with Fe to reform FeS due to its low electronic conductivity [22]. Based on theoretical calculation, the lithiation process will lead to a 200% volume change [15], resulting in a rapid capacity fading and a low coulombic efficiency. Interestingly, the lattice parameters of

FeSe almost remain unchanged during the Li-intercalation process, which indicates that FeSe maintains stable structure upon cycling [19]. However, the theoretical capacity of FeSe is relatively low (397 mAh g^{-1}). Herein, a double-anion compound of Fe$_2$SeS was prepared and its electrochemical properties were examined for lithium ion batteries. Our results demonstrated the good reversibility of electrochemical reaction between Fe$_2$SeS and Li. Relatively high capacity and flat discharge/charge plateaus of Fe$_2$SeS electrode make it a promising anode candidate for lithium ion batteries.

2. Experimental

In a typical synthesis, iron, selenium and sulfur powders (all 99.9%) with an element molar ratio of 2:1.5:1.5 were mixed by high energy ball milling. Excessive Se and S in mixture aimed to compensate Se and S loss during high temperature synthesis which would be processed later. Afterward the mixture was pressed to form a pellet and loaded into a tube furnace. High temperature annealing process was executed at 700 °C for 12 h to ensure the thorough reaction of Fe, Se and S. A constant flow of argon was applied to avoid oxidation of the pellet. After annealing, the furnace naturally cooled down to room temperature under constant flow of argon and the pellet was ground in an agate mortar to get dark gray powder.

X-ray diffraction (XRD) pattern and the morphology of the

product were investigated by Bruker D8 Advance diffractometer equipped with Cu Kα radiation ($\lambda = 0.15406$ nm) and field emission scanning electron microscopy (FESEM) (HITACHI, S-4800). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements were carried out by a JEOL 2010 TEM at 200 kV accelerating voltage. The X-ray absorption (XAS) data at the Fe K-edge of the lithiated and delithiated samples were recorded at room temperature in transmission mode using ion chambers at beam line BL14W1 of the Shanghai 15 Synchrotron Radiation Facility (SSRF), China.

The working electrode was made of Fe_2SeS (80 wt.%), carbon black (10 wt.%) and polyvinylidene fluoride (PVDF) (10 wt.%) coated on an aluminum foil substrate and was dried in a vacuum oven at 80 °C for 12 h. The mass loading of the working electrode was 1.5–2.0 mg cm^{-2}. Swagelok cells were assembled in an Ar-filled glove box by using Li metal as anode, 1 mol L^{-1} LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as electrolyte, and Celgard 2400 as separator. Galvanostatic charge–discharge measurements were carried out at room temperature with a battery test system (CT2001A, Wuhan Land Electronics). The cells were cycled between 1.0 and 3.5 V vs. Li$^+$/Li at C/10. Note that "C/n" means that the charge or discharge current is set up to achieve the nominal capacity (calculated assuming the Fe_2SeS as the only active material) in "n" hours. Cyclic Voltammogram (CV) tests were performed between 1.0 and 3.5 V on electrochemical working station (CHI660A, Shanghai Chenhua Instruments). The scanning rate was 0.1 mV s^{-1}.

3. Results and discussion

Fig. 1a shows the typical SEM image of as-prepared powder which exhibits irregular shape. The XRD pattern of as-prepared powder is shown in Fig. 1b. All diffraction peaks at 29.0°, 32.8°, 42.5°, 51.6° and 55.6° could be well assigned to (100), (101), (102), (110) and (103) reflection of hexagonal Fe_2SeS phase (JCPDS card no. 75-0609), indicating successful preparation of Fe_2SeS through high temperature solid state reaction. The XRD pattern of Fe_2SeS is entirely different from FeSe (JCPDS card no. 85-0735) and FeS (JCPDS card no. 04-0832), which suggests that Fe_2SeS is a new phase instead of FeSe or FeS phase.

Fig. 2a shows the first three cyclic voltammograms of Fe_2SeS electrode. In the first cycle, a couple of distinct redox peaks at 1.3 and 1.8 V was observed. The cathodic peak could be attributed to the reaction between Fe_2SeS and Li to form Fe, Li_2Se and Li_2S, while the anodic peak is probably due to the formation of Fe_2SeS phase again from Fe, Li_2Se and Li_2S. But the possibility of forming FeS and FeSe separately may also occur. In the second cycle, the cathodic peak shifts to 1.45 V while the anodic peak remains almost no change, implying the possible structure or composition change of Fe_2SeS after one cycle. The curves of the third cycle are almost identical to the second cycle, indicating good reversibility of Li/Fe_2SeS cell in the following cycles. Note that for all three cycles, only one pair of distinct redox peaks was observed. This result is entirely different from FeS [17] and FeSe [20,21], both presenting two pairs of redox peaks in CV curves.

The galvanostatic cycling profiles of the Fe_2SeS/Li cell cycled between 1.0 V and 3.5 V under a current density of 0.1 C are shown in Fig. 2b. The first discharge and charge curve of Fe_2SeS shows distinct plateaus at around 1.5 and 1.8 V, which is consistent with the above CV results (Fig. 2a). The initial discharge and charge capacities are 471 mAh g^{-1} and 436 mAh g^{-1}, respectively, giving a high initial coulombic efficiency of 92.56%. The discharge and charge plateaus of second cycle only shift a little and the capacities are almost not changed, indicating good reversibility of Fe_2SeS.

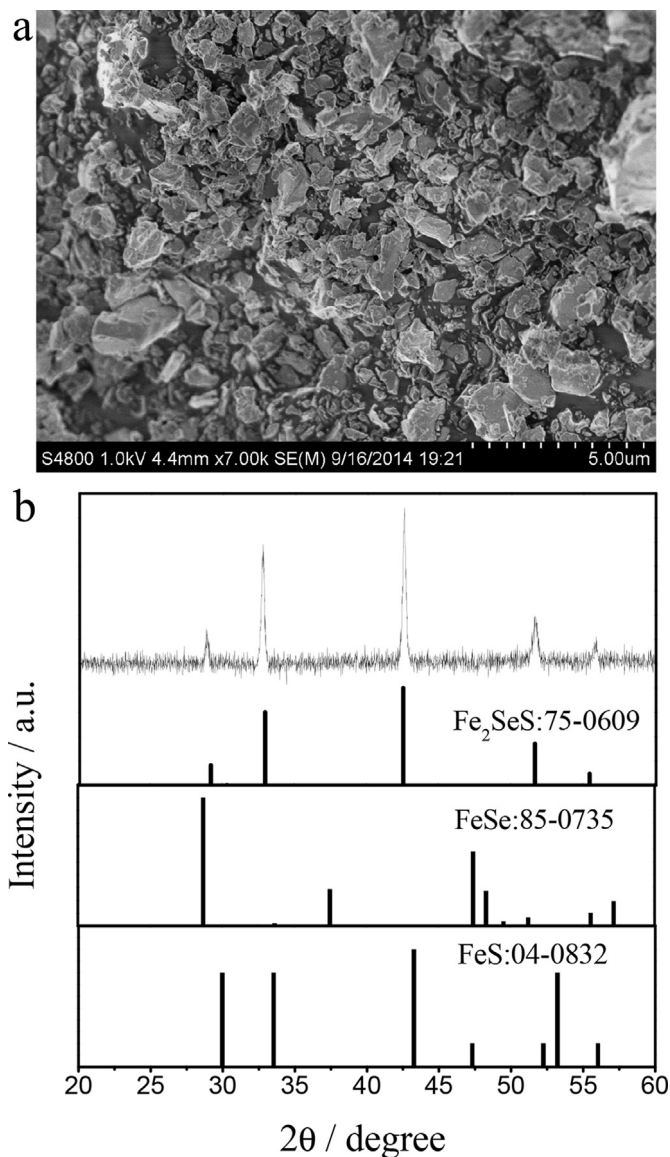The discharge capacity versus cycle number for FeSe, FeS and

Fig. 1. (a) SEM images of as-prepared Fe_2SeS powder and (b) XRD pattern of as-prepared Fe_2SeS powder and the standard XRD patterns of Fe_2SeS, FeSe and FeS.

Fe_2SeS cells are presented in Fig. 2c. FeSe and FeS were prepared using similar strategies of solid-state reactions as Fe_2SeS. However, comparing with FeSe and FeS, Fe_2SeS exhibits higher reversible capacity. After 100 cycles, a reversible capacity of 397.2 mAh g^{-1} was still retained. Since Fe_2SeS has higher theoretical capacity than FeSe calculated from conversion reaction, it is reasonable to deliver higher reversible capacity. Nevertheless, although FeS owns highest theoretical capacity, the reversible capacity is lowest among three compounds. We attributed this phenomenon to sulfur dissolution, which exists in lithium electrochemical reaction of many transition metal sulfides [23]. However, unlike to FeS, in which S is only bonded to Fe, S in Fe_2SeS is also bonded to Se, which may be helpful to alleviate sulfur dissolution and keep reversible capacity.

Fig. 2d shows the initial discharge curves of Fe_2SeS electrode at different current density (0.1 C, 0.2 C, 0.5 C, 1 C). It can be seen that the initial discharge capacity decreases with increasing the current density.

In order to investigate the electrochemical reaction mechanism of Fe_2SeS with lithium, *ex situ* XRD, TEM, SAED and synchrotron XAS were performed. The *ex situ* XRD data of the lithiated