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SnS₂ anode for rechargeable lithium battery

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Abstract

SnS₂ powder made by sonochemistry was applied and examined for anode material of Li ion battery. The annealed SnS₂ at 400°C showed a higher capacity of 600 mAh g⁻¹ than the non-annealed SnS₂. The cell with annealed SnS₂ anode and LiCoO₂ cathode worked well. From the results, SnS₂ material was revealed to be one of the candidates of the anode materials for future Li ion batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li ion battery; Anode; SnS₂; Li–Sn alloy; Sn

1. Introduction

Li ion battery has the highest energy density among commercial rechargeable batteries. Carbon materials (hard carbon, soft carbon, etc.) are commercially used as the anode material of Li ion battery. The theoretical capacity of carbon material is 372 mAh g⁻¹, while higher energy density battery is demanded. Under such a situation, new anode materials with higher capacity are required. In recent years, Li–Sn alloy compounds have attracted many researchers in the sense of application to the anode material of rechargeable Li battery because of its larger theoretical capacity than that of carbon materials. SnO₂ was attempted for the starting material with conversion to the Li–Sn alloy by electrochemical reduction. In order to use the Li–Sn alloy for the anode of rechargeable Li battery, some other Sn compounds might be the starting material for Li–Sn alloy. In this study, we have examined the possibility of using SnS₂ as a candidate of the anode for Li ion battery.

2. Experiment

The amorphous SnS₂ powder was prepared following the literature [1–6]. Aqueous solution of SnCl₄ and thioacetamide was sonicated for 30 min at room temperature under air

atmosphere. Amorphous SnS₂ was obtained as a precipitate. Part of resulting amorphous SnS₂ was annealed at 400°C to improve the crystallinity.

The SnS₂ powder was mixed with polyvinylidene fluoride hexafluoropropylene (PVdF-HFP) (10 wt.%) and carbon powder (10 wt.%) in THF solvent. The mixture was spread onto Ni form and dried, and it was pressed and used as the working electrode. The organic liquid mixture of ethylene carbonate (EC) and propylene carbonate with 1:1 volumetric ratio containing 1 M LiClO₄ was used as the electrolyte. Three electrodes type cell with counter and reference electrodes of Li foils was used for the characterization of SnS₂ anode, while two electrodes cell with the positive electrode containing LiCoO₂ was used for the battery test. Electrodes were prepared in a dry room and cells were assembled in an argon-filled globe box. Cyclic voltammetry method was applied in the potential range of 0–2 V versus Li/Li⁺, and the scanning rate was 0.1 mV s⁻¹. The SnS₂ anode was charged and discharged at constant current of 50 mA g⁻¹ in the potential range of 0–2 V versus Li/Li⁺. Two electrodes type cell was charged and discharged at constant current of 50 mA g⁻¹ between 1.5 and 4.2 V.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms for the SnS₂ electrodes for annealed and non-annealed samples. For the both samples, almost similar voltammograms were

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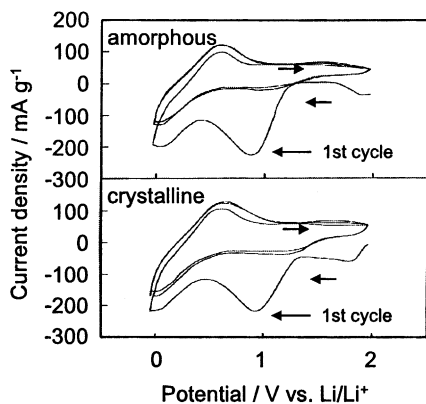


Fig. 1. Cyclic voltammograms for SnS_2 electrodes. Counter electrode: Li; electrolyte: 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$; potential range: 0–2 V vs. Li/Li^+ ; scan rate: 0.1 mV s^{-1} .

demonstrated. At the first potential sweeping towards the cathodic direction, a large cathodic current was observed around 0.9 V versus Li/Li^+ , while in the subsequent potential cycle no more large cathodic current was detected around 0.9 V versus Li/Li^+ . There appeared redox peak couple at 0.1 V versus Li/Li^+ in the cathodic scan and at 0.7 V versus Li/Li^+ in the anodic scan for all the cycle. From these results, similarly as the case of SnO_2 [7–11], the large cathodic irreversible current was supposed to exhibit the formation of Sn metal particle during the cathodic potential sweep from the SnS_2 powder with the Li_2S formation as follows, $\text{SnS}_2 + 4\text{Li} \rightarrow \text{Sn} + 2\text{Li}_2\text{S}$. The redox couple will be the charge–discharge reaction of Li with Sn particle, $x\text{Li} + y\text{Sn} \rightleftharpoons \text{Li}_x\text{Sn}_y$. Since the anodic peak is at 0.7 V versus Li/Li^+ , potential range of 0–2 V versus Li/Li^+ is enough for charge–discharge test. Therefore, charge–discharge test was done at the potential range of 0–2 V versus Li/Li^+ . Fig. 2 shows the potential curve of SnS_2 electrode under a constant current of 50 mA g^{-1} . The first cycle of both electrodes exhibits enormous irreversible capacity. That indicates that the formation of metallic Sn from the SnS_2 powder is similar to the SnO_2 electrode. During the

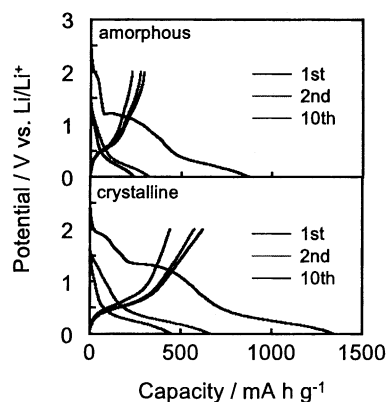


Fig. 2. Charge–discharge curves of SnS_2 electrode. Counter electrode: Li; electrolyte: 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$; potential range: 0–2 V vs. Li/Li^+ ; current density: 50 mA g^{-1} .

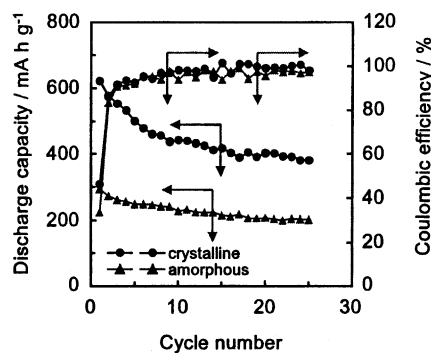


Fig. 3. Cycle performance of SnS_2 electrode. Counter electrode: Li; electrolyte: 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$; potential range: 0–2 V vs. Li/Li^+ ; current density: 50 mA g^{-1} .

subsequent cycle, the electrode was charged in the potential range of 0.5–0 V versus Li/Li^+ and discharged in the potential range of 0.5–0.7 V versus Li/Li^+ . The discharge capacity and coulombic efficiency for these electrodes are shown in Fig. 3. As compared with non-annealed SnS_2 electrodes, it is clear that the annealed SnS_2 has larger capacity. The initial capacity of annealed SnS_2 is above 600 mAh g^{-1} , and decreases gradually to 400 mAh g^{-1} , while the capacity of non-annealed SnS_2 decreases from 300 to 200 mAh g^{-1} . In the initial cycle, the efficiency was less than 50% and showed sudden jumping to 80% in the second cycle. After the third cycle, the efficiency was kept at the value of about 90–95%. These results indicate that the conversion of SnS_2 into Sn metal or Sn–Li alloy takes place in the initial cycle. Almost the same amount of charge was stored in the resulting metal compound in subsequent charge–discharge cycle as the charge of conversion in the first cycle. These results exhibit a good agreement with the results obtained by the cyclic voltammetry. Next, we applied the SnS_2 electrode to the Li ion cell using LiCoO_2 for cathode. Fig. 4 shows potential curve of the cell. It is clear that SnS_2 has a possibility to be used as an anode material of Li ion battery.

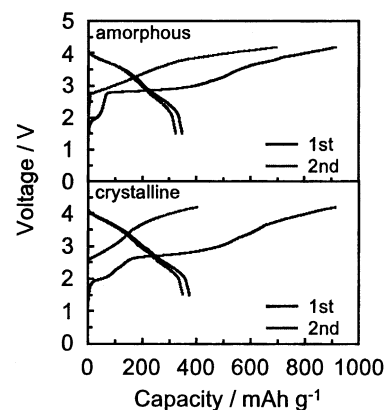


Fig. 4. Charge and discharge curves for SnS_2 electrode. Counter electrode: LiCoO_2 ; electrolyte: 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$; current density: 50 mA g^{-1} ; cut-off voltage: 4.2–1.5 V.

4. Conclusion

Amorphous SnS₂ and crystalline SnS₂ were studied in order to apply anode material in rechargeable lithium battery. The SnS₂ annealed at 400°C showed a capacity of over 600 mAh g⁻¹ at the initial stage. Non-annealed SnS₂ had the capacity of about 300 mAh g⁻¹. It was also revealed that SnS₂ could work as anode in Li ion battery using LiCoO₂ cathode. The annealed SnS₂ was revealed as a possible candidate for the lithium ion battery anode.

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