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Gallium (III) sulfide as an active material in lithium secondary batteries

Hiroshi Senoh[a,*], Hiroyuki Kageyama[a], Tomonari Takeuchi[a], Koji Nakanishi[b], Toshiaki Ohta[b], Hikari Sakaebe[a], Masaru Yao[a], Tetsuo Sakai[a], Kazuaki Yasuda[a]

[a] *Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*
[b] *Synchrotron Radiation Center (The SR Center), Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

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ABSTRACT

In an attempt to identify an active material for use in lithium secondary batteries with high energy density, we investigated the electrochemical properties of gallium (III) sulfide (Ga_2S_3) at 30 °C. Ga_2S_3 shows two sloping plateaus in the potential range between 0.01 V and 2.0 V vs. (Li/Li$^+$). The specific capacity of the Ga_2S_3 electrode in the first delithiation is ca. 920 mAh g^{-1}, which corresponds to 81% of the theoretical capacity (assuming a 10-electron reaction). The capacity in the 10th cycle is 63% of the initial capacity. *Ex situ* X-ray diffraction and X-ray absorption fine structure analyses revealed that the reaction of the Ga_2S_3 electrode proceeds in two steps: $Ga_2S_3 + 6Li^+ + 6e^- \leftrightarrows 2Ga + 3Li_2S$ and $Ga + xLi^+ + xe^- \leftrightarrows Li_xGa$.

1. Introduction

Lithium secondary batteries have been widely used because of their high energy characteristics. Various active materials have been proposed as novel electrodes. Sulfur is a promising active material because of its high theoretical capacity and relatively low cost [1]. To circumvent the limitations of sulfur (low electronic conductivity and a tendency to dissolve into the electrolyte), many attempts have been made to alloy sulfur with a metal to form a sulfide. A variety of transition metal-containing sulfides, such as FeS_2, NiS_2 and CuS, have been studied for use as cathode active materials [2–4].

Recently, some sulfides of *p*-block elements have been proposed as anode active materials [5–7]. For example, Kim et al. reported that a GeS_2 glass could serve as a new class of anode material because of its high Li$^+$ conductivity [5]. Hang et al. investigated the electrochemical properties of Li_2SiS_3 in a solid electrolyte and found that Li_2SiS_3 has a large capacity with small capacity degradation [6]. Quite recently, we found that a sulfide of an earth metal – aluminum sulfide (Al_2S_3) – has high specific capacity in the potential range between 0.01 V and 2.0 V vs. (Li/Li$^+$) [7].

In this study, we focused on another sulfide of an earth metal – gallium (III) sulfide (Ga_2S_3) – for use as an anode active material. Ga_2S_3 is a component of lithium-containing sulfide glass, which has been studied as a possible solid-state electrolyte material for use in lithium secondary batteries [8–10]. To our knowledge, there has been no previous report on the possible application of Ga_2S_3 as an anode material in lithium secondary batteries. If the complete lithiation of Ga_2S_3 is assumed ($Ga_2S_3 + 10Li^+ + 10e^- \leftrightarrows 2Li_2Ga + 3Li_2S$), the theoretical capacity would be 1137 mAh g^{-1}. This value is about three times as large as that of the conventional active material – graphite. In the present study, we examined the electrochemical properties of Ga_2S_3, and focused on its structural changes by means of *ex situ* X-ray diffraction and X-ray absorption fine structure analyses to understand the reaction mechanisms during galvanostatic cycles.

2. Experimental

Commercially available Ga_2S_3 powder (Kojundo Chemical Laboratory Co., Ltd., 99.99%) was used as-received for the electrochemical studies. SEM observation revealed that the Ga_2S_3 powder was composed of flaky particles of 2–3 μm in size. A slurry to form the working electrode was prepared by mixing the Ga_2S_3 powder, ketchen black as a conductive additive, and polyimide as a binder in a weight ratio of 80:5:15 in *N*-methyl-2-pyrrolidone. The prepared slurry was loaded onto copper foil as a current collector. The resultant electrode was dried and then roll-pressed to a thickness of about 60 μm. The electrode was heated at 300 °C for 1 h under vacuum to give stronger bonding between the anode material and the

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[*] Corresponding author. Tel.: +81 72 751 9612; fax: +81 72 751 9629.
E-mail address: h.senoh@aist.go.jp (H. Senoh).

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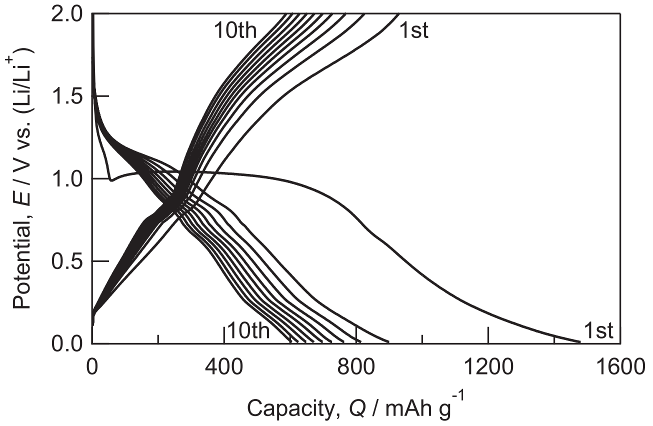

Fig. 1. Potential profiles of a Ga_2S_3 electrode in the 1st to 10th cycles.

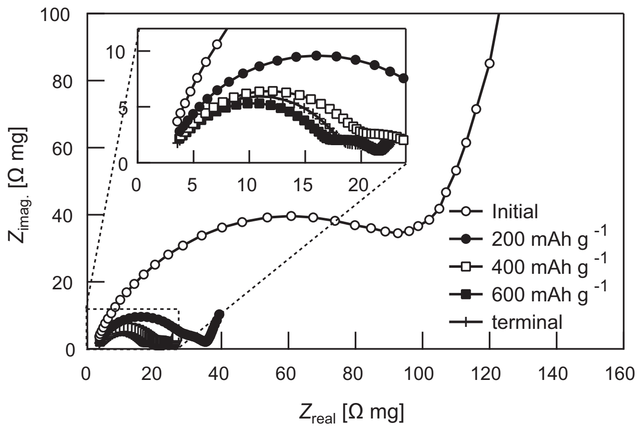

Fig. 2. Electrochemical impedance spectra of a Ga_2S_3 electrode during the 1st lithiation: initial, 200, 400, 600 mAh g^{-1} and terminal.

other materials. A blank electrode without Ga_2S_3 was also prepared at the same procedure.

A galvanostatic cycle test was performed in a half-cell (HS cell, Hohsen Corp.) constructed in an Ar-filled glove box. The counter electrode was Li foil (Honjo Metal Co., Ltd.). The separator was a porous polypropylene sheet (Asahi Kasei Chemicals Co., Ltd.). The electrolyte was 1 mol L^{-1} lithium hexafluorophosphate in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (Kishida Chemical Co., Ltd.). The cycle test was conducted at 30 °C using a charge/discharge unit (ABE1024-05R1, Electrofield). In the cycle test, the prepared working electrode was first reduced (lithiated) at a current density of 100 mA g^{-1} with a cutoff potential of 0.01 V, allowed to rest for 1 h, and then oxidized (delithiated) at the same current density with a cutoff potential of 2.0 V unless otherwise stated. During the cycle test, the electrochemical impedance spectra of the cell were measured in the frequency range of 20 kHz to 0.1 Hz with a perturbation of 10 mV against a rest potential (SI1280B, Solartron Instruments).

After the cycle test, the cell was disassembled inside the Ar glove box and the working electrode was washed with dimethyl carbonate to remove the electrolyte. *Ex situ* X-ray diffraction (XRD) analysis of the electrode was performed under an Ar atmosphere by covering it with a polyimide film to avoid any reaction with moisture and air. The XRD patterns were recorded with an XRD unit (RINT-2500, Rigaku Corp.) using Cu Kα radiation at room temperature. Ga K-edge X-ray absorption fine structure (XAFS) analysis of the electrode, which was sealed in a laminate pack in an Ar atmosphere, was carried out in the transmission mode by using an X-ray spectrometer (EXAC-820, Technos Co., Ltd.) at room temperature. S K-edge XAFS analysis of the electrode was performed at BL-10 of the SR Center, Ritsumeikan University [11]. Samples were prepared in an Ar-filled glove box, transferred, and loaded in the XAFS sample chamber in vacuum without being exposed to air. XAFS spectra were obtained in both the total electron yield mode and the partial fluorescence yield mode.

3. Results

Potential profiles of the Ga_2S_3 electrode during the cycle test are shown in Fig. 1. Prior to reduction, no reaction of the Ga_2S_3 electrode was observed in the potential range of 2.0–4.0 V. The first reduction curve shows a large plateau at ca. 1.0 V. This is mainly attributed to lithiation of the Ga_2S_3 electrode, as mentioned later. A slight increase in the potential in the early stages of the plateau is due to a decrease in the overpotential induced by the reaction resistance. This is confirmed by the electrochemical impedance analysis (Fig. 2). The large impedance of the cell before reduction (Initial) drastically decreases in the early stages of the plateau, and thereafter the impedance changes slightly. Naturally, while other factors such as nucleation of the product affect the impedance, there is a drastic decrease in impedance only in the early stages of the first reduction. As shown in Fig. 1, during the first reduction, the potential gradually decreases after the large plateau, and another plateau appears below 0.3 V. The total reduction capacity (ca. 1450 mAh g^{-1}) is beyond the theoretical capacity. There are at least two possible explanations for this over-reduction: the formation of a solid–electrolyte interface (SEI), which uses extra electric current, and the contribution from the capacities of ketchen black and polyimide. In the subsequent first oxidation (delithiation), the potential increases gradually and the capacity of the electrode exceeds 900 mAh g^{-1}. Overall, two sloping plateaus appear during the lithiation process (ca. 1.1 V and below 0.3 V) as well as the delithiation process (ca. 0.8 V and 1.7 V). All of the plateau regions gradually become narrow with an increase in the cycle number.

Cycle performance in the delithiation capacity of Ga_2S_3 is shown in Fig. 3. The capacity contributions of the over-reduction from the SEI, ketchen black and polyimide were subtracted out by using the blank electrode. The first delithiation capacity of Ga_2S_3 is 920 mAh g^{-1}, which is 81% of the theoretical capacity. The capacity decreases more rapidly in the initial five cycles than in the subsequent cycles. The capacity at the 10th cycle is close to 600 mAh g^{-1} (capacity retention: 63%). This is superior to that of Al_2S_3, the capacity of which dropped to 240 mAh g^{-1} after 10 cycles [7] (although the preparation of Al_2S_3 electrode by mixing Al_2S_3 powder with teflonized acetylene black is different from that of Ga_2S_3 electrode

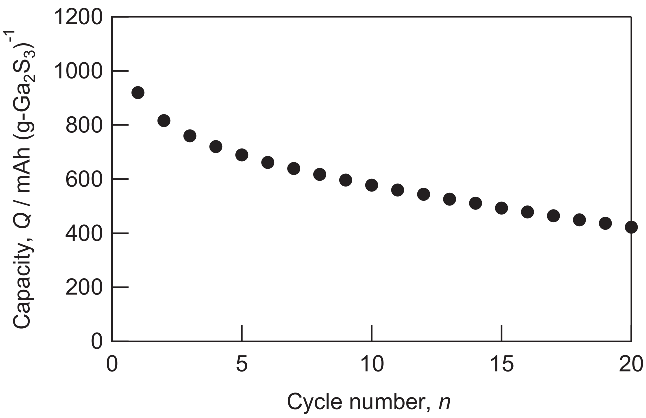

Fig. 3. Delithiation capacity of Ga_2S_3 at 100 mA g^{-1} corrected for the SEI, ketchen black and polyimide as a function of the cycle number.