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Preparation of needle-like α -Fe₂O₃ particles and influences of their morphology on the electrochemical behavior in all-solid-state lithium batteries

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Needle-like α -Fe₂O₃ particles with the length of 2 μ m and the width of 250 nm were prepared by thermal decomposition of β -FeOOH and the electrochemical performances in the all-solid-state cells were examined. The cell using needle-like particles with acetylene black as a conductive additive showed the first discharge capacity of about 700 mAh g⁻¹ at the current density of 0.064 mA cm⁻². The lithium ion and electron conduction path of the electrode was improved by using vapor grown carbon fiber as a conductive additive. The needle-like α -Fe₂O₃ particles were compared with α -Fe₂O₃ spherical particles; the suitability for the active material of all-solid-state batteries was investigated.

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1. Introduction

Fabrication of all-solid-state lithium batteries is desirable from the viewpoints of safety and reliability. We have studied all-solid-state batteries using the Li₂S–P₂S₅ solid electrolytes with high lithium ion conductivity.^{1)–4)} In the all-solid-state cells, working electrodes are composed of an active material, the solid electrolyte and a conductive additive. Electrochemical reaction would proceed at a solid-solid interface in the composite electrode. Morphology of the electrode materials is an important factor in order to form good solid-solid interfaces.

In our previous study, the influences of the sizes of active materials on the all-solid-state lithium cells have been investigated by using α -Fe₂O₃ spherical particles with various sizes.^{5),6)} The capacities increased with decreasing the particle sizes in the all-solid-state cells. It indicates that smaller active materials are effectively utilized because of increasing the contact area with solid electrolyte particles. The carbon conductive additives have been also focused in order to construct favorable solid-solid interfaces in all-solid-state cells.^{7),8)} It is found that the fibrous carbon material forms a continuous conducting path in an electrode, suggesting that the morphology of the electrode materials is also an important factor to improve the cell performance in the all-solid-state batteries.

In the present study, we focused on the morphology of α -Fe₂O₃ as an active material in composite electrodes for all-solid-state cells. Two types of α -Fe₂O₃ particles were prepared: needle-like particles were prepared by thermal decomposition of needle-like β -FeOOH particles prepared by a solution process; spherical particles were prepared also by a solution process. The electrochemical properties of needle-like α -Fe₂O₃ were measured and

compared with those of spherical α -Fe₂O₃. The influences of the morphology of active materials on electrochemical performances in the all-solid-state batteries were investigated.

2. Experimental

Needle-like α -Fe₂O₃ particles were prepared by thermal decomposition of needle-like β -FeOOH particles. Iron (III) chloride was dissolved in distilled water to obtain 1.0 M FeCl₃ solution. After the solution was maintained at 100°C for 120 h, the resulting product was collected by a centrifuge and washed three times with distilled water. The other powder obtained by the above described solution process was dried at 80°C over night. The other powder was heated at 500°C for 2 h at the heating rate of 10°C min⁻¹ to yield brownish powder.

The spherical α -Fe₂O₃ particles were prepared by a solution process described in our previous report.⁵⁾ 2.0 M FeCl₃ solution was mixed with 5.4 M NaOH solution and aged at 100°C for 8 days. The precipitation was washed three times and dried in *vacuo* at room temperature. The brownish powder was obtained.

X-ray diffraction (XRD) measurements were performed to identify crystalline phases. The microstructure and morphology of the samples were examined by using a scanning electron microscope (SEM). The BET specific surface area was determined from the nitrogen adsorption isotherm measurement.

All-solid-state electrochemical cells were assembled as follows.^{5),6)} The 80Li₂S·20P₂S₅ (mol%) glass-ceramic electrolyte with the particle size of about 5 μ m,⁸⁾ was prepared by the mechanical milling process and heating processes.¹⁾ A composite electrode was prepared by mixing of α -Fe₂O₃ (40 wt%), the solid electrolyte (60 wt%), and conductive additive (acetylene black (AB) (6 wt%) or vapor grown carbon fiber (VGCF) (4 wt%)) powders. The quantities of conductive additives required to provide enough electronic conductivity to the composite electrode were used.⁸⁾ The three-layered pellet con-

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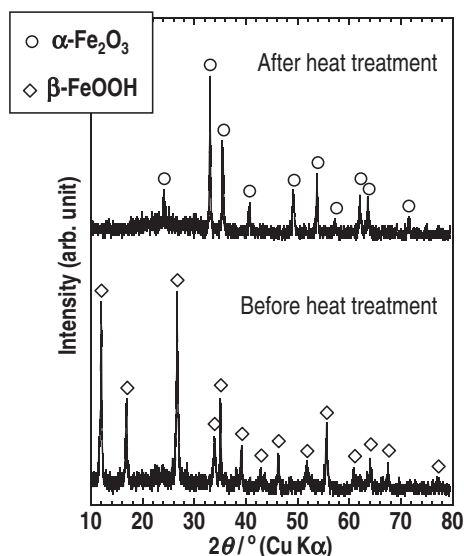


Fig. 1. XRD patterns of the powders prepared by a solution process before and after heat treatment at 500°C.

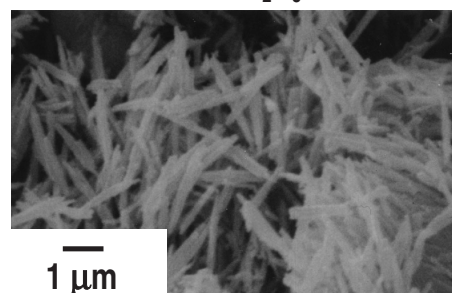
sisted of the composite electrode layer, the solid electrolyte layer and the Li-In alloy counter electrode layer was fabricated in a polycarbonate tube. Galvanostatic tests of the cells were conducted at the current densities of 0.064 and 0.26 mA cm⁻² at 25°C in an Ar atmosphere.

3. Results and discussion

Figure 1 shows a XRD pattern of the other powder prepared by a solution process. All the peaks were attributed to β -FeOOH. The XRD pattern attributed to α -Fe₂O₃ was observed after heat treatment at 500°C as shown in Fig. 1. The SEM image of α -Fe₂O₃ particles prepared by thermal decomposition is shown in **Fig. 2(a)**. Needle-like particles with the width of about 250 nm and the length of 2 μ m were observed. Needle-like particles were partially aggregated to form bundles. The β -FeOOH powder, which was precursor particles of needle-like α -Fe₂O₃, was composed of needle-like particles. Needle-like α -Fe₂O₃ particles, which kept the shape of the β -FeOOH particles, were obtained after the heat treatment.

Needle-like α -Fe₂O₃ particles were examined as an active material of all-solid-state cells with AB as a conductive additive; its electrochemical property was compared with that of spherical particles with the size of 250 nm as shown in Fig. 2(b). **Figure 3** shows the charge-discharge curves of the all-solid-state cells using the needle-like particles and the spherical particles up to the fifth cycle at 0.064 mA cm⁻². In the charge-discharge diagrams, the cell potential based on the Li-In reference electrode is denoted on the left axis and the potential calculated from the difference of potential between Li and Li-In is denoted on the right axis.⁹⁾ The cells were charged and discharged between 0.6 and 2.6 V (vs. Li). The profiles of the charge-discharge curves are similar to those in the conventional Li/ α -Fe₂O₃ cells using liquid electrolytes.^{10),11)} The first discharge capacities of the cells using needle-like particles and spherical particles were about 700 mAh g⁻¹ and 1050 mAh g⁻¹, respectively. The capacity of spherical particles is similar to the theoretical capacity of the full reduction of α -Fe₂O₃. The capacity of needle-like particles was smaller than that of spherical particles, because the needle-like particles were partially aggregated as shown in Fig. 2. The central part of the

(a) Needle-like α -Fe₂O₃



(b) Spherical α -Fe₂O₃

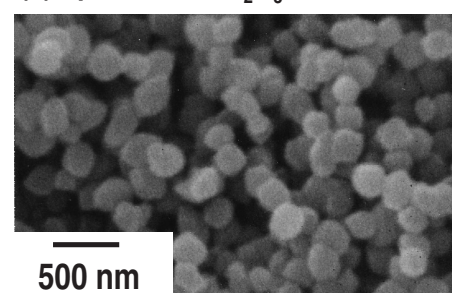


Fig. 2. SEM images of (a) needle-like α -Fe₂O₃ particles and (b) spherical α -Fe₂O₃ particles.

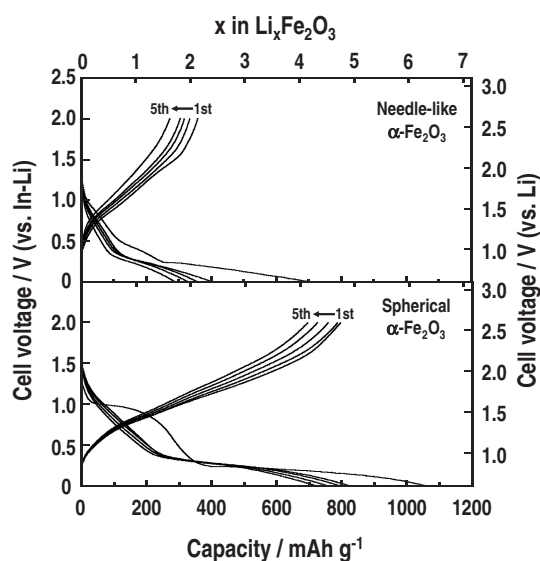


Fig. 3. Charge-discharge curves of all-solid-state cells using the needle-like α -Fe₂O₃ and the spherical α -Fe₂O₃ up to the fifth cycle. The cells were charged and discharged between 0.6 and 2.6 V (versus Li) at the current density of 0.064 mA cm⁻².

aggregations would become electrochemically inactive regions, which are unconnected with solid electrolyte particles and the conductive additive particles. In addition, the formation of suitable lithium ion and electronic conduction path in the composite electrode including the combination with needle-like particles and AB would be difficult. The capacities of both α -Fe₂O₃ particles gradually decreased with cycle number. In our previous study,⁵⁾ ex situ XRD measurements of the electrodes after cycling were performed to investigate the reaction mech-

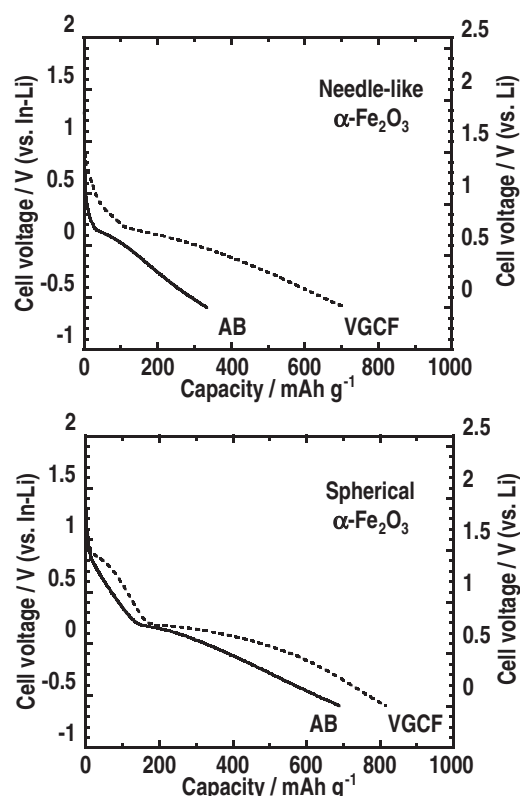


Fig. 4. First discharge curves of all-solid-state cells using the needle-like α -Fe₂O₃ and the spherical α -Fe₂O₃. The cells were discharged to 0 V (versus Li) at the current density of 0.26 mA cm⁻². Solid and broken lines denote the cell with AB and VGCF as conductive additives, respectively.

anism and the cause of the capacity loss. The conversion reaction mainly proceeded in the electrochemical reaction between α -Fe₂O₃ and lithium in the all-solid-state cells. After the full reduction of α -Fe₂O₃ in the all-solid-state cells, the peaks of metallic iron were observed. At the same time, amorphous Li₂O, which could not be detected by XRD measurements, would be formed. The peak intensity of iron increased with increasing the cycle number, and the peaks due to iron still remained even after the 20th charge.⁵⁾ The capacity loss would relate to the formation of the electrochemically inactive iron forming due to the volume change and aggregations of active materials during cycling.

We reported that a favorable lithium ion and electron conduction path in the all-solid-state In/LiCoO₂ cells can be formed by using VGCF as a conductive additive.^{7),8)} Addition of smaller amounts of VGCF, compared with AB, can provide enough electronic conductivity to the composite electrode because the fibrous shape of VGCF is effective in forming a continuous electron conduction path. The fibrous carbon was then applied to the Li-In/ α -Fe₂O₃ cells to improve electrochemical performances of the cells. **Figure 4** shows the first discharge curves of the cells using composite electrodes including AB and VGCF as conductive additives in combination with needle-like or spherical α -Fe₂O₃ particles. The cells were discharged to 0 V (vs. Li) at 0.26 mA cm⁻². Solid and broken lines denote the cells with AB and VGCF as conductive additives, respectively. The cells with VGCF showed the larger capacity than those with AB, even in the case using needle-like α -Fe₂O₃ particles with aggregation. The results indicate that the using VGCF as a conductive additive leads to high utilization of

active materials. The particle size of needle-like α -Fe₂O₃ was larger than that of spherical particles and the specific surface area of needle-like particles (13 m² g⁻¹) was smaller than that of spherical particles (20 m² g⁻¹). In addition, needle-like particles were partially aggregated. Thus, the needle-like particles prepared in this study were not expected to be suited for the active materials of all-solid-state batteries than the spherical particles. In the cells with VGCF, however, the difference of the capacity between the cells using needle-like particles and spherical particles was only 100 mAh g⁻¹. The combination of needle-like α -Fe₂O₃ and VGCF would form a favorable lithium ion and electron conduction path. The influence of the morphology of α -Fe₂O₃ particles on electrochemical performance of all-solid-state cells has not been clarified in detail because of the aggregation of needle-like α -Fe₂O₃. The use of needle-like α -Fe₂O₃ particles without aggregations is expected to be more favorable than the use of spherical particles.

4. Conclusions

The needle-like α -Fe₂O₃ particles with the length of 2 μ m and the width of 250 nm were prepared by thermal decomposition of β -FeOOH. The all-solid-state cells using needle-like particles with AB showed the first discharge capacity of about 700 mAh g⁻¹. The capacity was smaller than that of the cell using well-dispersed spherical particles with the sizes of 250 nm. However, the Li-In/needle-like α -Fe₂O₃ cell with VGCF showed the discharge capacity close to the Li-In/spherical α -Fe₂O₃ cell with VGCF. The combination of needle-like active materials and fibrous conductive additives would form a favorable lithium ion and electron conduction path, suggesting that the morphology of active materials is an important factor in the all-solid-state lithium batteries.

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