

Lithium intercalation into α -Fe₂O₃ obtained by mechanical milling of α -FeOOH

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Abstract

Crystalline α -Fe₂O₃ powder was prepared by the mechanical milling of crystalline α -FeOOH at room temperature in air. This result means that crystalline α -FeOOH is dehydrated by mechanical milling at room temperature. The obtained α -Fe₂O₃ powder worked as a rechargeable electrode material in lithium ion conductive organic electrolytes. The electrodes exhibited high discharge capacities of over 1000 mAh g⁻¹ corresponding to 6 Li per α -Fe₂O₃ at potentials ranging from the open circuit potential to 0.5 V (versus Li⁺/Li) in the first discharging (lithium insertion) process. This suggests that the valence deviation from Fe³⁺ in α -Fe₂O₃ to Fe⁰ may be caused by electrochemical reduction. In contrast, after the first discharge, the electrodes exhibited high charge capacities of more than 700 mAh g⁻¹ corresponding to 4.2 Li per α -Fe₂O₃ in the first charging (lithium extraction) process. The coulombic efficiency at the first cycle was about 70%, suggesting a valence deviation from Fe⁰ to Fe²⁺ or Fe³⁺ caused by electrochemical oxidation.

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1. Introduction

Lithium ion batteries with high energy densities have been developed as small energy devices for mobile electronic devices, such as cellular phones and notebook computers. Recently, there has been a rapid development of large lithium ion batteries as energy devices for electric vehicles. Iron oxide and iron oxyhydroxide are inexpensive and harmless materials and so it would be very interesting if they could be used to develop electrode materials for large lithium ion batteries. Many researchers have reported that α -Fe₂O₃ works as a lithium intercalation material [1–3]. Recently, Larcher et al. described the effect of particle size on lithium intercalation into α -Fe₂O₃ particles [4,5]. In this case, the electrodes consisted of nanosize α -Fe₂O₃ particles (n-Fe₂O₃) prepared by the hydrolysis of an acidic medium and micrometric α -Fe₂O₃ particles (M-Fe₂O₃) produced by Aldrich and Pro-

labo, respectively. These electrodes realized high capacities of 1400 and 1200 mAh g⁻¹, respectively, in the open circuit to 0 V potential range (versus Li/Li⁺) in the first discharge (lithium insertion) process. These results mean that about 8.3 Li per n-Fe₂O₃ and about 7.2 Li per M-Fe₂O₃ can react with lithium. Moreover, although M-Fe₂O₃ undergoes an irreversible phase transformation when a very small amount of lithium (0.03 Li) is inserted in the crystalline structure, n-Fe₂O₃ can react reversibly with up to one Li per n-Fe₂O₃ without phase transformation. Therefore, the particle size influences the cycle performance. In contrast, the mechanical milling technique is an effective process for synthesizing the electrode materials for batteries because fine powder is obtained directly [6–8]. Moreover, since the mechanical milling technique makes it possible to induce defects in the crystal structure, the synthesis of a new electrode material is also expected.

In this study, we synthesized fine α -Fe₂O₃ particles by mechanically milling α -FeOOH at room temperature in air and then evaluated their characteristics as lithium intercalation materials.

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2. Experimental

α -FeOOH (Kanto Chemical) powder was used as the starting material. The powder was milled with a planetary ball mill (Fritsch Pulverisette 7) rotating at 250 rpm at room temperature in air. The pots and balls were made of stainless steel (SUS 304) and zirconium oxide, respectively. The pot volume was 45 ml and there were 20 balls each 10 mm in diameter. X-ray diffraction measurements were carried out for powder obtained by mechanically milling the α -FeOOH for various lengths of time.

The electrode was prepared from the powder also obtained by mechanical milling for various time periods. A mixture consisting of the mechanically milled powder (72 wt.%), acetylene black (18 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%) dissolved in *N*-methyl pyrrolidinone (NMP) was stirred in air. After the mixture was painted on a nickel mesh, it was dried at about 80 °C in air and pressed for use as a working electrode. Then the electrodes were dried in a vacuum at 120 °C. A lithium sheet (approximately 500 μm thick) was used as a counter and a reference electrode. A mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1:1 volume ratio containing 1 mol dm^{-3} LiPF_6 was used as the electrolyte. A simple two-electrode cell was fabricated in a dry Ar-filled glove box. The electrode properties at room temperature were tested by charge–discharge measurements in the 0.5–3.0 V potential range (versus Li^+/Li).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the samples after mechanical milling for 0, 20, 60 and 100 h with α -FeOOH as the starting material at room temperature in air. In this case, the sample milled for 0 h indicates that the α -FeOOH powder was used as the starting material without mechanical milling. The card patterns of α -Fe₂O₃ and

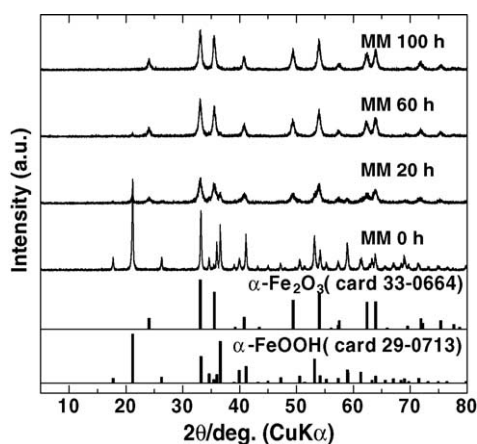


Fig. 1. X-ray diffraction patterns of the samples after mechanical milling for 0, 20, 60 and 100 h with α -FeOOH as the starting material at room temperature in air.

α -FeOOH are also shown in this figure. Weak and/or broad peaks of α -Fe₂O₃ were confirmed for all the samples after milling. However, peaks assigned to α -FeOOH were detected for the samples that were mechanically milled for 20 and 60 h. On the other hand, the peaks of the sample mechanically milled for 100 h are assigned only to α -Fe₂O₃. We found that crystalline α -Fe₂O₃ was synthesized from crystalline α -FeOOH without heat treatment. Therefore, the result suggests that crystalline α -FeOOH was dehydrated (reaction: α -FeOOH \rightarrow $1/2\text{Fe}_2\text{O}_3 + 1/2\text{H}_2\text{O}$) by mechanical milling at room temperature in air. In addition, we investigated the morphologies before and after mechanical milling using a scanning electron microscope (SEM). The morphology of α -FeOOH was needle-shaped. The morphology was very different for the sample milled for 100 h. The α -Fe₂O₃ powder milled for 100 h consisted of fine particles a few micrometers in diameter and their aggregation was also observed.

Fig. 2 shows the first, second, and third charge–discharge curves of α -Fe₂O₃ obtained after 100 h of mechanical milling. The first discharge curve was similar to that of an electrode consisting of nanosize α -Fe₂O₃ particles ($n\text{-Fe}_2\text{O}_3$) [4] reported previously. The electrode exhibited a high discharge capacity of about 1000 mAh g^{-1} corresponding to 6 Li per α -Fe₂O₃ in the open circuit potential to 0.5 V potential range (versus Li^+/Li) at a current density of 0.5 mA cm^{-2} during first discharge (lithium insertion) process. The result suggests that all the Fe^{3+} in the α -Fe₂O₃ changed the Fe^0 as a result of electrochemical reduction. The electrode after the first discharge exhibited a high charge capacity of 720 mAh g^{-1} corresponding to 4.3 Li per α -Fe₂O₃ in the 0.5–3.0 V potential range (versus Li^+/Li) at a current density of 0.5 mA cm^{-2} during the first charge (lithium extraction) process. The mechanically milled α -Fe₂O₃ powder functioned as a rechargeable electrode material in a lithium ion conductive organic electrolyte. However, we observed a gradual capacity degradation during the charge–discharge process for a cycling test in the 0.5 to 3.0 V potential range. These results suggest

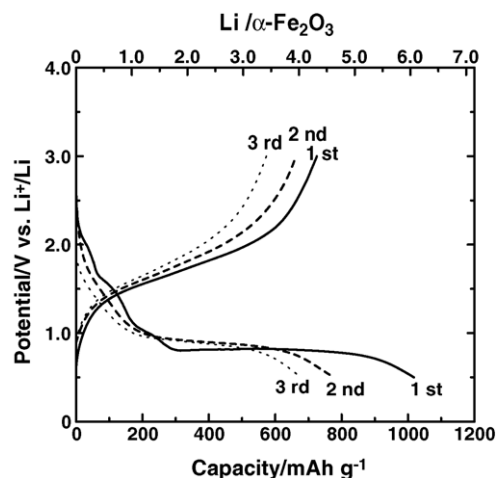


Fig. 2. First, second, and third charge–discharge curves of α -Fe₂O₃ obtained by mechanical milling for 100 h.

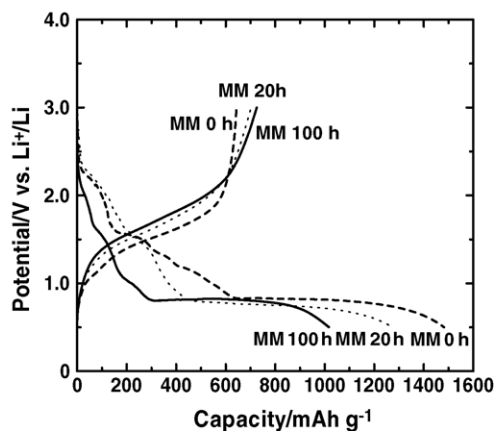


Fig. 3. First charge–discharge curves of samples milled for 0, 20, and 100 h.

that the mechanically milled α -Fe₂O₃ may cause fractures in the crystalline structure accompanied by a large amount of lithium insertion–extraction and electrochemical decomposition with the organic electrolyte.

The charge–discharge performance of the samples prepared at different milling periods was investigated. Fig. 3 shows the first charge–discharge curves of the samples milled for 0, 20, and 100 h. The first discharge capacities gradually decreased with increases in the mechanical milling periods. The sample milled for 0, i.e. α -FeOOH, exhibited a high discharge capacity of about 1500 mAh g⁻¹ corresponding to 5 Li per α -FeOOH in the open circuit to 0.5 V potential range (versus Li⁺/Li) at a current density of 0.5 mA cm⁻² for the first discharge (lithium insertion) process. Such a result is impossible to discuss in terms of the valence deviation of the transition metal Fe in α -FeOOH during the first discharge. The first discharge behavior of α -FeOOH seems to be similar to that of β -FeOOH as described previously [9]. In contrast, several potential steps are observed in the open circuit to >0.7 V potential range for the first discharge. These steps differ considerably for different milling periods. Once their potential steps had been observed, a long potential plateau for all the samples was observed at approximately 0.7 V. The lithium intercalation mechanism into α -FeOOH powder as a starting material and into mechanically milled α -Fe₂O₃ powder must be similar at 0.7 V. The lithium insertion at 0.7 V will be a typical heterogeneous reaction. On the other hand, their first charge curves are almost identical. Thus the same products must be obtained in the electrodes after the first discharge by electrochemical reduction.

Fig. 4 shows the mechanical milling time dependence of the first discharge capacity and the coulombic efficiency of samples obtained by mechanically milling α -FeOOH for various periods in the 0.5 to 3.0 V potential range (versus Li⁺/Li). Although the first discharge capacities gradually decrease with increases in the mechanical milling period, as described above, the coulombic efficiency at the first cycle is improved appreciably with increases in the mechanical milling period. In this case, the sample milled for 100 h achieved a coulombic efficiency of about 70%, suggesting a valence deviation

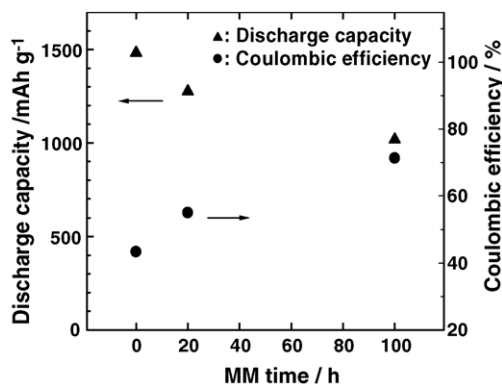


Fig. 4. Mechanical milling time dependence of first discharge capacity and coulombic efficiency of samples obtained by the mechanical milling of α -FeOOH for various periods.

from Fe⁰ to Fe²⁺ or Fe³⁺ resulting from electrochemical oxidation. The coulombic efficiency at the first cycle of the mechanically milled α -Fe₂O₃ was higher than that of an SnO electrode [10,11] and comparable to that of a CoO electrode made of nano-particles [12]. It is suggested that the electrochemical reaction mechanism of Li with the mechanically milled α -Fe₂O₃ powder must be similar to that found with transition-metal oxides, such as CoO.

Fig. 5 shows the cycle performance of samples milled for 0, 20, and 100 h. The capacity degradation of the powder milled for 100 h is smaller than that of the other powders. Consequently, we found that the cycle performance of mechanically milled α -Fe₂O₃ powder is better than that of α -FeOOH powder. However, all the samples exhibited a large capacity loss up to the 10th charge–discharge cycle in the 0.5 to 3.0 V potential range in nonaqueous electrolyte. This result suggests that the crystalline structure of the electrode materials is destroyed by a large number of lithium insertion–extractions and/or the electrode decomposes the organic electrolyte.

At present, we are undertaking a detailed investigation of the crystalline structure of electrode materials after various cut-off potentials at the first charge–discharge cycle and our goal is to improve the cycle performance of mechanically milled α -Fe₂O₃.

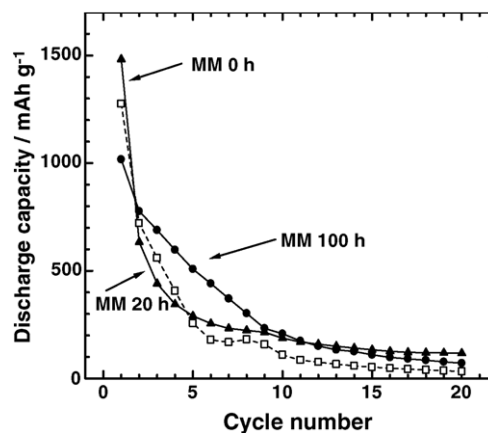


Fig. 5. Cycle performance of the samples milled for 0, 20, and 100 h.

4. Conclusion

Crystalline α -Fe₂O₃ powder was synthesized by mechanically milling crystalline α -FeOOH at room temperature in air. The mechanically milled α -Fe₂O₃ powder worked as a rechargeable high capacity electrode material in a lithium ion conductive organic electrolyte, suggesting that the Fe³⁺ in mechanically milled α -Fe₂O₃ must have changed the Fe⁰ as a result of electrochemical reduction. In this case, however, the cycle performance is very poor. If the cycle performance can be improved, α -Fe₂O₃ obtained by the mechanical milling of crystalline α -FeOOH appears to be a promising candidate as a high capacity electrode material for lithium ion batteries.

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