Transactions of the Materials Research Society of Japan 25 [1] 55-58 (2000)

Reversibility and Structure Change in Lithiation of β-$Fe_2O_3(K_{1+x}Fe_{11}O_{17})$ and γ-Fe_2O_3 under Electric Field

Shigeru Ito, Shunsuke Takahashi, Yoshitomo Omomo, Yuji Matsuura and Takashi Fujii
Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda Chiba 278-8510, Japan
Fax: 81-471-23-9890, e-mail: ito@ci.noda.sut.ac.jp

Abstract

Lithiation of β-$Fe_2O_3(K_{1.3}Fe_{11}O_{17})$ and γ-Fe_2O_3 was electrochemically performed. $K_{1+x}Fe_{11}O_{17}$ powder was lithiated up to $K_{0.5}Li_{33}Fe_{11}O_{17}$, in which valence of Fe seemed to be zero. The lithium in the product was extracted by the reverse reaction. The product containing large amount of lithium revealed broad peaks in the XRD pattern. The structure of lithiated β-Fe_2O_3 seemed to be amorphous. Similar results were obtained in the lithiation of γ-Fe_2O_3. On the other hand, lithiation was also performed chemically by the use of naphthalene-lithium; strong reducing agent. The extent of the lithiation was comparable to that in electrochemical lithiation and the crystal structure was destroyed after lithiation. The lithium in lithiated product was also chemically extracted by the oxidation using iodine. It was concluded that applying an electric field, β-Fe_2O_3 and γ-Fe_2O_3 reacted with lithium to produce amorphous materials containing Li^+ and metallic iron, and that the extractions of Li^+ proceeded.

Key words: Lithiation, Spinel structure, Amorphous, β-ferrite, γ-Fe_2O_3

1. INTRODUCTION

β-Fe_2O_3(K^+- β-ferrite: $K_{1+x}Fe_{11}O_{17}$, x=0.2-0.5) is a β-alumina analogue and has a layer structure consisting of alkali layers and spinel(γ-Fe_2O_3) blocks [1-3]. K^+ ions in the alkali layers of β-Fe_2O_3 can be exchanged with M^+ ion (M^+: Na^+, Rb^+, Cs^+, etc.)[4-5]. However, Li^+-β-ferrite, in which Li^+ ions were completely exchanged for K^+ ions, has not been reported. On the other hand, the lithiation of β-Fe_2O_3 will be possible if Fe^{3+} ions in γ-Fe_2O_3 layers are reduced to Fe^{2+}. Actually, $K_{1.2}Li_{2.2}Fe_{11}O_{17}$ containing lithium and Fe^{2+} was obtained by the reaction of $K_{1.4}Fe_{11}O_{17}$ and n-butyl-lithium (n-BuLi)[6]. However, a large amount of lithium was inserted into the β-Fe_2O_3 to produce $K_{1.3}Li_{11.5}Fe_{11}O_{17}$, using an electrochemical cell[7]. The amount of lithium was too large for the reduction of Fe^{3+} to Fe^{2+}. Furthermore, XRD patterns of the lithiated sample unchanged.

In this study, the lithiation process has been investigated. Especially, structure change, amount of lithium contained in β-Fe_2O_3, and the possibility of delithiation have been discussed on the basis of the application to the lithium secondary battery.

2. EXPERIMENTAL

2 .1 Electrochemical lithiation

K_2CO_3 and α-Fe_2O_3 powders were mixed with the composition of β-$Fe_2O_3(K_{1.3}Fe_{11}O_{17})$. The mixed powder was calcined at 900℃ for 1 h and the powder was then heated at 1200 ℃ for 5 h to produce β-$Fe_2O_3(K_{1.3}Fe_{11}O_{17})$. Three-electrode cell shown in Fig.1 was used in the experiment. The working electrode or cathode was prepared by pressing a mixed powder of $K_{1.3}Fe_{11}O_{17}$ or γ-Fe_2O_3 (20 mg each), acetylene black (20 mg) and PTFE binder (5 mg) on a Ti or Ni mesh current collector. The counter and reference electrodes were

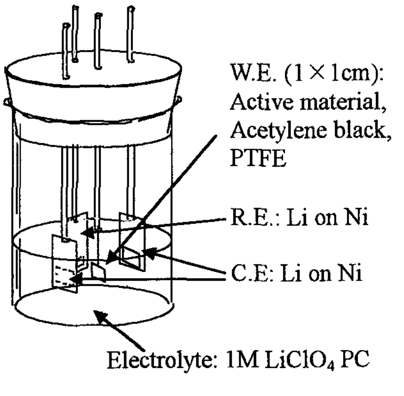

Fig.1 Electrochemical cell.

made by pressing lithium lump onto Ni mesh. $LiClO_4$ solution (1M) in propylene carbonate (PC) was used as an electrolyte. The cell was constructed in a dry box with Ar atmosphere. The cathode material after discharge or charge was identified by XRD analysis. The composition of Li, K and Fe in the cathode material was determined by flame analysis and atomic absorption analysis.

2.2 Chemical lithiation

The single crystals of β-Fe_2O_3($K_{1.3}Fe_{11}O_{17}$) were obtained by the method described elsewhere[8]. The crystals were vigorously stirred in an excess of 1.6 M solution of n-butyl-lithium (BuLi) in hexane to lithiate for 10 days at room temperature under nitrogen atmosphere.

Naphthalene-lithium was used as another lithiation reagent. The single crystals of β-Fe_2O_3 were lithiated at room temperature for 5 days in THF(tetrahydrofuran) solution of naphthalene and lithium. The lithiated sample was then washed by THF and THF dissolved naphthalene. The lithiated crystals were delithiated for 5 days at 60℃ by a 0.1 M solution of iodine in acetonitrile. The sample after delithiation was washed by acetonitrile. The lithiated and delithiated samples were identified by XRD. Fe^0 in the sample was quantitatively analyzed by dissolving Fe^0 into methanol solution of bromine, in which only Fe^0 was dissolved [9]. The residue containing Fe^{3+} and Fe^{2+} was dissolved by hydrochloric acid in an N_2 atmosphere to analyze Fe^{2+} content in the sample.

3.RESULTS AND DISCUSSION

3.1 Electrochemical lithiation

As previously reported[7], the discharge potential of the cell was about 1.5 V vs. Li/Li^+ at room temperature.

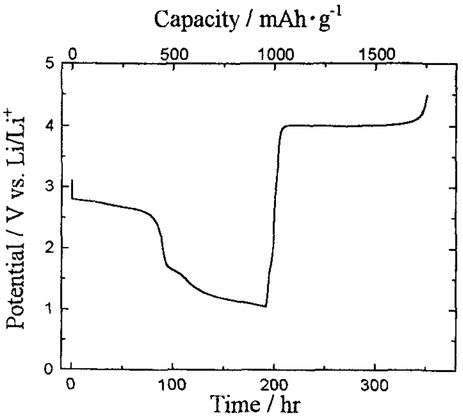

Fig.2 Discharge/charge curve for β-Fe_2O_3 at 60℃.
Current density: 0.1mA / cm^2

Fig.2 shows discharge and charge curves for β-Fe_2O_3($K_{1.3}Fe_{11}O_{17}$) at 60℃. Discharge potential increased to 2.7 V vs. Li/Li^+ by raising the temperature to 60℃. The potential decreased rapidly after 400 mAh/g of capacity. A large amount of lithium was detected in the cathode material by the chemical analysis. The composition at 950 mAh/g of discharge capacity was $K_{0.51}Li_{33}Fe_{11}O_{17}$, in which Fe^{3+} had to be reduced to Fe^0. This lithium content is nearly equal to that from the current integration. In charge step, the lithium content decreased to 0.50 in $K_{0.53}Li_{0.50}Fe_{11}O_{17}$. Lithium was almost perfectly extracted from the sample with $K_{0.51}Li_{33}Fe_{11}O_{17}$. Reversibility was confirmed in the cell. However, in the sample excessively discharged the cell was impossible to charge.

$LiCoO_2$, which has been generally used as a cathode active material, shows the capacity of about 130 mAh/g in 4 V vs. Li/Li^+ range[10]. On the other hand, the β-Fe_2O_3 has a very large capacity of 400 mAh/g, in spite of the low discharge potential of about 2.7 V vs. Li/Li^+. This capacity is over the capacity assigning the reduction of Fe^{3+} to Fe^{2+}. It is deduced that Fe^{3+} is reduced to Fe^0.

Fig.3 shows discharge and charge curves in cycle test. As the cycle was continued, discharge potential gradually decreased. In the 10th cycle, the discharge potential decreased to 1.5 V vs. Li/Li^+ at about 150 mAh/g of the capacity. However, the composition of cathode active material after the 10th cycle was $K_{0.51}Li_{0.50}Fe_{11}O_{17}$; i.e., lithium was almost completely extracted. This potential drop seemed not to be due to the deterioration of β-Fe_2O_3 cathode active material, but to be due to the structure of test cell.

Fig.4 shows the XRD patterns of the cathode active

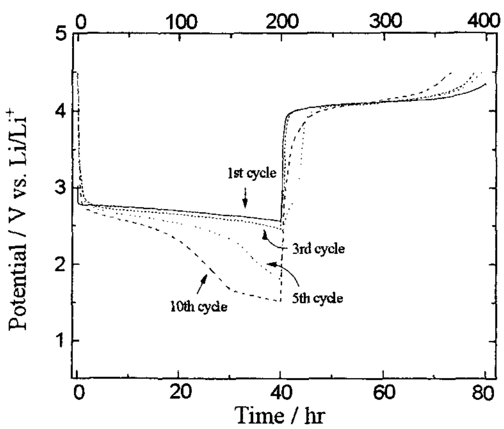

Fig.3 Discharge/charge curves for β-Fe_2O_3 at 60℃.
Current density: 0.1mA / cm

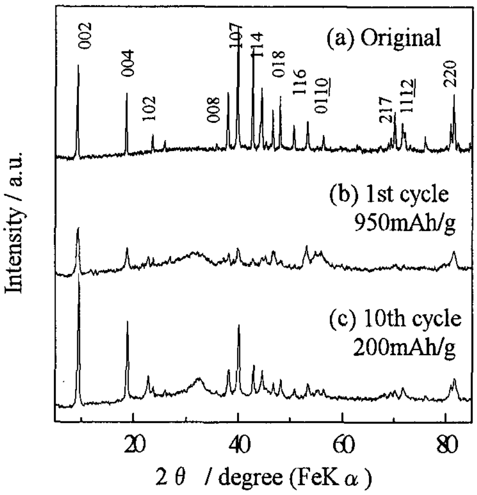

Fig.4 XRD patterns after electrochemical lithiation and extraction for β-Fe_2O_3.

material after cycle test. The lattice constants of cycled cathode materials were almost the same as those of the original one (a=0.5930 nm, c=2.380 nm). However the peak intensity with a large discharge/charge capacity was less than that with small capacity. Therefore, it seemed that a part of the grain was transformed into an amorphous phase by lithiation and delithiation, corresponding to the extent of the reaction.

If Li^+ ions were intercalated without destruction of β-structure, the lattice constants should be change. Therefore, the lithiation of β-Fe_2O_3 is not "Intercalation", but begins from the surfaces of β-Fe_2O_3 powder particles to form an amorphous phase containing Fe^0.

γ-Fe_2O_3, which is contained in β-structure as spinel block, was also used as a cathode active material. Fig.5 shows the discharge/charge curve for γ-Fe_2O_3 at 60℃. γ-Fe_2O_3 with a large specific surface area showed slightly excellent characteristics. This is due to the high reactivity of fine grains. Although the cell characteristics of γ-Fe_2O_3 was slightly excellent compared to those of β-Fe_2O_3, these are not large difference in discharge/charge characteristics of γ-Fe_2O_3 and β-Fe_2O_3. It is concluded that the discharge/charge characteristic of β-Fe_2O_3 is essentially equal to that of γ-Fe_2O_3.

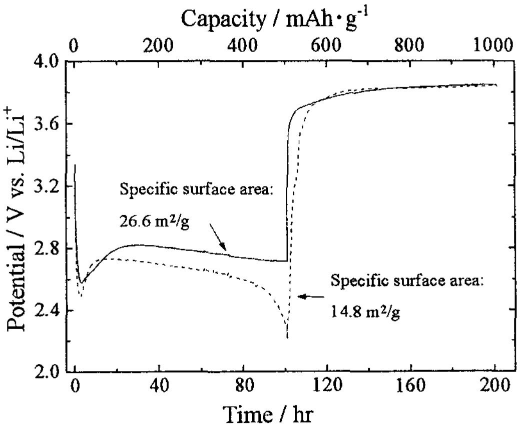

Fig.5 Discharge/charge curve for γ-Fe_2O_3 at 60℃. Current density: 0.1mA / cm^2

3.2 Chemical lithiation

A large amount of lithium was inserted by the electrochemical lithiation. To accept this amount of lithium, Fe^{3+} should be reduced to Fe^0. Detail investigation is needed. However, amount of the active material is too small to analyze valence of iron. PTFE and acetylene black also prevent the observation of the particles. Therefore, β-Fe_2O_3 was chemically lithiated and delithiated. Single crystals of β-Fe_2O_3 were ground to make powders with different particle sizes. This powder was then chemically lithiated by n-BuLi or naphthalene-lithium.

Fig.6 shows lithium content y of the sample lithiated by using n-BuLi as a function of particle size. $K_{0.99}Li_{1.7}Fe_{11}O_{17}$ was obtained in the sample with a small particle size of 5 μm. 7.4% of Fe^{2+} was detected in the sample $K_{0.99}Li_{1.7}Fe_{11}O_{17}$. On the other hand, large particle contained a small amount of lithium. It is concluded that the lithiation using n-BuLi is as follows,

$$K_{1+x}Fe^{2+}{}_xFe^{3+}{}_{11-x}O_{17} + yLi^+ + ye^- \rightarrow K_{1+x}Li_yFe^{2+}{}_{x+y}Fe^{3+}{}_{11-(x+y)}O_{17} \quad (1).$$

Similar XRD patterns were obtained in the samples before and after lithiation.

Lithium content was not so large in the lithiation using n-BuLi. Therefore, strong reducing agent naphthalene-lithium was used. Fig.7 shows lithium content, Fe^{2+} content and Fe^0 content in the sample. A

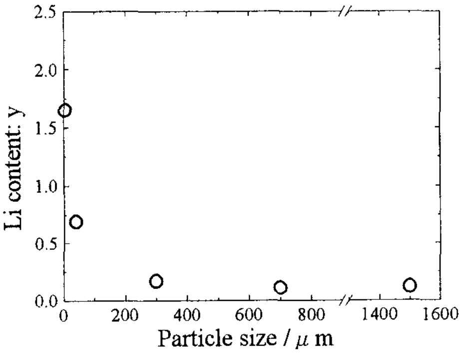

Fig. 6 Lithium content y in $KLi_yFe_{11}O_{17}$ lithiated by n-BuLi.

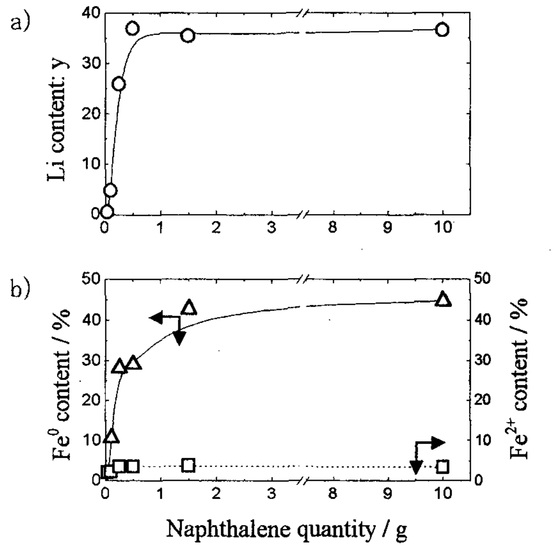

Fig.7 Lithium content y in $KLi_yFe_{11}O_{17}$, and Fe^0 and Fe^{2+} content as a function of naphthalene quantity.

large amount of lithium was detected, and the amount was independent of the particle size. The maximum value of lithium content y was 36, which is comparable to that of the electrochemically lithiated cathode active material. In this case, most of iron in β-Fe_2O_3 appeared to be Fe^0 followed by equation (2).

$$K_{1+x}Fe^{2+}{}_xFe^{3+}{}_{11-x}O_{17} + yLi^+ + ye^-$$
$$\rightarrow K_{1+x}Li_yFe^0{}_{1/3y}Fe^{2+}{}_x\,Fe^{3+}{}_{11-(x+1/3y)}O_{17} \quad (2).$$

For the existence of Fe^0, further investigation will be needed. In the XRD pattern of the completely lithiated sample, no peak was observed. The sample lithiated by naphthalene-lithium appeared to be amorphous. According to the SEM observation, the particles were cracked, as the lithiation proceeded. The sample lithated with y=36 was delithiated by acetonitrile solution of iodine. The lithium content y was decreased to 2.78. Therefore, the reversibility for the insertion and extraction of lithium was confirmed in the deeply lithiated sample, although the β-Fe_2O_3 was transformed into an amorphous phase.

4.CONCLUSIONS

In this study, extraordinary lithiation of β-Fe_2O_3 under electric field was investigated. The results were summarized below.

(1) β-Fe_2O_3 was electrochemically lithiated to form $K_{1.3}Li_{33}Fe_{11}O_{17}$ in which Fe^{3+} had to be reduced to Fe^0. This lithium content corresponds to 950 mAh/g of discharge capacity, which is much larger than that of conventional cathode active material for the lithium secondary battery.

(2) The lithium was almost perfectly extracted from the sample with $K_{0.51}Li_{33}Fe_{11}O_{17}$ in charge of the cell.

(3) The lithiation of β-Fe_2O_3 is not "Intercalation" holding the β-structure, but begins from the surface of β-Fe_2O_3 powder particles to form an amorphous phase.

(4) Similar discharge/charge characteristic was obtained using γ-Fe_2O_3 as a cathode material. It is concluded that the discharge/charge characteristic of β-Fe_2O_3 is essentially equal to that of γ-Fe_2O_3.

(5) β-Fe_2O_3 was transformed into amorphous phase by the chemical lithiation using naphthalene lithium. Fe^{3+} in β-Fe_2O_3 appeared to be Fe^0 according to the chemical analysis. The reversibility of lithiation and delithiation was also confirmed.

It is concluded that β-Fe_2O_3 is expected to be high capacity cathode active material for lithium secondary battery, although the discharge potential is relatively low.

ACKNOWLEDGMENT

This study was supported by Special Coordination Funds for Promoting Science and Technology from the Japanese Science and Technology Agency, to whom authors are deeply indebted. Authors are much indebted to Dr. T. Maruyama for the useful experimental suggestion.

REFERENCES

[1] J.P.Boilot, P.Colomban, G.Collin and R.Comes, Solid State Ionics, 1, 69 (1980)

[2] W.L.Roth and R.J.Romanczuk, J.Electrochem.Soc., 116(7), 975-980 (1969)

[3] T.Takahasi, K.Kuwabawa, and Y.Kase, DENKI KAGAKU, 43(8) (1975)

[4] B.Dunn and G.C.Farrington, Solid State Ionics, 9-10, 223 (1983)

[5] S.Nariki, S.Ito, K.Uchinokura and N.Yoneda, J.Ceram. Soc.Japan, 96, 186 (1988)

[6] Shigeru Ito, Takahiro Aoyama and Kazuo Akashi, Solid State Ionics, 113-115, 23-27 (1998)

[7] Shigeru Ito, Koichi Ui, Nobuyuki Koura and Kazuo Akashi, Solid State Ionics, 113-115, 17-21 (1998)

[8] S.Nariki, S.Ito and N.Yoneda, Ferrite, 101-104 (1992)

[9] JIS M 8213-1995

[10] N.Kumagaya and A.Yu, DENKI KAGAKU, 65(10), (1997)

(Received December 17,1999 ; Accepted February 15,2000)