

Chemical Lithiation/Delithiation of K^+ - β -Ferrite ($K_{1+x}Fe_{11}O_{17}$)

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The chemical lithiation/delithiation of K^+ - β -ferrite has been performed using butyllithium, lithium naphthalide (for lithiation), and iodine (for delithiation). In lithiation using butyllithium, the lithium content (y) in $K_{1+x}Li_yFe_{11}O_{17}$ was dependent on the average grain size of K^+ - β -ferrite single crystals; small grains (5 μ m) largely reacted with lithium to form $K_{0.99}Li_{1.65}Fe_{11}O_{17}$. Lithiation was performed by the reduction of Fe^{3+} to Fe^{2+} . Since the same X-ray diffraction (XRD) patterns were obtained before and after lithiation, the reaction seemed to be restricted to only near the grain surfaces. In lithiation using lithium naphthalide, the lithium content (y), which attained to be 36, was independent of the average grain size of K^+ - β -ferrite single crystals. This lithium content was remarkably large, compared to $y = ca. 1.6$ in lithiation using butyllithium. A large amount of Fe^0 (metal) was detected in the samples. According to scanning electron microscope (SEM) and XRD studies, not only pulverization of grains, but also destruction of the β -structure, occurred upon lithiation. On the other hand, delithiation of deeply lithiated samples was achieved by using iodine as an oxidant.

K^+ - β -ferrite was found in 1938 to be a magnetoplumbite-like compound by V. Adelsköld,¹ and was then clarified to have the same structure as β -alumina, known to be a superionic conductor.^{2–4} K^+ - β -ferrite, as well as β -alumina, has a layer structure alternating an alkali layer with potassium and oxygen and a spinel block with γ - Fe_2O_3 . The composition of K^+ - β -ferrite is expressed as $K_{1+x}Fe_{11}O_{17}$ ($0 < x < 0.5$), where x is the excess amount of potassium. This excess amount is compensated by the reduction of Fe^{3+} to Fe^{2+} ,^{5–6} although in β -alumina the oxygen atoms are in the alkali layer to compensate for any excess amount of alkali ions.

Considering the reduction of Fe^{3+} to Fe^{2+} , the authors constructed a lithium secondary battery using K^+ - β -ferrite as a cathode active material ($Li|1M LiClO_4 PCIK_{1.3}Fe_{11}O_{17}$).^{7–9} This battery revealed OCV, 3.2 V; discharge potential, 1.5 V vs. Li/Li^+ ; and capacity, 200 Ah kg^{-1} at room temperature. This capacity was larger than those of the conventional cathode active materials. After discharging, a large amount of lithium was contained in the cathode active material ($K_{1.3}Li_{6.8}Fe_{11}O_{17}$). After ten cycles of discharge/charge, no degradation was observed in this battery. However, the redox reaction in the cathode material was still unclear. M. Pernet et al. reported that in the lithiation of γ - Fe_2O_3 powder using butyllithium, Li^+ ions were inserted into octahedral vacancies in the defect spinel, and that a large amount of lithium was inserted with the first-order transition of spinel-rocksalt type to produce $Li_{0.86}Fe_2O_3$.¹⁰ Therefore, the lithiation was chemically examined by the reaction of butyllithium and K^+ - β -ferrite powder. The composition $K_{1.2}Li_{2.2}Fe_{11}O_{17}$ was obtained and Fe^{3+} in K^+ - β -ferrite was reduced to Fe^{2+} by the lithiation, according to a chemical analysis.¹¹ However, lithium hardly reacted with single crystals of K^+ - β -ferrite that were 1–2 mm in size. It appears that chemical

lithiation using butyllithium occurs near to the surface of K^+ - β -ferrite grains. On the other hand, K. M. Abraham et al. examined the chemical lithium insertion into α - and γ - Fe_2O_3 powder, using lithium naphthalide as a strong reductant, and obtained an amorphous phase containing lithium ($Li_xFe_2O_3$, $x \%$ 6).¹² This amorphous phase contained a large amount of lithium, compared to the product obtained by butyllithium. Therefore, further research may be required for K^+ - β -ferrite to clarify the redox reaction in the lithium secondary battery.

In this work, the lithiation of K^+ - β -ferrite single crystals was investigated by using butyllithium and lithium naphthalide. The relation between the amount of lithium and the structure of the product has been considered. In addition, the reversibility of the lithiation/delithiation was also examined using iodine as an oxidant.

Experimental

1. Preparation of K^+ - β -Ferrite Single Crystals. K^+ - β -ferrite single crystals, $K_{1.2}Fe_{11}O_{17}$, were obtained by a flux method using B_2O_3 – K_2O – KF .^{13–14} A mixed powder of B_2O_3 , K_2CO_3 , KF , and α - Fe_2O_3 (1:1:2:1 in molar ratio, 15 g in net weight) in a platinum crucible was heated at 1200 °C for 6 h, and then cooled to 700 °C at a cooling rate of 25 °C h^{-1} . The flux was removed by immersing the contents in 2 M HNO_3 for 3 days at 50 °C (1 M = 1 mol dm^{-3}). The obtained single crystals were sieved with average grain sizes of 40, 300, 700, and 1500 μ m, respectively. The ground particles of single crystals were also used as samples with an average grain size of 5 μ m.

2. Lithiation of K^+ - β -Ferrite Single Crystals Using Butyllithium. K^+ - β -ferrite single crystals (0.4 g, 5–1500 μ m) were immersed in 20 ml of 1.6 M butyllithium hexane solution for 5 or 10 days at room temperature under an inert nitrogen atmosphere. After the reaction with butyllithium, the sample was washed with hexane and distilled water, and then dried for 1 h at 120 °C in air.

3. Lithiation of K^+ - β -Ferrite Single Crystals Using Lithium Naphthalide. To prepare lithium naphthalide, first 0.04–10 g of naphthalene was dissolved in 20 ml of tetrahydrofuran, and then an excess amount of lithium (0.2–2 g) was added to the solution. K^+ - β -ferrite single crystals (0.4 g, 40 or 1500 μm) were immersed in the solution for 5 days at room temperature. The product was washed with tetrahydrofuran and tetrahydrofuran containing naphthalene, and then dried for 1 h at room temperature in vacuum. To remove oxygen and moisture from the reaction system, these experiments were carried out in a vacuum dry box filled with argon. Tetrahydrofuran was previously dried with molecular sieves 3 A.

4. Delithiation of Lithiated Samples Using Iodine. Lithiated samples (0.2 g) obtained in section 2 or 3 were immersed in 20 or 100 ml of 0.1 M iodine acetonitrile solution for 5 days at 60 °C. After the reaction, the sample was washed with acetonitrile, and then dried by the same procedure as described in section 2 or 3. For the samples lithiated using lithium naphthalide, delithiation was carried out in a vacuum dry box filled with argon. Acetonitrile was previously dried with molecular sieves, 3 A, to remove any moisture in the reaction system.

5. Characterization. The chemical compositions of K^+ - β -ferrite single crystals and lithiated/delithiated samples were determined by atomic absorption spectroscopy (Shimadzu, AA-630-12). The contents of metal iron and Fe^{2+} ions were determined by following JIS M 8213-1995. The crystalline phase of samples was identified by X-ray diffraction with $\text{Fe } K\alpha$ radiation (Rigaku CN 2013). In this measurement, a sample obtained using lithium naphthalide was ground in a vacuum dry box filled with argon, and the sample holder was wrapped with polyethylene film. The lithiated samples were observed by scanning electron microscope (Akashi, ALPHA-9).

Results and Discussion

1. Lithiation and Delithiation Using Butyllithium and Iodine. 1.1. Lithiation Using Butyllithium.

Figure 1 shows the lithium content (y) in $\text{K}_{1+x}\text{Li}_y\text{Fe}_{11}\text{O}_{17}$ after lithiation for 10 days as a function of the average grain size of K^+ - β -ferrite single crystals. Only a small amount of lithium reacted with single-crystal grains having an average grain size $> 700 \mu\text{m}$, e.g., $\text{K}_{1.19}\text{Li}_{0.12}\text{Fe}_{11}\text{O}_{17}$ was obtained by using grains with 1500 μm .

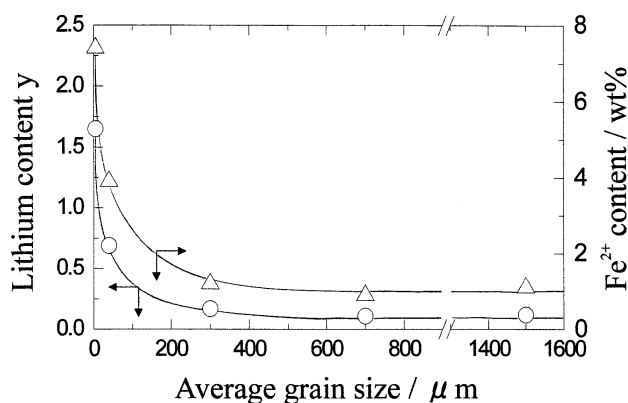


Fig. 1. Lithium content y in $\text{K}_{1+x}\text{Li}_y\text{Fe}_{11}\text{O}_{17}$ and Fe^{2+} content after lithiation for 10 days using butyllithium as a function of average grain size of K^+ - β -ferrite single crystals.

On the other hand, small grains (5 μm) largely reacted with lithium to form $\text{K}_{0.99}\text{Li}_{1.65}\text{Fe}_{11}\text{O}_{17}$. The lithium contents correlated with the amount of Fe^{2+} , as shown in Fig. 1. The grains with 5 μm contained 7.4 wt% of Fe^{2+} . Assuming that the lithiation is described by the following equation, 7.4 wt% corresponds to $y = 1.3$, in accordance with the result of a chemical analysis ($y = 1.65$):

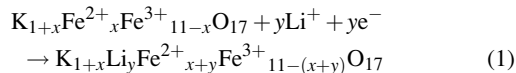


Figure 2 shows the XRD patterns and the lattice constants of samples lithiated for 10 days. The XRD patterns of lithiated samples were the same as that of the original K^+ - β -ferrite. No relation was recognized between the lattice constants and the lithium content (y). However, M. Pernet et. al. reported that Li^+ ions were inserted into the vacancies of $\gamma\text{-Fe}_2\text{O}_3$ to increase the lattice constants.¹⁰ If Li^+ ions are inserted into the $\gamma\text{-Fe}_2\text{O}_3$ layers in K^+ - β -ferrite, the lattice constants should be increased. On the other hand, the interlayer distance of K^+ - β -ferrite was decreased by inserting alkali ions in the alkali layers, because of the electrostatic attractive force.¹⁵ If Li^+ ions are inserted into the alkali layers of K^+ - β -ferrite, the electrostatic force must decrease the interlayer distance. Therefore, the intercalation of Li^+ ions does not occur in the reaction of butyllithium and K^+ - β -ferrite. Considering that the lithium content (y) de-

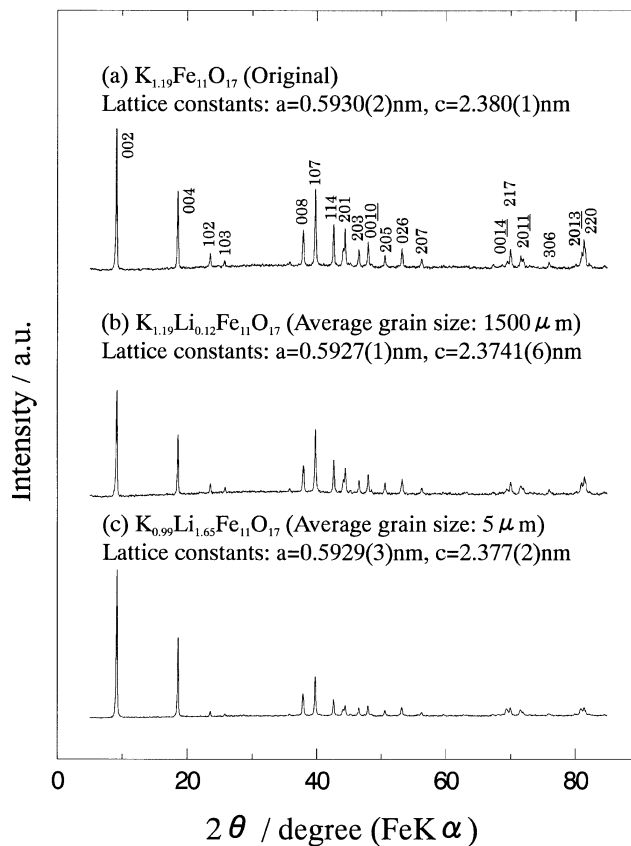
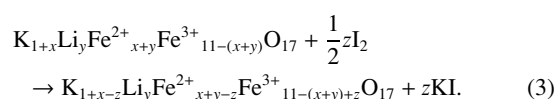
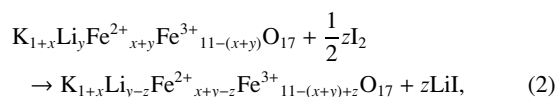


Fig. 2. XRD patterns of the samples lithiated for 10 days using butyllithium.

depends on the average size of single crystal grains of K^+ - β -ferrite, the reaction may be restricted to only near the surfaces of the grains.

1.2. Delithiation Using Iodine. Delithiation was performed for a sample lithiated for 10 days. Table 1 gives the compositions and Fe^{2+} contents of the delithiated samples. K^+ and Li^+ ions were decreased by delithiation using iodine. $K_{0.81}Li_{1.39}Fe_{11}O_{17}$ was obtained using a sample with 5 μm in average grain size. The Fe^{2+} content decreased corresponding to the decrease in the K^+ and Li^+ ions. It seems that K^+ and Li^+ ions are removed by the oxidation of Fe^{2+} to Fe^{3+} according to the following equations:



However, the delithiated sample still contained lithium, which seemed to be in a relatively stable state.

The XRD pattern of the delithiated sample was the same as those of the original K^+ - β -ferrite and the lithiated sample. The lattice constants of the delithiated sample with the composition of $K_{0.81}Li_{1.39}Fe_{11}O_{17}$ were $a = 0.5931(3)$ nm and $c = 2.379(1)$ nm, which were similar to those of the lithiated sample. This was because the lithiation and delithiation occurred near the surface of the grains.

2. Lithiation and Delithiation Using Lithium Naphthalide and Iodine. **2.1. Lithiation Using Lithium Naphthalide.** Figure 3 shows the lithium content (y) in $K_{1+x}Li_yFe_{11}O_{17}$ after lithiation for 5 days as a function of the weight of naphthalene in 20 ml of tetrahydrofuran. In lithiation using lithium naphthalide, naphthalene radical anions, which are formed by the reaction of lithium and naphthalene, attack K^+ - β -ferrite to reduce Fe^{3+} ions. As shown in Figs. 3(a) and 3(b), the lithium content (y), which attained to 36 for 1.5–10 g of naphthalene, was independent of the average grain size of K^+ - β -ferrite. This lithium content, which is remarkably large compared to $y = ca. 1.6$ obtained by butyllithium, resulted from the potential difference in butyllithium and lithium naphthalide (1 and 0.5 V vs. Li/Li^+ , respectively).¹⁶ Assuming the reduction of Fe^{3+} to Fe^{2+} in the lithiation shown in Eq. 1, the maximum content of lithium (y) is 11. For $y = 36$, Fe^{3+} in K^+ - β -ferrite must be complete-

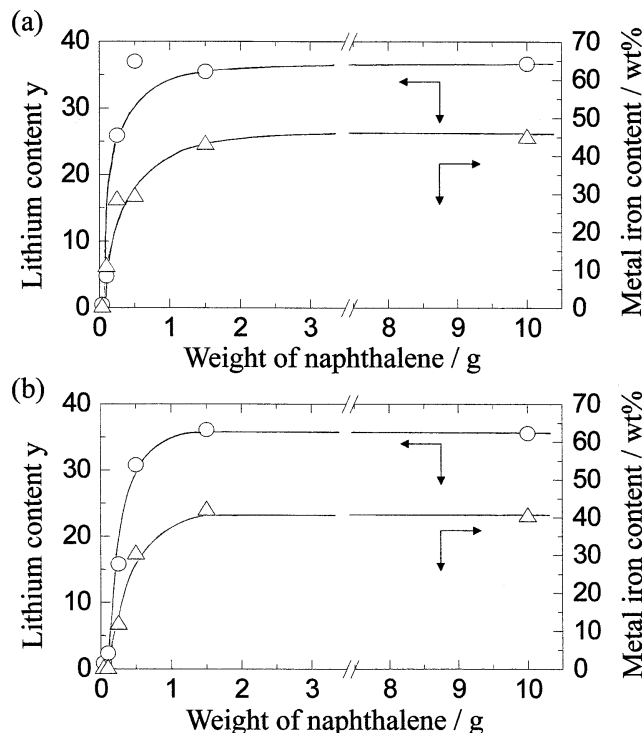
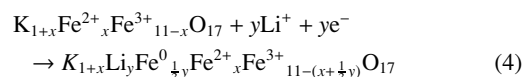


Fig. 3. Lithium content y in $K_{1+x}Li_yFe_{11}O_{17}$ and metal iron content after lithiation for 5 days using lithium naphthalide as a function of weight of naphthalene in 20 ml of THF. $K_{1+x}Fe_{11}O_{17}$ used; Average grain size: (a) 1500 μm , (b) 40 μm , Net weight: 0.4 g.

ly reduced to Fe^0 (metal). Figure 3 also shows the metal iron content. In this lithiation, a large amount of Fe^0 was detected as 45 wt%. However, the Fe^{2+} content was 2–6 wt%, corresponding to $y = 0.3$ –1.3. Lithiation using lithium naphthalide seems to proceed as follows:



According to Eq. 4, the reaction is completed with $y = 33$. An excess amount of lithium in the experimental data of $y = 36$ may be ascribed to $LiOH$ produced by residual H_2O in the reaction system.

Figure 4 shows SEM photographs of samples lithiated for 5 days. Single crystal grains pulverized from the surface, even for $y = 0.48$. As the lithiation proceeded, fine grains were observed in the sample. Figure 5 shows XRD patterns of samples lithiated for 5 days. The intensities of the peaks decreased in a sample containing a large amount of lithium. The diffraction peaks completely disappeared in a sample with $y = 36.7$. It was concluded that not only the pulverization of grains, but also the destruction of the β -structure, occurred in lithiation using lithium naphthalide.

2.2. Delithiation Using Iodine. The amorphous phase containing a large amount of lithium was delithiated. Table 2 gives the compositions, Fe^{2+} contents and metal-iron contents of the delithiated samples. The delithiation of a sample with $y =$

Table 1. Compositions and Fe^{2+} Contents of the Samples Delithiated for 5 Days Using Iodine

Average grain size μm	Composition (Fe^{2+} content/wt%)	
	After lithiation ^{a)}	After delithiation
1500	$K_{1.19}Li_{0.12}Fe_{11}O_{17}$ (1.1)	$K_{1.03}Li_{0.11}Fe_{11}O_{17}$ (0.8)
700	$K_{1.15}Li_{0.11}Fe_{11}O_{17}$ (0.9)	$K_{1.04}Li_{0.11}Fe_{11}O_{17}$ (0.7)
300	$K_{1.16}Li_{0.17}Fe_{11}O_{17}$ (1.2)	$K_{1.05}Li_{0.14}Fe_{11}O_{17}$ (0.8)
40	$K_{1.02}Li_{0.69}Fe_{11}O_{17}$ (3.9)	$K_{0.78}Li_{0.48}Fe_{11}O_{17}$ (1.2)
5	$K_{0.99}Li_{1.65}Fe_{11}O_{17}$ (7.4)	$K_{0.81}Li_{1.39}Fe_{11}O_{17}$ (5.4)

a) Lithiated for 10 days using butyllithium.

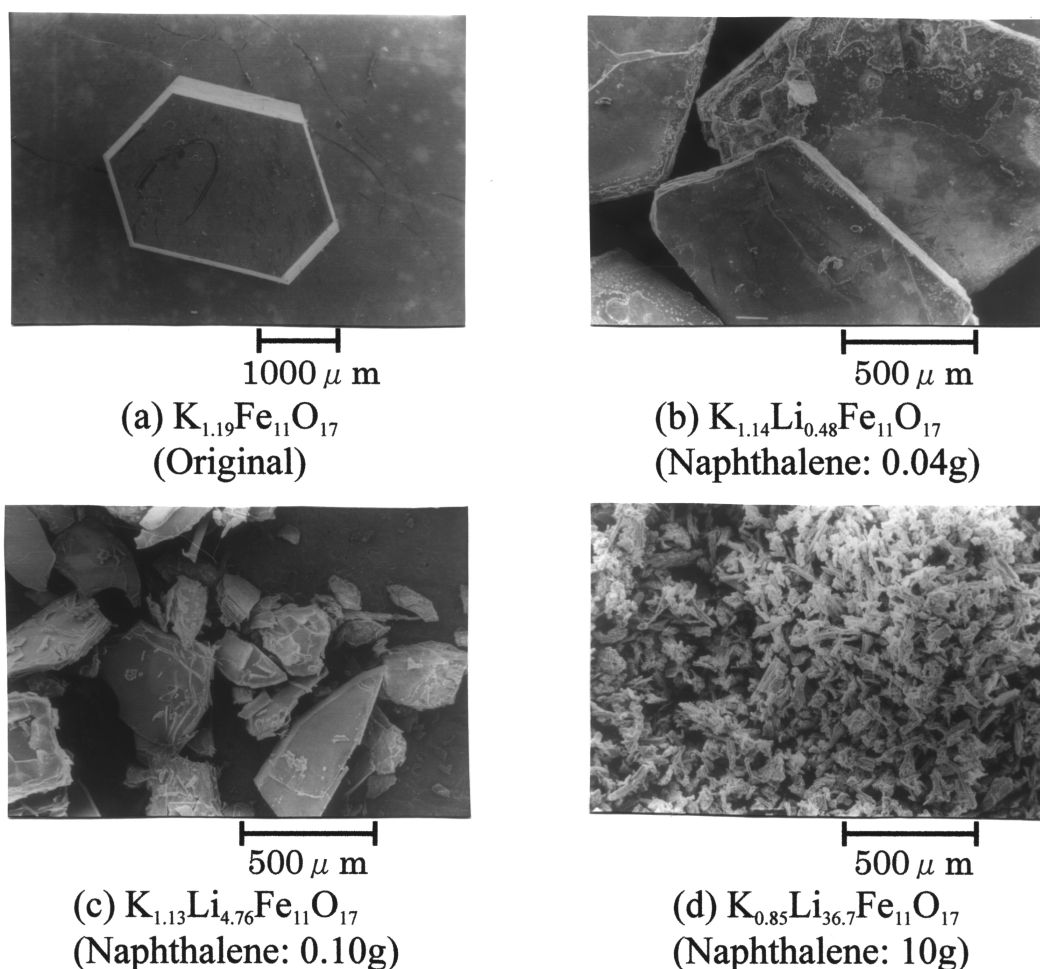


Fig. 4. SEM photographs of a K^+ - β -ferrite single crystal and the samples lithiated using lithium naphthalide.

36.7 proceeded to decrease the lithium content to $y = 2.78$. The Fe^{2+} content was 16 wt% in a sample with $y = 2.78$, whereas no metal iron was detected. A large amount of lithium was removed by the oxidation of metal iron using iodine.

Figure 6 shows the XRD patterns of the delithiated samples. The patterns in Figs. 6(b), 6(c), 6(d), and 6(e) were similar to those of the lithiated samples in Figs. 5(b), 5(c), 5(d), and 5(e), respectively. The destroyed structure after the lithiation was not recovered by delithiation.

2.3. Structure of the Lithiated Sample. From the result of an X-ray analysis, the lithiated sample was found to be amorphous. On the other hand, the material contained a large amount of Fe^0 . However, Fe atoms could not exist in the amorphous phase with the zero valency. Therefore, we deduce that the lithiated material consisted of nano-sized mixture of Li_2O and Fe (metal). Further work will be required to clarify the structure of the amorphous phase of the lithiated sample.

Conclusions

In this work, the chemical lithiation/delithiation of K^+ - β -ferrite was performed using butyllithium, lithium naphthalide (for lithiation), and iodine (for delithiation).

In lithiation using butyllithium, the lithium content (y) was dependent on the average grain size of K^+ - β -ferrite single crystals. The maximum content of lithium was $y = 1.65$ in $\text{K}_{1+x}\text{Li}_y\text{Fe}_{11}\text{O}_{17}$, when the average grain size was 5 μm . Lithiation was performed by the reduction of Fe^{3+} to Fe^{2+} . The same XRD patterns were obtained before and after lithiation. Lithiation using butyllithium may be restricted to only near the surfaces of the grains.

In lithiation using lithium naphthalide, the lithium content (y), which attained to 36, was independent of the average grain size of K^+ - β -ferrite single crystals. A large amount of Fe^0 (metal) was detected. The single-crystal grains pulverized from the surface. Furthermore, destruction of the β -structure occurred to form an amorphous phase.

Delithiation using iodine occurred for a sample lithiated using lithium naphthalide. It is expected that a lithium secondary battery using K^+ - β -ferrite as a cathode active material would have a large capacity.

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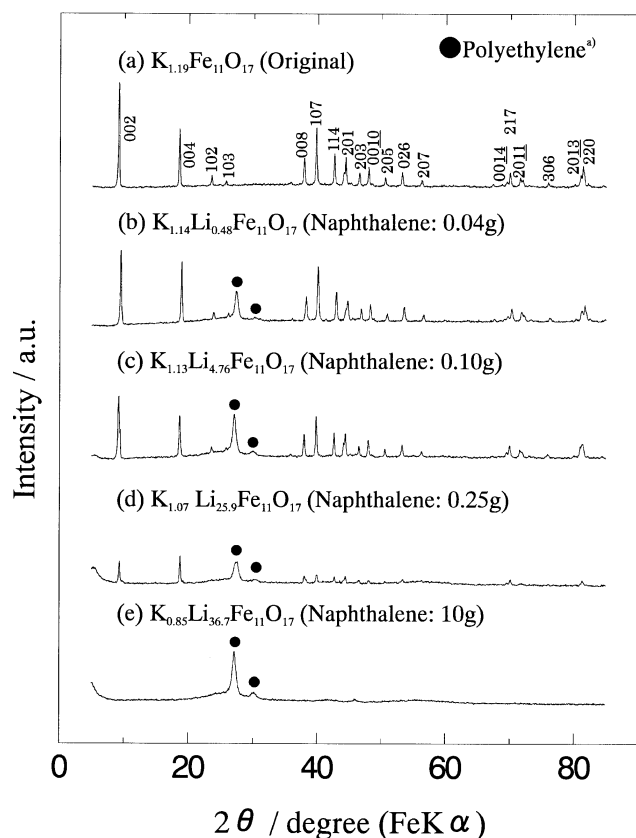


Fig. 5. XRD patterns of the samples lithiated for 5 days using lithium naphthalide. a) X-ray samples were covered with polyethylene film to prevent the exposure to air.

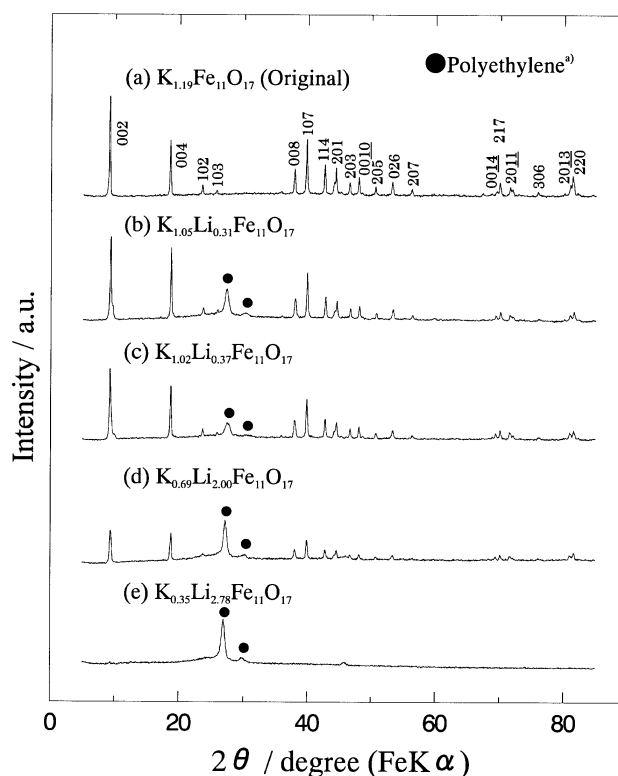


Fig. 6. XRD patterns of the samples delithiated for 5 days using iodine. Patterns (b), (c), (d), and (e) were obtained by the delithiation of the lithiated samples shown in Figs. 5(b), 5(c), 5(d), and 5(e), respectively. a) X-ray samples were covered with polyethylene film to prevent the exposure to air.

Table 2. Compositions of the Samples Delithiated for 5 Days Using Iodine

Composition (Metal iron content/wt%, Fe ²⁺ content/wt%) After lithiation ^{a)}	After delithiation
K _{1.14} Li _{0.48} Fe ₁₁ O ₁₇ (— ^{b)} , 2.0)	K _{1.05} Li _{0.31} Fe ₁₁ O ₁₇ (— ^{b)} , 1.4)
K _{1.13} Li _{4.76} Fe ₁₁ O ₁₇ (10.7, 2.3)	K _{1.02} Li _{0.37} Fe ₁₁ O ₁₇ (— ^{b)} , 2.2)
K _{1.07} Li _{25.9} Fe ₁₁ O ₁₇ (28.2, 3.6)	K _{0.69} Li _{2.00} Fe ₁₁ O ₁₇ (— ^{b)} , 6.6)
K _{0.85} Li _{36.7} Fe ₁₁ O ₁₇ (44.7, 3.3)	K _{0.35} Li _{2.78} Fe ₁₁ O ₁₇ (— ^{b)} , 16.0)

a) Lithiated for 5 days using lithium naphthalide.

b) —; No detection.

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