

## Application of FeOOH derivatives for a secondary lithium battery

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### Abstract

Three kinds of FeOOH derivatives were prepared from FeOCl using the ion exchange reaction of  $\text{Cl}^-$  ion in FeOCl with  $\text{OH}^-$  and  $\text{CH}_3\text{O}^-$ . The reaction products were identified as  $\gamma$ -FeOOH, the amorphous FeOOH including aniline, and  $\text{FeO}(\text{OCH}_3)$ . The amorphous FeOOH including aniline showed a much better performance as cathode of the rechargeable lithium battery than that of  $\gamma$ -FeOOH and  $\text{FeO}(\text{OCH}_3)$ . The discharge behavior of  $\gamma$ -FeOOH was similar to that of  $\text{FeO}(\text{OCH}_3)$ . From these results, it was found that the aniline interacted with FeOOH matrix played an important role for the high discharge potential (more than 3.0 V versus  $\text{Li}/\text{Li}^+$ ) and the high discharge capacity (more than  $200 \text{ mA h g}^{-1}$ ) of the amorphous FeOOH including aniline.

### Introduction

The rechargeable lithium battery has been investigated extensively, because of its high potentiality for energy storage. There are some problems for its use in practical cells. For example, the rechargeability of the cell is not sufficient. This is caused by the chemical and the electrochemical characteristics of the lithium anode and the cathode material. In order to develop an excellent cathode material for the rechargeable cell, many kinds of transition metal oxides and chalcogenides have been investigated. The  $\text{LiCoO}_2$  cathode has been studied extensively, because of its high discharge potential, 4.0 V versus  $\text{Li}/\text{Li}^+$  [1].  $\text{MnO}_2$ , which is the most common cathode material for the primary lithium cell, have been modified by using  $\text{LiOH}$  [2]. Some iron oxides have been investigated as the cathode of lithium batteries [3-5]. Most of the iron compounds decompose during the discharge and charge cycles. Recently, the modification of FeOCl, which is a layered compound, has been conducted by Kanamura *et al.* [6].

In this study, the discharge and charge characteristics of three kinds of FeOOH derivatives prepared from FeOCl,  $\gamma$ -FeOOH,  $\text{FeO}(\text{OCH}_3)$ , and the amorphous FeOOH including aniline, were examined and the effect of the crystal structure on the discharge and charge characteristics is discussed.

### Experimental

Three kinds of FeOOH derivatives,  $\gamma$ -FeOOH, the amorphous FeOOH including aniline, and  $\text{FeO}(\text{OCH}_3)$  were prepared by using the ion exchange reaction of  $\text{Cl}^-$  ion in FeOCl with  $\text{OH}^-$  ion or  $\text{OCH}_3^-$  ion. FeOCl was prepared by heating of the mixture

of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and FeCl<sub>3</sub> according to the ref. 6. For the preparation of  $\gamma$ -FeOOH, the intercalation compound of FeOCl and 4-aminopyridine was used as an intermediate which has a high reactivity on OH<sup>-</sup> ion. FeOCl was immersed into acetone containing 4-aminopyridine (mole ratio of FeOCl/4-aminopyridine=4/1) and then heated at 100 °C for one week. The prepared FeOCl(4-aminopyridine)<sub>1/4</sub> was washed with acetone and then dried under vacuum at 60 °C for one day. The formation of FeOCl(4-aminopyridine)<sub>1/4</sub> was confirmed by X-ray diffraction method (XRD) and FT-IR spectroscopy. The chemical composition was determined by chemical analyses and atomic absorption method. The FeOCl(4-aminopyridine)<sub>1/4</sub> was immersed in an aqueous solution containing 1.0 M LiOH for three days. The product was washed with water and then dried under vacuum at 80 °C for three days. The identification of the reaction product was conducted by XRD method.

For the preparation of the amorphous FeOOH including aniline, the intercalation compound of FeOCl and aniline was used as an intermediate. FeOCl was immersed into an aqueous solution containing aniline (mole ratio of FeOCl/aniline=4/1) for three days with stirring of the solution. The product was washed with water and acetone and then dried under vacuum at 60 °C.

The preparation of FeOOCH<sub>3</sub> was done by the reaction of FeOCl with CH<sub>3</sub>OLi in methanol. The reaction products were analyzed by XRD method, FT-IR spectroscopy, chemical analyses, and atomic absorption method.

The cathode pellet (30 mg) was prepared by pressing the mixture of the cathode material, acetylene black, and polytetrafluoroethylene (PTFE) at a weight ratio of 50:45:5, at 3 ton cm<sup>-2</sup>. Propylene carbonate containing 1.0 M LiBF<sub>4</sub> was used as electrolyte. Lithium metal was used as reference and counter electrodes. The potential changes of the cathode materials prepared in this study during the galvanostatic discharge and charge cycles at 0.5 mA were measured. The discharge and charge cycles were conducted in an argon dry box at room temperature.

## Results and discussion

Figure 1(a) shows the XRD pattern of the reaction product from FeCl<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. All peaks were clearly observed and identified as FeOCl. The space group of FeOCl was assigned to Pmnm. The strongest peak at  $2\theta=11.19^\circ$  corresponds to the interlayer spacing which was calculated to be 0.790 nm. The peak intensity corresponding to (0 k 0) planes was stronger than that of other index planes, because of high orientation of the crystal. Figure 1(b) shows the XRD pattern of the product prepared from the reaction of LiOH and the intercalation compound of FeOCl and 4-aminopyridine, which is identified as  $\gamma$ -FeOOH. The peak intensity corresponding to (0 k 0) planes was stronger than that of other planes. This is the indication for the high orientation of the crystals. The scanning electron microscopic (SEM) observations indicate that the particle shape and size of the reaction product were very similar to those of FeOCl whose particle shape is planar. The main peak of  $\gamma$ -FeOOH was broader than that of FeOCl. From these results, we may conclude that the crystallinity of  $\gamma$ -FeOOH was lower than that of FeOCl. Figure 1(c) shows the XRD pattern of the reaction product obtained from the reaction of the intercalation compound of FeOCl and aniline with water. This pattern indicates that the phase is much more amorphous than that of  $\gamma$ -FeOOH. These peaks were in agreement with those of  $\gamma$ -FeOOH. From the SEM observation, we conclude that the particle's shape and size of this compound were also similar to FeOCl. Figure 1(d) shows the XRD pattern

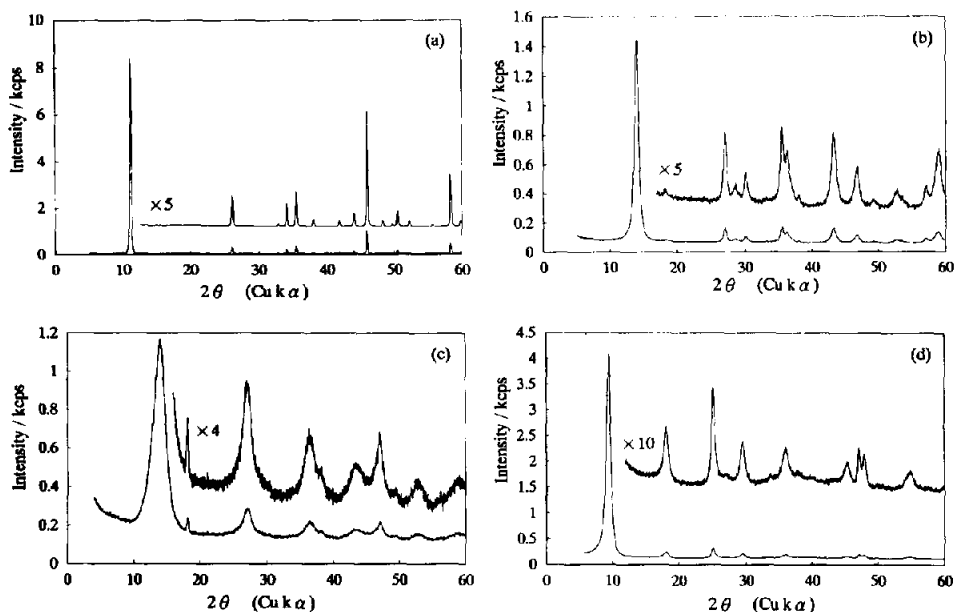


Fig. 1. X-ray diffraction patterns of: (a) FeOCl; (b)  $\gamma$ -FeOOH; (c) the amorphous FeOOH including aniline, and (d) FeOOCH<sub>3</sub> prepared in this study.

TABLE 1

Lattice parameters of FeOCl derivatives

Derivative	<i>a</i>	<i>b</i>	<i>c</i>
$\alpha$ -FeOOH <sup>a</sup>	3.86	6.31	3.14
FeOCl(4AP) <sup>b</sup>		13.6 <sup>c</sup>	
$\gamma$ -FeOOH	3.88	6.30	3.13
FeOOCH <sub>3</sub>	4.02	10.06	3.90
FeOCl	3.77	7.90	3.30

<sup>a</sup>The amorphous FeOOH including aniline.

<sup>b</sup>The intercalation compound of FeOCl and 4-aminopyridine.

<sup>c</sup>Interlayer distance.

of the reaction product of FeOCl and CH<sub>3</sub>OLi. The XRD peaks were assigned to those of FeOOCH<sub>3</sub>. The main peak at  $2\theta = 8.783^\circ$  was broader than that of FeOCl. The same phenomenon was observed in the XRD pattern of  $\gamma$ -FeOOH. The ion exchange of Cl<sup>-</sup> in FeOCl with OH<sup>-</sup> or OCH<sub>3</sub><sup>-</sup> may produce the stress in the reaction products. The lattice parameters of the reaction products, which were obtained from the XRD patterns, are summarized in Table 1.

Figure 2 shows the FT-IR spectra of these compounds. The absorption due to the vibration of the chemical bond between Fe and O was observed around the wavenumber of 500 cm<sup>-1</sup> [7-9]. The absorption peak near 500 cm<sup>-1</sup> was observed in all spectra. The spectrum of FeOCl shows one kind of Fe-O bond. On the other hand, the spectra of  $\gamma$ -FeOOH, the amorphous FeOOH including aniline, and FeOOCH<sub>3</sub>

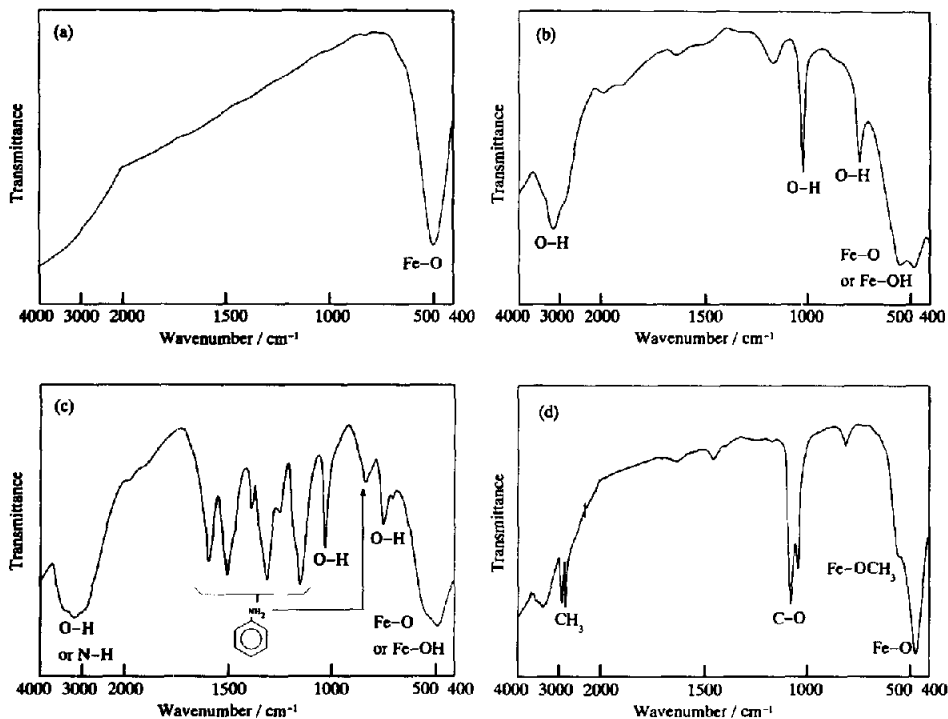


Fig. 2. FT-IR spectra of: (a) FeOCl; (b)  $\gamma$ -FeOOH; (c) the amorphous FeOOH including aniline, and (d) FeOOCH<sub>3</sub> prepared in this study.

show the presence of the two kinds of Fe-O bonds in their structure, which can be assigned to the vibration of the chemical bonds of Fe-O and Fe-OR (R=H or CH<sub>3</sub>). The absorption peak near 3000 cm<sup>-1</sup> was attributed to O-H. The peak assignments in these spectra were described in each Fig. From these assignments (and chemical analysis, see below), it can be seen that the products are FeOCl, FeOOH, FeOOH including aniline and FeOOCH<sub>3</sub>.

The chemical composition of these products were determined by the chemical analyses for carbon, hydrogen, nitrogen, and oxygen and the atomic absorption method for iron. The results are summarized in Table 2. The chemical composition of these products is in agreement with that of FeOCl, FeOOH, FeOOH(aniline)<sub>1/4</sub> and FeOOCH<sub>3</sub>.

From these analyses, a scheme of the structures of the reaction products were illustrated in Fig. 3. The structure of the product prepared from the reaction of the intercalation compound of FeOCl and aniline with water might be determined by XRD as  $\gamma$ -FeOOH. However, the presence of aniline was confirmed by the FT-IR spectrum. If aniline remains in the interlayer space of  $\gamma$ -FeOOH, the interlayer distance should be larger than that of  $\gamma$ -FeOOH. The result of the XRD method was inconsistent with that of FT-IR. The density of the product was measured by pycnometer and estimated to be 2.34, which was roughly half times as large as that of  $\gamma$ -FeOOH. This result indicates that the interlayer distance of the product is expanded. These results can be understood by the presence of two phases of FeOOH. One is the amorphous FeOOH including aniline, which has a larger interlayer spacing, and the other is  $\gamma$ -FeOOH.

TABLE 2  
Chemical composition of FeOCl derivatives (wt.%)

Derivative	C	H	N	Fe	Cl	O	C:N	Fe:N	Cl:Fe	C:Fe	O:Fe
$\alpha$ -FeOOH <sup>a</sup>	14.34	2.05	2.79	42.7	3.24	34.88	6.0:1.0	3.8:1.0	0.12:1.0		
$\gamma$ -FeOOH	1.25	1.07	0.17	61.7	0.92	34.90	8.5:1.0	91:1	0.02:1.0		2.0:1.0
FeOOCH <sub>3</sub>	9.86	2.69		49.1	1.59	36.8			0.05:1.0	0.93:1.0	2.6:1.0

<sup>a</sup>The amorphous FeOOH including aniline.

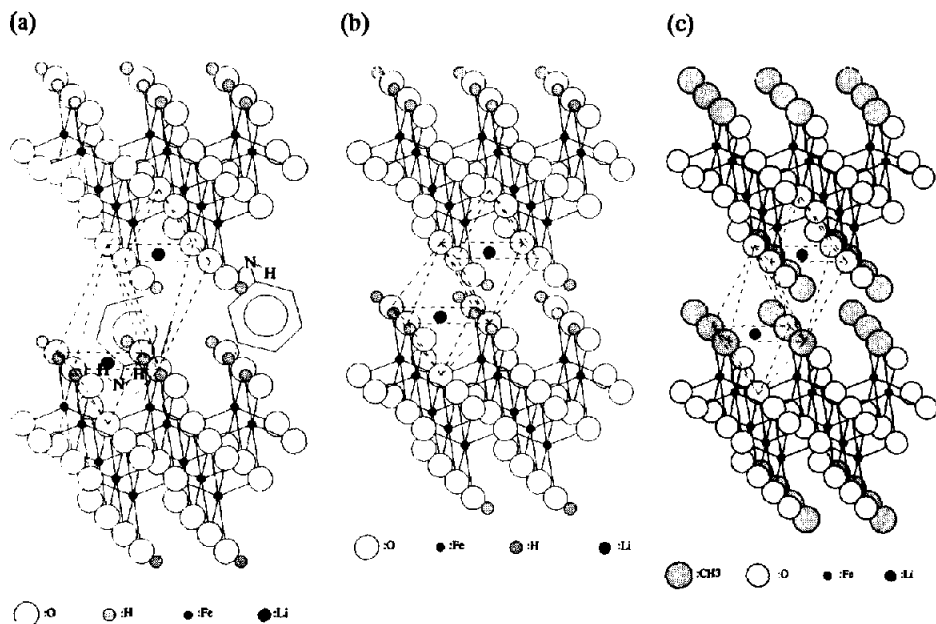


Fig. 3. Schematic illustrations of: (a) the amorphous FeOOH including aniline; (b)  $\gamma$ -FeOOH, and (c) FeOOCH<sub>3</sub>, prepared in this study.

The lithium insertion and extraction into/from these reaction products occur in the course of the discharge and charge cycle. The interstitial site for the lithium insertion are marked in Fig. 3. For all compounds, the interstitial site is surrounded by six anions. Lithium inserted into  $\gamma$ -FeOOH is surrounded by five OH<sup>-</sup> ions and one O<sup>2-</sup> ion, octahedrally. This octahedral site for lithium is slightly distorted, because of the difference in the bond length between Fe—O and Fe—OH. In the case of FeOOCH<sub>3</sub>, the octahedral site for lithium is also distorted and different from that of  $\gamma$ -FeOOH, as expected from the lattice parameters shown in Table 1. In the case of the amorphous FeOOH including aniline, the similar arrangement may be expected.

Figure 4 shows the discharge and charge curves of these compounds at the first and the tenth cycles under galvanostatic conditions. The discharge and charge potentials were different among these compounds. The discharge potential of the amorphous FeOOH including aniline was higher than that of  $\gamma$ -FeOOH and FeOOCH<sub>3</sub>. The discharge potential of these cathodes may be related to the physical state of the interstitial site for lithium. The interstitial site for lithium in FeOOCH<sub>3</sub> is different from that in  $\gamma$ -FeOOH, as shown in Fig. 3. However, the discharge behavior of  $\gamma$ -FeOOH at the first cycle was similar to that of FeOOCH<sub>3</sub>. This indicates that the effect of such a structural difference in structure of the interstitial site on the discharge behavior of the FeOOH derivatives is not so strong. From this result, it may be expected that the discharge behavior of the amorphous FeOOH including aniline is not so different from that of  $\gamma$ -FeOOH and FeOOCH<sub>3</sub>. But the discharge behavior of the amorphous FeOOH including aniline is much better than that of  $\gamma$ -FeOOH and FeOOCH<sub>3</sub>. The major difference is that aniline remains in the structure of the amorphous FeOOH including aniline. Probably such an aniline may interact with

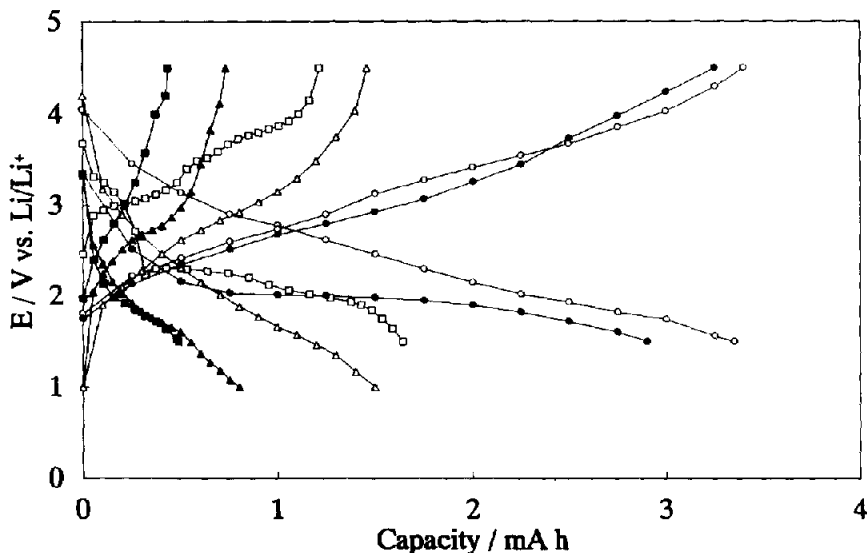


Fig. 4. Discharge and charge curves of FeOOH derivatives: (●) 1st discharge and charge curves of the amorphous FeOOH including aniline; (○) 10th discharge and charge curves of the amorphous FeOOH including aniline; (▲) 1st discharge and charge curves of  $\gamma$ -FeOOH; ( $\Delta$ ) 10th discharge and charge curves of  $\gamma$ -FeOOH; (■) 1st discharge and charge curves of FeOOCH<sub>3</sub>, and (□) 10th discharge and charge curves of FeOOCH<sub>3</sub>.

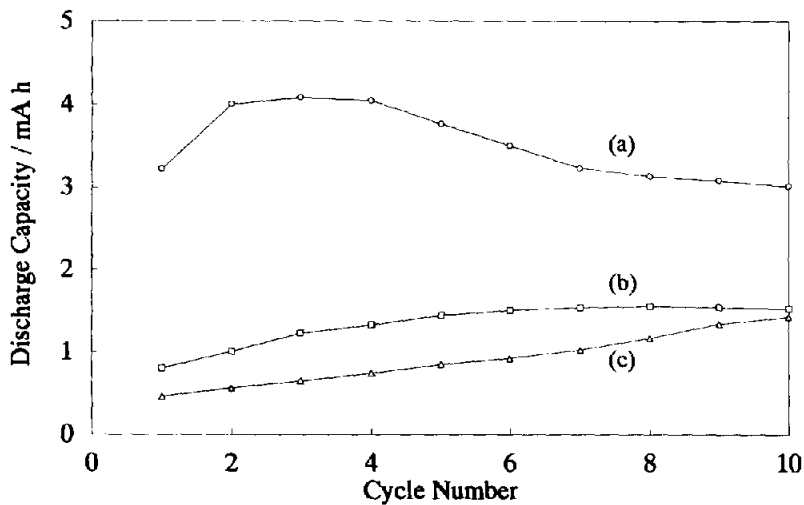


Fig. 5. Discharge capacity change during the discharge and charge cycles of: (a) the amorphous FeOOH including aniline; (b)  $\gamma$ -FeOOH, and (c) FeOOCH<sub>3</sub>.

FeOOH matrix and may arise the amorphous nature. As a result of such an interaction between FeOOH and aniline, the excellent discharge behavior of the amorphous FeOOH including aniline would be obtained.

Another interesting feature of the discharge and charge characteristics of these cathodes is that the discharge potentials of  $\gamma$ -FeOOH, FeOOCH<sub>3</sub>, and the amorphous FeOOH including aniline become higher during the discharge and charge cycles. Especially  $\gamma$ -FeOOH and FeOOCH<sub>3</sub> discharge capacities increased markedly during the discharge and charge cycles. This may be caused by a physical property change of these cathodes. As a result of such a change, the polarization would become smaller during the discharge and charge cycles. In the case of the amorphous FeOOH including aniline, the discharge capacity did not change. This fact indicates that the polarization of the amorphous FeOOH including aniline is not so large, originally.

Figure 5 shows the discharge capacity change during the cycles. The discharge capacity of the amorphous FeOOH including aniline was estimated to be at least 3 mA h (200 mA h g<sup>-1</sup>) which was two times as large as that of  $\gamma$ -FeOOH and FeOOCH<sub>3</sub>. The amount of lithium which can be inserted into the host matrix depends on the physical state of the interstitial site for lithium or on the kinetics of the insertion of lithium. The high discharge capacity and high discharge potential of the amorphous FeOOH including aniline may be related to the suitable physical property of the interstitial site for lithium which may be caused by the presence of aniline in the host matrix.

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