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THE DISCHARGE AND CHARGE CHARACTERISTICS OF FeOCl MODIFIED BY AN ORGANIC COMPOUND

KIYOSHI KANAMURA, NOBUYUKI IMANISHI, MASASHI FUJIWARA and ZEN-ICHIRO TAKEHARA*

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida-Hommachi, Sakyo-ku, Kyoto 606 (Japan)

Summary

FeOCl is a layered compound that is used as a cathode material in lithium primary batteries. FeOCl intercalated by lithium is unstable and decomposes into α-Fe, LiCl, and Li_2O during discharge. Therefore FeOCl cannot be used as cathode material for a lithium secondary battery. In this study, FeOCl was modified by the intercalation of a basic organic compound in order to improve its stability during discharge. The stability of FeOCl depends on the basicity of the organic compound, and 4-aminopyridine, pyridine, and 2-vinylpyridine are sufficiently basic to stabilize its structure during discharge.

Introduction

Layered compounds have been developed as cathode materials for lithium secondary batteries. For example, the transition metal dichalcogenides, TiS_2, MoS_2, $NbSe_2$, etc., are well known [2] and so far, most investigations have been concentrated on their electrochemical and chemical properties.

Oxyhalides of the transition metals, for example, FeOCl and VOCl, are also layered compounds. The intercalation of lithium into FeOCl has been investigated by some workers and it is supposed that the structure of FeOCl intercalated by lithium is unstable and decomposes [1, 3, 4]. The discharge products of FeOCl, confirmed by X-ray diffraction, are α-Fe, LiCl, and Li_2O [1]. Though FeOCl can be used as lithium primary battery cathode material it cannot be used for a lithium secondary battery.

In this study, FeOCl modified by the addition of various organic compounds has been investigated in an attempt to improve its stability when intercalated by lithium.

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*Author to whom correspondence should be addressed.

Experimental

FeOCl was prepared by heating a mixture of α-Fe_2O_3 and $FeCl_3$ in a sealed glass tube [4] and then modified by the intercalation of a basic organic compound. This was carried out as follows: acetone containing FeOCl and one of each of the organic compounds 4-aminopyridine (4-AP), pyridine (PY), pyradine (PA), and 2-vinylpyridine (2-VP) were heated in sealed Pyrex tubes at 80 - 100 °C. The interlayer distances of the modified FeOCl were larger than that of FeOCl itself, and are summarized in Table 1. The electronic conductivities of the modified FeOCl were larger than that of FeOCl.
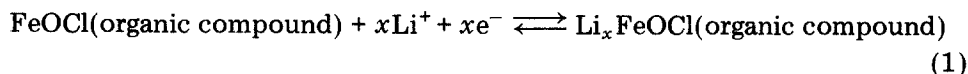
TABLE 1

Interlayer distances of FeOCl intercalated by various organic compounds

	(010)2θ	Interlayer distance (Å)
FeOCl	11.38	7.917
FeOCl(4-AP)$_{1/4}$	6.38	13.57
FeOCl(pyridine)$_{1/n}$	6.89	12.82
FeOCl(pyradine)$_{1/n}$	6.80	12.99
FeOCl(2-VP)$_{1/n}$	6.40 - 6.90	13.80 - 12.80

A mixture of FeOCl or modified FeOCl, conductive material (acetylene black), and binding material (Teflon), with a weight ratio of 80:15:5, were compressed at a pressure of 3 ton cm^{-2}. FeOCl and modified FeOCl cathodes were discharged galvanostatically in propylene carbonate containing 1.0 M $LiBF_4$. The stabilities of FeOCl and modified FeOCl intercalated by lithium were examined using X-ray diffraction (XRD) and electron probe microanalysis (EPMA).

Results and discussion

Figure 1 shows the discharge and charge curves of FeOCl and four kinds of modified FeOCl. The discharge capacities of FeOCl and FeOCl intercalated by pyradine, FeOCl(PA), were larger than the theoretical capacities calculated from the amount of active material when the intercalation of lithium was the main reaction in the course of the discharge. In this case, the reaction is described as:

$$FeOCl(\text{organic compound}) + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{Li}_x FeOCl(\text{organic compound})$$

$$(1)$$

However, the FeOCl and FeOCl(PA) intercalated by lithium were unstable and they could not be charged. Therefore, the discharge reaction of FeOCl and FeOCl(PA) will proceed with the decomposition of the discharged com-
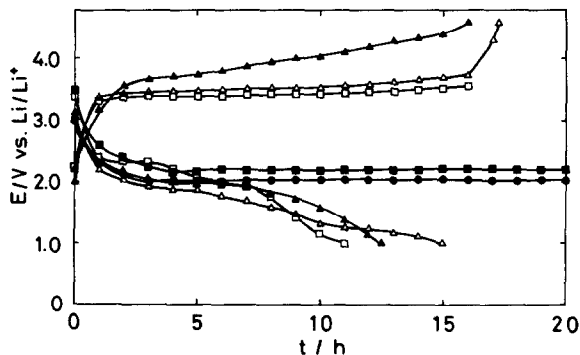
Fig. 1. The discharge and charge curves of FeOCl intercalated by 4-aminopyridine ($\triangle$), pyridine ($\square$), 2-vinylpyridine ($\blacktriangle$), pyradine ($\blacksquare$), and FeOCl ($\bullet$) in propylene carbonate containing 1.0 M LiBF$_4$ at 1 mA cm^{-2}.

pound. The discharge reaction of FeOCl was investigated in ref. 1, and it was supposed that the decomposition compounds were α-Fe, LiCl, and Li$_2$O. The discharge reaction of FeOCl can be described by the following equation:

$$FeOCl + 3Li^+ + 3e^- \longrightarrow \alpha\text{-Fe} + LiCl + Li_2O \tag{2}$$
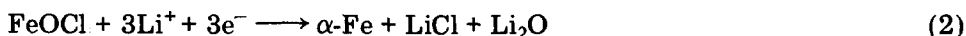
On the other hand, FeOCl intercalated by 4-AP, PY and 2-VP could be charged after the first discharge. Their discharge capacities were almost in agreement with the theoretical capacities estimated from the intercalation of lithium into them. From these results, it can be seen that some organic compounds intercalated into FeOCl result in the high stability of the discharge compound. Though FeOCl itself cannot be used as cathode material for a lithium secondary battery, FeOCl intercalated by an organic compound can.

Figure 2 shows X-ray diffraction patterns of FeOCl(4-AP) discharged to various degrees, where the degree of discharge was calculated in accordance
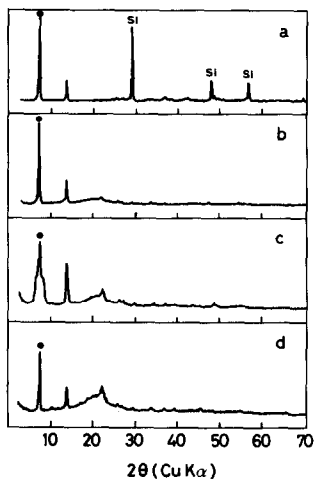

Fig. 2. X-ray diffraction patterns of FeOCl(4-aminopyridine) discharged by 20% (a), 50% (b), 100% (c), and after the first cycle (d).

with reaction (1). The main peak at $2\theta = 6.38°$ corresponds to the interlayer distance, which was calculated as 13.57 Å. The main peak did not shift during the course of the discharge. It is considered that lithium intercalates into the interlayers of FeOCl(4-AP) without any great structural change. In other words, the stability of FeOCl(4-AP) intercalated by lithium seems to be greater than that of FeOCl. The main peak broadened but it did not shift. The structure of FeOCl(4-AP) may become random with the intercalation of increasing quantities of lithium. The main peak after charge was sharp, and was almost the same as that before discharge. These XRD patterns indicate that the reversibility according to reaction (1) is high.
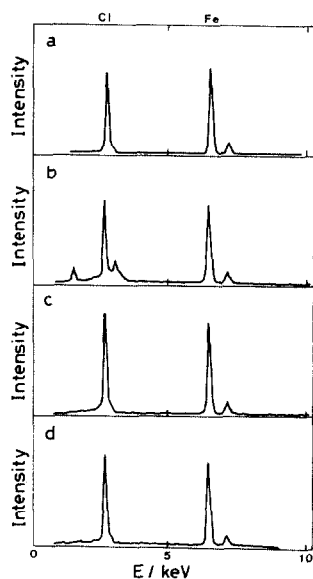

Fig. 3. The EPMA patterns of FeOCl(4-aminopyridine) before discharge (a), discharged by 20% (b), discharged by 80% (c), and after the first cycle (d).

Figure 3 shows the EPMA results, from which the ratio of Fe atoms to Cl atoms in FeOCl (4-AP) intercalated by lithium can be easily estimated. If only reaction (1) takes place during the discharge, the ratio of Fe atoms to Cl atoms does not change. The absolute ratio of Fe to Cl cannot be estimated from EPMA results, but it is easy to determine whether the ratio of Fe atoms to Cl atoms changes. During the first cycle, the ratio of Fe atoms to Cl atoms scarcely changes. If decomposition took place during discharge, the intensity of the Cl atoms would decrease with respect to that of the Fe atoms. By contrast, in the case of FeOCl, the intensity of the Cl atoms does decrease as the discharge proceeds. These facts indicate that lithium is reversibly intercalated into, and deintercalated from, FeOCl(organic compound).

In order to confirm the intercalation of lithium into FeOCl(organic compound), the amount of intercalated lithium was measured using an

TABLE 2

The x values of Li$_x$FeOCl(4-aminopyridine) discharged to various depths

Depth of discharge (%)	Experimental value*	Theoretical value**
20	0.18	0.20
40	0.33	0.40
60	0.58	0.60
80	0.79	0.80

*From atomic absorption measurement.
**From the quantity of electricity consumed.

atomic absorption procedure. Table 2 gives the experimental values, and also the theoretical values calculated from the quantity of electricity consumed. The experimental and theoretical values were in good agreement. From these results, it is confirmed that only lithium intercalation takes place during discharge.

The stability of FeOCl intercalated by lithium was improved by the intercalation of an organic compound. However, FeOCl intercalated by pyradine decomposed as discharge proceeded. Its discharge characteristics were very similar to that of FeOCl. The organic compounds contain a nitrogen atom which has a lone pair of electrons. The charge transfer complex is formed from the organic compounds and FeOCl [5, 6]. The characteristics of the charge transfer complex, for example, the bonding energy, depend on the properties of the organic compound, which plays the role of electron donor. In other words, the basicity of the organic compound is very important for the stability of the FeOCl intercalated by lithium. The basicity of pyradine is the weakest of the four organic compounds. It is important for the stability of FeOCl intercalated by lithium that the highest basic organic compound be chosen. In this study, four different organic compounds were intercalated into FeOCl, and the stability of the FeOCl(organic compound) was determined. If a more basic organic compound is intercalated into FeOCl, the discharge and charge characteristics will be improved immensely.

Figure 4 shows the discharge and charge curves of FeOCl intercalated by 4-AP. The discharge capacity decreased gradually with increasing cycle number. These results show that the stability of FeOCl(4-AP) decreases with increasing cycle number, and FeOCl(4-AP) decomposes gradually during discharge or charge. Figure 5 shows the results of EPMA on FeOCl(4-AP) before the first discharge and after the tenth cycle. The intensity of the Cl atoms after cycling decreased by comparison with that before cycling. This indicates that decomposition of FeOCl(4-AP) takes place during cycling, with a resultant decrease in the discharge capacity.

Figure 6 shows cyclic voltammograms of FeOCl(4-AP) and 4-aminopyridine in propylene carbonate with 1.0 M LiBF$_4$. A Pt plate was used as
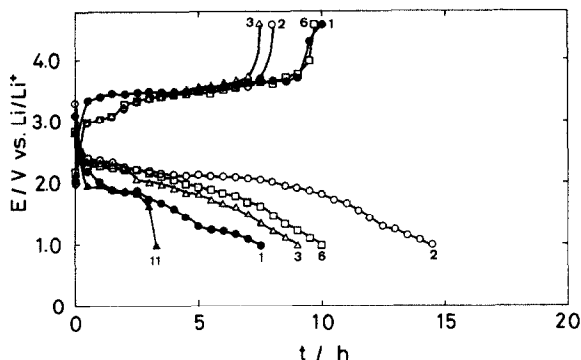
Fig. 4. The discharge and charge curves of FeOCl(4-aminopyridine) in propylene carbonate containing 1.0 M LiBF$_4$ at 1.0 mA cm^{-2}. The figures by the curves indicate cycle numbers.
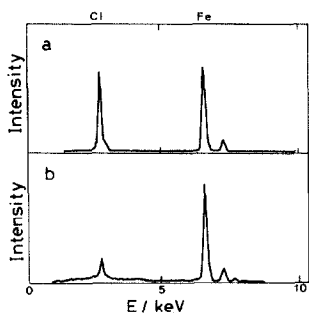

Fig. 5. The EPMA patterns of FeOCl(4-aminopyridine) before discharge (a) and after the tenth cycle (b).
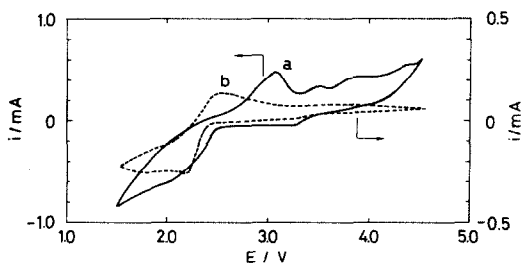
Fig. 6. Cyclic voltammograms of FeOCl(4-aminopyridine) (a) and 4-aminopyridine (b) in propylene carbonate containing 1.0 M LiBF$_4$. Sweep rate: (a) 1 mV s^{-1} (b) 50 mV s^{-1}.

working electrode for the cyclic voltammetry of 4-aminopyridine. The cyclic voltammogram of FeOCl shows that in addition to the intercalation of lithium into FeOCl(4-AP), other reactions occur in the discharge and charge potential region. 4-aminopyridine was oxidized and reduced in the discharge and charge potential region. The redox behavior of 4-aminopyridine dissolved in propylene carbonate is different from that intercalated into FeOCl. However, it may be that 4-aminopyridine is oxidized and reduced in the discharge and charge potential region of FeOCl(4-AP). If 4-aminopyridine is oxidized or reduced and changes to an inert compound, the discharge and charge characteristics will change in the course of the discharge and charge cycles. Since the organic compound intercalated into FeOCl stabilizes the structure of FeOCl(4-AP) during the discharge and charge cycles, the oxidation or reduction of 4-aminopyridine will result in a decrease in the discharge capacity. In order to improve the cycle life of FeOCl intercalated by an organic compound, a compound stable in the FeOCl discharge and charge potential region must be used as cathode material for lithium secondary batteries.

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