November, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 3609—3613 (1989)

The Discharge Characteristics of FeOCl in an Aprotic Organic Solvent

Zen-ichiro TAKEHARA,* Kiyoshi KANAMURA, Nobuyuki IMANISHI, and Chen ZHEN
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Yoshida Hommachi, Sakyo-ku, Kyoto 606

(Received March 1, 1989)

The discharge reaction of FeOCl was investigated and the discharge products were identified by XRD and EPMA. Lithium and solvent co-intercalate into FeOCl during the early stage of the discharge, in the low lithium concentration range in the FeOCl solid matrix (Li_xFeOCl, $x<0.6$). Such compounds are stable. However, at higher concentrations of lithium, FeOCl co-intercalated by lithium and solvent gradually decompose to yield α-Fe and other compounds. The results show that three electrons are consumed during the discharge. On the other hand, the discharge curve of FeOCl in propylene carbonate containing 1.0 M $LiBF_4$ indicates only a single charge transfer step. Therefore, the reaction mechanism of FeOCl can be explained by the intercalation of lithium in FeOCl followed by the decomposition of the intercalation compound formed between FeOCl, lithium and the solvent. The structure of FeOCl intercalated by lithium changes during the course of immersion in various solvents. This fact indicates that the solvent can easily intercalate into FeOCl and deintercalate from FeOCl. Such a behavior may arise from a weakening of the interaction between FeOCl layers after lithium intercalation, since the intercalation of lithium into FeOCl influences the chemical bonds in FeOCl. As a result, the interaction between FeOCl layers becomes weaker. Therefore, the intercalation and deintercalation of the solvent can easily take place. The stability of the FeOCl structure after cathodic reduction does not depend only on the concentration of lithium in FeOCl, but also on the kind of solvent.

Layered compounds have been investigated and used as a cathode material for lithium batteries, since lithium ions can be intercalated into their van der Waals gap. The transition metal dichalcogenides, e.g. TiS_2 and MoS_2, are representatives of the most popular layered compounds. On the other hand, some of the transition metal halogenide oxides are also classified as layered compounds. Particularly, iron chloride oxide (FeOCl) has been investigated by some workers in order to be utilized as a cathode material for lithium secondary batteries.[1-3]

In this study, the intercalation of lithium into FeOCl was investigated. The stability of the FeOCl host matrix intercalated with lithium and its structural changes during the course of lithium intercalation are discussed in order to understand the discharge reaction mechanism of FeOCl when in contact with a propylene carbonate electrolyte.

Experimental

FeOCl was prepared by heating on an α-Fe_2O_3 and $FeCl_3$ mixture in a 3:4 mole ratio in sealed and evacuated Pyrex glass tube at 350 °C in an electric furnace for 3 days according to the method of Kikkawa et al.[4] The reaction products were washed fully for 1 day with water to remove excess $FeCl_3$ and washed again with acetone and then dried. The products, thus prepared, were identified by a comparison of the X-ray diffraction (XRD) results of Lind.[5] In this study the prepared FeOCl had the same structure as Lind's with respect to the XRD measurement. Cathode composites were prepared by compressing a mixture of FeOCl, a conducting material (acetylene black), and a binding agent (PTFE) in a weight ratio of 80:15:5. The apparent surface area was 0.785 cm^2. These electrodes were discharged at a constant current in propylene carbonate (PC) containing 1.0 M $LiBF_4$ (1 M=1 mol dm^{-3}). Lithium metal was used as both the reference electrode and the counter electrode. PC was distilled under vacuum. $LiBF_4$ was also dried at 150 °C under vacuum for 2 days. The structural changes of the host matrix along with the discharge process were traced by the XRD method. The samples for X-ray analysis were wrapped with a thin poly(vinylidene dichloride) film in order to avoid any reaction with oxygen and water from the air. Oxygen and water cannot permeate through the thin film during X-ray analysis. The measurement was conducted from $2\theta=70°$ to $2\theta=4°$ at a scan rate of 1° min^{-1}. The iron and chlorine contents of the active materials were analyzed by Electron Probe Micro Analysis (EPMA). All procedures, except for XRD and EPMA, were performed under an argon atmosphere at room temperature.

Results and Discussion

Figure 1 shows the discharge curves of FeOCl at two different current densities in PC containing 1.0 M $LiBF_4$. The discharge curve of FeOCl is different from that of TiS_2. In the case of lithium intercalation into

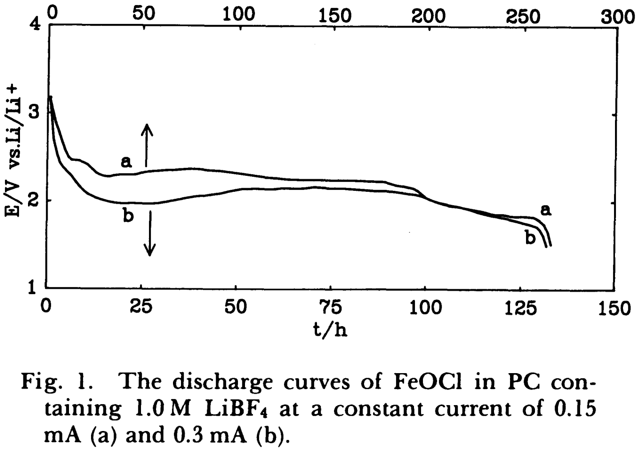

Fig. 1. The discharge curves of FeOCl in PC containing 1.0 M $LiBF_4$ at a constant current of 0.15 mA (a) and 0.3 mA (b).

TiS_2, the S-shaped discharge curve shows a typical simple intercalation of lithium into the host matrix, which takes place during the discharge.[1] For FeOCl, however, the profile of the electrode potential goes through a minimum during the initial period of discharge and then reaches to a potential plateau of about 2 V vs. Li/Li^+. Finally, the electrode potential sharply decreases to more cathodic potentials of about 1.5 V vs. Li/Li^+. Apparently, the discharge reaction may proceed via a single-step charge-transfer reaction.

When lithium intercalates into an interlayer of FeOCl, one electron reaction occurs during the discharge in aprotic solvents containing a lithium salt. Such a reaction can be written as

$$FeOCl + xLi^+ + xe^- \rightarrow Li_xFeOCl\ (0<x<1). \qquad (1)$$

The valence of the iron in FeOCl decreases from three to two during the intercalation of lithium. Therefore, the theoretical capacity can be calculated to be 10 mA h from the weight of FeOCl included in the composite of the cathode material (weight of FeOCl=40 mg). The theoretical discharge duration is also calculated to be 33.4 hours (discharge current=0.3 mA). If the discharge was terminated at 1.9 V vs. Li/Li^+, the observed capacity was 30 mA h, which was about three times that of 10 mA h. This means that another reaction takes place in the course of the reduction of FeOCl. The observed capacity corresponds to that expected from the conversion of the iron valence from three to zero.

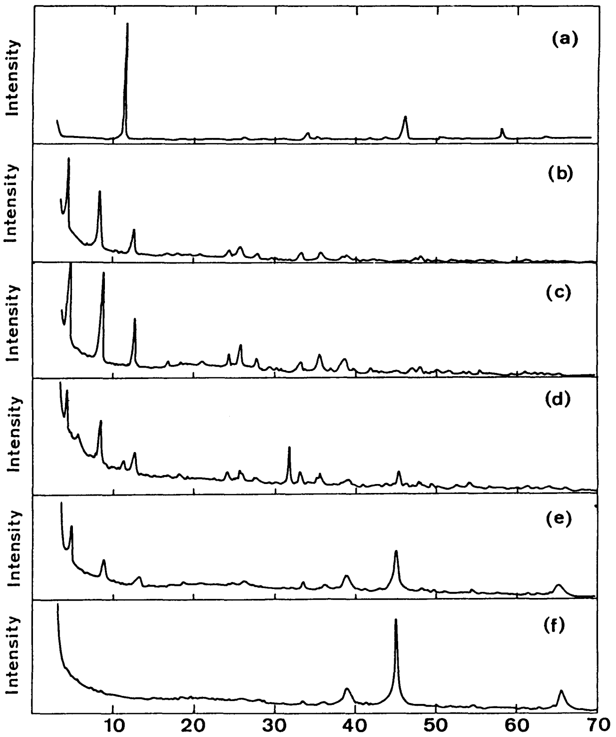

Fig. 2. X-Ray diffraction patterns of FeOCl before and after discharge. Discharge current=0.3 mA. (a) FeOCl, (b) $Li_{0.2}FeOCl$, (c) $Li_{0.6}FeOCl$, (d) LiFeOCl, (e) Li_2FeOCl, (f) Li_3FeOCl, where x in Li_xFeOCl corresponds to the mole ratio of lithium to iron. All the samples had been immersed in PC for one week after discharge.

In order to confirm such a discharge reaction, X-ray diffraction analyses of the discharge products were performed. The X-ray diffraction patterns of FeOCl discharged in PC containing 1.0 M $LiBF_4$ are summarized in Fig. 2. All of the XRD results shown in Fig. 2 were for the stable structures after one week had passed. Figure 2 (a) shows the X-ray diffraction patterns of FeOCl before the discharge. The main peak at $2\theta=11.2°$ corresponds to the van der Waals gap of FeOCl. Figure 3 shows the structure of FeOCl.[5,6] It has a b-axis preferred orientation with an interlayer distance of 7.9 Å. From these patterns, it can be seen that the structure of FeOCl changes during a discharge. During the early stages of a discharge ($Li_{0.2}FeOCl$), its structure is quite different from that before the discharge. However, regarding this point, it must be noted that the stabilization of the structure requires a certain time after intercalation. As shown in Fig. 4, the structure of $Li_{0.2}FeOCl$ changed with the immersion time in PC. From the patterns it can be seen that the structural change was complete after two days. The new peaks in Figs. 2 (b) and (c) correspond to an expanded gap, for which the distance between FeOCl layers is 10.5 Å. Such a large interlayer distance cannot be explained by the intercalation of lithium

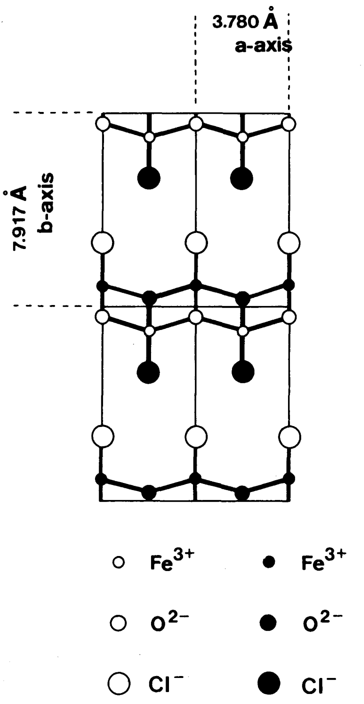

Fig. 3. Schematic illustration of the structure of FeOCl.

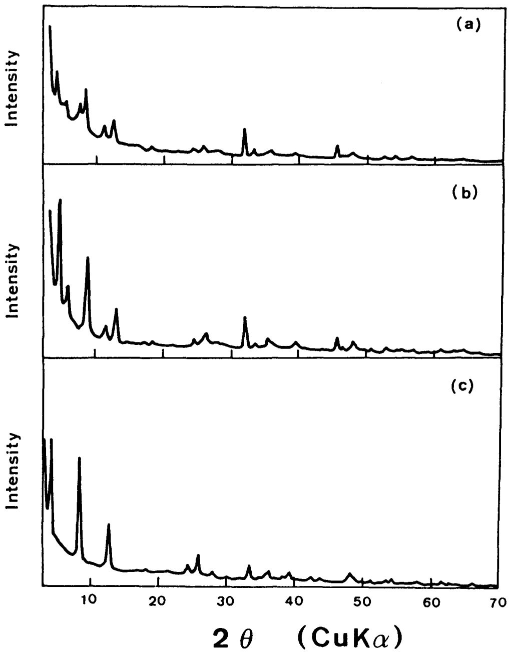

Fig. 4. X-Ray diffraction patterns of Li$_{0.2}$FeOCl after immersion in PC for one hour (a), seven hours (b), and two days (c).

alone, since lithium is smaller than 1 Å. The large interlayer expansion results from the intercalation of lithium and the solvent. The molecular size of PC is about 5 Å. If PC intercalates into the FeOCl interlayer, the interlayer distance between Fe atoms could expand from 7.9 to 10.5 Å.

The X-ray diffraction pattern of Li$_{0.6}$FeOCl showed the same peaks as Li$_{0.2}$FeOCl (Fig. 2), indicating the formation of FeOCl intercalated by lithium and solvent. After sitting for two weeks, such a structure remained unchanged. These results indicate that the intercalation compound of FeOCl with lithium and the solvent is formed during a discharge and is stable in the region from $x=0$ to $x=0.6$, where x corresponds to the ratio of lithium to iron.

Figure 5 shows XRD patterns of Li$_{0.6}$FeOCl which were discharged in PC and then immersed in various solvents. These XRD patterns were similar, except in the case of acetonitrile (ACN) and dimethoxyethane (DME). From the XRD patterns, no structural change could be observed. However, the peaks slightly shifted to a lower or higher angle. After the immersion in tetrahydrofuran (THF) or dimethylformamide (DMF), the three peaks shifted toward a higher angle. On the other hand, they shifted toward a lower angle after immersion in dimethylsulfoxide (DMSO) or γ-butyrolactone (γ-BL). In this way, the structural change of FeOCl intercalated by lithium was caused by immersion in various solvents. This fact indicates that an exchange of the solvent in the interlayer of FeOCl takes place between PC and the bulk solution, such as THF, DMSO, γ-BL, and DMF. However, XRD patterns after the immersion in ACN or DME indicated a structural change of Li$_{0.6}$FeOCl. Such a phenomenon can be understood by the strength of the interaction between solvent and FeOCl host matrix. The weak interaction between FeOCl layers may also be the main cause of the solvent exchange. The weak interaction between FeOCl interlayers results in the poor stability of Li intercalated FeOCl.

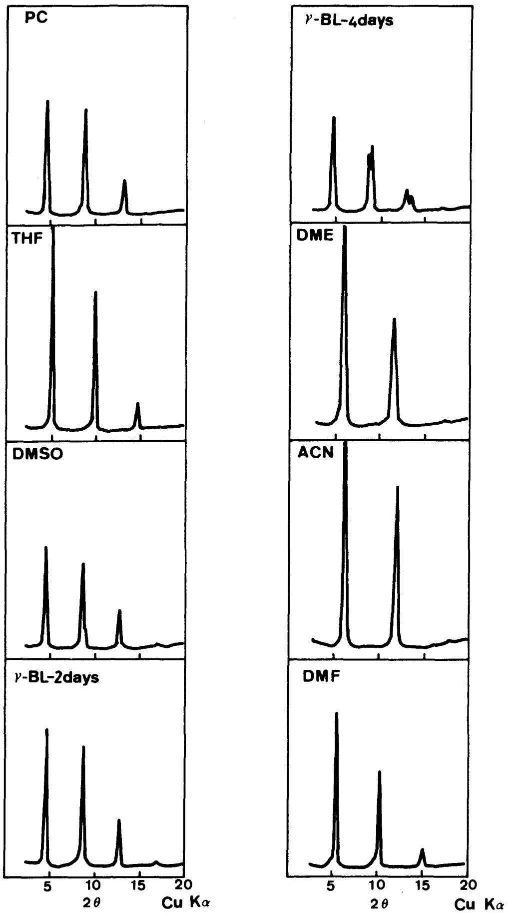

Fig. 5. X-Ray diffraction patterns of Li$_{0.6}$FeOCl after the immersion in THF, DMSO, γ-BL, DMF, DME, ACN, and PC for two days and γ-BL for four days.

However, Li$_x$FeOCl ($x<0.6$) had to be treated carefully, because the stability of these compounds sharply decreased with increased drying time. X-Ray diffraction patterns of Li$_x$FeOCl ($x<0.6$) changed with the drying time under vacuum, as showed in Fig. 6. When Li$_x$FeOCl samples were removed from the experimental cell and then kept in an argon dry box for one or two weeks, the structure of the discharged FeOCl changed to an amorphous-like type. It seemed that the solvent being intercalated into the FeOCl deintercalated from the FeOCl interlayer while drying. On the other hand, Li$_x$FeOCl samples, which were kept in solvent for one or two weeks, were very stable and their X-ray peak positions did not change. From these results, it can be seen that the stability of

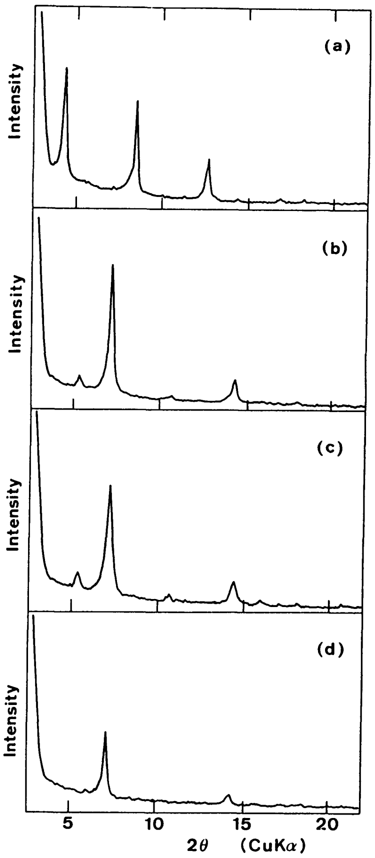

Fig. 6. The structural change of $Li_{0.2}FeOCl$ during drying under vacuum at 80 °C for 0 min (a), 25 min (b), 45 min (c), and 65 min (d).

Li_xFeOCl is dependent upon the solvent intercalated into the FeOCl interlayer.

On the contrary, X-ray diffraction patterns of Li_xFeOCl ($x>1$) were very different from those of Li_xFeOCl ($x<0.6$), as shown in Figs. 2 (b), (c), (d), (e), and (f). The main peaks at $2\theta=12.62°$, 8.42°, and 4.24°, decrease when more lithium is inserted into the FeOCl. Moreover, some new peaks appear at $2\theta=45°$ and 66°, and increase with the lithium content. These new peaks in Fig. 2 (f) correspond to those of α-Fe. This tendency increases when more lithium is added. In Li_3FeOCl, X-ray peaks at the lower-angle region disappeared and new peaks increased in intensity and sharpness. Thus, FeOCl was reduced to α-Fe through the intermediate product. Apparently, three electrons are consumed during the discharge reaction of FeOCl. The electron number expected from the results of the X-ray diffraction method was in agreement with that expected from the observed discharge capacity. However, the decomposition of the intercalation compound of FeOCl is a very complex process. The X-ray diffraction pattern of Li_2FeOCl shows that other compounds besides α-Fe are formed during the decomposition. These compounds could not be identified by the XRD method.

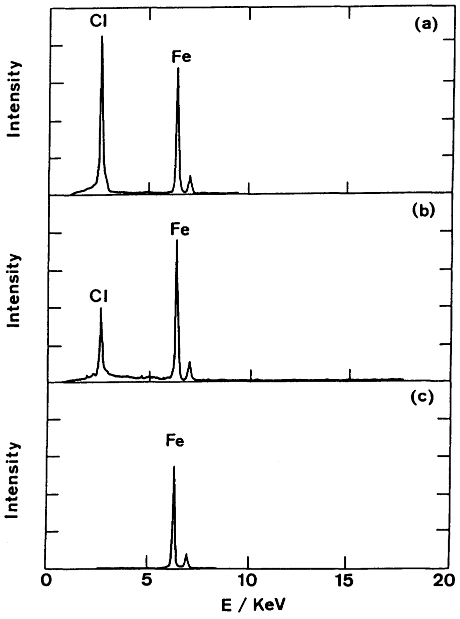

Fig. 7. EPMA results for FeOCl (a), Li_3FeOCl (b), and Li_3FeOCl washed by PC (c).

Elementary analyses of the discharge products of FeOCl were performed by using EPMA. Figure 7 shows the results. Before the discharge, the intensities of the iron and chloride peaks were almost the same, as shown Fig. 7(a). On the other hand, after the three-electron discharge of FeOCl, the chloride peak decreased to about one half that of iron, as shown in Fig. 7 (b). This result indicates that chloride was lost from the FeOCl structure during reduction. This sample was fully washed with PC and again analyzed for chloride. The result is shown in Fig. 7(c). The chloride peak became even smaller, and it was proved that chloride existed as a soluble species (LiCl). Part of the chloride ion remains in the cathode composite as LiCl, since the solubility of LiCl in PC is not very high.

The overall reaction of FeOCl can be assumed to be

$$FeOCl + 3Li^+ + 3e^- \rightarrow \alpha\text{-}Fe + LiCl + Li_2O. \qquad (2)$$

However, Li_2O and LiCl were not detected by the XRD method.

Thus, the kinetics of the discharge reaction of FeOCl in an aprotic solvent are not simple. To summarize, as the discharge proceeds, lithium and solvent intercalate into the FeOCl interlayer. As a result, $Li_x(PC)FeOCl$ ($x<0.6$) is formed, which is a stable product in PC. With the proceeding of the discharge reaction, $Li_x(PC)FeOCl$ ($x>0.6$) decomposes to yield α-Fe as the discharge product.

The intercalation compound of FeOCl with lithium was stable in the region of low lithium concentrtion. However, with increasing lithium concentration, FeOCl decomposes and α-Fe is formed. Such a decomposition permits a three-electron reaction of FeOCl. As a result, the capacity of FeOCl in primary cells is attractive. On the other hand, FeOCl cannot be utilized as the cathode material of a secondary lithium cell, because such a displacement reaction is not reversible. However, if this decomposition reaction could be somehow interrupted, it has the possibility of being utilized in a secondary battery. Further, it is seen that one possible way might be to insert another solvent into the FeOCl gap leading to a stable structure.

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