

# Preparation of a FeOCl derivative with pyrrole and its performance as a cathode material in a secondary lithium battery system

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## Abstract

A FeOCl derivative is prepared in water using pyrrole ( $a_{py}$ -FeOOH). The X-ray diffraction pattern of the product is similar to  $\gamma$ -FeOOH. From chemical analyses and the FT-IR spectrum, it is found that pyrrole remains in the product with an atomic ratio of Fe:N = 3:1. From discharge/charge cycling tests, it is confirmed that  $a_{py}$ -FeOOH is rechargeable and has a specific capacity of 60 mAh g<sup>-1</sup> between 2.0 and 4.5 V on the 20th discharge. When *N*-methylpyrrole (which has similar structure) is used instead of pyrrole, the derivative yields larger capacity during ten cycles.

**Keywords:** Pyrrole; *N*-methylpyrrole; Ion-exchange reaction; Cathode materials; Iron

## 1. Introduction

Since iron compounds are advantageous cathode materials for lithium batteries in terms of reduced cost, attempts have been made to find suitable iron-based cathode materials. Several iron compounds have been proposed, e.g., FeOCl [1,2], iron-phthalocyanine [3], Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> [4]. Of these compounds, FeOCl is the most interesting because of its reactivity.

When FeOCl is used as the cathode material in secondary lithium batteries, it undergoes irreversible degradation in the region of  $x > 0.3$  in Li<sub>x</sub>FeOCl to give  $\alpha$ -Fe, LiCl and Li<sub>2</sub>O [2]. It is claimed that the Fe–Cl bond is broken at the beginning of this decomposition. Thus, exchanging the Fe–Cl bond with another might improve the stability against Li<sup>+</sup> ion intercalation. Accordingly,  $\gamma$ -FeOOH [5] and FeOCH<sub>3</sub> [6] have been prepared from FeOCl using ion-exchange reactions. From discharge/charge cycling tests, it has been found that the performance in lithium batteries is far from practical, though the stability towards Li<sup>+</sup> ion intercalation is slightly improved.

By contrast, amorphous FeOOH containing aniline ( $a_{an}$ -FeOOH), prepared from FeOCl stirred with aniline in H<sub>2</sub>O, is a promising material for practical lithium batteries [7]. It

has also been reported that aniline remains in the  $a_{an}$ -FeOOH. Fourier-transform infrared spectroscopy (FT-IR) analysis showed [8] that the aniline is not exactly monomeric but is similar to the emeraldine base. The results obtained from FT-IR measurements also revealed that the state of aniline in the  $a_{an}$ -FeOOH was transformed during discharge/charge cycling [9]. Moreover, differences in the aniline content of  $a_{an}$ -FeOOH affects both the discharge capacity and the cycling behavior [5,10]. From these results, it is clear that aniline exerts an important influence on the mechanisms of the discharge and the charge reactions.

Aniline is a typical monomer that can be polymerized either electrochemically or chemically to become a conducting polymer [11–14]. Thiophene and pyrrole are also known to be polymerized with both methods and to have interesting properties [14–18]. In a previous paper [19], we reported 'FeOOH including thiophene ( $a_{th}$ -FeOOH)' is rechargeable. This compound was prepared by using an ion-exchange reaction that was triggered by the intercalation of 2,2-bithiophene (dimer of thiophene) into FeOCl [19]. By analogy, it is expected that pyrrole will react with FeOCl to remain in the structure and to have electrochemical properties similar to  $a_{an}$ -FeOOH and  $a_{th}$ -FeOOH. The work reported here tests this hypothesis.

## 2. Experimental

### 2.1. Reaction of pyrrole and FeOCl in H<sub>2</sub>O

FeOCl was prepared from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Wako, 99.9 wt.%) and anhydrous FeCl<sub>3</sub> (Mitsuwa, 99 wt.%) by the standard technique described in Ref. [20]. 2 g of FeOCl and pyrrole (Wako, 99 wt.%; 1/3 mol per FeOCl) were immersed in distilled water (100 cm<sup>3</sup>) and then stirred for 24 h at room temperature. As pyrrole is unstable in air, it was treated in an argon-filled glove box and sealed under an argon atmosphere immediately prior to mixing with FeOCl and water. The mole ratio of pyrrole to aniline was determined by the composition of FeOCl intercalated with polypyrrole [21].

The final reaction product was a black powder. This was removed from solution and, in succession, washed thoroughly with water and acetone (Wako, 99.5 wt.%). Finally, the powder was dried under vacuum at 100 °C for more than 24 h. All the above reagents were used as-received.

### 2.2. Characterization of reaction product

The structure of the reaction product was analysed by X-ray diffraction (XRD, Rigaku RINT 1500) with Cu K $\alpha$  radiation, and by Fourier-transform infrared spectroscopy (FT-IR, Nicolet SXR-600) with the KBr method. Chemical analysis for C, H, N, and Cl was conducted to determine the chemical composition of the reaction product. The iron content was measured by atomic absorption spectroscopy using a Hitachi Z-6100 unit. The apparent density of the product was estimated by a common method using a pycnometer; toluene was used as a solvent.

### 2.3. Electrochemical performance of reaction product

The electrochemical performance of the reaction product as a cathode material was investigated at 35 °C with a standard three-compartment electrochemical cell. The cathode composite was prepared by mixing the reaction product, carbon black (Denka Black) and polytetrafluoroethylene (PTFE) powder (Daikin, M-12), 50:45:5 by weight. About 40 mg of this mixture was pressed onto titanium expanded metal at 2 t cm<sup>-2</sup> to make a pellet of 10 mm in diameter. Lithium foil (Honjo metal Co., Ltd., 99.9 wt.%) was used for both the reference and the counter electrodes. Propylene carbonate with 1.0 M LiClO<sub>4</sub> (Mitsubishi Petrochemical Co., Ltd., battery grade) was used as the electrolyte. Discharge/charge cycling tests were conducted galvanostatically at 0.5 mA cm<sup>-2</sup> using a battery charge/discharge unit (Hokuto Denko Co., HJ-201B). A rest time of 1 h was applied between each discharge/charge cycle.

All electrochemical measurements were performed in an argon-atmosphere glove box. The materials (except for the electrolyte) were dried under vacuum before introduction into the glove box.

## 3. Results and discussion

### 3.1. Characterization of reaction product

As a result of the reaction between FeOCl and pyrrole in water, the colour of the powder changed from the blue violet of FeOCl into black.

Fig. 1 shows the XRD patterns for FeOCl and the products. The intercalation of pyrrole into the FeOCl interlayers during the early stages of the preparation reaction expands the interlayer distance from 7.917 to 15.12 Å (Fig. 1(b)). This interlayer distance is larger than that of FeOCl(Ppy)<sub>0.34</sub> prepared in acetonitrile, viz., 13.21 Å [21]. This may indicate a co-intercalation of water. After 24 h, weaker and broader peaks appeared; these can be assigned to  $\gamma$ -FeOOH (Fig. 1(c)) [22]. This phenomenon was also observed [7] for the preparation of a<sub>an</sub>-FeOOH, but pyrrole reacts more quickly. For example, the XRD pattern for FeOCl transfers to that for  $\gamma$ -FeOOH after 24 h when pyrrole is used, but takes 3 days when aniline is used.

Pyrrole also remains in the final product; this is revealed by the FT-IR spectrum for the derivative (Fig. 2(a)). The characteristic absorption found in the region between 700 and 1700 cm<sup>-1</sup> is very close to that for chemically polymerized polypyrrole(FeCl<sub>4</sub><sup>-</sup>) rather than monomeric pyrrole [21,23]. Two broader absorption peaks, at around 500 and 3000 cm<sup>-1</sup>, are also observed in the FT-IR spectrum. The former peak can be assigned to the Fe–O bond and the latter to –OH stretching or –NH stretching. Finally, an O–H bending absorption peculiar to  $\gamma$ -FeOOH is present at ~1020 cm<sup>-1</sup> [24,25]. From the chemical composition of the reaction product (Table 1), the ratio Fe:O is nearly 1:2.

The above results indicate that the composition of the inorganic substance in the product is FeOOH. C and N are found in the product also (Table 1), the ratio of these atoms is 3.99:1. This supports the existence of the organic compound

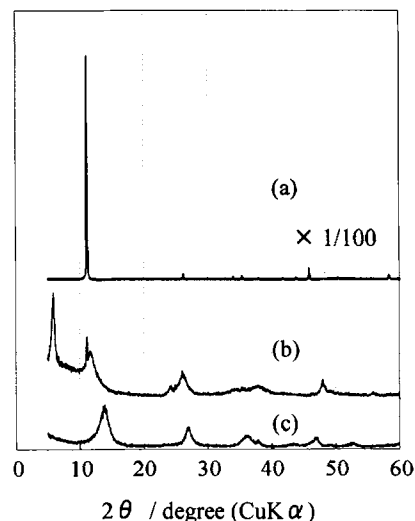


Fig. 1. XRD patterns for: (a) FeOCl; (b) FeOCl stirred with pyrrole in water for 12 h, and (c) FeOCl stirred with pyrrole in water for 24 h.

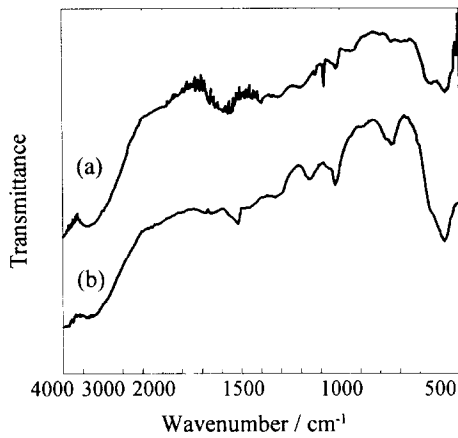


Fig. 2. FT-IR spectra for FeOCl stirred with: (a) pyrrole in water for 24 h, and (b) *N*-methylpyrrole for 24 h.

Table 1  
Chemical analysis of FeOCl stirred with pyrrole in water

Wt. %					
C	H	N	Fe	Cl	O
13.66	1.38	3.99	48.70	5.47	26.81
Atomic ratio					
C:N	Fe:N		Fe:O		Fe:Cl
3.99:1	3.06:1		1:1.92		1:0.18

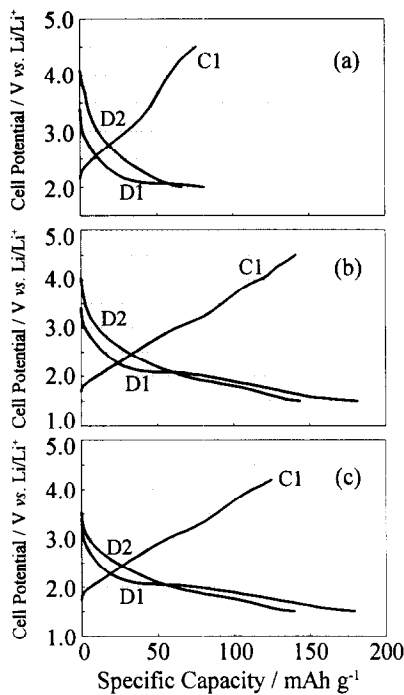


Fig. 3. Discharge and charge curves for cells with  $a_{py}$ -FeOOH in 1.0 M  $\text{LiClO}_4$ /propylene carbonate at a current density of  $0.5 \text{ mA cm}^{-2}$ : (a) 2.0 to 4.5 V; (b) 1.5 to 4.5 V; and (c) 1.5 to 4.2 V. D1, D2, and C1 refer to first discharge, second discharge, and first charge, respectively.

in the reaction product, i.e., a pyrrole-related substance. The ratio of Fe atoms to N atoms, which is considered to corre-

spond to the mole ratio of the FeOOH matrix and the pyrrole monomer unit is 3:1. This is the same ratio as at the beginning of the reaction. From characterization by XRD, FT-IR and chemical analyses, it is concluded that the final reaction product is 'FeOOH including pyrrole ( $a_{py}$ -FeOOH)' as has been reported for  $a_{an}$ -FeOOH and  $a_{th}$ -FeOOH [7,19]. XRD measurements suggest the presence of  $\gamma$ -FeOOH, but given the apparent density of the final product, this can be considered to be a by-product. The measured density ( $2.08 \text{ g cm}^{-3}$ ) was far from the theoretical value for  $\gamma$ -FeOOH, viz.,  $4.0 \text{ g cm}^{-3}$  [22].

### 3.2. Electrochemical performance of reaction product

The discharge/charge curves for a cell with  $a_{py}$ -FeOOH as a cathode material are given in Fig. 3. In the voltage range of 2.0 to 4.5 V, the capacity on the first discharge is  $80 \text{ mAh g}^{-1}$  (Fig. 3(a)). The value on the following charge is smaller despite the fact that the discharge voltage is greater. The cycling performance of this cell during 20 cycles is presented in Fig. 4(a). The discharge capacity decreases to  $60 \text{ mAh g}^{-1}$  on the 20th cycle. This capacity of  $a_{py}$ -FeOOH was compared with that of  $a_{an}$ -FeOOH by preparing three samples of the latter (FA1/2, FA1/4, FA1/8) with different amounts of aniline [10]. Except during the early cycles, the discharge capacity of  $a_{an}$ -FeOOH increases with increasing aniline content. On the 20th discharge, sample FA1/2 (which has the smallest aniline content and the smallest discharge capacity of the three samples) delivered a specific capacity of  $160 \text{ mAh g}^{-1}$  under the same test conditions as the present study. The sample of  $a_{an}$ -FeOOH with the largest aniline content (i.e., FA1/8) had a specific capacity of  $210 \text{ mAh g}^{-1}$ . By contrast,  $a_{py}$ -FeOOH has a much lower capacity — the value is insufficient for practical use. When the discharge cutoff

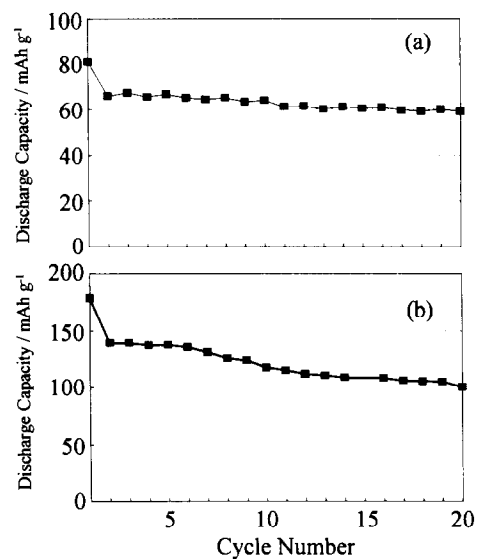


Fig. 4. Cycling properties during 20 cycles for cells with  $a_{py}$ -FeOOH in 1.0 M  $\text{LiClO}_4$ /propylene carbonate at a current density of  $0.5 \text{ mA cm}^{-2}$ : (a) 2.0 to 4.5 V, and (b) 1.5 to 4.2 V.

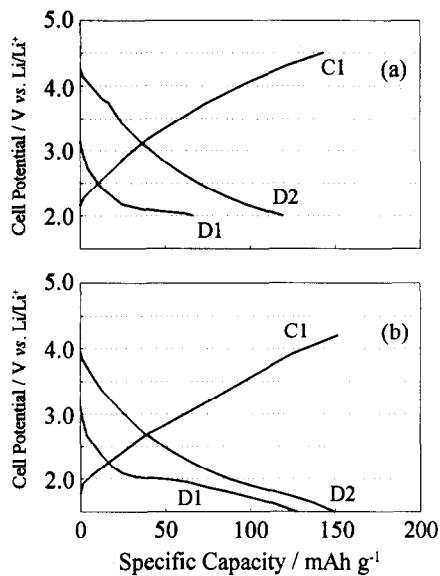


Fig. 5. Discharge and charge curves for cells with  $a_{\text{mpy}}\text{-FeOOH}$  in 1.0 M  $\text{LiClO}_4$ /propylene carbonate at a current density of  $0.5 \text{ mA cm}^{-2}$  in voltage range: (a) 2.0 to 4.5 V, and (b) 1.5 to 4.2 V. D1, D2, and C1 refer to first discharge, second discharge and first charge, respectively.

voltage is lowered to 1.5 V (Fig. 3(b)), the capacity increases to  $180 \text{ mAh g}^{-1}$  on the first cycle. The cycling properties of  $a_{\text{py}}\text{-FeOOH}$  between 1.5 and 4.2 V are displayed in Fig. 4(b). The discharge capacity decreases monotonously from 180 to  $100 \text{ mAh g}^{-1}$  (20th discharge). Changing the charge cutoff voltage to 4.2 V produces no significant decrease in the discharge capacity (Fig. 3(c)).

The intercalative polymerization of *N*-methylpyrrole has also been reported by Kanatzidis et al. [21]. The use of poly(*N*-methylpyrrole) as the conducting polymer in electric devices has been suggested [26,27]. Thus, it is expected that *N*-methylpyrrole remains in the product to form 'FeOOH including *N*-methylpyrrole ( $a_{\text{mpy}}\text{-FeOOH}$ )' as the result of a preparation reaction that is identical with the method for  $a_{\text{an}}\text{-FeOOH}$  and  $a_{\text{py}}\text{-FeOOH}$ . Rechargeability of the product can also be expected. *N*-methylpyrrole has a structure in which a methyl group is combined with a N atom of pyrrole. By virtue of this structural similarity, an identical amount intercalates in the FeOCl and remains in the final product to give a discharge capacity equal to that of  $a_{\text{py}}\text{-FeOOH}$ .

The corresponding XRD pattern can be assigned to  $\gamma\text{-FeOOH}$  with a rather broader full width at half-maximum ( $2.53^\circ$ ; 1.5 times that for  $a_{\text{py}}\text{-FeOOH}$ ) [22]. Fe–O, –OH in  $\gamma\text{-FeOOH}$  [24,25] and characteristic absorption peaks assigned to *N*-methylpyrrole [28] are found in the FT-IR spectrum (Fig. 2(b)). The atomic ratios are: C:N = 5.1:1; Fe:N = 1:0.34; Fe:O = 1:2.0; Fe:Cl = 1:0.15. Thus it is concluded that the final product can be represented as  $a_{\text{mpy}}\text{-FeOOH}$  with 0.34 mole of *N*-methylpyrrole in one mole of FeOOH.

The discharge/charge curves for  $a_{\text{mpy}}\text{-FeOOH}$  have almost the same shape as those for  $a_{\text{py}}\text{-FeOOH}$  (Fig. 5). The decline of the second discharge curve, however, is smaller. On the

other hand, the cycling properties of these derivatives, especially during the early stages, differ markedly. This is contrary to expectation. Over a voltage range of 2.0 to 4.5 V, the discharge capacity for  $a_{\text{mpy}}\text{-FeOOH}$  increases after the first charge to 4.5 V and then it decreases monotonously (Fig. 6(a)). For cycling between 1.5 and 4.2 V (Fig. 6(b)), the same phenomenon is observed. This behaviour is similar to that displayed by  $a_{\text{an}}\text{-FeOOH}$  and  $a_{\text{th}}\text{-FeOOH}$  [7,19].  $a_{\text{py}}\text{-FeOOH}$  and  $a_{\text{mpy}}\text{-FeOOH}$  have the largest contents of organic material in all the FeOCl derivatives prepared to date. The discharge/charge curves and cycling properties of these two compounds are quite different despite the similarity in organic content. This may be due, in part, to the chemical stability with respect to the air or to the moisture of the organic compound; pyrrole was stirred with FeOCl in water under air during the preparation of  $a_{\text{py}}\text{-FeOOH}$  though pyrrole is unstable in air. The difference during preparation may arise as follows. At the early stages of the preparation, that is the intercalation process, some molecules of pyrrole associate in advance of intercalation and interaction with the iron atoms in FeOCl because of its poor stability in water. On the other hand, *N*-methylpyrrole is sufficiently stable in water to intercalate and interact with the iron atoms. In other words, it is supposed to be mixed more microscopically. This model can be indirectly supported by the apparent density of the powder. The interlayer distance of FeOCl intercalated with pyrrole and *N*-methylpyrrole in acetonitrile is 13.21 [21] and 12.13 Å, respectively. Thus, FeOCl intercalated with *N*-methylpyrrole has a smaller space in the interlayer and this leads to a larger value in apparent density. Given this fact, the apparent density of  $a_{\text{mpy}}\text{-FeOOH}$  should be larger than that of  $a_{\text{py}}\text{-FeOOH}$ . The measured density of  $a_{\text{py}}\text{-FeOOH}$  and  $a_{\text{mpy}}\text{-FeOOH}$  is 2.08 and  $1.91 \text{ g cm}^{-3}$ , respectively. This may be

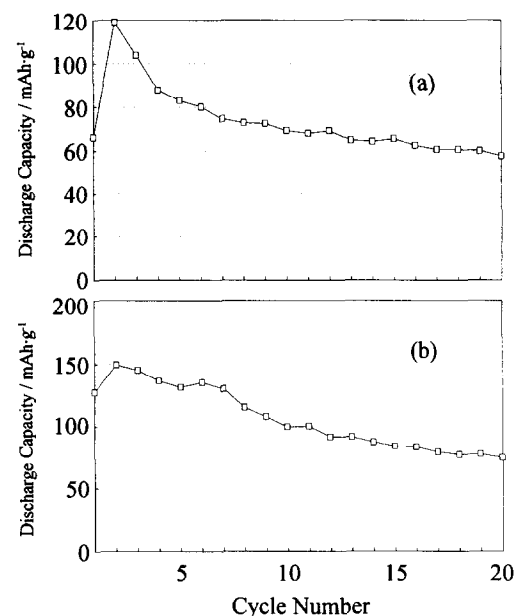


Fig. 6. Cycling properties during 20 cycles for cells with  $a_{\text{mpy}}\text{-FeOOH}$  in 1.0 M  $\text{LiClO}_4$ /propylene carbonate at a current density of  $0.5 \text{ mA cm}^{-2}$  in voltage range: (a) 2.0 to 4.5 V, and (b) 1.5 to 4.2 V.

an indirect proof that *N*-methylpyrrole is mixed in the inorganic substance more microscopically.

With respect to the correlation of the discharge capacity and the content of organic substance, the discharge capacity of a<sub>an</sub>-FeOOH, which had smaller organic content, was larger than the above two derivatives. a<sub>th</sub>-FeOOH also had a smaller organic content and a larger discharge capacity but, in this case, a different preparation method was applied. From these results, it is concluded that not only the content of the organic substance but also certain properties (chemical or physical) of its residual in the derivative affect the discharge/charge performance. In order to improve the discharge/charge properties of the FeOCl derivative, it is very important to determine the properties that essentially determine the discharge voltage or capacity. Accordingly, a study has been made of the discharge/charge properties of FeOCl derivatives with various kinds of organic compound, such as mono-substituted anilines.

Through the preparation of 'a<sub>x</sub>-FeOOH (*x* = an, py, th, mpy)', important conclusions have been made concerning the selection of *x*.

1. All the four organic compounds studied, an (aniline), py (pyrrole), mpy (*N*-methylpyrrole), th(2,2-bithiophene), can intercalate into the FeOCl interlayer, which induces the ion exchange of Cl<sup>-</sup> to OH<sup>-</sup>. When choosing thiophene as *x*, the preparation reaction did not proceed and there was no intercalation of thiophene into FeOCl [19]. Kanatzidis et al. [21] explained that the possibility of intercalation could depend on an oxidation (polymerization) potential of *x*. These authors conducted the intercalation reaction using acetonitrile as solvent. By contrast, water was used here, except for the preparation of a<sub>th</sub>-FeOOH.

2. The compounds can associate or polymerize chemically or electrochemically [11–18,26,29,30]. These properties result in an organic compound remaining in the FeOOH. When FeOCl intercalated with 4-aminopyridine (FeOCl(4-AP)<sub>1/4</sub>) was stirred in water or an aqueous solution of NaOH, only a trace amount of 4-AP remained in the reaction product (assigned to γ-FeOOH by XRD analysis) [5]. It has not been possible to find any reports of chemical or electrochemical polymerization of 4-AP.

3. The compounds can interact with FeOOH, especially with iron atoms. For the intermediate of preparation, that is FeOCl intercalated with *x*, it is confirmed that electric conductivity is improved compared with raw FeOCl [21,31]. Though only a<sub>an</sub>-FeOOH appears to be the candidate for the cathode material of practical batteries in these four derivatives, it is considered that the cathode performance of the FeOCl derivatives can be improved. We have many kinds of compounds that fulfill these three criteria.

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