

# $\beta$ -FeOOH, a new positive electrode material for lithium secondary batteries

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## Abstract

Beta-iron oxy-hydroxide, which exhibits a  $(2 \times 2)$  tunnel-type structure similar to that of  $\alpha$ - $\text{MnO}_2$ , was found to intercalate reversibly lithium in the tunnels. This material exhibits a potential slightly higher than 2 V with a capacity of 275 mAh/g and very good cyclic reversibility. X-ray Photoelectron Spectroscopy (XPS) investigation of discharged material showed that iron is reduced to the divalent state, and the lithium incorporated in the tunnels was purely ionic. This explains the good reversibility of this electrode material. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron oxy-hydroxide; Tunnel structure; Lithium battery; XPS

## 1. Introduction

So far,  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  materials have found applications in small-scale batteries for computers and portable phones. However, for large-scale lithium batteries, the use of these materials is very limited due to the high cost of cobalt and nickel. For this reason, iron compounds seem to be very attractive for the production of large-scale lithium batteries because of its large natural abundance and low cost. Several crystalline modifications of  $\text{LiFeO}_2$  have been proposed, including high-temperature cubic phase with a disordered structure of NaCl type, low-temperature tetragonal phase, the metastable monoclinic phase, and the layered phase [1–5]. However, all these iron oxide-based materials were found either to be electrochemically inactive or of poor activity, mainly because of decomposition of the materials and the collapse of the structure caused by the iron displacement to the lithium site during the extraction of lithium. To obtain an active iron-based material, we investigated more stable structures where the possibility of structural collapse is eliminated. One of the principal candidates is  $\beta$ -FeOOH, which exhibits a tunnel-type

structure where iron atoms are strongly bonded to the framework that constitutes the tunnels.

## 2. Experimental

$\beta$ -FeOOH was prepared by the hydrolysis process. First,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in warm  $\text{H}_2\text{O}$  and was subjected to slow hydrolysis. During the reaction, a progressive precipitation took place. The precipitate was filtered, washed extensively with water, then dried at  $100^\circ\text{C}$  in an oven. At the end of the washing process, a small amount of chlorine ions remained inside the tunnels, as deduced from the elemental analysis, which gave a composition of  $\beta\text{-FeOOHCl}_{0.087}$ . The obtained material was characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The XPS experiments were carried out on an SSX-100 equipment. The surface of the samples was cleaned by argon sputtering to eliminate any surface contamination before experiment. The electrochemical performances of the material was carried out in a glass cell using  $\text{LiClO}_4/(2\text{EC} + 2\text{DMC} + \text{DEC})$  as electrolyte at a current density of  $0.1 \text{ mA}/\text{cm}^2$ . The potential range for charging and discharging the cell was 0.5–4.2 V.

Fig. 1 shows the XRD pattern of  $\beta$ -FeOOH. The material could be indexed as a tetragonal phase with unit cell parameters of  $a = 10.54 \pm 0.05 \text{ \AA}$  and  $c = 3.03 \pm 0.05 \text{ \AA}$ . In this case, this structure can be described as a tunnel-type structure comprising large channels of type  $(2 \times 2)$ , where

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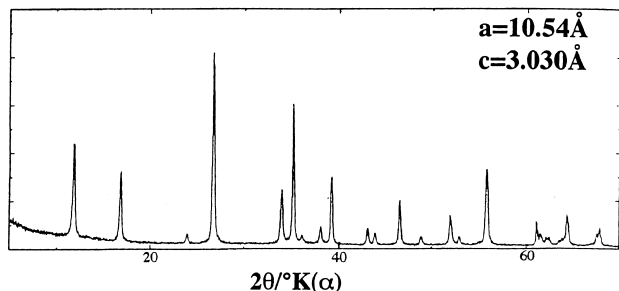


Fig. 1. X-ray diffraction pattern of  $\beta$ -FeOOH.

lithium can be accommodated during the intercalation process. Our first thought was to exchange hydrogen ions with lithium ions to obtain  $\text{LiFeO}_2$  with a tunnel-type structure. However, a tentative ion exchange between  $\beta$ -FeOOH and excess  $\text{LiCl}$  dissolved in methanol at  $100^\circ\text{C}$  for 3 days was unsuccessful. Ion chromatography analysis of the product indicated no lithium was present at the end of the exchange process. After detailed investigation of the structure of  $\beta$ -FeOOH [3], hydrogen was found to be strongly bonded to oxygen, which constitutes the main framework of the structure as shown in Fig. 2. The  $(2 \times 2)$  channels were either empty or partially occupied by chlorine atoms if the washing process is not completed. Therefore, we decided to try to insert lithium in these empty tunnels by just discharging  $\beta$ -FeOOH.

Fig. 3 shows the charge and discharge curves of  $\beta$ -FeOOH material. The test was conducted in a glass cell using  $\text{LiClO}_4/(2\text{EC} + 2\text{DMC} + \text{DEC})$  as electrolyte at a current density of  $0.1 \text{ mA/cm}^2$ . First, the cell was discharged to intercalate lithium ions in the tunnels and then charged to extract them. At the first discharge, the cell shows a plateau at around 2 V with a homogeneous one-phase reaction and a capacity of over 275 mAh/g. This result indicates that proton de-intercalation is very

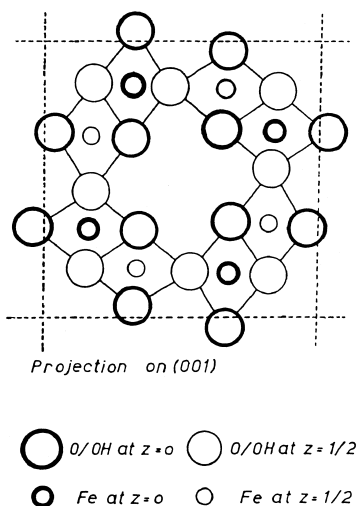


Fig. 2. Representation of tunnel structure of  $\beta$ -FeOOH.

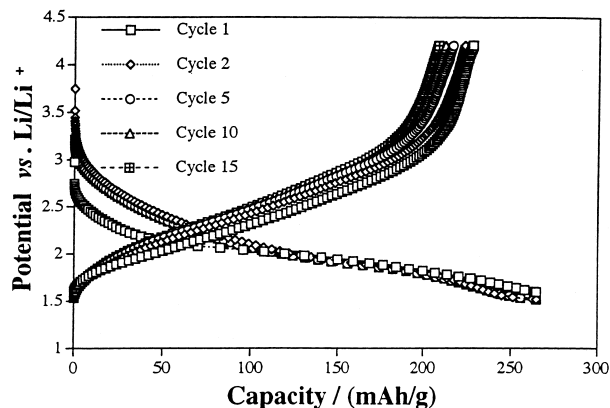
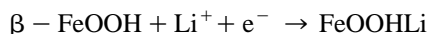


Fig. 3. Charge and discharge curves of  $\beta$ -FeOOH. Test was conducted in glass cell using  $1 \text{ M LiClO}_4/(2\text{EC} + 2\text{DMC} + \text{DEC})$  electrolyte. Cell was first discharged a current density of  $0.1 \text{ mA/cm}^2$ .

difficult, and only lithium intercalation and de-intercalation occur according to the following reaction:



The observed capacity is very close to the theoretical one (283 mAh/g) deduced from this reaction. This result indicates that almost one lithium ion could be intercalated and extracted from the tunnels, as also indicated by ion chromatography of discharged material, which gave a composition of  $\text{FeOOHLi}_{0.91}$ . During the second discharge, the potential of the cell increased slightly to between 2.5 and 2 V. The overall discharge capacity of the material after 15 cycles remained similar to that of the first cycle (275 mAh/g), indicating that this material cycles very well.

XPS was used to analyze the discharged material in order to confirm the reduction of trivalent iron to the divalent state and determine the nature of lithium incorporated in the tunnels upon discharging. Figs. 4 and 5 show the XPS emission spectrum of Fe 2p of  $\beta$ -FeOOH before and after discharge, respectively. The position of the Fe  $2p_{3/2}$  peak of  $\beta$ -FeOOH before discharge (712.54 eV) is consistent with that of trivalent iron reported in  $\text{Fe}_2\text{O}_3$  [6]. After the first discharge, the Fe 2p peaks are shifted toward low binding energy. This decrease in the binding energy is due to the increase in the electronic distribution of Fe,

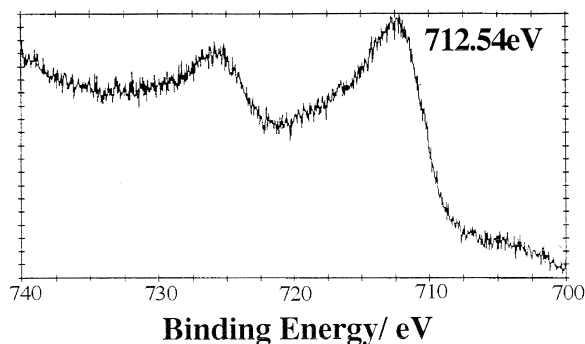


Fig. 4. Fe 2p emission spectrum of  $\beta$ -FeOOH before discharge.

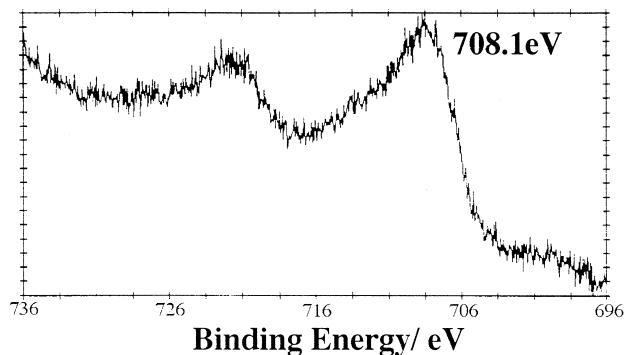


Fig. 5. Fe 2p emission spectrum of FeOOHLi<sub>0.91</sub> after first discharge.

which strengthens the screening effect between the nucleus and the Fe2p electron, resulting in weaker interactions between the nucleus and the Fe2p electron. As a result, lower energy is needed to extract the electron from the Fe2p level. The observed binding energy of discharged material (708.1 eV) is consistent with divalent Fe reported in XPS handbook tables [6]. This result indicates that during lithium insertion in the tunnels, trivalent iron is reduced to the divalent state.

Fig. 6 shows the XPS emission spectrum of Li 1s for discharged  $\beta$ -FeOOH. The position of the Li 1s peak (57.1 eV) is very close to that of LiCl (56.9 eV) where lithium is purely ionic. This result indicates that the lithium existing

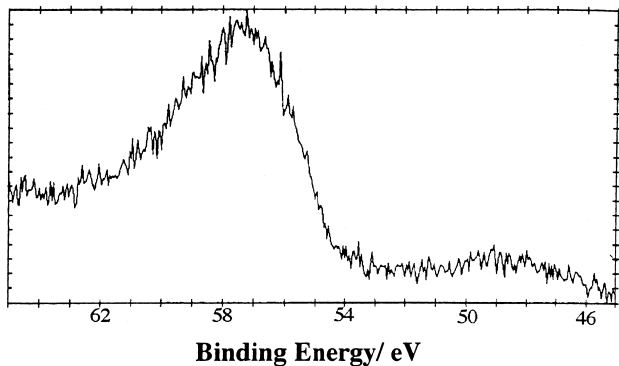


Fig. 6. Li 1s emission spectrum of FeOOHLi<sub>0.91</sub> after discharge.

in the tunnel after discharging the material is purely ionic. Therefore, the observed good cyclic reversibility of the material could be correlated with the pure ionic character of lithium ions located in the tunnels, which can be freely extracted and intercalated back without any alteration.

Preliminary results from a cyclic voltammetry scan of  $\beta$ -FeOOH showed that this material exhibits two more sharp reduction peaks, at 1.5 V and 0.7 V in addition to the 2 V peak. This result suggests that additional lithium is inserted in the tunnels. The overall discharge capacity at 0.5 V cut off voltage is about 1100 mAh/g. Further studies are underway to clarify the nature of the additional lithium and assess the structural stability of the discharged material.

### 3. Conclusion

$\beta$ -FeOOH was found to intercalate reversibly lithium in the (2 × 2) tunnels. The material cycle very well in the 2-V region and exhibits a large discharge capacity of 275 mAh/g with no fading after repeated cycling. The good cyclic reversibility, which is attributed to the high ionic character of lithium incorporated in the tunnels and the stability of the tunnel structure, make this material an attractive low cost cathode material for large rechargeable lithium batteries. However, when discharged to 0.5 V, the material exhibits three voltage plateaus at 2.3, 1.5 and 0.7 V and has an over all discharge capacity of 1100 mAh/g.

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