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Short communication

# β-FeOOH thin film as positive electrode for lithium-ion cells

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ABSTRACT

β-FeOOH thin film was prepared on the surface of a foamed Ni substrate by liquid phase deposition (LPD) method with a chemical equilibrium reaction between metal-fluoro complex and oxyhydroxide to make a low-cost and environmentally friendly positive electrode for high-power batteries. The new film electrode, with a thickness of 316 nm, was found out to give a large discharge capacity of 260 mAh $g^{-1}$ at 0.05 C rate even without an electro-conductive material. Furthermore, the electrode also showed good discharge performance with the retention of 69.9% at 10–0.05 C current rate, which means a promising positive active material for high-power use.



## 1. Introduction

Lithium-ion cells have been successfully commercialized by using $LiCoO_2$ $LiNiO_2$, and $LiMn_2O_4$ positive active materials in order to realize a higher operation voltage above 4 V especially for cellular phones and laptop computers. However, a low-cost and environmentally friendly positive active material has been recently expected as the alternative even with a lower operation voltage. In such a situation, an iron-based material is considered to be one of the candidates many researchers have studied on $LiFePO_4$ [1–3], $LiFeO_2$ [4,5], and $Fe_2O_3$ [6]. $LiFePO_4$ has been extensively studied for the commercial base whereas there are still problems to solve the drawback of high-rate discharge performance. β-FeOOH [7–9], which has a tunnel structure, is very attractive as a positive active material for 2-volt class lithium secondary cells on the point of a large delivered discharge capacity over 250 mAh $g^{-1}$. However, the practical high-rate discharge performance has not been cleared so far. Meanwhile, lithium-ion diffusion distance in an active material is one of the important factors to improve the discharge performance. At this viewpoint, it is considered to be effective to shorten the distance by thin film technology. The liquid phase deposition (LPD) method is one of the processes for preparing a thin film from an aqueous solution in electrical and optical fields [10–12]. Since this method takes advantage of the chemical equilibrium reaction between metal-fluoro complex and oxide, a homogeneous thin film is formed on the various kinds of substrates compared with other deposition techniques.

In this work, β-FeOOH thin film prepared by the LPD method has been investigated for the effect of morphology on the discharge performance together with the structure change in the Li-insertion process as a positive active material for high-power batteries.

## 2. Experimental

### 2.1. Preparation of β-FeOOH thin film electrode

α-FeOOH particle was first dissolved in 1.0 mol $dm^{-3}$ to Fe-ion concentration of 0.073 mol $dm^{-3}$ to give a parent solution. The $H_3BO_3$ solution was also prepared with distilled water at the concentration of 0.7 mol $dm^{-3}$. A treatment solution was then prepared by mixing the parent solution and the $H_3BO_3$ to concentrations of 7.3 mmol $dm^{-3}$ and 0.055 mol $dm^{-3}$, respectively. A foamed Ni substrate was immersed into the treatment solution with sonication at room temperature and then removed at different times. Finally, the film electrode was obtained after drying in a vacuum for 5 h at 80 °C.

### 2.2. Structure and electrochemical performance

The film morphology was investigated by scanning electron microscopy (SEM) analysis using JEOL JSM-T330A. The crystalline structure in the Li insertion process was identified by X-ray diffractometry (XRD) using Rigaku RINT2400.

Electrochemical performance was investigated by using three-terminal glass cells with a metallic Li foil as counter and reference

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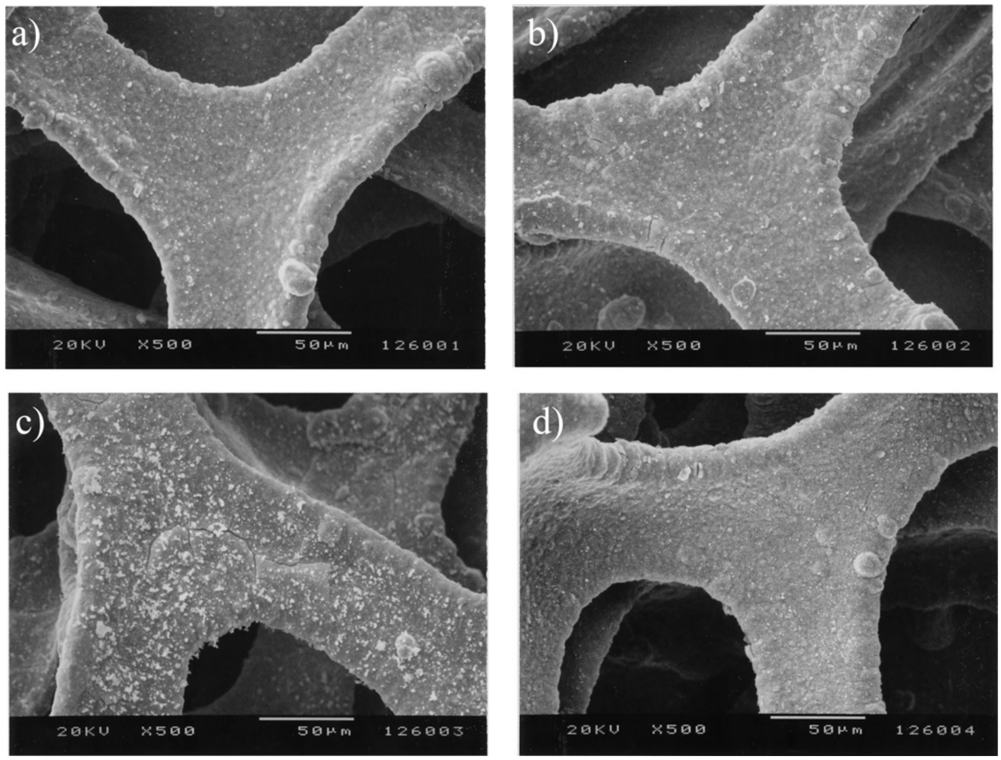


**Fig. 1.** Surficial SEM images of β-FeOOH thin film positive electrodes prepared by LPD method for (a) 1, (b) 2, (c) 4, and (d) 6 h.

electrodes in a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) in the volume ratio of 1:1 containing 1.0 mol dm$^{-3}$ $LiClO_4$. The positive electrode was discharged to 1.8 V vs. Li/Li$^+$ at different constant current rates based on one electron reaction of FeOOH at 25 °C. Charge was performed to 4.3 V vs. Li/Li$^+$ at the rate of 0.05 C at 25 °C in any electrochemical experiment.

## 3. Results and discussion

### 3.1. Film morphology

Surficial SEM images of β-FeOOH thin film obtained at immersion times of 1, 2, 4, and 6 h are shown in Fig. 1. Cross-sectional SEM images are also shown in Fig. 2. The films obtained for 1

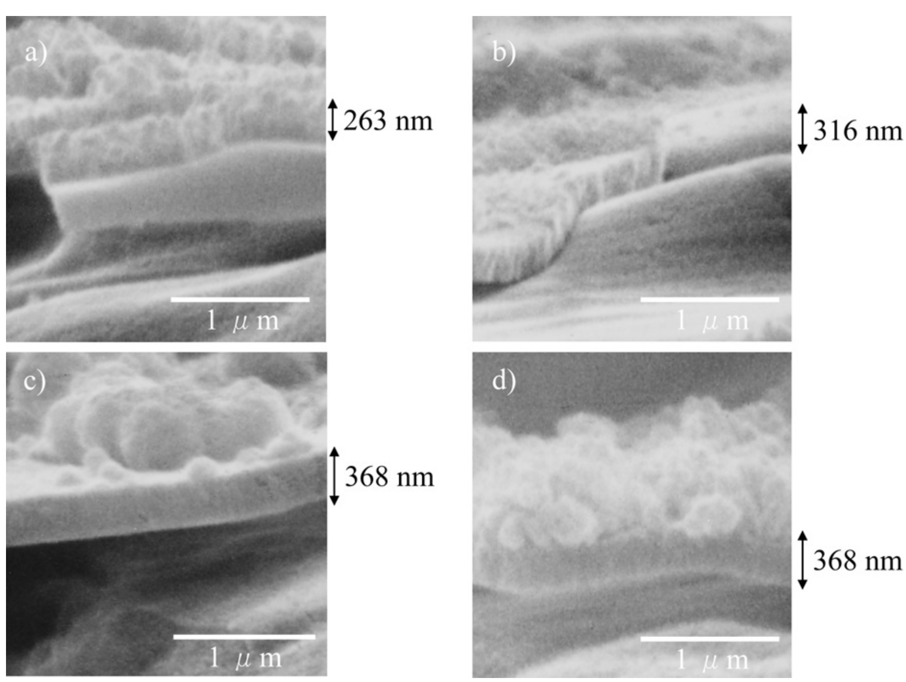


**Fig. 2.** Cross-sectional SEM images of β-FeOOH thin film positive electrodes prepared by LPD method for (a) 1, (b) 2, (c) 4, and (d) 6 h.

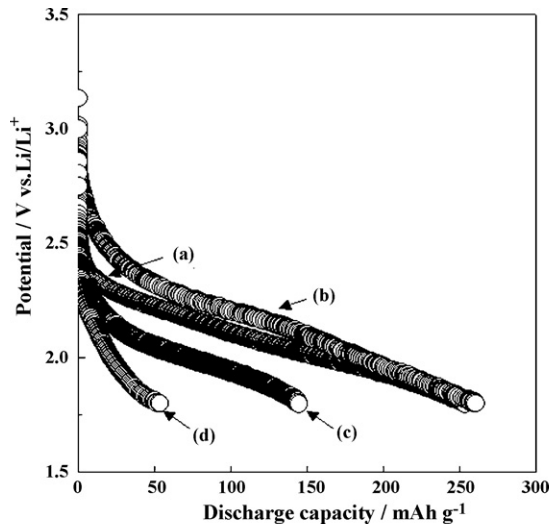


**Fig. 3.** Discharge characteristics of β-FeOOH thin film positive electrodes prepared by LPD method for (a) 1, (b) 2, (c) 4, and (d) 6 h at the rate of 0.05 C.

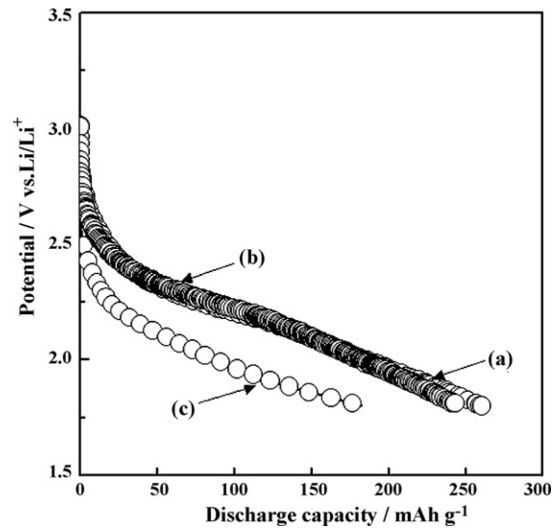


**Fig. 5.** Discharge characteristics of β-FeOOH thin film positive electrode prepared by LPD method for 2 h at the rates of (a) 0.05, (b) 0.1, and (c) 10 C.

and 2 h show columnar and uniform-flat morphology, respectively. However, the films obtained for 4 and 6 h show quite a different nature constructing of particles on the film surface of the electrodes. It was reported that low concentration of $H_3BO_3$ leads to the formation of β-FeOOH particles by this method [10]. Therefore, β-FeOOH particles are considered to be formed on the film surface of the electrode due to the decrease in the $H_3BO_3$ concentration. The thickness of film obtained for 1 h was found out to be 263 nm with columnar morphology. The columnar morphology is considered to be obtained at the beginning of the immersion time since the film growth is mainly vertical to the substrate by this deposition reaction. The thickness increased with the immersion time up to 368 nm to be uniform morphology by the horizontal growth and was then stabilized due to the change of nature, that is a formation of particles. From these results, the different film morphology can be classified; i.e. columnar film, uniform-flat film, particle-included film.

### *3.2. Effect of film morphology on discharge characteristics*

Initial discharge characteristics of electrodes with different β-FeOOH thin films obtained for 1, 2, 4, and 6 h by LPD method are shown in Fig. 3. The uniform-flat film electrode gave the largest discharge capacity of 260 mAh $g^{-1}$ at 0.05 C current rate even without an electro-conductive material. The columnar film electrode is suggested to give a larger polarization even at 0.05 C current rate especially at the beginning of discharge. Moreover, β-FeOOH particles are considered to cause drastic capacity decay due to the lack of electro-conductivity especially between each particle while discharging. Therefore, the optimum morphology of β-FeOOH thin film electrode is uniform and flat without columns and particles to give better electrochemical performance.

### *3.3. Structure change*

The calculated lattice constant change in the Li-insertion process is shown in Fig. 4. The uniform-flat film obtained for 2 h is assigned to β-type FeOOH tetragonal structure with the lattice constant $a$ = 1.054 nm and $c$ = 0.301 nm corresponding to the high crystallinity. The former lattice constant decreases according to the Li insertion and reaches $a$ = 1.041 nm at the discharged potential of 1.8 V vs. Li/$Li^+$. However, the latter lattice constant increases according with Li insertion and reaches $a$ = 0.304 nm at the discharged potential of 1.8 V vs. Li/$Li^+$. Each small amount of change is consid-

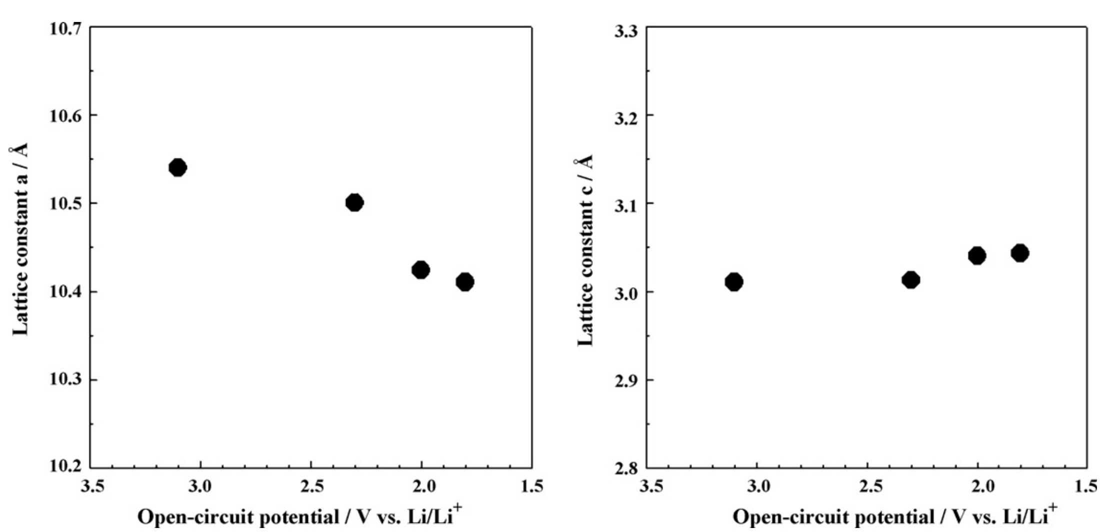


**Fig. 4.** Change in lattice constant $a$ and $c$ of β-FeOOH thin film as a function of open-circuit potential.

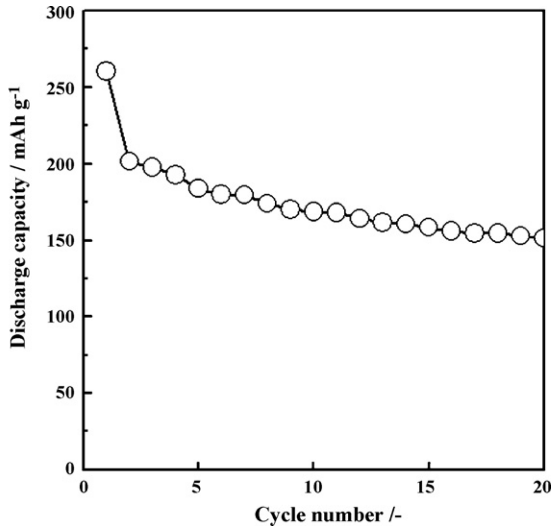


**Fig. 6.** Cycle performance of β-FeOOH thin film positive electrode prepared by LPD method for 2 h at the rate of 0.05 C.

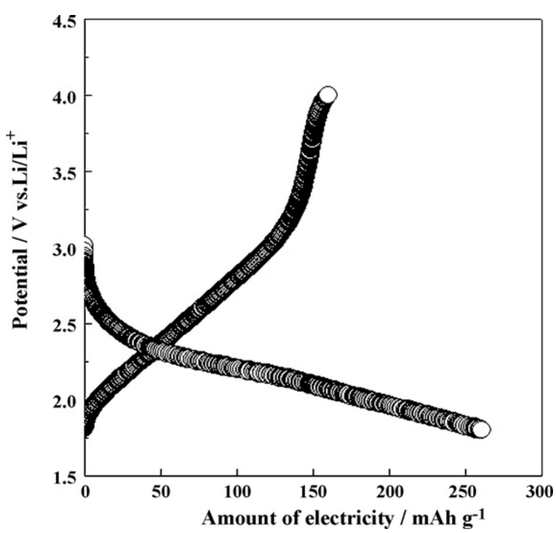


**Fig. 7.** Discharge and charge characteristics of β-FeOOH thin film positive electrode prepared by LPD method for 2 h at the rate of 0.05 C.

ered to be shown that lithium-ion is inserted in the tunnel structure smoothly without a drastic distortion. Accordingly, good cycle performance will be expected for the electrode with this material.

### *3.4. High-rate discharge and cycle performance*

Discharge performance of β-FeOOH thin film electrode obtained for 2 h is shown in Fig. 5. Discharge capacity retention at 10–0.05 C rate is a high value of 69.9%, which means that the electrode essentially gives excellent discharge performance. This value is much higher than $LiFePO_4$ positive active material without carbon coating, which was reported previously [13]. Non-carbon coating $LiFePO_4$ positive electrode shows almost no discharge capacity at 10 C rate. This result is anticipated as a very promising candidate of the material required for high-power batteries. Cycle performance of the electrode is shown in Fig. 6 together with the initial discharge and charge characteristics also given in Fig. 7. This electrode gave stable performance after the 2nd cycle though drastic capacity decay was caused at the 1st cycle. This capacity decay can be confirmed by the low coulombic efficiency at the 1st cycle shown in Fig. 7. This fact is suggested to be caused by the lack of electro-conductivity between the film and substrate due to the volume change during discharge and charge processes.

## 4. Conclusions

β-FeOOH thin film has been successfully prepared by LPD method as a new positive active material for high-power batteries. The different film morphology can be easily obtained by the control of deposition time, which are classified into columnar, uniform-flat, and particle-included films. The electrode of uniform-flat film with a thickness of 316 nm was found out to give a large discharge capacity of 260 mAh $g^{-1}$ at 0.05 C rate even without an electro-conductive material. Furthermore, the electrode also gave a high discharge capacity retention of 69.9% at 10–0.05 C rate. The columnar film electrode was suggested to give a larger polarization even at a low current rate of 0.05 C especially at the beginning of discharge. Moreover, β-FeOOH particles are considered to cause the lack of electro-conductivity especially between each particle due to the volume change during discharge. Therefore, the optimum morphology is concluded to be uniform-flat film without columns and particles to give better discharge performance. These facts mean that the electrochemical property is strongly dependent on the morphology of film obtained by LPD method. From these results, the uniform-flat β-FeOOH film electrode will be expected as a very promising candidate for a positive electrode for high-power batteries.

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