



Short communication

Surface reaction of β -FeOOH film negative electrode for lithium-ion cellsT. Tabuchi^{a,b,*}, Y. Katayama^b, T. Nukuda^b, Z. Ogumi^a^a Graduate School of Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan^b Corporate R&D Center, GS Yuasa Corporation, Nishinosho, Kisshoin, Minami-ku, Kyoto 601-8520, Japan

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ABSTRACT

Electrochemical performance of β -FeOOH thin film has been investigated for a low-cost and environmentally friendly negative electrode with a large capacity. The electrode was found out to give an initial large discharge capacity of 864 mAh g^{-1} and good cycleability with a constant value around 700 mAh g^{-1} at subsequent cycles. In the first charge process, one electron change reaction proceeded from the initial rest potential of $3.04\text{--}1.65 \text{ V vs. Li/Li}^+$, resulting in the formation of divalent product FeOOH. Further charging caused the surface film formation like solid electrolyte interface (SEI) between 1.65 V and $1.18 \text{ V vs. Li/Li}^+$ together with the reduction of Fe compound from divalent to partially zero-valent, followed by its film growth from 1.18 V to $0.07 \text{ V vs. Li/Li}^+$.

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1. Introduction

Lithium-ion cells have been successfully put into practical use by applying a carbon material to a negative electrode especially for mobile phones and personal computers despite the less theoretical capacity of 372 mAh g^{-1} . It is partly because there still was an insoluble matter with respect to pure metallic Li which gives much larger value of 3861 mAh g^{-1} . Recently, commercial-based cells have been strongly required to enhance the energy density with an increase in electric power consumption for various portable devices. Therefore, many researchers have extensively studied on larger-capacity negative active materials such as Si [1–5], Sn [6,7], SnCo [8], CoO [9,10], and Co_3O_4 [11] besides metallic Li as the alternative of a carbon material which is limited to increase the energy density. As the problem of such materials, capacity decay with cycling is mainly caused by the volume change in the Li-insertion and extraction processes. Meanwhile, the cost and environment are also important issues to be discussed in our battery field so that an electrode material should be developed in consideration of these solutions. In such a situation, an iron-based material is attractive to solve the problem of cost and environment compared with the other transition metal compounds such as CoO [9] which has been a focus to give a large capacity of 700 mAh g^{-1} and good cycleability. As the iron-based material, it was reported that Fe_2O_3 has a large capacity of more than 700 mAh g^{-1} [12]. However, it was concluded that Fe_2O_3

is a promising candidate as a large-capacity electrode material for lithium-ion batteries if the cycle performance can be improved. β -FeOOH is one of the attractive compounds due to a large capacity of 1100 mAh g^{-1} [13]. However, a basic technique for improving the cycle performance under the condition through a deep reduction potential as a negative electrode has not been proposed on this material. In this work, β -FeOOH has been investigated as a negative active material with the different geometric effect between the film and particle on the electrochemical performance. Moreover, the surface reaction of β -FeOOH has been studied by using the thin film electrode as a simple model, which can eliminate an electroconductive material and binder, by means of X-ray photoelectron spectroscopy (XPS) and AC impedance measurement.

2. Experimental

2.1. Preparation of β -FeOOH thin film electrode

β -FeOOH thin film was formed on a foamed Ni substrate to make a negative electrode by liquid phase deposition (LPD) method [14–16] which is one of the soft processes for preparing from an aqueous solution in electrical and optical fields. α -FeOOH particle was first dissolved in $1.0 \text{ mol dm}^{-3} \text{ NH}_4\text{F}\cdot\text{HF}$ (Nacalai Tesque Inc.) to Fe-ion concentration of $0.073 \text{ mol dm}^{-3}$. The H_3BO_3 aqueous solution was also prepared with distilled water to the concentration of 0.7 mol dm^{-3} . These solutions were then mixed to Fe-ion and H_3BO_3 concentrations of 7.3 mmol dm^{-3} and $0.055 \text{ mol dm}^{-3}$, respectively. A foamed Ni substrate was immersed into the mixed solution with sonication for 2 h at room temperature. Finally, the film electrode (hereinafter called; β -FeOOH thin film electrode) was obtained after drying in a vacuum for 5 h at 80°C . This condition

* Corresponding author at: Corporate R&D Center, GS Yuasa Corporation, Nishinosho, Kisshoin, Minami-ku, Kyoto 601-8520, Japan. Tel.: +81 75 312 0415; fax: +81 75 312 2129.

E-mail address: toru.tabuchi@jp.gs-yuasa.com (T. Tabuchi).

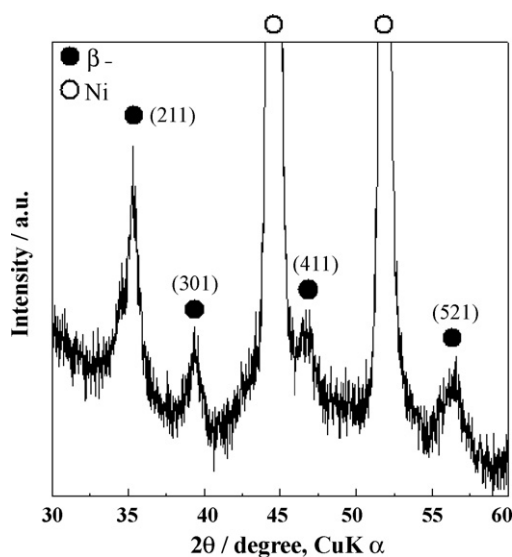


Fig. 1. XRD pattern of β -FeOOH thin film.

is based on our previous result in order to obtain a flat thin film of 316 nm thick with uniform-flat morphology, which was confirmed by scanning electron microscopy (SEM) [17].

2.2. Preparation of β -FeOOH particle electrode

β -FeOOH particles were prepared as previously reported [13]. An electrode with β -FeOOH particles (hereinafter called; β -FeOOH particle electrode) was also prepared for the purpose of comparison with the film-shape geometry. β -FeOOH particles with an average diameter of 1.3 μm , acetylene black (AB) as an electro-conductive material, and polyvinylidene fluoride (PVDF) as a binder were first mixed in the ratios of 75:10:15 in the solid mass with N-methyl-2-pyrrolidone solvent to prepare a slurry. The slurry was then loaded in a formed Ni substrate to be the density of 6.7 mg cm^{-2} . Finally, the electrode was obtained after drying in a vacuum for 5 h at 80 $^{\circ}\text{C}$.

2.3. Analysis and electrochemical measurement

The thin film was identified by X-ray diffractometry (XRD) using Rigaku RINT2400 at a scanning rate of 0.25 $^{\circ}\text{ min}^{-1}$ in the 2θ range from 30 $^{\circ}$ to 60 $^{\circ}$ with Cu K α radiation. The change in a valence state of Fe was analyzed by XPS using Shimadzu/Kratos AXIS-HS with a tube voltage of 10 kV and a filament current of 15 mA.

Electrochemical measurement was performed by using three-terminal glass cells with a metallic Li foil as counter and reference 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 $_4$. Both β -FeOOH electrodes were charged to 0.00 V and then discharged to 2.50 V vs. Li/Li $^{+}$ at 25 $^{\circ}\text{C}$ at the rate of 0.05 C on the basis of one electron change reaction. Impedance spectroscopy was also conducted in the charge and discharge processes at the frequency ranging from 0.1 Hz to 10 kHz. The measurement was normally carried out with a potential amplitude of 5 mV.

3. Results and discussion

3.1. Identification of β -FeOOH thin film

XRD pattern of the film is shown in Fig. 1. The peaks were clearly detected at around 35.2 $^{\circ}$, 39.3 $^{\circ}$, 46.7 $^{\circ}$, and 56.4 $^{\circ}$, assigning to (2 1 1), (3 0 1), (4 1 1), and (5 2 1) diffraction lines, respectively. All peaks can be identified to β -FeOOH except that of Ni substrate. Therefore,

the final product was confirmed to be β -FeOOH without any other phases.

3.2. Charge–discharge characteristics and cycle performance

Charge and discharge characteristics of β -FeOOH thin film electrode are shown in Fig. 2. The electrode showed the total electricity of 1213 mAh g^{-1} in the first charge process from the initial rest to the cutoff potential of 0.00 V vs. Li/Li $^{+}$ together with two plateaus which occur clearly at around 1.50 V and 0.80 V vs. Li/Li $^{+}$. Slight potential inflection was also confirmed at around 2.30 V vs. Li/Li $^{+}$. Moreover, the electrode was found out to give an initial large discharge capacity of 864 mAh g^{-1} . Accordingly, the charge and discharge efficiency is calculated to 71.2% at the 1st cycle. However, potential plateau was indefinite in the discharge process from the fully charged state to the cutoff potential of 2.50 V vs. Li/Li $^{+}$. The amount of charged electricity drastically decreased between the 1st and 2nd cycle. The efficiency at the 2nd cycle was improved to 87.3%. Moreover, the discharge capacity was found out to stabilize around 700 mAh g^{-1} with the similar potential behavior at subsequent cycles. This fact means the same electrochemical reaction proceeds in the discharge process after the 2nd cycle. Charge and discharge characteristics of β -FeOOH particle electrode are shown in Fig. 3. The charged electricity and discharge capacity were 1659 mAh g^{-1} and 958 mAh g^{-1} , respectively. It should be noted that these large values include the influence of acetylene black which can be also inserted and extracted with Li in the electrochemical processes. The discharge capacity drastically decreased with cycling in contrast with the thin film electrode. This reason is suggested to be due to the lack of electro-conductivity caused by the isolation of particles during charging and discharging. Change in discharge capacity of both electrodes is shown in Fig. 4 for comparison. The thin film electrode gave better cycle performance with a stable capacity around 700 mAh g^{-1} after the 4th cycle. This reason suggests that electrical contact in the electrode can be maintained by forming the thin film, which means that cycle performance is strongly dependent on the geometry of β -FeOOH active material.

3.3. Change in atomic valence of Fe

Change in the peak of Fe $_{2p}$ binding energy is shown in Fig. 5 to confirm the valence state in the charging process. The Fe $_{2p}$ peak

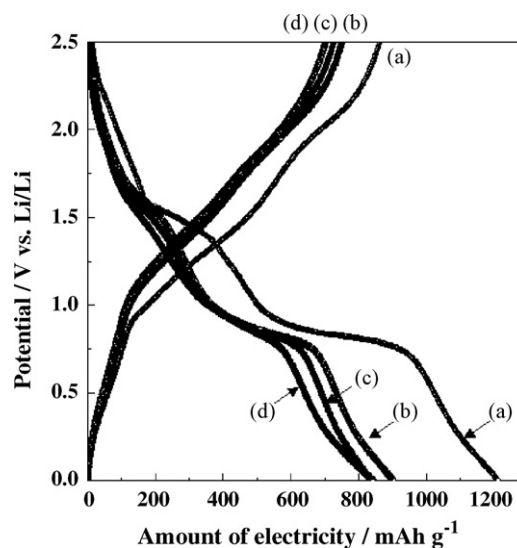


Fig. 2. Charge–discharge characteristics of β -FeOOH thin film negative electrode at the (a) 1st, (b) 2nd, (c) 3rd, and (d) 18th cycle.

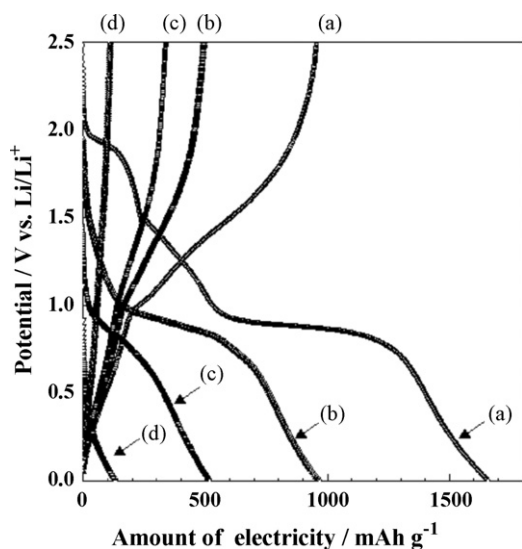


Fig. 3. Charge–discharge characteristics of β -FeOOH particle negative electrode at the (a) 1st, (b) 2nd, (c) 3rd, and (d) 18th cycle.

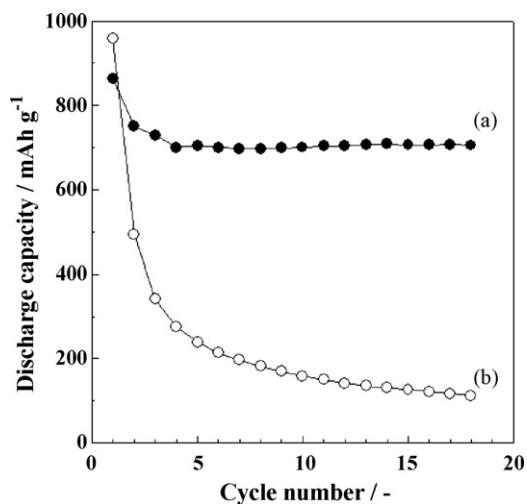


Fig. 4. Cycle performance of negative electrode with β -FeOOH (a) thin film and (b) particles.

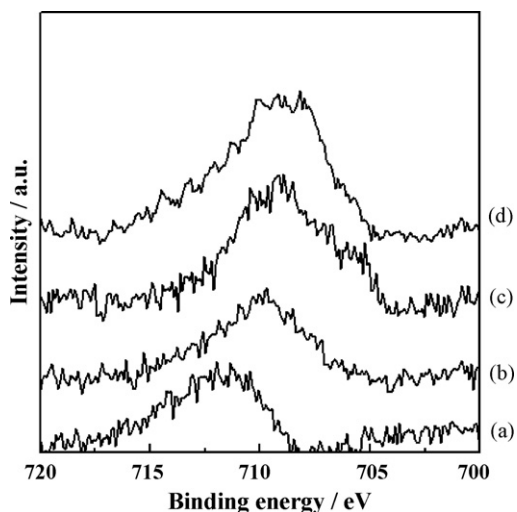


Fig. 5. Change in Fe_{2p} XPS spectra of β -FeOOH thin film negative electrode at different potentials of (a) 3.04 V, (b) 1.65 V, (c) 1.18 V, and (d) 0.70 V vs. Li/Li^+ .

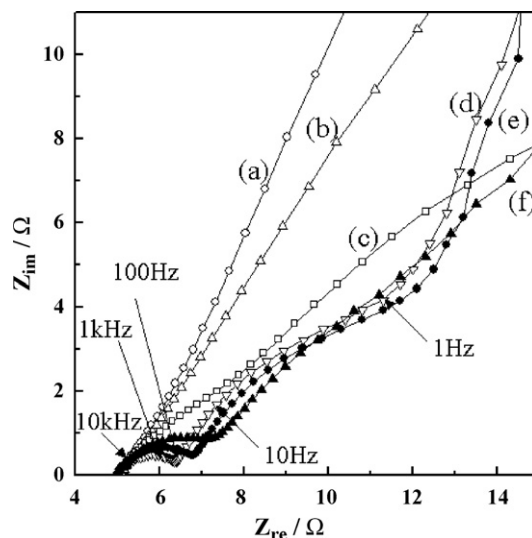
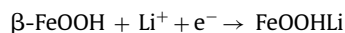


Fig. 6. Cole–cole plots obtained by AC impedance analysis of β -FeOOH thin film negative electrode at different potentials of (a) 3.04 V, (b) 1.89 V, (c) 1.65 V, (d) 1.18 V, (e) 0.70 V, and (f) 0.07 V vs. Li/Li^+ in the charge process.

appeared at 712 eV at the rest potential of 3.04 V vs. Li/Li^+ , which means as-prepared β -FeOOH film. This value is derived from trivalent Fe. The peak clearly shifted from 712 eV to around 709 eV by charging from the rest potential to 1.65 V vs. Li/Li^+ . This lower position is suggested to show a divalent state derived from FeOOHLi compound on the basis of one electron change reaction as previously reported [13].



The slight potential inflection at around 2.30 V vs. Li/Li^+ is mainly caused by this reaction. The peak slightly changed to the further low value with a shoulder formed at around 706 eV by the reduction to the potential of 1.18 V vs. Li/Li^+ . It is considered that this shoulder peak is derived from zero-valent Fe. This fact suggests that the electrochemical reaction proceeds inhomogeneously by Li-insertion in the range from 1.65 V to 1.18 V vs. Li/Li^+ including the first potential plateau around 1.50 V vs. Li/Li^+ . The peak position almost remains unchanged in the range from 1.18 V to 0.70 V vs. Li/Li^+ including the second potential plateau around 0.8 V vs. Li/Li^+ . Therefore, Fe compounds from divalent to zero-valent state still remain at 0.70 V vs. Li/Li^+ after the second potential plateau.

3.4. Impedance analysis

Change in cole–cole plots of β -FeOOH thin film electrode at different potentials in the first charge process is shown in Fig. 6. The plots at the beginning of 3.04 V vs. Li/Li^+ were formed with a simple line, which means a blocking electrode. The line was gradually inclined to a lower angle as the potential decreased, and then started to change into a slight strained curve at 1.65 V vs. Li/Li^+ suggesting to the end of one electron change reaction from the results by XPS analysis. The behavior was drastically changed to be two semi circles, which was clearly formed in the potential range between 1.65 V and 1.18 V vs. Li/Li^+ . Moreover, the semi circle at higher frequency was slightly enlarged with the potential decreased, though the behavior was similar between 1.18 V and 0.70 V vs. Li/Li^+ . However, the semi circle at lower frequency almost disappeared at 0.07 V vs. Li/Li^+ . In the discharge process, the semi circle at higher frequency became a little smaller at 0.99 V vs. Li/Li^+ and then again changed to be a simple line at the end of 2.66 V vs. Li/Li^+ as shown in Fig. 7. In order to study on the semi circle at higher frequency, the effect of different potential amplitudes was

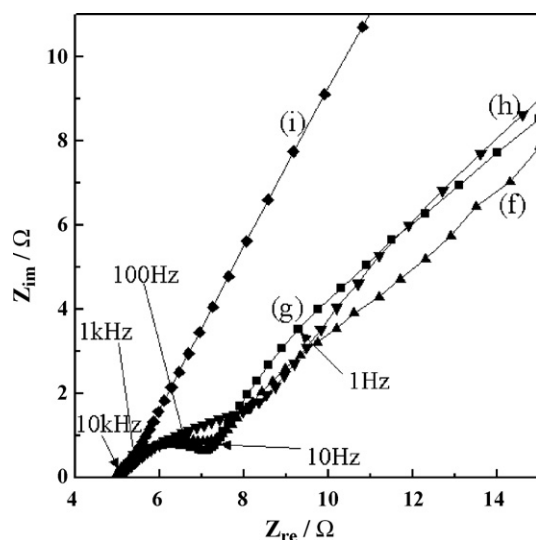


Fig. 7. Cole-cole plots obtained by AC impedance analysis of β -FeOOH thin film negative electrode at different potentials of (f) 0.07 V, (g) 0.99 V, (h) 1.97 V, and (i) 2.66 V vs. Li/Li⁺ in the discharge process.

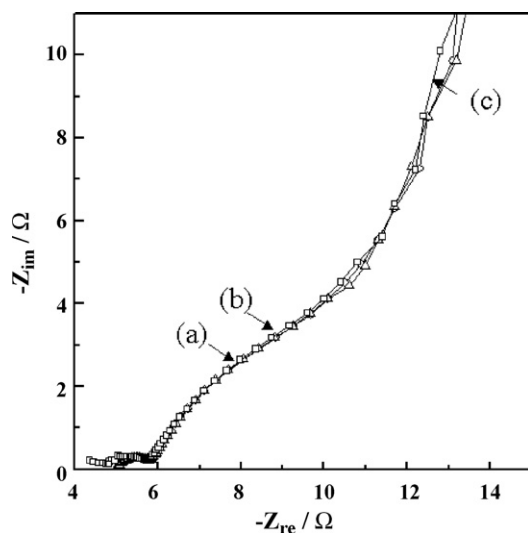


Fig. 8. Cole-cole plots obtained by AC impedance analysis of β -FeOOH thin film negative electrode at the potential of 0.70 V vs. Li/Li⁺ with different amplitudes of (a) 5 V, (b) 10 V, and (c) 50 mV.

also investigated at 0.70 V vs. Li/Li⁺ after 3 cycles as shown in Fig. 8. The semi circle was almost unchanged at the different potential amplitudes of 5 mV, 10 mV, and 50 mV. Interfacial reaction resistance should be strongly dependent on the potential amplitude. Therefore, it is considered that the semi circle at higher frequency is derived from the surface film like SEI formed between β -FeOOH

and electrolyte. Accordingly, the reaction of surface film is suggested to start in the range between 1.65 V and 1.18 V vs. Li/Li⁺ in the first charge process. The resistance increased with the further low potential down to 0.07 V vs. Li/Li⁺, which means increase in thickness of the surface film.

4. Conclusions

β -FeOOH thin film electrode was found out to give an initial large discharge capacity of 864 mAh g⁻¹ and good cycleability with a constant value around 700 mAh g⁻¹ at subsequent cycles. However, β -FeOOH particle electrode gave less cycleability due to the lack of electro-conductivity. Therefore, cycle performance is found out to be strongly dependent on the geometry of β -FeOOH active material. In the charge process, the thin film electrode showed a slight potential inflection around 2.30 V vs. Li/Li⁺ and two plateaus which occur clearly around 1.50 V and 0.80 V vs. Li/Li⁺. The inflection around 2.30 V vs. Li/Li⁺ is mainly caused by the one electron change reaction resulting in the divalent product of FeOOHLi. The reduction is suggested to proceed with the mixture of FeOOHLi and partly zero-valent state in the range between 1.65 V and 1.18 V vs. Li/Li⁺ including the first potential plateau around 1.50 V vs. Li/Li⁺. The reaction of surface film formation also started from this potential range. However, the surface film is still unstable considering the increase in resistance, based on the semi circle at higher frequency, at the lower potential down to 0.07 V vs. Li/Li⁺. Furthermore, the subsequent reduction in the range from 1.18 V to 0.07 V vs. Li/Li⁺ including the second potential plateau around 0.80 V vs. Li/Li⁺ is suggested to proceed from divalent to completely zero-valent state together with the increase in thickness of the surface film.

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