

β -FeOOH Thin Film Formed on the Surface of Carbon Materials by Liquid Phase Deposition Method for Positive Active Material of Lithium Secondary Cells

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Abstract

β -FeOOH thin film has been successfully formed on the surface of acetylene black (AB) and mesocarbon microbeads (MCMB) by liquid phase deposition (LPD) method. The new positive electrode with active material of β -FeOOH on the surface of AB was found to show good charge-discharge reversibility with the potential range between 1.8 and 4.0 V vs. Li/Li⁺ and a high capacity of 300 mAh g⁻¹ corresponding to the utilization value of 99% of theoretical capacity for one electron reaction. The delivered capacity of positive electrode was reached to the value of 123 mAh g⁻¹ even at high rate discharge of 86 CmA on the basis of the theoretical capacity. Therefore, β -FeOOH thin film formed on the surface of AB will be promising candidate for a positive active material of lithium secondary cells with high power performance.

1 Introduction

The lithium transition-metal oxide such as LiCoO₂, LiNiO₂, and LiMn₂O₄ has been used as a positive active material for 4 V-class lithium-ion cells. However, these oxides are rather costly and not environment-friendly material. On the other hand, iron-based compounds are attractive as positive active materials because of abundance, inexpensiveness, and nontoxicity. Therefore, the compounds such as β -FeOOH^{1,2)}, γ -FeOOH³⁾, LiFeO₂^{4,5)}, LiFePO₄^{6,7)}, and Fe₄[Fe(CN)₆]₃⁸⁾ have been extensively investigated for the positive active material. β -FeOOH with a (2 × 2) tunnel-type structure was found to be intercalated

reversibly lithium ion into the tunnels and show very large discharge capacity of 275 mAh g⁻¹.¹⁾ The charge-discharge reaction for β -FeOOH is one electron change as shown in equation (1) and its theoretical discharge capacity is 302 mAh g⁻¹.¹⁾



β -FeOOH powder prepared by conventional hydrolysis process¹⁾ has contained the contamination of 10% Cl⁻ and H₂O, though the β -FeOOH is a promising candidate as positive active material for lithium secondary cells.

On the other hand, β -FeOOH thin film was prepared uniformly on a glass substrate by liquid phase deposition (LPD) method as reported for the electronic material field.^{9, 10)} The feature of this method is the application of the hydrolysis equilibrium reaction of a metal-fluoro complex and

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F⁻ consumption with boric acid or aluminum metal. Metal oxide or oxyhydroxide thin film was prepared with little contamination in the product.

In this report, we will describe a possibility on the application of β -FeOOH thin film formed on the surface of different carbon materials of AB and MCMB by LPD method for positive active material of lithium secondary cells.

2 Experimental

2.1 Synthesis of β -FeOOH thin film on the surface of carbon material

α -FeOOH particle (Kojundo Chemical Laboratory Co., Ltd.) was dissolved in 1.0 mol dm⁻³ NH₄F·HF (Nacalai Tesque Inc.) to be a concentration of 0.073 mol dm⁻³ FeOOH-NH₄F·HF aqueous solution. H₃BO₃ (Nacalai Tesque Inc.) was dissolved in deionized water to be a concentration of 0.7 mol dm⁻³. These solutions are mixed to be whole quantity 150 ml of 0.0073 mol dm⁻³ FeOOH and 0.55 mol dm⁻³ H₃BO₃ with deionized water to prepare the treatment solution.

AB (Denki Kagaku Kogyo Co., Ltd.) and MCMB (Osaka Gas Co., Ltd.) were used as substrate for deposition of β -FeOOH thin film. The former specific surface area is 68 m²g⁻¹ and its average particle diameter is 0.5 μ m with chain structure. The later area is 1 m²g⁻¹ and its diameter is 25 μ m with spherical structure, respectively. These carbon materials of 0.3 g were immersed into the treatment solution of 150 ml for 1 h, 2 h, 4 h, and 8 h at 35 °C. β -FeOOH thin film was deposited on the surface of AB or MCMB by the immersion into the treatment solution. The products were filtrated, washed with distilled water, and dried at 60 °C.

The crystalline structure of formed β -FeOOH thin film was investigated by X-ray diffraction (XRD) analysis. The mass amount of β -FeOOH on the carbon materials was determined by the calculation from the result of inductively-coupled plasma (ICP) analysis.

2.2 Preparation of β -FeOOH positive electrode

The β -FeOOH thin film formed on carbon material, AB as an electro-conductive material, and polyvinylidene fluoride (PVdF) (Kureha Chemical

Industry Co., Ltd.) as a binder were mixed in the mass ratios of 80 : 5 : 15 with N-methyl-2-pyrrolidone (NMP) solvent to prepare a slurry. β -FeOOH positive electrode was obtained by filling into a foamed-nickel collector with the slurry and drying in vacuum at 60 °C for 5 h.

2.3 Electrochemical measurement

Charge-discharge test was conducted in three-electrode flooded-type glass cell. The metallic lithium was used as the counter and reference electrodes. The electrolyte was a mixed solution of ethylene carbonate (EC) and diethylcarbonate (DEC) (1 : 1 in the volume ratio) containing 1.0 mol dm⁻³ LiClO₄. The cell was discharged to 1.8 V vs. Li / Li⁺ and then charged to 4.0 V vs. Li / Li⁺ at a constant current density of 0.1 mA cm⁻². Moreover, the discharge current density of the high rate test was 0.1, 1, 5, and 10 mA cm⁻². All of the electrochemical measurements were carried out in an Ar filled in dry box with the concentration of H₂O less than 1 ppm at 25 °C.

3 Results and discussion

3.1 Synthesis of β -FeOOH thin films

XRD patterns of β -FeOOH thin films obtained by immersion for 2 h in the treatment solution are shown in Fig. 1. The diffraction peak positions of film on the surface of different carbon materials of AB and MCMB, were corresponded to JCPDS card of β -FeOOH (No. 341266, Fig. 1 (c)). β -FeOOH on the surface of AB and MCMB are assigned to tetragonal structure with the lattice constants of $a = 10.45 \pm 0.02$ Å and $c = 3.039 \pm 0.008$ Å. This result means that crystalline structure of obtained β -FeOOH film is not dependent on the kind of carbon material.

The change in mass amount of β -FeOOH deposited on the surface of carbon materials is shown in Fig. 2 as a function of immersion time. The mass amount of β -FeOOH deposited on the surface of AB is drastically increased at the beginning of immersion time and becomes constant after 2 h. The reason is that Fe³⁺ in the treatment solution is consumed for deposition reaction of β -FeOOH. On the other hand, mass amount of β -FeOOH deposited on the surface

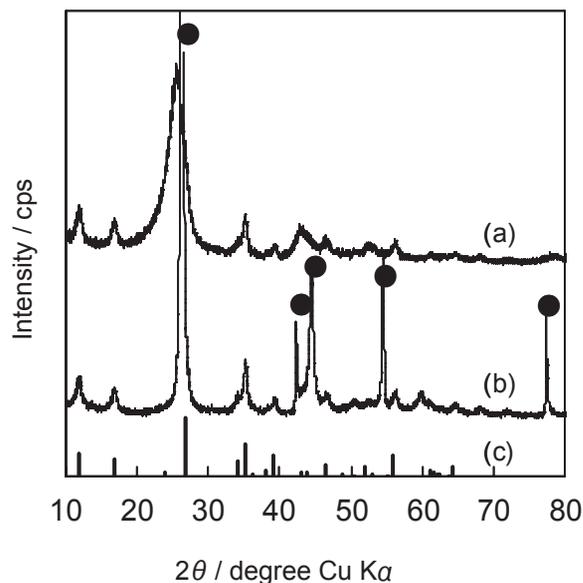


Fig. 1 XRD patterns of β -FeOOH deposited on carbon material of acetylene black (a), mesocarbon microbeads (b), and by JCPDS card No. 341266 (c). ●: Peaks of carbon.

of MCMB is gradually increased up to the immersion time of 8 h. The reason is considered that Fe^{3+} in the treatment solution is gradually consumed because of small specific surface area contacted between MCMB and the solution. Furthermore, it is found that mass amount of β -FeOOH deposited on the surface of AB is larger than that of MCMB judging from the result of Fig. 2. This fact is considered to be that the thickness of β -FeOOH film deposited on the surface of AB is thinner than that of MCMB, because the specific surface area of AB is larger than that of the latter case.

3. 2 Electrochemical performance of β -FeOOH electrode

The initial discharge-charge characteristics of β -FeOOH electrodes are shown in Fig. 3. β -FeOOH electrode using AB as a substrate is found to give a high discharge capacity of 300 mAh g^{-1} . The value is corresponded to the utilization value of 99% on the basis of theoretical capacity. β -FeOOH electrode using MCMB as a substrate shows a discharge capacity of 266 mAh g^{-1} . The value is corresponded to the utilization value of 88% on the basis of theoretical capacity. Moreover, The both β -FeOOH electrodes show average discharge potential of 2.2 V

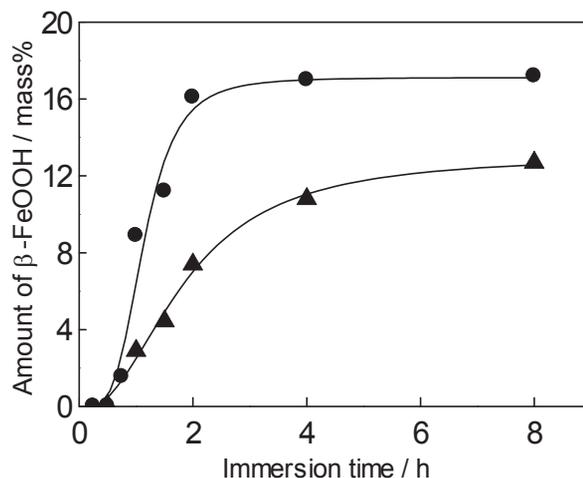


Fig. 2 Change in mass amount of β -FeOOH deposited on carbon material of acetylene black (●) and mesocarbon microbeads (▲) as a function of immersion time.

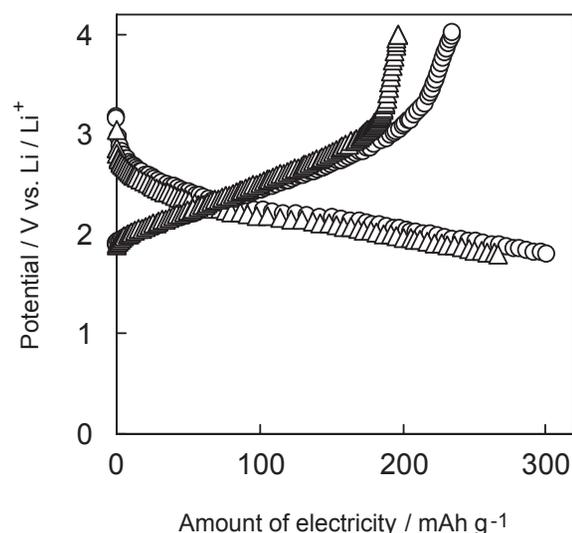


Fig. 3 Initial discharge-charge characteristics of β -FeOOH positive electrode with different carbon materials of acetylene black (○) and mesocarbon microbeads (△).

Charge: 0.1 mA cm^{-2} to 4.0 V vs. Li/Li⁺.
Discharge: 0.1 mA cm^{-2} to 1.8 V vs. Li/Li⁺.
Electrolyte: 1 mol dm^{-3} LiClO₄ of EC / DEC mixed solution.

vs. Li/Li⁺ and good discharge-charge reversibility. The cycle performances of electrodes are shown in Fig. 4. Discharge capacities of both electrodes are found to be decreased at the several cycles remarkably and gradually stable with further cycles. The reason of capacity decay at the beginning seems

to be that lithium ion is difficult to be sufficiently de-intercalated from the tunnel of β -FeOOH by this applied charge condition of simple constant current method judging from the low value of ratio of charge input to discharge capacity as shown in Fig. 5. Furthermore, it is found out that cycle performance of β -FeOOH electrode is not dependent on the kind of carbon materials.

Discharge capacity of the β -FeOOH electrode with different carbon materials of AB and MCMB as a function of discharge current is shown in Fig. 6. The delivered capacity of the electrode with AB is found to be reached to the large value of 123 mAh g⁻¹ even at high rate discharge of 86 CmA on the basis of theoretical capacity of 302 mAh g⁻¹. The delivered capacity of the electrode with MCMB is also found to be reached to the value of 56.4 mAh g⁻¹ even at high rate discharge of 81 CmA. The reason is consider to be that diffusion length of lithium ion in β -FeOOH film with AB is shorter than that with MCMB, because the thickness of the film on the former carbon is smaller than that on the latter one. Therefore, β -FeOOH thin film formed on the surface of AB will be promising candidate for a positive

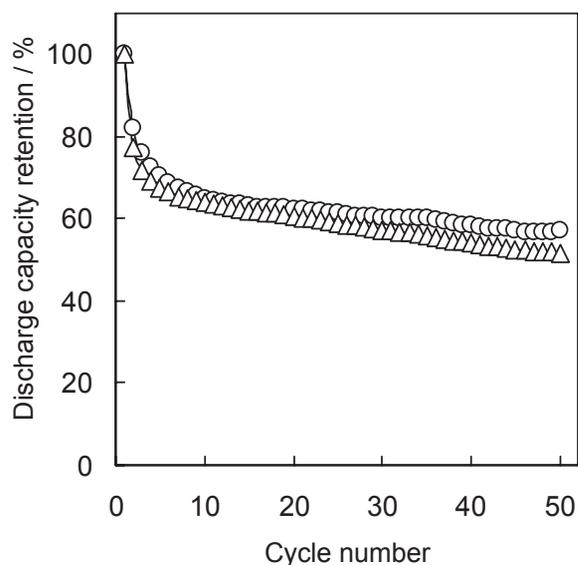


Fig. 4 Cycle performance of β -FeOOH positive electrode with different carbon materials of acetylene black (\circ) and mesocarbon microbeads (\triangle). Charge: 0.1 mA cm⁻² to 4.0 V vs. Li/Li⁺. Discharge: 0.1 mA cm⁻² to 1.8 V vs. Li/Li⁺. Electrolyte: 1 mol dm⁻³ LiClO₄ of EC / DEC mixed solution.

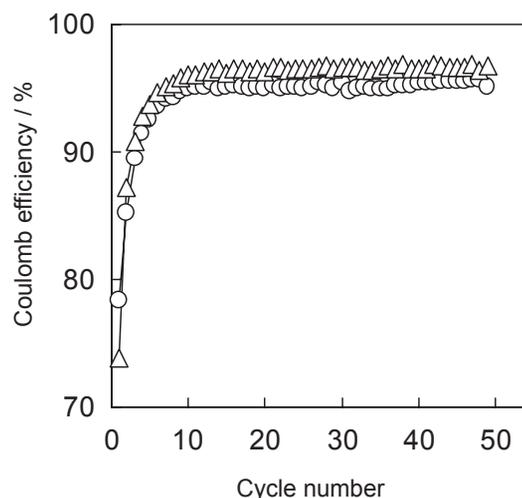


Fig. 5 Change in ratio of charge input to discharge capacity of β -FeOOH positive electrode with different carbon materials on acetylene black (\circ) and mesocarbon microbeads (\triangle). Charge: 0.1 mA cm⁻² to 4.0 V vs. Li/Li⁺. Discharge: 0.1 mA cm⁻² to 1.8 V vs. Li/Li⁺. Electrolyte: 1 mol dm⁻³ LiClO₄ of EC / DEC mixed solution.

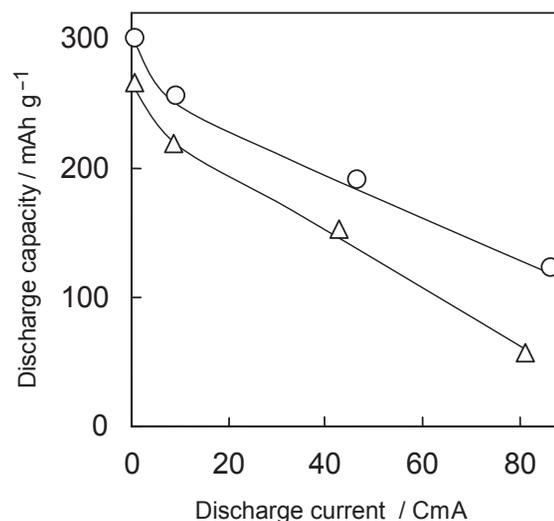


Fig. 6 Discharge performances of β -FeOOH positive electrode with different carbon materials of acetylene black (\circ) and mesocarbon microbeads (\triangle). The value C is based on theoretical capacity of β -FeOOH. Discharge: 0.1, 1, 5, and 10 mA cm⁻² to 1.8 V vs. Li/Li⁺. Electrolyte: 1 mol dm⁻³ LiClO₄ of EC / DEC mixed solution.

active material of lithium secondary cells with high power performance.

4 Conclusions

β -FeOOH thin film has been successfully formed on the surface of AB and MCMB by LPD method. The charge-discharge characteristics and cycle performances of β -FeOOH positive electrode have been also investigated. The results are summarized as follows.

- 1) The β -FeOOH electrode using AB as a substrate was found out to show large discharge capacity of 300 mAh g^{-1} corresponding to the utilization value of 99% of the theoretical capacity.
- 2) The β -FeOOH electrode gave a good high rate discharge performance. Especially, the delivered capacity of the β -FeOOH electrode with AB was reached to the large value of 123 mAh g^{-1} even at high rate discharge of 86 CmA on the basis of theoretical capacity.

References

- 1) K. Amine, H. Yasuda, and M. Yamachi, *J. Power Sources*, **81–82**, 221 (1999).
- 2) A. Funabiki, H. Yasuda, and M. Yamachi, *J. Power Sources*, **119–121**, 290 (2003).
- 3) H. Sakaebe, S. Higuchi, K. Kanamura, H. Fujimoto, and Z. Takehara, *J. Electrochem. Soc.*, **142**, 360 (1995).
- 4) K. Kanno, T. Shirane, Y. Kawamoto, Y. Takeda, M. Takano, M. Ohashi, and Y. Yamaguchi, *J. Electrochem. Soc.*, **143**, 2435 (1996).
- 5) K. Ado, M. Tabuchi, H. Kobayashi, H. Kageyama, O. Nakamura, Y. Inaba, R. Kanno, M. Takagi, and Y. Takeda, *J. Electrochem. Soc.*, **144**, L177 (1997).
- 6) A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada, and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1609 (1997).
- 7) A. Yamada, S. C. Chung, and K. Hinokuma, *J. Electrochem. Soc.*, **148**, A224 (2001).
- 8) N. Imanishi, T. Morikawa, J. Kondo, R. Yamane, Y. Takeda, O. Yamamoto, H. Sakaebe, and M. Tabuchi, *J. Power Sources*, **81–82**, 530 (1999).
- 9) S. Deki, N. Yoshida, Y. Hiroe, K. Akamatsu, M. Mizuhata, and A. Kajinami, *Solid State Ionics*, **151**, 1 (2002).
- 10) S. Deki, *GS News Technical Report*, **62** (2), 46 (2003).