



Short communication

Synthesis of composite electrode materials of FeOOH-based particles/carbon powder and their high-rate charge–discharge performance in lithium cells

Hideyuki Morimoto^{a,*}, Kazuhiko Takeno^b, Yuuki Uozumi^a, Ken-ichi Sugimoto^a, Shin-ichi Tobishima^a

^a Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

^b NTT DOCOMO, INC., 3-6 Hikarino-oka, Yokosuka-shi, Kanagawa 239-8536, Japan

ARTICLE INFO

Article history:

Received 26 January 2011

Received in revised form 14 March 2011

Accepted 16 March 2011

Available online 23 March 2011

Keywords:

Lithium cell

Composite electrode material

FeOOH

High-rate charge–discharge

Amorphous

Iron oxide

ABSTRACT

Composite electrode materials of FeOOH-based particles and carbon powder were prepared with and without heat treatment of composite powder. The composite powder was obtained by hydrolyzing mixed aqueous solutions of FeCl₃, Ti(SO₄)₂ and electron conducting carbon powder as acetylene black (AB) or Ketjen black (KB). FeOOH-based materials formed in the presence of Ti(IV) ions became amorphous and/or low crystalline structure. The composite powder worked as lithium insertion electrode materials in lithium cells using nonaqueous electrolytes including lithium ions. The electrodes exhibited a good cycle performance at large charge–discharge current densities over 5 mA cm⁻² (4 A g⁻¹ per weight of active material). In addition, it was found that the cycle performance was effective process to be improved by the heat treatment of the composite materials. The composite materials such as amorphous FeOOH, α-Fe₂O₃, TiO₂ and electron conductive powder obtained by the heat treatment are one of the promising candidates as electrode materials for energy storage devices, such as lithium-ion batteries and hybrid electrochemical supercapacitors.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Energy storage devices of high-rate charge–discharge operations have been strongly demanded to use as power sources of hybrid cars or electric vehicles. For example, there are researches to enhance the energy density of electric double layer capacitors (EDLC) comprised of active carbon electrodes and the power density of lithium-ion secondary batteries comprised of lithium intercalation electrodes. In addition, a nonaqueous asymmetric hybrid electrochemical supercapacitor comprised of active carbon as the positive electrode material, lithium intercalation material (Li₄Ti₅O₁₂) as the negative electrode, and the nonaqueous solution including lithium ions (1 mol dm⁻³ LiPF₆ in 2:1 volume ratio of ethylene carbonate (EC):dimethyl carbonate (DMC)) was reported to exhibit high power and high energy density [1]. In this case, nano-structured Li₄Ti₅O₁₂ exhibited high capacity even at high-rate charge–discharge. The energy density of the new devices was consequently greater than that of EDLC. Thus, it is very important to use excellent high-rate intercalation electrode materials for an asymmetric hybrid electrochemical supercapacitor.

Composite powders of transition metal oxides such as TiO₂ [2], MnO₂ [3] and γ-Fe₂O₃ [4] and electron conducting carbon powder

such as acetylene black (AB) have recently been synthesized and the new electrodes consisting of them have exhibited good high-rate intercalation performances in nonaqueous electrolytes including lithium ions. On the other hand, Amine has reported that crystalline β-FeOOH with a (2 × 2) tunnel-type structure, which is inexpensive and harmless material, has worked as a positive electrode material for lithium secondary batteries [5]. The low-crystalline β-FeOOH positive electrode showed a discharge capacity of 230 mAh g⁻¹ in the potential range of 4.3 V and 1.6 V vs. Li/Li⁺ and better cycle performance than the high-crystalline one [6].

We have reported that composite electrode materials consisted of needle-like fine particles of high crystalline β-FeOOH with a (2 × 2) tunnel-type structure and carbon powder have been prepared by hydrolyzing 0.1 mol dm⁻³ FeCl₃ aqueous solution in which carbon powder were dispersed at low temperature of 80 °C, and have exhibited good high-rate charge–discharge performances in nonaqueous solutions including lithium ions [7]. For an enhancement of the electrode performances during high-rate charge–discharge, it will be necessary to prepare the fine particle and to improve a stabilization of crystalline structure for the lithium insertion–extraction and an electric conductivity of β-FeOOH. β-FeOOH particles have been synthesized from FeCl₃ aqueous solutions containing Ti⁴⁺, Cr³⁺, Cu²⁺, and Ni²⁺ and their structures have been investigated [8]. Ti⁴⁺ inhibited crystallization and particle growth of β-FeOOH by coprecipitation with Fe³⁺. Composite electrode materials prepared by using FeCl₃ aqueous solution containing Ti⁴⁺ will be advantageous for a high-rate

* Corresponding author. Tel.: +81 277 30 1383; fax: +81 277 30 1380.
E-mail address: morimoto@chem-bio.gunma-u.ac.jp (H. Morimoto).

charge–discharge because they will give a fast diffusion speed and a short diffusion length of lithium ions.

In this paper, composite materials consisted of fine powder of FeOOH–TiO₂ and carbon powder were prepared by a hydrolysis method using FeCl₃ aqueous solution containing Ti⁴⁺ in which electron conducting carbon powder (AB or KB) was dispersed. Then heat treatment was carried out the carbon composite materials. The high-rate charge–discharge performance was estimated, and the effects on the addition of Ti transition metal were investigated by comparison with composite electrode materials containing crystalline β-FeOOH formed without the presence of Ti(IV) ions.

2. Experimental

FeCl₃·6H₂O (Kanto chemical) and ca. 27% Ti(SO₄)₂ (aq.) (Kanto chemical) were used as starting materials. FeCl₃ (aq.) prepared by dissolving FeCl₃·6H₂O in distilled water and Ti(SO₄)₂ (aq.) were mixed in nominal element ratio of Fe:Ti=9:1 (Ti/(Fe+Ti)=0.1). After the solution was stirred for 24 h at 80 °C, the powder formed in the solution was collected by the centrifugal separator. It was washed with distilled water. Then acetylene black (AB; specific surface area 68 m² g⁻¹) or Ketjen black (KB; specific surface area 1270 m² g⁻¹) as carbon powder was put and dispersed in the solutions. It was stirred for 24 h at 80 °C and the powder in the solution was removed by filter and washed with distilled water. Then heat treatment was carried out for 1 h at 350 °C in air. Composite powder of crystalline β-FeOOH and AB was obtained by means of the hydrolysis of 0.1 mol dm⁻³ FeCl₃ (aq.) [6]. Composite powder of α-Fe₂O₃ and AB was prepared by heat treatment of composite powder of β-FeOOH and AB. A content of the active material in the composite powder was determined from the weight change. X-ray diffraction measurements were carried out to examine crystalline structure. The electrodes consisting of the composite materials were prepared from the slurry of the composite powder (90 wt%) and polyvinylidene fluoride (PVdF, 10 wt%) dissolved in N-methyl pyrrolidinone (NMP) as a binder. The electrode material slurry spread on the nickel mesh of the collector was dried at 80 °C. It was pressed and dried in vacuum at 120 °C. It was used as a working electrode. Lithium sheet of ca. 500 μm in thickness was used as a counter electrode and a reference electrode. The mixture of propylene carbonate (PC) containing 1 mol dm⁻³ LiClO₄ was used as the electrolyte. Electrochemical three-electrode cells (beaker cell) were constructed in a dry argon-filled glove box. The electrochemical cells were discharged and charged between 1.5 and 4.0 V (vs. Li/Li⁺) under various constant current densities. Cyclic voltammetry (CV) measurements were carried out between 1.0 and 4.0 V (vs. Li/Li⁺) at room temperature.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of products formed with and without Ti⁴⁺. The carbon powder is not in the products. The β-FeOOH peaks of powder formed in a solution without Ti(SO₄)₂ are sharp. The peaks of sample prepared by hydrolyzing of FeCl₃+Ti(SO₄)₂ (aq.) became broad. The weak peaks contributed to anatase-TiO₂ appear. Therefore their results mean that the powder of amorphous and/or low crystalline β-FeOOH and anatase-TiO₂ (amorphous FeOOH-based materials) were formed. Similar results were obtained for carbon composite material prepared by hydrolyzing FeCl₃+Ti(SO₄)₂ (aq.) except that the weak peaks contributed to β-FeOOH were detected. It was confirmed by scanning electron microscope (SEM) observations that the addition of Ti(SO₄)₂ has changed the shape of particles and decreased particle size as shown in Fig. 2. The results of XRD measurements and SEM observations suggested that both crystalline structure and the shape of particles were changed by adding of Ti(SO₄)₂. Fig. 3

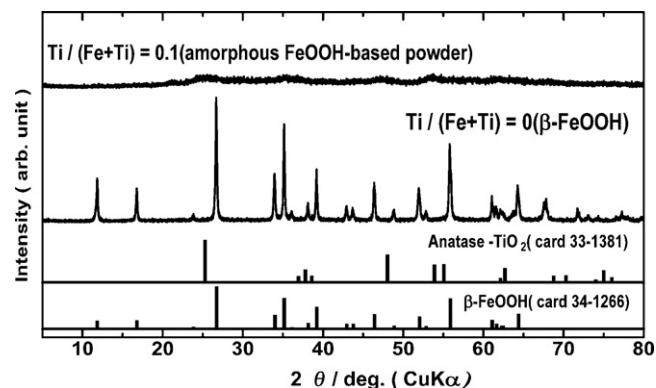


Fig. 1. X-ray diffraction patterns of products formed with and without Ti⁴⁺. The samples are free from carbon.

shows TEM images of the AB composite powder of β-FeOOH and amorphous FeOOH-based powder. It was found that morphology of particle of the AB composite powder of amorphous FeOOH-based powder made by adding Ti(SO₄)₂ is different compared with that of the particle of the AB composite powder of β-FeOOH. The content (wt%) of the deposit in the composite powder was estimated from the difference between the weight of carbon powder (AB) using as a starting material and the weight of the carbon composite material. The content of the deposit in composite powder formed with and without Ti⁴⁺ was calculated to be around 25 and 19 wt%, respectively. Fig. 4 shows first charge–discharge curves of carbon composite electrodes formed with and without Ti⁴⁺. The abscissa in Fig. 4 was drawn as a capacity per weight of the deposit (active material) in the composite electrodes. The composite electrodes exhibit the high capacity over 150 mAh g⁻¹ at the high current density of 5.0 mA cm⁻². Their curves show the different potential behavior. The discharge potential gradually decreased without any step with an increase in time. The discharge behavior of the composite electrode material formed with Ti⁴⁺ was similar to that of the lithium insertion amorphous electrode materials. Such the results may be consistent with the view that

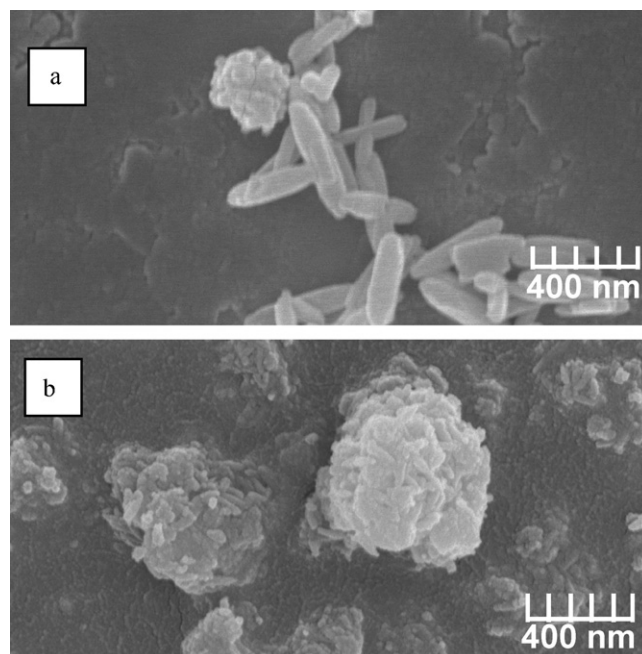


Fig. 2. SEM images of β-FeOOH and amorphous FeOOH-based powder.

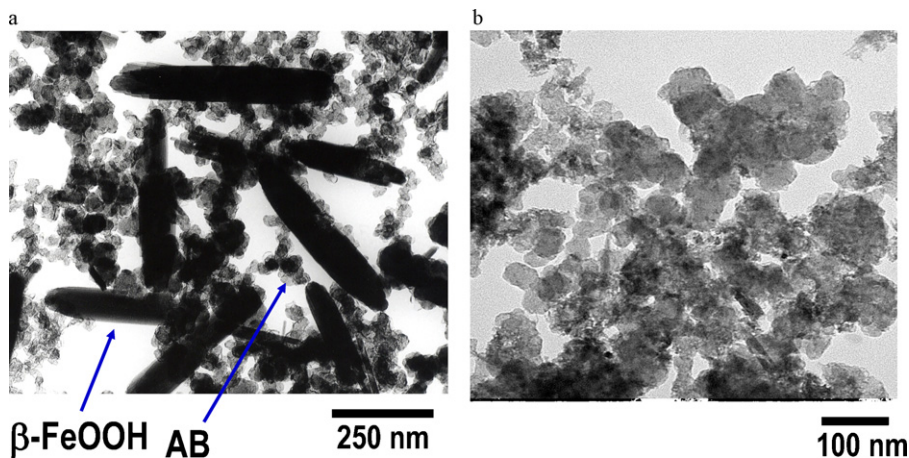


Fig. 3. TEM images of (a) the AB composite powder of β -FeOOH and (b) amorphous FeOOH-based powder.

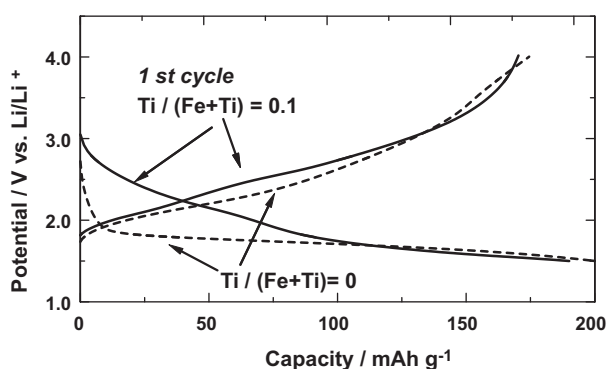


Fig. 4. First charge–discharge curves of composite electrodes formed with and without Ti^{4+} .

X-ray diffraction patterns of the sample formed with Ti^{4+} show halo. Fig. 5 shows the cycle performance of composite electrodes at constant current density of 5.0 mA cm^{-2} between 1.5 and 4.0 V. Cycle performance of the composite electrode formed with Ti^{4+} is superior to that formed without Ti^{4+} . It was confirmed by X-ray diffraction measurement that the crystalline structure of β -FeOOH after charge–discharge measurement has been broken. It can be presumed that the amorphous and/or low crystalline samples of β -FeOOH inhibit the volume change in the insertion–extraction reaction of lithium ions for the electrodes and bring about the formation of the fine particles to maintain better electronic contact during charge–discharge. Therefore the composite electrode

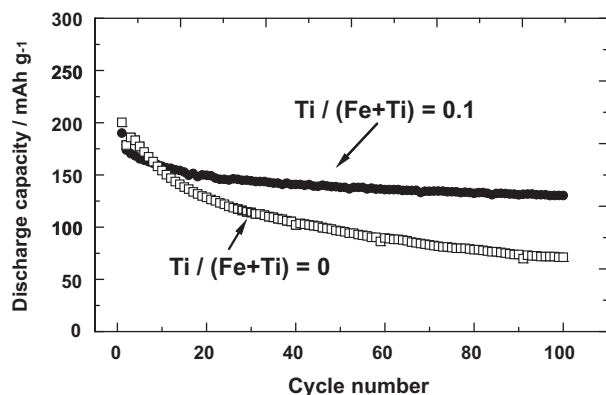


Fig. 5. Cycle performance of composite electrodes at constant current density of 5.0 mA cm^{-2} between 1.5 and 4.0 V.

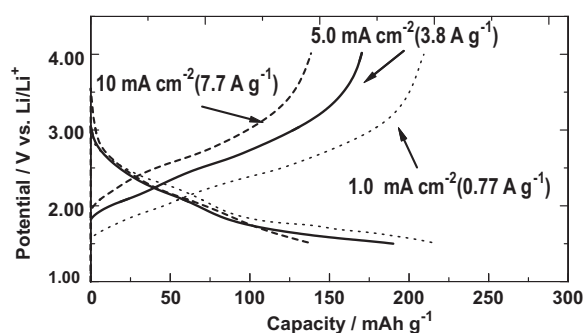


Fig. 6. First charge–discharge curves of the composite material formed in a solution including $\text{Ti}(\text{SO}_4)_2$ at the various current densities ($1, 5,$ and 10 mA cm^{-2}).

formed with Ti^{4+} must exhibit the good cycle life. Fig. 6 shows first charge–discharge curves of the composite material formed with Ti^{4+} at the various current densities ($1.0, 5.0,$ and 10 mA cm^{-2}). The composite material works as a rechargeable electrode and exhibits the high capacity over 125 mAh g^{-1} even at the high current density of 10 mA cm^{-2} (around 7.5 A g^{-1}). Fig. 7 shows cycle performances of composite electrodes formed with Ti^{4+} at the constant current densities of 5.0 and 10 mA cm^{-2} between 1.5 and 4.0 V. Capacity retention at the current density of 10 mA cm^{-2} is superior to that at the current density of 5.0 mA cm^{-2} . The electrodes show good cycle life, suggesting that the amount of the lithium insertion into active material may influence the cycle properties.

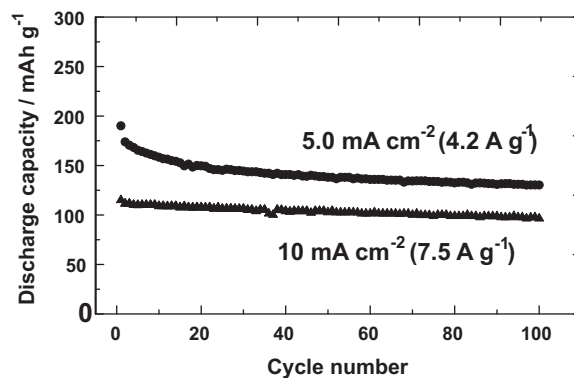


Fig. 7. Cycle performance of composite electrodes formed in a solution including $\text{Ti}(\text{SO}_4)_2$ at the constant current densities of 5.0 and 10 mA cm^{-2} between 1.5 and 4.0 V.

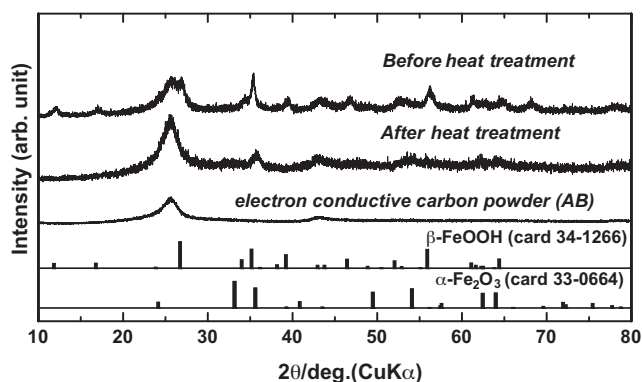


Fig. 8. X-ray diffraction patterns of the samples before and after heat treatment of the composite powder of amorphous FeOOH and AB.

Fig. 8 shows X-ray diffraction patterns of the samples before and after heat treatment of the composite powder of amorphous FeOOH and AB. The sample before heat treatment shows the weak peaks due to β -FeOOH and AB in the halo pattern. On the other hand, the sample after heat treatment also shows halo patterns but the peaks due to β -FeOOH disappeared and the weak peaks due to α -Fe₂O₃ were observed. It was suggested that the sample should maintain the amorphous structure and α -Fe₂O₃ was formed by thermal decomposition of β -FeOOH at 350 °C in air (2β -FeOOH \rightarrow α -Fe₂O₃ + H₂O). It was confirmed by scanning electron microscope (SEM) observations that the particle size before and after heat treatment of amorphous FeOOH-based material was about 80 nm. Fig. 9 shows FT-IR spectra of the particles before and after heat treatment for β -FeOOH and amorphous FeOOH-based materials without AB. Spectra due to TiO₂ were confirmed by FT-IR measurements for amorphous FeOOH without AB. Thus, for carbon composite material before heat treatment, it is suggested that amorphous FeOOH, β -FeOOH, TiO₂ and AB are to present. For the sample after heat treatment, it suggested that amorphous FeOOH, α -Fe₂O₃, TiO₂ and AB are to present. Component of composite powder of amorphous FeOOH and KB was similar to that of the composite powder of amorphous FeOOH and AB described above. Fig. 10 shows the first cyclic voltammogram of the samples before and after heat treatment of the composite materials of amorphous FeOOH-based powder and AB powder. Sharp redox peaks were not observed for both electrodes. The behavior was characteristic with regard to that of other amorphous electrodes. Fig. 11 shows first charge–discharge curves of the electrode materials before and after heat treatment of the composite materials of the amorphous FeOOH-based powder and AB powder. The abscissa in Fig. 11 was drawn as a capacity per weight of the FeOOH-based amorphous materials (active materials) in the composite electrodes. First discharge potential of both composite electrodes

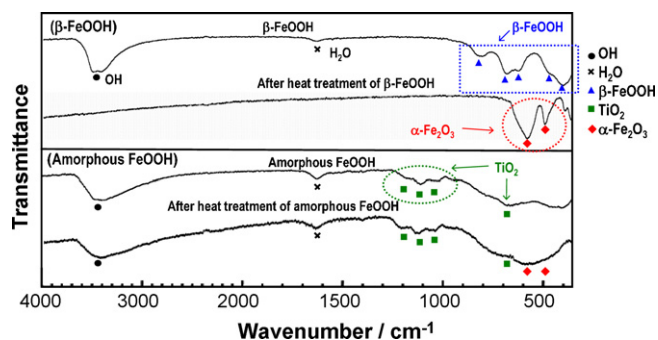


Fig. 9. FT-IR spectra of the particles before and after heat treatment for β -FeOOH and amorphous FeOOH-based materials without AB.

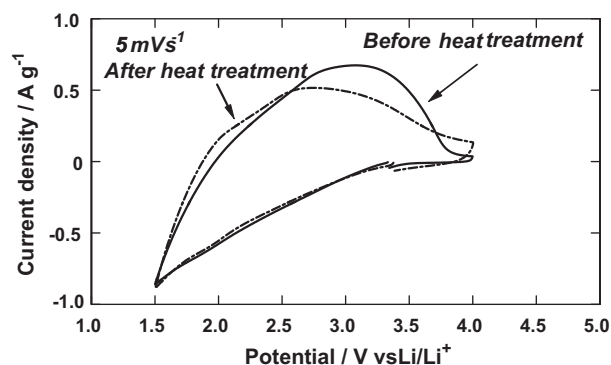


Fig. 10. First cyclic voltammogram of the composite materials of amorphous FeOOH-based powder and AB powder.

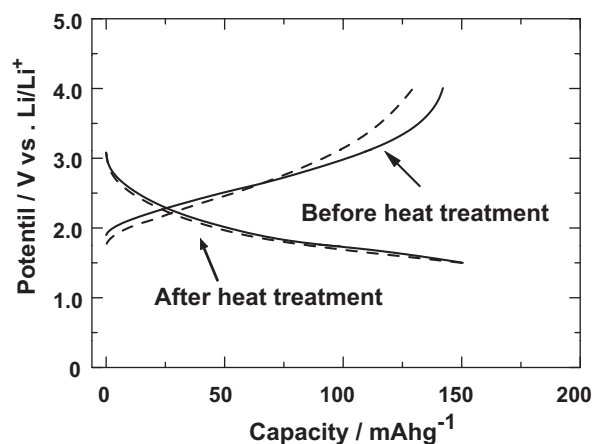


Fig. 11. First charge–discharge curves of the electrode materials before and after heat treatment of the composite materials of the amorphous FeOOH-based powder and AB powder.

gradually decreased without any step with an increase in time as showed in Fig. 6, suggesting that the electrode materials had amorphous structures. Fig. 12 shows cycle performance the various composite electrodes with AB during cycling. Both the composite electrodes exhibit the capacities over 150 mAh g⁻¹ during first discharge. The capacity degradation of the composite electrode after heat treatment is small compared with that before heat treatment during a few cycles. The crystalline structure of β -FeOOH in the composite material before heat treatment may be unstable to the

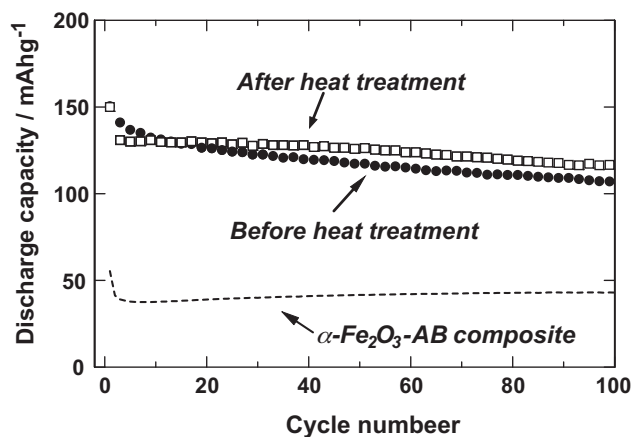


Fig. 12. Cycle performance of the various composite electrodes with AB during cycling.

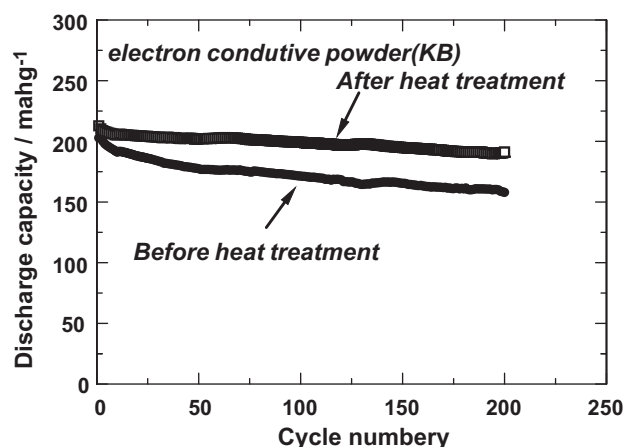


Fig. 13. Cycle performance before and after heat treatment of the composite powder of amorphous FeOOH and KB.

electrochemical lithium insertion–extraction during a few cycles because it was conformed by X-ray diffraction measurements that crystalline β -FeOOH had been amorphous after 100 cycle for Li/electrolyte/ β -FeOOH–AB cell. Li/electrolyte/ α -Fe₂O₃–AB cell, on the contrary, exhibited good cycle performance but the discharge capacity (45 mAh g⁻¹) decreased. Since the electrode material obtained by heat treatment of amorphous FeOOH-based material was free from the crystalline β -FeOOH, the capacity degradation during cycling will be inhibited. It may be noted that heat treatment was effective process to improve the cycle performance. Fig. 13 shows cycle performance of the electrodes before and after heat treatment of the composite materials of amorphous FeOOH and KB. The electrodes after heat treatment exhibit the high capacity over 200 mAh g⁻¹ and superior cycle performance. It was found that the properties of the composite electrodes depended on the electron conducting carbon powder.

4. Conclusions

β -FeOOH formed in the presence of Ti(IV) ions became amorphous and/or low crystalline materials. The composite material containing carbon prepared in the presence of Ti(IV) ions worked as a lithium insertion electrode in nonaqueous electrolytes including lithium ions. The electrodes maintained the high capacity at large charge–discharge current density. Cycle performance of the composite electrode formed in the presence of Ti(IV) ions is superior to that formed without Ti⁴⁺. The capacity retention was excellent at large charge–discharge current density. The composite materials are one of the promising candidates as electrode materials for energy storage devices that require high-power operations. We are studying on a role of Ti transition metal and/or TiO₂.

The composite electrode materials of amorphous FeOOH and carbon were improved by heat treatment under thermal decomposition temperature of carbon powder. Amorphous FeOOH and crystalline α -Fe₂O₃ after heat treatment must be based on the high stability for electrochemical lithium insertion–extraction. The composite electrodes of amorphous FeOOH and KB after heat treatment exhibit the high capacity and superior cycle performance. Since KB powder have higher specific surface area than that of AB powder, electron and lithium ion conducting network of the composite powder using KB should produce optimum conditions for electrochemical reactions.

References

- [1] G.G. Amatucci, F. Badway, A.D. Pasquier, T. Zheng, J. Electrochem. Soc. 148 (2001) PA930.
- [2] M. Hibino, K. Abe, M. Mochizuki, M. Miyayama, J. Power Sources 126 (2004) 139.
- [3] M. Hibino, H. Kawaoka, H.S. Zhou, I. Honma, J. Power Sources 124 (2003) 143.
- [4] M. Hibino, J. Terashima, T. Yao, J. Electrochem. Soc. 154 (2007) A1107.
- [5] K. Amine, H. Yasuda, M. Yamachi, J. Power Sources 81–82 (1999) 221.
- [6] A. Funabiki, H. Yasuda, M.J. Yamachi, Power Sources 119–121 (2003) 290.
- [7] H. Morimoto, K. Takeno, Y. Uozumi, K. Sugimoto, S. Tobishima, Electrochemistry 73 (2005) 336.
- [8] T. Ishikawa, R. Katoh, A. Yasukawa, K. Kandori, T. Nakayama, F. Yuse, Corros. Sci. 43 (2001) 1727.