FULL PAPER

Synthesis of $\text{H}_2\text{Ti}_{12}\text{O}_{25}$ containing fine carbon particles by impregnation method using porous titanium hydroxide

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$\text{H}_2\text{Ti}_{12}\text{O}_{25}$ (HTO) is a negative-electrode oxide material for Li-ion batteries with high capacity and repetition stability. To improve the conductive performance of HTO, porous titanium hydroxide powder containing fine carbon particles was synthesized by hydrolyzing TiOSO_4 solution with fine carbon particles, and a HTO containing fine carbon particles was synthesized by impregnation method using its porous titanium hydroxide. The charge–discharge properties of this sample were characterized, and its Li insertion and extraction performance was generally higher than that of HTO without C prepared by solid-state and impregnation methods.

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Key-words : $\text{H}_2\text{Ti}_{12}\text{O}_{25}$, Li-ion battery, Porous titanium hydroxide, C-composite, Impregnation method

[Received December 20, 2018; Accepted April 3, 2019]

1. Introduction

$\text{H}_2\text{Ti}_{12}\text{O}_{25}$ (hereafter “HTO”) is one of the most attractive negative electrode materials for Li-ion batteries.^{1)–6)} Titanium oxide-based materials generally have poor conductivities, and conductive additives such as a carbon black are added during electrode fabrication. To improve the conductive performance, various methods have been developed, including reducing the particle size,^{7),8)} doping with metal ions,^{9),10)} coating with conductive materials,^{11),12)} and using composites with conductive materials.^{13),14)}

We previously reported an improvement in the electrochemical performance of submicrometer-sized HTO synthesized from $\text{Na}_2\text{Ti}_3\text{O}_7$ ground by ball-milling.⁵⁾ We also reported a new synthesis process for creating smaller-sized HTO without grinding using the impregnation method.⁶⁾ In this method, the titanium source was porous titanium hydroxide synthesized by hydrolyzing titanium oxide sulfate (TiOSO_4) solution. When fine carbon particles as conductive additives were suspended in the solution, it was possible to synthesize porous titanium hydroxide containing fine carbon particles that became nucleation centers. By using this titanium hydroxide, it was possible to synthesize HTO containing fine carbon particles, termed “C-composite HTO”.

In this study, we synthesized C-composite HTO by the impregnation method and investigated the effect of the C-

composite on the electrochemical properties at different current densities (10, 100, and 200 mA/g).

2. Experimental

2.1 Synthesis of C-composite HTO

C-composite porous titanium hydroxide was synthesized by TiOSO_4 solution with fine carbon particles using urea as follows: 6.25 g titanium oxide sulfate hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$, $x = 2\text{--}5$, Alfa Aesar, A. Johnson Matthey Co.) was dissolved in ion-exchange water with 7 cm³ sulfuric acid (assay 95%, Wako Pure Chemical Industries). Fine carbon particles (50 or 100 mg) (Super C65, Imerys Graphite & Carbon Belgium SA) and 30 g urea (assay 99%, Kojundo Chemical Laboratory Co.) were added to the solution, and the volume was adjusted to 250 cm³ with ion-exchange water. Urea is hydrolyzed to NH_3 and CO_2 by heating, and NH_3 functions as a precipitant. The solution was heated in a glass flask at 368 K for 1.5 h while stirring. The solution vessel was then cooled in water to stop the hydrolysis reaction, and the resulting product was washed thrice with ion-exchange water using ultrasonic agitation and centrifuging (3000 rpm, 10 min). The sample was then dried at 333 K for 12 h. About 2.5 g of C-composite titanium hydroxide was obtained during one experiment. Hereafter, the C-composite titanium hydroxides synthesized with fine carbon particles of 50 and 100 mg are referred to as TH-1 and TH-2, respectively. For comparison, titanium hydroxide without fine carbon particles was synthesized (referred to as TH-3).

The obtained sample was immersed in 216 g/dm³ Na_2CO_3 (assay 99%, Kojundo Chemical Laboratory Co.) solution at a concentration of 1 g sample per 100 cm³ solution, and ultrasonically dispersed for 5 min. The sample

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[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.127.P6-1>

was separated by filtration and dried at 333 K for 12 h. It was then heated at 1073 K for 10 h in Ar gas at a heating rate of 10 K/min, and C-composite $\text{Na}_2\text{Ti}_3\text{O}_7$ was obtained.

C-composite HTO was synthesized by Na^+/H^+ ion-exchange of C-composite $\text{Na}_2\text{Ti}_3\text{O}_7$ and sequentially annealed as follows: the sample was immersed in 0.5 M HCl for three days at 333 K at a concentration of 1 g sample per 250 cm^3 solution, washed with ion-exchange water, and dried at 333 K for 12 h. The sample was finally annealed at 553 K for 5 h in Ar gas, affording C-composite HTO. Hereafter, the C-composite HTO synthesized using sample TH-1 and TH-2 are referred to as HTO-1 and HTO-2, respectively. For comparison, HTO samples without C-composite were prepared by impregnation and solid-state methods (referred to as HTO-3 and HTO-4, respectively).^{1),6)}

2.2 Characterization of samples

Morphological and elemental analysis of the samples was performed by scanning electron microscopy (SEM, JSM-5400 and JCM-6000, JEOL) with energy dispersive X-ray spectrometry (EDS). The structural properties of the sample were studied using X-ray diffractometry (XRD, RINT2550V, Rigaku Co.). The C-content of the sample was measured as follows: C-composite HTO was first heated at 1073 K for 10 h in Ar gas to completely dehydrate the sample. The dehydrated sample was then subjected to thermogravimetric analysis (TG, TG-DTA2000, Mac Science) in air from 298 to 1073 K. Assuming that the compound remaining after the TG analysis was TiO_2 , the observed weight loss represented the C-content of the sample.

Electrochemical Li insertion and extraction experiments were conducted using Li coin-type cells. The working electrode was formed by mixing sample:acetylene black:polytetrafluoroethylene at a ratio of 5:5:1 (mg) and sequentially pressing the mixture onto an Al mesh 15 mm in diameter under a pressure of 20 MPa. The electrical test cell was constructed in a stainless-steel coin-type configuration. The counter electrode was a Li foil 20 mm in diameter, and the separator was a microporous polypropylene sheet. The electrolyte was a solution of 1 M LiFP_6 in a 50:50 mixture of ethylene carbonate and diethyl carbonate by volume (Kishida Chemical Co., Ltd.). The cell was constructed in an argon-filled glove box, and electrochemical measurements were performed at 298 K with a battery charge–discharge system (HJ-SD8, Hokuto Denko Co.). The measurement voltage ranged from 3.0 to 1.0 V, and the current densities per unit mass of the HTO sample were 10, 100 and 200 mA/g. The specific capacities of the samples were calculated on the basis of only HTO weight except C-content.

3. Results and discussion

3.1 Synthesis of C-composite HTO

Figure 1 shows SEM images of the titanium hydroxide samples with different amounts of fine carbon particles.

Fig. 1. SEM images of the titanium hydroxide samples with different amounts of fine carbon particles. (a): Titanium hydroxide synthesized with 50 mg fine carbon particles (Sample TH-1). (b): Titanium hydroxide synthesized with 100 mg fine carbon particles (Sample TH-2). (c): Titanium hydroxide synthesized without fine carbon particles (Sample TH-3).

Samples TH-1 and TH-3 had similar morphologies, consisting of spherical particles about $2\text{ }\mu\text{m}$ in diameter, with some aggregation. Because no fine carbon particles were observed in sample TH-1 by SEM, they were believed to be incorporated in the titanium hydroxide sample. However, sample TH-2 had spherical particles about $2\text{ }\mu\text{m}$ in diameter together with much smaller particles. Because the area containing these smaller particles contained a large amount of carbon based on EDS point analysis, many fine carbon particles were considered to be aggregated, existing separately rather than being incorporated in the titanium hydroxide particles. The C-contents of samples TH-1 and TH-2 were 1.0 and 6.5 wt %, respectively. This indicates that it is difficult to synthesize C-composite titanium hydroxide with large amounts of fine carbon particles using this method. The X-ray diffraction patterns of the samples indicate an anatase-like amorphous structure.

Fig. 2. SEM images of HTO samples synthesized by impregnation and solid-state methods. (a): HTO sample synthesized by impregnation method using sample TH-1 (Sample HTO-1). (b): HTO sample synthesized by impregnation method using sample TH-2 (Sample HTO-2). (c): HTO sample synthesized by impregnation method using sample TH-3 (Sample HTO-3). (d): HTO sample synthesized by solid-state method without C-composite (Sample HTO-4).

Figure 2 shows SEM images of HTO samples synthesized by impregnation and solid-state methods. Samples HTO-1 and HTO-3 were aggregated with more anisotropic particles, such as needle and rod-like particles, and they showed minimal difference in particle shape. At this time, the existence of fine carbon particles could not be observed, as shown in Fig. 2(a). However, sample HTO-2 was aggregated with more anisotropic and much smaller particles, which may have been fine carbon particles, and many HTO and fine carbon particles were considered to exist separately. Sample HTO-4 synthesized by the solid-state method was aggregated with less anisotropic particles, which were large compared with the samples prepared by the impregnation method.

Figure 3 shows an XRD pattern for sample HTO-1. Other samples prepared by the impregnation method gave similar XRD patterns, and that for the sample prepared by the solid-state method was also similar except that the peak at $2\theta = 24.6^\circ$, corresponding to the (110) plane,^{4),15)} was generally smaller.⁶⁾

3.2 Electrochemical Li insertion and extraction evaluation of C-composite HTO

Figure 4 shows the first cycle of electrochemical Li insertion and extraction curves for the HTO samples except for sample HTO-2, due to inadequate C-composite sample, at different current densities. **Figure 5** shows the relationship between the specific capacities and current densities of these samples at the first and tenth cycles. Flat potential plateaus were observed for all experiments at

Fig. 3. XRD pattern for HTO sample synthesized by impregnation method using sample TH-1 (Sample HTO-1).

approximately 1.5 V (versus Li/Li^+) for Li insertion and at 1.6 V or above for Li extraction. Voltage differences in the flat potential plateaus between samples were rarely observed at 10 and 100 mA/g. Small differences were observed at 200 mA/g due to the lack of aging, and the difference decreased as the cycle number increased. The specific capacities of these samples decreased with current density because Li insertion and extraction could not be followed up at higher current densities due to the poor conductive performance. The specific capacities of sample HTO-1 were usually higher than those of the other samples. As the electrical conductivities of the powder compact of these samples were out of range (below $1 \times 10^{-7} \text{ S}$), it is difficult to quantitatively compare the

Fig. 4. Electrochemical Li insertion and extraction curves for the HTO samples at the first cycle. Sample HTO-1: HTO sample synthesized by impregnation method using sample TH-1. Sample HTO-3: HTO sample synthesized by impregnation method using sample TH-3. Sample HTO-4: HTO sample synthesized by solid-state method without C-composite. Sample HTO-2 was not tested due to inadequate C-composite sample.

Fig. 5. Relationship between specific capacities and current densities of HTO samples. Sample HTO-1: HTO sample synthesized by impregnation method using sample TH-1. Sample HTO-3: HTO sample synthesized by impregnation method using sample TH-3. Sample HTO-4: HTO sample synthesized by solid-state method without C-composite. Sample HTO-2 was not tested due to inadequate C-composite sample.

Fig. 6. Cycling performance of the HTO samples at 200 mA/g. Sample HTO-1: HTO sample synthesized by impregnation method using sample TH-1. Sample HTO-3: HTO sample synthesized by impregnation method using sample TH-3. Sample HTO-4: HTO sample synthesized by solid-state method without C-composite. Sample HTO-2 was not tested due to inadequate C-composite sample.

conductive performances of these samples. However, the Li insertion and extraction reaction of sample HTO-1 was considered to occur more easily than with other samples because the smaller particle size and C-composite were contributed to improving the conductive performance by shortening the electrical conductive path.

Figure 6 shows the cycling performance of the HTO samples at 200 mA/g. A reversible Li insertion-extraction performance with a relatively high capacity exceeding 180 mAh/g was observed for sample HTO-1, about 10 mAh/g larger than that of HTO without C synthesized by the impregnation method (sample HTO-3) and about 25 mAh/g larger than that of HTO without C synthesized by the solid-state method (sample HTO-4). The improvement can be explained by the increasing utilization rate of the HTO sample due to its smaller sample size and the C-composite. The discharge capacity retention rate of sample HTO-1 was 98% after 100 cycles.

4. Conclusion

We developed C-composite HTO by an impregnation method. This showed an improved performance as the negative electrode of a Li-ion battery because of an enhanced conductive performance due to a smaller particle size and the C-composite.

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