Synthesis of H$_2$Ti$_{12}$O$_{25}$ with anisotropic morphology by impregnation of Na$_2$CO$_3$ solution into porous titanium hydroxide

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H$_2$Ti$_{12}$O$_{25}$ (HTO) is a negative-electrode oxide materials used in Li-ion batteries that has higher capacity and repetition stability. We developed a new process for synthesizing Na$_2$Ti$_6$O$_{13}$ by impregnation of Na$_2$CO$_3$ solution into porous titanium hydroxide and synthesized Na$_2$Ti$_3$O$_7$ with higher anisotropic morphology. HTO with higher anisotropic morphology was synthesized by ion-exchange using soft-chemical synthesis and subsequent annealing. The HTO with higher anisotropic morphology was smaller and exhibited better performance in its Li insertion and extraction than that derived from Na$_2$Ti$_3$O$_7$ synthesized by the solid-state method.

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1. Introduction

Li-ion batteries are widely used for energy storage in cell phones, portable computers, and other electronic devices due to the advantages of high energy density, high working voltage, and long cycle life. They are also attractive for electric vehicles and stationary storage of electricity for homes. Currently, graphite-based materials are commercially used as a negative electrode in Li-ion batteries. However, they suffer from a poor rate-capability, solvent co-intercalation, and serious safety problems during repeated charge–discharge cycling, such as the formation of dendritic deposits of metal lithium. Other negative electrode materials are currently being investigated to replace the graphite-based materials. Among these, titanium oxide-related materials such as Li$_2$Ti$_3$O$_5$, TiO$_2$, TiO$_2$B and H$_2$Ti$_{12}$O$_{25}$ (hearafter “HTO”) have attracted great interest as negative electrode materials for new Li-ion batteries with long-term cycling stability, reliable safety and good rate-capability.

HTO is one of the most attractive negative electrode materials for Li-ion batteries. It has reversible electrochemical Li insertion and extraction profiles at 1.55 V vs. Li/Li$^+$ similar to Li$_4$Ti$_5$O$_{12}$ and higher charge and discharge capacities (over 200 mAh/g) than that of Li$_4$Ti$_5$O$_{12}$. HTO can be synthesized by Na$^+/H^+$ ion-exchange with Na$_2$Ti$_6$O$_{13}$ using soft-chemical synthesis and subsequent annealing. To improve the electrochemical performance of HTO, we previously synthesized HTO from Na$^+/H^+$ ion-exchangers of Na$_2$Ti$_3$O$_7$ with an isotropic shape. Because the particle size of the precursor Na$_2$Ti$_3$O$_7$ is smaller than that of Na$_2$Ti$_3$O$_7$, the HTO sample synthesized from Na$_2$Ti$_3$O$_7$ had smaller particles than that synthesized from Na$_2$Ti$_3$O$_7$ as well as superior electrochemical performance. However, Na$_2$Ti$_3$O$_7$ could only be Na$^+/H^+$ ion-exchanged through an Na$^+/Li^+$ ion-exchanger, while Na$_2$Ti$_3$O$_7$ can be directly Na$^+/H^+$ ion-exchanged. Therefore, Na$_2$Ti$_3$O$_7$ is a better precursor than Na$_2$Ti$_3$O$_7$ from the viewpoint of HTO production. We also studied the improvement in electrochemical performance of HTO synthesized from Na$_2$Ti$_3$O$_7$ ground by ball-milling. The ball-milled Na$_2$Ti$_3$O$_7$ had a 0.2 µm average particle size, and the charge and discharge capacities of HTO synthesized from Na$_2$Ti$_3$O$_7$ ground by ball-milling exceeded that of an HTO sample without treatment. The initial coulombic efficiency was decreased because of the reactivity between the electrolytic solution and smaller particles less than 0.2 µm in size formed by overgrinding during ball-milling. These results indicate that the electrochemical performance of HTO depends on the morphology of the starting compound, such as its particle size and shape. In the present study, we developed a new synthesis process for creating smaller-size Na$_2$Ti$_3$O$_7$ without grinding, synthesizing it by the impregnation of Na$_2$CO$_3$ solution into porous titanium hydroxide and subsequent heating. The obtained Na$_2$Ti$_3$O$_7$ was evaluated, and HTO was synthesized by ion-exchange using soft-chemical synthesis and subsequent annealing. In addition, the electrochemical properties of the obtained HTO sample was evaluated.

2. Experimental

2.1 Synthesis of Na$_2$Ti$_3$O$_7$ by impregnation

Porous titanium hydroxide was synthesized by self-hydrolysis of titanium oxide sulfate (TiOSO$_4$) solution as follows: 6.25 g titanium oxide sulfate hydrate (TiOSO$_4$·xH$_2$O, x = 2–5, Alfa Aesar, A. Johnson Matthey Co.) was dissolved in an ion-exchange water with 7 cm$^3$ sulfuric acid (Assay 95%, Wako Pure Chemical Industries, Ltd.) and adjusted to 250 cm$^3$ by ion-exchange water. The solution was heated in a glass flask at 358 K for 1.5 h while being stirred. The solution vessel was then cooled in water to stop the self-hydrolysis reaction and the resulting product was washed three times with ion-exchange water using ultrasonic agitation and centrifuging (3000 rpm, 10 min). After that, the sample was dried at 333 K for 12 h. About 0.5 g of titanium hydroxide was obtained in one experiment.

The obtained sample was immersed in Na$_2$CO$_3$ (Assay 99%, Kojundo Chemical Laboratory Co., Ltd.) solution at a rate of 1 g sample against 100 cm$^3$ solution, and dispersed for 5 min by ultrasonic agitation. The concentrations of Na$_2$CO$_3$ solution were...
between 144 and 240 g/dm$^3$. The samples were separated by filtration and dried at 333 K for 12 h. The samples were then heated at 1073 K for 10 h in air at a 10 K/min heating rate.

2.2 Synthesis of HTO by soft-chemical synthesis and annealing

When the above-mentioned sample consisted almost entirely of Na$_2$Ti$_3$O$_7$, Na$^+$/$\text{H}^+$ ion-exchange of the sample was conducted by soft-chemical synthesis. The sample was immersed in 0.5 M HCl solution for three days at 333 K at a rate of 1 g sample against 250 cm$^3$ solution, similar to the conditions in previous literature, and an H$_2$Ti$_3$O$_7$ sample was obtained. After the acidic treatment, the produced H$_2$Ti$_3$O$_7$ sample was washed by ion-exchange water, and then dried at 333 K for 12 h. An HTO sample was synthesized by annealing the H$_2$Ti$_3$O$_7$ sample at 533 K for 5 h in air.

2.3 Characterization of sample

The morphologies of the samples were observed by scanning electron microscope (SEM, JSM-5400, JEOL Ltd.), and the constituent elements of the sample were analyzed by energy dispersive X-ray spectrometer (EDS, JED-2100, JEOL Ltd.). The structural properties of the sample were studied using an X-ray diffractometer (XRD, RINT2550V, Rigaku Co.). Specific surface areas and pore sizes of the sample were measured by a volumetric gas adsorption technique (BELSORP-mini, BEL JAPAN, Inc.).

Electrochemical Li insertion and extraction experiments were performed using Li coin-type cells. The working electrode was prepared by mixing HTO sample: acetylene black: polytetrafluoroethylene = 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 cells were constructed in a stainless steel coin-type configuration. The counter electrode was a 20 mm diameter Li foil. The separator was a microporous polypropylene sheet. A solution of 1 M LiPF$_6$ in a 50:50 mixture of ethylene carbonate and diethylcarbonate by volume (Kishida Chemical Co., Ltd.) was used as the electrolyte. Cells were constructed in an argon-filled glove box, and electrochemical measurements were carried out at 298 K by a battery charge-discharge system (HJ-SD8, Hokuto Denko Co.). The measurement voltage ranged between 3.0 and 1.0 V, and the current density per unit mass of the HTO sample was 10 mA/g.

3. Results and discussion

3.1 Synthesis of Na$_2$Ti$_3$O$_7$ by impregnation

Figure 1(A) presents an SEM image and EDS result for the titanium hydroxide sample. The sample consisted of almost spherical particles 1–5 μm in diameter, with some particles aggregated with each other. The sample included no Na and only a little S, such as sulfate-ions. This S could be removed by immersion in an alkali solution, such as Na$_2$CO$_3$. The sample exhibits the X-ray diffraction pattern of an anatase-like amorphous structure. The specific surface area of this sample was 150 m$^2$/g and the average pore size was 3.7 nm. These results indicate that the obtained sample was a porous particle.

Figure 1(B) presents a typical SEM image and EDS result for the titanium hydroxide sample after impregnation with Na$_2$CO$_3$ solution. The sample morphology after impregnation was almost the same as that of the as-synthesized sample. In addition, the EDS result reveals that the sample included Na. Based on these results, we concluded that Na$_2$CO$_3$ was impregnated into the porous titanium hydroxide.

Figure 2 presents SEM images of the samples heated at 1073 K after impregnation into different concentrations of Na$_2$CO$_3$ solution. For comparison, the SEM image of Na$_2$Ti$_3$O$_7$ sample synthesized by the solid-state method was added. Figure 3 presents a schematic diagram of the synthesis of sodium titanate using the impregnation method and solid-state method. The samples were aggregated with higher anisotropic particles, such as needle and rod-like particles, independent of the concentration of Na$_2$CO$_3$ solution. On the other hand, the sample synthesized by solid-state method was aggregated with lower anisotropic particles. The formation of these particles with higher anisotropic morphologies could be considered to occur as follows. As seen in the schematic diagram of Fig. 3, Na$_2$CO$_3$ impregnated in the porous titanium hydroxide particle exists in or on any points of titanium hydroxide. During heat treatment, many nuclei of Na$_2$Ti$_3$O$_7$ were synthesized in or on the porous titanium hydroxide by a solid-state reaction of titanium hydroxide and Na$_2$CO$_3$ at first, and then Na$_2$Ti$_3$O$_7$ crystals were grown. As a result, many Na$_2$Ti$_3$O$_7$ crystals were formed from one porous titanium hydroxide particle, and each crystal had an anisotropic shape because of crystal growth with a specific orientation. Because the general solid-state reaction did not have many nuclei due to limited contact with titanium oxide and Na$_2$CO$_3$, the obtained sample had a similar morphology with titanium oxide particles.
Figure 4 presents XRD patterns for the above samples. Many peak positions for all samples were in agreement with Na$_2$Ti$_3$O$_7$ (JCPDS No.31-1329), but the peak intensities were considerably different from the JCPDS data due to the anisotropic morphology. Samples impregnated by Na$_2$CO$_3$ solution with the concentrations between 190 and 216 g/dm$^3$ [samples (c) and (d) in Fig. 4] included little impurity phase, such as Na$_2$Ti$_6$O$_{13}$ and Na$_4$Ti$_5$O$_{12}$. The average major and minor axes of sample (d) measured by SEM were 2.45 and 0.47 $\mu$m, and the specific surface area was 1.78 m$^2$/g. When the sphere approximation diameter ($D$) was calculated by the formula: $D = 6/(S \rho)$, where $S$ and $\rho$ are the specific surface area and density of the sample. $D$ of sample (d) was 0.98 $\mu$m, which was smaller than that of Na$_2$Ti$_3$O$_7$ created by the solid-state method (about 1.6 $\mu$m). Therefore, the Na$_2$Ti$_3$O$_7$ sample with smaller size could be synthesized by impregnation method. Synthesis of Na$_2$Ti$_3$O$_7$ sample with different particle size is considered to be next subject.

3.2 Soft-chemical synthesis of HTO and annealing of Na$_2$Ti$_3$O$_7$ synthesized by impregnation

Figure 5 presents an SEM image and XRD pattern of an HTO sample synthesized from sample (d). For comparison, the SEM image and XRD pattern of an HTO sample synthesized by the solid-state method was added. Because only the chemical composition of the sample could be changed by soft-chemical synthesis, the sample morphologies rarely change before and after treatment. Therefore, the HTO sample synthesized from sample (d) was aggregated with higher anisotropic particles, similar to the Na$_2$Ti$_3$O$_7$ sample before treatment, and the HTO sample synthesized by the solid-state method was aggregated with lower anisotropic particles. The XRD pattern of sample (d) was almost the same as that of the solid-state method and the peak of 2$\theta = 24.6^\circ$, which corresponds to (110),$^{39}$ was generally larger. The results of both SEM and XRD suggest that the HTO obtained by the impregnation method consists of particles with higher anisotropic structure.

3.3 Electrochemical Li insertion and extraction evaluation of HTO sample synthesized by impregnation

Figure 6 depicts the electrochemical Li insertion and extraction properties for the above HTO sample. A flat potential plateau was observed at approximately 1.5 V (versus Li/Li$^+$) for the first Li insertion reaction. The initial charge (discharge) capacity was
248 (221) mAh/g, with an initial coulombic efficiency of 89%. The initial charge (discharge) capacity of the HTO derived from Na$_2$Ti$_3$O$_7$ synthesized by the solid-state method was reported to be 247 (213) mAh/g, and coulombic efficiency was 86%. The improvement of the initial coulombic efficiency can be explained by the smaller sample size.

Figure 7 depicts the cycling performance of the HTO sample synthesized by impregnation. A reversible Li insertion-extraction performance with a relatively high capacity exceeding 210 mAh/g was observed at about 1.55 V, about 10 mAh/g larger than that of the solid-state method. The improvement can be explained by increasing an utilization rate of the HTO sample due to smaller sample size. The discharge capacity retention rate was 96% after 100 cycles, similar to that of the solid-state method.

4. Conclusion

We developed a new method of synthesizing HTO with higher anisotropic morphology by impregnation of Na$_2$CO$_3$ solution into porous titanium hydroxide. This HTO sample had better performance as a negative electrode of a Li-ion battery because it had higher discharge capacity and coulombic efficiency than that synthesized from Na$_2$Ti$_3$O$_7$ by the solid-state method.

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