Charge/discharge Behavior of Triclinic LiTiOPO₄ Anode Materials for Lithium Secondary Batteries

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ABSTRACT

Triclinic LiTiOPO₄ fine powders were synthesized via low-temperature thermal treatment. First, amorphous fine powders were prepared by mechanical milling (MM) treatment of a mixture of the starting materials (Li₂CO₃, TiO₂, and P₂O₅) at room temperature. The mechanically milled amorphous powder formed a triclinic LiTiOPO₄ crystal below 700°C in air. The mechanically milled powders before heat treatment barely worked as an active material at ca. 0.1 C rate in the potential range of 1.0 to 3.0 V versus Li/Li⁺ in lithium cells. On the other hand, the triclinic LiTiOPO₄ compounds obtained by the crystallization of the mechanically milled amorphous powders at 700°C in air worked as anode materials in lithium cells. The triclinic LiTiOPO₄ electrode materials exhibited capacities of around 100 mAh g⁻¹. The average operation potential was around 1.7 V (vs. Li/Li⁺). The triclinic LiTiOPO₄ pristine compound when used as an anode caused a phase transition into an orthorhombic compound during lithium insertion (charge process). The orthorhombic compound changed into a triclinic phase during lithium extraction (discharge process). The triclinic LiTiOPO₄ electrodes exhibited a good cycle performance in the potential range of 1.0 to 3.0 V versus Li/Li⁺. It is suggested that the crystalline phase changes reversibly during charge/discharge.

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1. Introduction

In the development of high-performance storage batteries such as lithium-ion secondary batteries, it is necessary to enhance their energy density, cycle life, and safety. Transition metal phosphate compounds with polyanionic structure frameworks have been researched as cathode and anode materials for high energy density and/or highly safe lithium-ion batteries. S. Okada et al. reported the electrochemical, structural, and spectroscopic characteristics of orthorhombic olivine LiMPO₄ (M = Co, Fe, Ni, or Mn) as high-voltage cathode active materials for lithium secondary batteries.¹ On the other hand, Ti-based M'_{0.5}TiOPO₄ (M' = Fe, Co, Ni, or Cu) materials have been researched and developed as high-capacity anode materials for lithium secondary batteries.^{2–9} Y. Kee and co-workers reported the synthesis of rhombohedral LiTi₂(PO₄)₃ and orthorhombic Li_{1.5}Ti₂(PO₄)₃ via the sol-gel method and the investigation of their use as anode materials for rechargeable Li-ion batteries.¹⁰ S. Patoux and C. Masquelier reported that LiTiPO₅/Super P carbon (SP carbon; MMM Carbon, Belgium) electrodes worked as active materials using cyclic voltammetry (CV) measurements and galvanostatic intermittent titration techniques (GITT).¹¹ Y. Fu and co-workers reported that carbon-coated orthorhombic LiTiOPO₄ (LiTiOPO₄/C) obtained after calcination in Ar atmosphere at 650°C for 3 h exhibited a limited discharge capacity with a value of 100 mAh g⁻¹ even at a current rate of 0.1 C cycling in the potential range of 0.5–3.0 V.¹² The potential plateau during lithium insertion was at around 1.5 V versus Li/Li⁺, accompanied by the reduction of Ti⁴⁺ to Ti³⁺. The framework of the orthorhombic LiTiOPO₄ pristine material was preserved during the insertion of the first lithium ion: orthorhombic LiTiOPO₄ + xLi⁺ + xe⁻ → orthorhombic Li_{1+x}TiOPO₄ (0 ≤ x ≤ 1). Generally, the triclinic

and orthorhombic phases of the LiTiOPO₄ composition are known. However, the charge/discharge behavior and electrode reaction mechanism of triclinic and/or amorphous LiTiOPO₄ electrodes have almost never been investigated in lithium cells.

On the other hand, mechanical milling (MM) techniques using a high-energy ball mill are often used for the preparation of amorphous and crystalline inorganic oxide-based materials.^{13–21} In general, the specificity of the MM method enables the preparation of fine powders during room temperature and/or low-temperature thermal treatment. Such MM methods are adapted for the preparation of electrode and solid electrolyte materials for energy and sensor devices.

In this study, amorphous powders were synthesized by MM treatment of a mixture with the nominal composition LiTiOPO₄. Triclinic LiTiOPO₄ compounds were prepared by heat treatment of the mechanically milled amorphous powders. The crystallization temperature of the mechanically milled amorphous powder was investigated by differential thermal analysis (DTA). The mechanically milled amorphous and triclinic LiTiOPO₄ materials were investigated as anodes in the potential range of 1.0 to 3.0 V versus Li/Li⁺ for a lithium cell using organic electrolyte solutions. The electrode reaction mechanism was investigated through the charge/discharge behavior and ex-situ X-ray diffraction (XRD) patterns of the electrode surfaces after the charge/discharge cycles.

2. Experimental

2.1 Preparation of the triclinic LiTiOPO₄ electrode materials

Li₂CO₃ powder (Wako Pure Chemical Industries, Ltd., 99%), TiO₂ (Wako Pure Chemical Industries, Ltd., 99.9%), and P₂O₅ (Wako Pure Chemical Industries, Ltd., 97%) were used as starting

materials. MM treatment was carried out on mixtures of the starting materials with a LiTiOPO_4 composition using a planetary ball mill (Fritsch, p-7) at a rotation speed of 450 rpm for 20 h at room temperature under a dry Ar atmosphere. Stainless steel pots and zirconia balls were used for the ball milling. The volume of the pots and number of balls were 45 mL and 10, respectively. The diameters of the balls were 10 mm. Mechanically milled powders were heat-treated at 700°C for 2 h in air. XRD measurements (Rigaku, MiniFlex) with $\text{CuK}\alpha$ radiation were performed to estimate the crystalline phase before and after heat treatment of the mechanically milled powders. The experimental conditions were as follows: tube voltage, 30 kV; tube current, 15 mA; scan speed, 2°min^{-1} ; and sampling width, 0.01° . Differential thermal analysis (DTA; Rigaku, Thermo plus TG8120) of the mechanically milled powder was performed under air flow at a heating rate of $10^\circ \text{C min}^{-1}$. The particle size and morphology was estimated by scanning electron microscopy (SEM; JEOL, JSM-6510).

2.2 Preparation of the electrodes

The working electrodes were fabricated from the synthesized powder (75 wt%), acetylene black (AB) powder (15 wt%), and polyvinylidene fluoride (PVDF, 10 wt%). The mixture of the synthesized powder and the acetylene black powder was stirred with a PVDF binder solution with 1-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was painted onto the Al sheet (thickness: 15 μm) of the current collector and dried at 80°C. The slurry-painted Al sheet was dried under vacuum at 120°C. The sheet was cut. The electrode sheets were then pressed and dried under vacuum at 120°C (content of active material: 2.0–2.5 mg cm^{-2} , electrode density: 1.0–1.1 g cm^{-3}).

2.3 Electrochemical measurements

The electrochemical measurements were carried out using 2032 coin cells. These cells comprise a lithium metal counter electrode (Honjo Metal Co., Ltd., lithium sheet thickness = 0.5 mm) and a working electrode (electrode density: 1.0–1.1 g cm^{-3}). The electrolyte was 1 mol dm^{-3} LiPF_6 in a mixed solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 volume ratio).

CV measurements were carried out in the potential range of 1.0 to 3.0 V versus Li/Li^+ during a sweep rate of 0.5 mV s^{-1} at room temperature. Charge/discharge cycle measurements with a constant current (CC) density of 0.05 mA cm^{-2} during the cycles were carried out in the potential range of 1.0 to 3.0 V versus Li/Li^+ using a battery charge/discharge system (HOKUTO DENKO Corp., model HJ100ISM8). In this case, the lithium insertion into an electrode indicates a charge process. The charge/discharge rate (C rate) was calculated based on the theoretical capacity (ca. 162 mAh g^{-1}) of LiTiPO_5 . The crystalline structure of the electrodes after the charge/discharge cycles were investigated by ex-situ XRD measurements.

3. Results and Discussion

Figure 1 shows the XRD patterns of the powders before and after MM treatment of the mixtures of Li_2CO_3 , TiO_2 , and P_2O_5 (nominal composition: LiTiOPO_4) as the starting materials. The peaks of the starting materials disappeared and halo patterns were observed after MM, although small peaks due to anatase-type TiO_2 and rutile-type TiO_2 were observed.

Figure 2 shows the DTA curve of the amorphous powders after MM. An exothermic peak was observed at around 600°C during the heating processes. Such a result can be attributed to the crystallization of the amorphous material. It is suggested that the triclinic LiTiOPO_4 compound is formed by low-temperature thermal treatment in air. Figure 3 shows the XRD patterns of the powders (LiTiPO_5 (700°C)) obtained by heat treatment of the mechanically milled amorphous powder at 700°C for 2 h. Diffraction peaks

Figure 1. XRD patterns of the powders before and after MM treatments of mixtures of Li_2CO_3 , TiO_2 , and P_2O_5 (nominal composition: LiTiOPO_4) as the starting materials.

Figure 2. DTA curve of the amorphous powders after MM.

Figure 3. (Color online) XRD patterns of the powders (LiTiPO_5 (700°C)) obtained by heat treatment of the mechanically milled amorphous powder at 700°C for 2 h.

assigned to triclinic LiTiOPO_4 (card No.; PDF#01-077-0994) were observed in the LiTiPO_5 (700°C) sample after heat treatment. The exothermic peak shown in Fig. 2 corresponds to the crystallization of the triclinic LiTiOPO_4 phase from the amorphous powder. The

Figure 4. SEM images of the powders a) before and b) after the heat treatment of the amorphous powder (MM powder) obtained by MM treatment.

Figure 5. (Color online) Cyclic voltammograms for 5th cycle of MM powder and LiTiPO_5 (700°C) electrodes in the potential range of 1.0 to 3.0 V versus Li/Li^+ at room temperature.

crystallization temperature of the mechanically milled amorphous powder was ca. 570°C. Triclinic LiTiOPO_4 compounds were synthesized by relatively low-temperature thermal treatments. The triclinal compound obtained by crystallization of the mechanically milled amorphous powder changed into an orthorhombic compound after heat treatment at 850°C in air. The triclinic compound will be a low-temperature phase of orthorhombic LiTiOPO_4 compound.

Figure 4 shows the SEM images of the powders a) before and b) after heat treatment of the amorphous powder (MM powder) obtained by MM treatment. Fine particles with diameters less than 1 μm were observed in both the amorphous (MM powder) and triclinic LiTiOPO_4 (LiTiPO_5 (700°C)) samples. In addition, the aggregation of the fine particles was confirmed. On the other hand, particle growth by thermal processing was not confirmed.

Figure 5 shows the cyclic voltammograms for the 5th cycle of the MM powder and LiTiPO_5 (700°C) electrodes in the potential range of 1.0 to 3.0 V versus Li/Li^+ at room temperature. The oxidation and reduction currents were barely observed for the MM powder electrode under the experimental conditions. On the other hand, the redox current for the LiTiPO_5 (700°C) electrode was observed. It was found that the lithium insertion reaction into

Figure 6. (Color online) First discharge/charge curves in the potential range of 1.0 to 3.0 V versus Li/Li^+ of MM powder and LiTiPO_5 (700°C) electrodes at a current density of 0.05 mA cm^{-2} at room temperature.

triclinic LiTiOPO_4 occurred. After insertion, the electrode materials are able to undergo lithium extraction. The reduction and oxidation peak potentials were observed at ca. 1.54 V and 1.89 V (vs. Li/Li^+), respectively. These potentials are close in value to those reported previously for orthorhombic electrode materials.¹² The peak potentials should be the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple in the triclinic LiTiOPO_4 compound.

Figure 6 shows the first discharge/charge curves in the potential range of 1.0 to 3.0 V versus Li/Li^+ of the MM powder and LiTiPO_5 (700°C) electrodes at a current density of 0.05 mA cm^{-2} at room temperature. Both the electrodes worked as active materials in the lithium cells. The charge and discharge capacities of the LiTiPO_5 (700°C) electrode (ca. $x = 0.72$ in $\text{Li}_{1+x}\text{TiPO}_5$ during charge) were ca. 117 and ca. 102 mAh g^{-1} per unit weight of LiTiPO_5 at approximately 0.1 C rate, respectively. The initial coulombic efficiency of LiTiPO_5 (700°C) electrode was ca. 87%. The main factor affecting irreversible capacity is indicated that the crystalline structure changes accompanying the electrochemical reaction of LiTiOPO_4 electrode is partially irreversible and/or the electrical conductive path for the electrode is broken. The charge/discharge potential during the first cycle was around 1.7 V (vs. Li/Li^+). On the other hand, the charge/discharge potential of the MM powder electrode was around 2.5 V (vs. Li/Li^+). The capacities were ca. 10 mAh g^{-1} per unit weight of MM powder. Amorphous materials obtained from MM would barely work as an active material during ca. 0.1 C charge/discharge because the amorphous materials show relative low electrical conductivity. However, TiO_2 materials, which exist in the amorphous materials obtained from the MM, would work as an active material.

Figure 7 shows the discharge capacity retention of the MM powder and LiTiPO_5 (700°C) electrodes. Both electrodes exhibited a good cycle performance. Figure 8 shows the ex-situ XRD patterns of the LiTiPO_5 (700°C) electrode surfaces before the first charge/discharge, after the 1st charge, 1st discharge, 10th charge, and 10th discharge. The XRD patterns of the electrode surfaces before the first charge/discharge were assigned to triclinic LiTiOPO_4 . On the other hand, the active materials after the 1st charge were changed into orthorhombic compound. The electrode surfaces after the 1st discharge were assigned to triclinic LiTiOPO_4 . The results were the same after the 10th charge and 10th discharge. Thus, triclinic LiTiOPO_4 underwent a phase transition into an orthorhombic compound during lithium insertion into the lithium cells. The orthorhombic compound underwent a phase transition into the

Figure 7. (Color online) Discharge capacity retention of MM powder and LiTiPO_5 (700°C) electrodes.

Figure 8. (Color online) Ex-situ XRD patterns of LiTiPO_5 (700°C) electrode surfaces before first charge/discharge, after 1st charge, 1st discharge, 10th charge, and 10th discharge.

triclinic compound during lithium extraction. Reaction mechanism of triclinic LiTiOPO_4 mentioned in this study has been not reported for the orthorhombic LiTiOPO_4 active material.^{11,12} It is suggested that the crystalline phase changes reversibly during charge/discharge. Triclinic LiTiOPO_4 is expected to show a superior cycle performance.

4. Conclusions

Triclinic LiTiOPO_4 compounds were prepared by heat treatment of amorphous powders obtained using an MM technique. The crystallization temperature of the mechanically milled amorphous powder was lower than 600°C. Triclinic LiTiOPO_4 compounds were synthesized by relatively low-temperature processing. The mechan-

ically milled amorphous materials barely worked as an active material in the potential range of 1.0 to 3.0 V versus Li/Li^+ for the lithium cells. On the other hand, the triclinic LiTiOPO_4 compounds obtained from the crystallization of the amorphous powder at 700°C worked as anode materials in the lithium cells. The triclinic LiTiOPO_4 electrode materials exhibited a capacity of ca. 100 mAh g^{-1} at around 1.7 V (vs. Li/Li^+) and a good cycle performance in the potential range of 1.0 to 3.0 V versus Li/Li^+ . The electrode reaction mechanism suggests that the crystalline phase changes reversibly during charge/discharge in the potential range of 1.0 to 3.0 V versus Li/Li^+ .

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