Spray-Drying Synthesized Lithium-excess Li$_{4+x}$Ti$_{4.95-x}$Nb$_{0.05}$O$_{12-\delta}$ and its Electrochemical Property as Negative Electrode Material for Li-ion Batteries

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Li$_{4+x}$Ti$_{4.95-x}$Nb$_{0.05}$O$_{12-\delta}$ (x = 0.11 ~ 0.13) materials were synthesized by using a spray-drying method followed by heat treatment at 600 ~ 900 C in air. Chemical and structural studies of the final products were done by X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) etc. The optimum synthesis condition of the materials was examined in relation to the electrochemical characteristics including charge-discharge cycling tests. The charge-discharge cycling results of several the Nb-substituted samples indicated that the samples prepared at heat treatment temperature of 700 C for 12 h showed best cycling performance with the discharge capacity of 175 ~ 140 mAh g$^{-1}$ at the discharge rate of 0.5 ~ 3 C.

Key Words : Li-ion Battery, Spray-Drying, Nb Doping, Lithium-excess

1 Introduction

Li$_4$Ti$_4$O$_{12}$ (theoretical capacity 175 mAh g$^{-1}$) is a promising negative electrode material for lithium-ion batteries due to its good structural stability during cycling.$^6$ The material was mainly synthesized by a conventional solid-state reaction method from anatase-type TiO$_2$ and LiOH or Li$_2$CO$_3$ as the starting materials. The method generally requires a prolonged time at high temperature for obtaining the pure phase material. Furthermore, impurity phases such as rutile-type TiO$_2$ (r-TiO$_2$) and Li$_2$TiO$_3$ as the starting materials. The method generally requires a prolonged time at high temperature for obtaining the pure phase material. Thus, it is hard to obtain a single phase Li$_4$Ti$_4$O$_{12}$ any containing any impurity phase such as TiO$_2$ and Li$_2$TiO$_3$ through this methods.$^6$ To overcome the synthetic disadvantages, synthesis using aqueous reaction method, such as sol-gel,$^7$ emulsion-gel,$^8$ spray pyrolysis$^9$ and hydrothermal methods,$^{10}$ has been reported. Additionally, the rate performance of the material is very low due to poor electronic conductivity (< 10$^{-11}$ S cm$^{-1}$).$^{11}$ Recently, to improve the electrode performance, V,$^{12}$ and Ti$^{4+}$ substitutions of the Ti$^{4+}$ in Li$_4$Ti$_4$O$_{12}$ have been reported.$^{13,14}$ In our previous work, we have reported the synthesis and electrochemical characteristics of lithium-excess Li$_{4+x}$Ti$_{4.95-x}$O$_{12-\delta}$ (x = 0.06 ~ 0.08, \( \delta = 0.11 ~ 0.14 \)) prepared by a spray-drying method. Rietveld refinement of the neutron diffraction pattern revealed that the excess lithium is located at the lithium and titanium layer of 16d site in the spinel structure with Fd-3m under oxygen defect.$^{15}$ In this study, we have tried to synthesize a single phase Nb-substitution Li$_{4+x}$Ti$_{4.95-x}$Nb$_{0.05}$O$_{12-\delta}$ material by spray-drying method for a large-scale production.

2 Experimental

Li$_{4+x}$Ti$_{4.95-x}$Nb$_{0.05}$O$_{12-\delta}$ was synthesized by a spray-drying method as follows. Li$_2$CO$_3$ (3.18 g) and titanium tetraisopropoxide (29.00 g) and niobium ethoxide (0.30 g) dissolved in ethanol (20 ml) were added to aqueous solutions consisting of (COOH)$_2$·2H$_2$O (25.20 g) in distilled water (400 ml). The molar ratio of Li/Ti + Nb) was controlled at 0.860. The solutions were stirred overnight at 80 C for 3 h at room temperature, and spray-dried using a spray dryer (SD-1000, EYELA) to obtain the precursors under the input temperature of 160 C and output temperature of 100 C. The obtained precursors were heat treated at 600 ~ 900 C for 12 h in air.

The powder X-ray diffraction (XRD, Rint 2200, Rigaku) measurements were performed to identify the synthesized materials. The lattice parameters for the materials were calculated by the least squares method using the main diffraction peaks based on a cubic structure (Fd-3m). The oxidation states of the synthesized materials were measured by X-ray photon electron spectroscopy (XPS, PHI 5600 spectrometer, Perkin-Elmer) with monochromatic Mg-Ka (h\( \nu = 1256 \) eV). The specific surface areas of the materials were measured by Brunauer-Emmett-Teller (B. E. T.) method using nitrogen adsorption (BEL SORP MINI, BEL JAPAN Inc). Prior to measure the surface area, the materials were dried for 24 h under vacuum. The chemical analysis of lithium and titinate components of the prepared samples was carried out by inductively coupled plasma mass spectrometry (ICP-MS, ICP-8000, SHIMAZU). The electrochemical measurements were performed using an R2032 coin-type cell.

For the measurements, the electrodes were prepared as follows. The synthesized samples were mixed with acetylene black and a polyvinylidene difluoride (PVdF) powder binder in the weight ratio of 88 : 6 : 6 to make a N-methyl-2-pyrrolidinone (NMP) solution slurry. The prepared slurry was then spread on aluminum foil using a doctor blade and dried to remove the NMP at 80 C for 3
h in air. After drying, the aluminum foil was roll-pressed and punched out as a disk having an 11.28 mm diameter, furthermore dried at 80°C overnight under vacuum. 1.0 M LiPF₆ in ethylene carbonate and dimethyl carbonate (30 : 70 in volume) was used as the electrolyte, and Celgard 2325 was used as the separator. For assembling the cell, the prepared sample as a working electrode and lithium metal foil as the counter electrode were used. The assembly of the cell was performed in an argon-filled glove box (DBO-1NK-1U-2, Miwa Mfg Co., Ltd.). The assembled cells were cycled between the voltages of 3.0 and 1.2 V at current densities of 17.5 ~ 525 mA g⁻¹ (1C = 175 mA g⁻¹) at 25°C.

3 Results and Discussion

3.1 Characterization of Li₁ₓTi₆₋ₓNbₓO₁₂₋₄ phase prepared by spray-drying method

The XRD patterns of Li₁ₓTi₁₆₋ₓNbₓO₁₂₋₄ formed from heat-treating the spray-dry precursors at 600 ~ 900°C for 12 h in air are shown in Fig. 1. As seen in the figure, at heat-treated temperature of 600°C, a small amount of unknown impurity phase was contained in the product. At 700 ~ 900°C, however, the main diffraction peaks were attributed to the formation of the pure Li₁ₓ−ₓTi₁₆₋ₓNbₓO₁₂₋₄ phase and indexed with cubic crystal system and the space group of Fd-3m. As seen in Table 1, the a-lattice parameters of the samples heat-treated at 600 ~ 900°C were 8.362(7) ~ 8.366(9) Å, which are larger than the literature value, 8.360(0) Å for non-substituted Li₁₀Ti₁₄O₂₅.¹⁰

By XPS results, the oxidation states of Ti and Nb in the synthesized samples were 4+ and 5+, respectively. The ionic radii of Li⁺, Ti⁴⁺ and Nb⁵⁺ are 0.76, 0.605 and 0.64 Å, respectively.¹¹ Thus, the a-lattice parameters of the Nb-substituted samples may be increased by substitution of Nb⁵⁺ for Ti⁴⁺.

ICP-MS results and surface areas of the samples are shown in Table 1. As seen in the table, the observed Nb/(Ti + Nb) ratios nearly equal to the starting ratio of 0.50. Meanwhile, the Li/(Ti + Nb) ratios are clearly lower than the starting ratio of 0.860, probably due to evaporation of the lithium component during calcination of the spray-dry precursor, however, higher than the stoichiometric value of Li/(Ti + Nb) = 0.800. The surface area of the samples decreased with increasing heating temperature, and the sample at 900°C showed the largest area of 2.43 m² g⁻¹. The neutron diffraction measurement and the rietveld refinement of the sample prepared done on the ICP analytical result (Table 1) indicated that the excess amounts of lithium, x = 0.11, and niobium in Li₁₁₁Ti₁₁₆Nb₀₀₅O₁₂₋₄ are substituted for the titanium at the octahedral 16d site under the oxygen defect.

3.2 Electrochemical characteristics of samples prepared by a spray-drying method

The initial charge-discharge curves of the samples obtained by at heat-treating at the temperatures of 600 ~ 900°C in the starting Li/(Ti + Nb) of 0.860 are shown at several C-rates in Fig. 2. As can be seen in the figure, the discharge plateau is observed at about 1.5 V, in any Nb-substituted sample which is in agreement with that for non-substituted Li₁₀Ti₁₄O₂₅.¹⁰ The sample (a) obtained at 600°C showed lower capacity, probably due to formation of impurity phases based on the XRD results. The sample (b) prepared at 700°C represented the highest discharge capacity among the Nb-substituted samples.

The discharge capacities of Li₁₀Ti₁₄O₂₅ (b) in Fig. 2 and Li₁₁₁Ti₁₁₆Nb₀₀₅O₁₂₋₄ (c) in Fig. 2 samples are given at several C-rates in Fig. 3. As a function of the cycle number, Li₁₁₁Ti₁₁₆Nb₀₀₅O₁₂₋₄ represented the better rate performance than non-Nb substituted material, while maintaining a higher capacity of 139 mAh g⁻¹ at the higher 3C rate. Thus, the Nb-substituted sample obtained at 700°C showed the most excellent cycling performance.

<table>
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<tr>
<th>Table 1</th>
<th>Chemical composition, a-lattice parameters and surface area of Li₁ₓ₋ₓTi₁₆₋ₓNbₓO₁₂₋₄ (x = 0.11 ~ 0.13) obtained from heat-treating the spray-dry precursor at 700 ~ 900°C for 12 h in air.</th>
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<tr>
<td>Calculination temperatures/°C</td>
<td>Starting ratios of Li/(Ti + Nb)</td>
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<tr>
<td>700</td>
<td>0.860</td>
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probably due to the formation of a single phase and the structural stability with Nb-substitution and further the largest surface area.

4 Conclusion
We have synthesized lithium-excess Li$_{1+x}$Ti$_{1.55-x}$Nb$_{0.05}$O$_{12-d}$ ($x = 0.11 \sim 0.13$) materials as the negative electrode for Li-ion batteries using a spray-drying method. When the precursors heat-treated at 700 \textdegree{}C, the pure phase not containing an impurity phase was obtained based on the XRD results. The chemical compositions of these final products obtained by an ICP-MS analysis are shown to be Li$_{1+x}$Ti$_{1.55-x}$Nb$_{0.05}$O$_{12-d}$ ($x = 0.11 \sim 0.13$) with lithium excess composition. Such a pure Li$_{1+x}$Ti$_{1.55-x}$Nb$_{0.05}$O$_{12-d}$ ($x = 0.11 \sim 0.13$) phase formed at calcination temperature of 700 \textdegree{}C showed excellent cyclability and superior rate capability (140 mAh g$^{-1}$ at 3C rate).

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References

Fig. 2 First charge-discharge curves of Li$_{1.0}$Ti$_{1.55}$Nb$_{0.05}$O$_{12-d}$ ($x = 0.11 \sim 0.13$) formed from heat-treating the spray-dry precursor at (a) 600 \textdegree{}C, (b) 700 \textdegree{}C, (c) 800 \textdegree{}C, (d) 900 \textdegree{}C for 12 h and (e) Li$_{1.0}$Ti$_{1.51}$O$_{11.87}$ from heat-treating 700 \textdegree{}C for 12 h at different current densities.

Fig. 3 C-rate performance of Li$_{1.1}$Ti$_{1.8}$Nb$_{0.05}$O$_{11.86}$ and Li$_{1.0}$Ti$_{1.51}$O$_{11.87}$ formed from heat-treated the spray-dry precursor at 700 \textdegree{}C for 12 h.