Hydrothermal synthesis of Li$_4$Ti$_5$O$_{12}$ nanoparticles using a supercritical flow reaction system

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The cubic Li$_4$Ti$_5$O$_{12}$ nanoparticles were continuously synthesized in supercritical water using a flow hydrothermal reaction system. Ti-sols (M-6, A-6) and Ti(SO$_4$)$_2$ were used as the Ti source. Initial Li/Ti molar ratio was varied with the LiOH concentrations. The syntheses were carried out at temperatures from 350 to 410°C, at pressure of 30 MPa, and for residence times from 10 to 26 s. X-ray diffraction (XRD), transmission electron microscopy (TEM), BET surface area, and Dynamic light scattering (DLS) technique were used to characterize the samples. Single phase of Li$_4$Ti$_5$O$_{12}$ was achieved under supercritical conditions at initial Li/Ti molar ratio > 2.5 from Ti-sol (M-6) and > 2 from Ti-sol (A-6), respectively, whereas single phase was not obtained from Ti(SO$_4$)$_2$ solution even at initial Li/Ti molar ratio of 10. It requires the pH range over 12 to prepare the single phase Li$_4$Ti$_5$O$_{12}$. As-synthesized samples exhibited the diffuse scattering (111) and missing (311) reflections due to a disorder in Ti-O framework, whereas the presence of these two reflections indicates reordering of the Ti sublattice after annealing.

Key-words: Lithium titanate, Nanoparticles, Hydrothermal synthesis, Supercritical water, Flow reaction system, Lithium ion battery

1. Introduction

Rechargeable Li-ion batteries have attracted much attention as power sources for portable electronic devices, hybrid electric vehicles (HEV) and electric vehicles (EV) due to high energy density and high electromotive force. In present commercial Li-ion batteries, graphite is a widely used as anode material, whereas it has some problems for the safety and rate performance required for the applications in HEV and EV. Spinel lithium titanate, Li$_4$Ti$_5$O$_{12}$ (LTO), has recently attracted great interest as an alternative anode material to graphite. LTO affords low cost, environmental friendliness, and enhanced safety.

LTOs have been synthesized by various methods, such as solid-state reaction, sol–gel, solvothermal, and hydrothermal techniques. Since solvothermal and hydrothermal routes are suitable for preparing fine and uniform powders of high purity in a single step without requiring expensive reagents, nanosized LTO spinel powders have been synthesized under hydrothermal and solvothermal conditions up to 200°C. Recently, LTO powders with high rate capability have been prepared using supercritical hydrothermal synthesis in batch process since supercritical water (SCW) is a new reaction media to synthesize nanomaterials based on the beneficial properties of SCW such as low viscosity, high diffusivity, zero surface tension, and an environmentally benign solvent. In addition, supercritical water gives favorable reaction field for nanoparticle formation owing to the enhancement of the reaction rate and high supersaturation based on the nucleation theory due to lowering the solubility. However, large-scale production is thought to be difficult and it takes long reaction time for heating and cooling process due to the usual batch process. A flow supercritical hydrothermal process would appear to have good potential as continuous process because the short reaction times could allow high through put synthesis. While as far as we know, the synthesis of LTO materials via flow hydrothermal process has been reported by Laumann et al. They used titanium isopropoxide and lithium metal dissolved in ethanol as starting materials. In this paper, the synthesis of nanocrystalline LTO has been conducted from water soluble Ti and Li sources by continuous hydrothermal method.

2. Experimental section

2.1 Hydrothermal synthesis

Titanium dioxide solids (Taki Chemical Co Ltd.; Tynoc M-6: TiO$_2$ 6%, crystallite size 5 nm, pH 3.4, Tynoc A-6: TiO$_2$ 6% pH 10), Titanium sulfate [Ti(SO$_4$)$_2$: Wako Chemicals, pH <1] and lithium hydroxide (LiOH; 85% Wako Pure Chemicals Co. Ltd.) were used as starting materials. The TiO$_2$ sol was dispersed into distilled water, and the concentration of Ti was adjusted to 0.05, or 0.2 M, respectively. The concentration of LiOH was adjusted in the range from 0.1 to 0.6 M. Schematic diagram of the flow reactor system used in this study was shown in Fig. 1. Each of the Ti-sol and LiOH solution were fed forward to a reactor by high-pressure pumps (Nihon Seimitsu Kagaku NP-KX-500) at a flow rate of 5 g/min, and these two streams were mixed at the first mixing point, MP1. On the other hand, distilled water was fed by another high-pressure pump at a flow rate of 40 g/min and heated to an appropriate temperature by an electric furnace. The reactant mixture of Ti sol and LiOH was mixed with the supercritical water at the second mixing point MP2. The temperature and pressure of the hydrothermal reactions were set to be 350–410°C and 30 MPa, respectively. The reactant was maintained at 350 to 410°C in a 1/8 inch SUS tube reactor.
diameter: 1.25 mm and length: 13.5 m). After the prescribed reaction time period, hydrothermally treated mixture reaction was quenched by cooling at the end of the reactor. The product solution was depressurized with a back pressure regulator (Tescom Corporation 26-1761: 200-10,000PSIG). Particles were recovered as a slurry solution, separated with a membrane filter (pore size 0.025 μm) as aggregation, washed with pure water, and then dried at 60°C in an electric oven for 24 h. Experimental conditions for each run are given in Table 1. Reaction (residence) time, t, was calculated using the following equation:

\[ t = \frac{V}{F} (\rho_298 / \rho_T) \]

where \( F \) is the total flow rate (g/s) and \( V \) is the reactor volume (cm³). \( \rho_298 \) and \( \rho_T \) are densities of pure water (g/cm³) at 298 K and reaction temperature and pressure. The reaction time was calculated to be 25.9, 23.3, 14.4 and 10.1 s using the density of 0.644, 0.579, 0.357, and 0.251 g/cm³ at 350, 370, 400 and 410°C, respectively.

As the post-treatment, the as-synthesized samples were annealed in the electric furnace under air conditions and kept at constant temperature in the range of 400–1000°C for 3 h to confirm the thermal stability of the prepared phases.

### 2.2 Characterization

The crystal structure of the products was determined by X-ray diffraction measurement (XRD; Rigaku Co. Ltd., Model RINT 2000). Particle size and the morphology of the obtained particles were examined by transmission electron microscopy (TEM; FEI Co., Model TECNAI-G2). The elemental contents were measured with an inductively coupled plasma (ICP) atomic emission spectrometer, Seiko instruments SPS7800, after dissolving the products in conc. nitric acid. BET surface area of the particles was measured by nitrogen adsorption and desorption apparatus (QUANTACHROME Co. Ltd., CHEMBET 3000). The particle size in a dispersed solution was evaluated with the DLS (dynamic light scattering) method (Otsuka Electronics Co. Ltd. FDLS-3000). The mean particle size was calculated using the cumulant analysis.

### 3. Results and discussion

Figure 2 shows XRD profiles of the products from 0.05 M Ti-sol(M-6) and 0.1 M LiOH as Ti and Li sources at various

![Fig. 1. Schematic diagram of the hydrothermal flow reaction system. MP represents the mixing point and BPR stands for Back pressure regulator.](image)

![Fig. 2. XRD patterns of as-synthesized powders formed from Ti-sol(M-6) as Ti source under the conditions. (a) (350°C, 30 MPa), (b) (370°C, 30 MPa), (c) (400°C, 30 MPa), and (d) (410°C, 30 MPa). (○): Anatase, (●): Lithium titanate.](image)
hydrothermal temperatures. Since residence time varies with the density of water, the residence time decreases with an increase in the hydrothermal temperature. It is seen that the XRD profile for the sample prepared at 350°C [Fig. 2(a)] can be assigned to Anatase even in the longest residence time. It is noteworthy that the broad peaks at ca. 2θ = 18.5, 43.5 and 62.9° for the products at 370°C or higher can be assigned to the (111), (400) and (440) peaks for the spinel Li4Ti5O12 (JCPDS 49-0207) whereas the peaks for Anatase were also recognized.

Based on the XRD data file for the spinel Li4Ti5O12 (JCPDS 49-0207), the d(111) of 4.8 Å and d(311) of 2.7 Å are the strongest and pronounced peaks. The broadening of d(111) and apparent absence of d(311) reflections were reported for the hydrothermally synthesized LTO samples which are characteristic of the spinel structure that the Ti occupies both available types of octahedral sites (16c and 16d) with approximately the same probability. Accordingly, diffuse scattering in the range corresponding to (111) reflection and missing (311) reflection can be attributed most likely to a disorder in Ti-O framework. The ordering of Ti-O framework by annealing will be discussed later.

3.1 The effect of Li/Ti molar ratio

Since the anatase phase was coexisted in the hydrothermal products under supercritical conditions, initial Li/Ti molar ratio was varied in the range from 2.0 to 4.0 to obtain the single phase of Li4Ti5O12, using Ti-sol(M-6). XRD patterns of the products are presented in Fig. 3 and pH values for the product solutions were listed in Table 1. The observed diffraction patterns show that all of the prepared materials are single phase of Li4Ti5O12 except for the product from initial Li/Ti molar ratio of 2 where the pH value for the filtrates was lower than 12.

Figure 4 shows XRD profile of the products from Ti-sol(A-6) at various initial Li/Ti molar ratios. In the case of Ti-sol(A-6), single phase of LTO was achieved at initial Li/Ti molar ratio of 2.0, whereas anatase phase was coexisted in the presence of LTO at the Li/Ti molar ratio of 1.0 and 1.5 where the pH values for the filtrates were lower than 12. Figure 5 shows XRD profile of the products from Ti(SO4)2 at various initial Li/Ti molar ratios. In the case of Ti(SO4)2, single phase of LTO was not obtained even at initial Li/Ti molar ratio of 10 where the pH value was lower than 11. Besides, corrosion and blockage took place in the case of initial Li/Ti molar ratio of 2.0 and 3.0 whereas anatase phase was coexisted in the presence of LTO at the lower Li/Ti molar ratio of 10. In the Ti(SO4)2 solution, excess amount of sulfuric acid is added to prevent the hydrolysis of titanium ions, a large excess amount of LiOH might be required to prepare the single phase LTO from Ti(SO4)2 solution. In contrast, the titania is completely converted to a ternary oxide (LTO) at pH 12 or higher if the Li:Ti molar ratio in the reaction mixture exceeds 2:1 or 2.5:1 from Ti-sol(A-6), and M-6, respectively. Therefore, pH is the key for preparing the single phase of Li4Ti5O12.

The chemical compositions, specific surface area, and mean particle size measured by DLS for the as-synthesized powders are listed in Table 1. Specific surface area for the as-synthesized samples are over 90 m²/g whereas those for the Run No. 11 and 12 samples prepared from Ti(SO4)2 were less than 10 m²/g. The specific surface area correlated with the mean particle size (MPS) measured by DLS which is aggregated particle size in dispersed solution.

Figure 6 shows representative TEM micrographs of the hydrothermal products from various Ti sources. These micrographs revealed that the synthesized products from Ti-sols (M-6, A-6) were all nanometer-sized particles. The particles synthesized from Ti-sols at 400°C [Figs. 6(a) and 6(b)] showed relatively uniform particle size with aggregated form. In contrast, the parti-
cles synthesized from Ti(SO₄)₂ at 400°C [Fig. 6(c)] showed large particle size over micron size. The particle sizes observed by TEM were consistent with the crystallite sizes calculated from the XRD line-broadening (20–50 nm).

3.2 Effect of annealing temperature

To improve the crystallinity of the materials, hydrothermally prepared samples were annealed at various temperatures (400, 600, 800, and 1000°C) for 3 h. Figures 7(a) and 7(b)–7(e) show the XRD profiles of as-synthesized sample at 400°C(a), and after annealing at 400(b), 600(c), 800(d), and 1000°C(e). In the annealed samples, additional peaks were appeared at d spacing of 4.82Å(2θ = 18.4°) and 2.53Å(2θ = 35.5°) which can be indexed as (111) and (311) reflections within the spinel structure, indicating that reordering of Ti sublattice upon annealing. These peaks increased with an increase in the annealing temperature and maximized at 800°C. The morphologies of the samples after annealing at 400, 600, 800 and 1000°C were characterized by TEM. The TEM images of the as-synthesized sample(a) and after annealing at 400(b), 600(c), and 800°C(d) are shown in Fig. 8. It can be seen from the micrographs that the particles are in the range of several 10 nm to 50 nm and particle size did not change during the annealing process up to 400°C. However, particles become larger as the annealing temperature increased at 800°C or higher, suggesting that agglomerated particles were sintered. TEM results were supported with the specific surface area (SSA) which were gradually decreased up to 600°C, then dropped at 800°C or higher. The SSA values were 82.3, 38.2, 0.6 and 0.2 m²/g for the samples annealed at 400, 600, 800 and 1000°C, respectively.

4. Conclusion

In this study, the Lithium titanate (LTO) nanoparticles were synthesized by hydrothermal flow reaction system with various Ti sources [Ti-sol(M-6,A-6) and Ti(SO₄)₂] and LiOH as starting materials. XRD analyses revealed that the LTO single phase was achieved under supercritical conditions at the initial Li/Ti molar ratios >2.5 for Ti-sol(M-6) and >2.0 for Ti-sol(A-6), whereas the LTO single phase could not be obtained from Ti(SO₄)₂ solution even in the initial Li/Ti molar ratio of 10.

Supercritical hydrothermal reaction system is convenient tool for nanoparticles production since it can continuously produce under rapid reaction times in the seconds order with a single step. Although resulting LTO nanoparticles have a high degree of crystal strain due to the disordered titanium in spinel structure, reordering can be achieved by the annealing at 400°C or higher.

References
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