

Li₄Ti₅O₁₂ Synthesis with High Specific Surface Area and Single Phase

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Abstract

We have investigated a novel Li₄Ti₅O₁₂ synthesis with high specific surface area, high crystallization and single phase and its mechanism. The method was performed with a solid phase synthesis by using CH₃COOLi·2H₂O and anatase TiO₂ via Li₂TiO₃ as an intermediate in pre-sintering at 500°C and sintering at 750°C. This result showed specific surface area of 12 m²/g and single phase-Li₄Ti₅O₁₂ by applying the high specific surface anatase TiO₂ as a precursor.

Keywords

Li₄Ti₅O₁₂, Solid Phase Synthesis, Specific Surface Area, SEM, TEM

1. Introduction

A negative electrode in lithium ion secondary battery has applied C₆ graphite to intercalate lithium ions. The graphite expands by overcharge to intercalate them more than stoichiometry. To solve the expansion, materials with keeping a crystal structure have been developed [1]. Hence, Li₄Ti₅O₁₂ consisting of a spinel structure has been expected for not changing the structure or size by intercalating the lithium ion [2] [3]. Furthermore, it is superior to the graphite in stability of charge capacitance under a high temperature or fast charge-discharge cycle [4]-[6]. On the other hand, an electrical conductivity is low like an insulator, and effects of a carbon doping or metal ions by adding V⁵⁺, Mn⁴⁺, Fe³⁺, Mg²⁺ and Ag⁺ have been investigated for the higher conductivity [7]-[14]. Especially the carbon doping has been available, and attempted by a sol-gel or spray-dry method in a liquid phase [15]-[17].

Li₄Ti₅O₁₂ synthesis methods have been known as solid phase, sol-gel, hydrothermal or co-precipitation method. The solid phase method has surpassed others in industrialization to be easy and controllable for the synthe-

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sis, while it is difficult to obtain homogeneous grain size. The small grain size needs lower sintering temperature, but the higher crystallization requires the higher sintering temperature. Furthermore, the solid phase method has been studied for the improvement in these points [18] [19].

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ for the negative electrode requires high crystallization, single phase, small grain size and high specific surface area to perform an excellent property. Especially, the high specific surface area is important to intercalate many lithium ions into the crystal efficiently. We have investigated the synthesis method for the high specific surface area with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of the completely single phase by the solid phase reaction. In this study, we attempted the synthesis by applying anatase TiO_2 of the different specific surface area via a pre-sintering.

2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesis was carried out by using $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.) as a Li source that was melted with low temperature at about 300°C , and 30 or $50\text{ m}^2/\text{g}$ anatase TiO_2 (Toho Titanium Co., Ltd.) as a Ti source. The first synthesis process was mixed with the $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ and TiO_2 with Li:Ti = 4:5 by ball milling (Fritsch, Pulversitte 7) at 1 h, rotating speed at 320 rpm and orbital speed at 110 rpm in agate mortar and balls. The mixed powder was pre-sintering at 500°C with $10^\circ\text{C}/\text{min}$, 1 h in air, and an intermediate was formed. Furthermore, the intermediate was mixed by the ball milling for rotating speed at 320 rpm and orbital speed at 110 rpm at 1 h similarly, and was sintered at 700°C and 750°C with $10^\circ\text{C}/\text{min}$ at 1 h in air.

The obtained powder was identified by XRD (Rigaku Corp., Rint 2000) at scanning step 0.02 deg and scanning speed 5 deg/min by $\text{CuK}\alpha$, and was also measured by BET specific surface area (Shimadzu Corp., Flow-Sorb III 2305) at 0.1 g sample, gas flow rate $80\text{ cm}^3/\text{min}$ in N_2 and current 50 mA, after degassing the sample with heating at 160°C at 2 h. Particle size of the obtained sample was observed by FE-SEM (Hitachi, Ltd., S-4200), and crystalline estimation tried with TEM (JEOL Ltd., JEM-2100).

3. Results and Discussion

3.1. XRD Measurements

We yielded the intermediate by pre-sintering a mixture of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ and anatase TiO_2 at 500°C , and showed XRD patterns as (a); a green line in **Figure 1(A)** and **Figure 1(B)** by applying the $30\text{ m}^2/\text{g}$ and $50\text{ m}^2/\text{g}$ anatase TiO_2 respectively. The intermediate was identified with unreacted TiO_2 and Li_2TiO_3 known as a sub-phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Li_2TiO_3 has been understood by a phase diagram of $\text{Li}_2\text{O}-\text{TiO}_2$ among TiO_2 , Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which shows an accurate mixed rate at Li and Ti atoms [20]. A Ti site of Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is common in center of an octahedron, while a Li site exists in a tetrahedron in the case of Li_2TiO_3 . Li_2TiO_3 show inactivity as the electrode not to charge and discharge Li ions [21].

To obtain $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the intermediate was sintered at 700°C , and the identification was shown as (b); a red line in the XRD patterns, which obtained main $\text{Li}_4\text{Ti}_5\text{O}_{12}$ peaks and slight peaks of Li_2TiO_3 , and was not able to confirm the unreacted TiO_2 . This result is not enough to obtain a single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at the sintering temperature although all unreacted TiO_2 is consumed. Then, effect of the specific surface area by applying the $30\text{ m}^2/\text{g}$ or $50\text{ m}^2/\text{g}$ anatase TiO_2 was not confirmed in **Figure 1(A)** and **Figure 1(B)**. In the sintering temperature at 750°C , the single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was obtained by applying either specific surface area of the anatase TiO_2 as shown in (c); a blue line in the patterns. On the other hand, the peak intensity was strong by applying the anatase TiO_2 of $50\text{ m}^2/\text{g}$ than that of $30\text{ m}^2/\text{g}$, which would be superior to the crystallization.

Now, to estimate the synthesized rate of the single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$, we defined a single phase rate in a following equation.

$$\text{Single phase rate (\%)} = [S(\text{Li}_4\text{Ti}_5\text{O}_{12}) / \{S(\text{Li}_2\text{TiO}_3) + S(\text{Li}_4\text{Ti}_5\text{O}_{12})\}] \times 100$$

Here, “S” shows area of the peaks. The value was nearly same in 86% in **Figure 1(A)** and 89% in **Figure 1(B)** at 700°C , and was 100% at 750°C in any cases. Consequently, the effect of the specific surface area in the anatase TiO_2 does not be indicated by the single phase rate, while the sintering temperature gave the great effect.

3.2. SEM Observation

The intermediate was produced by the pre-sintering the mixture of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ and anatase TiO_2 at 500°C , and was showed in **Figure 2(A)**; $30\text{ m}^2/\text{g}$ and **Figure 2(B)**; $50\text{ m}^2/\text{g}$ anatase TiO_2 . These results showed two

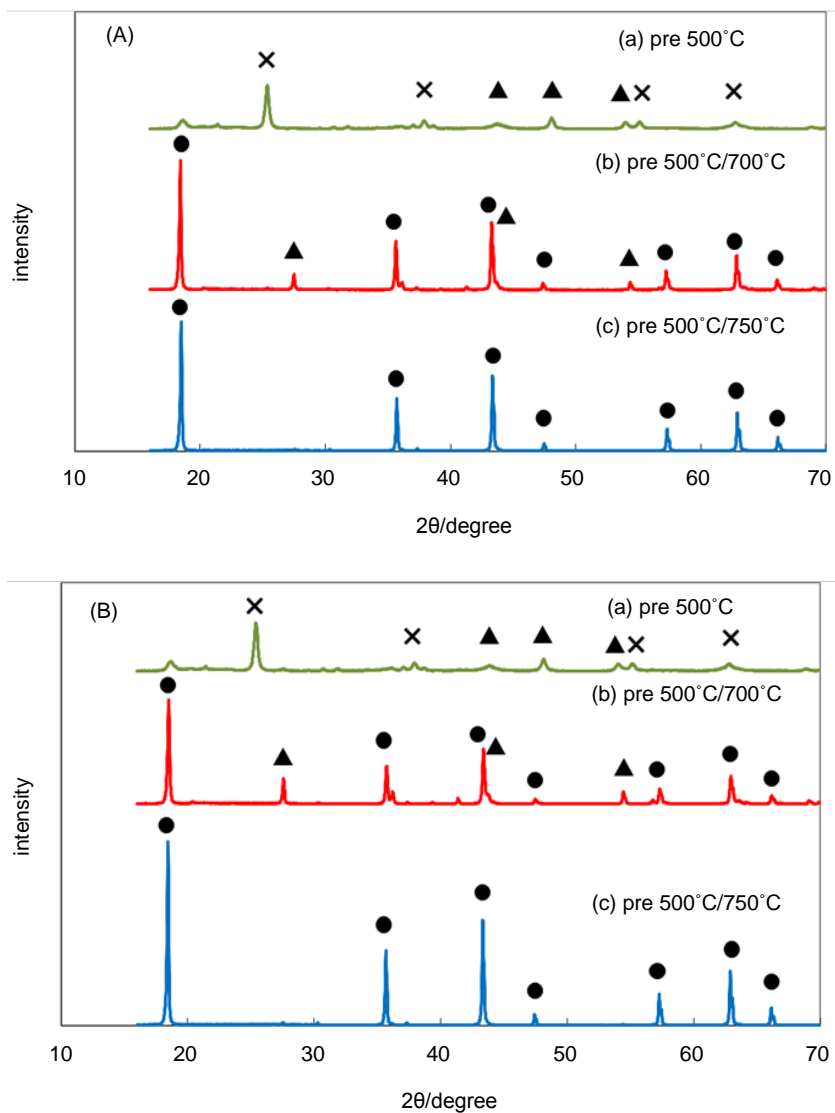


Figure 1. XRD patterns of (A) applying the (30 m²/g); and (B) 50 (m²/g) anatase TiO₂ respectively, addition to (a) pre-sintering temperature at 500 (°C); (b) sintering temperature at 700 (°C); and (c) at 750 (°C) after the pre-sintering. The mark shows ●: Li₄Ti₅O₁₂; ▲: Li₂TiO₃; and ×: TiO₂.

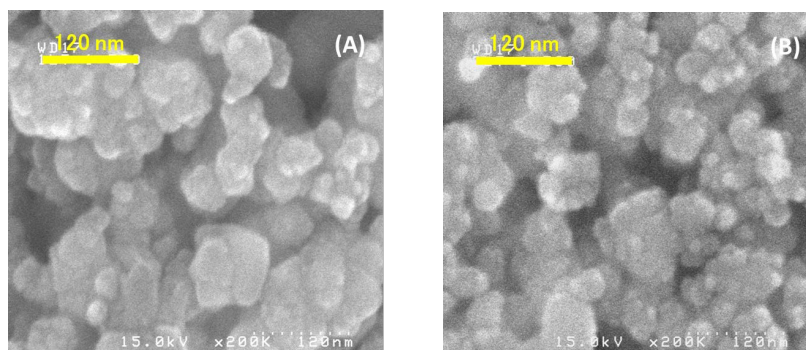


Figure 2. SEM images of the intermediate synthesized by applying (A) 30 (m²/g); (B) 50 (m²/g) anatase TiO₂ after pre-sintering at 500 (°C).

grain species to differ from contrast, which will indicate the unreacted TiO_2 and Li_2TiO_3 as shown in the XRD pattern. The intermediate would consist of the heterogeneous parts by them. The average grain size of the intermediate was different from 60 nm at **Figure 2(A)** and 30 nm at **Figure 2(B)**, and the specific surface area was about $26.6 \text{ m}^2/\text{g}$ and $33.0 \text{ m}^2/\text{g}$ respectively. The specific surface area of the applying anatase TiO_2 will give the effect to the average grain size and specific surface area of the intermediate.

Figure 3 showed homogeneous grains without almost the contrast by the sintering at 700°C or 750°C , especially the heterogeneous parts was not observed at 750°C at all. In fact, the single phases rate is 100%, which would support acquisition of the single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$. While the average grain size trended for greater with the high temperature about **Figure 3(A)**; 101 nm, **Figure 3(B)**; 83 nm, **Figure 3(C)**; 124 nm and **Figure 3(D)**: 87 nm, it will show no much change by applying the $50 \text{ m}^2/\text{g}$ anatase TiO_2 . Similarly, the specific surface area was about (a); $8.3 \text{ m}^2/\text{g}$, (b); $14 \text{ m}^2/\text{g}$, (c); $5.1 \text{ m}^2/\text{g}$ and (d): $12 \text{ m}^2/\text{g}$, hence the single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was obtained with high specific surface area by the $50 \text{ m}^2/\text{g}$ anatase TiO_2 at sintering temperature of 750°C . Furthermore, the crystallization will be higher by the grain of a horned shape.

3.3. TEM Observation

Figure 4 shows TEM images at pre-sintering temperature of 500°C . The minute TiO_2 particles will encircle the Li_2TiO_3 at the $50 \text{ m}^2/\text{g}$ anatase TiO_2 specially, which may take advantage of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesis by the following sintering. These images did not indicate a clear morphology like a facet in this pre-sintering, and would show a very low crystallization.

TEM images show the samples by the sintering temperature of 700°C or 750°C in **Figure 5**. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles would be the higher crystallization to form at an angular grain which included the facets in the morphology, while the sintering temperature and the specific surface area of the anatase TiO_2 would hardly give the effect for the synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ not to be obtained about the clear differences. The morphology have been reported about the synthesis by using nano-particle or nano-wire TiO_2 , which have described that the nano-particle or nano-wire $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was obtained on keeping the TiO_2 morphology like a mold [22] [23]. This knowledge will suggest the synthesis mechanism for the solid phase synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which the (002) face of Li_2TiO_3

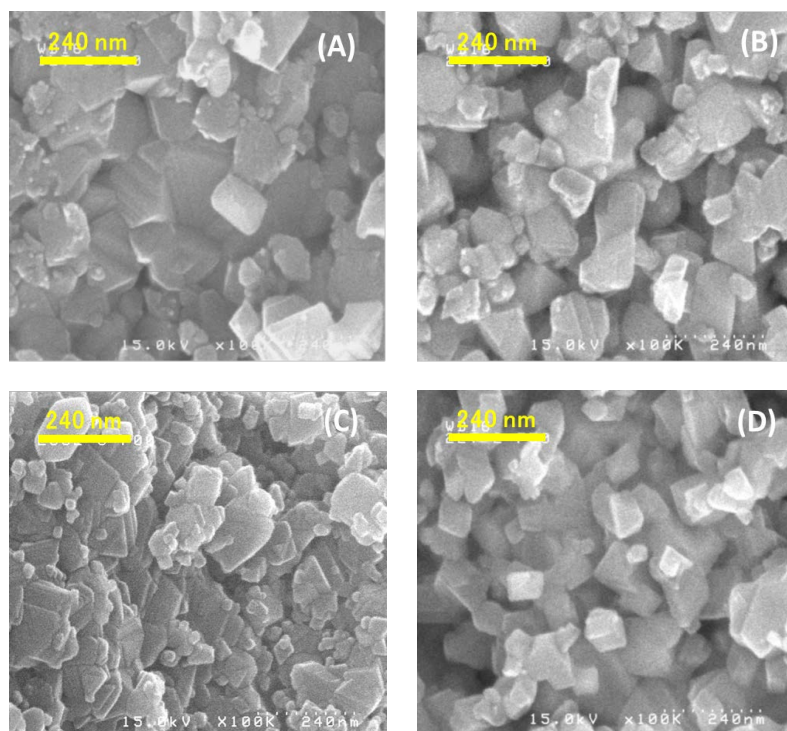


Figure 3. SEM images of the synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which is (A) 700°C , by the $30 \text{ (m}^2/\text{g)}$; (B) 700°C , by the $50 \text{ (m}^2/\text{g)}$; (C) 750°C , by the $30 \text{ (m}^2/\text{g)}$; (D) 750°C , by the $50 \text{ (m}^2/\text{g)}$ anatase TiO_2 .

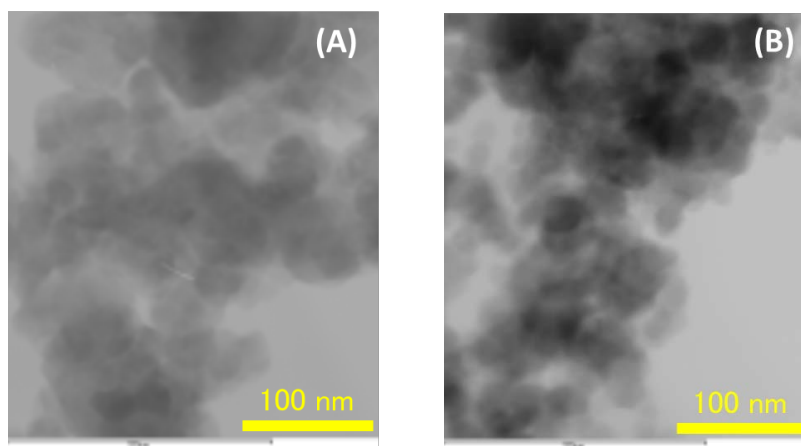


Figure 4. TEM images of the intermediate synthesized by applying (A) 30 (m²/g); (B) 50 (m²/g) anatase TiO₂ after pre-sintering at 500 (°C).

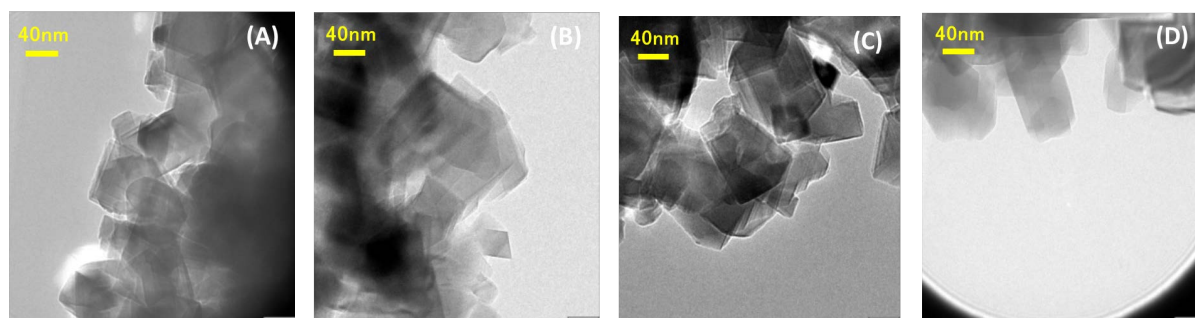


Figure 5. TEM images of the synthesized Li₄Ti₅O₁₂ which is (A) 700 (°C), by the 30 (m²/g); (B) 700 (°C), by the 50 (m²/g); (C) 750 (°C), by the 30 (m²/g), (D); 750 (°C), by the 50 (m²/g) anatase TiO₂.

plays a role of the mold in the spinel structure. These may show that the mobility of titanium ions is improved to close to the (002) Li₂TiO₃ and the (111) Li₄Ti₅O₁₂.

4. Conclusion

We attempted the single phase Li₄Ti₅O₁₂ synthesis with the higher specific surface area by using CH₃COOLi·2H₂O as a Li source that was melted with low temperature at about 300 °C, and 30 or 50 m²/g anatase TiO₂ as a Ti source. The synthesis method obtained Li₄Ti₅O₁₂ by the sintering at 700 °C or 750 °C via Li₂TiO₃ as the intermediate in pre-sintering at 500 °C. Then, the single phase Li₄Ti₅O₁₂ was obtained with 12 m²/g specific surface area and the higher crystallization at 750 °C. The mechanism may give a suggestion as the improvement of mobility for the titanium ions.

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