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Single Phase $Li_4Ti_5O_{12}$ Synthesis for Nanoparticles by Two Steps Sintering

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Abstract

$Li_4Ti_5O_{12}$ has been noticed about a negative electrode of a high powered and safe lithium ion secondary battery. These properties require single phase, high crystallization, larger specific surface area and fine nanoparticles. This study carried out the noble synthesis of $Li_4Ti_5O_{12}$ using a solid phase synthesis by two steps sintering. These results showed $Li_4Ti_5O_{12}$ of 6.1 $m^2 \cdot g^{-1}$ and diameter of 110 nm with the single phase and high crystallization. Li_2TiO_3 will play an important role in this reaction, obtained by pre-sintering as a precursor.

Keywords

Lithium Ion Secondary Battery, $Li_4Ti_5O_{12}$, Solid Phase Synthesis, Sintering, Nanoparticle

1. Introduction

Lithium ion secondary batteries have been noticed for many applications to high performances recently, and the developments have been performed [1]. For example, material development of negative electrode has been concerned with safety. The material is currently graphite, which has layer structure and is intercalated by lithium ions into the layers. On the other hand, the graphite is not safe to expand with overcharge to intercalate amount of lithium ions over the stoichiometry into the layer. Therefore, noble materials have been investigated instead of the graphite to prevent ignition by internal short-circuit [2]. The noble materials need some properties, whose crystal structure shows no change and high stability with intercalate lithium ions. Furthermore, the synthesis is easy and inexpensive to mass production. Here, we have studied $Li_4Ti_5O_{12}$ as superior negative electrode materials [3].

$Li_4Ti_5O_{12}$ has spinel structure and $LiMn_2O_4$ does likewise, which is applied to the positive electrode in the lithium ion secondary battery. The properties of $Li_4Ti_5O_{12}$ are hardly expanded by the overcharge, and high stabil-

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ity in cycles of discharge and charge. The synthesis methods are known as solid phase synthesis, sol-gel process, hydrothermal synthesis, coprecipitation method and vapor phase deposition method. Especially, the solid phase synthesis is a good method for industrial processes, which is simple and easy to control composition of a chemical compound. However, it has some problems, such as a low reactivity, a control of fine particle size and a production of by-products. The synthesis developments have been performed to solve them [4] [5].

Consequently, the synthesis method is needed to produce $Li_4Ti_5O_{12}$ of a single phase, fine nano-size particles and a high crystalline in order to show high performance as the battery. A synthesis process has been performed by sintering with low temperatures by a two-step process of a pre-sintering at 400˚C - 500˚C and a sintering at 700˚C - 750˚C, because we have tried to synthesize a single phase and fine nano-size $Li_4Ti_5O_{12}$.

2. Experimental

$Li_4Ti_5O_{12}$ synthesis was carried out by using $CH_3COOLi{\cdot}2H_2O$ (Wako Pure Chemical Industries, Ltd.) as a Li source that was melted with low temperature at about 300˚C, and anataseTiO_2 (Toho Titanium Co., Ltd.) as a Ti source. The first synthesis process was mixed with the $CH_3COOLi{\cdot}2H_2O$ 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 400˚C, 450˚C and 500˚C with 10˚C/min, 1 h in air, and a precursor was formed. Furthermore, the precursor was mixed by the ball milling at 1 h similarly, and was sintered at 700˚C and 750˚C with 10˚C/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 CuKα, and was also measured by BET specific surface area (Shimadzu Corp., FlowSorb III 2305) at 0.1 g sample, gas flow rate 80 cm^3/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. Pre-Sintering

Precursor was formed by pre-sintering the $CH_3COOLi{\cdot}2H_2O$ and TiO_2 mixed powder at 400˚C, 450˚C and 500˚C in air, and showed in **Figure 1**. These indicated unreacted TiO_2 and sub-phase Li_2TiO_3 of $Li_4Ti_5O_{12}$ under any temperature. This relationship is known as a phase diagram of Li_2O-TiO_2 among TiO_2, Li_2TiO_3 and $Li_4Ti_5O_{12}$, which shows an accurate mixed rate at Li and Ti atoms [6]. Ti site of Li_2TiO_3 and $Li_4Ti_5O_{12}$ is common in center of an octahedron, while Li site exist a tetrahedron in the case of Li_2TiO_3. Hence, Li_2TiO_3 shows inactivity as the electrode not to charge and discharge Li ions [7].

SEM images were shown about the precursors in **Figure 2**. These indicated that average grain size increased with the pre-sintering temperature at 50 nm, 70 nm and 75 nm under 400˚C, 450˚C and 500˚C. Simultaneously,

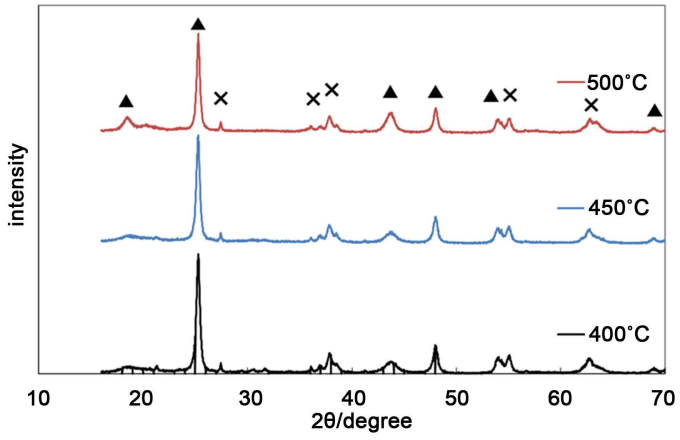

Figure 1. XRD patterns of the samples pre-sintered at 400˚C (black line), 450˚C (blue line) and 500˚C (red line), which show ▲; Li_2TiO_3 and ×; TiO_2.

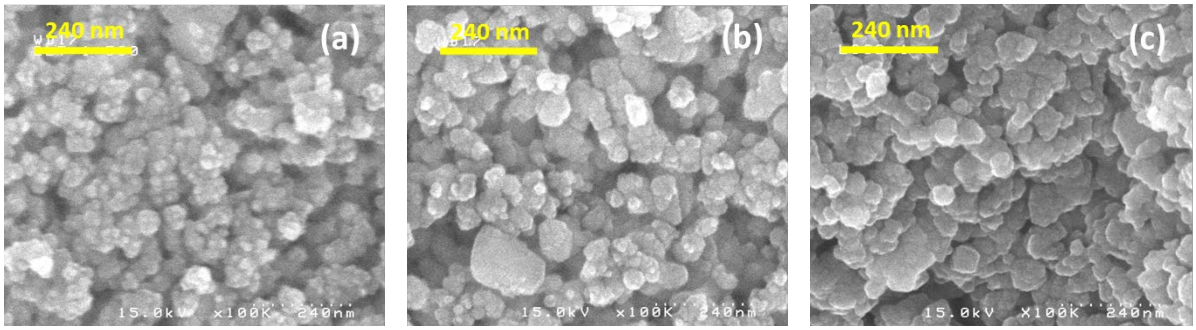

Figure 2. SEM images of the samples for the pre-sintering temperature of (a) 400˚C, (b) 450˚C and (c) 500˚C.

BET specific surface area presented 27.7 $m^2 \cdot g^{-1}$, 26.6 $m^2 \cdot g^{-1}$ and 26.2 $m^2 \cdot g^{-1}$ under 400˚C, 450˚C and 500˚C. The images of the grain observed two types as deference of contrast at 400˚C in **Figure 2(a)**, and showed a uniform contrast with the high temperature. These results might indicate a localization of unreacted TiO_2 and sub-phase Li_2TiO_3 in keeping with XRD patterns. This tendency may confirm TEM images in **Figure 3**, which will show a low crystallization with corresponded to XRD not to observe facet areas.

3.2. Sintering

XRD peaks of samples ware showed at sintering temperature of 700˚C and 750˚C in **Figure 4** and **Figure 5**. Peaks intensity of Li_2TiO_3 decreased, while those of $Li_4Ti_5O_{12}$ increased with pre-sintering temperature at 700˚C sintering in **Figure 4**. Single phase of $Li_4Ti_5O_{12}$ was obtained at the pre-sintering temperature of 500˚C in **Figure 5**, however the peaks intensity indicated the similar tendency about pre-sintering temperature with the sintering temperature of 700˚C. Here, we defined a single phase rate to estimate it, which utilized the peaks area of them at shown in following equation.

$$\text{single phase rate } (\%) = \left[I\left(Li_4Ti_5O_{12}\right) \Big/ \left\{ I\left(Li_2TiO_3\right) + I\left(Li_4Ti_5O_{12}\right) \right\} \right] \times 100$$

The value at 700˚C was 80%, 84% and 86% at the pre-sintering temperature of 400˚C, 450˚C and 500˚C, which were advantageous with the high pre-sintering temperature. Furthermore, the value at 750˚C was 92%, 99% and 100% similarly, and we could obtain the single phase $Li_4Ti_5O_{12}$ at 750˚C. These results will show that the sub-phase Li_2TiO_3 give effects for the $Li_4Ti_5O_{12}$ synthesis.

A surface separation of (002) face of Li_2TiO_3 at 4.80 Å is very close to that of (111) face of $Li_4Ti_5O_{12}$ at 4.83 Å in the spinel structure, which $Li_4Ti_5O_{12}$ would be able to form from Li_2TiO_3 with holding the structure [8]. The knowledge will show that $Li_4Ti_5O_{12}$ was synthesized via Li_2TiO_3 by the pre-sintering, and the single phase was obtained at 750˚C in this process.

SEM images of the samples showed in **Figure 6**. The average grain size was observed at about 90 nm in any samples at sintering temperature of 700˚C in **Figures 6(a)-(c)**, and the BET specific surface area was about 10.5 $m^2 \cdot g^{-1}$ for any samples. Similarly, it was at 110 nm under 750˚C in **Figures 6(d)-(f)**, and was 7.3 $m^2 \cdot g^{-1}$, 6.3 $m^2 \cdot g^{-1}$ and 6.1 $m^2 \cdot g^{-1}$ in the specific surface area. The grain size of the single phase $Li_4Ti_5O_{12}$ have reported about 600 nm in the solid phase synthesis under 850˚C at 12 h by boll-milling [9]-[11], and Guerfi has especially reported the grain size of 150 nm by mixing graphite into the ball mill [9]. On the other hand, we could synthesize that of grain size of 110 nm via Li_2TiO_3 at 750˚C by the two steps sintering method.

TEM images of the samples showed in **Figure 7**, and the shape of the grain indicated uniformity in any samples. Furthermore, morphology was improved at the sintering temperature of 750˚C compared with at 700˚C, and facets in the grain were observed by a crystal growth. The morphology have been reported about the synthesis by using nano-particle or nano-wire TiO_2, which have described that the nanoparticle or nanowire $Li_4Ti_5O_{12}$ was obtained on keeping the TiO_2 morphology like a mold [12] [13]. This knowledge will provide a synthesis mechanism for this two steps sintering method, which the (002) face of Li_2TiO_3 plays a role of the mold in the spinel structure. These may show the reason why the surface separation of the (002) Li_2TiO_3 has very close it in the (111) $Li_4Ti_5O_{12}$.

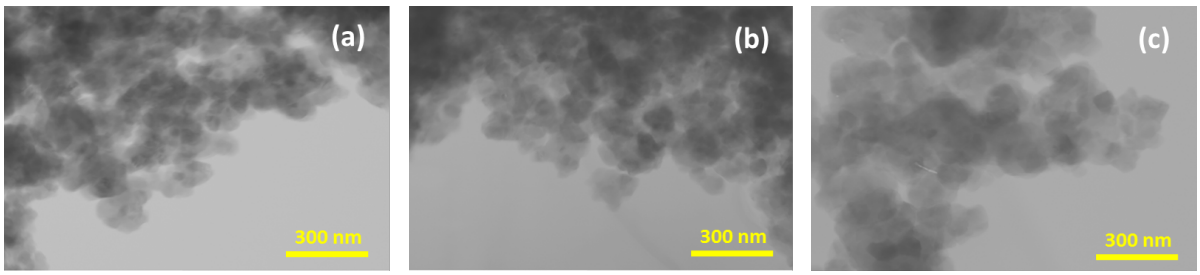

Figure 3. TEM images of the samples for the pre-sintering temperature of (a) 400˚C, (b) 450˚C and (c) 500˚C.

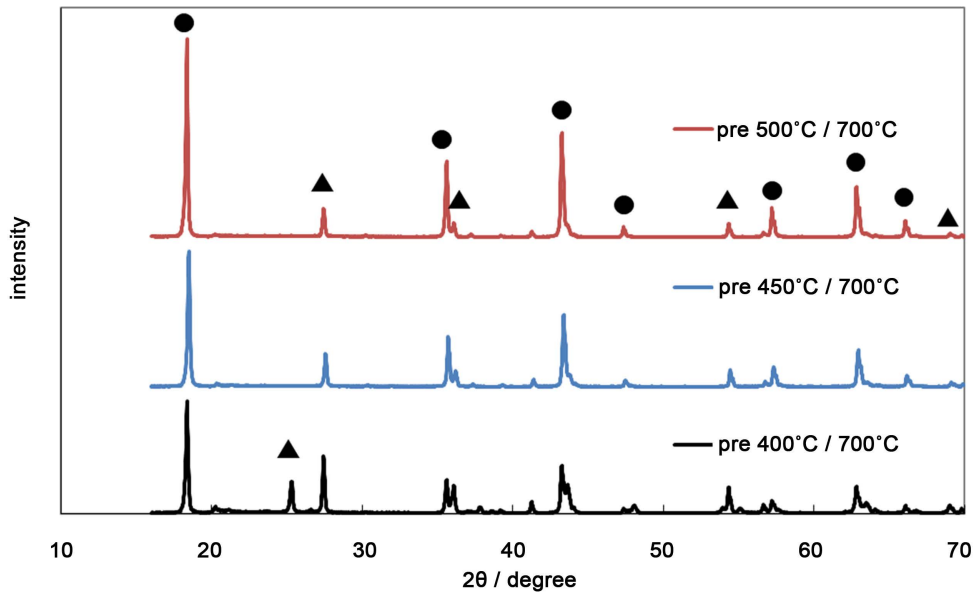

Figure 4. XRD patterns of the samples sintered at 700˚C with the pre-sintered temperature of 400˚C (black line), 450˚C (blue line) and 500˚C (red line), which show ●; $Li_4Ti_5O_{12}$ and ▲; Li_2TiO_3.

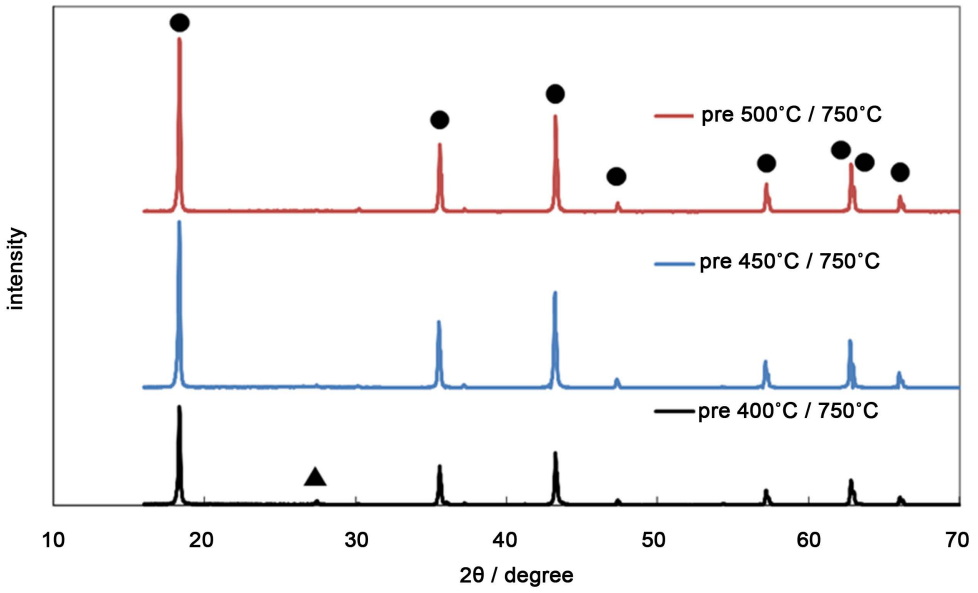

Figure 5. XRD patterns of the samples sintered at 750˚C with the pre-sintered temperature of 400˚C (black line), 450˚C (blue line) and 500˚C (red line), which show ●; $Li_4Ti_5O_{12}$ and ▲; Li_2TiO_3.

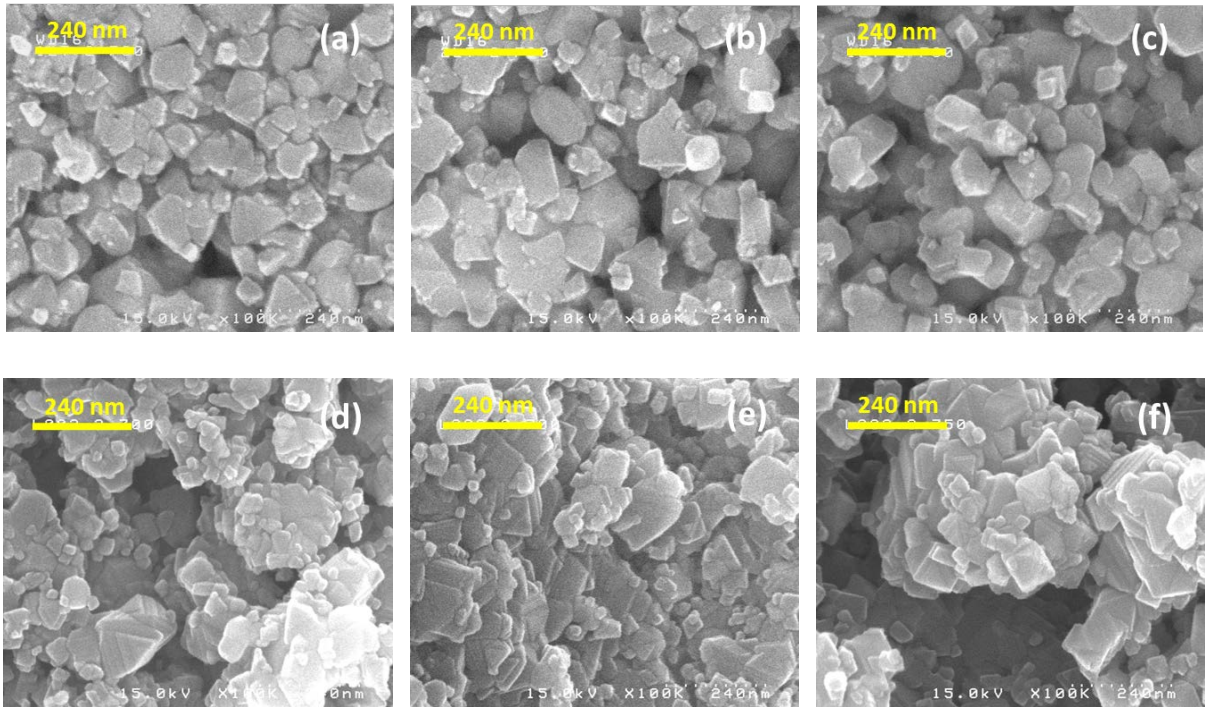

Figure 6. SEM images of the samples sintered at 700˚C with the pre-sintered temperature of (a) 400˚C, (b) 450˚C and (c) 500˚C; and at 750˚C with the pre-sintered temperature of (d) 400˚C, (e) 450˚C and (f) 500˚C.

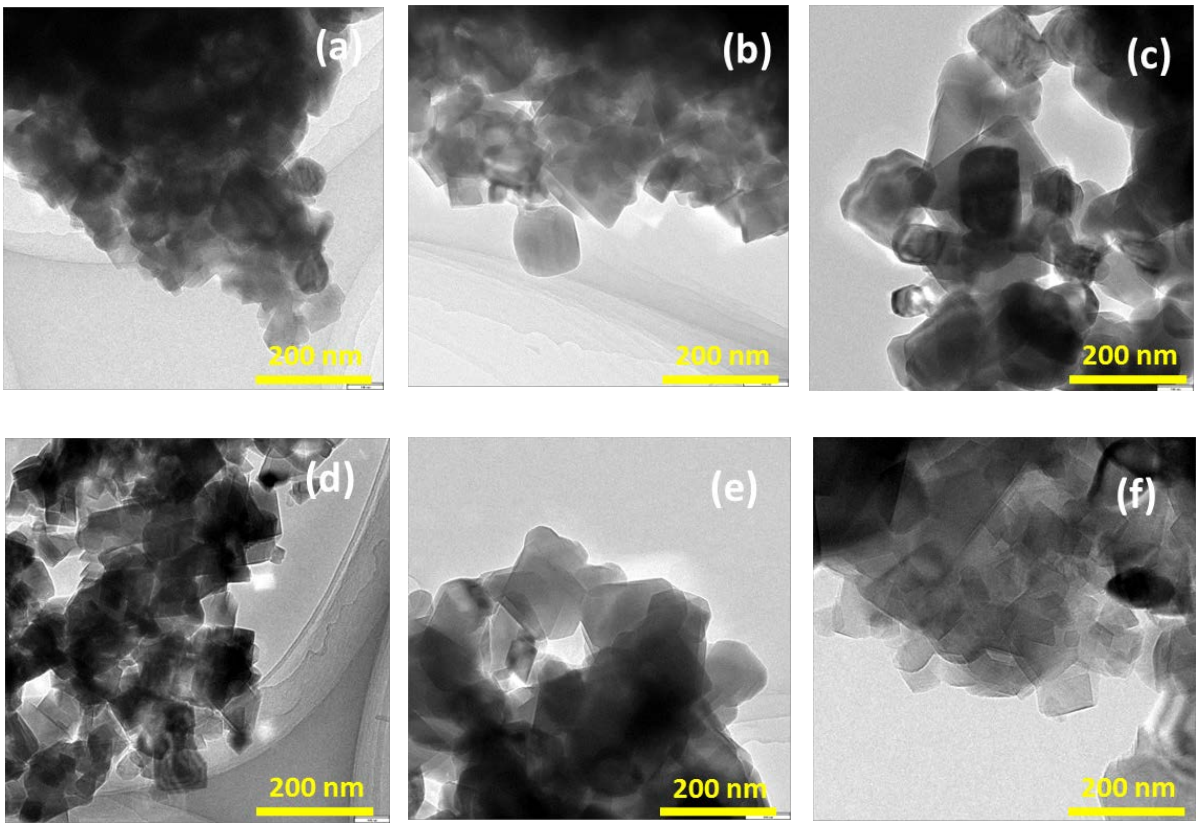

Figure 7. TEM images of the samples sintered at 700˚C with the pre-sintered temperature of (a) 400˚C, (b) 450˚C and (c) 500˚C; and at 750˚C with the pre-sintered temperature of (d) 400˚C, (e) 450˚C and (f) 500˚C.

4. Conclusion

Single phase $Li_4Ti_5O_{12}$ was synthesized by the two-step sintering via Li_2TiO_3. The method especially obtained the fine nanoparticles at about 110 nm and 6.1 $m^2 \cdot g^{-1}$ under sintering temperature of 750˚C. The process will bring about expectation for the mass production in the industry.

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