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SHORT COMMUNICATION

Synthesis and structural properties of lithium titanium oxide powder as-synthesized by two step calcination process

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Abstract−A two-step calcination synthesis, considering the potential for mass production, of lithium titanium oxide powder was carried out to fabricate a single $Li_4Ti_5O_{12}$ phase, which is useful for anode electrode material of Li-based rechargeable battery as well as an electrode for supercapacitor. The final composition is controlled by adding more TiO_2 powder into powder gained at one calcination process during the two calcination process. We investigated the influence of excess TiO_2 on the structural characteristics of lithium titanium oxide synthesized by the two-step calcination method. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) measurements showed that the as-synthesized powder had a spinel crystal structure as well as A composition of 4 : 5 : 12. In addition, a high resolution transmission electron microscopy (HRTEM) analysis revealed that the fabricated powder exhibited a single crystalline phase formation. These results indicated that the powder synthesized in the one-step calcination process showed coexistence crystalline phases, which are the $Li_4Ti_5O_{12}$ and $Li_{2.39}Ti_{3.4}O_8$ phase. However, in the two-step calcination process, the powder synthesized showed the single crystalline $Li_4Ti_5O_{12}$ phase. A very uniform grain size of the as-synthesized powder was shown in a field emission scanning electron microscopy (FESEM). These results suggested that the two-step calcination process can be used for synthesis of single crystalline $Li_4Ti_5O_{12}$ powder with uniform grain shape and provide motivation to pursue mass production of lithium titanium based oxide powder for bulk type batteries.

Key words: Lithium Titanium Oxide, Two Step Calcination Process, Oxygen Content, Rechargeable Battery, High Resolution Transmission Electron Microscopy

INTRODUCTION

Rechargeable lithium ion batteries are used extensively because they have better electrochemical properties and are more environmentally friendly than other rechargeable batteries [1], such as NiCd and/or Pb based batteries. In addition, they can be stored for long periods of time in products such as the percussion cap in the blasting parts of a missile. Moreover, they are suitable in tiny bionic products and in the development of bionics.

Research on rechargeable lithium ion batteries has focused on improving their electrochemical performance such as capacity, cyclability and stability. Recently, many efforts for increasing the cathode electrode performance have been tried, and some highly stable cathode materials compared with Li-Co-O or Li-Ni-O based materials have been developed. Those stable cathode materials increase the battery stability during use periods at relatively high temperatures. However, we have the instability of Li metal or Li ion based anode. The Li batteries with Li based anode show explosion at elevated temperature due to this instability. Stable anode, therefore, should be developed in order to replace the Li based anode. Among many candidates, Si, Sn and/or Li-Ti-O are focused on by many research groups. Even though Si and Sn based anode materials have high energy capacity, those have extremely poor initial efficiency and cyclability, and it is hard to use these materials as stable anode over time. Li-Ti-O based materials or series are very attractive as anode candidate material because of high chemical stability at high temperature and the high reversibility of the lithium insertion reaction. This enables the development of batteries with a prolonged life cycle [2], although they have high Li-insertion voltage as shown in the series below compared with Si and Sn.

In 1971, Deschanvres et al. reported that the spinel oxides $Li_{1+x}Ti_{2-x}O_4$ ($0 \le x \le 1/3$), for the space group Fd3m, had a cubic crystalline structure [3]. In the early 1990s, Dhan, Thackeray, and Ohzuku et al. electrochemically characterized these oxides [4-7]. The end members of the series, that is $LiTi_2O_4$, showed metallic behavior with a dark blue color (superconducting below 11 K), and $Li_4Ti_5O_{12}$ showed a semiconducting behavior with a white color [2]. Despite this difference, both of these materials exhibit similar Li-insertion electrochemistry. For example, the formal potentials of the Li-insertion are 1.36 V to 1.338 V for $LiTi_2O_4$ and 1.55 V to 1.562 V for $Li_4Ti_5O_{12}$ [4].

In this work, we synthesized lithium titanate ($Li_4Ti_5O_{12}$; LTO) powders with single crystalline structure by a two-step calcination process and investigated the structural properties in order to develop a mass production based fabrication process since the two-step calcination process is one of the good mass production methods [8].

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In general, it is very hard to form the single crystalline phase of LTO by conventional calcination method. That is, the formation of a single crystalline phase of LTO is very difficult by single-step calcination following mixing the Li_2CO_3 and TiO_2 powders with atomic ration of 4 : 5. Therefore, we focus on the formation of single crystalline phase of the LTO in this study.

EXPERIMENTAL

Powders of Li_2CO_3 and TiO_2 (Kojundo Co. Ltd.) with a purity of 99.9% both are used for the raw materials to synthesize LTO. The Li_2CO_3 and TiO_2 powders were thoroughly mixed in a rotary mill with rotation speed of 500 rpm for 24 hours by using ZrO_2 ceramic balls, and ethanol was used as a dispersing medium. The atomic ratio of Li_2CO_3 and TiO_2 was calculated from weight percentage ratio of Li_2CO_3 and TiO_2 to control the composition of the as-synthesized powder. At the first stage, the atomic ratio of Li and Ti was 2.38 : 1.

After finishing the mixing step, we dried the mixture for 24 hours at 100 °C. The powders obtained from the drying process were then calcinated for 5 hours at 900 °C. The second ball milling was conducted for 24 hours, and we conducted the final heat treatment for 5 hours at 1,050 °C to form the crystalline structure of LTO powder. This powder was named by pseudo-LTO.

In order to synthesize stoichiometric LTO, we added TiO_2 powder into the as-synthesized pseudo-LTO powder. Finally, we applied the same process to the crystalline structure LTO powder, which made the Li and Ti atomic ratio of 4.1 : 5. Namely, the powder mixture had a 10% Li excess content. Fig. 1 shows the detailed procedure.

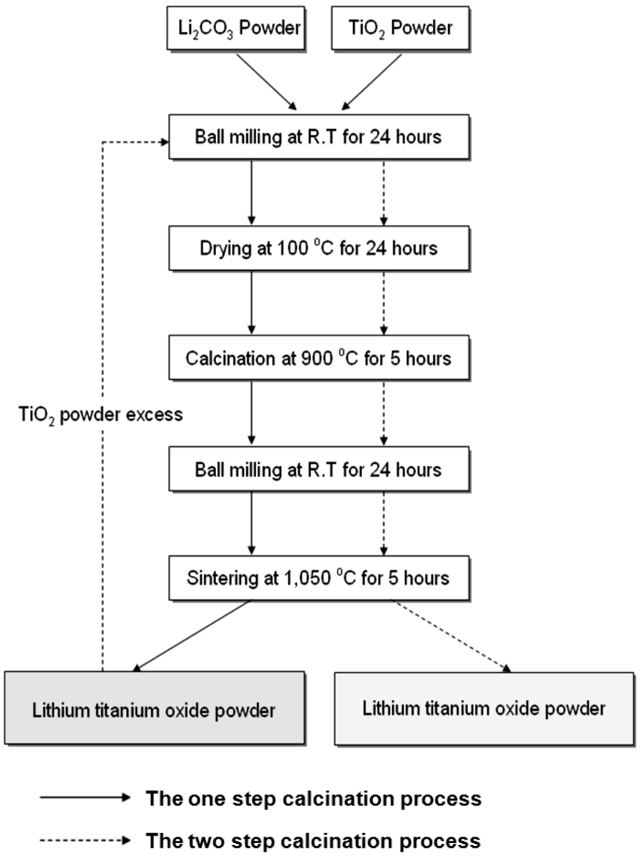
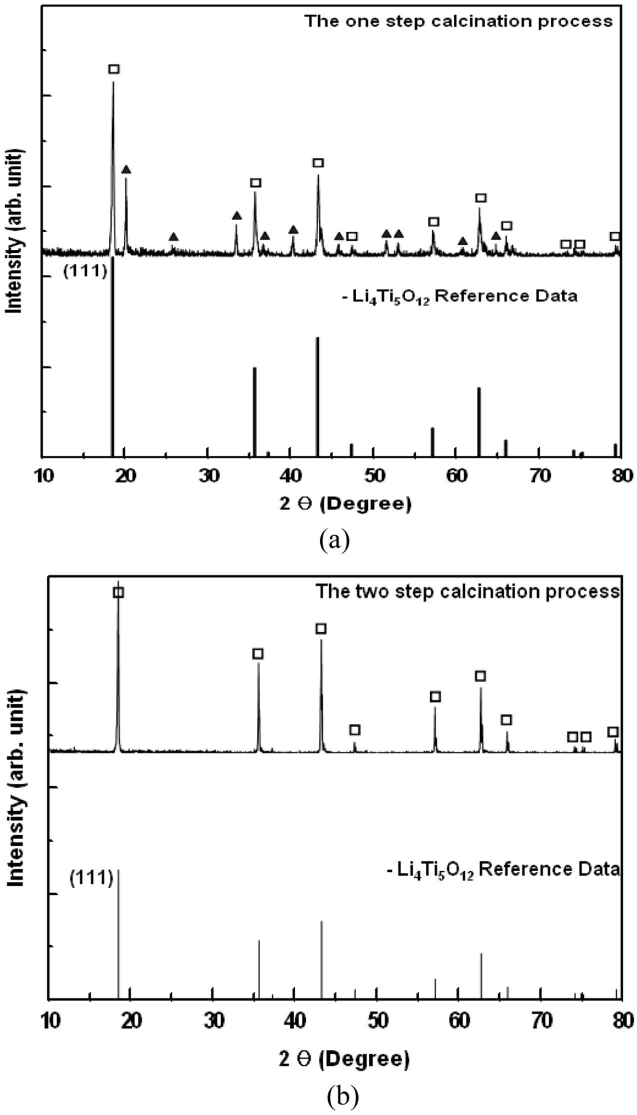


Fig. 1. A detailed diagram of the two-step calcination powder process of LTO materials.

The structure and morphology properties of the as-synthesized LTO powder were investigated in order to reveal the crystallinity and crystal phase. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy measurements were taken to analyze the crystallinity and to compare with reference LTO powder, respectively. The as-synthesized LTO grain shape and size were identified by field emission scanning electron microscopy (FESEM). In addition, for the existence of the phase analysis, dark field images of transmission electron microscopy (TEM) and high resolution TEM (HRTEM) analysis were carried out to confirm the defects and phases in the as-synthesized LTO grain.

RESULTS AND DISCUSION

The as-synthesized LTO powder had a very white color without



(a)

(b)

Fig. 2. XRD curve of as-synthesized (a) pseudo-LTO and (b) LTO powders.

any different color dots, while the pseudo-LTO powder showed a little bit light blue by the naked eye. This means that the LTO and pseudo-LTO have different physical properties such as crystallinity and/or composition from each other.

Wide angle XRD measurements in 2 theta range of 10-80° were conducted to distinguish the crystalline difference between the LTO and pseudo-LTO as shown in Fig. 2. Compared with the reference XRD patterns by JCPDS # 490207, the as-synthesized LTO and the pseudo-LTO showed single crystallinity and multi-crystallinity, respectively.

Fig. 2(a) shows the XRD patterns of the as-synthesized pseudo-LTO powder. There are several peaks in the $Li_4Ti_5O_{12}$ powder and they agree well with those of the $Li_4Ti_5O_{12}$ reference XRD patterns. Not only the (111) peak at 2 theta of 18° but also peaks not shown in the JCPDS # 49207 patterns were observed in the XRD pattern. The precise investigation of the JCPDS indicated that the pseudo-LTO powder has $Li_{2.39}Ti_{3.4}O_8$ (▲). These results indicated that the as-synthesized pseudo-LTO consists of multi-crystalline phases with different atomic ratio of Li/Ti as well as residual Li_2O without a reaction with Ti. The formation of multiphases agrees well with our previous result [8]. Fig. 2(b) shows the results of the XRD patterns for the as-synthesized LTO powders as the two-step process. The LTO powder as-synthesized by the two-step process shows the existing single phase. Also, all peaks for as-synthesized LTO at the two-step process were in good agreement with those observed for reference $Li_4Ti_5O_{12}$ data (JCPDS #490207). Furthermore, the intensity ratios of peak to peak were coincident with each other. Even though it is hard to speculate the reason for the formation of a single crystalline phase, it can be explained by the chemical reactions with non-LTO phase and TiO_2. This chemical reaction might have lower activation energy for the formation of LTO phase than that by Li_2CO_3 and TiO_2 reaction, which induced LTO phase formation easily during calcination at the same temperature.

Fig. 3 shows the FT-IR absorption bands for the as-synthesized LTO powder by the one- and two-step calcination process. The absorption band of the as-synthesized LTO sample is similar to the reference $Li_4Ti_5O_{12}$ phase. There are two absorption bands whose centers are located at 488 cm^{-1} and 649 cm^{-1} at the LTO synthesized by the two calcination method and reference LTO between 400 cm^{-1} and 1,000 cm^{-1} can clearly be observed [9]. Also, the two absorption bands correspond to the symmetric stretching vibration, and we observed an absorption band formed by the reaction of CO_2 on TiO_2 at the 1,430 cm^{-1}. In addition, no other peaks induced by non LTO phase can be observed, while the pseudo-LTO powder shows some extra peaks in the FT-IR bands. Therefore, the phase of the as-synthesized LTO by the two step is the same as the pure $Li_4Ti_5O_{12}$ phase. This result agrees well with XRD analysis result.

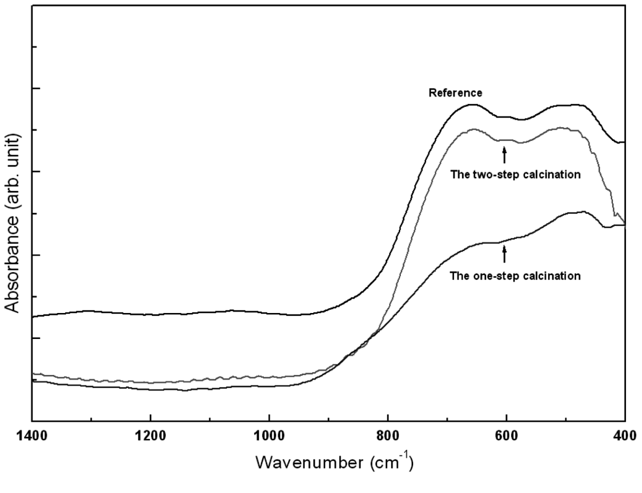
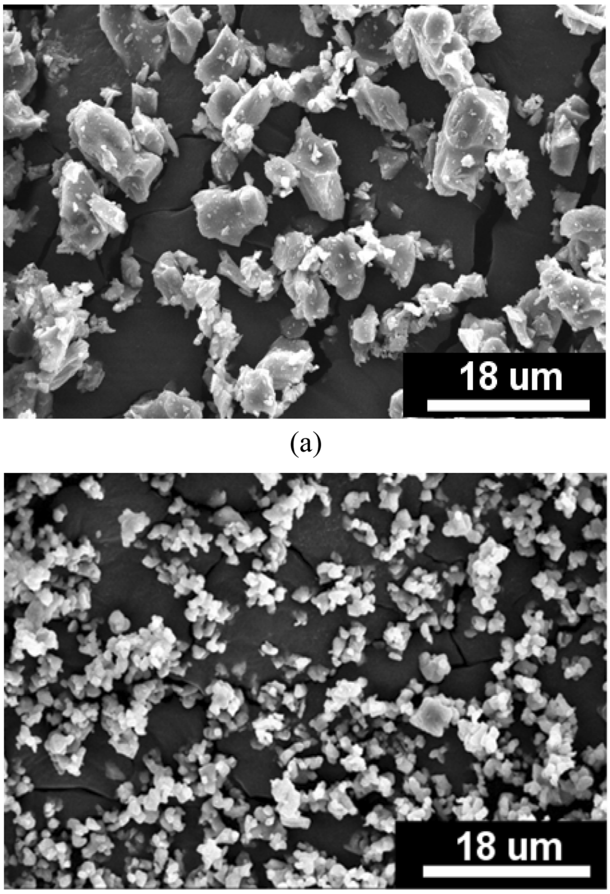


Fig. 3. FT-IR absorption bands for the LTO powder as-synthesized by the one- and two-step calcination process.



(a)

(b)

Fig. 4. FESEM images of the pseudo-LTO (a) and the LTO (b) powders.

Fig. 4 shows the FESEM images of the pseudo-LTO (a) and the LTO (b) powders. Generally, the particle size may be due to the temperature and time during the calcination process in the conventional solid state method [10]. The particle size (0.8 μm) of the LTO powder is much smaller than that (8 μm) of the pseudo-LTO powder. Thus, the particle size results in a relatively large particle size (0.8 μm), or larger than in the electrode materials field. But the particle size is enough to satisfy the high rate requirement in the rechargeable battery.

Fig. 5 shows TEM and HRTEM images showing the pseudo-LTO (a) and the LTO (b) powders. Also, just as in the HRTEM result, the pseudo-LTO powder shows two different crystalline phases at the as-synthesized by the first step calcination. But the LTO powder synthesized by the two calcination method shows that the grown LTO is well crystallized in the framework spinel structure without any indication of crystallographic defects such as dislocations or

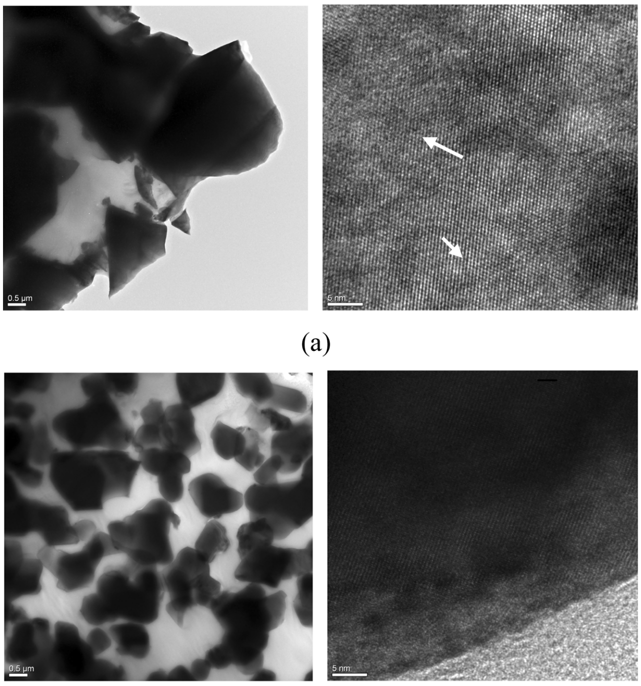


Fig. 5. TEM and HRTEM images of the pseudo-LTO (a) and the LTO (b) powders.

misfits. These results suggest that the LTO powder of single crystalline phase synthesized by the conventional powder two-step calcination method, considering the potential for mass production, includes single crystalline phases if it has excess TiO_2 content.

CONCLUSIONS

We synthesized LTO powders by using conventional powder two-step calcination method and analyzed structural properties when the LTO had excess TiO_2. The XRD pattern, high-resolution TEM images show the existence of single crystalline phases of LTO powder. As shown by FESEM and TEM measurements, the LTO had smaller grains with an increase in TiO_2 content. These results indicate that the excess lithium in the LTO powder synthesized by the conventional powder two-step calcination method, considering the potential for mass production, induces the formation of single crystalline phases.

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