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Synthesis and structural properties of lithium titanium oxide powder

Soo Ho Kim, Kwang Hoon Lee, Baek Seok Seong*, Gyeung-Ho Kim, Jong Sung Kim*** and Young Soo Yoon†**

Department of Advanced Technology Fusion, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea
*Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon 305-600, Korea
**Nanomaterial Research Center, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, Korea
***Department of Chemical and Biological Engineering, Kyungwon University,
Bokjung-dong, Sujung-gu, Seongnam-si, Gyounggi-do 461-701, Korea
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Abstract−Recently, lithium titanium oxide material has gained renewed interest in electrodes for lithium ion rechargeable batteries. We investigated the influence of excess Li on the structural characteristics of lithium titanium oxide synthesized by the conventional powder calcination method, considering the potential for mass production. The lithium excess ratio is controlled by using different weight of Li_2CO_3 powder during calcination. X-ray diffraction (XRD) measurement for the synthesized powder showed that the lithium titanium oxide material with excess lithium content had a spinel crystal structure as well as a different crystal one. In addition, high resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM) measurement revealed that the lithium titanium oxide powders with a lithium excess ratio of 5-20% exhibited a two phase formation. Inductively coupled plasma - atomic emission spectrometer (ICP-AES) and energy dispersive x-ray spectroscopy (EDX) measurements were used to analyze composition of the lithium titanium oxide powder. These results suggested that the conventional calcination method, considering the potential for mass production, formed two phases according to the Li excess amount in initial raw materials.

Key words: Lithium Titanium Oxide, Rechargeable Battery, ICP-AES, HRTEM, Mass Production, Li Excess

INTRODUCTION

Recently, various techniques, such as the sol-gel process, powder calcination process, and hydrothermal process, have been used to synthesize lithium transition metal oxide materials for excellent lithium rechargeable batteries [Sun et al., 1998; Doh et al., 2002; Park et al., 2005; Rho et al., 2002]. Research on rechargeable lithium batteries has focused on enhancing their electrochemical performance and investigated electrodes and electrolyte materials. Electrode materials have been studied more extensively since the performance of the Li battery strongly depends on the structural properties of the electrode materials than those of other components constituting the battery. Among the plethora of different electrode materials, such as $LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.8}Co_{0.2}O_2$ and $Li_{1+x}Ti_{2-x}O_4$; $(0 \leq x \leq 1/3)$, many researchers have recently reported that the $Li_{1+x}Ti_{2-x}O_4$ has not only easy charge/discharge properties, but also excellent recycling performance. Based on these reports, the $Li_{1+x}Ti_{2-x}O_4$; $(0 \leq x \leq 1/3)$ series can be considered for developing rechargeable lithium ion batteries, particularly to serve as an anode material. Moreover, the $Li_{1+x}Ti_{2-x}O_4$; $(0 \leq x \leq 1/3)$ series shows a high reversibility of the lithium insertion reaction, which would make it possible to develop batteries with a very long cycle life. Even though the lithium insertion potential of this series is about 1.5 V versus lithium/lithium-ion [Jovic et al., 2003], it has been studied widely due to the advantages mentioned above. A unique property of $Li_4Ti_5O_{12}$ is that 'a' lattice parameter of its cubic crystal was increased only slightly from 8.36 Å to 8.37 Å upon the insertion (intercalation-deintercalation) of lithium by investigators, and the results of our experiment yielded similar results as well. It is, therefore, considered a 'zero-strain' insertion compound. In addition, this material is one of the good candidates synthesized by classical calcination method. This unique structural property is the cause for the extremely good charge/discharge cycle life of the $Li_4Ti_5O_{12}$ electrode in lithium cells.

Spinel oxides $Li_{1+x}Ti_{2-x}O_4$; $(0 \leq x \leq 1/3)$ (space group Fd3m) with cubic crystal structure were revealed in 1971 Deschanvres et al. [1971] and electrochemically characterized in the early 1990s by Dhan, Trackeray, and Ohzuku et al. [Colbow et al., 1989; Ferg et al., 1994; Ohzuku et al., 1995]. Subsequently, encouraged by its 'zero strain' lithium insertion properties, a number of investigators studied $Li_4Ti_5O_{12}$ for use as electrodes in lithium and lithium-ion batteries [Scharner et al., 1999]. Recent, XRD studies were conducted by Scharner et al. at the constant potentials corresponding to lithium insertion and extraction [Prosini et al., 2001].

The demand for a manufacturing process of the lithium transition metal oxide materials for mass production has been growing for the last several years. Therefore, in this paper, we should like to investigate the phase formation of lithium titanium oxide synthesized by a conventional powder calcination process, considering the potential for mass production.

This paper is intended as an investigation of Li-Ti-O electrode materials that are considered to be another phase, which are $Li_{1+x}Ti_{2-x}O_4$; (x: 1/3) by adding 5 wt%, 10 wt% and 20 wt% lithium excess ratio. We would make it possible to describe the coexistence of the two distinct phases of $Li_4Ti_5O_{12}$ with each phases as mentioned above due to 5 wt%, 10 wt% and 20 wt% lithium excess ratio used by stoi-

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†To whom correspondence should be addressed.
E-mail: ysyoon@konkuk.ac.kr

chiometric analysis and verifying used X-ray diffraction (XRD), field emission scanning electron microcopy (FESEM), inductively coupled plasma - atomic emission spectrometer (ICP-AES), energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Consequently, our investigation yielded remarkable results after each given condition, that the $Li_4Ti_5O_{12}$ might consist of mixed two phases which the 5 wt% excess lithium are $Li_{1.26}Ti_{1.66}O_4$ (space group Fd-3ms). In the 10 wt% excess lithium condition, the $Li_4Ti_5O_{12}$ and $Li_{2.39}Ti_{3.4}O_8$ (space group number Pnma) existed by the two mixed phases. Finally, in the 20 wt% excess lithium condition, the $Li_{1.072}Ti_{1.67}O_4$ (space group number Pbnm) and $Li_4Ti_5O_{12}$ (space group number Fd-3m) existed by two mixed phases.

EXPERIMENTAL

Lithium titanium oxide ($Li_4Ti_5O_{12}$) powders were synthesized from Li_2CO_3 and TiO_2 (Kojundo co. Ltd, 99.9%) as starting materials. Li_2CO_3 and TiO_2 were thoroughly mixed in a rotary mill for 24 hours with ceramic balls, and ethanol was used as the dispersing medium. At this time, the excess content ratio of lithium was controlled by the weight percentage ratio (wt%) between Li_2CO_3 and TiO_2 ($Li_2CO_3 : TiO_2$=1.05 : 1, 1.1 : 1, 1.2 : 1). The dry was processed for 24 hours at a temperature of 100 °C. The obtained lithium titanium oxide powders were calcinated at a temperature of 900 °C for 5 hours. The next step was ball milling for 24 hours after the calcination method was finished. Finally, heat treatment at 1,050 °C was performed for 5 hours to form the crystalline structure of LTO; the procedure is shown in detail in Fig. 1.

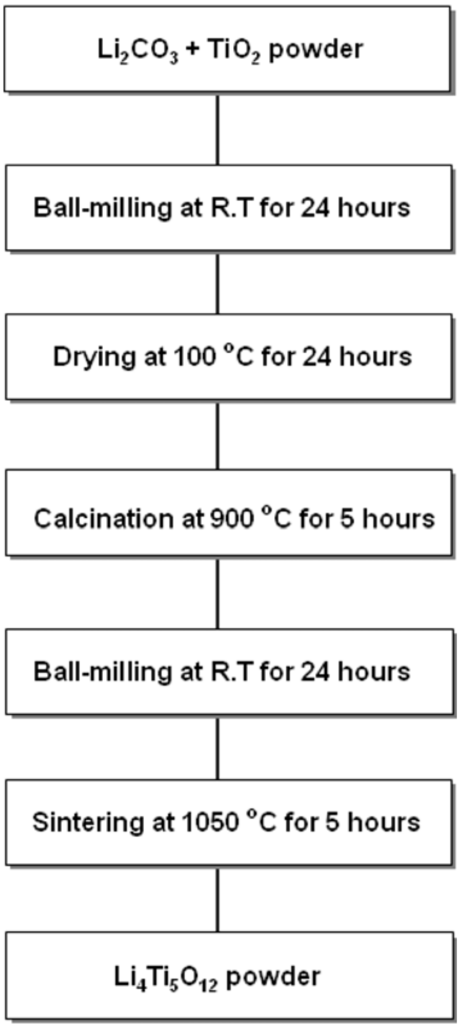


Fig. 1. A detailed diagram of the powder sintering process of $Li_4Ti_5O_{12}$ materials as a lithium excess ratio.

The structure and morphology properties of the as-synthesized LTO powder were analyzed by several measurements. An XRD (Philips X'pert MPD) measurement was taken to analyze the structure characteristics. And, for the coexistence of the two distinct phase analysis, TEM with HRTEM were performed. The surface observation of the samples was carried out with FESEM (Hitachi S-4200). The composition analysis of LTO powder by increase of lithium excess ratio was examined with ICP-AES and EDX.

RESULTS AND DISSCUSION

1. Structure Analysis of Lithium Titanium Oxide Material

At each excess lithium condition, the composition of the as-synthesized LTO powder was analyzed, whose metal groups and oxygen contents were measured by ICE-AES and EDX, respectively, since ICP-AES cannot be used to measure the oxygen contents. By comparing ICP-AES and EDX results, the final composition of the as-synthesized powder can be determined. Table 1 shows the results. Based on ICP-AES and EDX data, the relative molar ratios according of the excess lithium are shown in Table 2. Compared with calculation of molar ratio, the as-synthesized LTO powders with excess lithium of 5, 10 and 20 wt% in initial starting materials showed different lithium and oxygen ratio, as confirmed by ICP-ASE and EDX results. This difference might induce different compositions consisting of Li, Ti, and O is considered by thing which is used creating other phase at LTO synthesis. In addition, the as-synthesized LTO powders showed the coexistence of different crystalline phase. This result agrees well with XRD analysis result.

Fig. 2 shows the result of the XRD patterns for the as-synthesized LTO powder with excess lithium content ratio. Several peaks for $Li_4Ti_5O_{12}$ powder were in good agreement with those observed

Table 1. ICP-AES anlysis of the as-synthesized LTO powder

	Compositional analysis (wt%)	
	Lithium	Titanium
5 wt%	6.18	51.3
10 wt%	6.96	50.5
20 wt%	6.52	49.1

Table 2. The molar ratio of each component according to the excess lithium

	Molar ratio		
	Lithium	Titanium	Oxygen
5 wt%	4.10	5	12.40
10 wt%	4.70	5	12.65
20 wt%	4.55	5	13.55

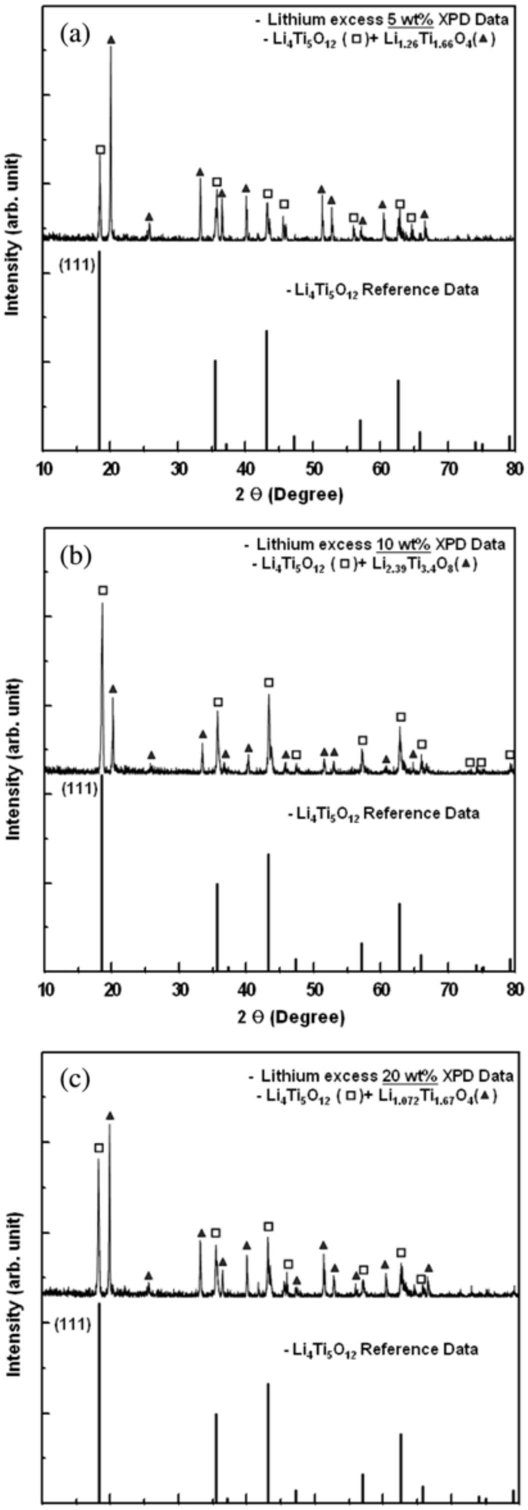


Fig. 2. XRD curve of the $Li_4Ti_5O_{12}$ materials as a (a) lithium excess 5 wt%, (b) 10 wt%, (c) 20 wt%.

for reference $Li_4Ti_5O_{12}$ data (JCPDS #490207), and a main peak corresponding to the (111) plane was observed in the XRD pattern of all of the as-synthesized LTO powders, regardless of the excess lithium content. This result indicates that the as-synthesized LTO powder through a conventional powder calcination method is $Li_4Ti_5O_{12}$ with a spinel type structure (space group Fd-3m, #227). A different phenomenon shown in XRD analysis is that full width half maximum (FWHM) values measured at the main peak (111) plane of the as-synthesized LTO powder with a lithium excess ratio of 5, 10, 20 wt% were 0.17, 0.21, 0.16°, respectively.

Also, the as-synthesized LTO powders show they existed by mixed two phases as excess lithium. In the case of a lithium excess ratio of 5 wt%, the as-synthesized LTO powder exhibits that it consists of the $Li_4Ti_5O_{12}$ phase and $Li_{1.26}Ti_{1.66}O_4$ phase, which means the conventional calcinations form two phases of the LTO powder if the starting material has excess lithium content. The lithium excess ratios were 10 wt% and 20 wt%, in this case; the first ratio is two different

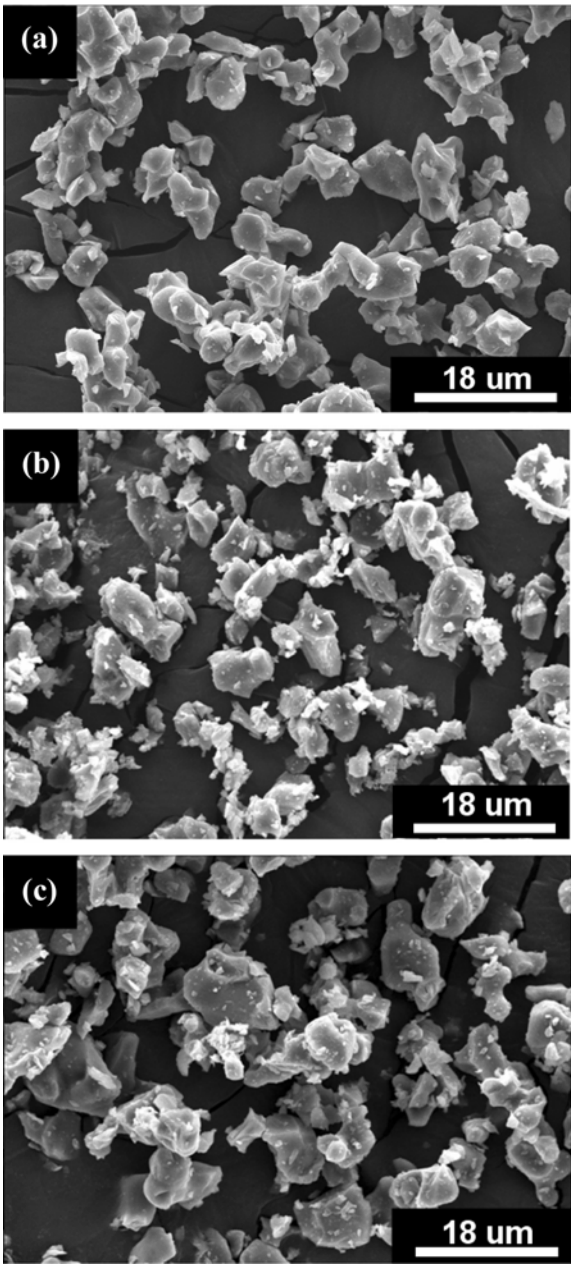
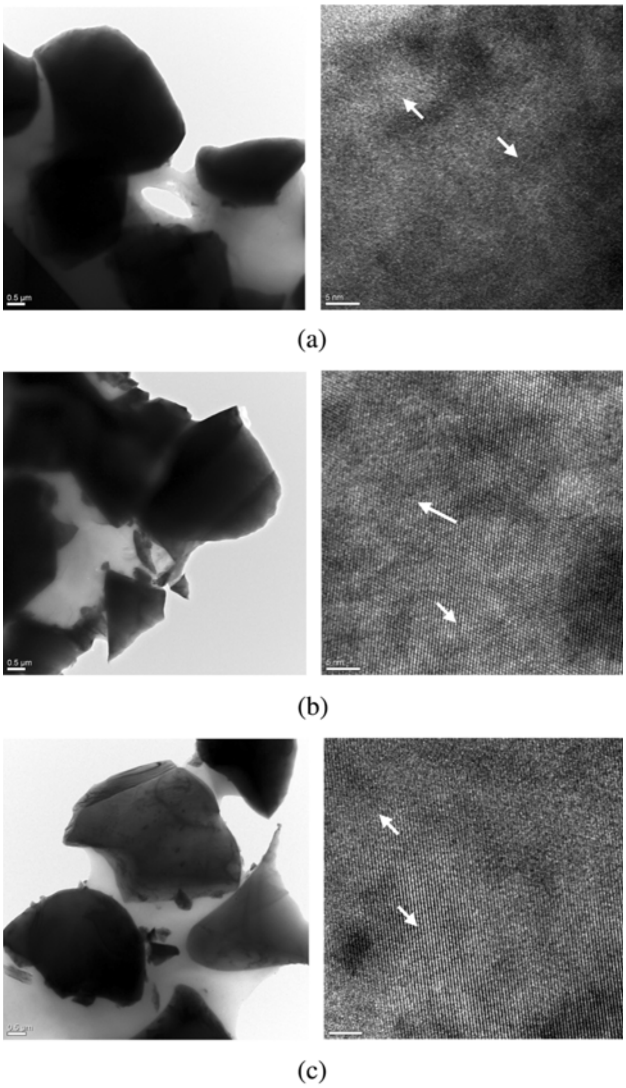


Fig. 3. FESEM images for $Li_4Ti_5O_{12}$ materials synthesized as a lithium excess ratio (a) 5 wt%, (b) 10 wt% and (c) 20 wt%.



(a)

(b)

(c)

Fig. 4. TEM and HRTEM for $Li_4Ti_5O_{12}$ materials synthesized as (a) lithium excess 5 wt%, (b) 10 wt% and (c) 20 wt%.

crystalline phases, which are the $Li_4Ti_5O_{12}$ and $Li_{2.39}Ti_{3.4}O_8$ phase; the second is an $Li_4Ti_5O_{12}$ and $Li_{1.072}Ti_{1.67}O_4$ phase, respectively. As a result, the lithium that remains was used to create another phase.

2. Surface Morphology Analysis of the LTO Powder

Fig. 3 and Fig. 4 show the FESEM and TEM for the as-synthesized LTO powder with the excess lithium content. The particle size grew from about 4 um to 9 um with the increase of the excess lithium content. Furthermore, according to the increase of the lithium excess ratio, the as-synthesized LTO powders had many small particles. Fig. 4 is TEM and HRTEM images showing the LTO powders with the lithium excess ratio. As the lithium excess increased, the lattice constant of samples was measured by 8.41, 8.45, and 8.47 Å, respectively. Also, just as in the HRTEM result, the LTO powder showed two phases that exist according to increase of the lithium excess ratio. These results suggest that the LTO powder synthesized by the conventional powder calcinations method, considering the potential for mass production, includes two distinct crystalline phases if it has excess lithium content.

CONCLUSIONS

We synthesized the LTO powders by using conventional powder calcination method and analyzed structural properties when the LTO had excess lithium. The XRD pattern, high-resolution TEM images and ICP-AES result show the coexistence of two different crystalline phases of LTO powder that had been incorporated in lithium excess. As shown by FESEM and TEM measurements, the LTO had larger grains with an increase in lithium content. These results indicate that the excess lithium in the LTO powder synthesized by the conventional powder calcinations method, considering the potential for mass production, induces the formation of two different crystalline phases.

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