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Effect of heat treatment on electrochemical characteristics of spinel lithium titanium oxide

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Abstract−Spinel structured LTO (lithium titanium oxide), $Li_4Ti_5O_{12}$, materials have gained renewed interest in electrodes for lithium-ion batteries. Powder precursors were mixed by HEBM (high energy-ball mill) and $Li_4Ti_5O_{12}$ was formed by calcinations at high temperature. The influence of excess Li on the structural characteristics of lithium titanium oxide was investigated. According to the XRD and SEM analysis, uniformly distributed $Li_4Ti_5O_{12}$ particles were synthesized. $Li_4Ti_5O_{12}$ had different characteristics due to the precursor sizes and the heat treatment temperatures. LTO from micro TiO_2 showed the highest discharge capacity at 750 °C for 12 h. LTO from nano TiO_2 showed the highest discharge capacity at 700 °C for 12 h. Lithium-ion battery with $Li_4Ti_5O_{12}$ anode and lithium metal cathode showed the capacity of 170 mAh/g at 1.0-3.0 V.

Key words: Lithium-ion Battery, Anode, Lithium Titanium Oxide, Spinel

INTRODUCTION

Recently, mobile electronics have become very popular such as digital cameras, PDAs, notebook computers, portable video games, MP3 players, and mobile phones. As the technology is developed, the electronics become smaller and the battery must have light weight and high capacity. To have high capacity, the development of anode and cathode materials becomes the key issue [1].

The electrode of the lithium ion battery must have high energy and power density. To increase the capacity of the battery, the capacity of the electrode must be increased or the working voltage of the electrode must be high. Ionic conductivity, electron conductivity, reversibility of oxidation and reduction, and thermal and chemical stability is also very important to the electrode [2]. It must be cheap, easily obtainable, non-toxic, and easily manufactured.

Graphite is currently used for the commercial lithium ion battery. The reaction mechanism of the graphite anode is the intercalation and deintercalation of lithium ion between the layers of the graphite, which is very stable in cyclic operation. Graphite has very low working voltage, so it has high voltage. However, it has the disadvantage of forming an SEI (solid electrolyte interface) during the first charge/discharge cycle.

Spinel $Li_4Ti_5O_{12}$ has been studied by many researchers in order to make up for the weak point of the graphite. The average voltage of LTO (lithium titanium oxide) is 1.55 V (Li/Li^+) and it has an L-shaped discharge curve. The great advantage of this material is the easy charge/discharge characteristics and good cycle ability. It can be called as a 'zero strain' material because the change of lattice parameter is less than 0.1% during the intercalation and deintercalation procedure [3]. The graphite shows an SEI formation during the initial charge/discharge cycle. However, LTO can avoid the reaction with electrolyte and SEI is not formed [4]. Recently, many articles have been published about lithium transition metal oxide as an anode material [5,6].

In this research, Li_2CO_3 and micro-size or nano-size TiO_2 were used as precursors. The capacity change and cycle ability were tested with the manufactured LTO as a function of temperature. XRD and TG-DTA were used to observe the structural change, and the surface morphology was tested with SEM. Charge/discharge characteristics were tested with a battery cycler.

EXPERIMENTS

The precursors were mixed with a planetary ball mill, called an HEBM (high energy ball mill) because chemical reaction can occur by mechanical activation during the pulverization of the powder with balls [7]. Li_2CO_3 (Aldrich Chemical Co.) and nano size (avg. 21 nm) or micro size (≤5 μm) TiO_2 (Aldrich Chemical Co.) were used as precursors. 10Ø zirconium balls with powder were rotated for 2 h at 300 rpm inside zirconium bowl. The weight ratio of ball to powder was 5 : 1.

The mixed powder was heated in box furnace under air at different time and temperature. The temperature range was 600-900 °C and the heating times were 3, 6, and 12 h with the heating rate of 5 °C/min. The procedures of powder manufacturing, active material analysis, and electrochemical measurement are explained in Fig. 1.

To make the anode electrode, manufactured LTO was used as the active material. AB (acetylene black, Denka black Co.) was used as a conductor and 8% PVDF (polyvinylidene fluoride) [in NMP (1-methyl-2-pyrrolidinone)] was used as a binder. NMP was used to adjust the viscosity. Different amount of NMP was used depending on the nano or micro size TiO_2. The weight ratio of active material, conductor, and binder was 87 : 8 : 5, and the mixture was stirred in an homogenizer at 5,000 rpm for 1 h. The mixture was cast on Cu foil with the doctor-blade method and dried in oven at 80 °C for 3 h. It was cut into 5×7 cm^2 size and pressed at 120 °C with roll press to reduce the thickness by 30%. The resulting material was

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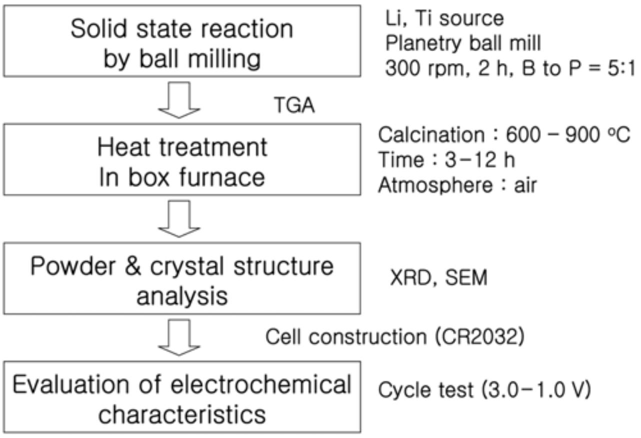


Fig. 1. Manufacturing procedure of coin-type cell for LTO.

dried in a vacuum oven at 80 ºC for one day.

The battery cell was assembled in a dry room where the relative humidity was less than 0.3%. The electrode characteristics were tested with a half cell. LTO was used as the working electrode and lithium metal foil was used as a counter electrode. Porous PP (polypropylene, Cellgard 2500) was used as a separator. A mixture of EC, EMC and DMC (1 : 1 : 1 in v/v) with 1M $LiPF_6$ was used as an electrolyte. CR2032 coin cell was assembled to test the electrical characteristics.

TGA (thermogravimetric analyzer, TA Instruments) was used to analyze the weight loss by increasing the temperature at 5 ºC/min up to 900 ºC. SEM (scanning electron microscope, JSM-6300, JEOL) was used the surface morphology of the sample. Structural changes of LTO treated at different temperature was analyzed by XRD (X-ray diffraction, D-5005, Bruker) using Cu Kα radiation (λ=1.5418 Å).

RESULTS AND DISCUSSION

TGA was used to determine the composition and decomposition temperatures. Fig. 2(a) shows that the weight loss occurs at 400 ºC for the sample of micro TiO_2 and Li_2CO_3 and maximum weight loss occurs at 640 ºC. In case of nano TiO_2 and Li_2CO_3, 2.5% weight loss occurs up to 100 ºC due to the vaporization of moisture, and weight change stops over 600 ºC as shown in Fig. 2(b) [8]. Theoretical weight loss is 17.5% during the formation of LTO from the starting material. TGA data shows that the weight loss is 16.0% in case of micro TiO_2 and 18.6% in case of nano TiO_2.

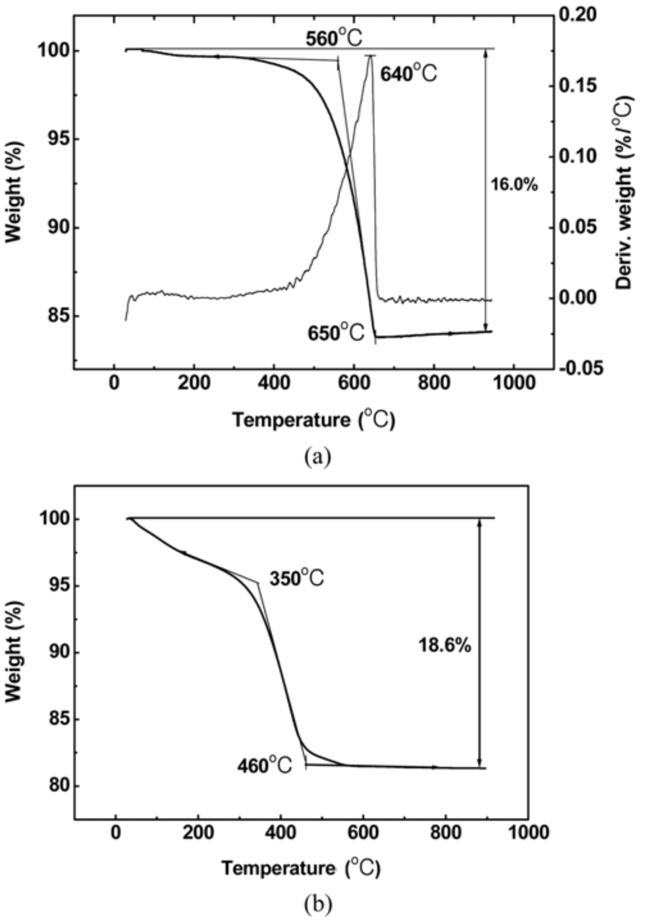


Fig. 2. TGA curve of (a) micro TiO_2 and Li_2CO_3 and (b) nano TiO_2 and Li_2CO_3.

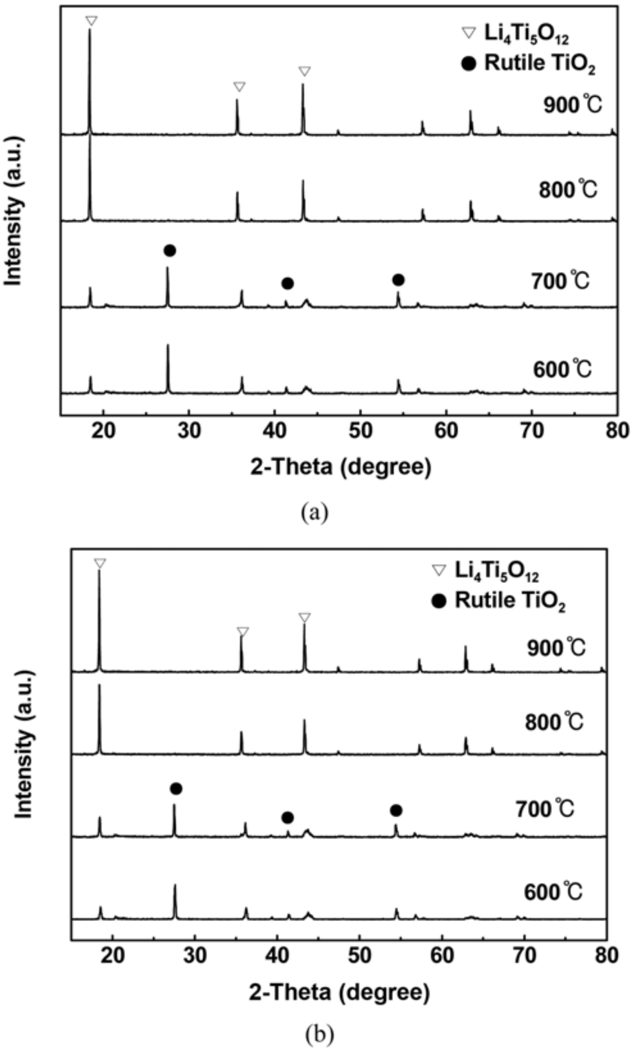


Fig. 3. XRD patterns of $Li_4Ti_5O_{12}$ after calcining micro TiO_2 and Li_2CO_3 for (a) 3 h and (b) 6 h.

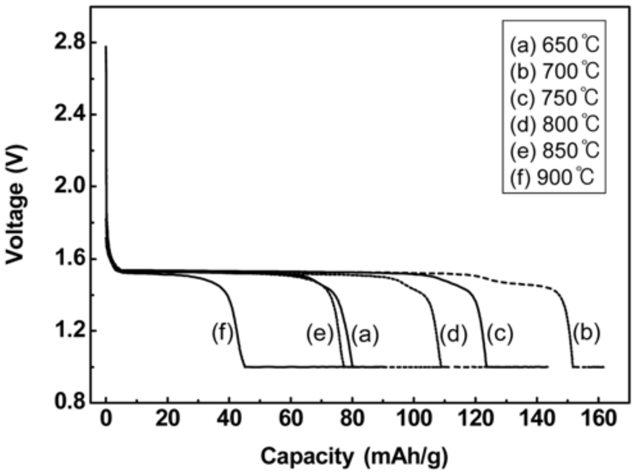


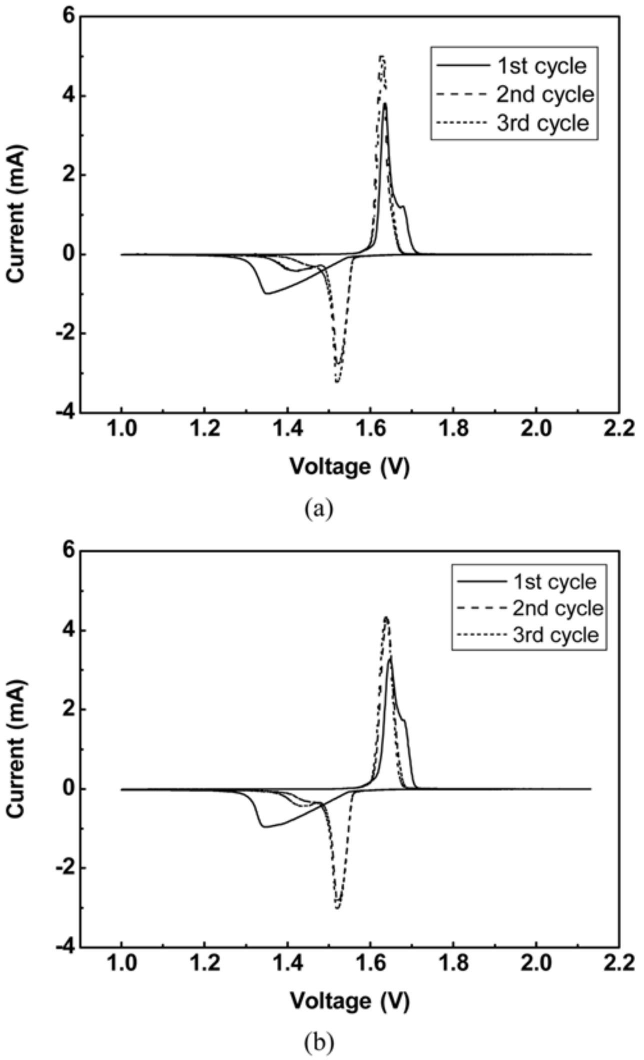
Fig. 4. 10th discharge curves of LTO after calcining nano TiO_2 and Li_2CO_3 at (a) 650, (b) 700, (c) 750, (d) 800, (e) 850 and (f) 900 °C for 12 h between 1.0-3.0 V at 1C rate.

The XRD patterns of LTO are shown in Fig. 3 at different heating temperatures of 600, 700, 800, and 900 °C. LTO was manufactured from micro TiO_2 and Li_2CO_3. Fig. 3(a) is 3 h heat treatment and Fig. 3(b) is 6 h treatment, and both patterns show very similar shapes. Samples at 600 and 700 °C show both LTO peaks and rutile TiO_2 peaks, so the temperatures are not enough to formulate LTO [9]. Heat treatments at 800 and 900 °C show complete LTO peaks. The phase transition from precursors to LTO occurs between 700 and 800 °C [10].

Charge and discharge curves were measured between the cut-off voltages of 1.0 and 3.0 V. Fig. 4 shows the discharge curves at 10^{th} cycle of the LTO manufactured from nano TiO_2 and Li_2CO_3. The samples were heated at 650, 700, 750, 800, 850 and 900 °C for 12 h, and the sample of 700 °C shows the highest capacity [11]. Fig. 4 shows that LTO is a very stable anode material with constant voltage, but it also shows a large capacity change depending on the heat treatment condition. As the heat treatment temperature went up, the formation of LTO became more complete. The samples treated at 700 °C showed highest discharge capacity. At that temperature the phase transition was almost complete, and the crystal size might have been very small. As the treatment temperature went up, the crystal size became larger, which means the small size crystal has higher electrical capacity than the large crystal.

Constant discharge voltage occurs at approximately 1.5 V, and the capacity of that range is 50 to 80% of the total capacity. Charge voltage is 1.6 V (Li/Li^+), and it is very close to the discharge voltage. This is due to the two phase reaction of Ti^{4+}/Ti^{3+} redox couple. This voltage is relatively high to be used as an anode material. High voltage cathode material can be used with LTO anode because LTO anode shows a good recycle ability and a constant voltage plateau.

Electrochemical characteristics of LTO were measured with CV (cyclic voltammetry) method during the oxidation and reduction reaction. The measurement was cycled three times with the voltage scan rate of 0.2 mV/sec. Fig. 5 shows the CV curves of LTO, and the 2^{nd} and 3^{rd} cycles show the apparent oxidation and reduction reaction peaks. As discharge curves in Fig. 4 show the voltage plateau at approximately 1.5 V (Li/Li^+), the voltage due to the oxidation and reduction reaction can be identified in Fig. 5. During the discharge process Li^+ and electron enter into the LTO electrode, so reduction occurs at LTO at 1.52 V. During the charge process Li^+ and electron leave from the LTO and oxidation occurs [12]. Plus current peak is due to the oxidation and minus current peak is due to the reduction.

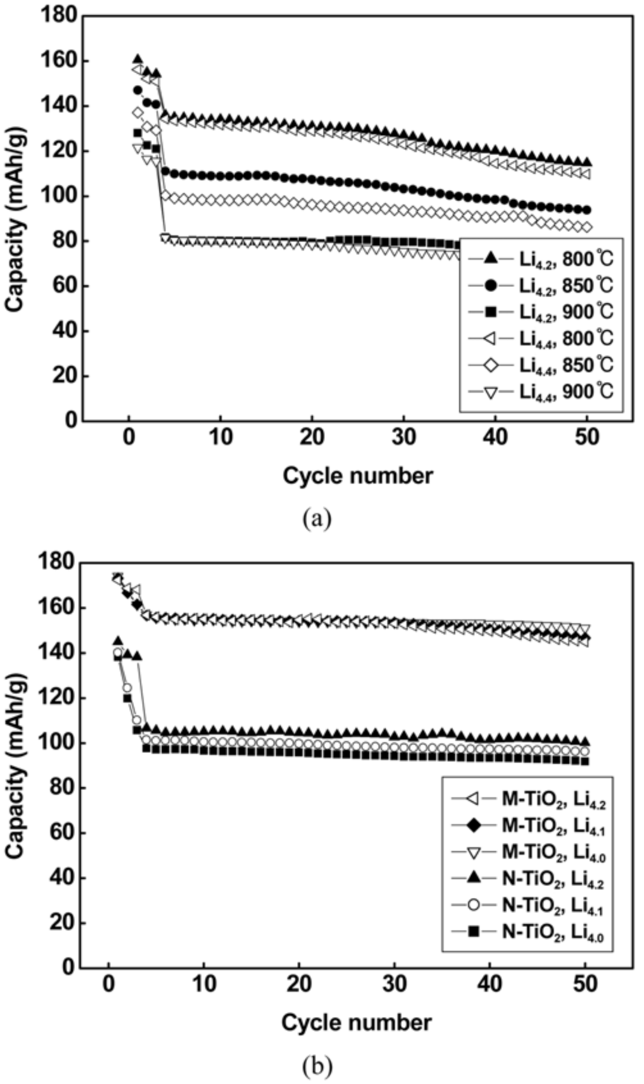


(a)

(b)

Fig. 5. Cyclic voltammogram of LTO after calcining (a) micro TiO_2 and Li_2CO_3 at 750 °C for 12 h and (b) nano TiO_2 and Li_2CO_3 at 700 °C for 3 h.

The discharge capacities of LTO at different amounts of lithium are shown in Fig. 6. The stoichiometric amount of lithium was 4.0 for $Li_4Ti_5O_{12}$ preparation. However, a slightly large amount of lithium was used because there is a chance that the lithium can be vaporized during the heat treatment. Fig. 6(a) shows that the lithium amount of 4.2 shows slightly higher capacity than that of 4.4. Heat treatment temperature of 800 °C shows the highest discharge capacity. Fig. 6(b) shows the difference between micro and nano TiO_2, and micro size titania shows higher discharge capacity that nano size titania. Heat treatment temperature was fixed at 900 °C for 3 hr. The lithium amount was changed from 4.0 to 4.2, and the discharge capacities are very close for the micro TiO_2. However, lithium amount of 4.0 shows slightly higher capacity than 4.2 for the nano TiO_2 [7].



(a)

(b)

Fig. 6. Discharge capacities of $Li_4Ti_5O_{12}$ after calcining (a) nano TiO_2 and Li_2CO_3 for 12 h and (b) at different ratio of TiO_2 at 900 °C for 12 h.

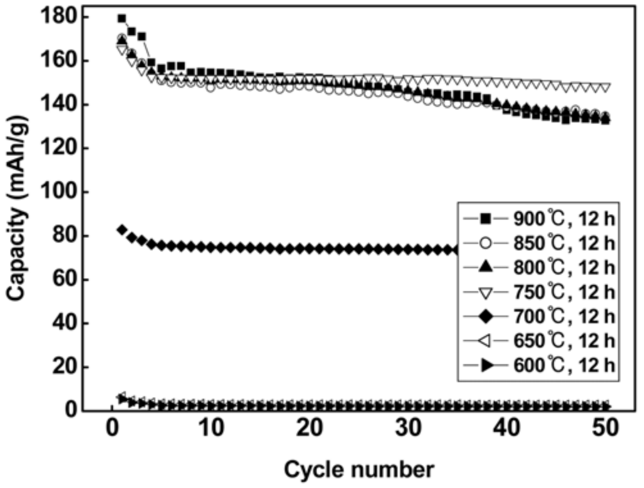


Fig. 7. Discharge capacities of $Li_4Ti_5O_{12}$ after calcining micro TiO_2 and Li_2CO_3 for 12 h.

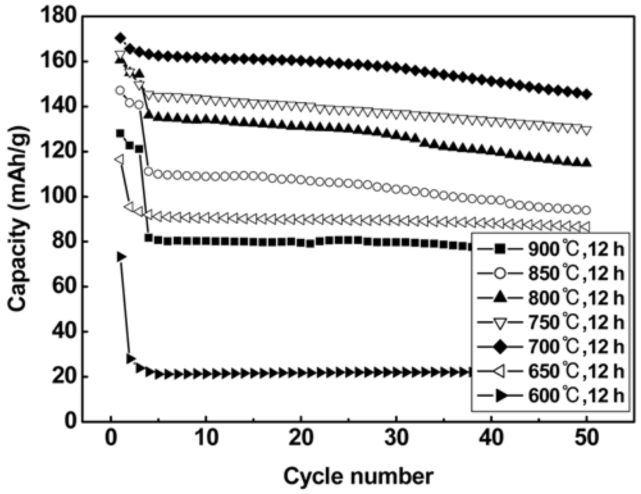


Fig. 8. Discharge capacities of $Li_4Ti_5O_{12}$ after calcining nano TiO_2 and Li_2CO_3 for 12 h.

Fig. 7 shows the discharge capacities of LTO manufactured from micro TiO_2 and Li_2CO_3 at different temperatures from 600 °C to 900 °C for 12 h. The discharge capacities are almost zero below 650 °C, and 700 °C shows very low capacity. This is very consistent with the XRD results of Fig. 3. $Li_4Ti_5O_{12}$ peaks are negligible below 700 °C and are present above 800 °C. That means $Li_4Ti_5O_{12}$ peaks start to form between 700 and 800 °C. The best cycle performance is shown at 750 °C heat treatment, and the discharge capacities decrease slightly above 800 °C heat treatments.

Fig. 8 shows the discharge capacities of LTO manufactured from nano TiO_2 and Li_2CO_3 at different temperatures from 600 °C to 900 °C for 12 h. Sample treated at 700 °C shows the highest discharge capacity, and 600 and 650 °C heat treatment show low capacity. Above 750 °C heat treatment the capacities become decreased. Compared to Fig. 7 the optimum temperature of nano TiO_2 is °C 700, while micro TiO_2 shows the optimum temperature at 750 °C. As the particle size becomes smaller, the melting point is lower. This may be the reason that the nano size TiO_2 has lower optimum temperature than micro size TiO_2.

CONCLUSIONS

TGA data showed that LTO with micro TiO_2 had weight loss from 560 °C to 650 °C and LTO with nano TiO_2 showed weight loss from 350 °C to 460 °C. Heat treatment at 600 °C and 700 °C showed the rutile TiO_2 peaks, and heat treatment above 800 °C showed only $Li_4Ti_5O_{12}$ peaks. The weight loss of LTO with micro TiO_2 was 16.0% and that with nano TiO_2 was 18.6%. XRD data showed that $Li_4Ti_5O_{12}$ was formed between 700 °C and 800 °C. Lithium molar ratio of 4.2 showed the optimum discharge capacity. LTO with micro TiO_2 showed the highest discharge capacity at 750 °C for 12 h. LTO with nano TiO_2 showed the highest discharge capacity at 700 °C for 12 h.

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