

# Novel Synthesis Method and Electrochemical Characteristics of Lithium Titanium Oxide as Anode Material for Lithium Secondary Battery

Han-Joo Kim\* and Soo-Gil Park<sup>†</sup>

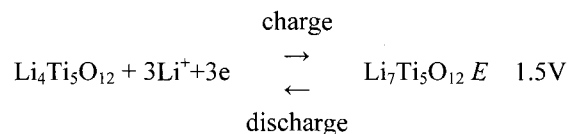
**Abstract** - Lithium titanium oxide as anode material for energy storage prepared by novel synthesis method.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  based spinel-framework structures are of great interest material for lithium-ion batteries. We describe here  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  a zero-strain insertion material was prepared by novel sol-gel method and by high energy ball milling (HEBM) of precursor to form nanocrystalline phases. According to the X-ray diffraction and scanning electron microscopy analysis, uniformly distributed  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles with grain sizes of 100nm were synthesized. Lithium cells, consisting of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode and lithium cathode showed the 173 mAh/g in the range of 1.0 ~ 3.0 V. Furthermore, the crystalline structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  didn't transform during the lithium intercalation and deintercalation process.

**Keywords:** Lithium secondary battery, Lithium titanate, Anode, Sol-gel process

## 1. Introduction

It's getting more important to get high performance, high efficiency and portable convenience for batteries according to advanced science technology. The emerging market for hybrid vehicles (HEVs) presents a challenge to identify low-cost materials with high power performance. A key element in HEVs is the battery which must have high power capability. On the other hand, energy density is reduced for this application compared to that required for pure electric vehicles (Es). For Li-ion batteries,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can be used with high-voltage cathodes (5 V) as  $\text{LiCoPO}_4$  [1], or 4 V cathodes as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$  and with a 3.5 V cathode,  $\text{LiFePO}_4$  [2,3]. For use in HEVs, the major concern is safety. The mid-discharge voltage of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  close to 1.55 V versus  $\text{Li}^+/\text{Li}$  is very promising for a large number of battery applications [4,5]. The electrochemical activity occurs at a voltage higher than 1.0 V. Thus, the electrode does not experience the passivation of carbon materials and their inevitable electrolyte reaction. Commercial lithium secondary battery used carbon material as anode. However, it has a problem with structural destroy due to weak carbon-carbon bond, formation of lithium dendrite and passivation layer [6,7]. Insertion/extraction of Li into/from  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is known to proceed with little change of lattice dimensions and it is considered as a zero strain insertion compound [8~10]. The

corresponding electrochemical processes are:



Lithium reacts with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  according to the reaction because lithium insertion into the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel displaces tetrahedrally coordinated lithium ion into octahedral sites with the formation of a rock-salt-type  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  product. The safety remains a major issue for large scale-up Li-ion batteries, particularly when large amount of liquid electrolyte are used, because gas formation and electrolyte decomposition become very problematic. For this reason, it is essential that large scale Li-ion batteries use an anode (zero swelling). We have been studying carbonized phenol resin prepared by the pyrolysis of resole-type phenol resin as one of the most promising amorphous carbon materials for lithium secondary battery anode. In this work, we report the results of the X-ray diffraction measurements for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  together with SEM observation, electrochemical discharge and charge, and cyclic voltammetry.

## 2. Experimental

The starting materials, titanium isopropoxide and LiOH, were commercially available with purities of 99 and 99.5%, respectively. A mixture of  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  and LiOH (molar ratio Ti/Li of 1.25) was prepared by spray method. LiOH

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was solved in 2-methoxy ethanol 60 mL at 80 °C and mixed with titanium isopropoxide after mixture cooled down at room temperature. Precursors were evaporated until solvent dried up to 70 %. Then the mixed powder was separated from the solvent by dried at 110 °C with spray dryer. The powder was calcined at 850 °C for 5 h in air to form  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The homogeneous mixed phases were obtained by High energy ball milling (HEBM). A flow chart of the synthesis procedure is shown in Fig. 1.

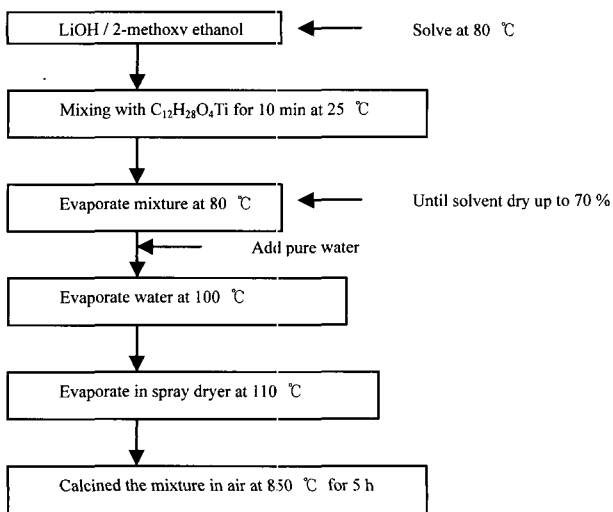


Fig. 1 Synthesis of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$

The samples were characterized by X-ray diffractometer and scanning electron microscopy before intercalation. A Hitachi S-70 SEM was used to monitor particle size at each synthesis step. The electrochemical measurement of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was carried out in 1-cm<sup>2</sup> laboratory cells with lithium metal as the counter and reference electrode. The initial cell chemistry is based on the following configuration: Li metal/electrolyte/  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with a liquid electrolyte ( $\text{LiClO}_4/\text{PC}$ ,  $\text{LiPF}_6/\text{EC}+\text{DEC}$ ). The working electrode was prepared from a paste mixture of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , carbon black for an electronic conductor additive and PVDF binder mixed in NMP. The paste was coated on Cu foil. The electrode was dried under vacuum at 85 °C for 24 h before electrochemical evaluation. CV and potentiostatic current transient experiment were also performed and recorded by using automatic polarisation equipment (HZ-3000, KOKUTO DENKO Co.). Galvanostatic intermittent discharge-charge experiments were conducted under constant current conditions by using automatic discharge and charge equipment (WBCS 3000, Won-A Tech. Co.). Cut-off voltages were 1.0 and 3.0 V vs  $\text{Li}/\text{Li}^+$  for discharge and charge processes, respectively. A scan rate of CV was 10 mV/s in a range of 1.0 ~ 3.0 V vs.  $\text{Li}/\text{Li}^+$ . All electrochemical experiments were conducted in an argon-filled glove box at room temperature

### 3. Results and Discussion

#### 3.1 Analysis

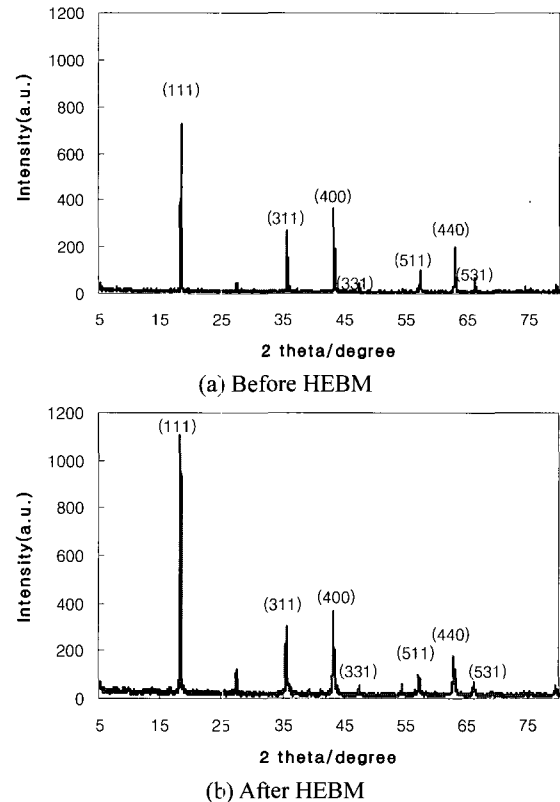


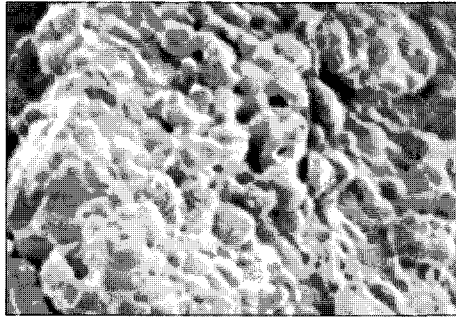
Fig. 2 XRD patterns of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particle

The formation of crystalline phase can be seen from the XRD patterns of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (Fig. 2). The XRD pattern of Fig. 2 correlates well with the report that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has a defective spinel-framework structure. The weak diffraction peak appeared at  $2\theta = 27.4$  in Fig. 2 indicated that Li-Ti-O phase may contain smaller amount of rutile phase  $\text{TiO}_2$ . The reason derived from the loss of Li in the precursor fired at 850 °C. The lattice parameter  $a$  was 8.368 Å by the least square method using 10 diffraction lines. Ohzuku et al.[1] reported  $a = 8.367$  Å and Rho et al.[3] also reported  $a = 8.365$  Å, which are in good agreement with our value  $a = 8.369$  Å. The dimensions of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  monocrystallines were estimated from the widths of the major diffraction peaks observed in Fig. 2(a), using the Scherrer formula:

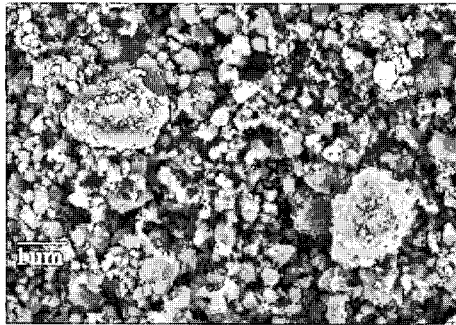
$$D_{hkl} \approx \frac{\beta \lambda}{B \cos \theta}$$

where  $D_{hkl}$  is the linear dimension of the coherent diffracting domain along a direction normal to the diffraction plane (hkl),  $\lambda$  X-ray wavelength (1.5418 Å),  $\beta$

the crystal shape constant (0.89),  $\theta$  the reflection angle of the peak, and B is the corrected full width at half maximum of the peaks in Fig. 2(a), the dimensions of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nano crystallines are 98nm(111), 102nm(311), 105nm(400), and 136nm(440), respectively.



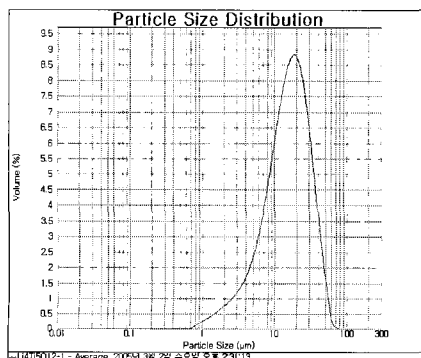
(a) Before HEBM



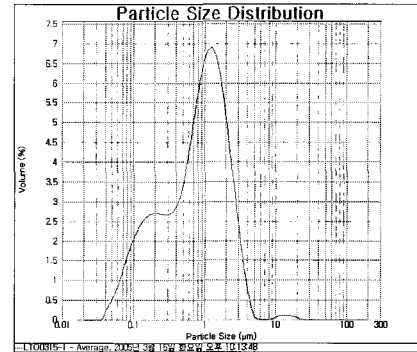
(b) After HEBM

Fig. 3 SEM images of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particle

Fig. 3 shows scanning electron micrographs of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . It is apparent that crystallines are regular nanoparticles with good dispersivity, and the average size of these nanoparticles is about 100nm, which is in good agreement with the XRD results. The size distribution of this material is depicted in Fig. 4. As is seen in this figure, the average particle size of after HEBM determined by the laser diffraction-scattering method is 1.098 $\mu\text{m}$ , exhibiting the coefficient of variation (CV) of 49.5% on a volume basis. In contrast, the average particle size of before HEBM is 17.8 $\mu\text{m}$ , and its CV value is 68.7%.



(a) Before HEBM



(b) After HEBM

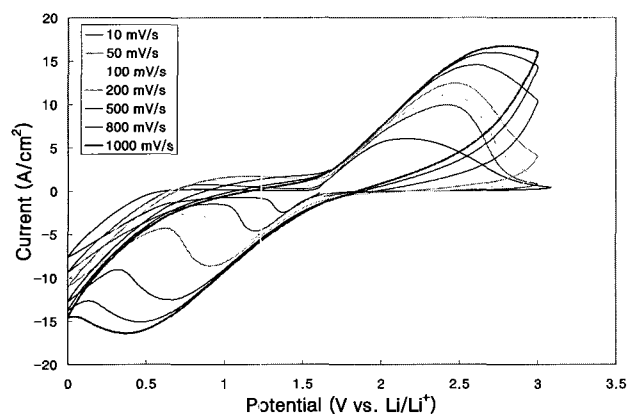
Fig. 4 Size distribution of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particle

### 3.2 Electrochemical Performance

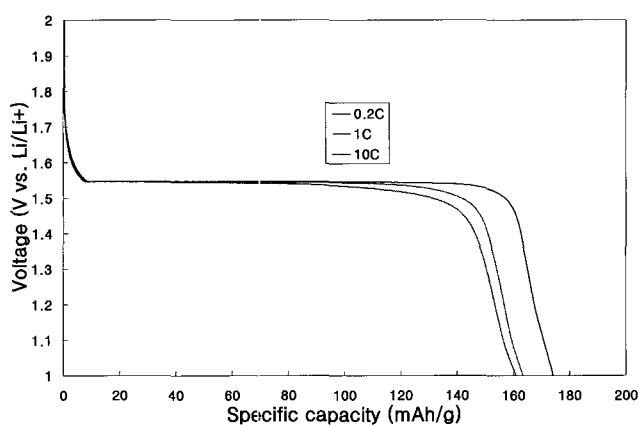
The electrochemical behavior of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was characterized by cyclic voltammogram as shown in Fig. 5. For all the voltammograms, the voltage was initially scanned from 0.0 to 3.0 V, and then back 0.0 V at a scan rate of 10 mV/s ~ 1000 mV/s. The oxidation peaks located at around 2.3 and the corresponding reduction peaks around 1.4 V. These results indicated that lithium extraction and insertion become easy with the increasing firing temperature, because higher degree of crystallinity gives rise to a more reversible Li transfer in three-dimensional frame work of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . One electrochemical peak appeared for both oxidation and reduction process indicating that both the insertion and extraction of lithium ions occur in one stage, which is in agreement with the previous reports by other methods [2, 5]. The specific capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was determined by discharge test at a constant current density of 0.3 mA/cm<sup>2</sup> between the cut-off voltages of 2.5 and 1.0 V. In order to give electrical contact to all the particles and also to supply electrolyte inside the cathode, acetylene black and teflon binder were used to prepare the anode. Fig. 5(b) shows the first discharge character of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The first discharge test was carried out between 2.5 and 1.0 V and the voltage dropped quickly down to below 2V and decreased as the reaction proceeded until the voltage reached about 1.51 V (initial 4.8 % of discharge capacity), after which the voltage was almost independent upon the degree of reduction (initial 53.9 % of discharge capacity) [3,8,9]. The voltage fell quickly below 1.51 V (initial 15.1% of discharge capacity). As the firing temperature decreased, capacity of the cell quickly drowned at the first discharge. The reason for the initial capacity difference results from the coexistence of impure phase ( $\text{TiO}_2$ ) and non-crystalline phase in samples.

The first discharge special capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is 173 mAh/g, which is higher than previous reports[8,9]. The increase of cell capacity derived from the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with more uniform particle distribution, smaller size (100nm),

and larger surface area. These characteristics are beneficial to the  $\text{Li}^+$  ion migration in the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  host and can improve reversibility and capacity of the cell.



(a) cyclic voltammogram



(b) constant current discharge

Fig. 5 Electrochemical performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Electrode

#### 4. Conclusion

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  has been successfully synthesized by new sol-gel method and phase purity and good stoichiometric product was obtained. Nano structure lithium titanate particles having an average size of 1.098  $\mu\text{m}$  and sharp size distribution of CV value of 49.5 % on a volume basis were prepared by HEBM. HEBM samples exhibited excellent cyclability and the first capacity was 173 mAh/g. When the discharge capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  determined at 0.2 C was taken as standard, the discharge capacity at 10 C was 86 %. These nanocrystalline samples showed good electrochemical performance. This work demonstrated that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with nano structure and good crystallinity was a promising negative electrode host..

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