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# Effects of the starting materials and mechanochemical activation on the properties of solid-state reacted $Li_4Ti_5O_{12}$ for lithium ion batteries

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## Abstract

$Li_4Ti_5O_{12}$ was synthesized by a solid-state reaction between $Li_2CO_3$ and $TiO_2$ for applications in lithium ion batteries. The effects of the $TiO_2$ phase and mechanochemical activation on the $Li_4Ti_5O_{12}$ particles as well as the corresponding electrochemical properties were investigated. Rutile $TiO_2$ was more desirable in acquiring high purity $Li_4Ti_5O_{12}$ than anatase due to the anatase to rutile phase transformation, which was found to be more rigid in the solid-state reaction than the intact rutile phase. Mechanochemical activation of the starting materials was effective in decreasing the reaction temperature and particle size as well as increasing the $Li_4Ti_5O_{12}$ content. The specific capacity depended significantly on the $Li_4Ti_5O_{12}$ content, whereas the rate capability improved with decreasing particle size due to the enhanced contact area and reduced diffusion path. Overall, a 200 nm-sized $Li_4Ti_5O_{12}$ powder with a specific capacity of 165 mAh/g could be synthesized by optimizing the milling method and starting materials.

*Keywords:* E. Batteries; Solid-state reaction; Mechanochemical activation; $Li_4Ti_5O_{12}$; Electrochemical properties

## 1. Introduction

$Li_4Ti_5O_{12}$ is a promising anode material for high power Li-ion batteries owing to its good cycle performance and little structural change during the $Li^+$ intercalation and de-intercalation process with a theoretical capacity of 175 mAh/g [1–5]. Since it shows a flat Li insertion potential of 1.55 V versus $Li/Li^+$, which is higher than the reduction potentials of common electrolyte solvents, it does not form a solid electrolyte interface during operation [2,6]. These properties can be a great merit for electric and/or hybrid vehicle applications of Li-ion batteries, which demand high power operation and long-term stability [7,8].

To produce high rate Li-ion batteries, a very fine active material is more desirable than a coarse one due to its shorter $Li^+$ diffusion path and greater electrode–electrolyte contact area for $Li^+$ intercalation and de-intercalation [9–11]. On the other hand, the properties of the particles depend significantly on the synthetic process and starting materials, which lead to final products with range of sizes and morphologies. Therefore, considerable effort is being made to enhance the electrochemical performance of batteries by optimizing the electrode materials, including the utilization of various synthetic methods, doping and coating with other materials [12–18]. Generally, a spinel-type $Li_4Ti_5O_{12}$ is synthesized by an economic solid-state reaction using $TiO_2$ and $Li_2CO_3$, which generally results in a significant amount of agglomeration and a coarse particle size. This is why wet chemical methods, such as hydrothermal and coprecipitation, have been attempted despite their high cost [19–22].

The synthesis of fine ceramic powders through a solid-state reaction with the aid of an advanced high energy mill was reported recently [23,24]. Compared to a conventional ball mill, the modern high energy mill shows much higher milling efficiency owing to its high speed rotor turning at up to several thousand rotations per minute. Their high energy input along with the use of small grinding media enables the achievement of very small particle sizes in a very short processing time

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[24,25]. The mechanochemical activation by heavy milling is the key process in the solid-state synthesis of nano-sized ceramic powders, for example $BaTiO_3$ [23,24], which alters the physicochemical properties of the starting materials. Finely milled starting materials enhance the solid-state reaction due to their high activity and decrease the reaction temperature and final particle size.

To the best of the authors' knowledge, there are no reports on the effect of mechanochemical activation for the starting materials on the formation of $Li_4Ti_5O_{12}$ powder. With this background, this study compared the effects of milling methods (ball milling and high energy milling) on the properties of $Li_4Ti_5O_{12}$ powder and the corresponding electrochemical properties. In addition, the effects of two different starting $TiO_2$ phases, i.e., anatase- and rutile-phased $TiO_2$, were also examined.

## 2. Experimental procedure

### 2.1. Starting materials

Commercial $Li_2CO_3$ and $TiO_2$ powders were used as Li- and Ti-precursors for $Li_4Ti_5O_{12}$ synthesis, respectively, where two different types of $TiO_2$ powders, i.e., anatase- and rutile-phase, were used to examine the phase effects. Table 1 lists the characteristics of the starting materials, including the manufacturer, mean particle size and purity.

### 2.2. Synthesis of the spinel $Li_4Ti_5O_{12}$

To synthesize 100 g of $Li_4Ti_5O_{12}$ powder, 32.19 g of $Li_2CO_3$ and 86.98 g of $TiO_2$, which correspond to a Li/Ti stoichiometric ratio of 4/5, were mixed with 200 g of de-ionized water after adding 2 wt.% of the ammonium salt of polycarboxylic acid (Cerasperse 5468-CF, San Nopco, Korea) with respect to the ceramic powder, as a dispersant. Formulated mixtures containing 2 different $TiO_2$ powders were exposed to high energy milling (MiniCer, Netzsch, Germany) for 3 h at a rotor speed of 3000 rpm with 0.4 mm $ZrO_2$ beads. The mixtures with the same formulation were also ball-milled for 24 h using 5 mm $ZrO_2$ balls for comparison. The four types of slurries were dried after milling at 100 °C in a rotary evaporator for uniform mixing. The dried powders are named AB, AH, RB and RH depending on the $TiO_2$ type and milling method, where A and R stand for anatase- and rutile-$TiO_2$, and B and H for ball-milled and high energy-milled, respectively. Each dried powder was heat-treated at 700, 800 and 900 °C for 3 h in air at a heating rate of 3 °C/min.

Table 1
Characteristics of the starting materials used in this study.

| Materials | Manufacturer | $D_{50}$ (μm) | Purity | Note |
|---|---|---|---|---|
| $Li_2CO_3$ | New Well, Korea | 3.80 | >99.9 | Broad size distribution |
| $TiO_2$ (anatase) | Hang Zhou Wan Jing, China | 0.08 | >99.0 | Highly agglomerated |
| $TiO_2$ (rutile) | Toho Titanium, Japan | 0.78 | >99.9 | 3.5 wt.% anatase $TiO_2$ contained |

### 2.3. Characterization of the particles

The dispersion stability of the particles associated with wet milling was examined by measuring the zeta potentials of the starting materials using an electroacoustic-type zeta potential analyzer (Zeta Probe, Colloidal Dynamics, USA) with and without a dispersant after adjusting the pH of the slurry using $NH_4OH$ and HCl. The morphologies of the starting materials before and after milling were characterized by scanning electron microscopy (SEM: S-4800, Hitachi using 15 kV and 10 μA with the working distance of 5–8 mm, Hitachi). The thermal decomposition behavior of 4 different combinations were examined by thermogravimetric analysis (TGA: SDT Q600, TA Instruments, USA) in a flowing air atmosphere at temperatures ranging from room temperature to 1000 °C with a heating rate of 5 °C/min. Room temperature XRD (RT-XRD: X'Pert-PRO MPD, Panalytical using Cu $K_\alpha$ line, 40 kV and 30 mA) and Rietveld refinement were performed for quantitative phase verification after heat treatment. In addition, high temperature XRD (HT-XRD: D/MAX-RB, Rigaku using Cu $K_\alpha$ line, 40 kV and 300 mA) was performed for the AH combination to confirm in situ the phases generated during heat treatment. For the measurements, the samples were heat-treated from room temperature to 800 °C in 100 °C steps and held at each measurement temperature for 3 min.

### 2.4. Electrochemical testing

To evaluate the electrochemical properties, an electrode paste composed of 80 wt.% $Li_4Ti_5O_{12}$, 10 wt.% Denka black and 10 wt.% poly(vinylidene fluoride) (PVdF, KF1300) was mixed and dispersed. The paste was then screen-printed on Al foil to form an electrode. The electrode plate was then pressed to enhance the interparticle contact and to ensure a better adhesion to the current collector. Coin-type half-cells (CR2032) were assembled with the composite electrode, Li foil as a counter electrode, and polyethylene film as a separator. The electrolyte used was 1.3 M $LiPF_6$ dissolved in a mixture of ethylene carbonate and ethylmethyl carbonate with a volume ratio of 1/2. The cell assembly was performed in a glove box filled with Ar gas, and the electrode was dried under vacuum at 120 °C to remove the moisture before filling the electrolyte. The galvanostatic charge–discharge measurements were performed in a potential range of 1.0–2.5 V (versus $Li/Li^+$) at different current conditions of 0.1*C* (17.5 mA/g)–4.0*C* (700 mA/g). The cells were charged and discharged for three cycles at each current density at 25 °C.

## 3. Results and discussion

### 3.1. Starting materials and their dispersion stability

Since a solid-state reaction occurs at the contact points of the starting materials, the use of very fine and uniformly dispersed