Effects of TiO₂ Source on the Electrochemical Performance of Li₄Ti₅O₁₂

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This study examined the formation mechanism of $Li_4Ti_5O_{12}$ by a ball mill assisted solid-state reaction between Li_2CO_3 and TiO_2 for applications in lithium ion batteries, also effects of TiO_2 source such as rutile type and anatase type on the electrochemical performance of $Li_4Ti_5O_{12}$. However, it is believed that the particle properties may depend significantly on the synthesis process and starting materials, which lead to final products with a range of sizes, morphologies, and even phases.

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 deintercalation process with a theoretical capacity of 175 mAh/g [1–5]. It is a spinel-type composite oxide allowing the reversible lithium insertion at room temperature via the reaction as follows:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \leftrightarrow Li_7Ti_5O_{12}.$$
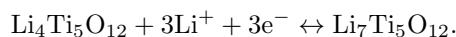
Three lithium atoms can insert into the lattice of $Li_4Ti_5O_{12}$ molecule with the formation of $Li_7Ti_5O_{12}$, resulting in a theoretical capacity of 175 mAh g^{-1}. During the insertion process, the phase structure of the oxide changes from a spinel type ($Li_4Ti_5O_{12}$) to a rock-salt type volume difference by less than 0.1%. 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 [6–8]. 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.

Commercial Li_2CO_3 and TiO_2 powders were used for $Li_4Ti_5O_{12}$ synthesis, respectively, where two different types of TiO_2 powders, i.e., anatase and rutile-phase were present.

2. Experimental

$Li_{4.25}Ti_5O_{12}$ with rutile TiO_2, $Li_{4.25}Ti_5O_{12}$ with anatase TiO_2 was synthesized by a facile solid state method and ball-milling treatment. Excess Li was provided to compensate for the loss of Li during synthesis. Ball mill treatment is capable of increasing reactivity of powders by reducing particle size, and increasing particle surface areas, which highly facilitate the completeness of solid-state reactions. The samples were prepared from Li_2CO_3, TiO_2 (anatase/rutile) molar ratio of Li and Ti was set at 4.25:5. In this method, starting materials Li_2CO_3, TiO_2 and ethanol were milled for 2 h at 400 rpm at ball mill, the resulting mixture in an oven which is set to 80 °C for alcohol dried up. The dried powder was then calcinated at 800 °C in argon atmosphere for 24 h to obtain the final grey powder of the samples. Samples were verified by X-ray diffraction (XRD) Bruker AXS D8, using Cu K_α radiation. The morphology and microstructure of samples were observed by scanning electron microscopy (LEO 440). The electrochemical performance was investigated by galvanostatic charge/discharge experiments. Two-electrode teflon cell was used to evaluate the electrochemical properties of both synthesized with rutile TiO_2, and anatase TiO_2, $Li_{4.25}Ti_5O_{12}$ electrodes. The electrochemical cells consisted of Li-metal sheet as a counter electrode and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate, EC/DEC, 1:1 vol.%, as a liquid electrolyte. Cell construction and sealing were carried out in an argon filled glove box. Galvanostatic cycling was performed between 1 V and 2.8 V with 1 C on an MLab Multi Channel battery tester.

3. Results and discussion

The XRD patterns of all powders are presented in Fig. 1. The diffraction peaks conform to spinel $Li_{4.25}Ti_5O_{12}$ structure (JCPDS file no. 49-0207) without obvious impurity phase. There is no significant change in the XRD pattern for the $Li_{4.25}Ti_5O_{12}$ (synthesized with anatase TiO_2-ball mill assisted) and (b) $Li_{4.25}Ti_5O_{12}$ (synthesized with rutile TiO_2-ball mill assisted). Calculated lattice parameters by Win Metric program were $a = 8.237$ (rutile) Å and $a = 8.236$ (anatase).

The crystallite sizes of $Li_{4.25}Ti_5O_{12}$ and the samples were prepared from Li_2CO_3, TiO_2 (anatase/rutile) are calculated from the Scherrer formula, $D = 0.94\lambda/\beta_{1/2}\cos(\Theta)$ and given in Table, where D is the crystallite size [mm], λ is the wavelength of the X-ray radiation (0.15418 nm for Cu K_α), Θ is the Bragg angle and $\beta_{1/2}$ is the full width half maximum (FWHM) of the diffraction peak measured at 2Θ in radians.

TABLE

Crystal size of samples.

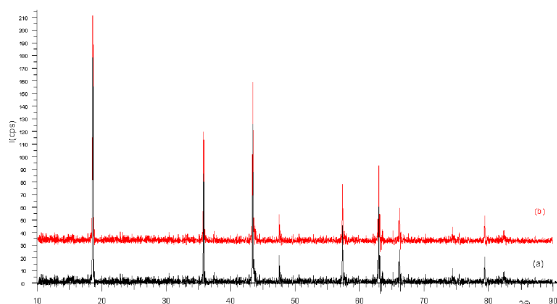| Compounds	Crystal size [nm]
$Li_{4.25}Ti_5O_{12}$ (synthesized with anatase TiO_2-ball mill assisted)	126
$Li_{4.25}Ti_5O_{12}$ (synthesized with rutile TiO_2-ball mill assisted)	154

Fig. 1. XRD pattern of Li$_{4.25}$Ti$_5$O$_{12}$, synthesized with: (a) anatase TiO$_2$-ball and (b) rutile TiO$_2$-ball mill assisted.
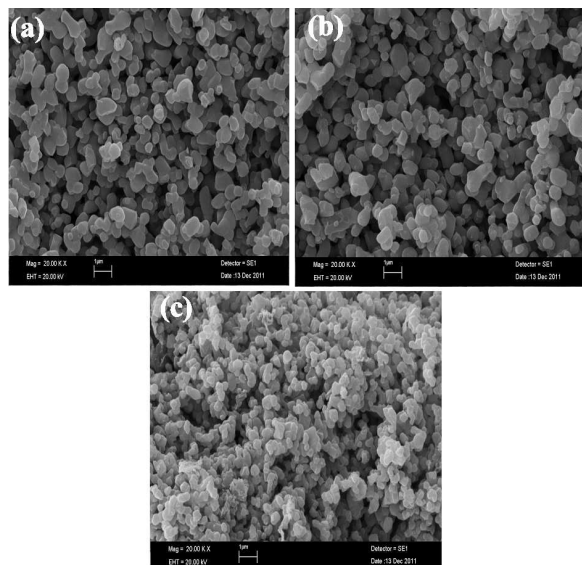

Fig. 2. SEM images of Li$_{4.25}$Ti$_5$O$_{12}$ synthesized with: (a) solid state method, (b) rutile TiO$_2$-ball, and (c) anatase TiO$_2$-ball mill assisted.

Figure 2 shows SEM images of the Li$_{4.25}$Ti$_5$O$_{12}$ powders, the crystallite size is about 150–170 nm Li$_4$Ti$_5$O$_{12}$ (synthesized with anatase TiO$_2$), and other sample which is synthesized with rutile TiO$_2$ 220–240 nm, and consequently these crystal sizes are smaller than in the Li$_4$Ti$_5$O$_{12}$ synthesized by the traditional solid-state method.

Figure 3 shows the continuous charge and discharge profiles of Li$_{4.25}$Ti$_5$O$_{12}$ (solid state method), Li$_{4.25}$Ti$_5$O$_{12}$ (synthesized with anatase TiO$_2$-ball mill assisted), Li$_{4.25}$Ti$_5$O$_{12}$ (synthesized with rutile TiO$_2$-ball mill assisted) performed at room temperature.

4. Conclusions

In this study we reported that the TiO$_2$ as the titanium source for the synthesis of Li$_4$Ti$_5$O$_{12}$ is very significant for the structure, morphology, and electrochemical performance of Li$_4$Ti$_5$O$_{12}$ synthesized by solid-state method.
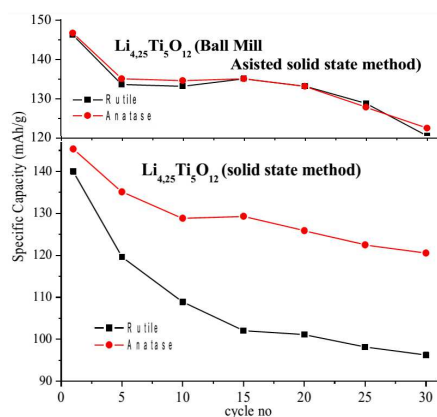

Fig. 3. Cycling performances of the samples synthesized with anatase TiO$_2$ and rutile TiO$_2$ with ball mill assisted and traditional solid state method.

In this work, TiO$_2$ with different crystal structure are prepared and used as the titanium source to investigate the effects of TiO$_2$ crystal structure on the performance of Li$_4$Ti$_5$O$_{12}$ anode material. It has been found that the structure, morphology, and electrochemical performance of Li$_4$Ti$_5$O$_{12}$ are influenced significantly by the TiO$_2$ crystal structure. After 30 cycles the Li$_{4.25}$Ti$_5$O$_{12}$ (synthesized with rutile TiO$_2$-ball mill assisted) loss of the capacity was about 18.94%, and Li$_{4.25}$Ti$_5$O$_{12}$ (synthesized with anatase TiO$_2$-ball mill assisted) loss of the capacity was about 11.56%. Consequently we can say that in this work, the Li$_4$Ti$_5$O$_{12}$ material using anatase TiO$_2$ shows best electrochemical performance.

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