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Facile synthesis of nano-Li$_4$Ti$_5$O$_{12}$ for high-rate Li-ion battery anodes

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Abstract

One of the most promising anode materials for Li-ion batteries, Li$_4$Ti$_5$O$_{12}$, has attracted attention because it is a zero-strain Li insertion host having a stable insertion potential. In this study, we suggest two different synthetic processes to prepare Li$_4$Ti$_5$O$_{12}$ using anatase TiO$_2$ nanoprecursors. TiO$_2$ powders, which have extraordinarily large surface areas of more than 250 m^2 g^{-1}, were initially prepared through the urea-forced hydrolysis/precipitation route below 100°C. For the synthesis of Li$_4$Ti$_5$O$_{12}$, LiOH and Li$_2$CO$_3$ were added to TiO$_2$ solutions prepared in water and ethanol media, respectively. The powders were subsequently dried and calcined at various temperatures. The phase and morphological transitions from TiO$_2$ to Li$_4$Ti$_5$O$_{12}$ were characterized using X-ray powder diffraction and transmission electron microscopy. The electrochemical performance of nanosized Li$_4$Ti$_5$O$_{12}$ was evaluated in detail by cyclic voltammetry and galvanostatic cycling. Furthermore, the high-rate performance and long-term cycle stability of Li$_4$Ti$_5$O$_{12}$ anodes for use in Li-ion batteries were discussed.

Introduction

Li$_4$Ti$_5$O$_{12}$ is one of the most promising anode materials for Li-ion batteries even though it has lower specific capacity (175 mAh g^{-1}) than does graphite (372 mAh g^{-1}). One of the unique properties of Li$_4$Ti$_5$O$_{12}$ is the negligible lattice change in the Li-ion insertion/desertion process, which provides good high-rate cycling stability [1]. The electrochemical properties of Li$_4$Ti$_5$O$_{12}$ are dependent on its method of preparation. The conventional solid-state, sol-gel [2], hydrothermal [3], spray pyrolysis [4], and combustion [5] methods have been proposed for Li$_4$Ti$_5$O$_{12}$ synthesis. Among these, the solid-state process is a simple method that is well suited for production scale-up. However, the solid-state process using TiO$_2$ as a starting precursor requires lengthy heating with Li salts at high temperatures in order to obtain highly crystalline Li$_4$Ti$_5$O$_{12}$ [6]. As a result, particle size control is more difficult than that in hydrothermal or sol-gel method, and the resultant larger particles lead to poor capacity retention and rate capability.

Herein, we demonstrate the preparation of highly crystalline nanosized Li$_4$Ti$_5$O$_{12}$ [nano-Li$_4$Ti$_5$O$_{12}$] with a uniform particle size via a urea-mediated wet process, in which a TiO$_2$ precursor with a large surface area is initially formed, followed by wet and solid-state processes with different Li sources, LiOH and Li$_2$CO$_3$, respectively. After subsequent heat treatment, the electrochemical performance of the resultant Li$_4$Ti$_5$O$_{12}$ as an anode for Li-ion batteries is evaluated and discussed.

Experimental procedure

Preparation of TiO$_2$ precursor

TiO$_2$ nanoparticles with an anatase structure were prepared using the urea-mediated precipitation method [7], in which 0.015 M titanium trichloride (20% in 3% hydrochloric acid, TiCl$_3$, Alfa Aesar, Ward Hill, MA, USA) and 3.0 M urea (99.3%, (NH$_2$)$_2$CO, Alfa Aesar, Ward Hill, MA, USA) were dissolved in deionized [DI] water at room temperature. The solution was heated at 90°C to 100°C for 4 h with magnetic stirring. Precipitates were obtained by centrifugation and repeated washing (five times with DI water and once with anhydrous ethanol). The powders were dried at 100°C for several hours in a vacuum oven.

Preparation of Li$_4$Ti$_5$O$_{12}$

Wet process

Stoichiometric amounts of the prepared TiO$_2$ nanopowder were dispersed in DI water by sonication for 2 h.

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A stoichiometric amount of LiOH (98%, Sigma-Aldrich, St. Louis, MO, USA) was then dissolved in the solution with stirring. The resulting white-colored suspensions were heated at 110°C to evaporate water. Finally, the powder was calcined at various temperatures in air to afford $Li_4Ti_5O_{12}$.

Solid-state process

For the solid-state process, Li_2CO_3 (99%, Sigma-Aldrich, St. Louis, MO, USA) was chosen as the Li source. The stoichiometric mixture was agitated for 24 h with a zirconia ball in absolute ethanol, dried, and calcined at various temperatures in air.

Characterization of TiO_2 precursors and $Li_4Ti_5O_{12}$ nanoparticles

The powders were characterized by X-ray powder diffraction [XRD] (D/max-2500 V, Rigaku, Tokyo, Japan), Brunauer-Emmett-Teller [BET] (Belsorp-mini II, BEL Japan Inc., Osaka, Japan) surface area determination, high-resolution transmission electron microscopy [HRTEM] (JEM-3000F, JEOL, Tokyo, Japan) at an accelerating voltage of 300 kV, and field-emission scanning electron microscopy [FESEM] (JSM-6700F, JEOL, Tokyo, Japan).

Electrochemical analysis

A mixture consisting of 70 wt.% of the active materials, 15 wt.% Super P carbon black (MMM Carbon, Brussels, Belgium), and 15 wt.% Kynar 2801 binder (PVDF-HFP, Arkema Inc., King of Prussia, PA, USA) was dissolved in 1-methyl-2-pyrrolidinone (Sigma-Aldrich, St. Louis, MO, USA) solvent for uniform dispersion of the active materials on a Cu foil to obtain positive electrodes. Then, the solvent was evaporated in a vacuum oven at 100°C. A Swagelok-type cell was assembled in an Ar-filled glove box in order to protect the cell from oxidation and moisture. A Li metal foil (negative electrode) and the prepared mixture (positive electrode) were saturated with a liquid electrolyte obtained by dissolving 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 by volume, Techno Semichem Co., Ltd., Sungnam, South Korea). $Li_4Ti_5O_{12}$ powders were analyzed by the galvanostatic discharge/charge cycling method and cyclic voltammetry [CV] measurements with a battery cycler (WBCS 3000, WonATech, Seoul, South Korea). Each cell was cycled through a voltage range of 1.0 to 2.5 V versus Li/Li$^+$.

Results and discussion
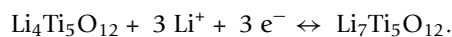
The XRD pattern (Figure 1a) for precursor powders indicated that they comprised anatase-phase TiO_2 (Joint Committee of Powder Diffraction System [JCPDS] #21-1272). The TiO_2 morphology was found to be flower-like clusters of 50 nm in size, which comprised tiny aggregated nanorods (Figure 1b). For this reason, the powder had an extremely large surface area, 267 m^2 g^{-1}, as confirmed by BET surface area measurements. In addition, the electron diffraction (selected area electron diffraction [SAED]) pattern of the selected area coincided with that of anatase TiO_2, as shown in the inset of Figure 1b.

In order to obtain nano-$Li_4Ti_5O_{12}$ with a sufficiently large surface area, the TiO_2 powders prepared as mentioned above were used as precursors. After mixing the TiO_2 precursor with LiOH and Li_2CO_3 through wet and solid-state processes, respectively, both mixtures were calcined at 700°C and 800°C and were found to mainly comprise the cubic $Li_4Ti_5O_{12}$ phase (JCPDS #49-0207; Figure 2). However, the $Li_4Ti_5O_{12}$ powders prepared through the wet process had an undesirable (Li-inactive) secondary phase, Li_2TiO_3 (JCPDS #33-0831), even after calcination at 800°C as confirmed by the XRD peak at $2\theta = 35.6°$. As opposed to the powders prepared by the wet process, those prepared through the solid-state process showed an almost pure $Li_4Ti_5O_{12}$ phase with negligible secondary phases.

Figures 3a, b show the typical FESEM and HRTEM images of the $Li_4Ti_5O_{12}$ powders prepared through the solid-state process. Small and uniformly sized $Li_4Ti_5O_{12}$ particles (50 to 100 nm) were obtained even if the calcination temperature was 700°C, which could be attributed to the unique TiO_2 nanoprecursors with extremely large surface areas. These $Li_4Ti_5O_{12}$ powders were further investigated by HRTEM, as shown in Figure 3c. The typical HRTEM image was recorded from a single particle with lattice fringes of approximately 0.496 nm, which corresponded to the (111) interplanar spacing in $Li_4Ti_5O_{12}$. The presence of single-phase $Li_4Ti_5O_{12}$ was also confirmed from the SAED patterns shown in the inset of Figure 3c.

Nanostructured electrode materials help in enhancing the performance of Li-ion batteries by providing higher electrode/electrolyte contact areas, shorter Li$^+$ diffusion lengths (L) in the intercalation host (smaller time constant (τ); $\tau = L^2/2D$, where D is the coupled diffusion coefficient for Li$^+$ and e$^-$), and better accommodation of the Li-ion insertion/extraction strain [8,9]. Figure 4 shows the electrochemical activity of nano-$Li_4Ti_5O_{12}$ powders that were prepared through the solid-state process. These CV measurements were carried out during the first cycle using a half cell with Li metal foil as the negative electrode, operating at 0.3 mV/s. Clear cathodic and anodic peaks appeared at approximately 1.46 and 1.7 V, respectively, for the Li intercalation/deintercalation, in accordance with the pair of peaks reported for $Li_4Ti_5O_{12}$ powders [10]. The following electrochemical reaction of $Li_4Ti_5O_{12}$ with Li has been suggested [11]:

$$Li_4Ti_5O_{12} + 3\ Li^+ + 3\ e^- \leftrightarrow Li_7Ti_5O_{12}.$$
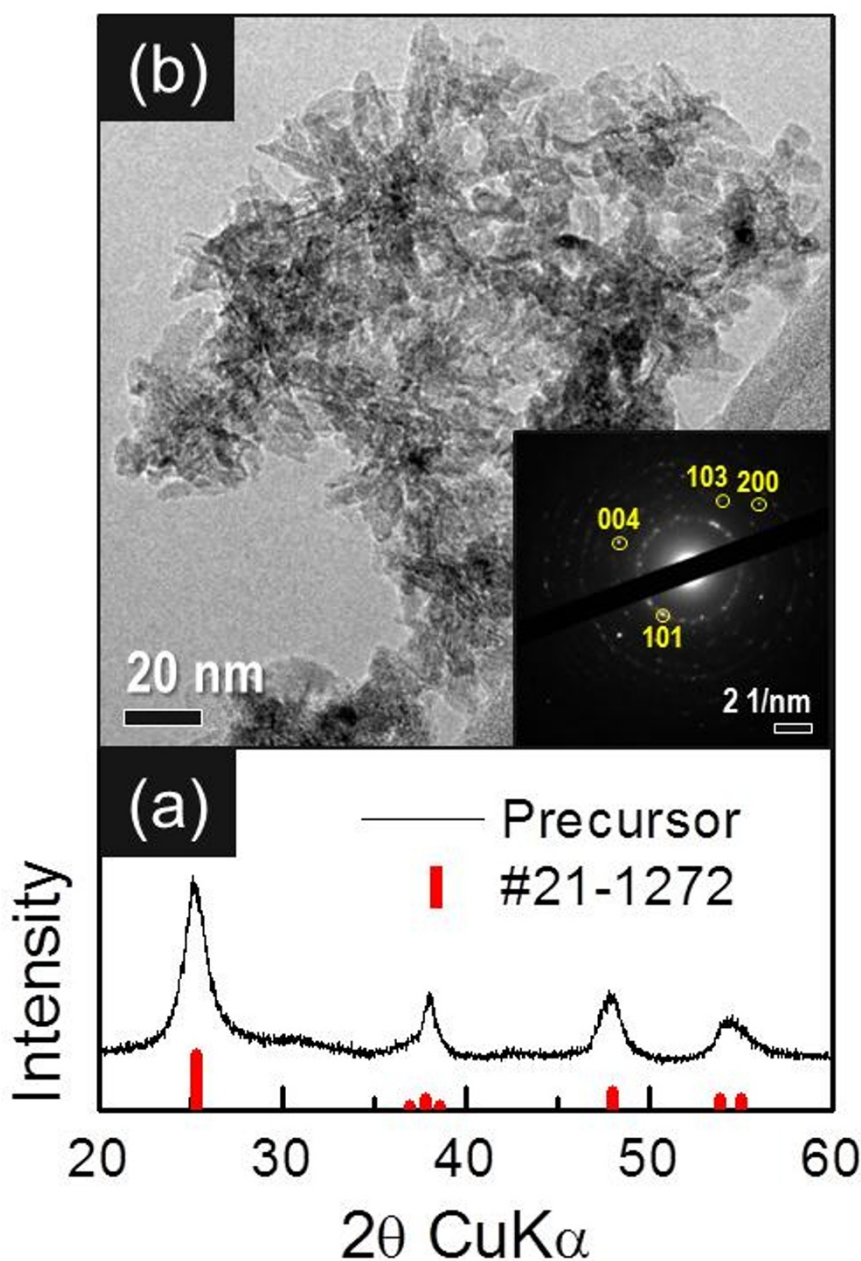
Figure 1 Characterization of TiO₂ products. (**a**) A typical XRD pattern. (**b**) A TEM image of TiO₂ precursor powders. The inset in (b) shows SAED patterns. (By Jin YH et al.).
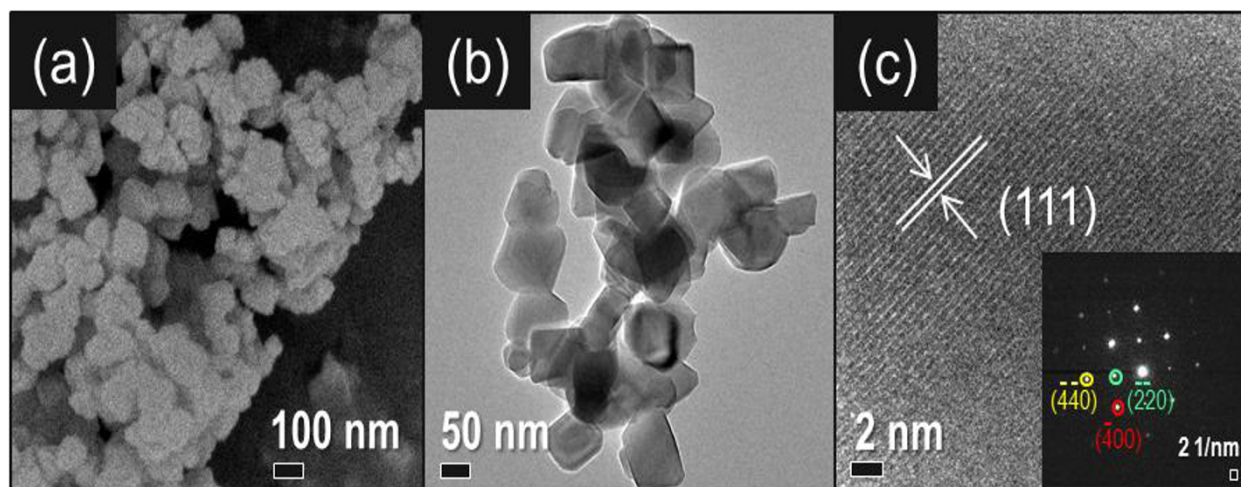
Figure 4b shows the galvanostatic cycling characteristics of nano-$Li_4Ti_5O_{12}$ powders that were prepared through the solid-state process. The first discharge capacity was 154 mAh g^{-1} over a voltage window of 1.0 to 2.5 V at a current rate of 1 C (175 mAh g^{-1}; here, C is defined as three Li ions per hour and per formula unit of $Li_4Ti_5O_{12}$ on the basis of the above equation). The reversible capacities were observed to be 135, 133, 131, 130, and 128 mAh g^{-1} after 100, 200, 300, 400, and 500

cycles, respectively. Indeed, it is interesting to note that the nano-$Li_4Ti_5O_{12}$ electrode in this study shows superior long-term cyclability and negligible variation in reversible capacity upon cycling (0.013% fading per cycle between 100 and 500 cycles).

Figure 5 shows the rate capability of the nano-$Li_4Ti_5O_{12}$ powders that were prepared through the solid-state process, for up to 20 C. The cells were charged and discharged at 1 C for the first 10 cycles, and then, the
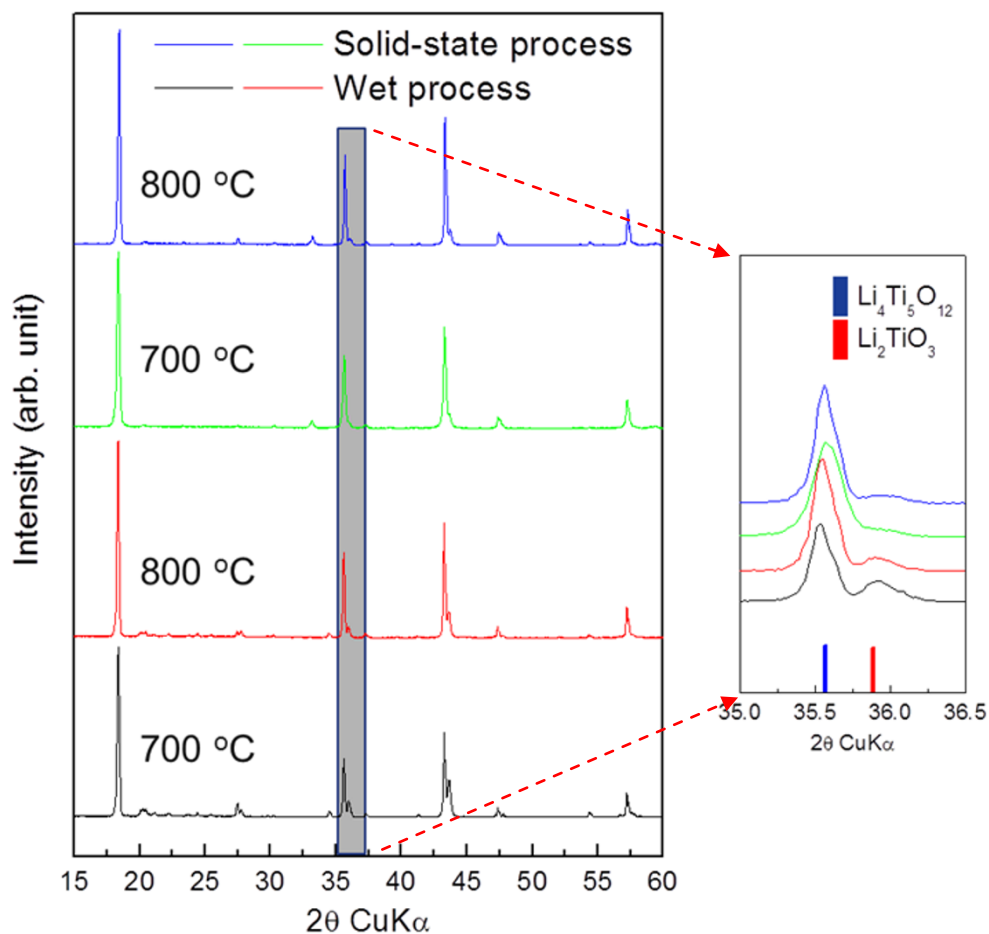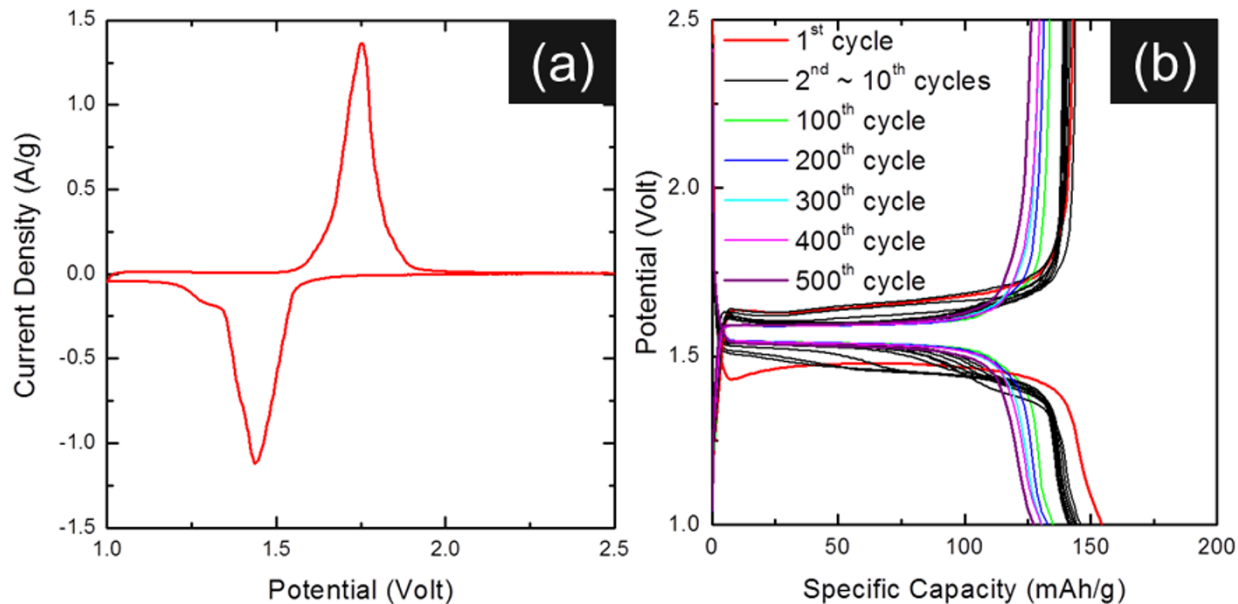
Figure 2 XRD patterns of Li$_4$Ti$_5$O$_{12}$ powders. Li$_4$Ti$_5$O$_{12}$ prepared through wet and solid-state processes and subsequently calcined at 700℃ and 800℃ for 4 h. (By Jin YH et al.).

**Figure 3 FESEM and HRTEM images**. (**a**) FESEM image of a typical Li$_4$Ti$_5$O$_{12}$. (**b**) Low-magnification HRTEM image of Li$_4$Ti$_5$O$_{12}$. (**c**) HRTEM image of Li$_4$Ti$_5$O$_{12}$ powders prepared through the solid-state process and subsequently calcined at 700℃ for 4 h. The inset in (c) shows SAED patterns. (By Jin YH et al.).

Figure 4 Electrochemical performance of Li$_4$Ti$_5$O$_{12}$. (**a**) A cyclic voltammogram of Li$_4$Ti$_5$O$_{12}$. (**b**) Charge-discharge profiles of Li$_4$Ti$_5$O$_{12}$ powders prepared through the solid-state process and subsequently calcined at 700°C for 4 h. (By Jin YH et al.).
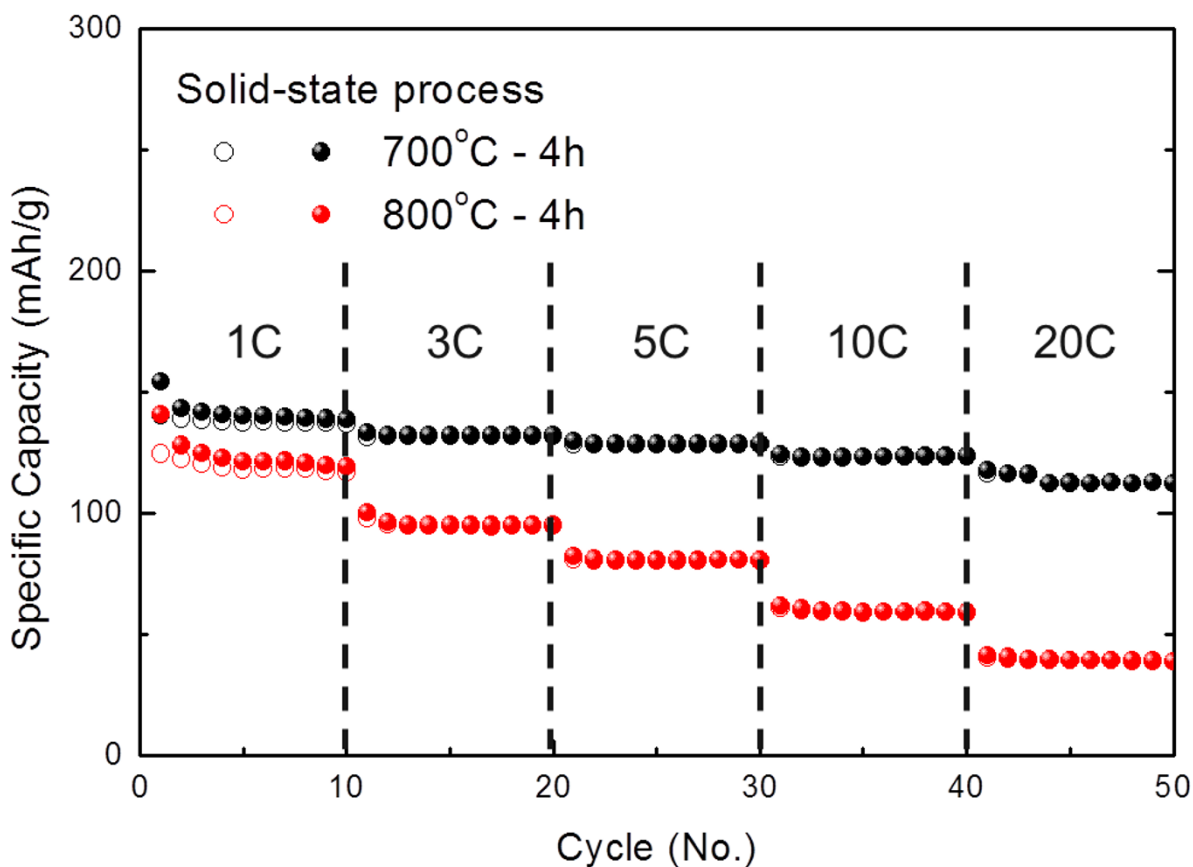
Figure 5 Rate capability of Li$_4$Ti$_5$O$_{12}$. Cycling behavior at different C values for Li$_4$Ti$_5$O$_{12}$ powders prepared through the solid-state process and subsequently calcined at 700°C and 800°C for 4 h. Solid and open circles indicate discharge and charge capacities, respectively. (By Jin YH et al.).

rate was increased in stages to 20 C. At a rate of 20 C, the capacity of the nano-$Li_4Ti_5O_{12}$ powders was still high: 112 mAh g^{-1}. This outstanding performance at high rates was much better than that afforded by any of the various types of $Li_4Ti_5O_{12}$ nanostructures such as nanowires and nanoparticles [3,12,13]. In particular, the nano-$Li_4Ti_5O_{12}$ powders calcined at 700°C exhibited better long-term cyclability as well as superior rate capabilities than those calcined at 800°C (Figure 5), possibly a result of the nanosize effect of the small particle size and large surface area.

Conclusion

In summary, spinel-type nano-$Li_4Ti_5O_{12}$ particles were synthesized by a solid-state process from a large-surface-area TiO_2 precursor and subsequent calcination at 700°C. The average particle size of these nano-$Li_4Ti_5O_{12}$ particles was 50 to 100 nm. High Li electroactivity was confirmed by CV experiments. The nano-$Li_4Ti_5O_{12}$ particles calcined at 700°C showed a high Li storage capacity of 128 mAh g^{-1} after 500 cycles at 1 C and superior cycle performance (112 mAh g^{-1}) even at a high rate of 20 C. The enhanced reversible capacity and cycling performance were attributed to the formation of highly crystalline, uniform nanoparticles, which make this nano-$Li_4Ti_5O_{12}$ a potential host material for high-powder Li-ion batteries.

Authors' contributions
Y-HJ carried out the TiO_2 and $Li_4Ti_5O_{12}$ sample preparation and drafted the manuscript. K-MM and H-WS fulfilled the electrochemical analyses. S-DS, I-SH, and K-SP participated in the microstructural analysis. D-WK designed the study, led the discussion of the results, and participated in writing the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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