

Research on spray-dried lithium titanate as electrode materials for lithium ion batteries

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Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been considered as a promising electrode material for lithium secondary batteries. In this work a spray drying process was developed to prepare porous and spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with Li_2CO_3 and rutile type TiO_2 as precursors and PVB as forming agent of pores. The experimental results showed that porous and spherical morphology of the spray-dried powders was maintained during the sintering and the subsequent heat treatment. The oxygen atmosphere was demonstrated important to the electrochemical performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. However, overtime heat treatment would result in superfluous loss of lithium content and therefore led to obvious decrease of charge and discharge capacities.

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1. Introduction

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ based materials displayed good Li ion intercalation and de-intercalation reversibility and exhibited no structural change (zero-strain insertion material) during charge–discharge cycling process. Moreover, they offered a main discharge platform close to 1.55 V versus Li^+/Li , which was above the reduction potential of most organic electrolytes and consequently, passive films with high resistances from the reduction of electrolytes could therefore be avoided on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface. The materials have been considered very promising in lithium ion batteries as anodic material while coupled with high voltage cathode such as 4 V LiMn_2O_4 , LiNiO_2 or LiCoO_2 to supply a cell with an operating voltage of approximately 2.5 or 5 V $\text{LiMn}_{2-x}\text{O}_4$ ($x = \text{Co}, \text{Ni}$) to provide 3.5 V operating voltage, or even as anodic materials coupled with lithium or carbon anode [1–3]. In addition, Amattucci et al. [4] ever reported an asymmetric electrochemical cell using nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as cathode and carbon as an-

ode which stored energy through pseudocapacitive reaction and more than 4000 cycles were obtained at cycling rates in the range of 10–50 °C.

So far, the spinel type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was mainly prepared by solid-state reactions from mechanical mixtures of anatase type TiO_2 and Li_2CO_3 or LiOH . The reactions typically occurred at 800–1000 °C for 12–24 h [5,6]. In our previous work, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were synthesized by solid-state reaction from rutile type TiO_2 , a natural and low cost type of titanium dioxide, and the powders displayed specific energy density as high as that prepared from anatase type TiO_2 , which was generally considered to be the most active Li^+ insertion host [7].

Nakahara et al. [8] ever reported excellent cycling performance of particulate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by spray drying process with LiOH and anatase type TiO_2 as precursors, it was found that granular morphology of the active $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was essential to the high rate capacity of the active materials.

In this paper, porous and spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were prepared by spray drying process with Li_2CO_3 and rutile type TiO_2 as precursors and PVB as forming agent of pores. Effects of heat treatment conditions on the electro-

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chemical performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were investigated by means of thermal analysis, microstructure observation and charge–discharge cycling test.

2. Experimental

2.1. Sample preparation

The stoichiometric amounts of precursors Li_2CO_3 (AR) and rutile type TiO_2 (99.9%) were mixed in alcohol solvent by rotary ball milling at a speed of 300 rpm for 2 h to form a slurry, then 6 wt.% polyvinyl butyral (PVB) was added and dissolved in the slurry and mixed for another 1 h. The homogeneous slurry obtained was spray-dried at the inlet and outlet temperatures of 150 and 80 °C, respectively. The dried spherical powders were heated at 950 °C for 24 h in a covered alumina crucible, afterwards, further heat treatments were taken under air circumstances at 850 °C for different periods. The powders were then ground gently for analyses and tests.

2.2. Characterization

DTA and TG profiles of the spray-dried precursors were determined at a heating rate of 10 K min^{-1} from ambient temperature to 900 °C. Phase analysis of the sintered and the further treated powders was performed on an X-ray diffractometer using $\text{Cu K}\alpha_1$ as the radiation source. The morphology and particle size of all powders were evaluated by scanning electron microscopy (SEM).

The electrochemical cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders was carried out with coin cells using lithium metal as the counter electrode at room temperature. The cells were based on the following configuration: Li metal(–)/electrolyte/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (+) with a liquid electrolyte (1 M solution of LiPF_6 in EC:DMC (1:1, v/v)). Microporous polypropylene film (Celgard) was used as the separator. The working electrode was prepared from a paste of 80 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 10 wt.% conductive carbon black and 10 wt.% PVDF binder in NMP solvent. The paste was coated on an aluminum foil by blade, and then dried under vacuum at 100 °C for 8 h before electrochemical evaluation. Cell assembly was made in a glove box (NAC AM-2) filled with pure argon. The charge–discharge characteristics of the cells were recorded in the potential range between 0.5 and 2.5 V using a LANDCT2001A computer-controlled galvanostat.

3. Results and discussion

3.1. Thermal analyses

Fig. 1 showed the DTA and TG profiles of the spray-dried precursor powders. An obvious endothermic peak at 71.8 °C indicated residual alcohol in the powders after the

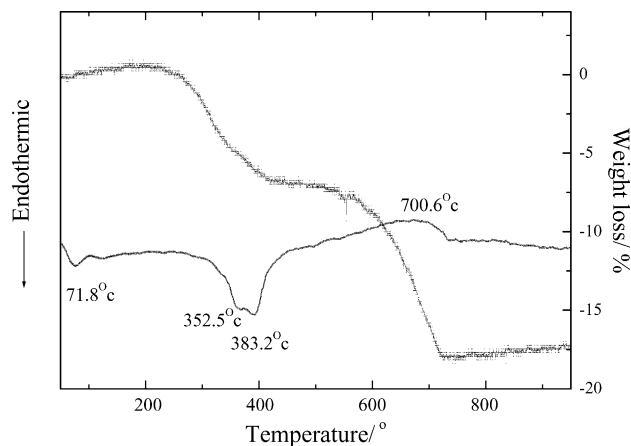


Fig. 1. DTA/TGA profiles of the spray-dried precursor powders.

spray drying. The endothermic peaks at 352.2 and 383.2 °C could be attributed to the decomposition of PVB and the pore forming agent contained in the powders. The corresponding weight loss up to the decomposition points was about 7 wt.% which was comparable to the weight percent of the PVB added to the powders. About 10 wt.% further weight loss was due to the decomposition of Li_2CO_3 precursor, corresponding to the broad exothermic band. The peak at 700.6 °C could be considered as the forming temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. No obvious thermal effect was found after 720 °C.

3.2. Phase analyses

Fig. 2 showed the XRD patterns of the powders sintered at 950 °C and treated further at 850 °C for various periods. It was found that the diffraction patterns of all the specimens were similar, with all the peaks indexable to the $Fd\bar{3}m$ space group. No obvious shift of the diffraction lines could be found, which indicated comparable cell parameters of all the specimens,

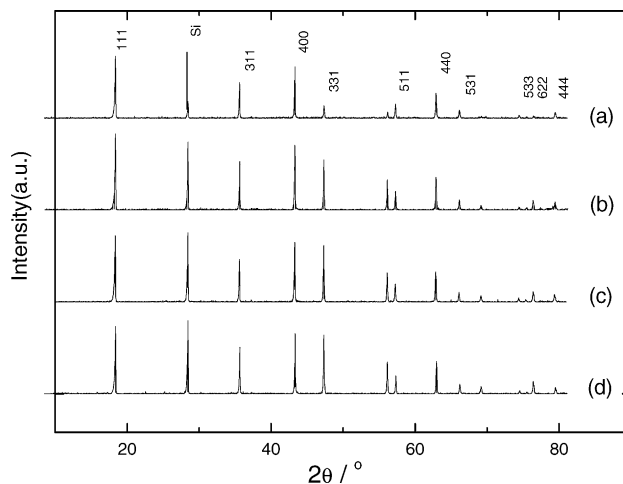


Fig. 2. XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders sintered at 950 °C for 24 h (a) and treated further at 850 °C for 4 h (b), 16 h (c) and 24 h (d).

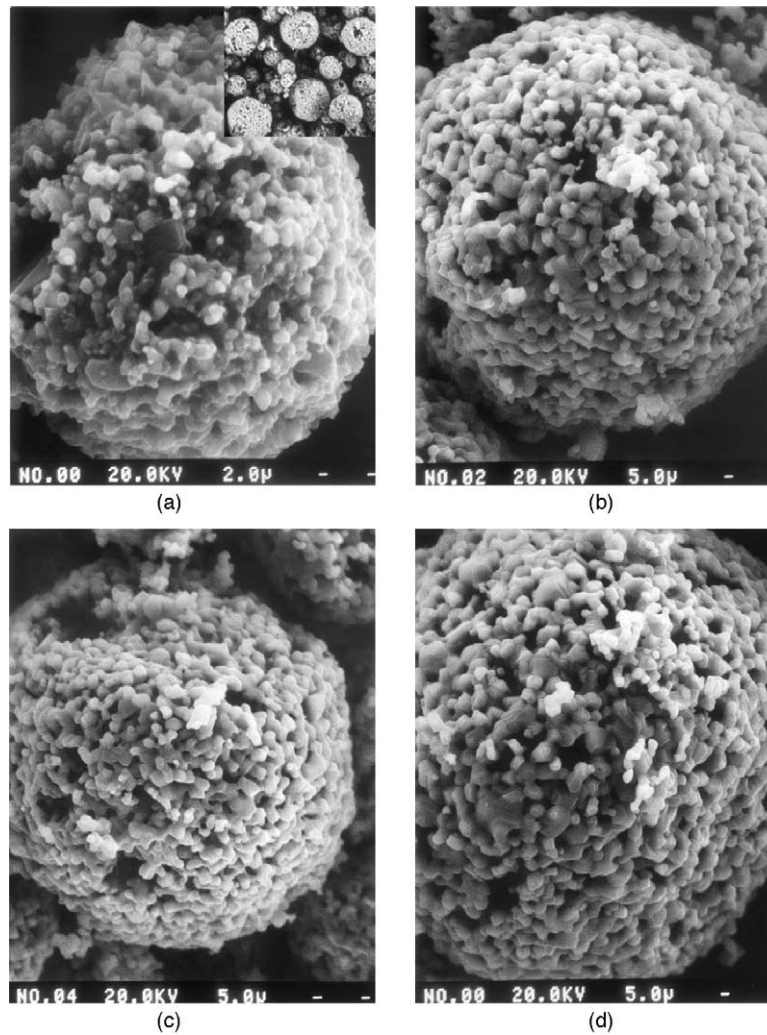


Fig. 3. Typical morphology of the spray-dried powder (a) and the powder sintered at 950 °C for 24 h (b) and further treated at 850 °C for 4 h (c) and 24 h (d).

but small difference of the intensities of the peaks at large angles was found as shown in the figure.

3.3. Morphology

Fig. 3 showed the morphology of the spray-dried precursor powders together with the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders sintered at 950 °C for 24 h and the powders further treated at 850 °C for 4 and 24 h, respectively. As seen, all powders showed spherical features. Typical sphere size of the spray-dried and the sintered powders was in the range of several microns to 20 μm. In the sphere of the spray-dried powders, different particle morphologies corresponding to different kinds of compound, i.e., Li_2CO_3 , TiO_2 and PVB in the precursor were found. After sintering, the spheres were enlarged in comparison with the spray-dried powders, indicating dilatation of the spheres during the decomposition of PVB and Li_2CO_3 . The porous feature of the sintered spheres was helpful to the penetration of the liquid electrolyte and even conducting agent carbon in the preparation of cathode. The size of the particles

in the sintered spheres was about 1 μm which was comparable to that prepared from LiOH precursor. As known [1], the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles prepared from LiOH tend to grow in larger size because of the much lower melting point of the LiOH which allows the products to crystallize and agglomerate into large particles whereas the higher melting point of Li_2CO_3 at about 723 °C enables the reaction to proceed to completion without a significant growth in the particle size of the product. It could be suggested according to Fig. 1 that during the preparation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ from spray-dried precursors containing Li_2CO_3 , TiO_2 and PVB, the decomposition of Li_2CO_3 happened during the synthesis instead of the melting of the lithium carbonate, which resulted in highly reactive precursors and improved the growth of the particles in the product.

3.4. Electrochemical cycling performances

Fig. 4 showed typical first charge–discharge cycling profiles between the cutoff voltages of 0.5 and 2.5 V of the spec-

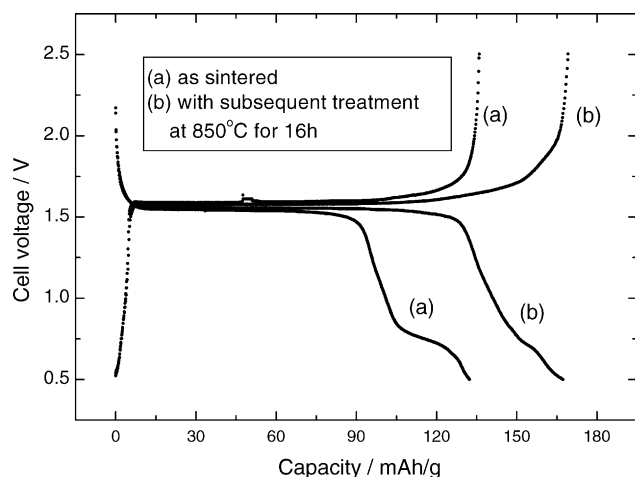


Fig. 4. Typical first cycling profile for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as sintered and thermally treated.

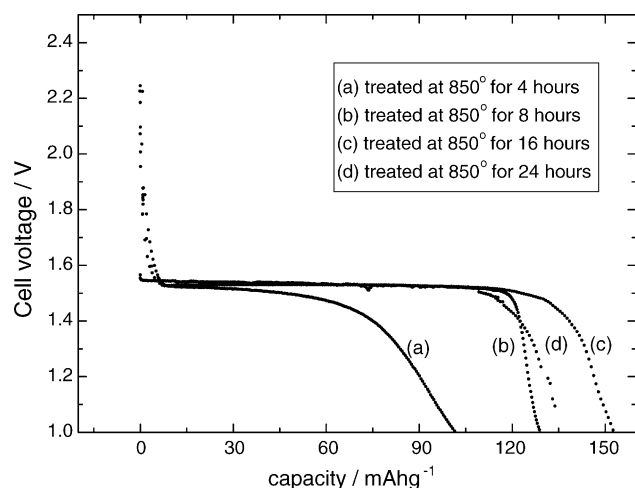


Fig. 5. First discharge profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated at 850°C for different times.

imen sintered at 950°C for 24 h and the specimen further treated at 850°C for 16 h. From the figure, we could see that the voltage dropped quickly to below 2 V and decreased as the reaction proceeded until the voltage reached about 1.53 V, after which the voltage was almost independent upon the degree of reduction. In addition to the 1.53 V platform, another one at 0.68 V was also observed in almost all samples and its capacity was different among all the specimens. It is noteworthy that the reverse of the minor platform (0.68 V) occurred at around 1.7V_{Li} in conjunction with the oxidation of Ti^{3+} to Ti^{4+} . The phenomenon was also reported by other research groups [9], which suggested a multi step restore of Ti^{4+} during the discharge period.

It was found that the further treatment under air was important to the specific capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ specimen. Fig. 5 demonstrated the effect of further thermal treating time on the first discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ specimens. Since the sintering took place inside a covered crucible where oxygen

was probably insufficient for the oxidation of the titanium in $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which led to the decrease of the $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio in the specimen and hence caused a lower specific capacity. In comparison with the normal solid-state reaction method, the oxidation of the spray-dried powders would be more difficult because of the bigger size of the spheres. The subsequent heat-treatment under air circumstances allowed the oxidation of the specimen to proceed further, and therefore effectively enhanced the specific capacity. It was noticeable that overtime treatment played a reverse role in the capacity of the powders, probably due to the overgrowth of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles as demonstrated in Fig. 3 and superfluous loss of lithium content during the treating process. According to the experimental results, 16 h would be considered as the best treating time for the sintered powders.

4. Conclusions

The spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with appropriate porosity have been synthesized by spray drying process from rutile type TiO_2 and with PVB as forming agent of pores. The oxygen atmosphere is very important to the formation of spinel type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase with high specific capacity. All specimens showed main discharge platform close to 1.53 V as well as a minor one at about 0.68 V. Overtime heat treatment of the specimens would result in superfluous loss of lithium composition and overgrowth of the particles and therefore reduced their capacity.

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