RHEOLOGICAL PHASE SYNTHESIS AND CHARACTERIZATION OF MICRO-SIZED $\text{Li}_4\text{Ti}_5\text{O}_{12}$ LINGLING XIE¹, XIAOYU CAO^{1*}, CHANGWEI LIU¹, CHIWEI WANG²¹*School of Chemistry and Chemical Engineering, Henan University of Technology,
Zhengzhou, 450001 People's Republic of China*²*Tianjin EV Energies Co., Ltd., Tianjin, 300112 People's Republic of China*

(Received: November 26, 2009 - Accepted: June 15, 2010)

ABSTRACT

Zero-strain anode material of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for lithium ion battery was successfully synthesized via the rheological phase reaction (RPR) method. The as-prepared powders were characterized by means of powder X-ray diffraction (XRD), scanning electron microscope (SEM) and particle size distribution analysis (PSD), and the electrochemical properties of the powders were evaluated by the galvanostatic discharge test and cyclic voltammetry (CV). The results revealed that well-crystallized uniform micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were obtained at 800 °C for different calcination times via the simple template-free rheological phase route. Among these RPR-derived $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders, one synthesized at 800 °C for 22 h displays the initial discharge capacity of 184.3 mAh/g and excellent characteristic of cyclic voltammetry.

Keywords: rheological phase synthesis; characterization; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; anode material; lithium ion batteries

INTRODUCTION

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as an anode material has received increasing interest over past years due to its potential applications in lithium ion batteries^{1,2,3,4,5,6}. Both the excellent Li intercalation/de-intercalation kinetics and structural stability make it achieve the good high-rate capability and reversibility^{6,7}. Apart from the cheapness and non-toxicity, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ also displays a flat voltage plateau located at about 1.5 V vs. Li/Li^+ , which is higher than the reduction potential of the conventional electrolyte solvents^{8,9}. This feature avoids the reduction of solvent and the formation of a solid electrolyte interface, which accordingly alleviate the potential problem of lithium deposition and render the material significantly safer than graphite. Thus, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ possesses a continuous interest to the lithium battery industry though the energy density of cell is slightly sacrificed when it is coupled with a 4 V cathode material.

At present, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been widely prepared by various synthetic methods. Among these preparation methods, the conventional solid state reaction is usually used to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder at high temperature starting from lithium salts and titanium oxides^{1,2,3,4,5,6,7}. These methods need large thermal energy and long reactive time, which may results in the undesirable large particle size and particle heterogeneity and accordingly incur an adverse effect on its electrochemical performances such as discharge capacity and rate capability. In particular, many high temperature calcination processes are made in a nitrogen or oxygen gas stream^{1,2,3,4,6,7}, which leads to the cost increase. As far as the soft chemistry synthesis methods such as the low temperature chemical lithiation method¹⁰, the sol-gel synthesis method¹¹, the macroemulsion synthesis method¹², the hydrothermal synthesis method¹³, the ball milling-assisted sol-gel method¹⁴ and spray pyrolysis method¹⁵ are concerned, the particle size of thus prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with various morphologies is much finer and more uniform compared with the conventional solid state synthesis powder due to preparing the precursors constituted of ultra-fine particles. As a consequence, the soft-chemical synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders display the high discharge capacity and excellent rate capability. However, many soft chemistry synthetic methods often suffer from the complicated operation and thereby are not suitable for the mass production in despite of a relative low calcination temperature.

In this work, we introduce a simple synthetic route for preparing the homogenized micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders by a rheological phase reaction method. It is a process of preparing compounds or materials from a solid-liquid rheological mixture. Firstly, the solid reactants are fully mixed in a proper molar ratio. Then a proper amount of water or other solvent is added to a solid-liquid rheological body where the solid particles and liquid substance are uniformly distributed. After further treatment, the final product is obtained. The structure, morphology and electrochemical properties of the as-synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders have been investigated.

EXPERIMENTAL

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder was prepared through a rheological phase reaction process. $\text{LiOH}\cdot\text{H}_2\text{O}$ and anatase TiO_2 were used as starting materials and fully mixed by grinding in a molar ratio of 4:5. A proper amount of redistilled water was added to obtain a rheological body and the mixtures were heated at 90 °C for 5 h in a cylindrical Teflon-lined stainless autoclave. After being dried at 120 °C, the precursor was moved into a furnace at 800 °C for 8 h, 16 h and 22 h in air, respectively and then cooled to room temperature to obtain final $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. All the reagents were analytical reagent grade and as received.

X-ray diffraction (XRD) analysis was carried out on an XRD-Pert Pro diffractometer (XPERT PRO MPD, Netherlands) with $\text{Co K}\alpha$ radiation source ($\lambda = 1.78901 \text{ \AA}$). The morphological feature of the as-prepared powders was observed on the SEM- JSM6380LA (JEOL, Japan). The analysis of particle size for the powders was carried out with Mastersizer-2000 (Malvern instruments, England) using a laser granulometer.

The working electrodes were composed of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders, acetylene black and polytetrafluoroethylene emulsion binder (60 wt.%) at a weight ratio of 8:1:1. The stainless-steel meshes were used as the current collectors. The CR2016 coin cells were assembled with pure lithium foil as a counter electrode, Celgard-2400 as the separator and 1 mol/L LiClO_4 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (v/v, 1:1) as the electrolyte. The discharge tests were performed at constant specific current of 30 mA/g with a cut-off voltage of 1.0 V in a multi-channel battery tester (Neware, Shenzhen) at 25 °C. The cells were assembled in an Argon-filled dry glove box. Cyclic voltammetry (CV) test was carried out on a CHI660A electrochemical workstation (Chenhua, Shanghai) at a scan rate of 0.05 mV/s using lithium foils as the reference and the counter electrodes.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of PRP-derived $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders heat-treated at 800 °C for different calcination times. It can be obviously seen from the XRD that all the powders display sharp diffraction peaks, indicating an enhanced degree of crystallinity. For the powder obtained at 800 °C for 8 h in Fig. 1(a), the main Bragg diffraction peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase have emerged apart from an impurity peak marked with asterisk (*); at about 20-21.99°. With prolonging the calcinations time from 8 h to 16 h and 22 h, all the peaks of as-prepared powders exhibit the characteristic diffraction lines of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase without any miscellaneous phase, which are identified as $\text{Li}_4^{(8a)}[\text{Li}_{1/3}\text{Ti}_{5/3}]^{(16d)}\text{O}_{12}^{(32c)}$ and indexed to the cubic system with space group $Fd\bar{3}m$.

Fig. 1: XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders calcined at 800 °C for different calcination times (a) 8 h, (b) 16 h, (c) 22 h

Fig. 2 presents a set of the different magnified SEM micrographs of RPR-derived $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders calcined at 800 °C for 8, 16 and 22 h, respectively. It is easily found that homogenized, uniform and smooth $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles are obtained in all situations. In the case of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder calcined at 800 °C for 8 h in Fig. 2(a-b), the particle sizes are about 1.3–3.9 μm in diameter. After heating at 800 °C for 16 and 22 h, the particles tend to become relative smaller and more dispersed. Moreover, Fig. 2(e-f) also displays that a lot of particles are nearly spherical in shape and dense in density, whereas no visible particle aggregation can be found. It is widely acknowledged that uniform micro-sized electrode-active powder with high tap density is very desirable to the practical application in lithium-ion batteries due to avoiding the side reactions at the interface between the electrolyte and the electrode caused by nano-sized particles. As a result, a high discharge capacity for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder calcined at 800 °C for 22 h is to follow on.

Fig. 2: Different magnified SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800 °C for different calcinations times (a-b) 8 h, (c-d) 16 h, (e-f) 22 h; (a, c and e) $\times 1000$, (b, d and f) $\times 2000$.

It should be pointed that particle size analysis can demonstrate the entire picture of the pattern where the particles are distributed in the bulk but SEM analysis only gives the magnification of the selected portion of the powder and represents the averaged out size of the particles. In order to understand the PSD of RPR-derived $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders, the PSD experiment is conducted and the result is shown in Fig. 3. It gives the particle size distribution in terms of percentage of total particle volume vs. particle diameter of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. As seen in Fig. 3(a-b), the distribution curves all presents one large population and two small shoulder peaks. However, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder calcined at 800 °C for 22 h has one large population and one small shoulder peak with a mean size of about 3.2 μm . Table 1 summarizes the selected particle size distribution data of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. $D_{10\%}$ denotes the maximal particle size when the volume percentage of the cumulate volume to the total volume amounts to 10%. The meaning of $D_{50\%}$ and $D_{90\%}$ can be analogical. It is noticed that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder synthesized at 800 °C for 22 h is superior to the other powders in the small and uniform-distributed particle size, and its mean particle size is only 3.215 μm .

Table 1.- Particle size distribution curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800 °C for different calcination times

Powders	$D_{10\%}$ (μm)	$D_{50\%}$ (μm)	$D_{90\%}$ (μm)
8 h	1.625	4.049	29.088
16 h	1.399	3.432	43.597
22 h	1.074	3.215	5.758

Fig. 3: Particle size distribution curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800 °C for different calcinations times (a) 8 h, (b) 16 h, (c) 22 h

In general, templates or surfactants are essential in the reaction system for preparing ultra-fine powders with homogenized particles. However, neither templates nor surfactants are used in this RPR process. This phenomenon should be related to the synthetic method and the reaction condition. During the synthesis of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ precursor, the surface area of the solid particles can be utilized efficiently while the contact between solid particle and fluid is close and uniform. Meanwhile, the heat exchange between them can be carried out easily and quickly. Therefore, the growth rates of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nuclei are likely to be identical and controllable. In the subsequent calcination process, the well-crystallized uniform micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were obtained. On the basis of the above-mentioned analysis, we tentatively deduce that the RPR process for the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders should be divided into three steps, as described in Fig. 4. Firstly, dissolved $\text{LiOH}\cdot\text{H}_2\text{O}$ can be immersed the particle gap of TiO_2 and coated on its particle surface to attain homogenized mixing of the raw materials. Next, $\text{LiOH}\cdot\text{H}_2\text{O}$ gradually loses crystal water and becomes LiOH under the heat-treatment condition. Lastly, with the calcination temperature heightening, the resultant LiOH and TiO_2 initiate chemical reactions on the solid-solid interface by losing hydroxyl and convert to $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Fig. 4: Schematic diagram of RPR process for forming micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.

The initial discharge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800°C for different calcination times are shown in Fig. 5. According to Fig. 5, the powders heated at 800°C for 8 h, 16 h and 22 h deliver the initial discharge capacity of 160.7 mAh/g, 178.8 mAh/g and 184.3 mAh/g, respectively. Meanwhile, there exists one typical flat discharge plateau located at about 1.46 V in the voltage curves for the lithium intercalation of three $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. Among them, the plateau of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder obtained at 800°C for 22 h is obviously elongated compared to the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800°C for 8 h and 16 h. The above phenomenon can be ascribed to the differences in the particle size of these powders. As was reported^{16,17,18}, the smaller grain size will result in a shorter diffusion path of Li^+ ions and effectively restrains the concentration polarization inside a porous electrode. At the same time, the small particle size means a large active area, which can dramatically lower the effective current density and reduce the electrochemical polarization^{16,18}. Consequently, the relative large particle size and presence of impurity decrease the discharge capacity of the powder synthesized at 800°C for 8 h. In contrast, RPR-derived powder calcined at 800°C for 22 h exhibits highest discharge capacity because of its more uniform and smaller particle size. In addition, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800°C for 22 h display a lower discharge plateau than that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800°C for 16 h. In the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, reduced discharge plateau will favor to achieve a high operation voltage when $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and other cathodes such as LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ and LiFePO_4 are assembled into lithium ion batteries.

Fig. 5: The initial discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained at 800°C for different calcination times (a) 8 h, (b) 16 h, (c) 22 h.

Fig. 6 shows the CV curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder prepared at 800°C for 22 h. It can be seen that there is one pair of redox peaks in the voltage range of 1.0–3.0 V, which should be attributed to the redox of $\text{Ti}^{4+}/\text{Ti}^{3+}$ couple. The well defined cathode and anode peak centered at 1.43 V and 1.75 V indicates a high crystallinity, as reflected in XRD patterns. Also, the profiles of CV curves

for the initial two cycles are almost overlapped, suggesting a stable crystal structure of zero-strain $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode¹.

In sum, RPR route processes great advantages for preparing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder with the homogenized particle. This green soft chemical synthesis method does not need any templates or surfactants. Especially, this method is suitable for producing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials in battery industry due to its simplicity and feasibility.

Fig. 6: Cyclic voltammograms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder obtained at 800°C for 22 h.

CONCLUSIONS

Rheological phase reaction derived $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders have been synthesized in this work. Well-crystallized uniform micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with narrow particle distribution range are obtained at 800°C for different calcination times. RPR-derived powder made at 800°C for 22 h yields the initial discharge capacity of as high as 184.3 mAh/g with a cut-off voltage of 1.0 V at a current rate of 30 mA/g owing to its reduced particle size. Besides, it also exhibits an excellent characteristic of cyclic voltammetry. Therefore, this RPR process demonstrates to be an effective and promising method for preparing a practical electro-active $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with uniform micro-sized particles when the large-scale production is concerned.

ACKNOWLEDGEMENT

This work was supported by the Key Science and Technology Project of Henan Province of China under the grant No. 092102210153.

REFERENCES

- Ohzuku, T.; Ueda, A.; Yamamoto, N. *J. Electrochem. Soc.* **142**, 1431, (1995).
- Zaghib, K.; Armand, M.; Gauthier, M. *J. Electrochem. Soc.* **145**, 3135, (1999).
- Zaghib, K.; Simoneau, M.; Armand, M. et al. *J. Power Sources* **81–82**, 300, (1999).
- Scharner, S.; Weppner, W.; Schmid-Beurmann, P. *J. Electrochem. Soc.* **146**, 857, (1999).
- Wang, G.X.; Bradhurst, D.H.; Dou, S.X. et al. *J. Power. Sources* **83**, 156 (1999).
- Panero, S.; Reale, P.; Ronci, F. et al. *Ionics* **6**, 461, (2000).
- Cheng, L.; Li, X.L.; Liu, H.J. et al. *J. Electrochem. Soc.* **154**, A692, (2007).
- Lu, W.; Belharouak, I.; Liu, J. et al. *J. Electrochem. Soc.* **154**, A114, (2007).
- Belharouak, I.; Sun, Y.K.; Lu, W. et al. *J. Electrochem. Soc.* **154**, A1083, (2007).
- Jiang, C.; Hosono, E.; Ichihara, M. et al. *J. Electrochem. Soc.* **155**, A553, (2008).
- Huang, J.J.; Jiang, Z.Y. *Electrochim. Acta* **53**, 7756, (2008).
- Huang, J.J.; Jiang, Z.Y. *Electrochem. Solid-State Lett.* **11**, A116, (2008).
- Tang, Y.F.; Yang, L.; Qiu, Z. et al. *Electrochem. Commun.* **10**, 1513, (2008).

- 14.- Yan, G.F.; Fang, H.S.; Zhao, H.J. et al. *J. Alloys Compd.* **470**, 544, (2009).
- 15.- Ju, S.H.; Kang, Y.C. *J. Power Sources* **189**, 185, (2009).
- 16.- Liang, H.G.; Qiu, X.P.; Chen, H.L. et al. *Electrochem. Commun.* **6**, 789, (2004).
- 17.- Cao, X.Y.; Xie, J.G.; Zhan, H. et al. *Mater. Chem. Phys.* **98**, 71, (2006).
- 18.- Cao, X.Y.; Xie, L.L.; Zhan, H. et al. *Inorg. Mater.* **44**, 886, (2008).