Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 6139–6143

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Hydrothermal synthesis of Zn-doped $Li_4Ti_5O_{12}$ with improved high rate properties for lithium ion batteries

Zhenwei Zhang[a], Liyun Cao[a,*], Jianfeng Huang[a], Sen Zhou[a], Yicheng Huang[a], Yingjun Cai[b]

[a] *Key Laboratory of Auxiliary Chemistry and Technology for Light Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, China*

[b] *National Engineering Laboratory for Cleaner Production, Chinese Academy of Sciences, Beijing 100190, China*

Received 2 November 2012; received in revised form 9 January 2013; accepted 10 January 2013
Available online 20 January 2013

Abstract

Hydrothermal method has been successfully used to synthesize a spheroidic zinc doped $Li_4Ti_5O_{12}$ ($Li_{3.95}Zn_{0.05}Ti_5O_{12}$) with large specific surface area. X-ray diffraction (XRD) and scanning electron microscope (SEM) are used to characterize the structure and morphology. The electrochemical properties are measured by the galvanostatic method and the results demonstrate that the $Li_4Ti_{3.95}Zn_{0.05}O_{12}$ has a large discharge capacity of 182.45 mAh/g at 0.1C. With the favorable transport channel caused by the doped Zn^{2+}, the $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ exhibits an enhanced high rate capacity of 122.38 mAh/g and better cyclic stability at 10C, which is promising for application in lithium ion batteries.

Keywords: Lithium titanate; Hydrothermal synthesis; Zinc dope; High rate capacity

1. Introduction

In the past few decades, lithium ion battery has attracted tremendous interests as promising power source in portable electronics and hybrid electric vehicles [1,2]. Recently, lithium titanate ($Li_4Ti_5O_{12}$) has been found to be a suitable candidate material for lithium ion battery. Spinel $Li_4Ti_5O_{12}$, as promising anode material, demonstrates many advantages compared to the conventional used graphite [3–6]. In the process of Li^+ intercalation and deintercalation, the $Li_4Ti_5O_{12}$ displays a good reversibility and structural stability and there is negligible change in the unit cell volume, which is called "zero strain" material [7–9]. The spinel lithium titanate possesses good lithium ion mobility and a long and stable voltage plateau at approximately 1.5 V versus Li^+/Li. However, the low intrinsic electronic conductivity of bulk $Li_4Ti_5O_{12}$ (merely 10^{-9} Scm^{-1}) restricts its high rate performance [2], which limits the wide application in the hybrid electric vehicles.

In recent years, much effort has been devoted to the exploration of $Li_4Ti_5O_{12}$ with various particle sizes and morphologies, hoping to enhance the discharge capacities and cycle performances at high rates. Coating with conductive materials (e.g., TiN, and Ag) [10–12] and doping with other metals (e.g., Mg^{2+},Zn^{2+}, Al^{3+}, V^{5+}) [13–15] have been researched, trying to improve the high rate electrochemical properties. In previous reports, Yuan et al. [16] reported the Zn^{2+} doped $Li_4Ti_5O_{12}$ in the form of $Li_{4-x}Ti_5O_{12}$ ($x=0$, 0.25, 0.5, 1) and Chen et al. [17] researched the $Li_4Ti_{5-x}Zn_xO_{12}$ prepared by the solid state method. Doping of zinc can increase the electronic conductivity and Li^+ ion conductivity.

The aim of the present work is to improve the electronic conductivity and high rate behaviors. In this paper, we report a hydrothermal synthesis of zinc doped $Li_4Ti_5O_{12}$ in the form of $Li_{3.95}Zn_{0.05}Ti_5O_{12}$. The hydrothermal synthesis is an even simpler and lower temperature method, compared with sol–gel and solid state methods. The spheroidic $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ measured by N_2 adsorption/desorption BET isotherms has demonstrated a great specific surface area and a good cycling performance at the high rate of 10C.

---

*Corresponding author. Tel./fax: +86 29 8616 8802.
E-mail address: skdzzw@163.com (L. Cao).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.01.032

2. Experiments

2.1. Sample preparation

All chemicals were used as received. The tetrabutyl titanate was mixed in ethylalcohol with stirring to form solution A. The starting reagents of $LiOH \cdot H_2O$ and $Zn(CH_3COO)_2$ weighed with the stoichiometric ratio in order to get the $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ were dissolved into 20 mL deionized water with stirring, forming an aqueous solution B and then dropwise added into the solution A with strong stirring for 1 h. After that, the mixture was transferred into stainless-steel autoclave at 180 °C for 24 h. The obtained precursor was calcinated at 600 °C for 10 h to get the final products. The crystal structure of the powders was characterized by X-ray diffraction (XRD, Rigaku D/max-2000) and the morphology was observed by scanning electron microscopy (SEM, S4800, Japan).

2.2. Electrode preparation and electrochemical characterization

Electrochemical measurements were performed using 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., $[O_2] < 1$ppm, $[H_2O] < 1$ppm). To fabricate the electrodes, a mixture of the synthesized $Li_{3.95}Zn_{0.05}Ti_5O_{12}$, acetylene black, and polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10 was pasted on pure copper foil. Pure lithium foil was used as the counter electrode. The electrolyte consisted of a solution of 1 M LiPF6 in ethylene carbonate and dimethyl carbonate (EC+DMC, 1:1 in volume). The charge/discharge tests were carried out using a LAND Celltest 2001 A (Wuhan, China) system between cutoff voltage of 2.5 and 1.0 V. The cyclic voltammetry (CV) was measured on a CHI660D electrochemical workstation.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ calcinated at 600 °C, which is much lower than that of 800 °C synthesized by sol–gel and solid state methods [6]. The diffraction peak of $Li_4Ti_5O_{12}$ named sample 1 in Fig. 1(a) coincides with the cubic spinel structure (JCPDS No. 49-0207) without obvious impurity. Correspondingly, the Zn doped $Li_4Ti_5O_{12}$ was named sample 2 in Fig. 1(a), which was very close to the pure $Li_4Ti_5O_{12}$ in XRD patterns. And there is an obvious increase of crystallinity after doped with Zn^{2+}. The XRD pattern in the Fig. 1(b) shows that the peaks of the Zn doped $Li_4Ti_5O_{12}$ shifted to smaller angels and indicated an enlarged lattice constant of the $Li_4Ti_5O_{12}$ according to the Bragg equation. This may be caused by two reasons: (1) the radius of Zn^{2+} (74 pm) is larger than Li^+ (68–70 pm) [16]. The doping of Zn will cause the lattice constant of the $Li_4Ti_5O_{12}$ increased; (2) meanwhile, the transition of a certain amount of Ti^{4+} to Ti^{3+} will cause the increase of the lattice constant from 60.5 pm to 67 pm, which are the main factors to explain the enlarged parameters and indicate that the Zn^{2+} has successfully entered the lattice of spinel $Li_4Ti_5O_{12}$.

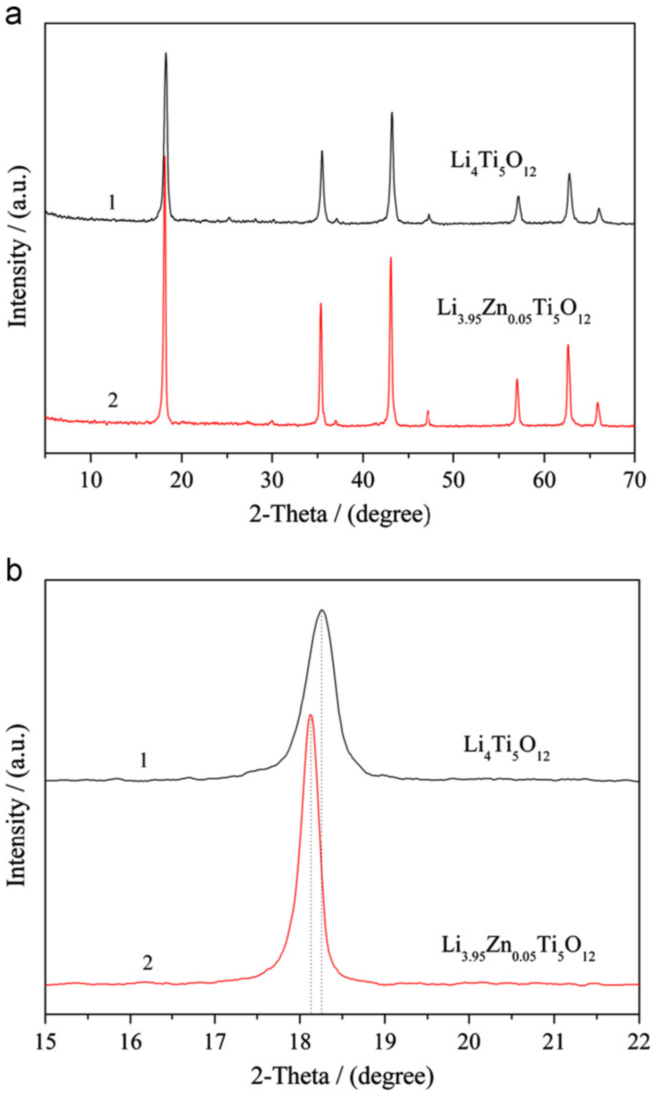
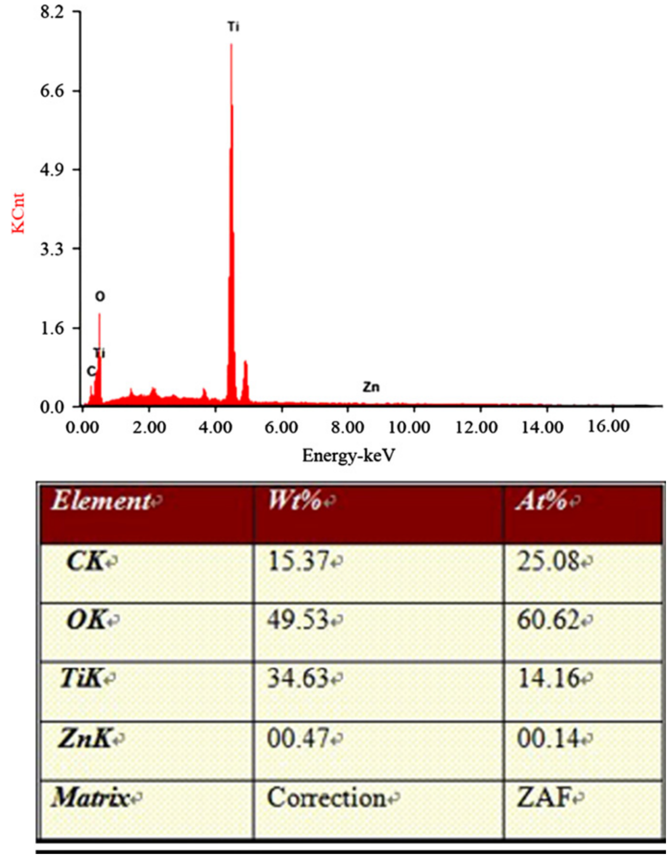


Fig. 1. (a) XRD patterns and (b) magnified (400) peaks of the $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$.

The Fig. 2 was the energy dispersive spectrum analysis (EDS) of the Zn doped $Li_4Ti_5O_{12}$. From the table of the element content, we can see that the molar ratio of Zn/Ti was 1/100 approximately. Meanwhile, with the doping of Zn^{2+} there must be a transition from Ti^{4+} to Ti^{3+} for the charge balance, which means that the doped Zn^{2+} can only replace the Li^+, forming the final $Li_{3.95}Zn_{0.05}Ti_5O_{12}$.

The SEM images of the $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ powders are shown in Fig. 3. The images in Fig. 3(b) and (d) show that the spinel $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ powders are assembled by many nanosheets. But the sheets of $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ with the thickness of several nanometers in Fig. 3(d) are thinner than that of dozens of nanometers of $Li_4Ti_5O_{12}$ in Fig. 3(b). Meanwhile, the loose and porous structure contributes to increase the specific



Element	Wt%	At%
CK	15.37	25.08
OK	49.53	60.62
TiK	34.63	14.16
ZnK	00.47	00.14
Matrix	Correction	ZAF

Fig. 2. The energy dispersive spectrum analysis of the Zn doped $Li_4Ti_5O_{12}$.

surface area of the products, which can provide more transport channels for lithium to insert into the electrode material and delay the capacity loss associated with the concentration polarization to higher current density [18]. The synthesis of Zn-doped $Li_4Ti_5O_{12}$ using hydrothermal method needs much lower temperature than other approaches like sol–gel and solid state methods [6–8],which need a high temperature over 800 °C. The sheets on the surface of the Zn-doped $Li_4Ti_5O_{12}$ may be melt into thick sheets and even bulks when calcinated at high temperatures by sol–gel or solid state methods, which will be disadvantageous for Li^+ to insert into the spinel $Li_4Ti_5O_{12}$ and decrease the discharge capacity.

Fig. 4 is the first-cycle charge/discharge curves of the $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ at 0.1C and 10C, respectively. Compared with 172 mAh/g of the $Li_4Ti_5O_{12}$, the first discharge capacity of $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ is 182.45 mAh/g at 0.1C. The capacity of $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ at 10C is 122.38 mAh/g, which is much larger than that of 90.6 mAh/g for the $Li_4Ti_5O_{12}$. It demonstrates that the Zn doped lithium titanate has a better high rate discharge capacity. This may be caused by the exaggerated lattice parameters, which is easier for Li to insert and diffuse in the bulk $Li_4Ti_5O_{12}$. The cycling performances of $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ at different rates are shown in Fig. 5. It is obvious that the Zn doped lithium titanate demonstrates larger discharge capacity and better cyclic stability at various rates, especially at high rate. For the doped $Li_{3.95}Zn_{0.05}Ti_5O_{12}$, the retention of the discharge capacity is 117.4 mAh/g after 20 cycles, which

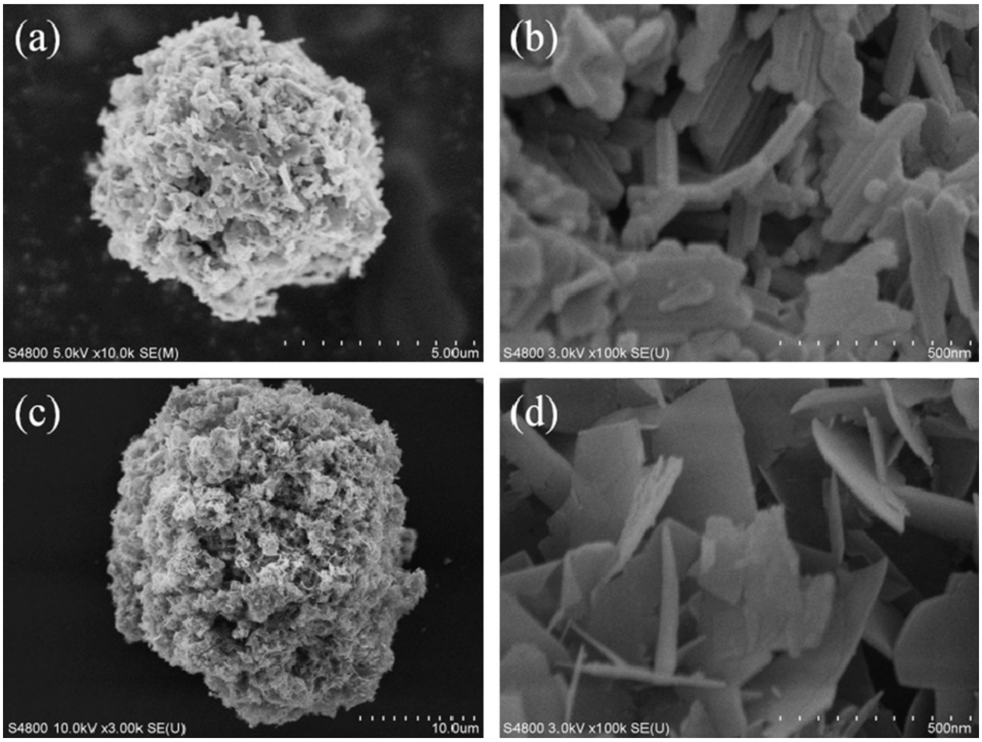


Fig. 3. SEM images of the $Li_4Ti_5O_{12}$ (a: × 10,000, b: × 100,000) and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ powders (c: × 3000, d: × 100,000).

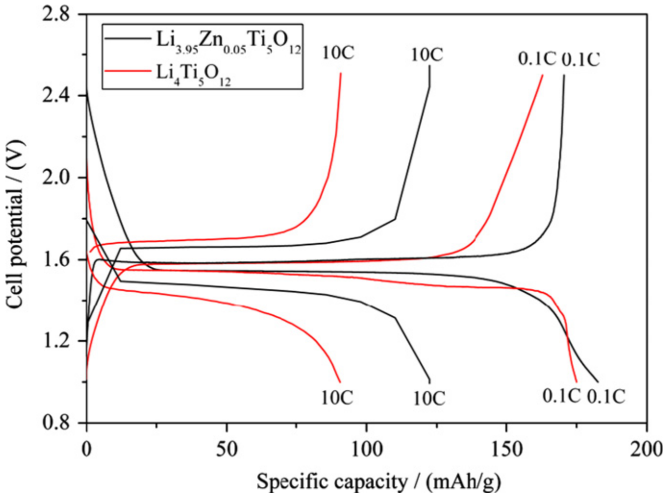


Fig. 4. Initial charge-discharge curves of pure $Li_4Ti_5O_{12}$ (0.1C and 10C) and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ (0.1C and 10C).

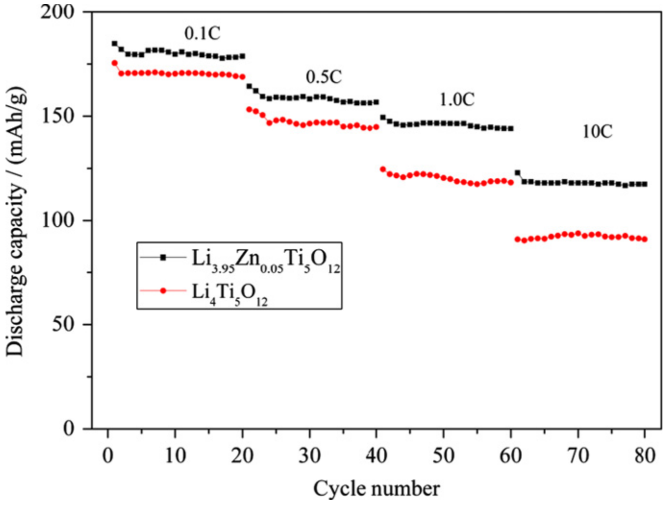


Fig. 5. Cycle performances of $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ at different rates.

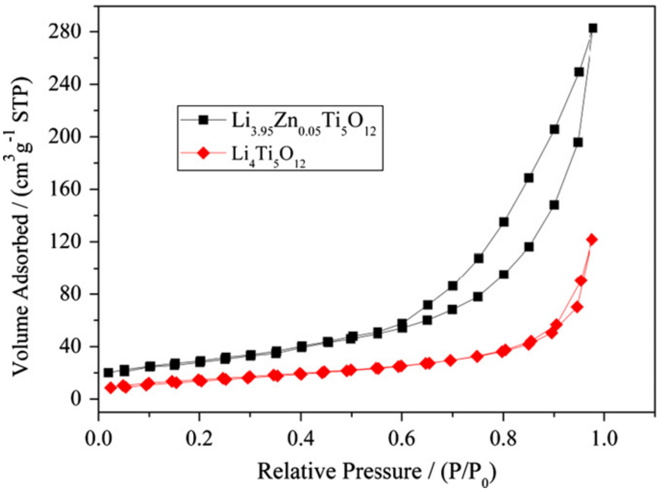


Fig. 6. N_2 adsorption/desorption BET isotherms of $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ and $Li_4Ti_5O_{12}$.

is approximately 30 mAh/g higher than that of the pure $Li_4Ti_5O_{12}$. It could be attributed to the large specific surface area, which increases the Li storage on the surface and adds the contact with the electrolyte, decreasing the concentration polarization to higher rates [19]. Moreover, the doping of zinc increases the lattice constant of $Li_4Ti_5O_{12}$, in which the Li^+ can transfer and diffuse faster. It also enhances the ion conductivity, which is beneficial to the high rate performance.

Fig. 6 shows the N_2 adsorption/desorption isotherms of the $Li_4Ti_5O_{12}$ and $Li_{3.95}Zn_{0.05}Ti_5O_{12}$. Both the isotherms reveal type VI with a representative H_1-type hysteresis loop, which are the characteristic of mesoporous materials [20,21]. The Brunauer–Emmett–Teller (BET) specific surface area of the $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ is 128.6 m^2g^{-1}, which exceeds a great many than that of pure $Li_4Ti_5O_{12}$ (64.3 m^2g^{-1}). Accordingly, the doping of zinc in $Li_4Ti_5O_{12}$ has increased the specific surface area obviously, which can provide more locations and channels for lithium to insert into the electrode material, and improved the high rates behaviors, indicating a promising wide application in the HEVs.

4. Conclusions

In summary, $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ powders have been successfully synthesized via a simple hydrothermal method. The results demonstrate that the $Li_{3.95}Zn_{0.05}Ti_5O_{12}$ with good crystallinity has a higher discharge capacity and specific surface area, which also exhibits better cyclic performance than the pure $Li_4Ti_5O_{12}$ prepared by the similar process. The specific capacities at 0.1C and 10C are 182.45 mAh/g and 122.38 mAh/g, respectively, which are much larger than the $Li_4Ti_5O_{12}$. Zn-doping is beneficial to the intercalation and deintercalation of Li^+, implying a promising use in the lithium ion batteries.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51072108, 51172134), Natural Science Foundation of Shaanxi Province of China (2010JM6001, 2010JM6017), International Science and Technology Cooperation Project of Shaanxi Province (2011KW-11) and the Graduate Innovation Foundation of Shaanxi University of Science and Technology.

References

[1] Y.F. Tang, L. Yang, S.H. Fang, Z. Qiu, $Li_4Ti_5O_{12}$ hollow microspheres assembled by nanosheets as an anode material for high-rate lithium ion batteries, Electrochimica Acta 54 (2009) 6244–6249.

[2] J.Z. Chen, L. Yang, S.H. Fang, S. Hirano, K. Tachibana, Synthesis of hierarchical mesoporous nest-like $Li_4Ti_5O_{12}$ for high-rate lithium ion batteries, Journal of Power Sources 200 (2012) 59–66.

[3] K. Ariyoshi, R. Yamato, T. Ohzuku, Zero-strain insertion mechanism of $Li[Li_{1/3}Ti_{5/3}]O_4$ for advanced lithium ion (shuttlecock) batteries, Electrochimica Acta 51 (2005) 1125–1129.

[4] K. Zaghib, M. Simoneau, M. Armand, M. Gauthier, Electrochemical study of $Li_4Ti_5O_{12}$ as negative electrode for Li-ion polymer rechargeable batteries, Journal of Power Source 81–82 (1999) 300–305.

[5] N.Q. Zhang, Z.M. Liu, T.Y. Yang, C.L. Liao, Z.J. Wang, K.N. Sun, Facile preparation of nanocrystalline $Li_4Ti_5O_{12}$ and its high electrochemical performance as anode material for lithium ion batteries, Electrochemistry Communications 13 (2011) 654–656.

[6] Z.W. Zhang, L.Y. Cao, J.F. Huang, J.P. Wu, D.Q. Wang, Y.J. Cai, Hydrothermal synthesis of $Li_4Ti_5O_{12}$ microsphere with high capacity as anode material for lithium ion batteries. Ceramics International, http://dx.doi.org/10.1016/j.ceramint.2012.09.036, in press.

[7] G.R. Hu, X.L. Zhang, Z.D. Peng, Preparation and electrochemical performance of tantalum-doped lithium titanate as anode material for lithium-ion battery, Transactions of the Nonferrous Metals Society of China 21 (2011) 2248–2253.

[8] J. Barker, M.Y. Saidi, J.L. Swoyer, Electrochemical insertion properties of lithium vanadium titanate, $LiVTiO_4$, Solid State Ionics 167 (2004) 413–418.

[9] L.J. Wang, X.X. Li, Z.Y. Tang, X.H. Zhang, Research on $Li_3V_2(PO_4)_3/Li_4Ti_5O_{12}/C$ composite cathode material for lithium ion batteries, Electrochemistry Communications 22 (2012) 73.

[10] M. Kundu, S. Mahanty, R.N. Basu, $Li_4Ti_5O_{12}/Li_3SbO_4/C$ composite anode for high rate lithium ion batteries, Materials Letters 65 (2011) 3083–3085.

[11] H.K. Kim, S.M. Bak, K.B. Kim, $Li_4Ti_5O_{12}$/reduced graphite oxide nano-hybrid material for high rate lithium-ion batteries, Electrochemistry Communications 12 (2010) 1768–1771.

[12] H. Kitaura, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, Fabrication of electrode–electrolyte interfaces in all-solid-state rechargeable lithium ion batteries by using a supercooled liquid state of the glassy electrolytes, Journal of Materials Chemistry 21 (2011) 118–124.

[13] L. Zhao, Y.S. Hu, H. Li, Z.X. Wang, L.Q. Chen, Porous $Li_4Ti_5O_{12}$ coated with N-doped carbon from ionic liquids for lithium-ion batteries, Advanced Materials 23 (2011) 1385–1388.

[14] T. Yuan, X. Yu, R. Cai, Y.K. Zhou, Z.P. Shao, Synthesis of pristine and carbon-coated $Li_4Ti_5O_{12}$ and their low-temperature electrochemical performance, Journal of Power Source 195 (2010) 4997–5004.

[15] C.H. Chen, J.T. Vaughey, A.N. Jansen, D.W. Dees, A.J. Kahaian, T. Goacher, et al., Journal of the Electrochemical Society 148 (2001) A102–A104.

[16] B. Zhang, H. Du, B. Li, F. Kang, Structure and electrochemical properties of Zn-Doped $Li_4Ti_5O_{12}$ as anode material in Li-ion battery, Electrochemical and Solid-State Letters 13 (2010) A36–A38.

[17] T.F. Yi, H.P. Liu, Y.R. Zhu, L.J. Jiang, Y. Xie, R.S. Zhu, Improving the high rate performance of $Li_4Ti_5O_{12}$ through divalent zinc substitution, Journal of Power Source 215 (2012) 258–265.

[18] W. Xia, W.Q. Meng, R.B. Yu, X.R. Xing, D. Wang, Y.F. Chen, M. Takano, An effective route for porous ferrihydrite preparation from layered double hydroxide precursors, Chemistry Letters 35 (2006) 656.

[19] X.Y. Lai, J.E. Halpert, D. Wang, Recent advances in micro-/nano-structured hollow spheres for energy applications: from simple to complex systems, Energy Environment Science 5 (2012) 5604.

[20] Z.W. Zhang, L.Y. Cao, J.F. Huang, D.Q. Wang, Y. Meng, Y.J. Cai, Temperature effect on spinel $Li_4Ti_5O_{12}$ as anode materials for lithium ion batteries, Electrochimica Acta 88 (2013) 443–446.

[21] M.D. Wei, K.W. Wei, M. Ichihara, H.S. Zhou, High rate performances of hydrogen titanate nanowires electrodes, Electrochemistry Communications 10 (2008) 1164–1167.