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Short communication

Synthesis of lithium insertion material $Li_4Ti_5O_{12}$ from rutile TiO_2 via surface activation

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ABSTRACT

The synthesis of spinel-type lithium titanate, $Li_4Ti_5O_{12}$, a promising anode material of secondary lithium-ion battery, from "inert" rutile TiO_2, is investigated. On the purpose of increasing the reactivity of rutile TiO_2, it is treated by concentrated HNO_3. By applying such activated rutile TiO_2 as the titanium source in combination with the cellulose-assisted combustion synthesis, phase-pure $Li_4Ti_5O_{12}$ is successfully synthesized at 800 °C, at least 150 °C lower than that based on solid-state reaction. The resulted oxide shows a reversible discharge capacity of ~175 mAh g^{-1} at 1 C rate, near the theoretical value. The resulted oxide also shows promising high rate performance with a discharge capacity of ~100 mAh g^{-1} at 10 C rate and high cycling stability.

1. Introduction

Graphite/carbon-related materials have been the most applied anodes in small size secondary lithium-ion batteries as power source of personal electronics, such as laptops, camcorders and digital cameras [1–3]. For larger size applications like electric vehicles and dispersed energy storage systems where high rate charge/discharge is frequently required, the carbon anode may suffer from serious safety problems. Due to the low lithium intercalating voltage of approximately 100 mV (vs. Li/Li^+), highly reactive metallic lithium forms easily under fast charge rate [4], which may deposit on the surface of electrode particles and has the high risk to react with the electrolyte or highly charged cathodes to result in combustion or explosion.

Recently lithium insertion oxides like $Li_4Ti_5O_{12}$ have acquired considerable attention as alternative anode to carbon/graphite in rechargeable lithium-ion batteries [5–9]. 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 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 ($Li_7Ti_5O_{12}$) [10], both structures have the same cubic lattice symmetry and a cell volume difference less than 0.1% [11]. Thereby, $Li_4Ti_5O_{12}$ is also named as a zero-strain lithium insertion material [11]. This is a beneficial feature ensuring a long cycling life. Similar to $LiFePO_4$ cathode, the two-phase mechanism for the lithium intercalation/de-intercalation results in an extremely flat discharge platform at around 1.55 V for $Li_4Ti_5O_{12}$. Such a medium discharge voltage is well above the formation potential of metallic lithium; as a result, the safety problem associated with carbon-based anode due to metallic formation during fast charge is effectively avoided by adopting the $Li_4Ti_5O_{12}$ anode. Although its medium level of discharge voltage discourages the application as a positive electrode, it can be coupled with a high-voltage electrode such as 4 V $LiMn_2O_4$ and $LiCoO_2$ or 5 V $LiCoPO_4$ to provide a cell with an operating voltage of 2.5–3.5 V [12].

One practical problem associated with coarse $Li_4Ti_5O_{12}$ anode is its poor rate performance because of its negligible electronic conductivity. Surface coating with conductive material such as amorphous carbon and reducing the grain size are the effective ways to minimize the electrode polarization resistance at high charge/discharge rate [13–17]. The decrease of grain size would not only lessen the diffusion distance for electron and lithium ion but also increase the surface area for interfacial reaction; consequently the rate performance can be effectively improved [15–17]. Consequently, the preparation of ultrafine $Li_4Ti_5O_{12}$ powder becomes one of the key steps towards the commercialization of $Li_4Ti_5O_{12}$

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anode in rechargeable lithium-ion batteries. Although nano-sized $Li_4Ti_5O_{12}$ has been successfully prepared in the literature using advanced techniques such as sol–gel process [18–21], up to now, the most attractive process for potential industrial application is still the solid-state reaction by applying cheap and abundant TiO_2 as the titanium source for lower costs.

It is well known that the rutile TiO_2 is the most suitable raw material for synthesis of $Li_4Ti_5O_{12}$ from the aspect of material availability, although the anatase TiO_2 can accommodate much more lithium in its crystal lattice compared to rutile TiO_2 [22–24]. In fact most of these studies reported that bulk rutile hardly inserts any lithium at room temperature. Consequently, very high calcination temperature is needed to facilitate the solid-state reaction between rutile TiO_2 and Li_2CO_3/LiOH to form $Li_4Ti_5O_{12}$ [25,26]. The high-temperature calcination, however, results in not only the difficulty in precise control of the cation stoichiometry, but also the serious sintering of the product, consequently, poor rate performance is frequently observed for the as-prepared sample.

Previously we successfully prepared high rate performance $Li_4Ti_5O_{12}$ oxide at reduced temperature via a cellulose-assisted combustion technique adopting anatase TiO_2 as the titanium source [27]. In this study, we reported the synthesis of $Li_4Ti_5O_{12}$ from more commercially available but more passive rutile TiO_2 at reduced temperature. A treatment of rutile TiO_2 by concentrated nitric acid significantly improved the reaction kinetics, consequently, a calcination temperature as low as 800 °C is sufficient to obtain a phase-pure $Li_4Ti_5O_{12}$ by adopting the cellulose-assisted combustion technique. The resulted anode material shows high rate performance and high cycling stability.

2. Experimental

2.1. Powder synthesis

The $Li_4Ti_5O_{12}$ oxides were synthesized by a cellulose-assisted combustion process adopting rutile TiO_2 as titanium source with excess 2 wt.% Li to compensate for the loss of Li followed by high-temperature calcination [27]. Cotton fiber, pre-activated by HNO_3, was applied as the cellulose. Commercial TiO_2 rutile powder with a surface area of 33.2 $m^2\,g^{-1}$, purchased from Hangzhou WAN JING New Material Co., Ltd. (China), is adopted as the titanium source. It is either applied directly as received or pretreated by concentrated HNO_3 (67%) at room temperature for 10 h. For comparison, $Li_4Ti_5O_{12}$ oxide was also synthesized by solid-state reaction adopting Li_2CO_3 and rutile TiO_2 as the raw materials.

2.2. Electrode fabrication

The electrochemical performance of $Li_4Ti_5O_{12}$ powders was carried out with coin-shape cells using metallic lithium film as the counter and reference electrode at room temperature (~30 °C). The cells are based on the configuration of Li metal (−) |electrolyte| $Li_4Ti_5O_{12}$ (+) with a liquid electrolyte (1 M solution of $LiPF_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1, v/v)). Microporous polypropylene film (Celgard 2400) was used as the separator. 85 wt.% $Li_4Ti_5O_{12}$ with 8 wt.% conductive Super P (NCM HERSBIT Chemical Co., Ltd., China) and 7 wt.% polyvinylidene fluoride (PVDF) binder homogeneously mixed in N-methyl pyrrolidinone (NMP) were prepared into viscous slurries for efficient deposition. The slurries were deposited on current collectors of copper foil (10 μm) by blade, which was pretreated by etching with 1 M nitric acid solutions followed by rinsing with water and then acetone. The electrode was then dried under vacuum at 100 °C for 12 h before electrochemical evaluation. Cell assembly was conducted in a glove box filled with pure argon.

2.3. Characterization

The crystal structures of the synthesized powders were examined by X-ray diffraction (XRD) using a Bruker D8 advance diffractometer with filtered Cu Kα radiation. The experimental diffraction patterns were collected at room temperature by step scanning in the range of $10^\circ \le 2\theta \le 80^\circ$. The specific surface area of the samples was characterized by N_2 adsorption at the temperature of liquid nitrogen using a BELSORP II instrument. Prior to analysis, the samples were treated at 100 °C for 3–5 h in vacuum to remove the surface adsorbed species.

The charge–discharge characteristics of the cells were recorded over the potential range between 1.0 and 3.0 V using a NEWARE BTS-5V50 mA computer-controlled battery test station at different rates of 1–40 C at 30 °C.

3. Results and discussion

3.1. Synthesis

The synthesis of $Li_4Ti_5O_{12}$ by traditional solid-state reaction applying rutile TiO_2 as reactant was first investigated. Stoichiometric amounts of Li_2CO_3 and rutile TiO_2 (as received) were well mixed by high energy ball milling (Fritsch, Pulveriette 6) at a rotation speed of 400 rpm for 2 h, the mixture was then submitted for calcination at various temperatures in air for a selected time (5–24 h). Fig. 1a shows the corresponding room temperature X-ray diffraction patterns of the powders calcined at 800–950 °C. After the calcination at 800 °C for 5 h, there was still considerable amount of rutile TiO_2 detected in the product by XRD. With the increase of calcination temperature and dwell time, the relative intensity of the spinel phase increased. However, minor amount of rutile TiO_2 was still detected even after the calcination at 950 °C for 24 h. In the literature, time-consuming intermitting grinding is needed to promote the solid-state reaction by breaking up the particle size and making intimating contact of the reactants to obtain pure phase $Li_4Ti_5O_{12}$ [28].

In our previous paper, we have demonstrated that the cellulose-assisted method can result in the reduced synthesis temperature of phase-pure $Li_4Ti_5O_{12}$ when adopting anatase TiO_2 as the titanium source. The cellulose can suppress the grain growth of anatase TiO_2 during the calcination on the one hand; the combustion process created instant high temperature to promote the phase reaction on the other hand. Consequently, nanocrystalline phase-pure $Li_4Ti_5O_{12}$ was obtained at a low calcination temperature of 750 °C [27]. The same technique was also adopted in this study on the purpose to reduce the synthesis temperature of $Li_4Ti_5O_{12}$ from rutile TiO_2. The sequence of materials addition was found to have significant effect on the phase formation with the optimal sequence of first impregnating the cellulose with a mixed solution of $LiNO_3$ and glycine, then with a suspension of TiO_2 and HNO_3 [27]. The same sequence was adopted for the synthesis of $Li_4Ti_5O_{12}$ from rutile TiO_2. Flame combustion was suddenly happened when the dried precursors were quickly heated up by an electrical oven at 250 °C, the combustion last for tens of seconds and left a primary product which took the morphology of the initial cellulose fiber. It was then pulverized and submitted for phase examination. Fig. 1b shows the XRD patterns of the primary product and that by further calcination at various temperatures for 5 h in air. After the calcination at 800 °C for 5 h, the rutile TiO_2 phase was still significant in the product based on the XRD results, although the relative intensity of spinel to rutile is several times that of the product calcined at the same temperature from the solid-state reaction. When the solid precursor was calcined at 850 °C for 5 h, the main spinel phase was formed and the diffraction peaks of rutile TiO_2

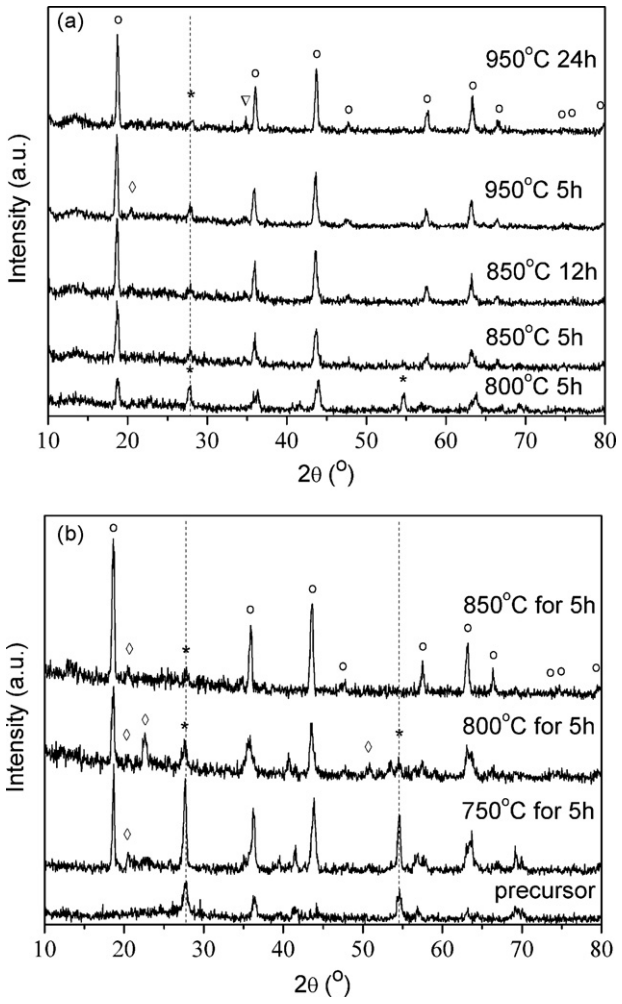

Fig. 1. XRD patterns of $Li_4Ti_5O_{12}$: (a) the pristine rutile TiO_2 as reactant prepared by solid-state reaction and (b) pristine rutile TiO_2 as reactant prepared by cellulose-assisted combustion and further calcined at different temperatures for 5 h. (o) Spinel $Li_4Ti_5O_{12}$, (*) rutile TiO_2, (◊) Li_2TiO_3, and (▽) Ti_2O_3.

phase were in very weak intensity. It suggests that a calcination temperature around 850 °C is needed by applying the cellulose-assisted combustion technique when adopting rutile TiO_2 as the reactant.

To reduce the synthesis temperature of $Li_4Ti_5O_{12}$ via the cellulose-assisted combustion technique, the rutile TiO_2 was activated by HNO_3 treatment at room temperature for 12 h. It was observed that the combustion behavior of the solid precursor is similar whether the rutile TiO_2 was acid treated or not. Fig. 2 shows the XRD patterns of the primary product prepared from the cellulose-assisted combustion technique by adopting the acid treated rutile TiO_2 as the titanium source and the samples after the further calcination of primary product at various temperatures for 5 h. The spinel phase, although in very weak intensity, started to appear in the primary product after the auto-combustion. After the further calcination at 750 °C for 5 h, the oxide displayed the main spinel phase together with weak rutile TiO_2 phase and Li_2TiO_3 phase. When the calcination temperature elevated to 800 °C, the TiO_2 phase was totally disappeared and a phase-pure spinel oxide was observed. It suggests that the $Li_4Ti_5O_{12}$ phase was successfully formed at around 800 °C. Compared to the results in Fig. 1, the synthesis temperature of a phase-pure $Li_4Ti_5O_{12}$ was effectively lowered.

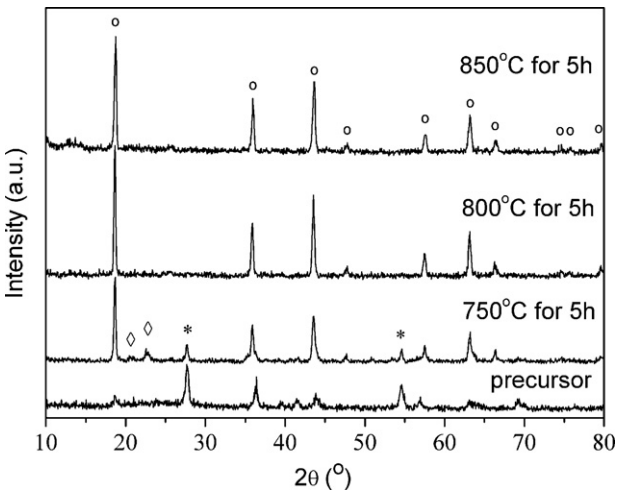

Fig. 2. X-ray diffraction patterns of the primary product and the samples after the further calcination at various temperatures for 5 h, prepared from the cellulose-assisted combustion technique by adopting the acid treated rutile TiO_2 as the titanium source. (o) Spinel $Li_4Ti_5O_{12}$, (*) rutile TiO_2, and (◊) Li_2TiO_3.

3.2. Electrochemical performance

The electrochemical performance of the various $Li_4Ti_5O_{12}$ oxides was then investigated at room temperature. Shown in Fig. 3 are the second discharge curves at various discharge rates of the $Li_4Ti_5O_{12}$ anodes synthesized from rutile TiO_2 by solid-state reaction after the calcination at 950 °C for 24 h (Fig. 3a), from the cellulose-assisted combustion technique applying rutile TiO_2 as titanium source after the calcination at 850 °C for 5 h (Fig. 3b), and from the cellulose-assisted combustion synthesis applying the acid treated rutile TiO_2 as the titanium source and after the calcination at 800 °C for 5 h (Fig. 3c). For the sample from the solid-state reaction, a discharge capacity of only 86 mAh g^{-1} was obtained at 1 C rate, much lower than the theoretic value of ~175 mAh g^{-1}. Furthermore, the capacity in the flat plateau was only about 35 mAh g^{-1}. With the increase of discharge rate the capacity decreased sharply, it retained only 40 mAh g^{-1} at 5 C rate. These results are much worse than that prepared by a sol–gel process, or by the cellulose-assisted combustion process by adopting anatase TiO_2 as the titanium source [19,27]. Two possible explanations for such poor performance are as follows. First there was still some minor impurity phase presented in the sample prepared from the solid-state reaction after the calcination at 950 °C for 24 h, suggesting the actual composition of the anode may deviate from the nominal composition of $Li_4Ti_5O_{12}$; second such high calcination temperature (950 °C) and prolonged calcination time led to the serious grain growth and the decrease of surface area. Kavan et al. studied the surface area and trace impurities on the electrochemical properties of $Li_4Ti_5O_{12}$ systematically [29]. Both resulted in a large polarization resistance for the lithium insertion into and extraction from the lattice. For the sample prepared from the cellulose-assisted combustion technique adopting rutile TiO_2 as reactant, much better discharge performance was obtained. A pretty flat discharge platform was observed at around 1.55 V at 1 C rate, in well agreement with the two-phase mechanism for the charge/discharge of $Li_4Ti_5O_{12}$ anode. The reversible discharge capacity of 117, 104, 87, 62, 44 and 32 mAh g^{-1} was observed at a discharge rate of 1, 2, 5, 10, 20 and 40 C, respectively. When adopting acid treated rutile as the raw material of titanium, a discharge capacity of 175, 140, 115, 92, 71, and 56 mAh g^{-1} was obtained at 1, 2, 5, 10, 20, and 40 C discharge rates, respectively. It suggests that the acid treatment greatly improved the rate performance of $Li_4Ti_5O_{12}$ as compared to that adopting rutile TiO_2 by the same cellulose-assisted combus-

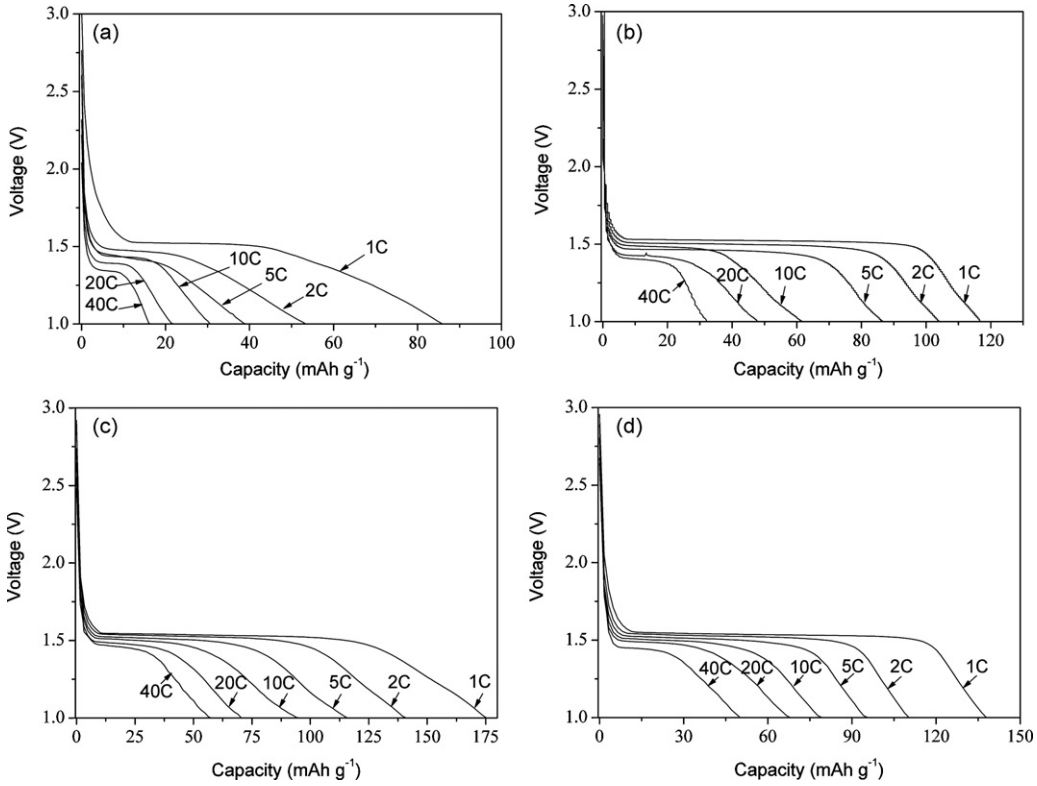

Fig. 3. The discharge profiles of the $Li_4Ti_5O_{12}$ oxides from 1 to 3 V at different rates, prepared by (a) solid-state reaction calcined at 950 °C for 24 h with rutile TiO_2 as reactant; (b) cellulose-assisted combustion process and further calcined at 850 °C for 5 h with rutile TiO_2 as reactant; (c and d) cellulose-assisted combustion process and further calcined at 800 and 850 °C for 5 h, respectively, with HNO_3-treated rutile TiO_2 as reactant.

tion synthesis. The performance of $Li_4Ti_5O_{12}$ is closely related with the grain size of the oxide. The surface area of $Li_4Ti_5O_{12}$ with rutile TiO_2 and acid treated rutile TiO_2 as the titanium source during the combustion synthesis is 1.09 $m^2\,g^{-1}$ (850 °C) and 2.78 $m^2\,g^{-1}$ (800 °C calcined), respectively. The improved $Li_4Ti_5O_{12}$ anode performance from the acid treated rutile TiO_2 raw material is likely associated with the increased surface area and accessible active area due to the reduced calcination temperature for obtaining pure phase $Li_4Ti_5O_{12}$ [29]. To support such assumption, the rate performance of $Li_4Ti_5O_{12}$ prepared by the cellulose-assisted combustion synthesis applying the acid treated rutile TiO_2 as titanium source and calcined at 850 °C was also conducted. As shown in Fig. 3d, a reversible discharge capacity of 137, 108, 94, 77, 63, and 49 mAh g^{-1} was observed at 1, 2, 5, 10, 20 and 40 C, much lower than that calcined at 800 °C, and only slightly improved as compared to that calcined at the same temperature with rutile TiO_2 as the raw material during the combustion synthesis. The surface area of the 850 °C calcined sample is 1.32 $m^2\,g^{-1}$, similar to that prepared from rutile TiO_2 and calcined at the same temperature (1.09 $m^2\,g^{-1}$).

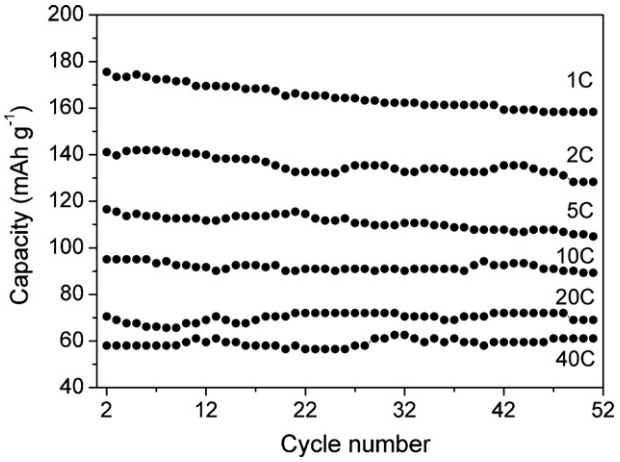

Fig. 4. Cycling performance at different discharge rates of the $Li_4Ti_5O_{12}$ prepared by the cellulose-assisted combustion process and further calcined at 800 °C for 5 h with acid treated rutile TiO_2 as reactant with the cut-off voltage from 1 to 3 V.

The cycling stability of the 800 °C calcined $Li_4Ti_5O_{12}$ prepared from cellulose-assisted combustion synthesis adopting acid treated TiO_2 is shown in Fig. 4. High cycling stability was observed. At 1, 2, 5, 10, 20 and 40 C rates, the decay in discharge capacity after the 51 cycles was only 9.7, 9.1, 9.9, 6.1, 2.1 and 2.6%, respectively. It suggests the high reversibility and stability of the Li-intercalation and de-intercalation through the as-prepared $Li_4Ti_5O_{12}$. Above results then highly promise the application of rutile TiO_2 in the synthesis of high performance $Li_4Ti_5O_{12}$ as lithium battery anode by simple acid treatment in combination with cellulose-assisted combustion synthesis.

4. Conclusions

With nitric acid treated rutile TiO_2 as the titanium source, phase-pure $Li_4Ti_5O_{12}$ anode powders were synthesized by a cellulose-assisted combustion process at a reduced temperature of 800 °C for 5 h calcination, more than 150 °C lower than that synthesized by standard solid-state reaction. Besides the contribution from the cellulose-assisted combustion synthesis, the decrease in synthesis temperature was also benefited from the nitric acid treatment of the rutile TiO_2, which improved the kinetics of rutile TiO_2, and then facilitated the phase reaction to form $Li_4Ti_5O_{12}$. The as-prepared $Li_4Ti_5O_{12}$ sample delivered a capacity of ~175 mAh g^{-1} at 1 C rate which near the theoretical value, and even reached ~100 mAh g^{-1} at a high discharge rate of 10 C with high cycling stability. Such

good electrochemical performance for as-synthesized $Li_4Ti_5O_{12}$ is likely associated with the increased surface area due to the reduced calcination temperature.

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References

[1] J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367.
[2] K. Nagajima, Y. Nishi, in: T. Osaka, M. Datta (Eds.), Energy Storage Systems for Electronics, Gordon and Breach Science Publisher, Singapore, 2000, p. 109, (Chapter 5).
[3] K. Sawai, Y. Iwakoshi, T. Ohzuku, Solid State Ionics 69 (1994) 273–283.
[4] D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller, Solid State Ionics 148 (2002) 405–416.
[5] R. Dominko, E. Baudrin, P. Umek, D. Arčon, M. Gaberščeka, J. Jamnik, Electrochem. Commun. 8 (2006) 673–677.
[6] J. Shu, Electrochim. Acta 10 (2009) 2869–2876.
[7] P.P. Prosini, R. Mancini, L. Petrucci, V. Contini, P. Villano, Solid State Ionics 144 (2001) 185–192.
[8] K Zaghib, M. Simoneau, M. Armand, M. Gauthier, J. Power Sources 81–82 (1999) 300–305.
[9] E.M. Sorensen, S.J. Barry, H.K. Jung, J.R. Rondinelli, J.T. Vaughey, K.R. Poeppelmeier, Chem. Mater. 18 (2006) 482–489.
[10] S. Scharner, W. Weppner, P.S. Beurmann, J. Electrochem. Soc. 146 (1999) 857–861.
[11] T. Ohzuku, A. Ueda, N. Yamamoto, J. Electrochem. Soc. 142 (1995) 1431–1435.
[12] A.D. Pasquier, I. Plitz, S. Menocal, G. Amatucci, J. Power Sources 115 (2003) 171–178.
[13] L. Cheng, X.L. Li, H.J. Liu, H.M. Xiong, P.W. Zhang, Y.Y. Xia, J. Electrochem. Soc. 154 (2007) A692–A697.
[14] G.J. Wang, J. Gao, L.J. Fu, N.H. Zho, Y.P. Wu, T. Takamura, J. Power Sources 174 (2007) 1109–1112.
[15] T. Yuan, R. Cai, K. Wang, R. Ran, S.M. Liu, Z.P. Shao, Ceram. Int. 35 (2009) 1757–1768.
[16] L. Kavan, M. Grätzel, Electrochem. Solid-State Lett. 5 (2002) A39–A42.
[17] D.H. Kim, Y.S. Ahn, J. Kim, Electrochem. Commun. 7 (2005) 1340–1344.
[18] C.M. Shen, X.G. Zhang, Y.K. Zhou, H.L. Li, Mater. Chem. Phys. 78 (2003) 437–441.
[19] Y.H. Rho, K. Kanamura, J. Solid State Chem. 177 (2004) 2094–2100.
[20] Y.J. Hao, Q.Y. Lai, Z.H. Xu, X.Q. Liu, X.Y. Ji, Solid State Ionics 176 (2005) 1201–1206.
[21] M. Venkateswarlu, C.H. Chen, J.S. Do, C.W. Lin, T.C. Chou, B.J. Hwang, J. Power Sources 146 (2005) 204–208.
[22] B.Z. Christiansen, K. West, T. Jacobsen, S. Atlung, Solid State Ionics 28–30 (1988) 1176–1182.
[23] W.J. Macklin, R.J. Neat, Solid State Ionics 53–56 (1992) 694–700.
[24] D.W. Murphy, F.J.D. Salvo, J.N. Carides, J.V. Waszczak, Mater. Res. Bull. 13 (1978) 1395–1402.
[25] S.H. Huang, Z.Y. Wen, X.J. Zhu, Z.X. Lin, J. Electrochem. Soc. 152 (1) (2005) A186–A190.
[26] S.H. Huang, Z.Y. Wen, X.J. Zhu, Z.H. Gu, Electrochem. Commun. 6 (2004) 1093–1097.
[27] T. Yuan, K. Wang, R. Cai, R. Ran, Z.P. Shao, J. Alloys Compd. 477 (2009) 665–672.
[28] H. Ge, N. Li, D.Y. Li, C.S. Dai, D.L. Wang, Electrochem. Commun. 10 (2008) 719–722.
[29] L. Kavan, J. Procházka, T.M. Spitler, M. Kalbáč, M. Zukalová, T. Drezen, M. Grätzel, J. Electrochem. Soc. 150 (7) (2003) A1000–A1007.