Short communication

Hybrid microwave synthesis and characterization of the compounds in the Li–Ti–O system

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Abstract

Hybrid microwave synthesis has been applied for preparation of $Li_4Ti_5O_{12}$, $Li_2Ti_3O_7$, Li_2TiO_3 and $LiTiO_2$ for the first time. Stepwise heating was used for avoiding the instantaneous release of gas by-product and obtaining well-shaped samples. The samples were characterized by powder X-ray diffraction, energy-dispersive X-ray analysis and scanning electron microscopy. The obtained samples have relatively uniform particle sizes. The electrochemical performance of $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$ were investigated. The first discharge capacity of $Li_4Ti_5O_{12}$ was $150\,mAh\,g^{-1}$ and $141\,mAh\,g^{-1}$ after 27 cycles and a very flat discharge and charge curve of $Li_4Ti_5O_{12}$ was shown at about 1.56 V. Similarly, $Li_2Ti_3O_7$ exhibits good cycle performance. The initial discharge capacity is $118\,mAh\,g^{-1}$ and 30th cycle is still $112\,mAh\,g^{-1}$.
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Keywords: Microwave synthesis; Lithium titanates; Li-batteries; Electrode materials

1. Introduction

Various compounds exist in the Li–Ti–O system, and they have attracted particular interest due to their potential applications. The lithium insertion behavior of the lithium titanates, such as $Li_4Ti_5O_{12}$, $Li_2Ti_3O_7$ and their solid solutions, has received intensive attention due to their promising applications as electrode materials in Li-batteries. $Li_4Ti_5O_{12}$ exhibits very flat discharge and charge curve, and it is considered as a "zero-strain" insertion compound because its structure does not change during charge–discharge processes. Additionally, this material exhibits a theoretical capacity as high as $175\,mAh\,g^{-1}$ [1–3]. $Li_2Ti_3O_7$ is also a promising electrode material with a maximum theoretical specific capacity of $235\,mAh\,g^{-1}$. The ramsdellite-type $Li_2Ti_3O_7$ has an open structure which allows the diffusion of lithium ions, and the structure change is no more than 2% even at high lithium intercalation [4–6]. Between room temperature and $50\,°C$ $Li_2Ti_3O_7$ exhibits an enhanced discharge capacity with increase of temperature [7]. As far as Li_2TiO_3 is concerned, it can be used as the breeding material in the blanket

of a nuclear reactor because it is effective in producing tritium atoms by lithium transmutation [8–11]. Furthermore, $LiTiO_2$ results from lithium insertion into TiO_2. Previously, $LiTiO_2$ was obtained by reaction of $LiTi_2O_4$ with BuLi or by electrochemical synthesis [12–14].

The phase equilibria in Li–Ti–O system have been systemically studied [15–17]. There are four compounds: Li_4TiO_4, Li_2TiO_3, $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$ in the binary phase system of Li_2O–TiO_2. Trimorphism was observed in the case of Li_2TiO_3: α-, β- and γ-phase. The α-Li_2TiO_3 is a metastable phase and it exits below $300\,°C$. The β-Li_2TiO_3 is monoclinic with a narrow range of solid solutions from 47% to 51% TiO_2, and undergoes an phase transformation to γ-Li_2TiO_3 at $1155\,°C$. The spinel $Li_4Ti_5O_{12}$ is stable until $1018\,°C$ and above which it decomposes to γ-Li_2TiO_3 and $Li_2Ti_3O_7$. The occurrence of $Li_2Ti_3O_7$ is established above $957 \pm 20\,°C$. Below this temperature, $Li_2Ti_3O_7$ transform into $Li_4Ti_5O_{12}$ and TiO_2. Additionally, in the binary phase system of Li_2O–Ti_2O_3, $LiTiO_2$ is the only established compound.
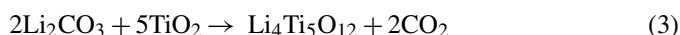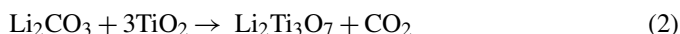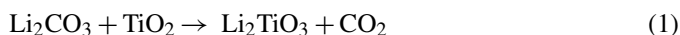
Various techniques, such as sol–gel [6,18–22] method, electrochemical method [14], solution combustion synthesis [23–25] and conventional solid-state reactions, were used to prepare lithium titanates. In recent years, the microwave synthesis has been used extensively as a new technique for material prepara-

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tion. Many inorganic materials [26–30] have been synthesized using the microwave method. Microwave synthesis has been known to provide a fast route for reactions in solid state, and it often occurs at lower temperatures than the conventional synthesis process. The higher reaction and cooling rates during microwave irradiation make the formation of metastable phases possible. The pioneer research on microwave synthesis of titanates was reported by Rao and coworkers, and they have obtained lithium lanthanum titanate from metal oxides [31]. Recently, we have successfully obtained the superconducting spinel phase and the non-superconducting ramsdellite phase of $LiTi_2O_4$ [32]. A review of the literature reveals no previous report on the microwave synthesis of lithium titanates. In order to study further the property of lithium titanates and improve the method of hybrid microwave synthesis, we tried to obtain lithium titanates ($Li_2Ti_3O_7$, $Li_4Ti_5O_{12}$, Li_2TiO_3 and $LiTiO_2$) and showed the promising applicability of the hybrid microwave synthesis.

2. Experimental

The starting materials are analytically pure Li_2CO_3, TiO_2 powders and high purity Ti powder (99.9%). Both TiO_2 and Li_2CO_3 were first dried at 200 °C for 3 h. They were mixed by mole ratio according to the following reactions:

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \tag{1}$$

$$Li_2CO_3 + 3TiO_2 \rightarrow Li_2Ti_3O_7 + CO_2 \tag{2}$$

$$2Li_2CO_3 + 5TiO_2 \rightarrow Li_4Ti_5O_{12} + 2CO_2 \tag{3}$$

The mixed powder was finely grounded and then pressed into a pellet (Ø20 mm) with a pressure of 9 MPa. The pellet surrounded by the mixed reactant powder was put in an alumina boat. Another alumina boat was used to cover the previous one to separate the reactants from the heating susceptor. Then, both boats were placed in the middle of an alumina crucible filled with SiC granules. The SiC granules were used as a heating susceptor because it could effectively absorb microwave radiation and withstand high temperature. An alumina plate was used as a lid of the crucible. A schematic illustration of microwave reactor setup is shown in Fig. 1. The reactor was placed in a domestic microwave oven (KE23B-W, Media, China) working at the frequency of 2.45 GHz and maximum power of 800 W. If the higher heating power (≥400 W) was applied at the beginning of
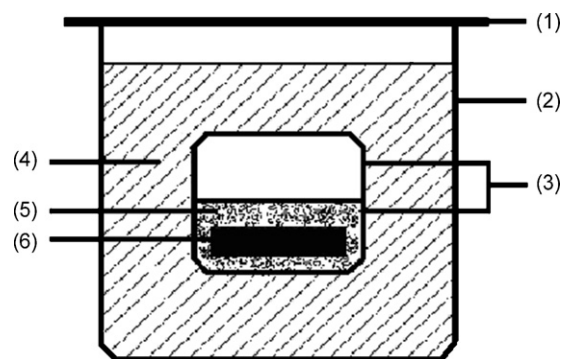

Fig. 1. Schematic illustration of microwave synthesis setup (1) Al_2O_3 plate, (2) Al_2O_3 crucible, (3) Al_2O_3 boat, (4) SiC granules, (5) reactant powder and (6) reactant pellet.

the hybrid microwave synthesis, the carbon dioxide gas would instantaneously release which result in the pellet crack with scattering debris. Therefore, the stepwise heating mode was chosen to reduce the release rate of carbon dioxide, so that well-shaped samples can be obtained. The detailed stepwise heating process is listed in Table 1. The samples were cooled to room temperature in an hour. Incidentally, the stepwise heating mode can be used for synthesis of other materials with gas by-product.

The $LiTiO_2$ sample was prepared using a two-stage synthesis route in argon. First, two intermediate compounds, Li_2TiO_3 and TiO, were prepared by the microwave synthesis. TiO was obtained at the power level of 800 W in 12 min in argon. The detailed experimental method has been described elsewhere [32]. The total reactions can be described as the following reactions:

$$TiO_2 + Ti \rightarrow 2TiO \tag{4}$$

$$Li_2TiO_3 + TiO \rightarrow 2LiTiO_2 \tag{5}$$

The obtained samples were characterized by powder X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX) and scanning electron microscope (SEM). The powder X-ray diffraction data was obtained using an M18X-AHF rotating-anode diffractometer with Cu Kα radiation. Lattice parameters were calculated using the least-square method with PowderX program [33]. The morphology and chemical composition were obtained using scanning electron microscope (XL30 S-FEG). The electrochemical properties of $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$ were performed using a Land automatic batteries tester. $LiPF_6$

Table 1
Preparation conditions and phase composition of lithium titanates by the hybrid microwave synthesis

Sample	Chemical composition	Microwave synthesis process[a]	Atmosphere	Phase composition
A1	$Li_4Ti_5O_{12}$	MH(I)	Air	$Li_4Ti_5O_{12}$, $Li_2Ti_3O_7$
A2	$Li_4Ti_5O_{12}$	MH(II)	Air	$Li_4Ti_5O_{12}$
B1	$Li_2Ti_3O_7$	MH(I)	Air	$Li_4Ti_5O_{12}$, TiO_2, $Li_2Ti_3O_7$
B2	$Li_2Ti_3O_7$	MH(II)	Air	$Li_4Ti_5O_{12}$, TiO_2, $Li_2Ti_3O_7$
B3	$Li_2Ti_3O_7$	MH(III)	Air	$Li_2Ti_3O_7$
C	Li_2TiO_3	MH(II)	Air	Li_2TiO_3, minor Li_2CO_3
D	$LiTiO_2$	MH(IV)	Argon	$LiTiO_2$, minor Li_2TiO_3 and Ti_2O

[a] MH(I): samples were successively heated using oven power of 160 W, 320 W, 480 W and 640 W, holding for 5 min at each power level. MH(II): MH(I) + 800 W for 4 min; MH(III): MH(I) + 800 W for 10 min; MH(IV): 480 W for 15 min.

(1 M) in ethylene carbonate/dimethyl carbonate was used as electrolyte. Electrodes were prepared by combining the active materials ($Li_4Ti_5O_{12}/Li_2Ti_3O_7$), carbon black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10. Cu foil is used as collector. The active material loadings are 0.018 g cm^{-2}. The electrodes were dried under vacuum at 80 °C for 10 h before use. The metallic lithium was used as the counter electrode. Celgard 2340 is used as the separator. The cells were assembled in a glove box filled with pure argon. All the electrochemical tests were carried out at room temperature. The charge–discharge cycle tests were performed at different current density of 0.35–4.0 mA cm^{-2} cycled between 1.0 V and 2.7 V.

3. Results and discussion

In order to obtain the single-phased samples, samples were prepared under different reaction conditions. Table 1 lists phase compositions of the representative samples obtained by different processes.

Fig. 2(a) shows the X-ray diffraction patterns of $Li_4Ti_5O_{12}$ prepared under different conditions. From the Li_2O–TiO_2 phase diagram [15–17], $Li_4Ti_5O_{12}$ is stable under 1018 °C. Therefore, the MH(I) process (see Table 1) with a lower oven power and shorter irradiation time, was first applied to prepare $Li_4Ti_5O_{12}$ (sample A1). It can be seen from Fig. 2(a), that most diffraction peaks of sample A1 belong to $Li_4Ti_5O_{12}$, and the remain-ing peaks can be attributed to the $Li_2Ti_3O_7$. Single-phased $Li_4Ti_5O_{12}$ (sample A2) can be obtained by the MH(II) process, and its diffraction patterns can be indexed by a cubic unit cell. The calculated lattice parameters are listed in Table 2.

The XRD patterns of $Li_2Ti_3O_7$ prepared at different reaction conditions are present in Fig. 2(b). Previously, $Li_2Ti_3O_7$ was prepared by solid-state reactions at 1100 °C and quenching in air, which was consistent with the Li_2O–TiO_2 phase diagram. Our samples were cooled to room temperature within an hour after the hybrid microwave heating. The cooling rate, higher than that in conventional solid-state synthesis, favors the fabrication of $Li_2Ti_3O_7$. Sample B1 prepared by the MH(I) process is a mixture of $Li_4Ti_5O_{12}$, TiO_2 and tiny $Li_2Ti_3O_7$. The major phase is target $Li_2Ti_3O_7$ and the minor phases are $Li_4Ti_5O_{12}$ and TiO_2 in sample B2 prepared by the MH(II) process. The experimental results indicate that longer heating time and higher power should be applied. So, the MH(III) process was further used, and single-phased $Li_2Ti_3O_7$ (sample B3) was obtained.

From Fig. 2(c), nearly single-phased β-Li_2TiO_3 was obtained by the MH(II) process. There are two extra diffraction peaks at $2\theta = 21.3°$ and 31.7°, corresponding to Li_2CO_3. Nearly single-phased $LiTiO_2$ was prepared with MH(IV) process in flowing argon. Its powder X-ray diffraction pattern was shown in Fig. 2(d). However, there are several weak impurities peaks in the diffraction pattern which can be attributed to Li_2TiO_3 and Ti_2O.
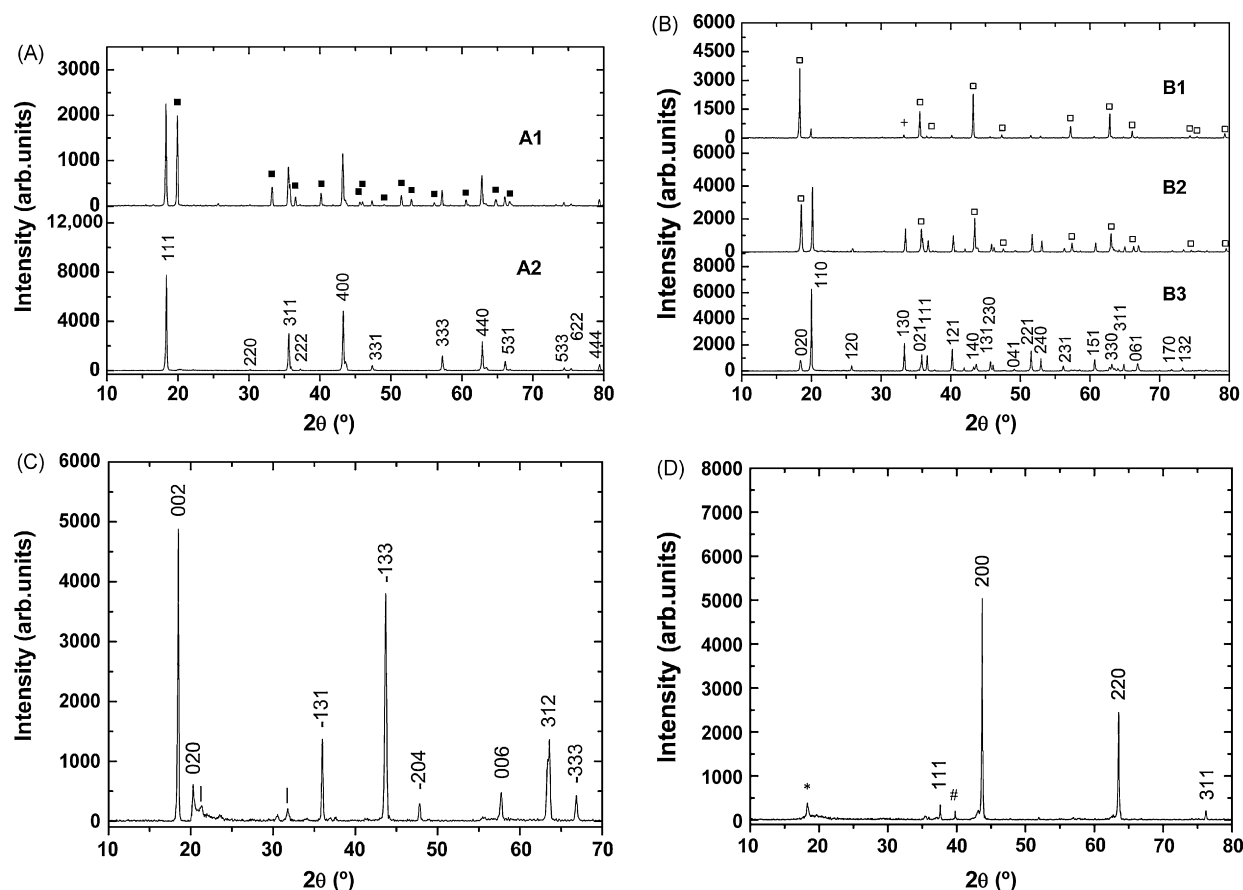

Fig. 2. XRD patterns of (a) $Li_4Ti_5O_{12}$ (■: $Li_2Ti_3O_7$), (b) $Li_2Ti_3O_7$ (□: $Li_4Ti_5O_{12}$, +: TiO_2), (c) Li_2TiO_3 (|: Li_2CO_3), (d) $LiTiO_2$ (*: Li_2TiO_3, #: Ti_2O) prepared by hybrid microwave synthesis.

Table 2
EDX analysis and lattice parameters of samples prepared by hybrid microwave synthesis

Phase composition	Sample	Elemental ratios[a]		Crystal structure	Unit-cell parameters (Å)
		Nominal	EDX		
$Li_4Ti_5O_{12}$	A2	0.417	0.432	Cubic	$a = 8.354$
$Li_2Ti_3O_7$	B3	0.429	0.448	Orthorhombic	$a = 5.010$, $b = 9.551$, $c = 2.942$
Li_2TiO_3	C	0.333	0.355	Monoclinic	$a = 5.068$, $b = 8.766$, $c = 9.656$, $\beta = 99.9$
$LiTiO_2$	D	0.500	0.529	Cubic	$a = 4.139$

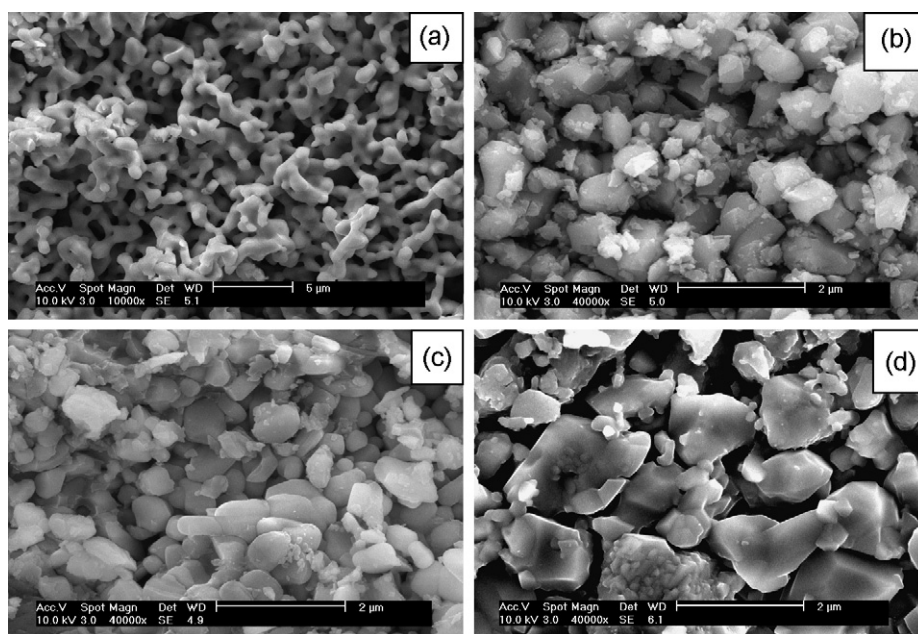[a] The elemental stoichiometric ratios of titanium and oxygen confirmed by EDX studies.

Fig. 3. SEM micrographs of lithium titanates prepared hybrid microwave synthesis. (a) $Li_4Ti_5O_{12}$, (b) $Li_2Ti_3O_7$, (c) Li_2TiO_3 and (d) $LiTiO_2$.

Fig. 3 shows the scanning electron microscopy (SEM) images of the single-phased samples. From Fig. 3(a), we can see that the $Li_4Ti_5O_{12}$ grains are connected with each other and their average size is around 1 μm. For $Li_2Ti_3O_7$, the most grains have similar sizes and the average particle size is around 1 μm (Fig. 3b). The samples of Li_2TiO_3 and $LiTiO_2$ (Fig. 3c and d) have irregular-shaped grains with an average size of around 1–2 μm. From above-mentioned data, lithium titanates with relatively homogeneous grain sizes were obtained by the hybrid microwave synthesis.

The stoichiometric ratios of titanium and oxygen in the products are evaluated using EDX measurements and the results are listed in Table 2. As Li is a light element, the content of Li atom cannot be determined using EDX. The EDX results revealed the ratios (Ti:O) are consistent with the nominal ratios within the experimental precisions.

The electrochemical behaviors of $Li_4Ti_5O_{12}$ and $Li_2Ti_3O_7$ were investigated. Fig. 4 shows the first discharge–charge cycle of $Li_4Ti_5O_{12}$. The cell was cycled between 2.7 V and 1.0 V. During the discharge and charge the $Li_4Ti_5O_{12}$ sample exhibits extremely flat curves at about 1.56 V, which means that there was a two-phase reaction based on the Ti^{4+}/Ti^{3+} redox couple [34,35]. The electrode exhibited an ini-

tial discharge capacity of 150 mA h g^{-1} with 0.35 mA cm^{-2} (Fig. 5), which is close to the previous results obtained using other synthesis method [20]. After 27 cycles, the discharge capacity is a nearly constant value. The initial discharge capacity with 3.2 mA cm^{-2} was 115 mA h g^{-1}, and the capacity after 10 cycles was 105 mA h g^{-1}. It indicates that
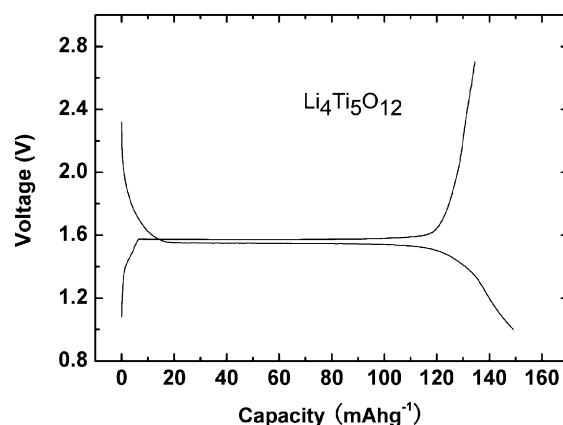

Fig. 4. Discharge/charge in initial first cycles of $Li_4Ti_5O_{12}$ prepared by hybrid microwave synthesis.

Fig. 5. Specific discharge capacity dependence on cycle number of $Li_4Ti_5O_{12}$ prepared by hybrid microwave synthesis at different current density.
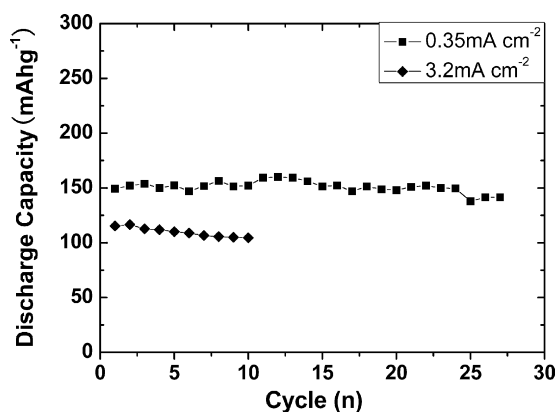

Fig. 7. Specific discharge capacity dependence on cycle number of $Li_2Ti_3O_7$ prepared by hybrid microwave synthesis at different current density.

the $Li_4Ti_5O_{12}$ electrode have better capacity retentivity and cycleability.

Fig. 6 shows the first discharge and charge curve of $Li_2Ti_3O_7$. The charge potentials are much different from the discharge ones, which is consistent with the previous reports. The discharge curve falls into three inclined parts, corresponding to voltage ranges of between 2.3 V and 1.6 V, 1.6 V and 1.5 V and 1.5 V and 1.2 V, respectively. The inclines attributed to two consecutive solid solutions and a biphasic region [4,5,7]. The initial discharge capacity of the sample is 118 mAh g^{-1} with a current density 0.35 mA cm^{-2}, and after 30 cycles it is still 112 mAh g^{-1} (Fig. 7). A good cyclic ability of $Li_2Ti_3O_7$ is confirmed experimentally by its capacity stability within 30 cycles. The discharge capacities of microwave synthesized $Li_2Ti_3O_7$ sample are smaller than that of sample obtained using solid-state reactions whose first discharge capacity is about 130 mAh g^{-1} with a 0.4 mA cm^{-2} current density [7]. For the larger current density of 4.0 mA cm^{-2}, the $Li_2Ti_3O_7$ sample exhibits an initial capacity of 88.35 mAh g^{-1}, and after 10 cycles it is still 86 mAh g^{-1}.

Finally, we would like to discuss the advantages of hybrid microwave synthesis of lithium titanates. The most remarkable advantage is the fast heating rate. Compared with the conven-
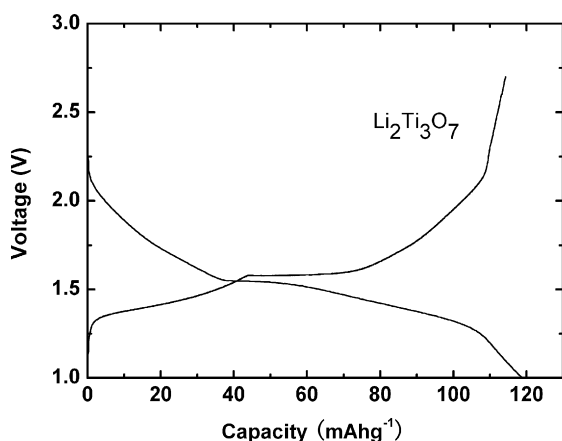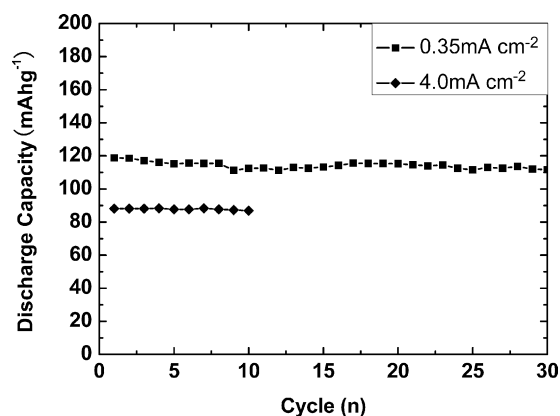
tional solid-state reactions that take several days, reactions in the microwave irradiation can be completed in 30 min. This would lead to the production of small particles with a narrow and uniform grain size distribution, which favors the better electrochemical behavior of electrode materials because small and uniform particle size results in a higher charge rate for intercalated anodes. Also, the energy resources were saved and the reaction parameters can be evaluated in a shorter time to optimize the desired chemistry. The additional advantage for this method is more atom economic. For example, in the typical sol–gel synthesis of $Li_4Ti_5O_{12}$, the product was obtained by drying, heating and calcining the mixture (solvent, metallic alkoxide and lithium salt). Compare to the sol–gel method, microwave synthesis is atom economic because all atoms in the reactants are retained in the final product (except the carbon dioxide from carbonate). Consequently, the hybrid microwave method is can be easily extended to synthesize other materials.

4. Conclusions

In this work, we have tried several microwave heating processes to obtain the single-phased lithium titanates. Stepwise heating processes were chosen to avoid the instantaneous release of carbon dioxide. Consequently, we have successfully obtained single-phased $Li_4Ti_5O_{12}$, $Li_2Ti_3O_7$ and nearly single-phased Li_2TiO_3 and $LiTiO_2$ samples.

The $Li_4Ti_5O_{12}$ sample, having a spinel-type crystal structure with $a = 8.354$ Å, and exhibits a stable cycleability with the initial discharge capacity of 150 mAh g^{-1} and discharge capacity of 141 mAh g^{-1} in the 27th cycle. The $Li_2Ti_3O_7$ sample have an orthorhombic crystal structure with $a = 5.010$ Å, $b = 9.551$ Å and $c = 2.942$ Å. It shows quite stable electrochemical performance with initial discharge capacity of 120 mAh g^{-1} and discharge capacity of 112 mAh g^{-1} in the 30th cycle. In the higher current density, the two compounds exhibit the better capacity retentivity and cycleability.

The microwave synthesis of lithium titanates is a new field. This paper presents the preliminary experimental results and there is still plenty of room for improvement of the hybrid microwave synthesis to prepare the lithium titanates samples

Fig. 6. Discharge/charge in initial first cycles of $Li_2Ti_3O_7$ prepared by hybrid microwave synthesis.

with higher purity and better electrochemical properties. We anticipate that the hybrid microwave method can be progressively used to synthesize other materials.

Acknowledgments

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