



Synthesis of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ –ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ composites under vacuum and their electrochemical properties



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ABSTRACT

Composites of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ –ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_2\text{Ti}_3\text{O}_7$) were prepared and evaluated for anode materials in lithium-ion batteries. Our experimental results turn out that sintering temperatures and carbon content play important roles in forming these composites. Under vacuum, it is found that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_2\text{Ti}_3\text{O}_7$ composites can be synthesized at around 600 °C under the help of citric acid. According to the XRD patterns, its reaction mechanism is suggested in this study. In addition, electrochemical testing demonstrates that the presence of $\text{Li}_2\text{Ti}_3\text{O}_7$ in the prepared sample modifies the charge/discharge behavior of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which makes it easily to monitor its SOC/SOD according to its voltage profile.

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1. Introduction

The study of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be tracked back to 1980s [1]. Since then, it has been extensively developed as an anode material for Li-ion batteries because of its superior lithiation/delithiation behavior, long cycle life and high safety [2–5]. However, the very flat charge/discharge voltage profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ brings up a difficulty in practical applications in which the voltages of batteries are monitored to tell their states of charge/discharge (SOC/SOD). In particular, it is impossible to predict the real-time SOC/SOD of a battery into which $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is assembled with LiFePO_4 [6].

To avoid over-charge/discharge of such a battery, ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ is designed to be added into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to modify its charge/discharge behavior [7] to change its flat voltage profiles to be slopes, which is studied as another anode material [8–11].

However, a noteworthy fact is that $\text{Li}_2\text{Ti}_3\text{O}_7$ is usually prepared at temperatures higher than 940 °C and then quenched immediately to avoid the transformation to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 [7,12–14]. In the present work, we report to synthesize the composite of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_2\text{Ti}_3\text{O}_7$ at much lower temperatures. Moreover, these composites demonstrate superior electrochemical properties.

2. Experimental

To prepare the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_2\text{Ti}_3\text{O}_7$ composites, stoichiometric amounts of Li_2CO_3 (5 wt.% in excess) and TiO_2 (molar ratio of Li to Ti is 4:5) were mixed and ball-milled in the disperser of ethanol. Then, the mixed slurry was dried at 80 °C. Finally, the dried mixture was pressed into pellets and heated at 500, 600, 650, 700 °C for 3 h under vacuum (10–20 Pa), denoted as S_0 -500, S_0 -600, S_0 -650 and S_0 -700, respectively. For the purpose of comparison, some of the pellets are heat-treated at 600 °C for 3 h in air, denoted as S_0 -600 (air).

To shed light on the influence of carbon on the formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_2\text{Ti}_3\text{O}_7$ composites, 10 and 20 wt.% of citric acid was incorporated initially with the starting materials. With the aforementioned procedure, the samples prepared from the citric acid (10 wt.% and 20 wt.%) included mixtures were called S_1 -600 and S_2 -600, respectively.

To explain the citric acid effect on the formation of $\text{Li}_2\text{Ti}_3\text{O}_7$, Li_2CO_3 (5 wt.% in excess) and TiO_2 with the molar ratio of 1:3 were mixed as described above, and calcined at 600, 650 and 700 °C for 3 h to obtain samples L600, L650 and L700. For the sake of comparison, a controlled sample was prepared with 20 wt.% citric acid at 600 °C, denoted as L600-C.

Powder X-ray diffraction (XRD) was conducted with a Rigaku TTRIII X-ray diffractometer equipped on graphite monochromatized high-intensity Cu K radiation, in steps of $0.02^\circ 2\theta$ and holding at each step for 2 s. The morphology and particle size of the samples were observed by scanning electron microscopy (SEM, XL30, Philips). The carbon content in the sample was determined by Elementar Analysensysteme GmbH-Vario EL III Element 68 Analyzer.

The working electrodes consisted of 90 wt.% active materials, 5 wt.% carbon black, and 5 wt.% polyvinylidene fluoride (PVDF) binder on aluminum foil current collector. After calendared and punched, electrodes were prepared with area of 1.33 cm² and loading of 3.0–5.0 mg. The cells were assembled in an Ar-filled glove box by using lithium foil as the counter electrode and a polypropylene film as the separator. The electrolytes were 1 M LiPF_6 dissolved in a mixture of ethyl carbonate (EC), dimethyl carbonate (DMC) with a volume ratio of 1:1. The cells were

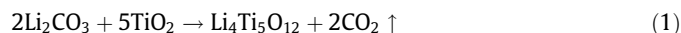
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galvanostatically charged and discharged between 1.0 V and 2.2 V vs. Li/Li⁺ at room temperature (27 °C) on the electrochemical test instrument (Guangzhou Qingtian Industry Co. Ltd., China). Herein, 1 C = 170 mA g⁻¹.

3. Results and discussion

Fig. 1A shows the XRD patterns of the samples prepared from Li₂CO₃ and TiO₂ as starting materials at different temperatures. The patterns of S₀-500 and S₀-600 are in good agreement with the published data for spinel Li₄Ti₅O₁₂ (JCPDS card #49-0207, Fd3m space group). Interestingly, only anatase TiO₂ and Li₂TiO₃ were obtained under the same heat-treatment with S₀-600 in air as shown in Fig. 1B. In terms of the suggested mechanism of Li₄Ti₅O₁₂ in air [15], our results indicate that Li₄Ti₅O₁₂ can form (reaction (1)) at much lower temperature as the pressure is reduced.



When the sintering temperature is increased to 650 and 700 °C under vacuum, patterns of S₀-650 and S₀-700 are dominated by spinel Li₄Ti₅O₁₂ and ramsdellite Li₂Ti₃O₇ (JCPDS card #340393, Pbnm space group). And the intensity of Li₂Ti₃O₇ becomes stronger with the increasing temperature, indicating the increase of its amount. At atmospheric pressure, it is suggested that Li₄Ti₅O₁₂ would decompose to Li₂Ti₃O₇ above 940 °C, following reaction (2) [16].

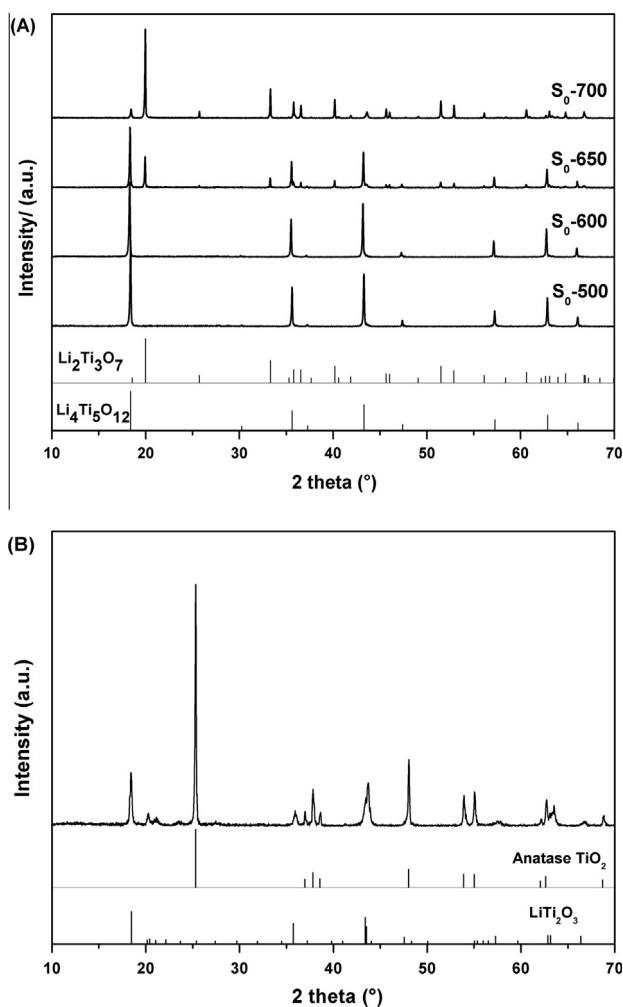
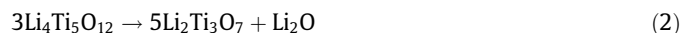


Fig. 1. XRD patterns of (A) S₀-500, S₀-600, S₀-650, and S₀-700, (B) S₀-600 (air).

Under vacuum, the reactions are pushed forward because of sublimation of lithium oxide is much easier. Due to the fast kinetics, the reaction can happen at lower temperature in vacuum than in atmospheric pressure. Consequently, the formation of Li₂Ti₃O₇ will take place at much lower temperature. As a result, Li₂Ti₃O₇ forms in the range of 600–650 °C in our study.

Fig. 2 shows the powder X-ray diffraction patterns of S₁-600 and S₂-600. All the diffraction peaks of S₁-600 can be ascribed to an ordered spinel Li₄Ti₅O₁₂. But in S₂-600, the XRD signals at around 2θ = 19.9°, 33.2° and 52.7° as marked by the arrows reflect detectable amounts of Li₂Ti₃O₇ phase. Why Li₂Ti₃O₇ formed at 600 °C in sample S₂-600, not in S₀-600? It is probably that the gases released from the pyrolysis of citric acid help lithium oxide to sublimate, which accelerates the decomposition reaction of the Li₄Ti₅O₁₂ (reaction (2)). No observation of Li₂Ti₃O₇ in S₁-600 is ascribed to the small amount of Li₂Ti₃O₇, which cannot be detected by XRD.

As shown in Fig. 3, the XRD patterns show that at 600 °C, the mixture of Li₂CO₃ and TiO₂ with the molar ratio of 1:3 tends to react to produce spinel Li₄Ti₅O₁₂, but TiO₂ remains, because of the lack of lithium oxide. It should be mentioned that the residual TiO₂ has a rutile structure, which is transformed from anatase TiO₂. Above 600 °C, Li₂Ti₃O₇ forms. And its amount increases as the

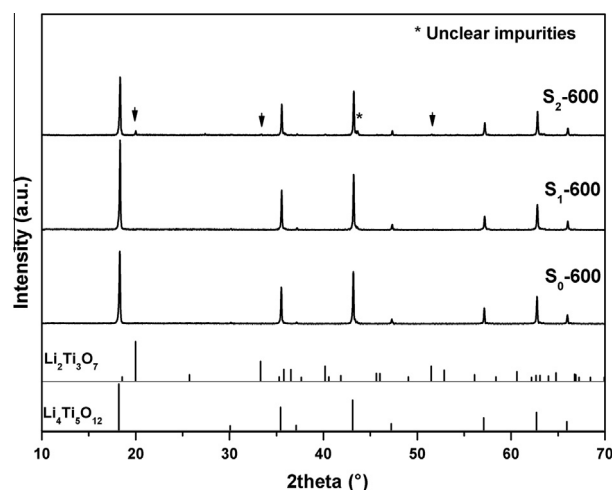


Fig. 2. XRD patterns of S₀-600, S₁-600, and S₂-600.

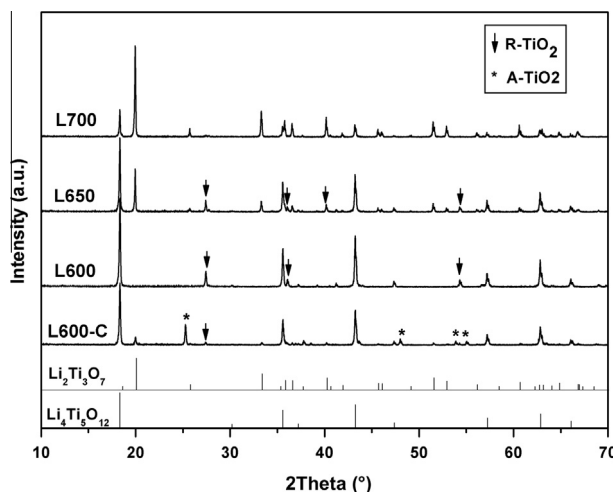


Fig. 3. XRD patterns of L600, L650, L700, and L600-C.

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