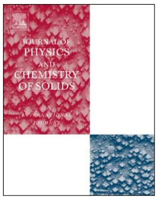
Journal of Physics and Chemistry of Solids 108 (2017) 25–29

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Zr doping effect with low-cost solid-state reaction method to synthesize submicron $Li_4Ti_5O_{12}$ anode material

Inseok Seo[a,*], Cheul-Ro Lee[a], Jae-Kwang Kim[b,*]

[a] *School of Advanced Materials Engineering, Research Center for Advanced Materials Development (RCAMD), Chonbuk National University, Baekje-daero 567, Jeonju 54896, Republic of Korea*
[b] *Department of Solar & Energy Engineering, Cheongju University, Cheongju, Chungbuk 360-764, Republic of Korea*

ARTICLE INFO

Keywords:
Lithium secondary battery
Lithium carbonate
Titanium oxide
Solid-state reaction
Zr-doped $Li_4Ti_5O_{12}$

ABSTRACT

To improve the electrochemical properties, fine Zr-doping $Li_4Ti_5O_{12}$ anode materials for rechargeable lithium batteries with a uniform particle size distribution were synthesized by a modified solid-state reaction using fine Li_2CO_3 and TiO_2 (anatase) powders as precursors with a Li:Ti molar ratio of 4:5. The use of fine Li_2CO_3 and TiO_2 (anatase) powders as precursors prevented the formation of ZrO_2 at 0.1 mol Zr-doping. XRD analysis revealed that the substitution of Zr for Ti leads to the increase of lattice parameters, allowing improved Li diffusion. The discharge capacity retention increased slightly with Zr-doping and the 0.1 mol Zr-doped $Li_4Ti_5O_{12}$ electrode achieved 99% retention of discharge capacity.

1. Introduction

Capacity degradation in Li-ion batteries is usually a result of structural failure due to the volume change of the anode material during charge and discharge. However, spinel-type $Li_4Ti_5O_{12}$ materials exhibit a long cycle life (Li-ion intercalation and de-intercalation) because of their zero-strain structure during charge and discharge [1–6]. The spinel $Li_4Ti_5O_{12}$ materials possess good Li-ion mobility and undergo a reversible electrochemical reaction. In addition, they show a good discharge plateau at 1.55 V versus Li^+/Li. This means greater stability compared to metallic Li or carbon materials because the high plateau potential can prevent the reduction of electrolytes on the electrode surface, as well as the growth of Li dendrites [7]. The flat plateau allows $Li_4Ti_5O_{12}$ to be a safe anode material alongside high capacity cathode materials [8,9]. This characteristic has attracted much attention for the application of $Li_4Ti_5O_{12}$ as anodes in Li-ion batteries. However, $Li_4Ti_5O_{12}$ has a low intrinsic electrical conductivity (10^{-13} S/cm) at room temperature [10]. In order to improve the electrical conductivity of $Li_4Ti_5O_{12}$, many researchers have attempted to prepare submicron or nano-sized $Li_4Ti_5O_{12}$ with carbon coating or cation doping [11–13]. The small sized $Li_4Ti_5O_{12}$ powders promote facile diffusion due to the reduced Li transport distance. In addition, carbon coating of the $Li_4Ti_5O_{12}$ surface improves electrical conductivity by constructing electron pathways [14,15], whereas cation doping improves electrical conductivity through the introduction of a cation at the Li or Ti site [16,17].

Until now, $Li_4Ti_5O_{12}$ has been synthesized by various processes, such as spray drying [18,19], sol-gel [20], and solid-state reaction [21] methods. Although the spray-drying method can produce powders with homogeneous mixing between Li_2CO_3 and TiO_2 powders, the produced powders must be crushed by a jet mill in order to produce submicron particles, which adds a step and increases the processing cost. In the case of the sol-gel method, the particle size can reach the submicron scale, but the processing has several disadvantages, including the relatively higher cost of raw materials, the presence of residual micropores after the synthesis, and the relatively longer reaction times. For these reasons, the sol-gel method is difficult to scale up for mass production. On the other hand, the solid-state method has several advantages over the above methods such as a simple synthesis route, low synthesis cost, and its ease of commercial application. However, production of homogeneous powders with submicron-sized particles is difficult by the solid-state reaction without controlling synthesis parameters such as milling time, type of precursor, heating temperature, and heating time etc. Moreover, reactive particles can affect their electrochemical performance [22,23].

In this paper, we propose an improved solid-state reaction for obtaining submicron Zr-doped $Li_4Ti_5O_{12}$ powders (Zr =0, 0.01, 0.05, 0.1 mol) with fine Li_2CO_3 powder and anatase-type TiO_2 powder as the starting materials. By using fine Li_2CO_3 (~1 μm) and TiO_2 (~1 μm) powders for the solid-state reaction, $Li_4Ti_5O_{12}$ with a particle size of ~1 μm and a uniform size distribution were achieved. Moreover, the effect of Zr-doping of the prepared $Li_4Ti_5O_{12}$ on structure and electrochemical performance was investigated.

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[*] Corresponding authors.
E-mail addresses: isseo@jbnu.ac.kr (I. Seo), jaekwang@cju.ac.kr (J.-K. Kim).

http://dx.doi.org/10.1016/j.jpcs.2017.04.011
Received 13 November 2016; Received in revised form 17 March 2017; Accepted 18 April 2017

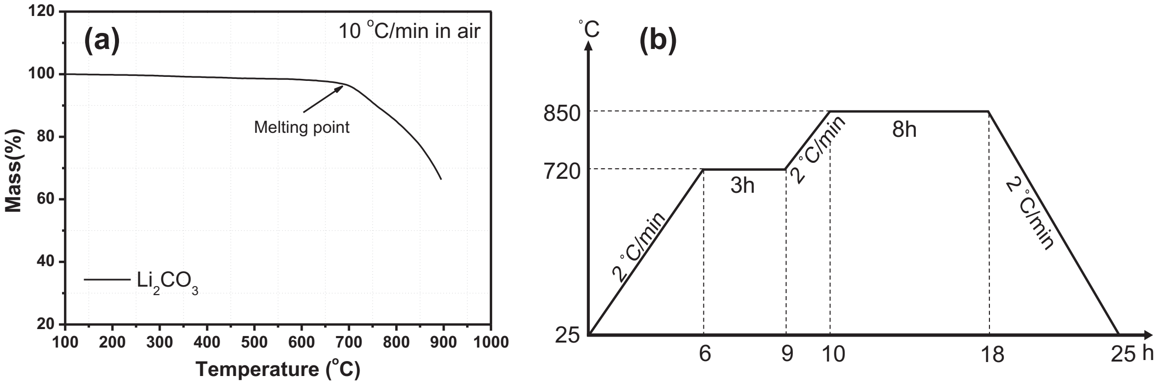

Fig. 1. (a) TGA results obtained for Li_2CO_3 and (b) schematic diagram of heat treatment for $Li_4Ti_5O_{12}$.

2. Experimental

In order to prepare $Li_4Ti_5O_{12}$ anode materials, fine Li_2CO_3 (Chengdu CCI, > 99.9%) and TiO_2 anatase (Samchun, 99.0%) were used as starting materials. The $Li_4Ti_5O_{12}$ was synthesized by solid-solid composite reactions using a Hosokawa Micron Nobilta instrument. In order to produce the pristine submicron-sized $Li_4Ti_5O_{12}$ powders, fine Li_2CO_3 powder (1.15 µm average diameter) and fine TiO_2 powder (1.2 µm average diameter) were mixed. For the preparation of Zr-doped $Li_4Ti_5O_{12}$, fine Li_2CO_3 powder (1.15 µm average diameter), fine TiO_2 powder (1.2 µm average diameter), and different Zr amounts (0.01, 0.05, and 0.1 M ratios) were mixed. The molar ratio of Li to Ti was 4:5. A batch of 300*g* was weighed and put into the instruments to mix the powders. The stirring speed was set to 3000 rpm and the operating time was 1 h. After mixing, the powders were sintered. Spinel-type $Li_4Ti_5O_{12}$ is usually synthesized by a solid-state reaction using Li_2CO_3 or LiOH and anatase-type TiO_2, with a sintering temperature of 800–1000 °C for 12–24 h [23,24]. In this study, the optimized temperature and time were 850 °C and 8 h, respectively. After heat treatment, the $Li_4Ti_5O_{12}$ powders were agglomerated without strong bonding. The agglomerated $Li_4Ti_5O_{12}$ was crushed using a mortar and a pestle.

The morphology, particle size, and distribution of the $Li_4Ti_5O_{12}$ powder were observed using scanning electron microscopy (SEM, Hitachi S-4200). To verify the structural phase and lattice parameters of the $Li_4Ti_5O_{12}$, X-ray diffraction (XRD) powder pattern data were collected on finely ground samples at room temperature with a Scintag XDS 2000 diffractometer using Cu K_α radiation (λ=1.5406 Å). It was operated at 40 kV and 30 mA in the 2θ range of 10–80° in continuous scan mode with a step size of 0.03° and scan rate of 2.0°/min.

The sample electrodes were prepared with $Li_4Ti_5O_{12}$, carbon black, and poly(vinyl difluoride) (PVdF) at a weight ratio of 85:10:5. The slurry was cast on Al foil and dried at 110 °C in vacuum for 8 h. The coil cells CR2032 were assembled with pure lithium foil as the counter electrode, an SK innovation CCS separator, and 1 M $LiPF_6$ EC: DMC (1:1) electrolyte in an argon-filled glove box. The charge-discharge cycling was galvanostatically performed with cut-off voltages of 1.0–2.6 V (versus Li/Li^+) at room temperature.

3. Results and discussion

Before heat-treating the mixed precursors for $Li_4Ti_5O_{12}$ preparation, the decomposition temperature of Li_2CO_3 was evaluated by TGA. TGA curves for pure Li_2CO_3 at a heating rate of 10 °C/min under air flow are shown in Fig. 1a. It can be clearly observed that the curve below 700 °C is very smooth, suggesting that the mass varies little at that temperature. No peaks (endothermic or other) are observed below 700 °C. Therefore, it can be concluded that no decomposition or phase change of Li_2CO_3 occurs below 700 °C. The decomposition temperature of fine Li_2CO_3 powder is slightly lower than that of normal-sized Li_2CO_3 powder. The decomposition temperature of fine Li_2CO_3 powder is below 700 °C; however, reference data show the value to be 720 °C [24]. Since the decomposition temperature of fine Li_2CO_3 powder is lower than that of normal-sized Li_2CO_3 powder, the fine powder could be decomposed and more easily diffused into TiO_2 powder than normal-sized Li_2CO_3 powder.

A schematic diagram of the heat treatment for $Li_4Ti_5O_{12}$ preparation is shown in Fig. 1b. The heating and cooling rates during the treatment were 2 °C/min. According to the TGA results, the melting point of the precursors was about ~690 °C. Thus, the temperature was maintained slightly higher than the melting point (~720 °C) for 3 h to allow Li diffusion into TiO_2 powder. The sintering temperature was maintained at 850 °C for 8 h. Spinel-type $Li_4Ti_5O_{12}$ is usually synthesized by a solid-state reaction using Li_2CO_3 or LiOH and anatase-type TiO_2, with the sintering temperature maintained at 800–1000 °C for 12–24 h [25,26]. In this study, the optimized temperature and operating time were 850 °C and 8 h, respectively.

Fig. 2a display the schematic structure of $Li_4Ti_5O_{12}$ and blue, green and red indicate is Ti atoms, Li atoms and O atoms, respectively. Li atoms occupy the tetrahedral (8a) sites, while the octahedral (16c) sites are randomly by lithium and titanium atoms. XRD powder patterns for the pristine $Li_4Ti_5O_{12}$ and the Zr-doped $Li_4Ti_5O_{12}$ materials are shown in Fig. 2b. The XRD data for the synthesized $Li_4Ti_5O_{12}$ powders are similar to the reference data, indexed to a cubic spinel structure with an Fd3m space group (JCPDS card No. 49-0207) [27,28], indicating that the minute amount of Zr doping does not affect the basic $Li_4Ti_5O_{12}$ structure. Although anatase TiO_2 powder was used as a starting material to synthesize $Li_4Ti_5O_{12}$, peaks corresponding to rutile or anatase TiO_2 did not appear. Moreover, in the reported study [29], a Zr doping amount > 0.1 M formed a ZrO_2 impurity, we found that in this study, also ZrO_2 related small intensity peak assigned at ~30° were appeared for all Zr-doped $Li_4Ti_5O_{12}$ samples. As Zr mole ratio increased, the XRD peak intensity assigned ~30° were very low and almost same. However, the ZrO_2 related peak did not appear for un-doped $Li_4Ti_5O_{12}$ samples. This result indicates that the modified solid-state reaction progressed well due to the fine particle size, which allowed the Li_2CO_3 and TiO_2 powders to be well mixed, thus facilitating Li diffusion into the TiO_2 powder. The peak position of the (111) planes of the Zr-doped $Li_4Ti_5O_{12}$ shifts to smaller angles (Fig. 2c), indicating an enlarged lattice constant of the $Li_4Ti_5O_{12}$ because of the substitution of Zr for Ti sites and the fact the ionic radius of Zr (0.079 nm) is larger than that of Ti (0.068 nm). The lattice parameters of Zr-doped $Li_4Ti_5O_{12}$ (Zr =0, 0.01, 0.05, 0.1 mol) samples calculated by Fullprof are a bout 8.355 Å, 8.356 Å, 8.357 Å and 8.362 Å, respectively. The expanded channels with the enlarged lattice constant are beneficial to the diffusion of Li-ions, thus improving the electrochemical performance of the anode.