

Characteristics of lithium titanate fabricated by an organic-inorganic solution route

Sang Jin Lee*

Dept. of Advanced Materials Science & Engineering, Mokpo National University, Muan, 534-729, Korea

A fine lithium titanate (Li_2TiO_3) powder was fabricated by an organic-inorganic solution route and its densification behavior was observed. Liquid-type ethylene glycol (EG) was used as an effective organic carrier for the dissolution of metal cations. Titanium isopropoxide and lithium nitrate were dissolved in the liquid-type ethylene glycol without any precipitation. The dried precursor gel showed a Li_2TiO_3 crystalline form at a low temperature of 300°C and a carbon-free Li_2TiO_3 was observed above 400°C. The calcined Li_2TiO_3 powder showed a soft and porous structure, and was ground easily to fine particles of 0.2 μm in size. The powder compact was densified to 91% theoretical density (TD) at a relatively low sintering temperature of 1200°C for 2 h. A significant densification was observed between at 800°C to 1100°C and the grain size was notably increased at 1200°C and above. After the abnormal grain growth, further densification was no longer observed because of the trapped pores in the over-sized grains.

Key words: Lithium titanate, Ethylene glycol, Synthesis, Sintering, Microstructure.

Introduction

Li_2TiO_3 is being evaluated as an alternative material to lithium metazirconate in the design of ceramic breeder blankets [1]. The phase Li_2TiO_3 exists in three modifications, α , β , and γ [2]. The α -phase is metastable at low temperature and transforms to the β -phase (monoclinic) at 300°C. The β -phase has a narrow homogeneity range and transforms to the γ -phase (cubic) at 1215°C [3]. In particular, an abrupt grain growth of Li_2TiO_3 around the temperature of β to γ transformation makes its densification difficult [4]. For applications, highly sinterable Li_2TiO_3 through a processable powder synthesis method is necessary. Li_2TiO_3 pellets have been prepared by various methods. The commonly employed method was direct mixing of the two oxides and then sintering of the powder compact [5]. As another chemical method, a solution combustion synthesis process using organics as the fuel was successfully developed [6]. Recently, as a new method, an organic-inorganic solution technique using polyvinyl alcohol (PVA) or ethylene glycol (EG) as a polymer carrier has been developed to establish an easier and highly productive form of soft solution processing [7-11]. PVA ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) can be also used as an organic carrier for the organic-inorganic solution route [11]. The PVA method only works with systems that are water-soluble. However, by using the polymerizing agent, EG, this process can

be extended to chemicals that decompose in water, such as titanium isopropoxide. At the optimal amount of EG polymer, the metal ions are dispersed in solution and a homogeneous polymeric network is formed. The EG method also has a distinct advantage over other sol-gel methods in that it is easier and cheaper.

In this study, highly sinetralbe Li_2TiO_3 powder was prepared by the EG method, and the crystallization behavior and powder morphology were examined. In addition, the synthesized powder was sintered and the densification behavior was compared with other sintered Li_2TiO_3 prepared by the solid-state and combustion methods.

Experimental Procedure

Titanium isopropoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and lithium nitrate (LiNO_3) were dissolved in stoichiometric proportion in liquid-type ethylene glycol. The amount of ethylene glycol was calculated using a ratio of total weight of metal ions from cation sources to the weight of ethylene glycol. In this experiment a 1 : 4 ratio was tried because all the cation sources were completely dissolved at this ratio. In a larger amount of ethylene glycol, 1 : 5 ratio, the cation sources were also dissolved, however, a minimum amount of ethylene glycol for dissolution was used in this experiment. The solution was allowed to gel for 48 h in a drying oven at 80°C. The dried gel was then heated in an air atmosphere for calcination and crystallization. Finally, the calcined Li_2TiO_3 powder was ball-milled with a zirconia media for 12 h. Isopropyl alcohol was used as a solvent for the wet-milling. The densification was conducted with the Li_2TiO_3 powder compacts made by pressing at 30 MPa into 10 mm diameter and 3 mm thick pellets. The pellets were sintered up to 1300°C for 2 h with a heating rate of 4 K

*Corresponding author:
Tel : +82-61-450-2493
Fax: +82-61-450-2490
E-mail: lee@mokpo.ac.kr

minute⁻¹. The crystallization behavior of the gel-type powders was examined using an X-ray diffractometer (Rigaku D/Max 2200) with CuK_a radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 8° minute⁻¹ and a sampling interval of 0.02°, over a range of 10-80° at room temperature. The morphologies of the crystallized powder and sintered samples were examined by scanning electron microscopy (SEM, Hitachi, S-3500N). The specimens were mounted on an aluminum stub and Au-Pd sputtered at 15 mA for 40 s. The average particle sizes of the ball-milled powders were measured by an electrophoretic light scattering spectrophotometer (ELS-8000, Photol, Tokyo, Japan). The sample cells were prepared by an ultra-sonicator for 20 minutes with a mixture of de-ionized water and powders at different pH conditions. The pyrolysis and decomposition behavior of the organic/inorganic precursor were monitored by simultaneous differential thermal analyzer and thermogravimetric analysis (DTA/TGA, Model STA 409, Netzsch GmbH, Selb, Germany) up to 1200°C, at a heating rate of 10 K minute⁻¹, in an air atmosphere. The densities of the sintered specimens at each temperature were estimated by the Archimedes' method using distilled water as a displacement liquid.

Results and Discussion

In a 1 : 3 ratio, titanium isopropoxide was not completely dissolved even with long time stirring. A transparent sol was obtained at a 1 : 4 ratio. The yellow-colored, dried precursor gel was sticky and hard, however, the calcined powder was white-colored and porous with soft agglomeration. The morphology of 400°C calcined powder and its particle size distribution are shown in Fig. 1. The particle shape was irregular and a wide particle size distribution, from 0.3 μm to 2.0 μm, was observed.

The crystalline development of the Li₂TiO₃ precursor at each temperature is presented in Fig. 2. The first crystallization of the monoclinic Li₂TiO₃ phase was observed at 300°C, and the peaks gradually developed as the temperature increased retaining the monoclinic

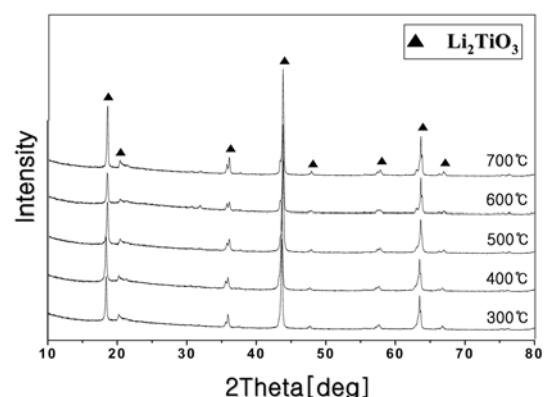


Fig. 2. XRD patterns of Li₂TiO₃ precursor prepared by EG method.

structure, which has a narrow homogeneity range [3]. The first crystallization temperature of 300°C was significantly lower in comparison with the case of solid-state reactions [4,6]. This may be due to the atomic-scale homogeneous mixing of cations by the effect of the polymer carrier. The Li₂TiO₃ powder crystallized at 300°C showed a bright grey color, however, the color changed to a white color at 400°C. The grey color may be due to the residual carbon derived from the pyrolyzed polymer, and this was examined by looking at the thermal decomposition behavior of the precursor. The result of thermal analysis of the organic-inorganic precursor is presented in Fig. 3. A large exothermic peak was observed at 272°C and this was due to the pyrolysis of ethylene glycol resulting from the breaking of the polymer structure and burn out of the resultant carbon by oxidation [12]. A significant weight loss was also observed at this temperature simultaneously by the removal of free organics and carbon. From this result, it is certain that all polymers were burned out by 272°C. However, in the real calcination process, some residual carbon may have existed to a slightly higher temperature. The removal of a large amount polymer, about 80 wt% of the total weight (Fig. 3), during the calcination process resulted in the porous and soft

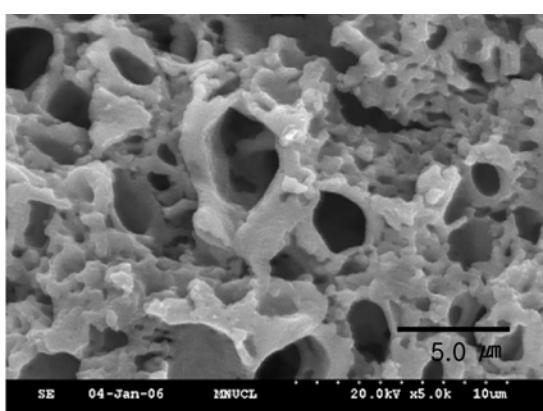


Fig. 1. SEM micrograph of calcined Li₂TiO₃ powder and its particle size distribution.

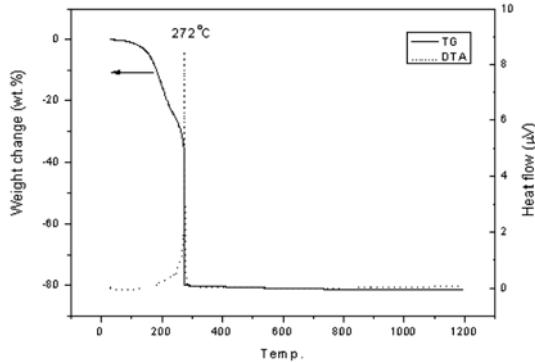


Fig. 3. The result of thermal analysis of the organic-inorganic precursor.

powder microstructure as shown in Fig. 1. In this study, carbon-free Li_2TiO_3 powder, obtained by calcination at 400°C , was used for the following ball-milling process.

In the milling process of the calcined Li_2TiO_3 powder, fine particles were easily obtained from the soft and porous powder structure. The particle sizes of the ball-milled, fine powders are presented in Fig. 4. The agglomerated, ball-milled powders were ultra-sonicated for 20 minutes in each pH solution, and then the average particle size and zeta potential at each suspension were measured. According to the zeta potential result, it can be seen that the agglomerated Li_2TiO_3 powder was well dispersed in the solution at pH 11. At this condition, the particle size was about $0.2 \mu\text{m}$ and the measured zeta potential was -42 mV .

The sintering behavior of the ball-milled Li_2TiO_3 powder compacts is shown in Fig. 5. A large increase of density was observed between at 800°C to 1100°C accompanied by about 16% linear shrinkage. However, a further large increase of density was no longer observed above 1100°C and finally stopped at 1200°C . The powder compact prepared by the ethylene glycol method showed a notably higher relative density of 91% at 1200°C in comparison with the 75% theoretical density of the sintered Li_2TiO_3 prepared by a solid-state reaction [4,6]. Actually, the densification of Li_2TiO_3 does not occur easily because of its fast grain growth behavior during the sintering process. The grain growth

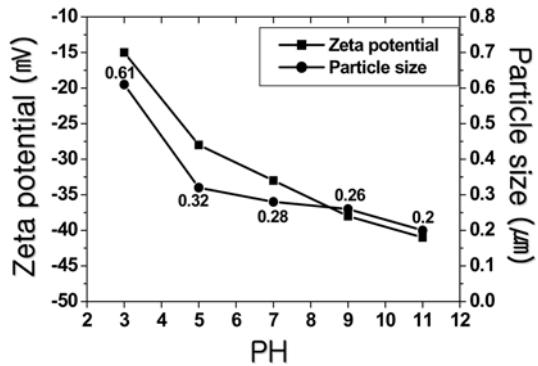


Fig. 4. Average particle size and zeta potential of ball-milled Li_2TiO_3 powders at each pH value.

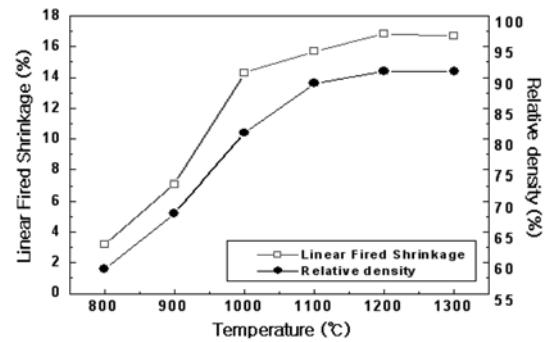


Fig. 5. Densification behavior of ball-milled Li_2TiO_3 powder compacts.

behavior is presented in Figs 6 and 7. The grain size in the densified Li_2TiO_3 at 1100°C was about $1.2 \mu\text{m}$ and some submicron-sized, the inter-granular pores were observed (Fig. 6). However, at a 100°C higher temperature (1200°C), a noticeable grain growth was observed and it resulted in pores trapped in the over-sized grains (Fig. 7). So, the densification needs to occur at a low temperature before the abnormal grain growth. In the ethylene glycol method, pure and fine Li_2TiO_3 powder was obtained by the simple ball milling process with a porous powder and it was densified up to 91% theoretical density below the temperature where abnormal grain growth started.

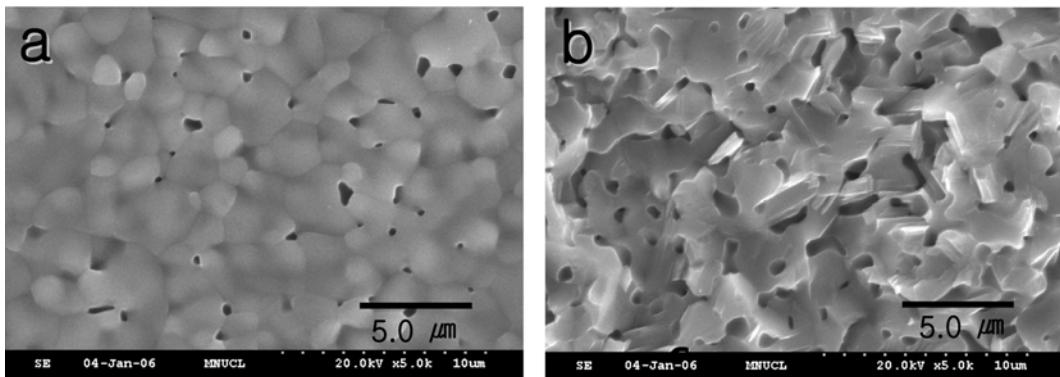


Fig. 6. SEM micrographs of Li_2TiO_3 sintered at 1100°C for 2h (a) surface, (b) fracture.

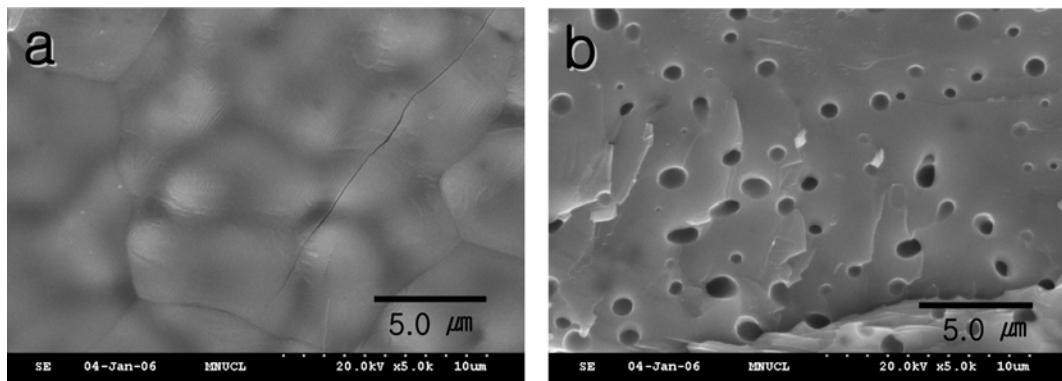


Fig. 7. SEM micrographs of Li_2TiO_3 sintered at 1200 $^{\circ}\text{C}$ for 2h (a) surface, (b) fracture.

Conclusions

The organic-inorganic solution route employing liquid-type ethylene glycol was successfully used for the fabrication of highly sinterable Li_2TiO_3 . The mixture of ethylene glycol and cation sources was homogeneous on an atomic scale. In particular, the polymeric network structure of ethylene glycol contributed to form a soft and porous calcined powder. The powder was crystallized to monoclinic Li_2TiO_3 at the low temperature of 300°C and the crystallized powder was capable of being ground to nano-sized powder by a simple ball milling process. The ball-milled powder showed an excellent sintering behavior at a relatively low temperature in comparison with other Li_2TiO_3 powders fabricated by a solid state reaction. A small grain size of 1.2 μm was observed in the densified Li_2TiO_3 sintered at 1100°C and then abnormal grain growth occurred at 1200°C without any increase of density. Finally, the simple, processable organic-inorganic solution route worked as a suitable method for making highly sinterable Li_2TiO_3 .

Acknowledgement

This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-D00387).

References

1. H. Hamilton, J. Nucl. Mater. 219 (1995) 274-283.
2. J. C. Mikkelsen, J. Am. Ceram. Soc. 63[5] (1980) 331-353.
3. H. Kleykamp, Fusion Eng. Design 61-62 (2002) 361-366.
4. C. H. Jung and J.Y. Park, J. Nucl. Mater. 341 (2005) 148-152.
5. C. E. Johnson, K.R. Kummerer, and E. Roth, J. Nucl. Mater. 155-157 (1988) 188-201.
6. C. H. Jung, J. Y. Park, S. J. Oh, H. K. Park, Y. S. Kim, D. K. Kim, and J. H. Kim, J. Nucl. Mater. 253 (1998) 203-212.
7. M. A. Gulgum, M. H. Nguyen, and W. M. Kriven, J. Am. Ceram. Soc. 82[3] (1999) 556-560.
8. M. H. Nguyen, S. J. Lee, and W. M. Kriven, J. Mater. Res. 14[8] (1999) 3417-3426.
9. S. J. Lee and W. M. Kriven, J. Am. Ceram. Soc. 81[10] (1998) 2605-2612.
10. S. J. Lee, E. A. Benson, and W. M. Kriven, J. Am. Ceram. Soc. 82[8] (1999) 2049-2055.
11. S. J. Lee, M. D. Biegalski, and W. M. Kriven, J. Mater. Sci. 14[7] (1999) 3011-3006.
12. K. Kiss, J. Madger, M. S. Vukasovich, and R. J. Lockhart, J. Am. Ceram. Soc. 49[6] (1996) 291-294.