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A polymer solution technique for the synthesis of nano-sized Li_2TiO_3 ceramic breeder powders

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Abstract

Nano-sized Li_2TiO_3 powder was fabricated by an organic–inorganic solution route. A steric entrapment route employing ethylene glycol was used for the preparation of the nano-sized Li_2TiO_3 particles. Titanium isopropoxide and lithium nitrate were dissolved in liquid-type ethylene glycol without any precipitation. With the optimum amount of the polymer, the metal cations (Li and Ti) were dispersed in the solution and a homogeneous polymeric network was formed. The organic–inorganic precursor gels were turned to crystalline powders through an oxidation reaction during a calcination process. The dried precursor gel showed the carbon-free Li_2TiO_3 crystalline form which was observed above 400 °C. The primary particle size of the carbon-free Li_2TiO_3 was about 70 nm, and the structure of the crystallized powder was porous and agglomerated. The powder compact was densified to 92% of TD at a relatively low sintering temperature of 1100 °C for 2 h.

1. Introduction

Lithium-containing ceramics have been considered as tritium breeding materials of the ITER test blanket module (TBM) for the DEMO reactor [1]. To date, considerable work has been done on the fabrication of Li_2TiO_3 pebbles, characterizing the tritium release behavior and developing a properties database [2–4]. The previous research has shown that Li_2TiO_3 has attractive properties that are better than those for other lithium-containing compounds. Li_2TiO_3-sintered body can be prepared by various methods. The most commonly employed method is an indirect mixing of the two oxides followed by compaction and sintering [5]. For this application, highly sinterable Li_2TiO_3 through a processable powder-synthesis method is necessary.

Ceramic powder processing is evolving in the direction of a chemical synthesis of the powders [6]. Methods based on a soft-solution processing provide powders with the desired properties. Recently, an organic–inorganic solution technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG ($HOCH_2CH_2OH$, ethylene glycol) as a polymer carrier has been developed to make the soft-solution processing easier and more productive [7–15]. The polymer ensures a homogeneous distribution of the metal ions in its polymeric network structure and it inhibits their segregation or precipitation from the solution. In the solution involving a polymer and nitrate ions, a continuous long chain polymer prevents a contact between the cations and it limits their agglomeration and precipitation [9–19]. In a water–soluble system, the PVA polymer only works with systems. However, by applying an EG polymerizing agent, the process can be extended to chemicals that decompose in water, such as metal-alkoxide (titanium isopropoxide). In particular, the ethylene glycol can act as an

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effective solvent for a wet chemical synthesis of a titanate powder because the water–soluble titanium salt is not available commercially [16,20]. At the optimal amount of an EG polymer, the metal ions are dispersed in a solution and a homogeneous polymeric network is formed.

In the present study, nano-sized Li_2TiO_3 powder is prepared by the EG method, and the effect of the polymer content, the crystallization behavior and the powder morphology are examined.

2. Experimental procedure

Titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$, TISO, Alfa Chem.) and lithium nitrate ($LiNO_3$, Aldrich Chem.) were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chem.). The amount of EG was calculated by using a ratio of the total weight of the metal ions from cation sources to weight of the EG. In this experiment a 1:4 ratio was tried. The transparent solution was then allowed to gel for 48 h in a drying oven at 80 °C. The dried gels were then calcined at various temperatures. The inside of the furnace was monitored through a window in the low temperature range (100–300 °C) to observe the explosive reaction. Finally, the calcined powders were planetary milled with a dia 5 mm zirconia media for 12 h. Isopropyl alcohol was used as a solvent for the milling, and the milling speed was 200 rpm.

The crystallization behavior of the gel-type precursor powders was examined as a function of the temperature, by using an X-ray diffractometer, with a scanning speed of 4°/min and a sampling interval of 0.02°. The crystallite size of the particles was calculated using the following Scherrer's equation from XRD data, $B - b = (\kappa \cdot \lambda)/(d \cdot \cos\theta)$, where, B is the half-value breadth (rad), b is the half-value breadth for materials of which crystallite size is larger than 100 nm, κ is the shape factor ($\kappa = 0.9$ at sphere), λ is the wave length of X-ray (Cu Kα; $\lambda = 0.15418$ nm), d is the crystallite size of Li_2TiO_3 (nm) and θ is the angle of diffraction (rad). The pyrolysis and decomposition behavior of the dried precursor were monitored by DTA-TG up to 1000 °C at a heating rate of 10 °C/min in an air atmosphere. The morphologies of the porous, crystallized powder and planetary milled powders were examined by scanning electron microscopy. Fig. 1 shows the details of the preparation process. In the case of pebble preparation, the polyvinylalcohol (PVA) solution was fabricated by dissolving 2 wt% of PVA in deionized water and spraying it onto the calcined and milled powders while they were being rolled with 150 rpm in a plastic jar. The primary wet-powder was sieved with 50 mesh screen. The sieved powder took the shape of granule-type spheres. For high-green density pebbles, these spheres were rolled again for several hours at various rolling speeds.

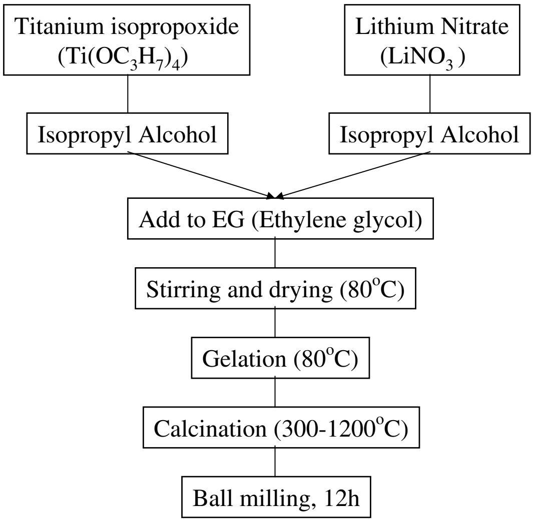

Fig. 1. Schematic diagram of the ethylene glycol method.

3. Results and discussion

During the synthesis of lithium monotitanate, soft-precipitates were formed in the solution of the ethylene glycol containing Ti-isopropoxide, due to the water in the precursor solution but they were dissolved after a stirring. The precursor solution with dissolved titanium isopropoxide and lithium nitrate has a pale yellow color. During the drying process at 80 °C, the transparent sol turned to a soft gel. The application of heating to the gel resulted in a charred foam structure.

Simultaneous DTA/TG results of the precursor gel from room temperature to 1000 °C are given in Fig. 2. In the TGA curve, the mass change occurred in three stages (1) 135 °C to 191 °C, (2) 210 °C to 257 °C and (3) 260 °C to 300 °C. The DTA showed two exothermic peaks at 170 °C and 235 °C, and one endothermic peak at 280 °C. In general, polymer decomposition occurs by two steps [21]. The first step is degradation of the polymeric structure by pyrolysis, which is then followed by oxidation of residual carbon. In the EG method, the first mass change was due to pyrolysis of EG resulting in breaking of bonds, removal of free organics from metal-ion sources and release of N_xO_y gases. An exothermic at 235 °C in the

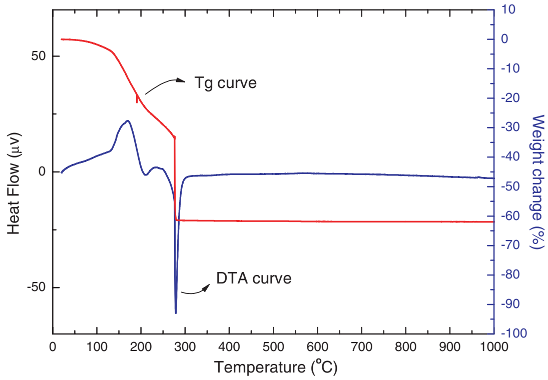

Fig. 2. DTA/TG curves for the dried precursor prepared by the ethylene glycol method (mass ratio of metal ions to EG is 1:4).

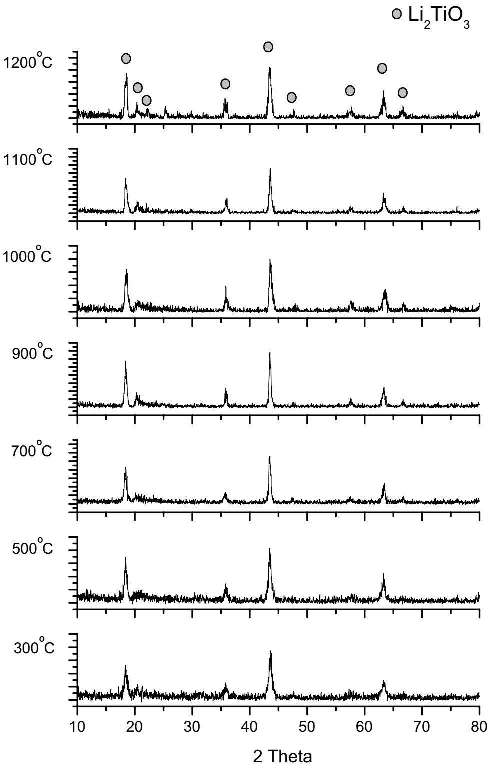

Fig. 3. XRD patterns of the Li_2TiO_3 prepared by the ethylene glycol method at the various calcinations temperature.

second weight change was due to the burn out of residual carbon by oxidation with CO and CO_2 gases form. The endothermic peak appeared at 280 °C, which was corresponded to the decomposition of Li–Ti-compound.

Fig. 3 shows the XRD results of the calcined precursor powders at different temperatures. Duration of calcinations time for these studies is 1 h holding at each calcinations temperature. The first crystalline form was observed at 300 °C, and the peaks were gradually enhanced as the temperature increased.

The powder morphologies of the crystalline Li_2TiO_3 derived from the 1:4 ratio material and the planetary ball-milled Li_2TiO_3 powder are shown in Fig. 4. The removal of the polymer during the calcination process resulted in a porous and soft agglomerated microstructure. The 400 °C crystallized Li_2TiO_3 powder showed agglomerated, fine particles of about 70 nm in size as shown in Fig. 4(a). The small particle size may also be due to the homogeneous mixing and relatively low crystallization temperature. The powder milled for 12 h showed submicrometer particles with an agglomeration (Fig. 4(b)). During the milling process, the efficiency was improved by the soft and porous powder structure in comparison with non-porous powders.

In Fig. 5, in order to examine the effect of the sintering temperature on the densification of the as-prepared pellets, the green compacts (the powders were synthesized by EG method, combustion synthesis and solid-state reaction) were sintered at temperatures from 800 to 1300 °C for 2 h and 4 h, respectively. In general, the increase of the sintering temperature raises the density of the compacts. The powder compact from the EG method (see solid cycle) showed a notably higher relative density of 92% TD at 1100 °C for 2 h (relative density (% TD) = measured density of the specimen/theoretical density of Li_2TiO_3, 3.43 g/cc). The compacts of combustion synthesis could be sintered to 82% of TD and solid-state one has 70% TD at a temperature 1100 °C. At a given temperature, the green compacts prepared from EG method-derived powders sinter to higher densities compared to the green compacts prepared from the combustion synthesis, solid-state reaction or reference results. This is because the EG

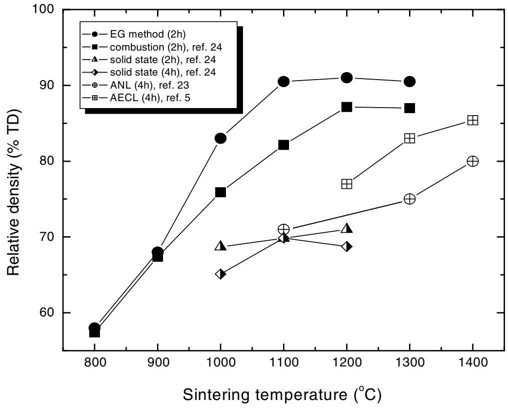

Fig. 5. Variation of the relative density of the Li_2TiO_3 pellets [5,23,24].

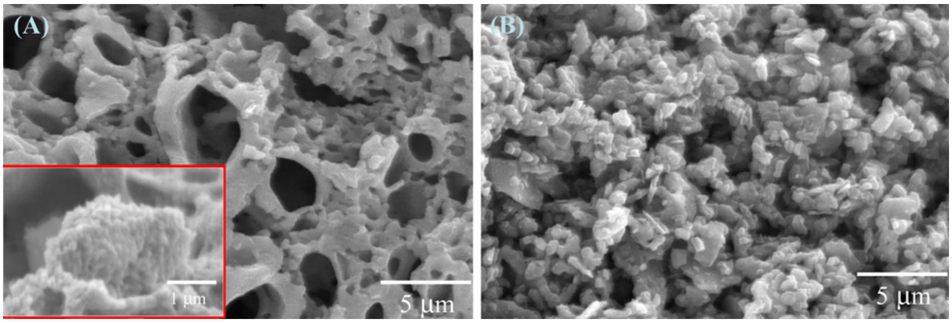

Fig. 4. SEM micrograph of the Li_2TiO_3 powder calcined at 400 °C. (a) Before planetary ball-milled and (b) after milled for 12 h.

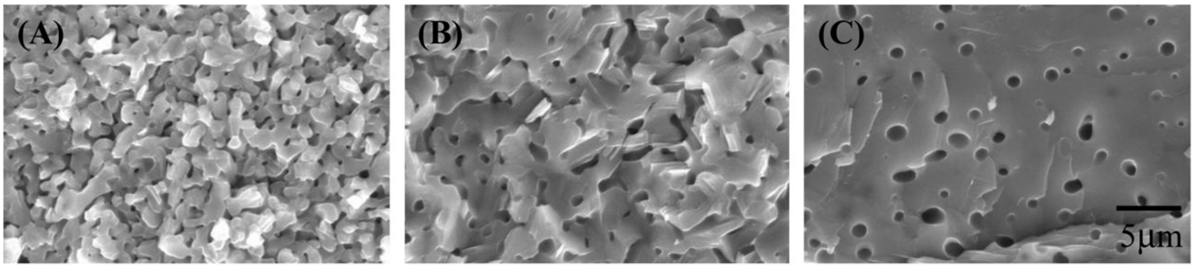

Fig. 6. SEM micrographs of the fractured surface of the Li_2TiO_3-sintered a (a) 1000 °C, (b) 1100 °C, and (c) 1200 °C, respectively.

powders have small particle size and higher surface areas and relatively larger soft particles compared to those of combustion synthesis or solid-state reaction powders. The EG powder has smaller crystallite size which helps in acceleration of the sintering at a relatively low temperature with result that no further holding time needs at high temperatures.

Actually, a densification of Li_2TiO_3 is not easy because of its fast grain growth at sintering temperature. A rapid grain growth results in several large pore traps in over-sized grains or on grain boundaries. This closed pore dose not removed during any additional sintering process. So, a densification should occur at a relatively low temperature before a rapid grain growth. According to the sintering results, there is no increasing densification up to 1300 °C, therefore the initiating temperature for a rapid grain growth was about 1100 °C. The sintered microstructures from the EG method are shown in Fig. 6. A rapid grain growth occurred and trapped pores in the grains were observed at 1200 °C for 2 h. The optimum temperature and time for sintering Li_2TiO_3 powders derived through the EG method is 1100 °C for 2 h.

In the pebbles by a dry-rolling granulation process (DRGP), the low-density pebbles became harder as the rolling time increased [22]. At the same time, the pebbles increased in size by combining with nearby powders from less dense pebbles. After a rolling for several hours, spherical particles with a higher green density were obtained. The pebbles were not deformed by handling and they were densified by the sintering process. Fig. 7 shows the change of the morphology of Li_2TiO_3 pebbles prepared by DRGP. Among the several processing parameters, binder content and particle size of the starting powder have a significant influence on rolling time and sphericity of the pebbles. As the particle size of the starting powder became smaller, the pebbles had a better sphericity. Therefore, decreasing the particle size of the starting powder may be a helpful method for an effective process control. Using the nano-sized Li_2TiO_3 powders prepared by the EG method, once the processing conditions are fixed, the DRGP should be a good process for the fabrication of impurity-free and mass produced pebbles.

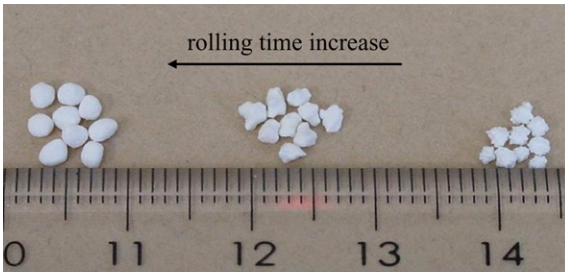

Fig. 7. Morphology change of the Li_2TiO_3 pebble by dry-rolling granulation process.

4. Conclusions

The ethylene glycol method was successfully used for the fabrication of Li_2TiO_3. This new method by employing water–insoluble chemicals as a source of the titanium ions has a distinct advantage over other chemical synthesis methods and is easier and cheaper. The simple, processable precursor could be synthesized by a steric entrapment of the cations using the ethylene glycol polymer to avoid a selective precipitation, the method produced a homogeneous mixing on a molecular scale. The porous powder crystallized at low temperature was capable of being ground to a nano-sized powder by a simple ball milling process, and the ball-milled powder showed an excellent sintering behavior at relatively low temperature. The ethylene glycol method is expected to find application to the synthesis of nano-sized Li_2TiO_3 powders because of its merits, such as being a cheap and simple process, and allowing an easy control of the crystalline form and particle size.

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