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Preparation of Amorphous Li_4SiO_4 Nanoparticles from Crystalline Raw Material by RF Thermal Plasma

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Abstract: Amorphous lithium ortholsilicate (Li_4SiO_4) nanoparticles which are promising material for solid electrolyte were synthesized by the RF thermal plasma. Micro-sized crystalline Li_4SiO_4 raw powder was evaporated in the thermal plasma, followed by the production of amorphous Li_4SiO_4 nanoparticles. The amorphization degree and particle size of product were compared in different powder feed rates, carrier gas flow rates, and working gases.

Keywords: RF thermal plasma, quenching, amorphous nanoparticle, solid electrolyte.

1. Introduction

A large free volume allows the application of glass materials to ion conductive solid material. Lithium orthosilicate (Li_4SiO_4) is one of ion conductive glass which is a promising material to substitute flammable organic liquid electrolyte used in a lithium-ion battery [1–3]. In order to use Li_4SiO_4 material as the solid electrolyte, amorphous nanoparticles are strongly required. It is because ionic conductivity is improved by increasing the mobility of lithium ion in an electrolyte.

Although a rapid quenching is required to produce amorphous nanoparticles from gas phase, it is difficult with conventional method due to limited quenching rate [4]. In the present work, the radio frequency (RF) thermal plasma was used to synthesize amorphous Li_4SiO_4 nanoparticles from the raw crystalline Li_4SiO_4 powder which is 10 μm in mean size. The RF thermal plasma can evaporates any kind of raw material with a large volume of high temperature region to produce nanoparticles form gas phase of each constituent element [5, 6]. Vaporized crystalline Li_4SiO_4 powder re-forms Li_4SiO_4 nanoparticles in amorphous phase, and crystallization and particle growth can be suppressed by the quenching process in the peripheral region of thermal plasma flame under adequate operating conditions. In order to control the particle size and crystallinity of Li_4SiO_4 nanoparticles, raw powder feeding rate and carrier gas flow rate were controlled in this work. In addition, effect of oxygen working gas on the synthesis process was also examined.

2. Experimental setup

A schematic diagram and operating condition of the RF thermal plasma system for the synthesis of amorphous Li_4SiO_4 nanoparticles is presented in **Fig. 1** and **Table 1**, respectively. The constant input power of 30 kW was provided by a RF power supply at the fixed frequency of 4 MHz. The operating pressure of inside a chamber where nanoparticles were synthesized was fixed at 101.3 kPa. Argon 5 L/min was used for inner gas which was introduced into the plasma torch around a powder injection probe. Two types of sheath gases which were introduced into the torch with swirl flow along the inner wall of a plasma confinement tube were compared to examine the influence of oxygen. Although main sheath gas was constant as argon 60 L/min, argon or oxygen 5 L/min was used as additional sheath gas. As raw material, crystalline

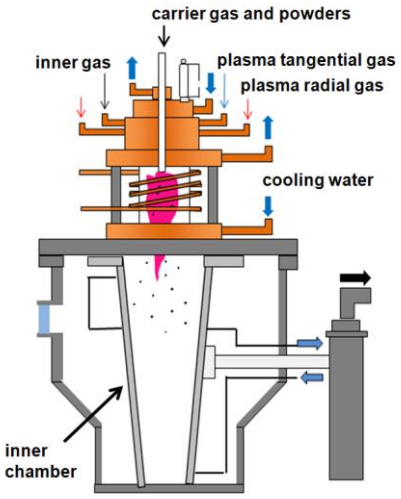

Fig.1 Schematic diagram of RF thermal plasma system for the synthesis of amorphous Li_4SiO_4 nanoparticles.

Table 1 Operating condition of RF thermal plasma system.

Input power [kW]	30
Operating pressure [kPa]	101.3
Inner gas [L/min]	Ar 5
Main sheath gas [L/min]	Ar 60
Additional sheath gas [L/min]	Ar 5.0 or O_2 5.0
Carrier gas [L/min]	Ar 2.5, 5.0, 7.5 or O_2 5.0
Powder feeding [mg/min]	50, 200, 600, or 1000

Li_4SiO_4 powder was injected into thermal plasma with argon or oxygen carrier gas. The flow rate of argon carrier gas was changed from 2.5 to 7.5 L/min, while the oxygen carrier gas flow rate was fixed at 5 L/min. The mean size of raw powder was about 10 μm with irregular shape. The feeding rate of raw powder was controlled by a powder feeder at 50, 200, 600, and 1000 mg/min.

Injected raw powder is evaporated by the high temperature of RF thermal plasma in the torch region. When vapors exceed the saturation vapor pressure with decreasing plasma temperature in the tail region of plasma flame, they form nuclei, and then nanoparticles start to grow. According to the quenching environment, growths of particle size and crystalline grain are limited producing amorphous Li_4SiO_4 nanoparticles. They were collected on the cooling wall of inner chamber. The morphology and size of products were observed by a transmission electron microscope (TEM, JEM-2010F, JEOL, Japan). In TEM images, 100 spherical particles were analyzed to estimate the average diameter of nanoparticles produced in each experimental condition. Since Li_4SiO_4 is well know material that absorbs CO_2 in low temperature and release it high temperature, the emission of CO_2 was observed by thermal gravimetric analysis (TGA, Thermo Plus, Rigaku, Japan) in inert helium environment. After the removal of CO_2 in the TGA, the elemental analysis of Li_4SiO_4 surface was conducted by X-ray photoelectron spectroscopy (XPS, JPS-9200, JEOL, Japan) to examine the change of material composition quantitatively.

The crystallinity of product was measured by X-ray diffraction (XRD, MiniFlex, Rigaku, Japan). In order to evaluate the amorphization degree of Li_4SiO_4, the method of internal standard was used in the present work. As a standard material, ZnO powder was employed. The standard curve was plotted from the intensity ratio of Li_4SiO_4 to ZnO in XRD measurement according to the composition of Li_4SiO_4 raw powder in the mixture of it and ZnO. In order to evaluate the amorphization degree (D_a), the intensity ratio of Li_4SiO_4 product after plasma treatment to ZnO was measured at a prescribed composition of Li_4SiO_4 product in the mixture of it and ZnO (X). At the same intensity ratio of Li_4SiO_4 product to ZnO, the composition of crystalline Li_4SiO_4 raw material in the mixture of it and ZnO (X') was found in the standard curve. The amorphization degree is evaluated follows:

$$D_a = \frac{X}{X - X'} \times 100 \qquad (1)$$

where, the unit of amorphization degree is %.

3. Result and Discussion

3.1 Effects of powder feeding rate

Measured XRD patterns in different powder feeding rates are shown in **Fig. 2**. The powder feeding rate was controlled in the range of 50 – 1000 mg/min at the fixed argon carrier gas flow rate of 5 L/min. Although characteristic peaks for crystalline Li_4SiO_4 raw material at each 2θ angle are also found after RF thermal plasma treatment, peak intensities are significantly decreased. This result means that synthesized material is amorphized Li_4SiO_4. In **Fig. 3**, the amorphization degree of Li_4SiO_4 is presented according to the powder feeding rate. It was decreased from 82% to 57% with increasing the powder feeding rate from 50 to 1000 mg/min. These results can be explained by the evaporative latent heat. Since a required heat to evaporate raw material increase with increasing the powder feeding rate, plasma temperature is decreased in the case of high powder feeding rate. Therefore, temperature gradient in the quenching region is decreased with increasing the powder feed rate. Since a rapid quenching with a steep temperature gradient suppresses the growth

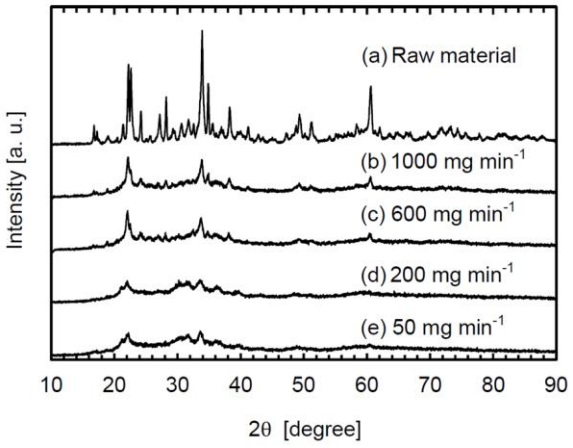

Fig.2 XRD patterns of raw Li_4SiO_4 powder and products according to powder feeding rate at 5 L/min argon flow rates for carrier and additional sheath gases.

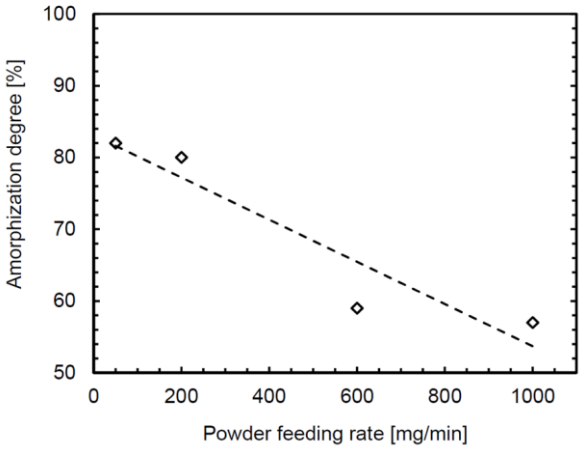

Fig.3 Amorphization degree of Li_4SiO_4 according to powder feeding rate at 5 L/min argon flow rates for carrier and additional sheath gases.

of crystalline grain, the amorphization degree is increased with decreasing the powder feeding rate. In addition, injected raw materials are easily evaporated in the upstream of thermal plasma leading to the radial diffusion of synthesized particles. Since the temperature gradient in the radial direction is higher than that in the axial direction of thermal plasma flow, a low powder feeding is advantageous to synthesize amorphous Li_4SiO_4 nanoparticles.

TEM images of products are presented in **Fig. 4**. After the RF thermal plasma treatment, the morphology of products is changed into the spherical shape and particle sized was significantly reduced from 10 μm to less than 100 nm. In the product, particle size was increased with increasing the powder feeding rate. It is because, a large number of vapors with a high powder feeding rate results in the growth of particle size. As a result, average particle sizes in cases of 200, 600, and 1000 mg/min were 38.4, 62.7, and 86.1 nm, respectively.

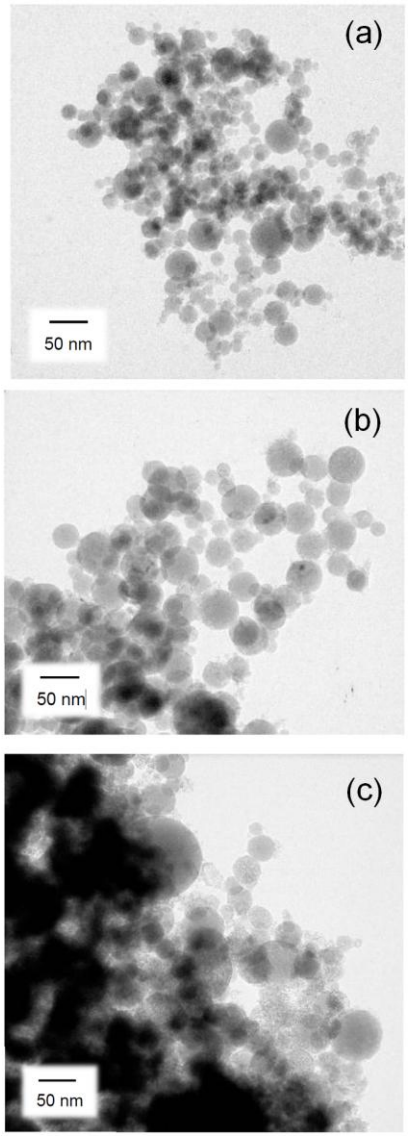

Fig.4 TEM images of synthesized amorphized Li_4SiO_4 nanoparticles in different powder feeding rates of (a) 200 mg/min, (b) 600 mg/min, and (b) 1000 mg/min at 5 L/min argon flow rates for carrier and additional sheath gases.

3.2 Effects of argon carrier gas flow rate

Effects of carrier gas flow rate on the amorphization degree and particle size of Li_4SiO_4 were also examined. As shown in **Fig. 5**, peak intensities for synthesized Li_4SiO_4 nanoparticles were similar each other even though the flow rate of argon carrier gas was changed. As a result, the amorphization degree of Li_4SiO_4 in **Fig. 6** is almost constant at around 80% in different argon carrier gas flow rates from 2.5 L/min to 7.5 L/min. Since the number of vapor in the process of particle growth is constant at the fixed powder feeding rate of 200 mg/min, the average particle size was about 40 nm regardless of the carrier gas flow rate.

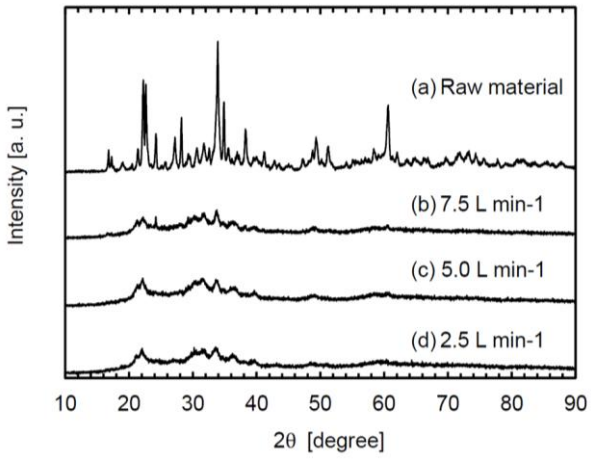

Fig.5 XRD patterns of raw Li_4SiO_4 powder and products according to the flow rate of argon carrier gas at the fixed powder feeding rate of 200 mg/min.

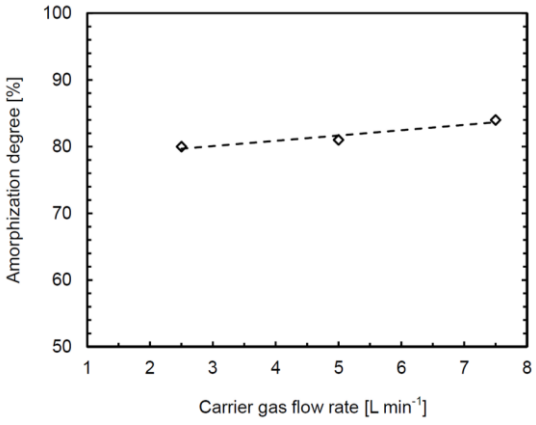

Fig.6 Amorphization degree of Li_4SiO_4 according to the flow rate of argon carrier gas at the fixed powder feeding rate of 200 mg/min.

3.3 Effects of oxygen working gas

As listed in **Table 1**, oxygen was used for additional sheath gas or carrier gas. At 10000 K, the thermal conductivity of oxygen is higher than that of argon at about twice [7]. Amorphization degrees with different working gas conditions are presented in **Fig. 7**. Compared with the case of pure argon condition, the amorphization degree of Li_4SiO_4 is slightly decreased when oxygen is used as additional sheath gas, whereas it is improved with oxygen carrier gas. However, the difference is negligible. Therefore, more thermally conductive working gas such as helium is required to change the amorphization degree.

Fig. 8 shows TGA results of synthesized amorphous Li_4SiO_4 nanoparticles which were exposed to air for 2 hours and 2 months. Since absorbed CO_2 in Li_4SiO_4 is released in a high temperature of several hundred degrees,

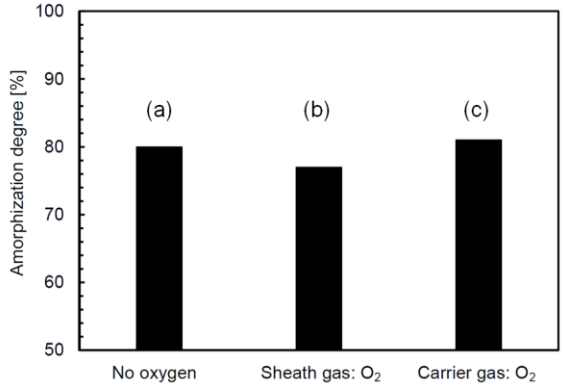

Fig.7 Comparison of amorphization degrees of Li_4SiO_4 with different working gas conditions of (a) pure argon, (b) oxygen additional sheath gas, and (c) oxygen carrier gas at 200 mg/min for powder feeding rate.

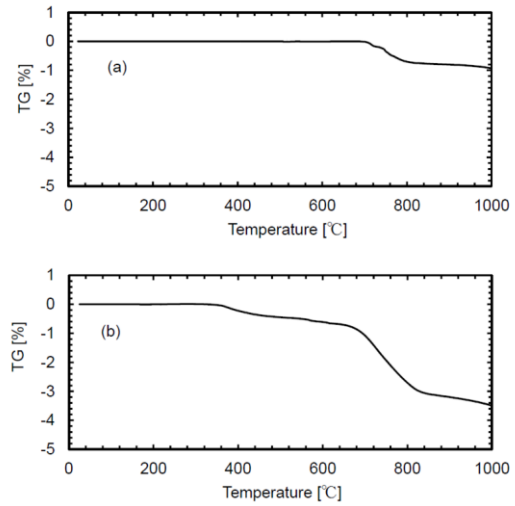

Fig.8 TGA results on amorphous Li_4SiO_4 nanoparticles to for (a) 2 hours and (b) 2 months after synthesized at 200 mg/min for raw powder feeding rate.

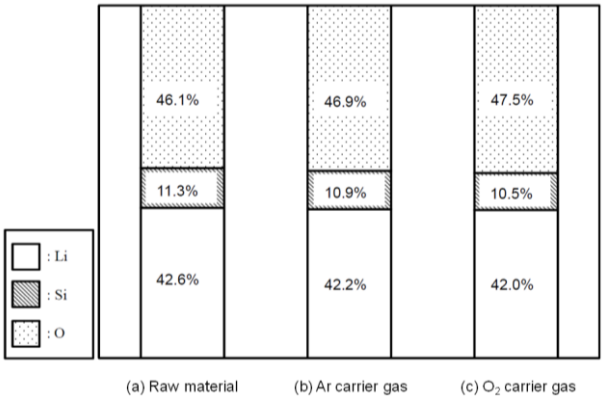

Fig.9 XPS results on (a) raw material and amorphous Li_4SiO_4 nanoparticles after RF thermal plasma treatment with (b) Ar carrier gas and (c) O_2 carrier gas at 200 mg/min for raw powder feeding rate.

the mass reduction is observed by increasing the temperature in TGA. After the removal of CO_2 from synthesized amorphous Li_4SiO_4 nanoparticles, XPS measurement was conducted. As shown in **Fig. 9**, surface composition seems to be unchanged after RF thermal plasma treatment. Therefore, it was confirmed that amorphous Li_4SiO_4 nanoparticles were synthesized form crystalline Li_4SiO_4 powder without the change of material composition.

4. Conclusion

Amorphous Li_4SiO_4 nanoparticles were synthesized from micro-sized crystalline Li_4SiO_4 raw powder by the RF thermal plasma. Growths of crystalline structure and particle size were suppressed by enhanced quenching rate and small amount of vapor in thermal plasma with a low powder feeding condition. Effects of carrier gas flow rate and oxygen working gas on the synthesis of amorphous Li_4SiO_4 nanoparticles were negligible. Therefore, the powder feeding rate is an important parameter to control the preparation of amorphous Li_4SiO_4 nanoparticles.

5. References

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