

Effect of particle size on the density and ionic conductivity of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ NASICON

Sang-Min Lee, Sung-Tae Lee, Dae-Han Lee, Sang-Hyung Lee, Sang-Soo Han and Sung-Ki Lim*

Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Kwangjin-gu, Seoul 143-701, South Korea

In this work, the correlation between density and ionic conductivity of the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ NASICON system is investigated. To control the densities of sintered pellets, particles with sizes of about 670 nm and 360 nm were used. XRD, SEM, density measurement, and electrochemical impedance spectroscopy were used to study the properties of the samples. The relative densities (theoretical density = 3.27 g/cm^3) of samples were measured at 91% and 96% for the 670 nm and 360 nm particles, respectively. Impedance spectroscopy data showed a significant increase of ionic conductivity in proportion to the density. The results indicate that the ionic conductivity of the sample not containing free zirconia from jet milling processing is higher than that of the sample containing free zirconia prepared by only ball-milled powder at the same density.

Key words: NASICON, Solid electrolyte, Density and Ionic conductivity.

Introduction

Sodium super ion conductors (NASICONs) are compounds with high sodium conductivity. NASICON compounds have high ionic conductivity, low thermal expansivity, and near isotropic mobility of ions. They are used as a solid electrolyte of sodium based batteries, in gas sensors, and as an ion selective electrode when ion-selective and high ionic conductivity are needed [1-3]. NASICON structures can be described in three-dimensional terms as they form a three-dimensional network structure; octahedra ZrO_6 is the corner-sharing tetrahedra SiO_4 and PO_4 , Na^+ ions are located therein [4, 5].

The most commonly studied NASICONs have the general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($1.6 < x < 2.2$). As ionic conductivity is generally increased by almost 2, the activation energy is lowered. NASICONs have a monoclinic structure at room temperature. Phase change occurs to a rhombohedral structure with high conductivity at $150 \sim 300^\circ\text{C}$ [6-8].

The easiest and most certain way to improve the ionic conductivity of the solid electrolyte is to increase the density. However, the problem is the formation of free zirconia due to the volatilization of P and Na in the NASICON synthesis step [9-11]. Free zirconia formation prevention, which can be controlled by adjusting the sintering conditions and the synthesis conditions, is essential to increase the density of NASICON.

Densification mainly occurs due to a change in free energy from the decrease in surface area and lowering

of the surface free energy. Free energy can be much higher when the precursor is a fine particle [12]. However, no detailed investigation has been carried out on increasing the conductivity by only the control of bulk density by the jet milling process, without the control of the condition of calcination or sintering process in NASICON. In this study, using a jet milling process, the effect of density on the conductivity without forming a free zirconia phase was investigated by adjusting the density of the sintered specimen by controlling the size of the NASICON powder.

Experimental

NASICON powder with a composition of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ($x = 2$) was prepared from the solid state reaction of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Junsei, JAPAN), ZrO_2 (Yakuri pure chemicals, JAPAN), and SiO_2 (Junsei, JAPAN). The powder was ball-milled in methanol with zirconia balls for 6 h. The mixture was dried at 90°C for 24 h, and the powder were calcined at 1100°C for 6 h. Part of the calcined powder was jet milled again to obtain a smaller particle size. The ball-milled powder and the jet milled powder were characterized using a laser diffraction particle size analyzer (Shimadzu Ltd.;SALD-200A). The ball-milled powder and the jet milled powder were mixed at a weight ratio of 3 : 1, 1 : 1, and 1 : 3. The pellets (25 mm diam. and 2 mm thick) were fabricated by uniaxial-pressing with a pressure of 100 bars and the samples were then sintered at 1210°C for 2 h. The other sample was prepared by only ball-milled powder and sintered at 1250°C for 2 h to use as a comparison group; the sample contained a free zirconia phase.

The phase analysis was performed using X-ray diffraction (XRD; Rigaku, D/max 2200) with $\text{Cu K}\alpha$

*Corresponding author:
Tel : +82-2-450-3500
Fax : +82-2-444-3490
E-mail: sklim@konkuk.ac.kr

radiation (40 kV, 30 mA). The samples were measured using the Archimedes method to calculate density. The surface morphology was observed by scanning electron microscopy (SEM; Model JSM-6380, JEOL).

The ionic conductivities of sintered pellets were measured by blocking silver electrodes using electrochemical impedance spectroscopy in the frequency range of 1 Hz to 3 MHz and the temperature range of 25 to 300 °C.

Results and Discussion

Fig. 1 shows the XRD pattern of the obtained

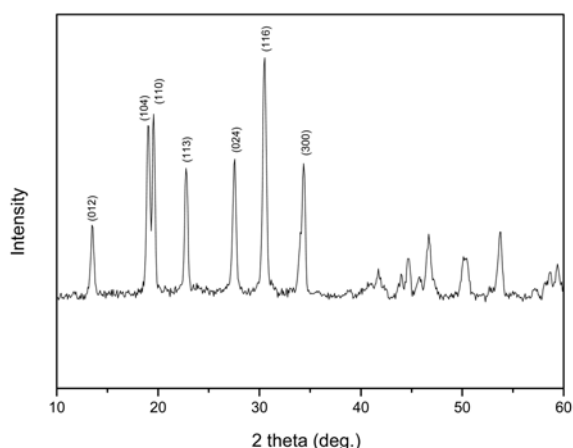


Fig. 1. XRD pattern of NASICON after calcination.

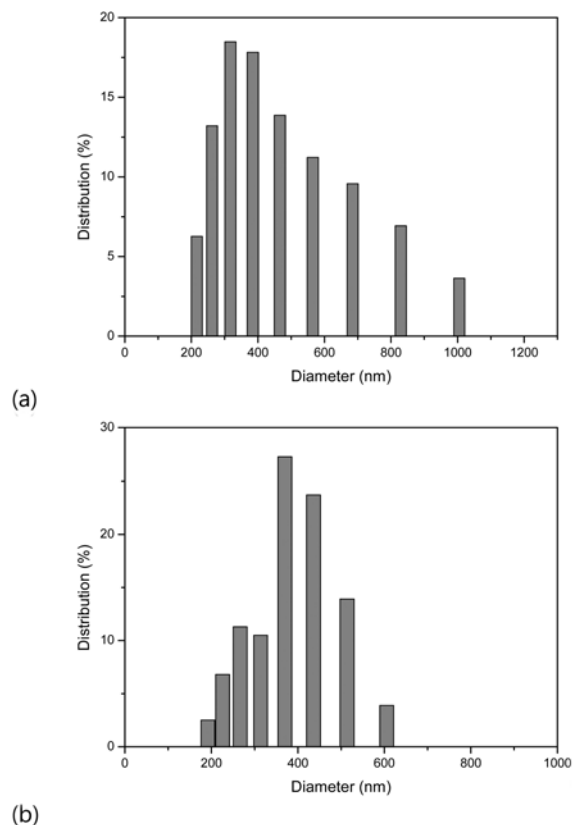


Fig. 2. Particle size distributions of NASICON powder: (a) after ball milling, (b) after jet milling.

Table 1. Bulk density and relative density of sintered pellets.

Weight ratio of jet milled powder: ball milled powder	0 : 1	1 : 3	1 : 1	3 : 1	1 : 0
Bulk density (g/cm ³)	2.97	3.01	3.04	3.12	3.14
Relative density (%)	91	92	93	95	96

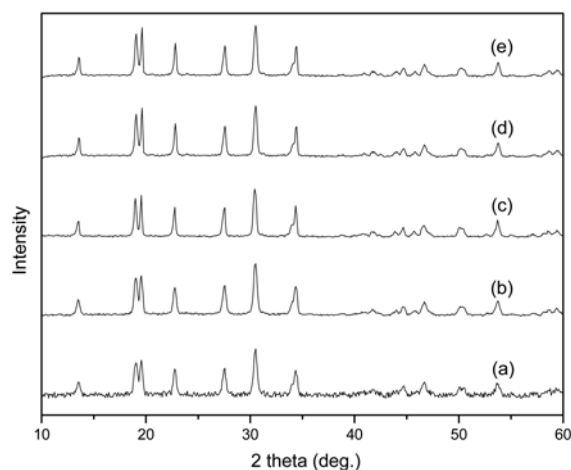


Fig. 3. XRD patterns of sintered (1210 °C, 2 h) NASICON pellets prepared using ratios of ball milled powder: jet milled powder at (a) 1 : 0, (b) 3 : 1, (c) 1 : 1, (d) 1 : 3, and (e) 0 : 1.

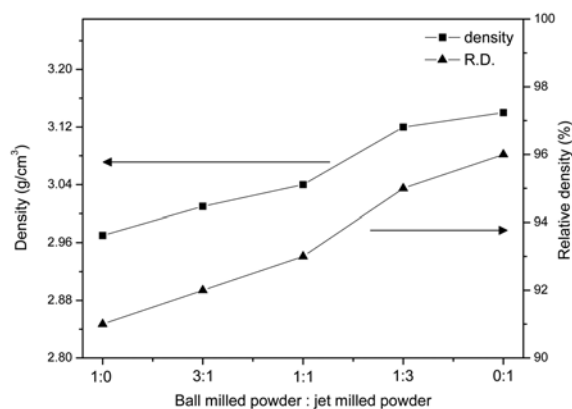
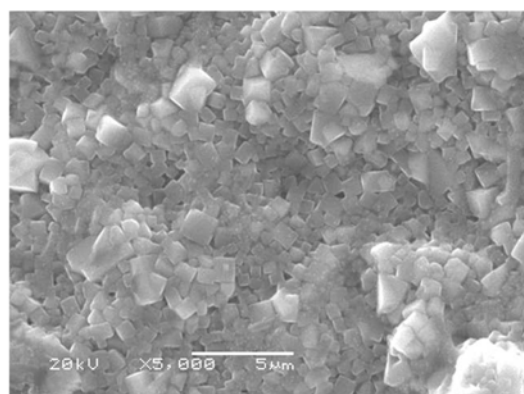


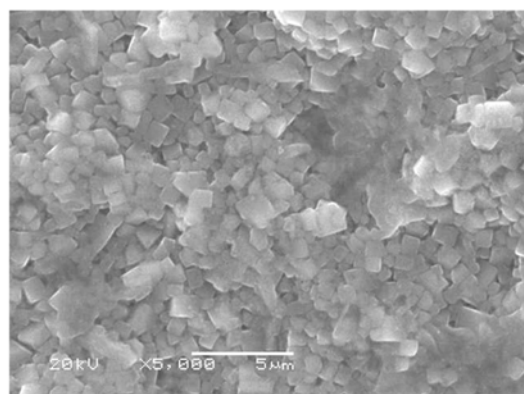
Fig. 4. Bulk densities and relative densities of sintered pellets.

NASICON powder after calcination. It is consistent with the NASICON pattern of JCPDS (#34-1334); also, there is no free zirconia peak. The results of particle size analysis are shown in Fig. 2. The average particle size of the ball milled powder was 600 nm, and the average particle size of the jet milled powder was 350 nm. Fig. 3 shows the XRD patterns of sintered pellets. NASICON is well maintained after sintering without free zirconia generated by the evaporation of P in the sintering process. All XRD patterns were the same and differences were not found. This means that the fine powder by jet milling does not affect the NASICON phase during the densification process.

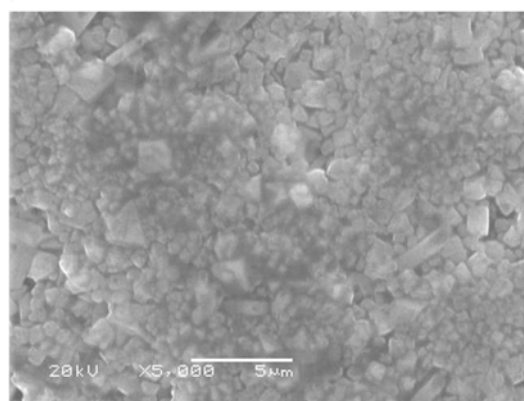
Results of the density measurement and bulk



(a)



(b)



(c)

Fig. 5. SEM images of sintered NASICON sample prepared with (a) only ball milled, (b) mixed powder (ball milled: jet milled = 1 : 1), and (c) jet milled.

densities in the cases of the samples prepared with only ball milled powder, mixed powder ratios of 3 : 1, 1 : 1, and 1 : 3 of ball milled powder and jet milled powder, and only jet milled powder, were 2.97, 3.01, 3.04, 3.12, and 3.14 g/cm^3 , respectively. Table 1 and Fig. 4 show the relative densities. The relative densities (theoretical density = 3.27 g/cm^3) of samples were calculated to be 91%, 92%, 93%, 95%, and 96%.

Figs. 5(a), 5(b), and 5(c) show SEM images of pelletized samples after sintering. The surface morphology of the samples was seen to have products with a uniform

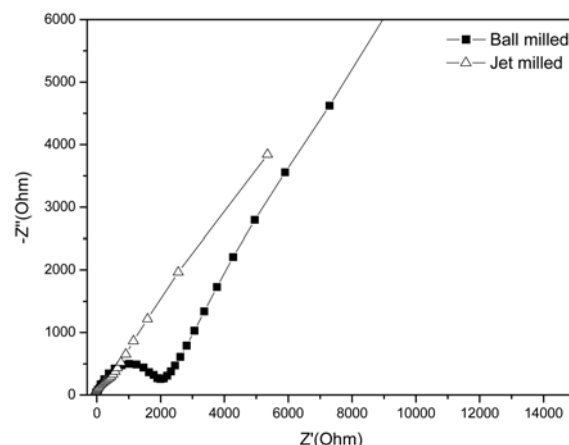


Fig. 6. Nyquist plots of sintered samples prepared with only ball milled powder and only jet milled powder at 200 °C

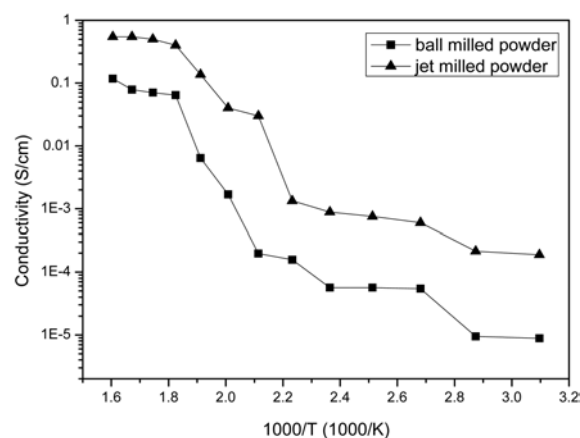


Fig. 7. Ionic conductivities of the samples prepared with only ball milled powder (■) and only jet milled powder (▲).

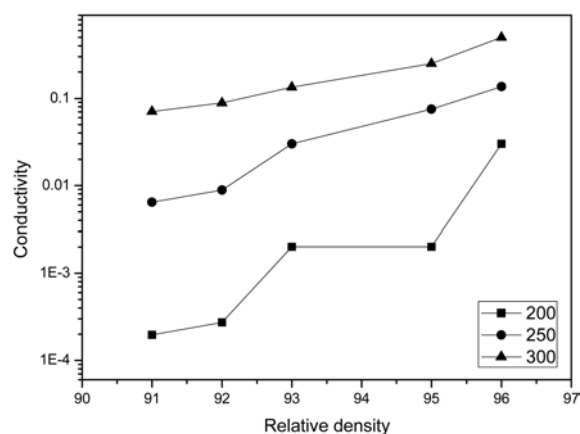


Fig. 8. Ionic conductivities vs. relative density; at 200 °C (■), 250 °C (●), and 300 °C (▲).

grain structure. However, the sample prepared using jet milled powder (Fig. 5(c)) seems to be denser (R.D = 96%). This is because fine powder acting as a catalyst during densification promotes the densification between grains. The small particle size of powder was expected to provide an advantage for the densification

behavior, because of the larger surface energy, which would enhance the neck formation in the initial sintering stage. An increase of the total surface area by decreasing the particle size led to a higher driving force operation during sintering [12].

Fig. 6 shows the Nyquist plots of sintered samples prepared only with ball milled powder and only jet milled powder at 200 °C. The sample prepared with only jet milled powder was seen to show lower resistance compared to that prepared with only ball milled powder. The ionic conductivity of the sample prepared with only jet milled powder is $1.37 \times 10^{-1} \text{ S cm}^{-1}$, which is 21.4 times higher than that of the sample prepared with only ball milled powder ($6.43 \times 10^{-3} \text{ S cm}^{-1}$) at 250 °C (Figs. 7, 8). The enhancements of the conductivity were ascribed to the improvement of density. It is clear from the results (Figs. 7, 8) that improving the density by controlling particle size can produce ionic conductivity.

Fig. 9 shows the XRD pattern of the sample containing the free zirconia phase. The pattern confirms the existence of the free zirconia phase. This is the outcome of the volatilization of P and Na during the high

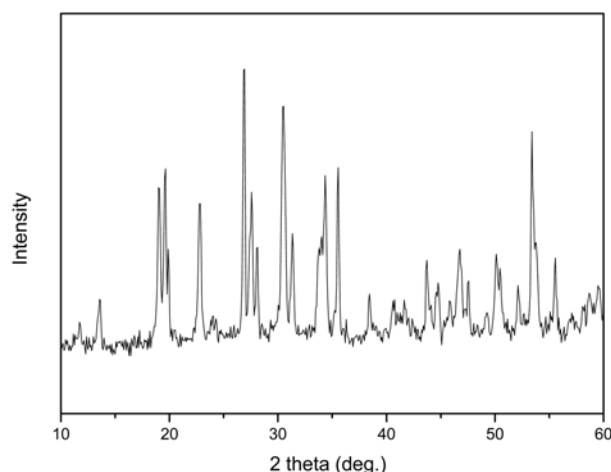


Fig. 9. XRD patterns of sintered NASICON pellets at 1250 °C, 2 h.

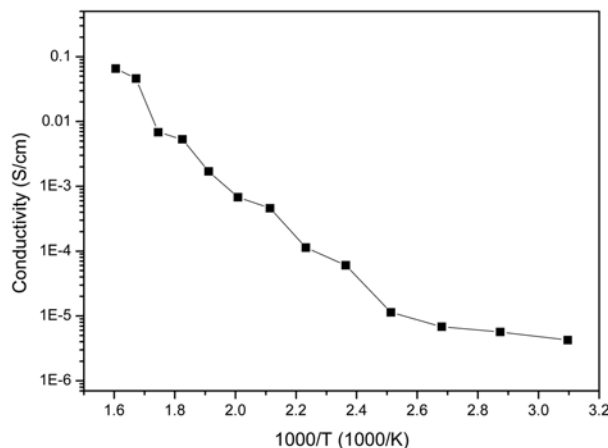


Fig. 10. Ionic conductivity of the samples containing free zirconia phase.

temperature sintering process. The measured relative density of the sample containing the free zirconia phase was 96%, which is equal to the value of the sample prepared only with jet milled powder. However, the ionic conductivity of the sample containing the free zirconia phase had definitely decreased. Fig. 10 shows the ionic conductivity of the sample containing the free zirconia phase (compare with fig. 7). It is certain that the process to reduce the particle size, such as the jet milling process, can improve ionic conductivity by increasing density, without the formation of a free zirconia phase.

Conclusions

Fine NASICON powder has the general formula of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, prepared using a jet milling method with an aim of enhancing ionic conductivity through increasing density. The ionic conductivity of the sample prepared with jet milled powder NASICON increased about 21.4 times compared with the ionic conductivity of the sample prepared with ball milled powder. This result has been attributed to the densification of NASICON fine powder. In the case of the sample containing the free zirconia phase, ionic conductivity was lower in spite of the same density. Controlling particle size by jet milling is successful in obtaining a high conductivity NASICON without any second phase of high thermal treatment.

Acknowledgments

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