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Preparation of NASICON Powder and Electrolyte

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A conventional ball-milling technique was used to produce NASICON powder. Fine component powders reacted easily to form the desired product at 1100°C or higher, whereas coarse component powders did not react completely even at 1170°C. The finer the grain size of the starting powders, the higher the bulk density of the NASICON electrolyte after sintering. Almost single phase NASICON electrolytes with a density of more than 95% of the theoretical density were fabricated by sintering for 40–60 h at temperatures between 1150 and 1170°C .

1. Introduction

NASICON (Na^+ super ionic conductor) solid solution has the chemical formula $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$ ($O \leq X \leq 3$). NASICON is a potential gas sensor material since sodium ions can move three dimensionally in the structure. The best conductivity is obtained at the composition $Na_3Zr_2Si_2PO_{12}$.[1–3] Practically, the materials are poor conductors at room temperature. However, the ionic conductivity increases rapidly with increasing temperature (0.2 $\Omega^{-1}cm^{-1}$ at 300°C). NASICON is a potential sensor material for CO_2, SO_X and NO_X gases, because of its high ionic conductivity, low volume change upon heating, and stable physical properties when absorbed by water.[4]

The first syntheses of NASICON powder were carried out using Na_2CO_3, ZrO_2 and $NH_4H_2PO_4$ using a ball-milling process involving two heating steps. The solid mixture was heated stepwise to decompose $NH_4H_2PO_4$ at about 700°C and Na_2CO_3 at about 900°C. In a one-step process, either Na_3PO_4 and $ZrSiO_4$ or Na_3PO_4, ZrO_2 and SiO_2 were used as the raw materials. Suitable reaction temperatures were known to be in the temperature range 1050–1250°C.[5]

Requirements[6] for a reversible solid electrolyte cell are: (1) The electrolyte conductivity must be entirely ionic. (2) Valence of the metallic ions in the salt must be unique. (3) Possible reaction of electrodes/electrolytes with the materials/gas used for construction of the cell should be avoided. (4) The cell must be constructed in such a way as to avoid the influence of thermoelectric forces. (5) The electrolytes should not be gas-permeable.

In the case of the NASICON electrolyte, the fifth criterion is essential. Below 90–95% of the theoretical density, open porosity leads to an ionic short circuit by the electrolytic (gas) solution which penetrates the bulk toward the internal reference electrode.

In the present work, fabrication of NASICON powder and electrolyte using the conventional ball-milling method is described.

2. Experimental

The procedure for preparing NASICON powder from the starting materials is outlined in Fig. 1.

The composition $Na_3Zr_2Si_2PO_{12}$ was chosen. The powder mixtures were made from reagent grade Na_3PO_4, ZrO_2 or $ZrSiO_4$ and SiO_2, using ball-milling techniques: powder I (coarse Na_3PO_4, ZrO_2, SiO_2), powder II (fine Na_3PO_4, ZrO_2, SiO_2) and powder III (fine Na_3PO_4, $ZrSiO_4$), as shown in Table 1.

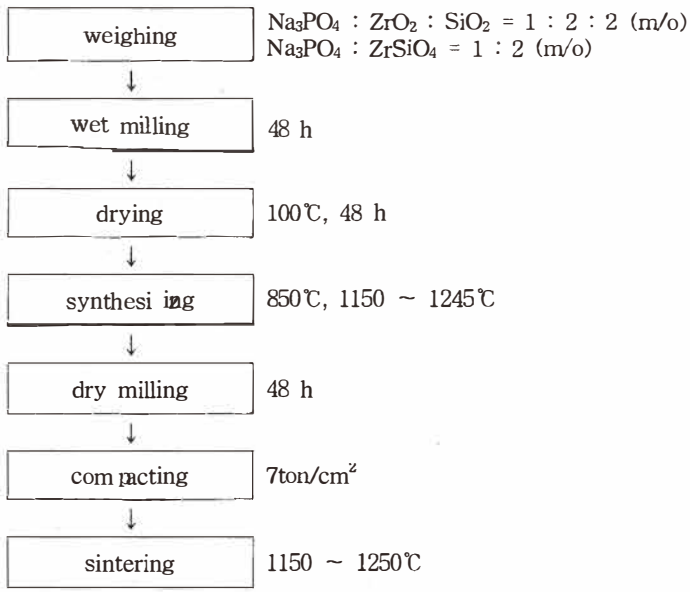

Fig. 1. Procedure for preparing NASICON powder and pellets.

Table 1
Average particle size of starting materials (μm).

Powder form	Na_3PO_4	ZrO_2	SiO_2	$ZrSiO_4$	Reacted mixture
Powder I (coarse)	32.3	56.8	36.1	–	97.0
Powder II (fine)	32.3	0.5	1.4	–	2.2
Powder III (fine)	32.3	–	–	0.5	0.5

The raw materials were ball-milled for 48 h, dried at 100°C for 48 h, and heated to temperatures between 1100 and 1245°C for 10 – 60 h. The synthesized NASICON powders were ground for 48 h and then pressed at 7 ton/cm^2 in a double-punch die for 10 min. The green pellets were then sintered in air at temperatures between 1150 and 1250°C. The heating rate for all samples was 1°C/min.

To identify the crystalline form of NASICON powder/pellets, X-ray analysis was performed with an X-ray diffractometer using CuK α radiation. Selected samples were polished and observed using a scanning electron microscope (SEM). Densities were measured using a standard immersion technique in distilled water and the laser scattering method.

3. Results and Discussion

3.1 *Synthesis of NASICON powder*

In the case of the coarse component powders, the synthesis was conducted at temperatures of 1170°C and 1236°C. Figs. 2(a) and 2(b) show X-ray diffraction patterns of NASICON powder formed at 1170°C for 10 h and at 1236°C for 60 h, respectively.

The presence of ZrO_2 as a second phase is clearly observed at temperatures above 1170°C with a large quantity of ZrO_2 at higher temperatures. For the fine component powders (powder II), which were synthesized at temperatures between 1100 and 1245°C, X-ray diffraction patterns are given in Figs. 3(a)–3(c). It can be seen that all the processes produced NASICON ceramics with a small quantity of ZrO_2 phase. All of the X-ray diffraction patterns, except those for the powders synthesized at 1100°C ($Na_3Zr_2Si_2PO_{12}$ phase according to JCPDS No. 35-412) indicate the presence of monoclinic NASICON and ZrO_2. The quantity of ZrO_2 increased as the reaction temperature increased.

As illustrated in Fig. 4(a) (as-polished sample) and Fig. 4(b) (as-fired sample), the X-ray diffraction patterns for the NASICON powders prepared from powder III show a noticeable NASICON phase with only a trace of ZrO_2. The shift in peaks between Figs. 4(a) and 4(b) might be due to a difference in the composition of ZrO_2. According to Quon *et al.*[7] an excess ZrO_2 is present on or near the surface of the pellets.

Considering the effects of different starting materials such as Na_3PO_4, ZrO_2 and SiO_2

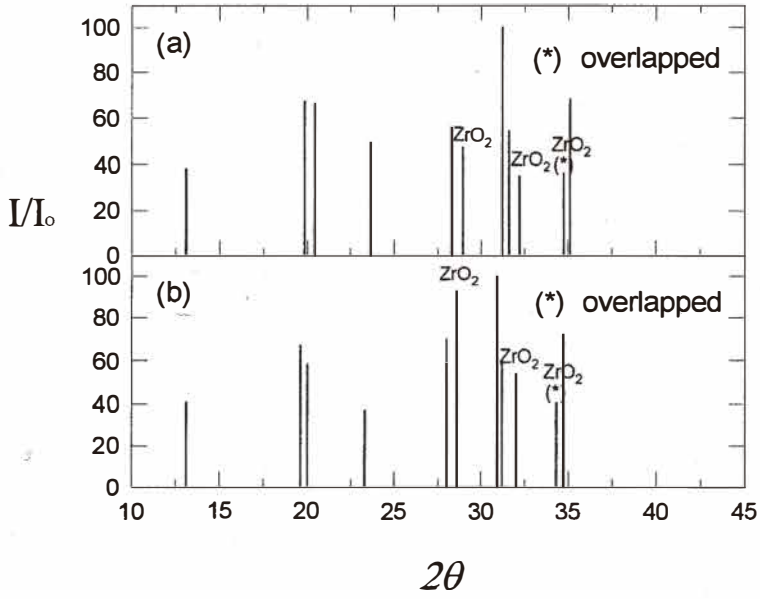

Fig. 2. X-ray diffraction patterns of NASICON powder formed from coarse component powders (powder I) at (a) 1170°C for 10 h (b) 1236°C for 60 h.

(powder I and powder II), and Na_3PO_4 and $ZrSiO_4$ (powder III) on the synthesis of a NASICON phase, powder III can be easily used to give a NASICON phase without the formation of ZrO_2 because there is no reaction between ZrO_2 and SiO_2.

3.2 *Fabrication of NASICON electrolyte*

The bulk density of the sintered pellets is a function of the particle size of the raw materials, the sintering temperature and the sintering time. The densities of NASICON electrolytes synthesized using coarse powder I were all low (below 87.9% of the theoretical density), regardless of the sintering conditions, as shown in Table 2.

Some samples prepared using the coarse component powders were contracted and distorted during sintering, presumably as a result of their low green densities. All of the green pellets fabricated from fine powders II and III had higher bulk densities than those of powder I after sintering. Ninety-six percent of the theoretical density, which is obtained at temperatures above 1150°C, is high enough for solid electrolytes.

In general, the finer the grain size of the starting powders, the higher the bulk density of the NASICON pellet. A similar observation was made in the work by Quon *et al.*[7] A commonly observed microstructural feature is the formation of pores and microcracks, as illustrated in Figs. 5(a) and 5(b). Therefore, the process must be carefully controlled to avoid crack formation during sintering.

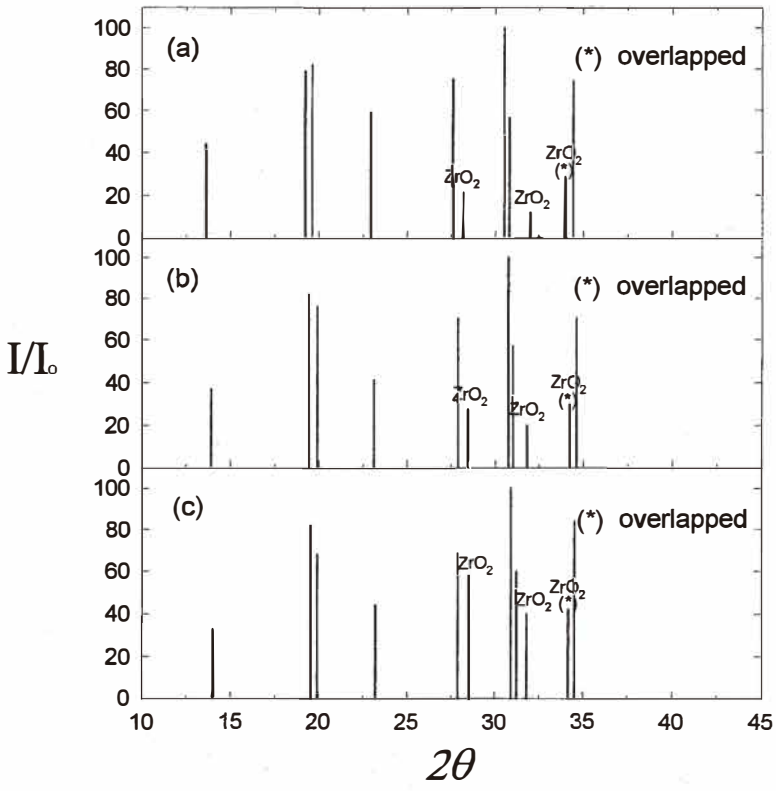

Fig. 3. X-ray diffraction patterns for fine component powders (powder II) synthesized at temperatures between 1100 and 1245°C. (a) 1100°C, 40 h (b) 1150°C, 60 h (c) 1245°C, 10 h.

4. Conclusion

NASICON (X = 2) powders and electrolytes were prepared using a conventional ball-milling technique and three component powders. Our conclusions are as follows.

(1) At reaction temperatures above 1100°C, the quantity of ZrO_2 increased as the reaction temperature increased. For the coarse powders, the reaction was incomplete even at 1170°C. On the other hand, the fine powders II and III reacted easily to form the desired product at temperatures above 1100°C.

(2) The ceramics produced from the fine component powders had significantly higher bulk densities than those produced from the coarse powders after sintering at temperatures above 1150°C. The samples obtained from the coarse component powders had low bulk densities even after sintering at temperatures above 1245°C, and developed pores and microcracks in some cases.

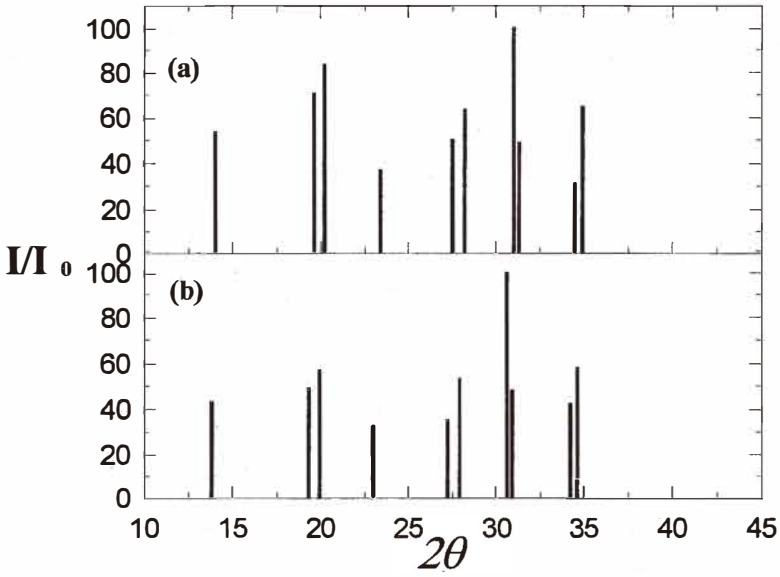

Fig. 4. X-ray diffraction patterns for as-polished sample (a) and as-fired sample (b) synthesized using powder III at 1150°C and 1200°C, respectively.

Table 2
Bulk densities of NASICON electrolytes and sintering conditions.

Powder form	Sintering condition	d/d_0 (%)*
Powder I (coarse)	1170°C, 10 h	68.5
	1200°C, 10 h	77.7
	1200°C, 15 h	82.0
	1245°C, 10 h	84.0
	1260°C, 30 h	87.9
Powder II (fine)	1100°C, 40 h	94.0
	1150°C, 60 h	96.0
	1700°C, 60 h	96.0–98.0
	1245°C, 10 h	96.0–98.0
Powder III (fine)	1150°C, 10 h	94.0
	1150°C, 40 h	96.0–98.0
	1200°C, 10 h	96.0–98.0

*d_0 is the theoretical bulk density

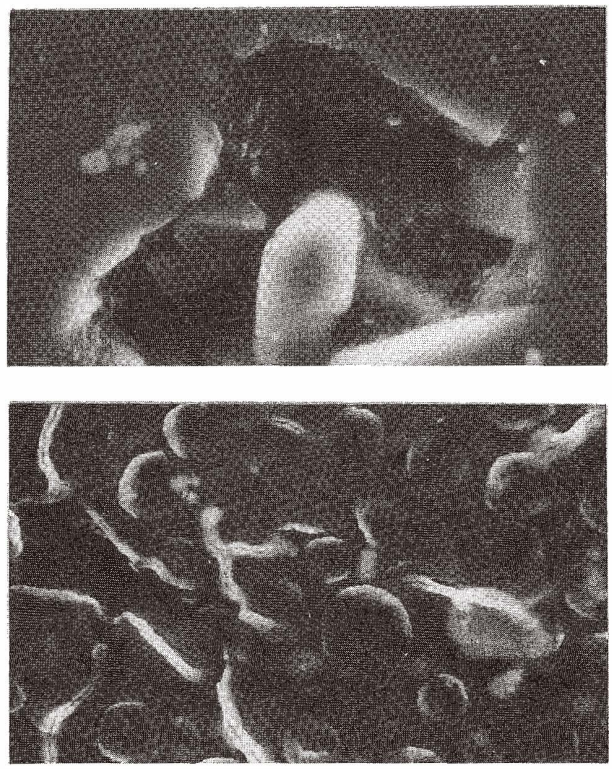

Fig. 5. SEM micrographs of NASICON electrolytes showing (a) pores and (b) microcracks.

It can be concluded that the optimal reaction and sintering conditions are 1150–1170°C for 40–60 h.

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