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FABRICATION OF NASICON ELECTROLYTES

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Abstract

Conventional ball-milling technique was used to synthesize NASICON powders. The NASICON powders were made from three kinds of component powders : coarse(ZrO_2, Na_3PO_4, SiO_2), fine (ZrO_2, Na_3PO_4, SiO_2) and fine ($ZrSiO_4$, Na_3PO_4) powders. The fine component powders were easily reacted to form the desired product at 1100℃ or higher, whereas incomplete reaction due to the coarse component powders occurred even at 1170℃. The finer the grain size of the starting powders was, the higher the bulk density of NASICON electrolyte after sintering was observed. Almost single phase NASICON electrolytes with more than 95% of the theoretical density, 3.27g/cm^3, could be fabricated by sintering for 40~60 hours at temperatures between 1150 and 1170℃.

요 약

NASICON 분말을 합성하기 위하여 볼밀링법을 사용하였다. 사용된 원료 분말은 3종류 였으며, 이것은 ZrO_2 + Na_3PO_4 + SiO_2의 미세 및 조립 분말, 그리고 $ZrSiO_4$ + Na_3PO_4의 미세 분말이다. 미세 분말은 1100℃ 혹은 그 이상의 온도에서 쉽게 반응하여 원하는 생성물로 바뀌었지만, 조립 분말을 사용하면 1170℃에서도 불완전한 반응이 일어났다. NASICON 전해질을 제조할 때, 원료 분말의 입도가 작을수록 소결 후의 밀도는 높아졌다. 이론적인 밀도(3.27g/cm^3)의 95% 이상의 단일상 NASICON 전해질은 1150~1170℃에서 40~60시간 소결할 때에 얻어질 수 있었다.

I. Introduction

NASICON (Na$^+$ super ionic conductor) solid solution has the chemical formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$($0 \leq X \leq 3$). The NASICON is of particular interest for gas sensor materials since it allows sodium ion to move three dimensionally in the structure. For the fast sodium ion transport, sodium ions are located in interstitial spaces of a rigid skeleton with ZrO_6 octahedra linked by corners to (P, Si)O_4 tetrahedra and occupy several kinds of sites whose size is a maximun at about X=2.[1-3] Thus the best conductivity is obtained for the composition $Na_3Zr_2Si_2PO_{12}$.[4-6] Practically, the materials are not so good sodium conductors at room temperature. However, the ionic conductivity increases rapidly with increasing temperature(0.2$\Omega^{-1}cm^{-1}$ at 300℃). The NASICON is a good candidate as a gas sensor material for gases CO_2, SO_X and NO/NO_X, because of its high ionic conductivity, little volume change upon heating, and unaltered physical properties when absorbed by water.[7]

In previous studies, the NASICON powders were prepared by the ball-milling technique,[8-9] the sol-gel process,[10-11] or the hydrothermal crystalline growth.[12] The first synthetic compounds of the NASICON powders were made

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from Na$_2$CO$_3$, ZrO$_2$ and NH$_4$H$_2$PO$_4$ by the ball-milling process involving two heating steps. The solid mixture is heated stepwise to decompose NH$_4$H$_2$PO$_4$ at about 700℃ and Na$_2$CO$_3$ at about 900℃. A one-step process utilizes either Na$_3$PO$_4$ and ZrSiO$_4$ or Na$_3$PO$_4$, ZrO$_2$ and SiO$_2$ as the raw materials. Suitable reaction temperatures are known to be in the range 1050~1250℃. In the sol-gel method, organo-metallic precursors such as Si(OC$_2$H$_5$)$_4$ and Zr(OC$_3$H$_7$)$_4$ in alcohol medium are the starting materials. They are quickly hydrolyzed by NaOH and NH$_4$H$_2$PO$_4$ aqueous solutions at approximately 60~80℃. Because the sol-gel route gives very fine powders, the sintering could be lowered considerably to avoid ZrO$_2$ formation observed by the classical way.[13] However, this method for forming NASICON compositions is time-consuming and expensive. The last process has been used for crystal growth of NASICON.

Requirements for a reversible solid electrolyte cell are commonly known as follows[14]: (1)The electrolyte conductivity must be entirely ionic. (2)Valence of metal ion in the salt must be unique. (3)Possible reaction of electrodes／ electrolytes with materials/gas used for construction of the cell should be avoided. (4)The cell must be constructed to avoid the influence of thermo-electric forces. (5)The electrolytes should not be gas-permeable.

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

In the present work, the fabrication of NASICON powders and electrolytes prepared by the classical ball-milling method are described as the simplest and least expensive process for the commercial production.

II. Experimental

The procedure for preparing NASICON powders from the starting materials is outlined in Fig. 1. The composition was chosen as Na$_3$Zr$_2$Si$_2$PO$_{12}$. The powder mixture was made from reagent grade Na$_3$PO$_4$, ZrO$_2$ or ZrSiO$_4$ and SiO$_2$, using the ball-milling technique(Table 1) : powder I (coarse Na$_3$PO$_4$, ZrO$_2$, SiO$_2$), powder II (fine Na$_3$PO$_4$, ZrO$_2$, SiO$_2$) and powder III(fine Na$_3$PO$_4$, ZrSiO$_4$).
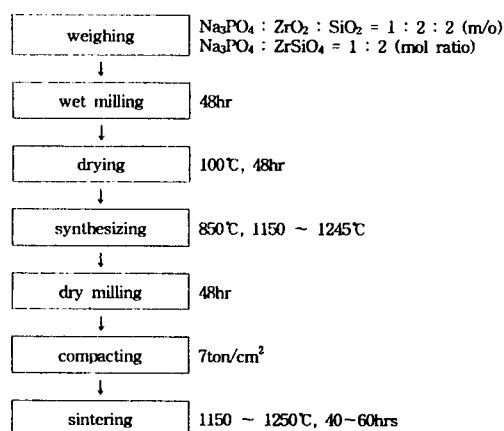

Fig. 1 Procedure for preparing NASICON powders and pellets.

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

Powder form	Na$_3$PO$_4$	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 hours to produce an intimate mixture of fine particles. The mixture was dried at 100℃ for 48 hours, heated at temperatures between 1100 and 1245℃ for 10 to 60 hours.

The synthesized NASICON powders were ground for 48 hours and then pressed at 7 ton/cm^2 in a double-punched die for 10 minutes. The green pellets were sintered in air at temperatures between 1150 and 1250℃. The heating rate for all samples was 1℃/min..

To identify the crystalline form of NASICON powders/pellets, X-ray analysis was performed with an X-ray diffractometer (XRD) using CuKα radiation. Selected samples were polished and observed in a Scanning Electron Microscope(SEM). Densities were measured using the standard immersion technique in distilled water and the Laser scattering method.

Ⅲ. Results and discussion

1. Synthesis of NASICON powders

In the synthesis of NASICON ceramics from their components, the microstructure of the final products could be controlled by using one or two reaction steps before sintering to transform practically reactants for the desired crystalline structure. An attempt was made at 850℃ for 30 minutes. Fig. 2 shows X-ray diffraction pattern for powder mixture prepared from powders of I and Ⅱ. All the components of powder mixtures were unreacted during the heating step, indicating no formation of NASICON phase.
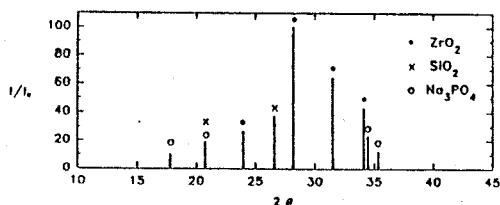

Fig. 2 X-ray diffraction pattern of powder mixture as-fired in air at 850℃ for 30 minutes.

The reaction of powder I was conducted to show Fig. 3 (a) and (b) which represented X-ray diffraction patterns of NASICON powders formed at 1170℃ for 10 hours and at 1236℃ for

60 hours, respectively. The presence of ZrO$_2$ as a second phase is clearly observed at temperatures above 1170℃ with a large amount of ZrO$_2$ at the higher temperature.
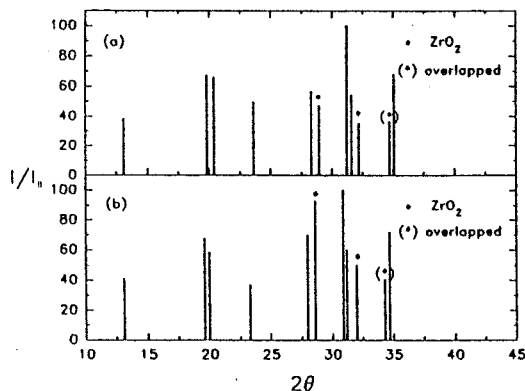

Fig. 3 X-ray diffraction patterns of NASICON powders formed from the coarse component powders(powder I) at (a) 1170℃ for 10hr and (b) 1236℃ for 60hr.

The fine component powders(powder Ⅱ) were reacted at temperatures between 1100 and 1245℃. X-ray diffraction patterns for these powders are given in Fig. 4 (a)-(c). The X-ray diffraction patterns at a given temperature show no difference for the reaction times longer than 40 hours and 10 hours in the temperature range of 1100~1170℃ and at 1245℃, respectively. It can be seen that all the processes led to NASICON ceramics with a small amount of ZrO$_2$ phase. All of the X-ray diffraction patterns, except for the powders obtained at 1100℃(Na$_3$Zr$_2$Si$_2$PO$_{12}$ phase according to JCPDS No. 35-412), indicate the presences of monoclinic NASICON and ZrO$_2$. Amounts of ZrO$_2$ were increased as the reaction temperature was raised. The ZrO$_2$ might result from two sources[9] : incomplete reaction of the raw materials and decomposition of the NASICON. It is postulated that the starting materials in the fine particulate solid form were completely reacted to NASICON and then decomposed to ZrO$_2$.
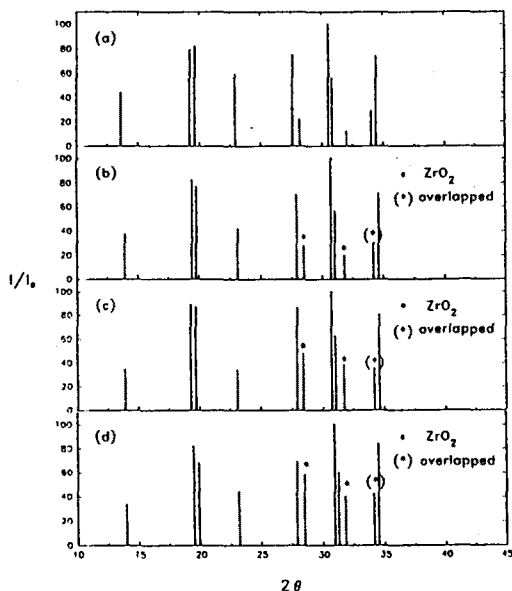
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Fig. 4 X-ray diffraction patterns of the fine component powders(powder II) heated at various temperatures between 1100 and 1245℃.

(a) 1100℃, 40hr   (b) 1150℃, 60hr

(c) 1170℃, 60hr and (d) 1245℃, 10hr

The synthetic method for NASICON powders disclosed by Pober[15] and described in detail by Lee,[16] utilizes Na_3PO_4 and zircon($ZrSiO_4$) as the raw materials. This is a process for making NASICON compositions from inexpensive starting materials and by one-step process. However, it should be noted that NASICON ceramics containing zircon as a minor second phase have higher resistivities than bodies containing ZrO_2.[17] As illustrated in Fig. 5(a) and (b), X-ray diffraction patterns for the NASICON powders prepared from the powder III as raw materials show noticeable NASICON phase only with a trace of ZrO_2.

A comparison of X-ray diffraction patterns for monoclinic NASICON(X=2) is given in Table 2. Our observation is in good agreement with the results obtained by LLoyd et al.[9] and Maruyama et al.[18], except for the peaks at 2θ =19.31 and 27.46. It is difficult to detect these peaks due to overlapping of peak and similar intensities. The similar observations were made by Sadaoka and Sakai[19] and Engell and Mortesen.[20]

Table 2. A comparison of X-ray diffraction patterns for monoclinic $Na_3Zr_2Si_2PO_{12}$

2θ [a]			d (nm)			I / I_0 [b]		
LLoyd	Maruyama	This study	LLoyd	Maruyama	This study	LLoyd	Maruyama	This study
30.5	30.5	30.7	0.2932	0.2932	0.2906	100	100	100
19.7	19.1	19.4	0.4507	0.4647	0.4565	90	84	83
19.1	19.6	19.9	0.4644	0.4530	0.4454	83	79	77
34.4	34.3	34.6	0.2604	0.2615	0.2588	83	59	71
27.7	27.4	27.8	0.3222	0.3255	0.3196	74	52	70
19.3	13.4		0.4596	0.6608		48	47	
30.8	27.0	31.0	0.2903	0.3303	0.2880	47	45	57
27.5	27.6		0.3248	0.3232		39	44	
23.0	22.9	23.1	0.3867	0.3884	0.3841	37	34	42
22.8			0.3896			36		
53.8		53.9	0.1704		0.1700	33		34
13.7		13.9	0.6482		0.6352			37
34.0	34.0	34.2	0.2633	0.2637	0.2618	32	32	30

a) CuKα radiation, λ =0.1542nm

b) I_0 is the intensity of the strongest peak

2. Fabrication of NASICON electrolytes

Uniaxial cold-pressing studies were conducted in a double punch die with the reacted NASICON powders at temperatures between 1150℃ and 1250℃. Overall heating and cooling rates were 1℃/min. to avoid crack formation during sintering. With the heating rate of 10℃/min., the sintered NASICON pellets obtained from the coarse component powders were glassy in appearance.

The bulk density of sintered pellets is a function of particle size of raw materials, sintering temperatures and times. The densities of NASICON electrolytes sintered with the coarse powder I were below 87.9% of the theoretical density, regardless of the sintering conditions, as shown in Table 3. Some samples prepared from the coarse component powders were contracted and distorted during sintering, presumably resulting from their low green densities.

All of green pellets of the fine powders II and III could be sintered to higher bulk densities. 96% of the theoretical density obtained at temperatures above 1150℃ is high enough for the solid electrolytes.

In Fig. 5(b) and (c), X-ray diffraction patterns indicate phases of polished and as-sintered surfaces, respectively. The sintered surface shows well-defined $ZrSiO_4$ peaks as well as NASICON's, whereas the polished surface shows no zircon but NASICON only. Because the zircon is present mainly near surface of the pellets, it is suggested that the loss of soda from the reactant Na_3PO_4 causes the subsequent precipitation of the zircon. The peak shift of the NASICON phase in Fig. 5(c) might be due to deficiency of zircon. In overall cases, the finer the grain size of the starting powders was, the higher the bulk density of NASICON pellets showed. Similar observation was available in the work by Quon et al.[11].

Table 3. Bulk densities of NASICON electrolytes as a function of sintering conditions

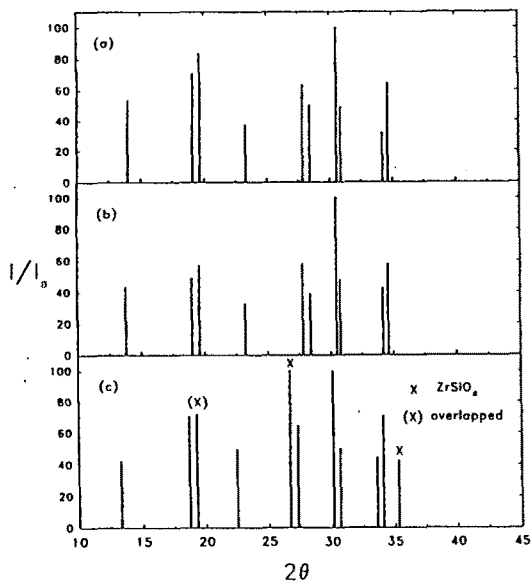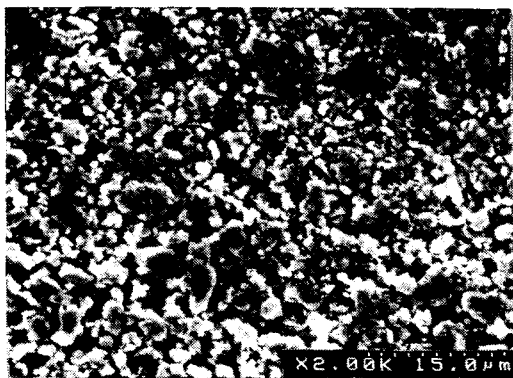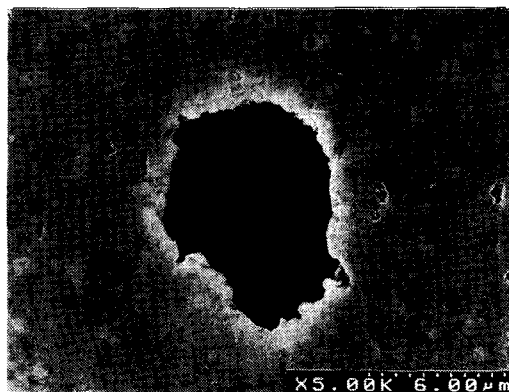| Powder form	sintering condition		d / d_0 (%)*
	Temperature(℃)	Time(hr)	
Powder I (coarse)	1170	10	68.5
	1200	10	77.7
	1200	15	82.0
	1245	10	84.0
	1260	30	87.9
Powder II (fine)	1100	40	94.0
	1150	60	96.0
	1170	60	96.0~98.0
	1245	10	96.0~98.0
Powder III (fine)	1150	10	94.0
	1150	40	96.0~98.0
	1200	10	96.0~98.0

* d_0 is the theoretical bulk density(3.27 g/cm³).

Fig. 5 X-ray diffraction patterns for (a), (b) the polished surfaces and (c) the as-sintered surface obtained from powder Ⅲ at 1150℃, 1200℃ and 1200℃, respectively.

Fig. 6 shows SEM micrograph of the surface of a compacted pellet before sintering. The microstructure of the sample contains large pores due to its relatively poor packing. Commonly observed microstructure feature is the formation of pores and microcracks by the improper heat treatment. as illustrated in Fig. 7(a) and (b). Thus. the process must be carefully controlled to avoid the crack formation during sintering.

(a)

(b)

Fig. 7 SEM micrograph of (a) pores (× 5,000) and (b)microcracks (× 5,000) in NASICON electrolytes prepared by improper thermal cycling.

Ⅳ. Conclusion

NASICON(X=2) powder and electrolytes were prepared by the classical ball-milling technique from three kinds of different powders. : powder Ⅰ(coarse ZrO_2, SiO_2, Na_3PO_4), powder Ⅱ(fine ZrO_2, SiO_2, Na_3PO_4) and powder Ⅲ(fine $ZrSiO_4$, Na_3PO_4). The mixtures were dried at 100℃ and heated at various temperatures between 1100 and 1245℃ for 10 to 60 hours. The synthesized NASICON powders were ground for 48 hours, pressed at 7 ton/cm^2 in die, and sintered in air at temperatures of 1150~1250℃. The present work

(× 2,000)

Fig. 6 SEM micrograph of the surface of green pellet.

suggests some conclusions as follows :

(1) All the component powder mixtures were unreacted during heating to 850℃ for 30 minutes.

(2) At reaction temperatures above 1100℃, amounts of ZrO_2 formed were increased as the reaction temperature was raised. For the coarse powders, incomplete reaction of raw materials occurred even at 1170℃. On the other hand, the fine powders II & III were easily transformed into the desired product at temperatures above 1100℃.

(3) The ceramics processed from the fine component powders could be sintered to significantly higher bulk density at temperatures above 1150℃. However, the samples obtained from the coarse component powders had low bulk density even at temperatures above 1245℃ and showed pores and microcracks in some cases.

It can be thus concluded that, optimal reaction and sintering conditions are found to be 1150~1170℃ for 40~60 hours.

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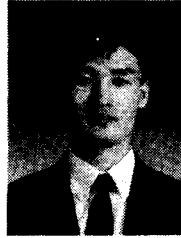[20] J. E. Engell and S. Mortesen, International Patent Classification G01N 27/30, 27/42, May, 1984

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