The Effects of the Addition of Silica Mol Fraction (x = 1.5; 2; 2.5) as a Solid Electrolyte on Ion Conductivity of NASICON (Na_{1-x}Zr_{2}Si_{x}P_{3-x}O_{12}) Using Solid-State Method

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Abstract. Energy is a very important in modern life and need innovations to develop it. One innovation is the application of energy for storage devices, such as batteries, capacitors, fuel cells, etc. For 30 years, the application of the NASICON (Na_{1-x}Zr_{2}Si_{x}P_{3-x}O_{12}) into the NASICON gas sensor material was successfully prepared by using solid-state method. The raw materials such as SiO₂, Na₂CO₃, ZrO₂, and NaH₂PO₄ with a little methanol were mixed in Ballmill equipment. The silica powder was made by the extraction of bagasse ash by using sol-gel method. The x-ray diffraction patterns showed that the result of silica extraction was amorphous and the NASICON structure was synthesized to bencmonic. The scanning electron microscopy results indicated that silica had non-uniform surface morphology and the NASICON had good surface morphology only on the form of Na₂Zr₂Si₃PO₁₂. The ionic conductivity of NASICON was shown on LCR Nyquist plot of the three compositions. The highest NASICON conductivity was found in the composition of x = 2.0, i.e. 1.142x10⁻⁸ S/m.

Keywords: silica, solid electrolyte, ion conductivity, NASICON

1. Introduction

NASICON is an acronym for sodium (Na) Super ionic Conductor, which usually refers to a family of solidss with the chemical formula of Na_{1+x}Zr_{2}Si_{x}P_{3-x}O_{12}, 0 < x < 3. In a broader sense, it is also used for similar compounds where Na, Zr, and/or Si are replaced by isovalent elements. NASICON compounds have high ionic conductivities, on the order of 10⁻² S/cm, which is a rival of those liquid electrolytes. They are caused by hopping of Na ions among interstitial sites of the NASICON crystal lattice [1].

The main application that envisaged for NASICON materials is as a solid electrolyte in a sodium-ion battery. Some NASICON exhibits a low thermal expansion coefficient (< 10⁻⁶ K⁻¹), which is useful for precision instruments and household ovenware. NASICONs can be doped with rare-earth elements, such as Eu, and used as phosphors. Their electrical conductivity is sensitive to molecules in the ambient atmosphere, a phenomenon that can be used to detect CO₂, SO₂, NO, NO₂, NH₃, and H₂S gases. Other NASICON applications include as catalysis, immobilization of radioactive waste, and sodium removal from water [1].
Besides, the production of bagasse ash from the waste of sugar cane industries was run over. On the other hand, the resulting ash was rich in silica of around 59%. It was as a raw material of silica gel and silica powder production. Generally, the silica gel was produced from the acidification of sodium silicate. Fabrication of sodium silicate was used commercially by reacting material which contain silica, for example, quartz sand, and soda ash in furnaces at temperatures of over 1300 °C [2]. It was clear that this technique consumes large amounts of energy, which can prevent the sugar industry from changing the ash into silica gel. Therefore, it would be advantageous to develop a simple, inexpensive, and low energy consuming method for the production of silica gel from the produced ash so that it can support the use of waste for the economic value-added products. Reported alkali extraction method can be used to increase the concentration of silica from rice husk ash using a low-temperature reaction[3].

This research concerned to analyze the effect of silica (SiO$_2$) addition from an extraction of bagasse ash by sol-gel/alkali method on the formation of NASICON.

2. Experimental Method

2.1. Chemicals
The chemical materials used in the experiment were Chloride Acid (99%, Merck), Sodium Oxide (99%, Merck), Sodium Dihydrogen Phosphate (99%, Sigma Aldrich), Zirconium Oxide (99%, Merck), Sodium Carbonate (99%, Sigma aldrich), and Methanol (99%, Merck). All chemical materials were used without further purification.

2.2. Preparation of Materials

2.2.1. Synthesis of Silica Powder. In this paper, two-step synthesis method was applied to synthesize the silica powder. The first step of the method was extraction. 10 gram of bagasse ash was added into 60 mL NaOH 2 M and then stirred and heated under boiling temperature for 1 hour. Then the extraction result was filtered to separate the extract and ash residue. Secondly, the extract was titrated by HCL for gelation. Next, the silica gel was aged for 18 hours and washed by demineralized water until the salt resulted from the titration process was not present. The pure silica gel was subsequently heated to degrade the water in an oven for 24 hours [4].

2.2.2. Preparation of NASICON (Na$_{1+x}$Zr$_2$Si$_x$P$_3$O$_{12}$). The NASICON material was produced by preparing SiO$_2$, ZrO$_2$, NaH$_2$PO$_4$, and Na$_2$CO$_3$ with proper compositions which were then mixed on a Ballmill with methanol sufficiently. The mol silica was varied to $x$=1.5, 2, and 2.5 to make the NASICON (Na$_{1.5}$Zr$_2$Si$_{1.5}$P$_3$O$_{12}$). The ball mill was rotated at a speed of 800 rpm for 4 hours. Then the result of pre-NASICON was calcined on horizontal furnace for 4 hours at 850 °C and was sintered by the same tool for 5 hours at 1000 °C [5].

2.3 General Characterization.
The samples were characterized by X-ray Diffraction (X’Pert PRO PANalytical) to know the phase and purity of the composing materials and NASICON. Scanning Electron Microscopy (FEI Inspect S50) was employed to know the morphology of the particle surface of silica and surface pellet of NASICON, and LCR meter was used to know the ionic conductivity of the super ionic conductor of NASICON.
3. Result and Discussion

3.1. Phase and Purity of Composing Materials

The results of x-ray diffraction analysis were shown in Figure 1. The phase of silica powder was amorf and 100% pure without impurities (Figure 1a) and the zirconia powder, sodium carbonat, and sodium dihydrogen phosphate phases were monoclic with suitable properties of conducting materials.

3.2. X-Ray Diffraction of NASICON

The results of x-ray diffraction analysis for NASICON which has been formed after the milling process for 4 hours in a ball mill with a rotation rate of 800 rpm are shown in Figure 2.a. The black line shows the diffraction pattern of the sample with the variable of silica mole fraction of $x = 1.5$. The formed NASICON has a chemical formula of $Na_{3.12}Zr_{2}Si_{2.12}P_{0.88}O_{12}$ and its crystal structure is monoclinic according to JCPDS 01-084-1317. While the red line shows the diffraction pattern of the sample with the variable of silica mole fraction of $x = 2$. The formed NASICON has a chemical formula of $Na_{3.1}Zr_{1.78}Si_{1.24}P_{1.76}O_{12}$ and its crystal structure is rhombohedral in accordane with JCPDS 01-077-1266 but this NASICON was not fully formed because an unreacting zirconia was still found. The blue line shows the diffraction pattern of the sample with the variable of silica mole fraction of $x = 2.5$. The formed NASICON has a chemical formula of $Na_{5.27}Zr_{0.5}Si_{2}P_{2.5}O_{12}$ and its crystal structure is rhombohedral according to JCPDF 01-087-0617.

The results of x-ray diffraction test for NASICON has done calcination to renew or change the shape of the crystal structure of the system that has been in the milling NASICON shown in Figure 2. The black line shows the diffraction pattern of the sample with variable silica mole fraction $x = 1.5$. NASICON formed has a chemical formula $Na_{3.12}Zr_{2}Si_{2.12}P_{0.88}O_{12}$ and its crystal structure is monoclinic according to JCPDS 01-084-1317. These results are similar to the diffraction test results before calcination. While the red line shows the diffraction pattern of the sample with variable silica mole fraction $x = 2$, NASICON formed has a chemical formula $Na_{3.25}Zr_{1.94}Si_{2}P_{2.5}O_{12}$ and its crystal structure is rhombohedral according to JCPDS 01-086-0987. After calcination, sample mole fraction $x = 2$ was
change. Such changes occur at concentrations of zircon and silica that had not yet reacted becomes react back when done calcination. On the blue line shows the diffraction pattern of the sample with variable silica mole fraction $x = 2.5$, NASICON formed has a chemical formula $\text{Na}_{3.4} \text{Zr}_2 \text{Si}_{2.4} \text{P}_{0.6} \text{O}_{12}$ and its crystal structure is rhombohedral according dengna JCPDF 00-036-0351. In addition to the mole fraction $x = 2$, variable mole fraction $x = 2.5$ also changes the chemical formula of sodium and phosphorus concentrations decline and the increase in the concentration of zirconia and silica. But the system did not change the crystal structure of monoclinic structure. In this variable there were silica and zirconia which have reacted yet.

Figure 2. X-ray diffraction pattern of NASICON with a fraction $x = 1.5$, 2 and 2.5 before (a) and after (b) calcination

3.3. Morphology of NASICON
Scanning electron microscopy (SEM) analysis was conducted on the powder NASICON that has heated and compacted to form pellets. The Figure 3. shown that the surface of the pellet did not have many changes in morphologies of before and after calcinating at 5000x magnification. However, the pellet surface becomes smoother and clearer morphology.

Figure 3. Result of Scanning Electron Microscopy of NASICON before and after of variated mol fraction of silica a&d) $x=1.5$, b&c) $x=2.0$, and c&f) $x=2.5$ at 5000x (30 µm)
On silica mole fraction \(x = 1.5\), NASICON particles were unevenly distributed, not uniform and it was bigger than a fraction \(x = 2.0\) and \(x = 2.5\) which is smaller in size and uniform across the surface of the pellet. The mole fraction \(x = 1.5\) is still appeared a raw material that did not react perfectly to the shape of particles obtained NASICON was no difference, irregular shape and are elongated fiber. Figure 4 shown the shape of NASICON surface with \(x = 2.0\) was impresive. The shape like a small sheet with diameter 500 nm. There were difference between before and after calcinating, from unregular shape to be sheet shape [7]. The figure was taken on magnification 75.000x.

Figure 4. Result of Scanning Electron Microscopy of NASICON before and after of variated mol silica \(x = 2\) with magnification of 75.000x (2 \(\mu\)m)

3.4. Ionic Conductivity of NASICON
To proof of NASICON that was made is Superconductor, we must characterized with LCR meter. The result of this analysis shown in Table 1. The table shown that the higher conductivity of NASICON which is obtained on fraction of mol silica \(x = 2.0\) as big as \(1.142 \times 10^{-8}\) S/m[8]. From the surface in this variable (Figure 4.) we could know that the transfer of ions sodium could move smoothly in charge and discharge. Figure 5 shown that the nyquist plot of NASICON with three variable. The optimum charge transfer was took placed in \(x = 2.0\) with 2 semicircle. There were two phenomenom in this figure, is chrate transfer on semicircle graph and diffusion on the body of NASICON on line straight graph.

| Variable x | F (Hz) | R (Ohm) | G (S)     | Conductivity (S/m) |
|------------|--------|---------|-----------|--------------------|
| 1.5        | 9541   | 4.97x10^5 | 2.94x10^{-7} | 1.083x10^{-9}    |
| 2.0        | 7543   | 2.8x10^6  | 3.37x10^{-7} | 1.142x10^{-8}    |
| 2.5        | 565    | 1.91x10^7 | 3.88x10^{-8} | 1.207x10^{-9}    |
Figure 5. Nyquist plot form LCR meter NASICON with mol fraction of silica a) x = 1.5, b) x = 2.0, and c) x = 2.5.

4. Conclusion
The addition of silica on the structure of NASICON can be impact on improving ion conductivity and uniformity of the surface structure. Silica was well prepared by sol-gel method had amorphous structure and the phase of NASICON were monoclinic structure. They were the result of x-ray diffraction analysis. The greatest value of ionic conductivity was $1.142 \times 10^{-8}$ S/m from x=2.0 from LCR analysis. The stable form from the effect of silica addition is Na$_3$Zr$_2$Si$_2$PO$_{12}$ by x=2.0.

5. References
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