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Research Article

The Effect of Unit Number Composition (x = 1.5; 1.6; 1.7; 1.8; 1.9; 2.0; 2.1, and 2.2) of Natrium Super Ionic Conductor (NASICON) as Solid Electrolyte on Ion-Sodium Batteries

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Abstract

The NASICON was originally used more for gas sensors because of its low ionic conductivity, thus limiting its application to sodium-based batteries. In this study, the synthesis of solid-state NASICON in the form ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) derived from Na_2CO_3, ZrO_2, SiO_2, and $NH_4H_2PO_4$, where SiO_2, is obtained by extracting from rice husk, then optimized by variating the x value of its composition, with variations of the x values (1,5, 1,6, 1,7, 1,8, 1,9, 2,0, 2,1 and 2,2) selected as a comparison determining the maximum conductivity obtaining from NASICONS, with calcination time ranges of 10 and 7 hours at 1100°C and 1250°C. The results of the analysis of the sample are characterized by specimens showing polycrystalline-shaped diffraction peaks. Furthermore, the characterization results of SEM show a more uniform morphological surface with increased variation of x values used, and the results of EDX analysis show that there are target compounds. Then, characterization using the LCR-Meter shows that the higher the variation of the x value, the higher the resulting conductivity. NASICON's ionic conductivity in the composition fails to reach the ideal standard of solid electrolyte conductiveness for the application of sodium ion batteries.

Keywords: Battery, conductivity, ion-sodium, NASICON, solid electrolyte

INTRODUCTION

In this modern era, the field of technology and information is developing rapidly. This is evidenced by numerous new inventions and sophisticated tools created in the field of technology and information. Various new tools are designed to meet the needs of people who continually seek to ease their daily tasks. This issue demands scientists to create electronic devices that are flexible, dynamic, and portable. Most of the electronic devices that are created also require flexible energy sources (Ellis & Nazar, 2012; Nishio & Furukawa, 2011). For example, batteries are portable energy storage components that can store electrical energy through various chemical processes, allowing the energy to be used at specific times. Batteries have become very important due to their reliability in providing energy for various electronic devices, from small gadgets like cell phones to larger tools such as electric vehicles. Seeing the crucial importance of battery usage today, it can be concluded that batteries are electronic components that currently play a very significant role in the development of technology

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itself. Without batteries, many devices we rely on daily would not function properly or might not function at all. Therefore, research and development of battery technology continue to be carried out to improve their efficiency, capacity, and safety to support various innovations in the field of technology and information (Dai, Mani, Tan, & Yan, 2017; Yu et al., 2023; Zhao, Zhang, Zhao, & Hou, 2020).

A battery is an energy storage device in which a reversible electrochemical process takes place with a high efficiency. Reversible reaction means that in a battery a chemical process can take place into electrical energy (the emptying process) and vice versa, from electrical to chemical power (the charging process) through the regeneration of the used electrodes by passing an electric current in the opposite polarity within the cell (Abdurrachim, Purwaningsih, & Pratiwi, 2016; Pal, Saha, Kumar, & Omar, 2020). The Sodium Super Ionic Conductor (NASICON) is one of the most promising solid electrolytes for assembling cheaper solid-state sodium batteries (Anantharamulu et al., 2011). Sodium-ion batteries have several advantages over lithium-ion batteries. The cost per kilowatt of sodium-ion batteries is estimated to be somewhat lower than that of lithium-ion batteries, which had an average cost of $137 per kilowatt in 2020. Additionally, sodium-ion batteries offer higher safety compared to lithium-ion batteries, and sodium is abundant and readily available in nature, whereas lithium is relatively scarce (Bell, Edney, Wheeler, Ingersoll, & Spoerke, 2014; Bui, Dinh, Okada, & Ohno, 2016).

NASICON (Sodium Super Ionic Conductor) with the molecular formula ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) was initially developed as a gas sensor due to its high conductivity. It was later adapted for use in Na^+-based batteries, which exhibit ionic conduction qualities similar to β-alumina and cubic stabilized zirconium. The NASICON material has a crystal structure that can be rhombohedral, monoclinic, triclinic, orthorhombic, or corundum-like, depending on its composition and sintering temperature. The composition of NASICON depends on the molar fraction expressed in the molecular formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, where x influences the molar fractions of Na, Si, and P. This compositional variation affects the structure of NASICON, as the addition of Si increases the number of Na atoms while decreasing the number of P atoms. These changes impact both the structure and properties of NASICON. Several researchers have investigated the effects of different compositions on its structure and electrical properties. Their investigations revealed that the highest NASICON conductivity is achieved with a composition of x=2.05 (Errahmah & Purwaningsih, 2016; Fang et al., 2018, 2018; Hwang, Myung, & Sun, 2017).

MATERIALS AND METHODS

Materials

The materials used in this research include Sodium Carbonate (Na_2CO_3), Zirconium Oxide (ZrO_2), Silica Oxide (SiO_2), Sodium Dihydrogen Phosphate ($NH_4H_2PO_4$), ethanol, and PVA. The SiO_2 used is extracted from rice husk using 3M NaOH. The main tools used in this research are a mortar, scale, sieve, oven, cylindrical mold, furnace, XRD, SEM-EDX, and LCR Meter.

Extraction of SiO_2 from Rice Husk

The extraction of silica from rice husk begins with the charring and ashing processes. Charring is conducted in a drum kiln, resulting in a black char with minimal ash, due to the limited air supply provided by the drum kiln equipped with a chimney, thus producing optimal rice husk char. The resulting rice husk ash is then washed with HCl to increase the purity of the silica. Washing with HCl is effective as it removes impurities present in the rice husk ash. This is consistent with the research by Guin & Tietz, (2015), which found that HCl washing produces a higher SiO_2 content compared to untreated ash, indicated by a more compact SiO_2 component structure.

Synthesis of NASICON

In this stage, the materials used are Na_2CO_3, ZrO_2, SiO_2, and $NH_4H_2PO_4$. Their molar ratios are calculated using stoichiometric calculations by varying the composition x, where x = 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2. From these variations, the mass ratios of each material for the NASICON synthesis will be determined. The materials are then mixed in containers corresponding to each x composition, and a series of solid-state processes is conducted. This begins with homogenizing the samples, followed by the first calcination at 1100˚C for 10 hours. After the first calcination, the samples are re-homogenized and then subjected to a second calcination at 1250˚C for 5 hours.

Characterization of NASICON

The characterization includes crystal structure analysis, morphology and composition analysis, and conductivity analysis of NASICON using XRD, SEM-EDX, and FPP (Four Point Probe).

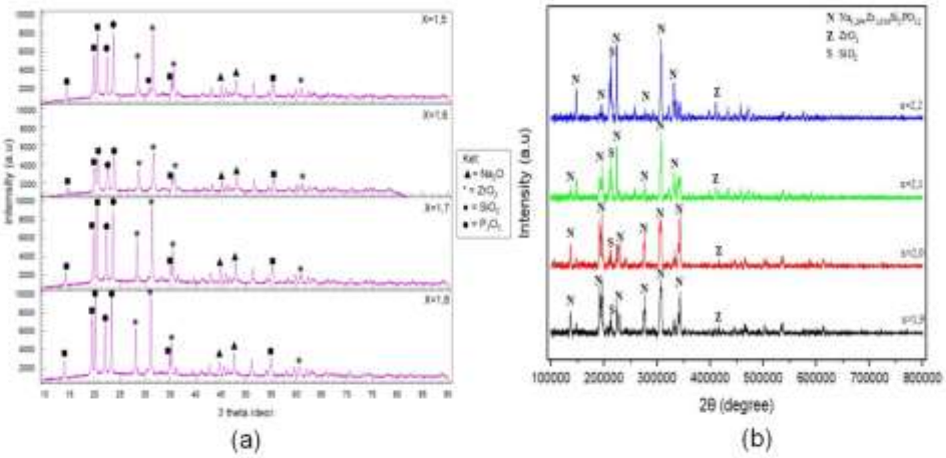
RESULTS AND DISCUSSION

Synthesis of NASICON

Sodium Super Ionic Conductor (NASICON) with the molecular formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ was synthesized using the solid-state method, followed by two stages of calcination at different temperatures. The materials ($NH_4H_2PO_4$, Na_2CO_3, ZrO_2, and SiO_2) were measured in their respective molar ratios according to the variations of x (x = 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2).

X-Ray Diffraction (XRD) Characterization Results

The NASICON compounds ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) with varying x values (x = 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2) were characterized using X-ray diffraction to determine the crystal structure and phases of the compounds formed in NASICON. The characterization was performed using a Cu source with a wavelength (λ) of 1.5405980 Å (0.15405980 nm) and a 2θ range of 10˚-90˚. The XRD test data produced XRD spectra showing the relationship between the scattering angle (2θ) and the intensity (I) of the spectrum peaks. To identify the peak positions of the NASICON constituent compounds, further data processing using OriginLab software was required. The X-ray diffraction characterization results analyzed using OriginLab software are shown in Figure 1.



(a) (b)

Figure 1. (a) NASICON diffractogram with x variations (x=1.5, 16, 1.7, and 1.8), (b) NASICON diffractogram with x variation (x=1.9; 2.0; 2.1; and 2.2).

Figure 1(a) indicates that this material is polycrystalline because multiple spectra are formed. X-ray diffraction characterization was analyzed using Origin Lab software to observe the changes in peak crystallinity produced. Then, the spectrum was compared with spectra generated from reference data in the Crystallography Open Database (COD).

To identify the presence of Sodium Oxide (Na_2O) from the spectrum, it can be compared with COD-Inorg #96-900-9064 data, indicating crystallinity forming at peaks 2θ (45.06 and 48.01) with a cubic crystal structure. Further, for the formation of crystallinity from Zirconium Oxide (ZrO_2), the spectrum was compared with COD-Inorg #96-152-5706 data, identifying it at angles 2θ (28.52, 31.52, 35.62, and 60.91) degree with a tetragonal crystal structure. Regarding Silica Oxide (SiO_2), comparing the spectrum with COD-Inorg #96-153-6410 data, it was identified at angles 2θ (22.45, 23.76, 28.52, 30.84, and 60.91) degree with a trigonal crystal structure (hexagonal axes). Then, for Phosphorus Pentoxide (P_2O_5), comparing the graph with COD-Inorg #96-231-1014 data, it was identified at angles 2θ (14.43, 19.86, 20.57, 35.22, and 55.35) degree with a trigonal crystal structure (hexagonal axes).

The addition of composition variations x (x = 1.9, 2.0, 2.1, and 2.2) in Figure 1(b) shows nearly identical diffraction patterns. Phase identification for each composition x indicates the presence of the NASICON phase ($Na_{3.94}Zr_{1.9}Si_2PO_{12}$ with ICDD #01-086-0988) with NASICON content percentages of 87% (x = 1.9), 85% (x = 2.0), 48% (x = 2.1), and 26% (x = 2.2). Qualitative analysis of NASICON also indicates the presence of zirconia ZrO_2 phase with ICDD #03-065-2357 and SiO_2 phase with ICDD #01-978-1422. The synthesized NASICON

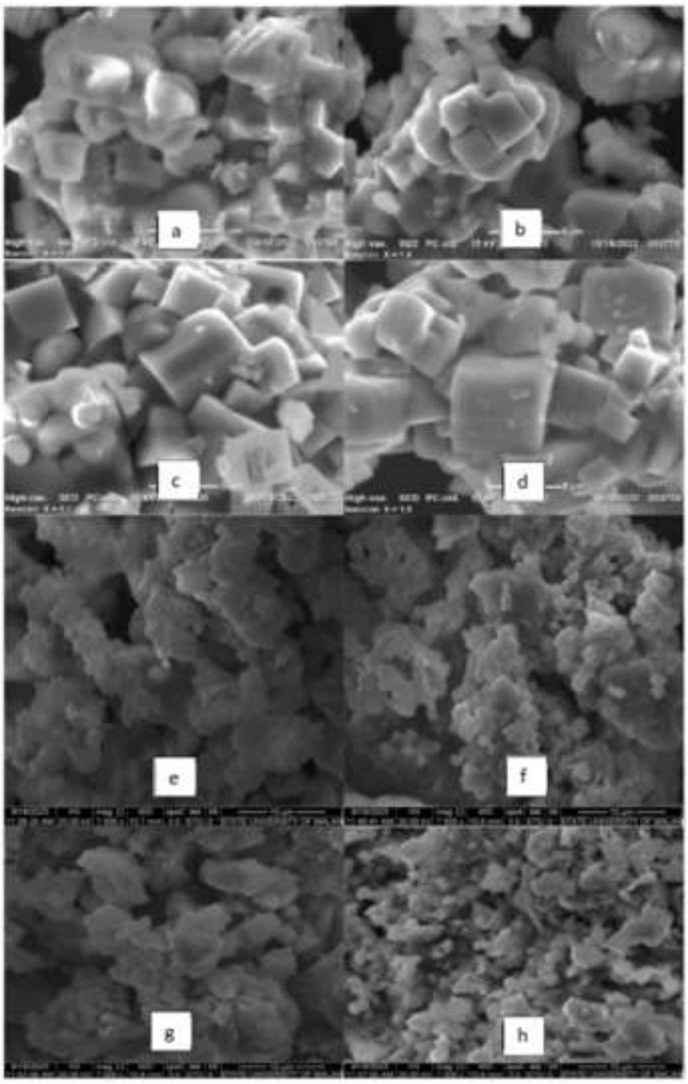


Figure 2. Morphological structure of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) samples at a magnification of 5000 times: (a) x=1.5, (b) x=1.6, (c) x=1.7, (d) x=1.8, (e) x=1.9, (f) x=2.0, (g) x=2.1, (h) x=2.2.

results are consistent with previous research; NASICON with crystal structure monoclinic was obtained in NASICON research with variable x = 1.5; 2 and 2.5 at sintering 1000°C. Another product of the synthesis is ZrO_3 (Zirconia). Due to the equilibrium reaction addition variable in the synthesis process, Zirconia reacted completely, but based on the diffraction data, Zirconia has not completely reacted, thus requiring efforts to increase the sintering temperature or re-sintering to produce single-phase NASICON (Jalalian-Khakshour et al., 2020; Zhao et al., 2020).

Based on the XRD characterization results, the crystal size can be calculated using the following equation:

$$D = \frac{K\lambda}{\beta \cos\ \theta}$$

Where, D = Crystal size, K = Crystal shape factor (0.9), λ = Wavelength of X-rays (1.5406 Å), β = Full Width at Half Maximum (FWHM) value (in radians), and θ = Diffraction angle (in degrees).

Morphology and Composition Analysis Results of Na_2CO_3 Using SEM-EDX

SEM-EDX testing was conducted to determine the morphology, particle size, and main constituent composition of NASICON samples from various composition variations of x, namely (x = 1.5; 1.6; 1.7; 1.8; 1.9; 2.0; 2.1; and 2.2). Images of the NASICON testing results using SEM-EDX shows in Figure 2.

In Figure 2 above, the SEM analysis results of NASICON with variations of x values (x=1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2) are shown. The surface morphology observed in the x value variations (x=1.5, 1.6, 1.7, and 1.8) initially appears semi-cubic, then becomes increasingly diverse forming tetragonal shapes. From the image above, it can be seen that the higher the x value composition, the more uniform the surface morphology displayed. It is evident that the displayed sizes have different diameters. Larger parts indicate protruding surfaces, while smaller parts signify recessed surfaces.

NASICON at x composition (x=1.9, 2.0, 2.1, and 2.2) shown in Image 2 exhibit different morphological shapes. The surface of each sample shows porosity. Image 2(h) (x=2.2) shows a different surface from other samples. Its surface is rougher or uneven with varying topography. This condition is influenced by the method, x composition, and synthesis process.

EDX analysis aims to provide information regarding the components of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) with variations of x values (x=1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2) both qualitatively and quantitatively. Qualitative analysis aims to identify the constituents of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$), while quantitative analysis aims to determine the amount of constituent elements present in NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$). The results of the EDX characterization are displayed in Table 1 and Figure 3.

Table 1. Atomic percentage results of NASICON EDX.

X Composition	Percentage of Atom (%)				
	Na	**Si**	**Zr**	**P**	**O**
1,5	7,86	18,85	16,01	14,33	27,62
1,6	7,75	22,08	14,98	14,24	27,57
1,7	7,80	19,88	16,24	14,66	27,55
1,8	6,04	27,38	14,79	12,19	29,08
1,9	19,6	6,2	4,2	2,0	68,1
2,0	18,4	8,2	5,5	2,7	65,1
2,1	23,9	5,8	6,0	1,8	62,5
2,2	21,5	7,3	6,1	2,2	62,9

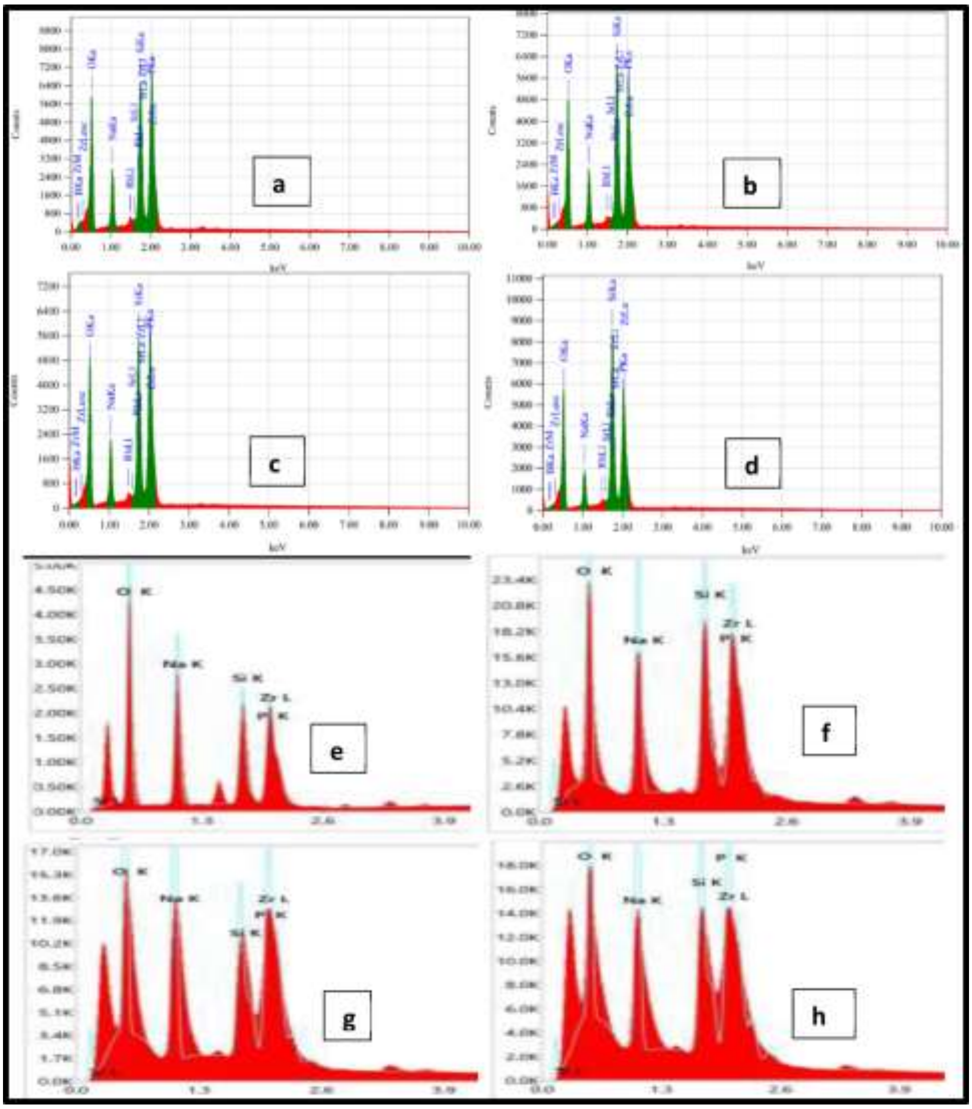


Figure 3. Spectrum of NASICON EDX results, where; (a) x=1.5, (b) x=1.6, (c) x=1.7, (d) x=1.8, (e) x=1.9, (f) x=2.0, (g) x=2.1, and (h) x=2.2.

The research results indicate that the percentage of sodium atoms tends to be larger than the number of atoms of other elements in various x composition variations. Sodium atoms reach their peak at x=2.1 with a percentage of 23.9%. With the increase in the x value, there is a change in the percentage of framework-forming atoms, such as silicon (Si), zirconium (Zr), and phosphorus (P), which can be interpreted as the impact of changing x composition on the distribution of elements in the crystal structure. Therefore, it can be concluded that variations in the x value can affect the stability of the compound by modifying the atom distribution.

The analysis of element percentages at x=2.1 shows optimal relative stability. At this value, the distribution of sodium atoms reaches its peak in line with a balanced distribution of framework-forming elements. The percentage of Si (5.8%), Zr (6.0%), and P (1.8%) atoms at x=2.1 indicates a relatively balanced distribution, creating a stable crystal framework. Therefore, the x=2.1 value can be considered as the optimal condition showing a good balance between sodium atoms and framework-forming elements, supporting structural stability in NASICON compounds.

Analysis of NASICON Conductivity Using FPP (Four Point Probe)

The purpose of this test is to determine the conductivity value of the samples produced. Conductivity is the ability of a material to conduct electric current. In this study, sample conductivity is measured using the Four Point Probe (FPP) method or the 4-probe method. It's called the 4-probe method because there are 4 contact points touched on the sample surface. These four contact points are arranged in a straight line with the distance between probes adjusted so that they have the same distance from each other. Electric current (I) is passed along the sample surface through the two outer probes, while voltage (V) is measured across the two inner probes.

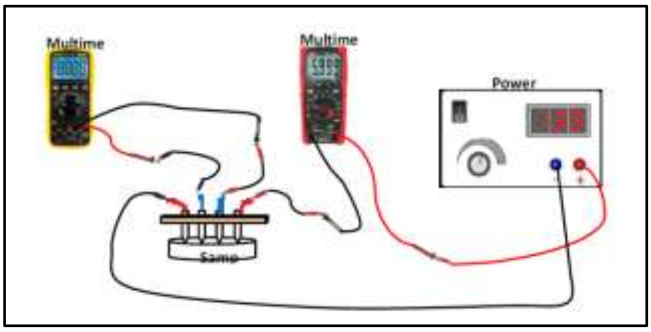


Figure 4. Conductivity Measurement Scheme

To calculate the conductivity value of a sample with a thickness greater than the distance between probes (s), the formula is as follows Equation 2:

$$\rho = 2\pi s\left(\frac{V}{I}\right) \qquad 2$$

The conductivity given by $\sigma\left(\frac{1}{\rho}\right)$ Where σ is resistivity (Ω/cm), ρ is conductivity (Ω/cm), V is voltage (V), I is current (A), and S is the distance between probes (cm). Here are the calculated conductivity values for each sample variation of composition x (x=1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2) as shown in the graph in Figure 5.

The conductivity test results indicate an increase in conductivity values with the addition of composition x in NASICON. At composition x=1.9, the conductivity is 2.06 x 10^{-5} Scm^{-1}, increasing at composition x=2.0 to 4.04 x 10^{-5} Scm^{-1} and experiencing a significant increase at x=2.1 and x=2.2 with conductivities of 7.15 x 10^{-4} Scm^{-1} and 6.92 x 10^{-4} Scm^{-1} respectively. Further analysis shows that the increase in conductivity is related to the addition of composition x, especially on the sodium component.

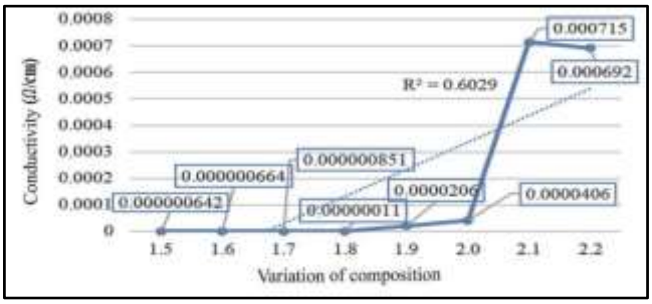


Figure 5. NASICON conductivity values

With the increase in the x value, the number of sodium atoms acting as charge carriers facilitates the movement of ions within the compound. Increasing the x composition can also enhance the ionic capacity, allowing the material to store or release more sodium ions during battery cycling or energy storage applications.

NASICON has a standard solid electrolyte conductivity for sodium-ion battery applications. Although there is an increase in conductivity with the increase in x value, the obtained conductivity does not reach the NASICON solid electrolyte conductivity standard. An ideal solid electrolyte has high ionic conductivity at room temperature (σ < 10 Scm^{-3}). NASICON with conductivity values (<10^{-4} Scm^{-1}) performs similarly to sodium β-alumina, thus NASICON with such conductivity potential to become a battery, but not at room temperature, but at 300°C (Errahmah & Purwaningsih, 2016).

CONCLUSION

The influence of composition x (x=1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2) on the crystal structure of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O$) indicates that each composition x exhibits diverse crystal structures or systems, showing the same diffraction pattern with varying peak heights. The formed crystal structures include cubic, trigonal (hexagonal axes), and monoclinic structures. The SEM-EDX analysis results indicate that variations in composition (x) in NASICON compounds significantly contribute to the distribution of elements within its crystal structure. Sodium atoms tend to have a higher percentage, reaching their peak at x=2.1 with a percentage of 23.9%. An increase in the value of x leads to a decrease in the percentage of framework-forming elements such as Si, Zr, and

P, indicating a change in the distribution of atoms within the crystal structure. The analysis of element percentages at x=2.1 demonstrates optimal relative stability, with a balanced distribution of sodium atoms and framework-forming elements. The conductivity increases with the increase in composition x, reaching its peak at x=2.1 with a conductivity value of 7.15 x 10^{-4}. Further analysis indicates that the increase in conductivity correlates with the increase in the molar fraction of sodium (Na) in the compound. An increase in the value of x enhances the number of sodium atoms as charge carriers, facilitating ion movement within the compound. However, the ionic conductivity of NASICON at these x variations does not reach the ideal standard for electronic conductivity, thus making it unsuitable for sodium-ion batteries.

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