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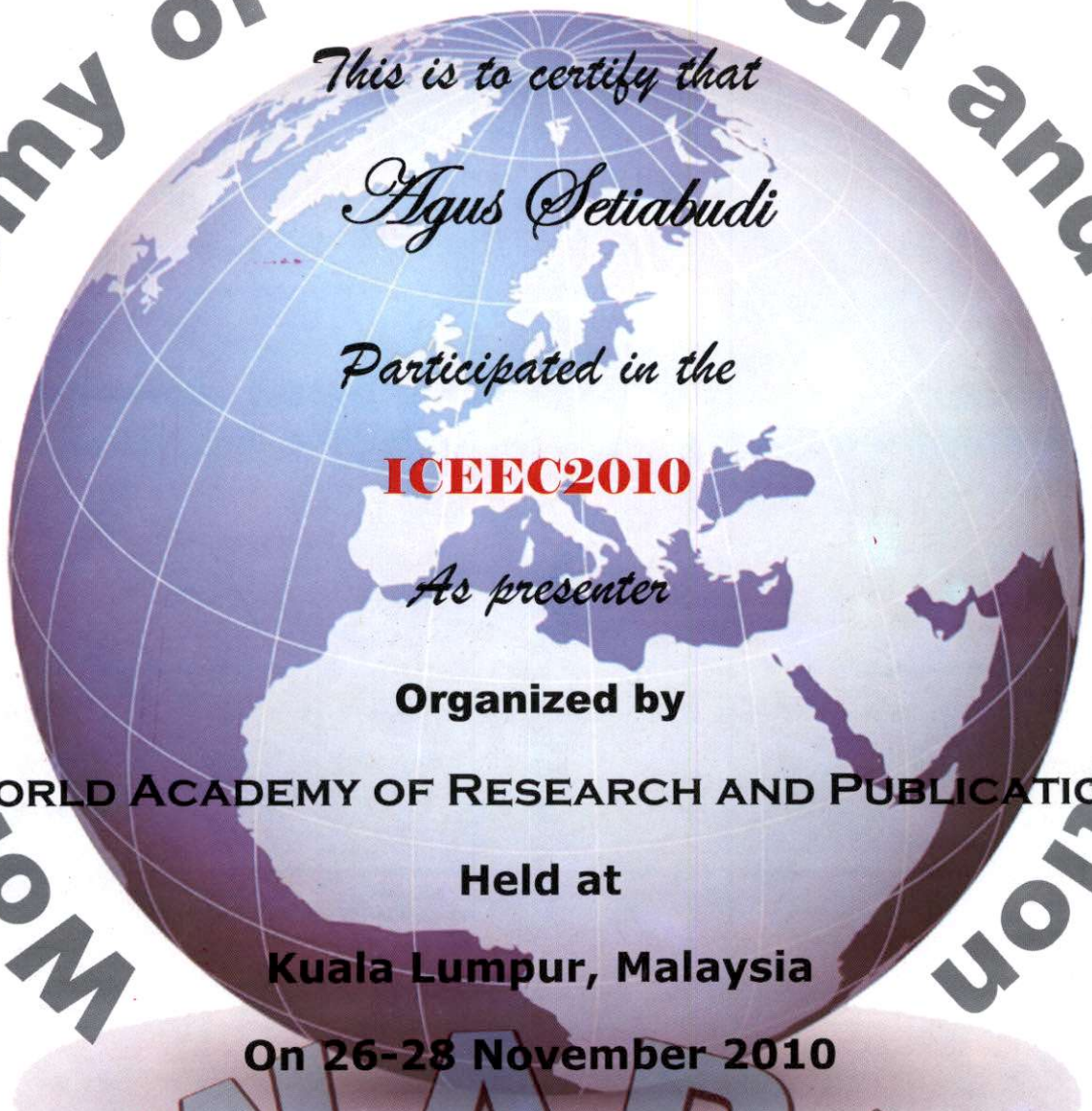

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Preparation and Characterization of Na^+-Based Solid Ionic Conductor and Its Performance As a NO_x Sensor in a Tailor-Made Cell

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Abstract

Natrium Super Ionic Conductor (NASICON) has been synthezised by a modified inorganic sol-gel method with organic acid as a sol stabilizer. The best calcination condition has been investigated by TG-DTA which showed that the reaction temperature occured at 975°C. Infrared Spectrofotometer (IR) was used to identify the vibration of some functional groups such as ZrO_6, SiO_4, and PO_4 at the wavenumbers of 400-750 cm^{-1} and 800-1100cm^{-1}. X-ray diffraction patterns described some specific peaks for NASICON in 2θ = 13, 19, 20, 24, 27.5, 30, and 33. XRF measurements were used to determine the composition of Na, Zr, Si, and P appropriate with the stoichiometry of NASICON, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ where x = 2.1. SEM analysis with magnification to 1500 times indicated that the synthesized materials were about 1 μm particle size with high homogeneity. A 10^{-3} S/cm^2 conductivity range was obtained from prepared NASICON measured both by Impedance Spectroscopy as well as tailor-made cells. Activity of prepared NASICON as a component for the sensor has been tested within an inert gas condition and in a variety of NOx concentrations. The results showed that the sensor cell ability to detect the existing NOx gas seen from the changes in current responses of NOx atmosphere compared to ambient conditions. A tendency of linearity between NOx gases concentration and current responses was also observed.

Keywords : Sol-gel; NASICON; Solid electrolyte; Sol stability.

1. Introduction

Nitrous Oxide (NOx) is one of the air pollution components with the highest toxicity levels [1]. These gases also contribute to the acid rain and photochemical fog which are dangerous to humans and water biotypes. Amperometric gas sensors have been widely used to determine the concentration of NOx in the air. Ionic conductor material with high conductivity is needed inside the sensor to transmit the current. *Natrium Super Ionic Conductor,* well-known as NASICON, is being developed as the material for sensors. Amperometric gas sensors have linear current responses with the concentration of NOx and have higher sensitivity than other electrochemical sensors [2].

A Solid-solid reaction has largely been used to synthesize NASICON because it is easier than the sol-gel method as shown by the previous research conducted by the author. However, the Sol-gel method produces NASICON with better homogeneity and higher conductivity. Nevertheless, this product is difficult to be synthesized because of the existing zirconium phosphate or zirconyl phosphate [3]. In general, acidic compounds are commonly used as the additive in producing NASICON through the sol-gel method.

In this paper, we focus our attention on the variation of additives with different concentration to stabilized NASICON. After it was prepared and characterized by several instrumentations analysis, NASICON was then applied as the sensor material to detect the presence of NOx gases through both qualitative and quantitative measurements. These results were expected to be used as the baseline to determine the range of concentration of the sensor cell.

2. Experimental

In this research, a preparation method was developed from a solid-solid reaction towards the sol-gel method. NASICON was prepared by mixing Na_2SiO_3, $ZrO(NO_3)_2$, $NH_4H_2PO_4$ in an aqueous phase with different acidic compounds, such as mallonic acid, tartaric acid, and citric acid. The concentrations of additives were also varied. The mixture was stirred to form sol and then it was dried to form xerogel. The xerogel was pelletized and then calcined at 750^0C for 1 hour and the second calcination was conducted at 1000^0C for 3 hours. The prepared material was then characterized by XRD, XRF, SEM, and FT-IR.

After NASICON was coated with Pt and $NaNO_2$, conductivity measurements were carried out at 150^0C to 400^0C. NASICON was applied in the inner space of the sensor cell with an NOx flow passed through the sensor and then the responses of current indicated the concentration of the NOx gases. The research design is shown schematically in Fig. 1.

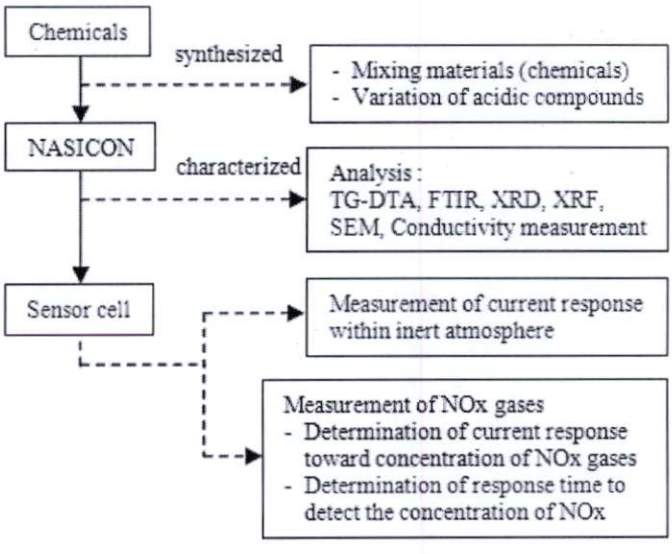


Figure 1. Experimental design

3. Results and Discussion

3.1. Sol Stability

The production of of zirconyl phosphate ($ZrOHPO_4$) or zirconium phosphate ($Zr(HPO_4)_2$) as a byproduct from the reaction between $ZrO(NO_3)_2$ and $NH_4H_2PO_4$ would precipitate and disturb the stability of the sol. To avoid this problem, an acidic compound was added to produce complex compounds with Zr^{4+} ion. These ions are easier to react with OH^- from base to form $ZrOH^{3+}$ (reaction 1) and then decompose into ZrO^{2+} (reaction 2). ZrO^{2+} then the result reacts with HPO_4^+ to form $ZrOHPO_4$ (reaction 3) [3].

$Zr^{4+} + OH^- \rightarrow ZrOH^{3+}$ $\quad K = 10^{14}$ (1)

$ZrOH^{3+} \rightarrow ZrO^{2+} + H^+$ $\quad K = 10^{0.7}$ (2)

$ZrO^{2+} + HPO_4^{2-} \rightarrow ZrOHPO_4$ $\quad K = 10^{19.5}$ (3)

In the formation of complex compounds, Zr^{4+} reacted with carbonyl group in acidic compounds to form RCOOZr as the following predicted reactions:

$Zr^{4+} + R(COOH)(COO)_2^{2-} \rightarrow [Zr(COO)_2(COOH)R]^{2+}$ (4)

$[Zr(COO)_2(COOH)R]^{2+} + H^+ \rightarrow [Zr(COO)(COOH)_2R]^{3+}$ (5)

The sol in which citric acid was used as an additive showed the highest stability. On the other hand, the variation of the citric acid concentration did not give any significant contributions to the differences in stability. The characteristics of sol are shown in Table 1.

TABLE I.

THE CHARACTERISTICS OF SOL

Additives	Color of sol & deposit	Stability (day)
No additive	White, no deposit	< 4
Mallonic	White, deposit (+)	< 4
Tartaric	White, no deposit	15
Citric (3M)	No color, no deposit	20
Citric (5.5M)	No color, no deposit	20
Citric (6,5)	No color, no deposit	20

3.2. TG-DTA study of conductor material

It can be seen immediately from Fig. 2, that approximately 58% of the mass dropped in the decomposition process during calcinations from 100^0C to 750^0C. Decomposition at 100-150^0C was indicated as water evaporation. Meanwhile, the other exothermic reactions occurred at 200-750^0C. These exothermic reactions were predicted due to oxidation of organic compounds [2] and decomposition of NH_4NO_3 during calcinations processes [4]. The formation of ZrO_2 tetragonal as predicted happened at 605^0C was in line with the previous research by Ignaszack et.al in 2005 [4]. The peaks at 975^0C did not cause mass change. Hence, this maximum temperature was predicted as the formation temperature of NASICON.

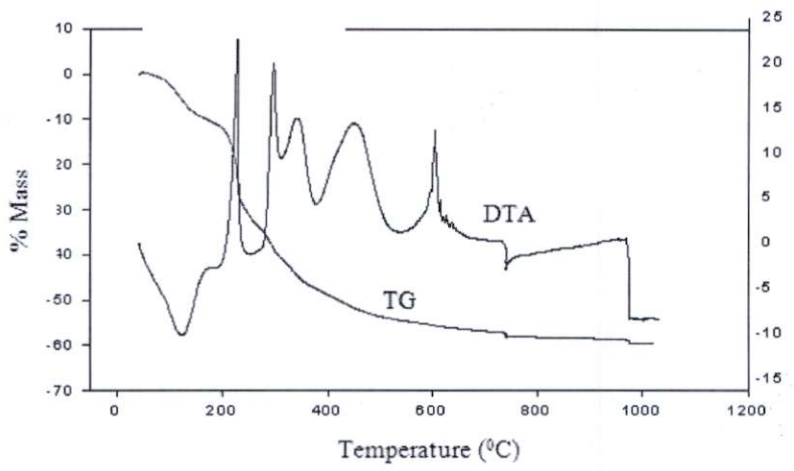


Figure 2. TG-DTA analysis of the NASICON

3.3. FT-IR analysis

IR spectra for material prepared with and without additives gave similar patterns as shown in Fig. 3. With references to the literatures [6,7] some peaks that appeared refer to the vibration of functional groups as listed in Table 2. Variation in additive concentrations did not give any significant differences in IR spectra as shown in Fig. 4. Meanwhile, IR spectra for the material calcined at 750^0C-1000^0C showed the differences as can be seen in Fig. 5, and we conclude that the calcinations' temperature influenced the material.

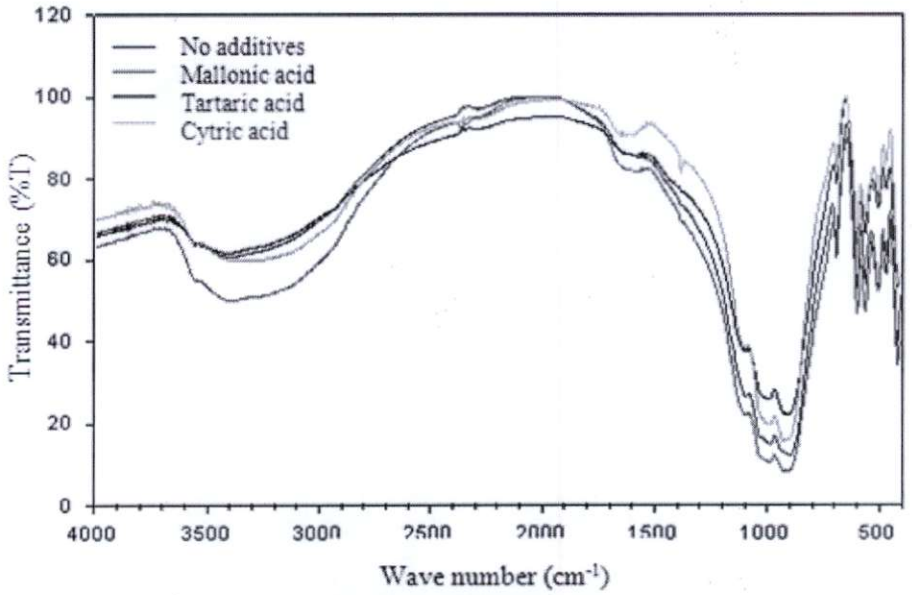


Figure 3. IR spectra for NASICON prepared with different additives

TABLE 2

LIST OF FUNCTIONAL GROUP VIBRATIONS IN NASICON

Adsorption peaks	Analysis
400-750 cm^{-1}	Vibration ZrO_6, PO_4 and SiO_4
470 cm^{-1}	Vibration ZrO_2
550-560 cm^{-1}	Vibration O—P—O,
600-900 cm^{-1}	Vibration Zr—O
850-1250 cm^{-1}	Vibration O—Si—O dan P—O—P
890-920 cm^{-1}	Vibration P—O—P
980-1080 cm^{-1}	Vibration PO_4^{3-} and SiO_4
1100-1150 cm^{-1}	Vibration PO^-

Having discovered that citric acid showed the best sol stabilization than the other additives, the investigation then continued to detect if concentration of additives influenced the chemical bond (functional group) of the NASICON prepared. The result indicated that there was no significant difference of the IR spectra from various citric acid concentrations.

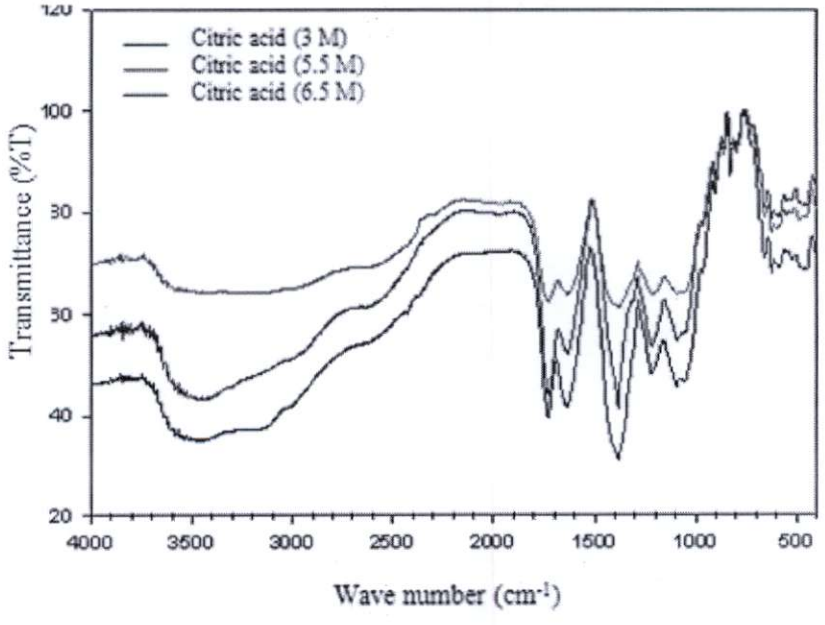


Figure 4. IR spectra of NASICON prepared with various concentration of citric acid

To trace the influence of the calcinations process, research was conducted at different calcinations' temperatures. The IR spectra for different calcinations temperatures are shown in Fig. 5.

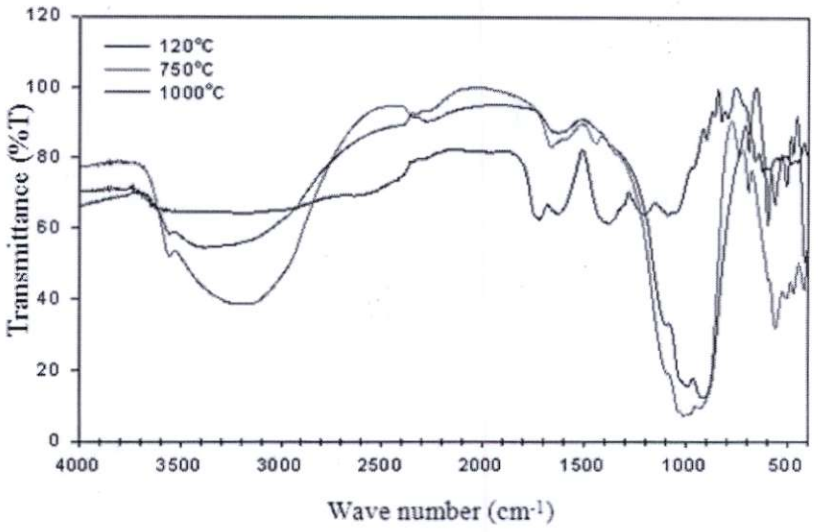


Figure 5. IR spectra of NASICON calcined at 750°C and 1000°C

3.4. XRD analysis

X-ray diffraction was used to identify the patterns of synthesized material to be compared with the XRD patterns of NASICON, as previously done by Mouzer et al [3]. The Difractogram pattern as described in Fig. 6 shows the peaks of NASICON at 2θ = 13, 19, 20, 24, 27.5, 30, 33, 42, 45, 46, 48, 50, 53, 57 and 60. There was another peak that was identified as contaminant from the formation of zirconia.

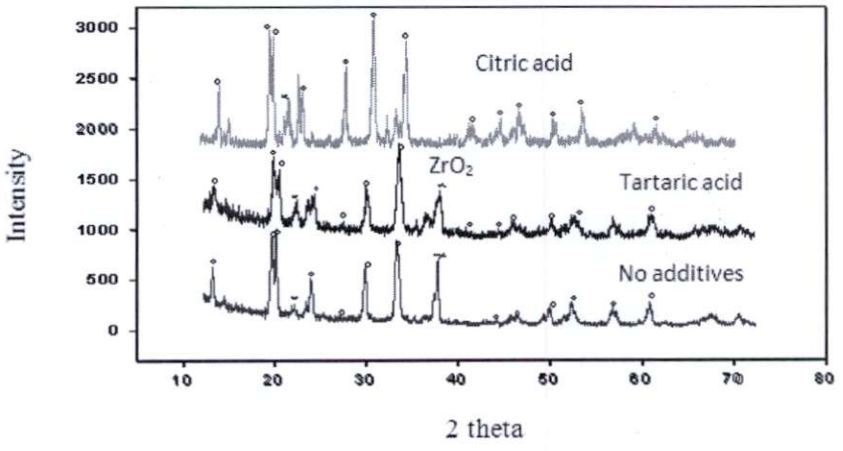


Figure 6. XRD pattern of NASICON with and without additives

It was concluded that using the citric acid in preparation processes of NASICON production gave less zirconia as a contaminant agent. Due to the characterization of sol prepared with different kinds of additives, citric acid reacted well with zirconia to form complex solution in which zirconia in a solid phase diluted, turning into an ionic phase. Meanwhile, the other additives did not react with solid zirconia as well as citric acid because of their lower K_{sp}. As a result, zirconia still remains in the final product.

3.5. XRF analysis

The importance of XRF analysis was to investigate the composition of elements in the NASICON prepared. Analysis was carried out for NASICON with and without additives to show the existence of Na, Zr, Si, and P as described in Table 3.

TABLE 3.

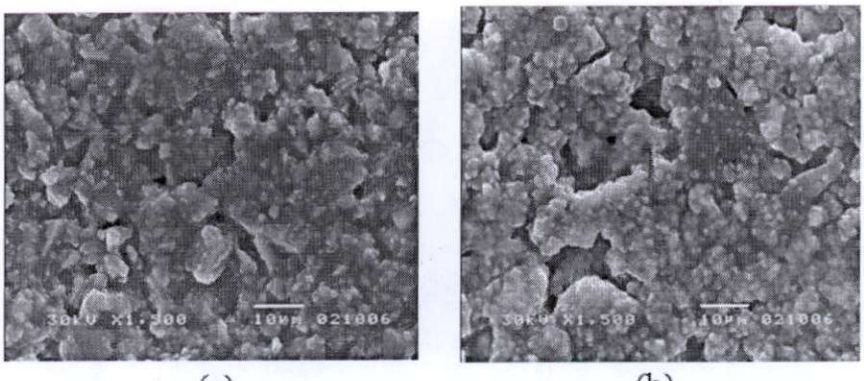
ELEMENTS OF NASICON WITH AND WITHOUT ADDITIVES

Additives		No additives	Tartaric acid
%Elements	Na	32.318	28.968
	Zr	31.148	38.923
	Si	23.484	22.336
	P	13.048	9.770
Predicted Formula		$Na_{2.7}Zr_{2.6}Si_{1.9}P_{1.1}$	$Na_{2.7}Zr_{3.6}Si_{2.1}P_{0.9}$

These results show that the chemical formula of prepared material fitted the stoichiometry of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$). It also can be seen that there was an exceeding of Zr in the NASICON composition that was revealed from the formation of ZrO_2 during the synthesis of NASICON. This fact was supported by XRD and FT-IR which illustrated the peaks of ZrO_2.

3.6. SEM analysis

Fig. 7 shows SEM images of the surface of synthesized NASICON with and without additives with magnification to 1500 times.



(a) (b)

Figure. 7. SEM analysis for NASICON (a) without additives and (b) with tartaric acid

Particles of NASICON which were prepared with tartaric acid revealed more homogeneity and the size was around 1 μm. The particles overlay one another. According to the research by Ignaszak, et.al in 2005 [4], the conductivity of material will be linear to its homogeneity.

3.7. Conductivity measurement

Measuring conductivity of NASICON was proposed to analyze the characteristics of the material. Figures 8, 9, and 10 describe the conductivity of NASICON added by citric acid with 3M, 5.5M, and 6.5M respectively, as a function of time. These measurements were carried out in different temperatures to find out the influence of temperatures in analysis of conductivity of ionic material.

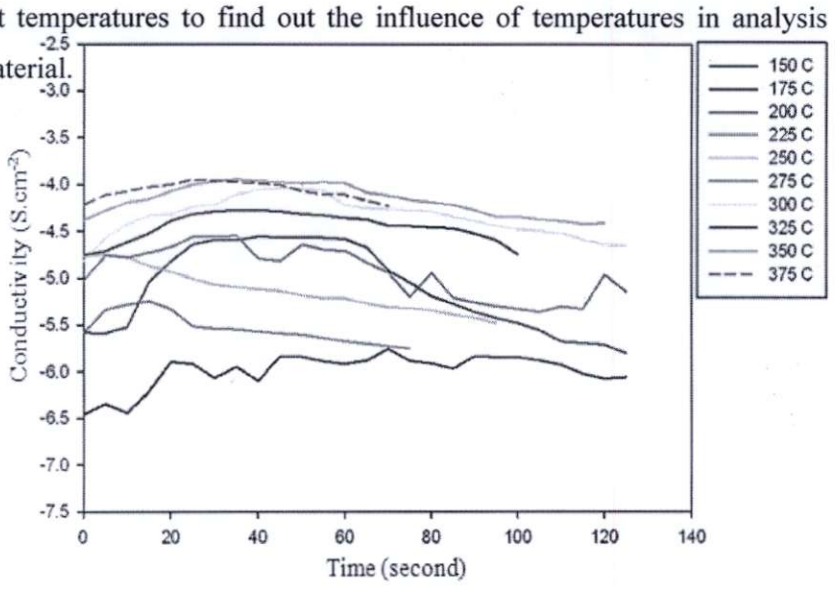


Figure 8. Conductivity of NASICON prepared with 3 M citric acid

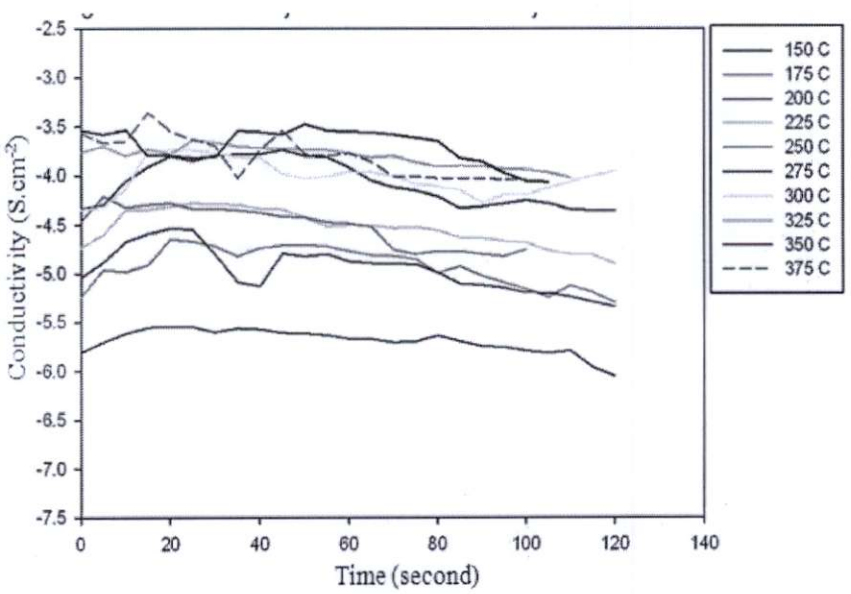


Figure 9. Conductivity of NASICON prepared with 5.5 M citric acid

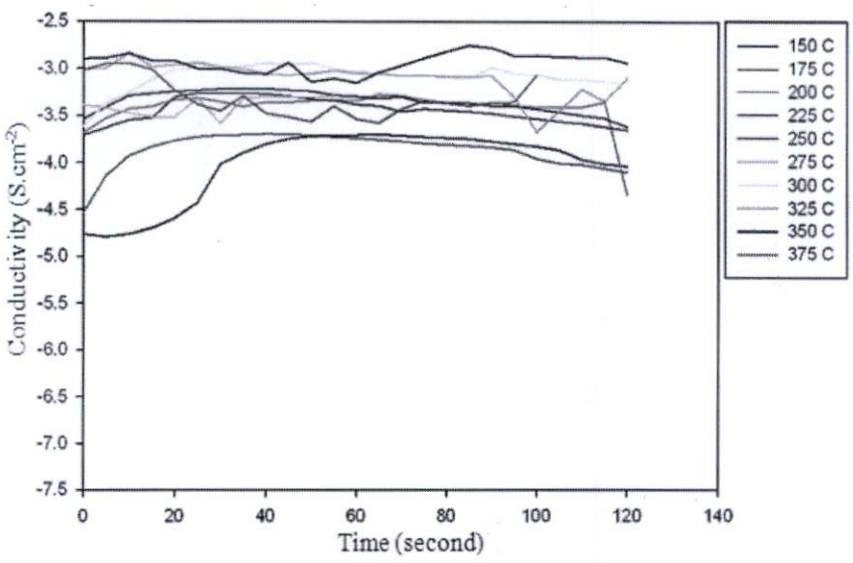


Figure 10. Conductivity of NASICON prepared with 6.5 M citric acid

Addition of 6.5 M citric acid gave the highest conductivity at the same range of temperature (150^0C – 375^0C) and showed that the optimum temperature was approximately at 350^0C. The next investigation was conducted to analyze the conductivity of some treatment applied to NASICON as shown in Fig. 11

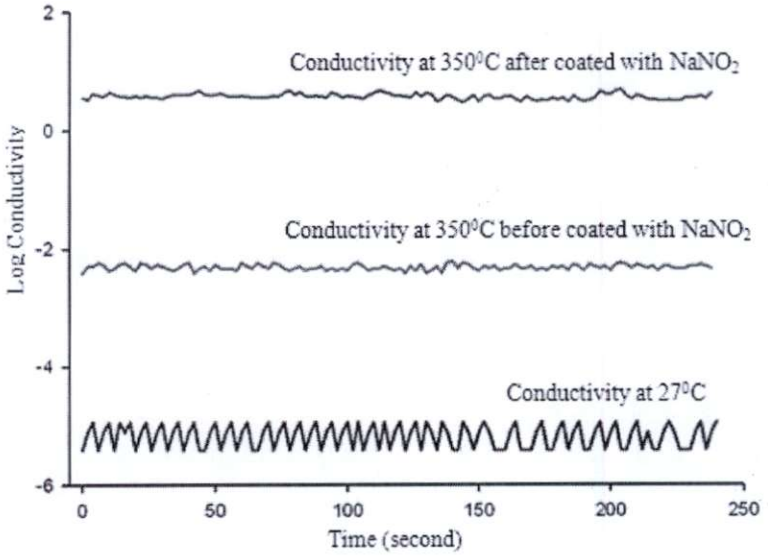


Figure 11. Conductivity of NASICON - 6.5 M citric acid measured at 350^0C with different treatments.

Conductivity measurements were conducted at several temperatures, 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 275 °C, 300 °C, 325 °C, 350 °C, 375 °C and 400 ^{0}C. Temperatures varied in order to observe the correlation between conductivity of ionic material toward increased temperatures. In general, the conductivity of NASICON rose with temperatures increased [5].

Fig. 8 shows that the conductivity of the prepared NASICON with citric acid 3M was log σ = -7.04 at 150^{0}C for the lowest point, meanwhile, log σ = -3.54 at 400^{0}C for the highest point. On the other hand, Fig. 9 shows that the conductivity of NASICON prepared with citric acid 5.5M had the lowest point of log σ = -8.15 at 150^{0}C and the highest point of log σ = -3.54 at 350^{0}C. However, Fig. 10 shows the highest conductivity among the three graphs with the range of conductivity of log σ = -4.47 at 150^{0}C to log σ = -2.75 at 350^{0}C.

The results suggest that increasing concentration of citric acid that was added to NASICON caused an upward trend in conductivity. It means that more citric acid addition leads to the stability of sol before further produced as NASICON. The conductivity of synthesized NASICON has fulfilled the requirement to be included as *a fast ionic conductor* and could be used as the component of the NOx gas sensor.

Fig. 11 illustrates the differences in conductivity between specific treatments. After being coated with $NaNO_2$, the conductivity of NASICON increased due to the possibility of the electrochemical reaction which occurs in ambient condition. However, the ambient condition consisted of many gases including NOx although in small concentrations. That is why the conductivity increased.

3.8. NASICON performance

Testing for the activity of NASICON was carried out in order to observe the feasibility of prepared material to be used as a component for the NOx gas sensor. These processes were conducted with NASICON-citric acid 6 M at 350^{0}C due to the highest conductivity of NASICON. These experiments provided information about the ability of NASICON to respond to the flowing NOx gases in particular concentrations.

The sources of the used NOx gases in the experiments were produced through thermal decomposition of $Ba(NO_3)_2$ and KNO_3.The gases were then diluted with Nitrogen and passed through the sensor cell for 125 second at 350°C with flow rate 20 mL/minute. The concentration of NOx was varied by different dilution processes. In these experiments, the concentrations of NOx were estimated by considering the physical variables such as mass of reacted, volume, pressure and temperature.

According to the stoichiometric reactions of thermal decomposition of $Ba(NO_3)_2$ and KNO_3, the reaction occurred at 300^0C as the following equitations :

$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + 1/2O_2$

$2KNO_3 \rightarrow K_2O + 2NO_2 + 1/2O_2$

Referring to the stoichiometric reactions, the concentration of NO_2 could be calculated by determining the loss of initial mol of $Ba(NO_3)_2$ as well as KNO_3. However, in these calculation methods, some assumptions were made, such as:

- The gases were considered to be ideal
- Thermal decomposition processes perfectly occurred
- The compositions of air were 79% N_2 and 21% O_2

The produced NOx were then analyzed using the prepared cell with NASICON coated Pt and $NaNO_2$ inside the cell. The results are shown in Fig.12.

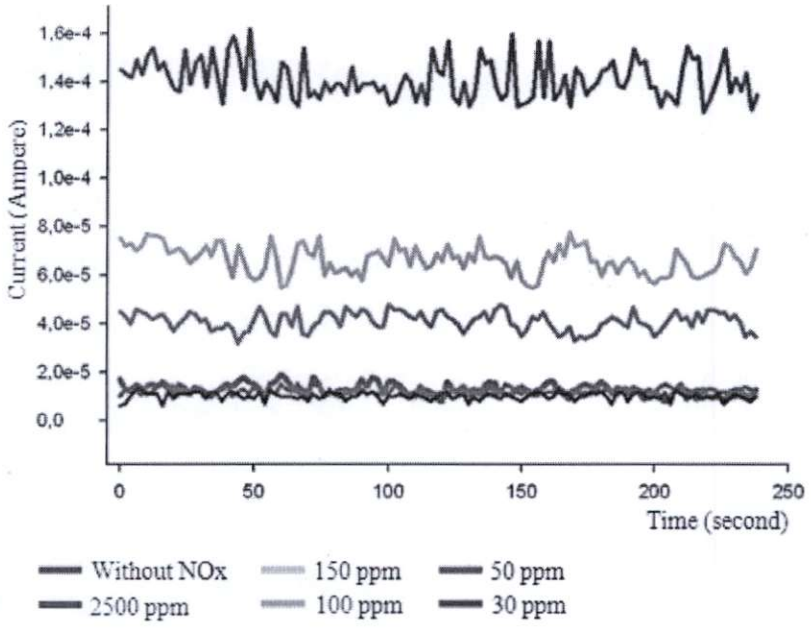


Figure 12. Current responses of NASICON in detecting NOx.

It can be interpreted from Fig. 12 that the conductivity levels in the ambient condition were lower than the conductivity levels in the flowing NO_2 conditions. It can be explained that in the flowing Nitrogen condition there was almost no NOx existence in the sensor cell so the electrochemical reaction inside the sensor could not occur. As a result, the conductivity levels were very low because almost no electrons were transmitted through the electrochemical processes in the sensor. Meanwhile, the ambient condition consisted of a little more NOx as part of air composition and caused the conductivity levels a little higher. On the other hand, in the flowing NO_2 conditions, the conductivity levels were slightly higher in line with the increasing of

NO_2 concentrations. Those facts indicated that there was a tendency of linearity between the increasing concentrations of NOx gases with the increasing conductivity levels of the sensor cell.

Conclusion

X-ray diffraction and FT-IR analysis showed that NASICON has been synthesized either through the solid-solid reaction or inorganic sol-gel method. SEM analysis illustrated that higher homogeneity was obtained from the NASICON prepared through the sol-gel method. The highest stability of NASICON was achieved by an addition of 6.5 M citric acid. The sensor showed the ability to detect NOx gases at the optimum temperature of 350°C. Qualitative analysis of the existing NOx gases was shown from the change of the current responses which corresponded to the qualitative analysis of the NOx concentration. The sensor was able to detect the NOx gases in various concentrations, 2500 ppm, 150 ppm, 100 ppm, 50 ppm, and 30 ppm. The current responses for 50 ppm and 30 ppm revealed approximately the same. It indicated the minimum range of NOx concentration that could be detected by this method. It is also concluded that there was a tendency of linearity between the increasing of NOx concentrations with the increasing of current responses.

Acknowledgments

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