

# DESIGNING THE NO<sub>x</sub> GAS SENSOR PROTOTYPE USING IONIC CONDUCTOR MATERIAL BASED ON NA<sup>+</sup>

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## Abstract

*Sodium Super Ionic Conductor* (NASICON) has been synthesized through solid-solid reaction and inorganic sol-gel method with citric acid as a sol stabilizer. The best calcination condition has been investigated by TG-DTA analysis and it showed that the formation of NASICON occurred in 975°C. Infra Red Spectrophotometer (IR) was used to identify the vibration of some functional groups for instance ZrO<sub>6</sub>, SiO<sub>4</sub>, and PO<sub>4</sub> in respectively wave number 400-750 cm<sup>-1</sup> and 800-1100cm<sup>-1</sup>. X-ray diffraction pattern described some specific peaks for NASICON in 2θ = 13, 19, 20, 24, 27.5, 30, and 33. XRF measurements allowed us to determine the composition of Na, Zr, Si, and P appropriate with the stoichiometric of NASICON, Na<sub>1+x</sub>Zr<sub>2</sub>Si<sub>x</sub>P<sub>3-x</sub>O<sub>12</sub> with x = 2,1. SEM analysis with magnification to 1500 times illustrated that the size of particle from synthesized material was about 1 μm with high homogeneity. Conductivity of NASICON which was measured by Impedance Spectroscopy as well as prepared cell showed in the range of 10<sup>-3</sup> S/m. The testing for activity of prepared NASICON as a component for sensor has been carried out within inert gas condition and also in variety of NO<sub>x</sub> concentrations. The results showed the ability of sensor cell to detect the existing NO<sub>x</sub> gas which can be seen from the changes of current responses in NO<sub>x</sub> atmosphere compared with ambient condition. In line with that, it was also concluded there was a tendency of linearity between NO<sub>x</sub> gases concentration and current responses.

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

## 1. Introduction

Nitrous Oxide (NO<sub>x</sub>), as one of the air pollution components, has the highest toxicity levels [7]. These gases also contribute to the acid rain and photochemical fog which are very danger for human and water biotype.

Amperometric gas sensors have been widely used to determine the concentration of NO<sub>x</sub> in the air. Ionic conductor material with high conductivity is needed inside the sensor to transmit the current. *Sodium Super Ionic Conductor*, much well known as NASICON, is being developed as the material for sensor. Amperometric gas sensors have linear current response with the concentration of NO<sub>x</sub> and have higher sensitivity than the other electrochemical sensors [4].

Solid-solid reaction was largely used to synthesize NASICON because it was easier than sol-gel method as the previous research that has been conducted by the author. However, Sol-gel method produces NASICON with better homogeneity and higher conductivity. Nevertheless, this product is quite difficult to be synthesized because of the existing of zirconium phosphate or zirconyl phosphate [5]. In general, acidic compounds are commonly used as the additive in producing NASICON through sol-gel method.

In this paper, we focused our attention on the variation of additive 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 existing of NO<sub>x</sub> gases 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, preparation method was developed from solid-solid reaction toward sol-gel method. NASICON was prepared by mixing Na<sub>2</sub>SiO<sub>3</sub>, ZrO(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> in aqueous phase with some different acidic compounds, such as malonic 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°C for 1 hour and the second calcination was conducted at 1000°C for 3 hours. The prepared material was then characterized by XRD, XRF, SEM, and FT-IR.

After NASICON was coated with Pt and NaNO<sub>2</sub>, conductivity measurements was carried out at 150°C to 400°C. NASICON was applied on the inner space of sensor cell with NO<sub>x</sub> flow passed through the sensor and then the responses of current indicated the concentrations of NO<sub>x</sub> gases. Research design is showed schematically in Figure 1.

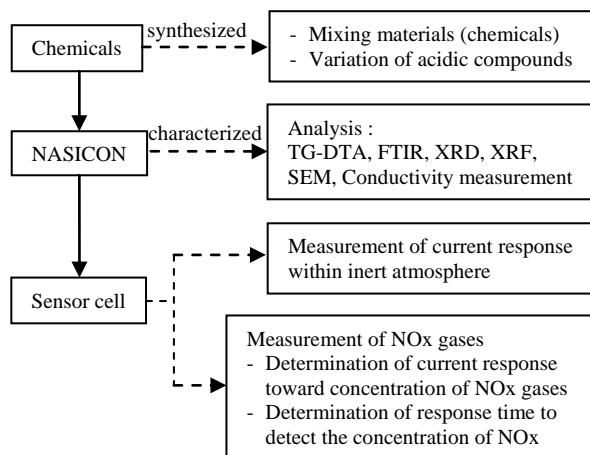


Figure 1. Research design

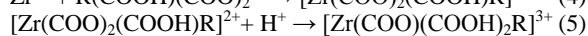
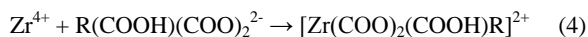
### 3. Results and discussion

#### 3.1. Sol stability

The existing of zirconyl fosfat ( $ZrOHPO_4$ ) or zirconium fosfat ( $Zr(HPO_4)_2$ ) as the byproduct from the reaction between  $ZrO(NO_3)_2$  and  $NH_4H_2PO_4$  will precipitate and disturb the stability of sol. Hence, to avoid the formation of ( $ZrOHPO_4$ ) or ( $Zr(HPO_4)_2$ ), acidic compound was added to produce complex compound with  $Zr^{4+}$  ion. These ions are easier to react with  $OH^-$  from base to form  $ZrOH^{3+}$  (reaction 1) and then decomposed into  $ZrO^{2+}$  (reaction 2).  $ZrO^{2+}$  then reacted with  $HPO_4^{2-}$  to form  $ZrOHPO_4$  (reaction 3) [5].



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



Sol which was prepared with citric acid showed the highest stability. On the other hand, variation of citric acid concentration did not give significant contribution to the differences of stability. The characteristics of sol are showed in Table 1.

Table 1. The characteristics of sol

Additives	Color of sol & deposit	Stability (day)
No additive	White, no deposit	< 4
Malonic	White, deposit (+)	< 4
Tartrat	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

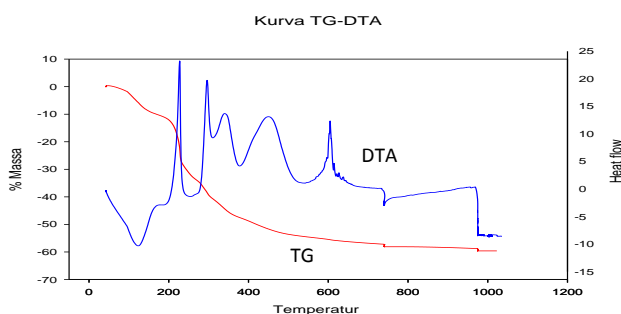


Figure 2. TG-DTA analysis of the NASICON

It can be immediately seen from Figure 2, there was approximately 58% mass dropped while decomposition process during calcinations from  $100^{\circ}C$  to  $750^{\circ}C$ . Decomposition at  $100-150^{\circ}C$  was indicated as water evaporation. Meanwhile, the other exothermic reactions occurred at  $200-750^{\circ}C$ . These exothermic reactions were predicted due to oxidation of organic compounds [4] and decomposition of  $NH_4NO_3$  during calcinations processes [3]. The formation of  $ZrO_2$  tetragonal was predicted happened at  $605^{\circ}C$ , inline with the previous research by Ignaszack et.al in 2005 [3]. The peaks at  $975^{\circ}C$  did not cause mass change. Hence, this maximum temperature was predicted as the formation temperature of NASICON.

#### 3.3. FT-IR analysis

IR spectra for material prepared with and without additives gave the similar pattern. With references to the literatures [4] some peaks that appeared refer to the vibration of functional groups as listed in Table 2.

Table 2. List of vibration of functional groups 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 $PO_4^{3-}$

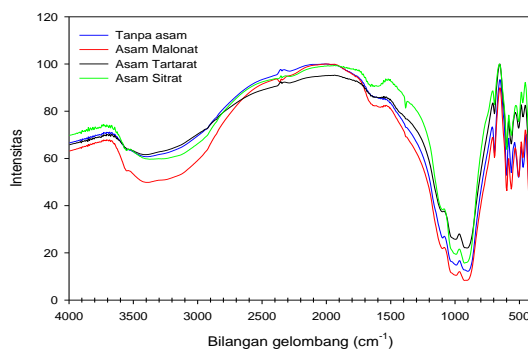


Figure 3. FT-IR spectra for NASICON with additives

Variation of additive concentrations did not give significant differences in IR spectra as showed in Figure 4. Meanwhile, IR spectra for material calcined at 750°C-1000°C showed the differences as can be seen in Figure 5, and we concluded that calcinations temperature influenced the material.

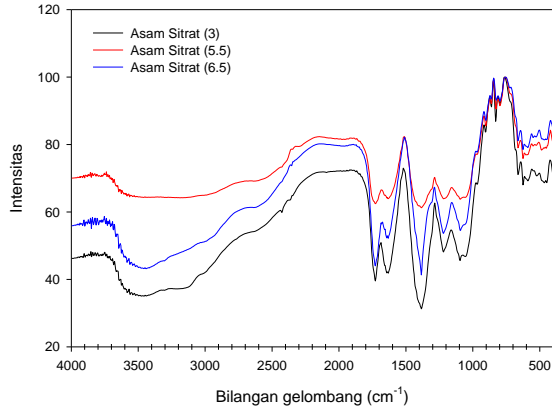


Figure 4. IR spectra with different additive concentrations

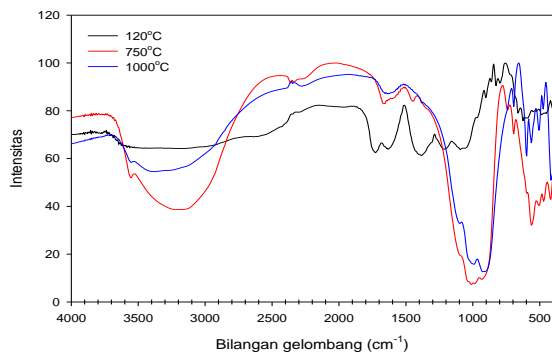


Figure 5. IR spectra with citric acid calcined at 750°C and 1000°C

### 3.4. XRD analysis

Diffractograph pattern as described in Figure 6 shows the peaks of NASICON at  $2\theta = 13, 19, 20, 24, 27.5, 30, 33, 42, 45, 46, 48, 50, 53, 57$  and  $60$ . There was another peak that identified as contaminant from the formation of zirconia.

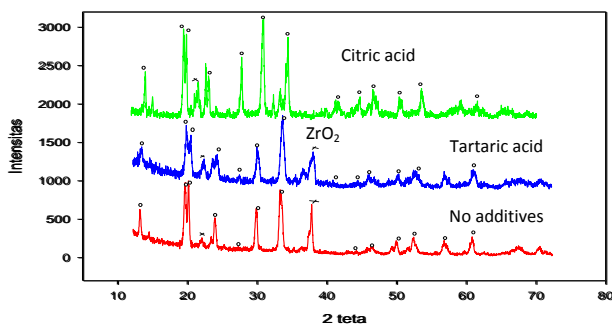


Figure 6. XRD pattern of NASICON

It was concluded that citric acid addition resulted the best product indicated by higher intensity levels of  $2\theta$ .

### 3.5. XRF analysis

XRF analysis for NASICON with and without tartaric acid showed the existing of Na, Zr, Si, and P as described in Table 3.

Table 3. Elements of NASICON prepared 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		$\text{Na}_{2.7}\text{Zr}_{2.6}\text{Si}_{1.9}\text{P}_{1.1}$	$\text{Na}_{2.7}\text{Zr}_{3.6}\text{Si}_{2.1}\text{P}_{0.9}$

This result shows the chemical formula for material prepared approaches the stoichiometry of NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ) which has rhombohedral symmetric. It also can be seen there was an exceeding of Zr in NASICON. It was predicted as the formation of  $\text{ZrO}_2$  within the synthesized material. This fact was supported by XRD and FT-IR which illustrated the peaks of  $\text{ZrO}_2$ .

### 3.6. SEM analysis

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

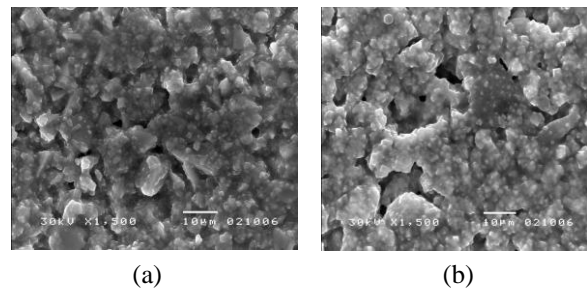
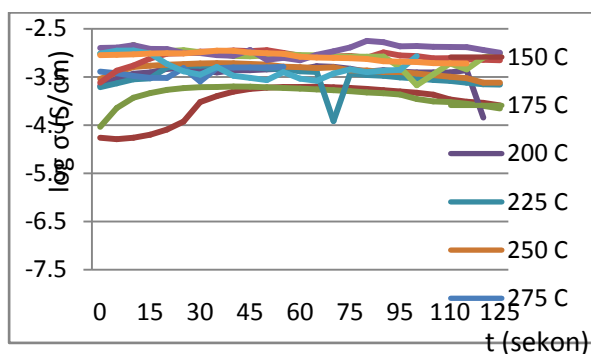
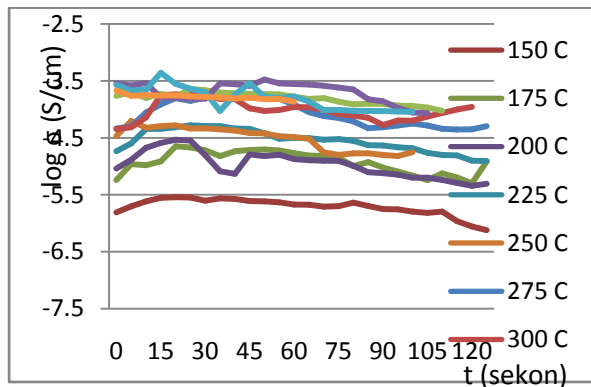
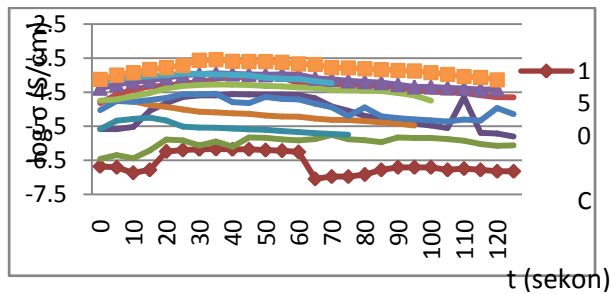


Figure. 7. SEM analysis for NASICON (a) without additives and (b) with tartaric acid

Particles of NASICON which prepared with tartaric acid revealed more homogeny and the size was around  $1 \mu\text{m}$ . The particles overlay one another. According to the research by Ignaszak, et. al in 2005 [3], the conductivity of material will be linier to its homogeneity.

### 3.7. Conductivity measurements

Measuring conductivity of NASICON was proposed to analyze the characteristic of the material. Figure 8, 9, and 10 describes the conductivity of NASICON added by citric acid with 3M; 5.5M; and 6M respectively, as the function of time. These measurements were carried out in difference temperatures to find out the influence of analysis temperatures toward the conductivity of ionic material.



Conductivity measurements were conducted in several temperatures, 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 275 °C, 300 °C, 325 °C, 350 °C, 375 °C and 400 °C. Temperatures were varied to observe the correlation between conductivity of ionic material toward increasing temperatures. In general, conductivity of NASICON rose with temperatures increased [1].

Figure 8 describes the conductivity of prepared NASICON with citric acid 3M was  $\log \sigma = -7.04$  at 150°C for the lowest point, meanwhile,  $\log \sigma = -3.54$  at 400°C for the highest point. On the other hand, Figure 9 shows the conductivity of NASICON prepared with citric acid 5.5M which had the lowest point of  $\log \sigma = -8.15$  at 150°C and the highest point was  $\log \sigma = -3.54$  at 350°C. However, Figure 10 shows the highest conductivity among the three graphs with the range of conductivity was  $\log \sigma = -4.47$  at 150°C to  $\log \sigma = -2.75$  at 350°C.

The result suggests 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 NASICON. The

conductivity of synthesized NASICON has filled the requirement to be included as *fast ionic conductor* and could be used as the component of NOx gas sensor.

### 3.8. Testing for the activity of NASICON ????

Testing for the activity of NASICON was carried out to observe the feasibility of prepared material to be used as the component for NOx gas sensor. These processes were conducted with NASICON-citric acid 6.5M at 350°C.

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## 4. Conclusions

## Acknowledgements

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