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Investigation of sensing mechanism of Nasicon electrocatalytic sensors in nitrogen dioxide and ammonia

Piotr Jasinski [a,] *, Anna Strzelczyk [b], Bogdan A. Chachulski [b], Maria Gazda [c], Grzegorz Jasinski [a]

[a] *Faculty of Electronics, Telecommunication and Informatics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland*

[b] *Chemical Faculty, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland*

[c] *Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland*

Abstract

In this paper a sensing mechanism of Nasicon electrocatalytic sensor in nitrogen dioxide and ammonia is investigated. Both gases are environmentally hazardous and contain nitrogen atom in the molecule. However, it seems that their sensing mechanism in electrocatalytic sensor could be totally different. Namely, the maximum sensitivity for each gas was obtained at different temperatures. Also, different auxiliary layers are formed for each gas.

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1. Introduction

Electrocatalytic sensors belong to family of electrochemical sensors with solid state electrolyte. Their sensing mechanism is based on application of periodically changing voltage and acquisition of current response. Obtained in this way current-voltage plot provides fingerprint information about ambient gases, which interact with sensor surface due to electrical excitation. So far relatively simple sensor structures have been investigated. Mostly, those structures consisted different types of electrolyte and metallic electrodes. We have been investigating those sensors before and it seems that Nasicon electrolyte with

* Corresponding author. Tel.: +48 58 347 1323; fax: +48 58 347 1757.
E-mail address:piotr.jasinski@eti.pg.gda.pl.

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platinum electrodes is very good structure for sensing mechanism investigation [1,2]. The structure shows unique response to different gases. So far, the major drawback of electrocatalytic sensor is related to instability due to formation of chemical phases on the sensor surface, which covers and block triple phase boundary. However, it was found that the sensors, which exposed and poisoned by nitrogen dioxide, can be at any time refreshed by short time high temperature treatment [3]. In order to improve sensor stability in different gases it is necessary to better understand the sensors sensing mechanism. This work aims to investigate Nasicon electrocatalytic gas sensor sensing mechanism in nitrogen dioxide and ammonia.

2. Experimental

In this paper, Nasicon ($Na_{2.8}Zr_2Si_{1.8}P_{1.2}O_{12}$) sensors with platinum electrodes were prepared and investigated. Namely, Nasicon powder was prepared by the conventional solid-state ball milling method from the zirconium oxide, silicon oxide and trisodium phosphate. The components were mixed in ball mill and annealed at 900°C. Obtained in this way powder was compacted into pellets (~12 mm in diameter and 1 mm thick) by iso-axial pressing. The pellets were sintered in air for 2 hours at 1100°C. Electrodes were made by coating both sides of the pellet with the platinum paste (ESL ElectroScience, ESL 5542) and firing at 900°C (surface area of 0.5 cm^2). Measurements were conducted in mixtures of high purity gasses: nitrogen dioxide or ammonia and synthetic air, which were supplied with a constant gas flow of 100 sccm maintained by mass flow controllers. The experiments were conducted in a tube furnace, which temperature was controlled with accuracy better than 0.5°C. The measurements were performed using the electrochemical interface Solartron SI 1287.

To obtain sensor sensitivity in nitrogen dioxide and ammonia, a triangular voltage excitation signal with the amplitude of 5 V and sweep rate of 50 mV/s was applied to the sensor. The electrical current was recorded during sensor polarization. On the current-voltage plot the peaks with different heights (maximum of the electric current) were visible for different concentrations of ammonia and nitrogen dioxide. This information was used to obtain sensors sensitivity *S* at different temperatures (1):

$$S = I_{max}\ (\text{in 100 ppm of gas}) / I_{max}\ (\text{in synthetic air}) \quad (1)$$

To investigate sensors sensing mechanisms XRD pattern of the electrode surface was investigated. Namely, a freshly fabricated Nasicon sensor was exposed to 100 ppm of ammonia or nitrogen dioxide at 200°C or at 350°C. At those temperatures the maximum sensitivity was recorded for each gas. When the temperature was stabilized the sensor was polarized (biased) with 1 V for 7 hours to form a sensing phase on the surface of electrode. The same sensing phase is formed during normal sensor operation, i.e. when the sensor is excited with triangular signal. On current- voltage plot it is reflected by the appearance of peaks due to electrochemical reaction of formation and decomposition of the phases. The surfaces of the sensors were investigated using X-ray diffractometry in order to determine the composition of the formed phase. XRD patterns were recorded with Cu Kα radiation at room temperature using Philips X'Pert Pro diffractometer. Qualitative phase analysis of diffraction pattern was carried out with ICDD PDF database.

3. Results

Nitrogen dioxide and ammonia contain nitrogen atom and both gases are environmentally hazardous. However, it seems that sensing mechanism of electrocatalytic sensor is not the same. The sensitivity level and the temperature of the maximum sensitivity are different (see Fig.1). Namely, for the nitrogen dioxide the maximum sensitivity of 34 was obtained at about 175°C, while for ammonia of 10 at about 350°C. To investigate sensors' sensing mechanism, freshly fabricated sensor structures were polarized at different

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temperatures in 100 ppm of nitrogen dioxide and ammonia. The electrodes of the sensors were investigated by XRD in order to determine phases, which were formed on the electrodes as the result of sensor electrical excitation. In Fig. 2. is presented XRD pattern of the sensor exposed to 100 ppm of nitrogen dioxide at 200°C and polarized with 1 V for 7 hours. It was found that on the negatively polarized electrode the chemical compound was formed (see Fig.2a), which does not exist on positively polarized electrode. The chemical compound was determined to be sodium nitrate or sodium nitrite and it is expected that this compound is formed and decomposed during normal sensor operation. Unfortunately, sodium nitrate and sodium nitrite show nearly the same XRD pattern, so it is impossible to distinguish between them. In Fig.2b is presented XRD pattern of the sensor exposed to100 ppm of NO_2 for 7 hours at 200°C and 350°C. The peak in XRD related to $NaNO_2/NaNO_3$ layer is much higher at 200°C than at 350°C. The sensitivity of the sensor at 200°C is much higher than at 350°C, what is in agreement with the hypothesis that the $NaNO_2$ or $NaNO_3$ is responsible for sensing mechanism of electrocatalytic sensors.

Contrary to the sensor exposed to nitrogen dioxide, in ammonia the surface of the negative (and possitive) sensor's electrode is free from any traces of $NaNO_2/NaNO_3$ both at 200°C and at 350°C.

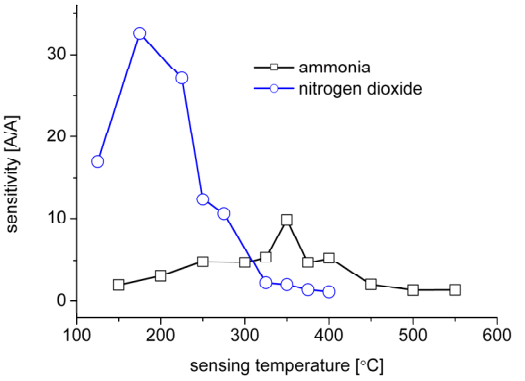

Fig. 1. Sensitivity plot of sensor exposed to 100 ppm ammonia and 100 ppm nitrogen dioxide at different temperatures.

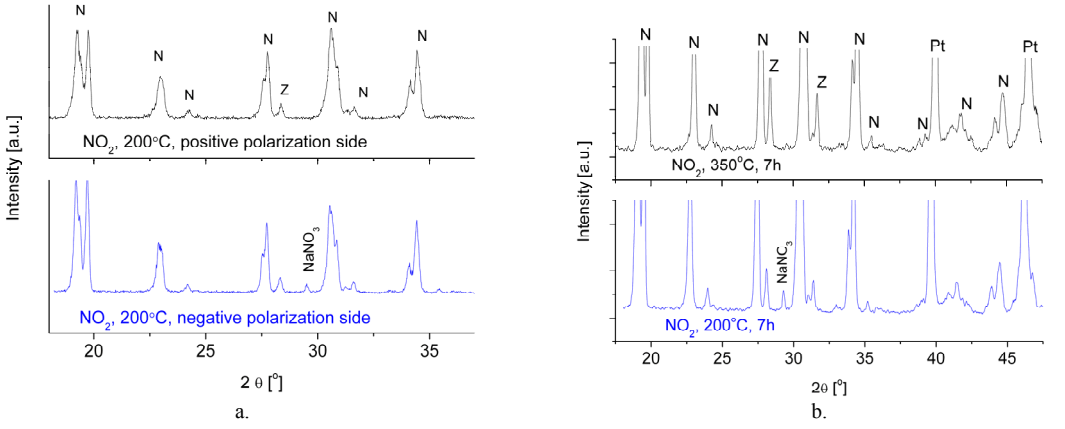

Fig. 2. XRD diffraction pattern of both sides of the sensors biased with the voltage of 1 V in 100 ppm of NO_2 for 7 hours at 200°C. (a) and negative polarization sides of the sensor at 200°C and 350°C (b). N – Nasicon, Z – zirconium oxide, Pt - platinium.

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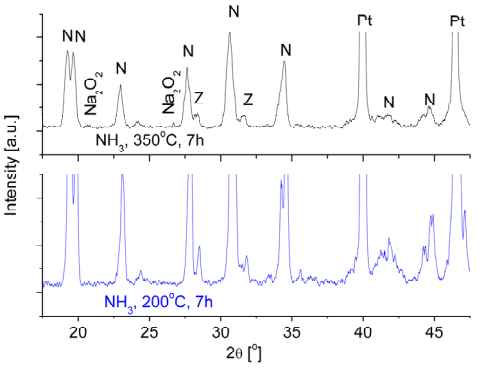

Fig. 3. XRD diffraction pattern of the sensors' negative polarization side. The sensors is biased with the voltage of 1 V in 100 ppm of NH_3 for 7 hours at 200°C and at 350°C. (N – Nasicon, Z – zirconium oxide, Pt - platinum)

Instead, small traces of sodium peroxide were detected at 350°C (see Fig.3). At 200°C the sodium peroxide is not detected, but at the same time the sensitivity of the sensor is lower than at 350°C. Therefore, it can be concluded that sensing mechanism of electrocatalytic sensor is different in nitrogen dioxide and ammonia. Namely, in nitrogen dioxide the sodium nitrate/nitrite is formed on the sensor electrode, while in ammonia the sodium peroxide.

4. Conclusions

In this paper the sensing mechanism of electrocatalytic Nasicon sensor in nitrogen dioxide and ammonia was investigated. It was found that the very high sensitivity in nitrogen dioxide at 200°C is related to sodium nitrate/nitrite formation, which at 350°C – much lower sensitivity in nitrogen dioxide - was barely detected. In case of the sensor exposed to ammonia, formation of sodium peroxide was detected. The amount of this phase is lower at 200°C than at 350°C, what is in agreement with sensitivity level at those temperatures.

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