Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 98 (2014) 129 – 132

Procedia Engineering

www.elsevier.com/locate/procedia

11th International Symposium on Systems with Fast Ionic Transport, ISSFIT 11

Electrocatalytic gas sensor with reference layer

Anna Strzelczyk[a], Piotr Lorenc[a], Grzegorz Jasinski[b]*,

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

Abstract

This paper presents studies of gas sensors prepared in ceramic technology with Nasicon as a solid electrolyte. Sensors work in the voltammetric mode thus based on the excitation of a sensor with a periodic potential signal while current response is recorded. The main aim is to investigate a $Bi_8Nb_2O_{17}$ reference layer influence on sensor properties. Sensors I-V characteristics in different concentration of nitrogen dioxide have been measured. Three different constructions of the sensor are compared.

Keywords: electrocatalytic sensor; gas sensor, nitrogen dioxide; solid state electrolyte

1. Introduction

In recent years electrochemical gas sensors based on solid state electrolytes have been intensively developed. They are easy to obtain, use and relative durable [1]. Nasicon is one of the most promising materials, which have been used in construction of gas sensors based on solid electrolytes. Most of these devices work in potentiometric or amperometric mode. However, some works are dedicated to sensors working in electrocatalytic mode [2, 3]. Reported results indicate that such sensors have enhanced selectivity [3]. Principle of operation of such sensors is based on the galvanic cell excitation with a periodic potential signal, while current response is recorded. When a voltage is applied to sensors electrodes an oxidation or a reduction of chemical species occurs. This results in a unique current-voltage (I-V) characteristic for each type and concentration of measured gas mixture. As a consequence gas concentration determination is possible.

Electrocatalytic sensors usually employs simple structure of a solid electrolyte and two metal electrodes [3, 4]. In this study electrocatalytic sensor with additional, reference layer is proposed. Our main goal was to check if presence

* Corresponding author. Tel.: +48-58-3471735; fax: +48-58-3486373.
E-mail address: grzegorz.jasinski@eti.pg.gda.pl

doi:10.1016/j.proeng.2014.12.499

of $Bi_8Nb_2O_{17}$ reference layer has any beneficial effect on sensor properties in case of electrocatalytic nitrogen dioxide sensor. In case of potentiometric gas sensor with such layer an improvement of sensor properties have been reported [5]. Properties of the sensors with and without this layer are compared.

2. Experimental

2.1. Sensor preparation

Nasicon pellets were prepared using the sol-gel method [6]. As a substrates $NH_4H_2PO_4$, $Na_2SiO_3{\cdot}9H_2O$ and $ZrO(NO_3)_2{\cdot}xH_2O$ were used. Aqueous solution of $ZrO(NO_3)_2$ was mixed with aqueous solutions of $NH_4H_2PO_4$ and $Na_2SiO_3{\cdot}9H_2O$ (molar ratio of components was 2:1:2) to form a sol. In order to obtain a gel, sol was heated at 100ºC for 12 hours and continuously dried at 100ºC to form xerogel. First calcination at 750ºC for 2 hours and afterwards sintering at 1000ºC for 12 hours were performed. Reference electrode material ($Bi_8Nb_2O_{17}$) was prepared from Bi_2O_3 and Nb_2O_5. These oxides were mixed at the molar ratio 4:1 (Bi_2O_3:Nb_2O_5). Calcination of oxides powders at 750ºC for 5 hours and sintering at 950ºC for 10 hours were performed.

One side of a Nasicon pellets was painted with Pt paste and then sintered at 900ºC. On the opposite side of pellet a layer of $Bi_8Nb_2O_{17}$ and Pt mixture was obtained in similar manner. Two kinds of sensor with reference layer were investigated, one with both electrodes exposed to the test gas mixture and other with Pt+$Bi_8Nb_2O_{17}$ electrode coated with dielectric sealing. Properties of these two sensors were compared with results obtained for the symmetrical sensor without the reference electrode. Investigated sensors structures are presented in Fig. 1 and referred later as a sensor 1, sensor 2 and sensor 3.

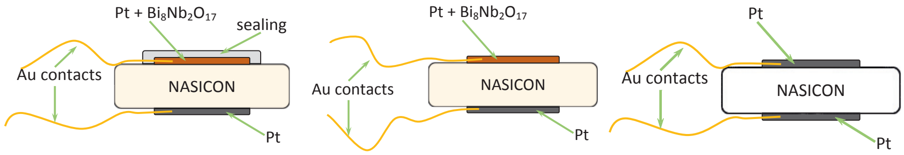

Fig. 1. Sensor 1 with additional layer sealed (a), sensor 2 with additional layer unsealed (b) and sensor 3 with symmetrical structure (c)

2.2. Sensor properties measurements

Measurement stand is presented in the Fig. 2. The measurements were performed using the electrochemical interface SI 1287 and a PC with suitable software for system control and data acquisition. Linearly changing voltage of symmetrical triangular shape (range from 5 V to –5 V) was used. Temperature was fixed to 300ºC.

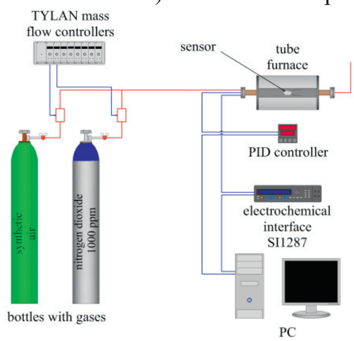

Fig. 2. Measurement stand

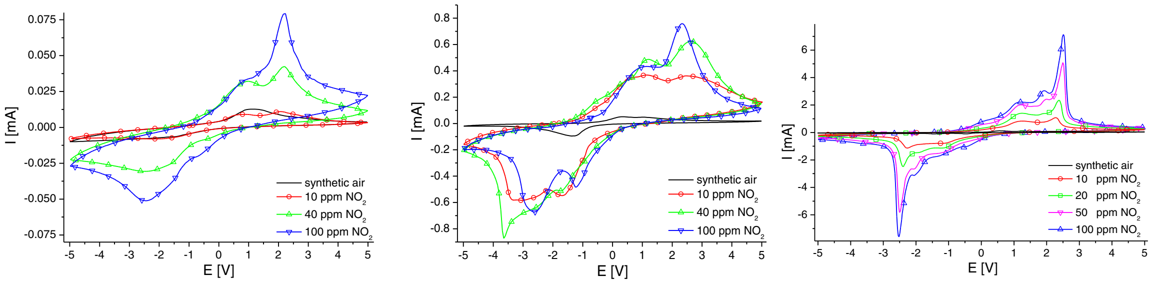

Fig. 3. Cyclic voltammograms at 300ºC measured for sensor 1 (a), sensor 2 (b) and sensor 3(c)

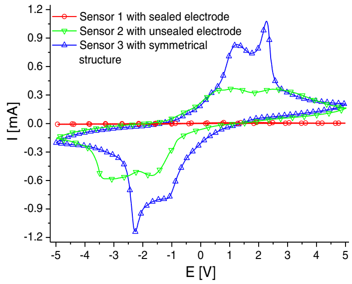

Fig. 4. Comparison between cyclic voltammograms measured for all sensors in 10 ppm NO_2

3. Results

3.1. Cyclic voltammetry

Current-voltage plots measured for all sensors in the atmosphere of the mixtures of synthetic air and nitrogen dioxide are shown in the Fig. 3. It is visible that in case of all sensors shape of obtained plots depends on the concentration of NO_2. In the Fig. 4 shapes of the I-V plots measured in the atmosphere containing 10 ppm of NO_2 for all investigated sensors have been compared. I-V plots measured for sensor 3 (Fig. 3c) with symmetrical structure are almost symmetrical. Characteristics registered for two sensors with additional reference layers are less symmetric. For sensor 1 with sealed electrode current-voltage plots (Fig. 3a) 'positive' peaks are much higher than negative peaks.

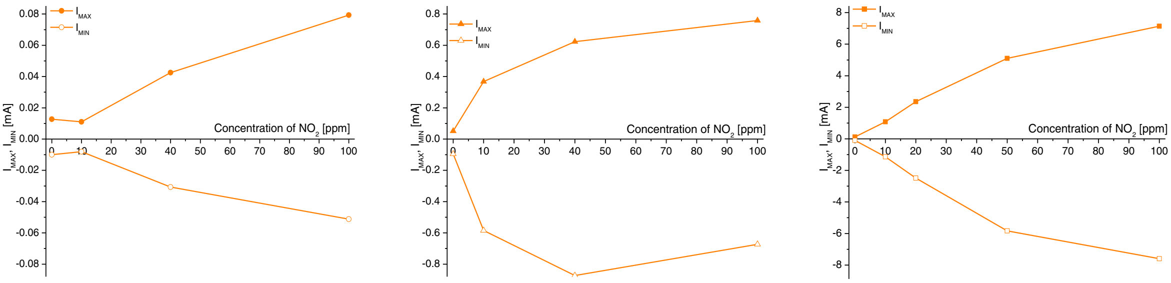

Fig. 5. Maximum current peak for different NO_2 concentrations sensor 1 (a), sensor 2 (b) and sensor 3 (c)

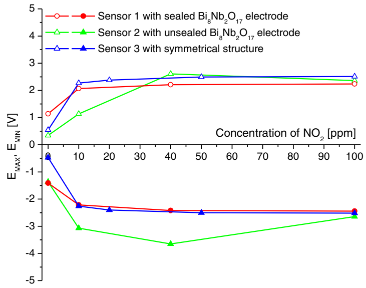

Fig. 6. Potential dependence of NO_2 concentration for all sensors.

3.2. Maximum peak current and potential dependence of NO_2 concentration

The maximum current peak value can be consider as a measure of the NO_2 concentration [4]. Maximum peak current dependences on NO_2 concentration are presented in the Fig. 5. I_{MAX} in the figure indicate maximum current value of 'positive' peaks and I_{MIN} maximum current value of 'negative' peak. In the most cases an increase of NO_2 concentration causes an increase in the current value. In the Fig. 6 values of potentials corresponding to the I_{MAX} and I_{MIN} are presented. This is the potential, in which chemical reaction occurring on the sensor electrodes is the fastest. This potential is almost independent of the NO_2 concentration and sensor structure. Only in case of sensor 2 values of potentials corresponding with I_{MIN} are slightly different.

Value of registered currents strongly depends on structure of the sensor. The highest values of the currents were recorded for the sensor without additional layers. This can be explained by the fact that electrochemical reaction can freely occur on both electrodes. In case of the sensor with sealed reference electrode reactions occur mainly on unsealed Pt electrode, alternately oxidation and reduction. In case of sensor 2 one of the electrodes active area is reduced by presence of $Bi_8Nb_2O_{17}$ layer.

4. Conclusions

In this work properties of the electrocatalytic sensors based on Nasicon and $Bi_8Nb_2O_{17}$ with different construction were investigated. Voltammetric response of this sensors in different NO_2 concentrations have been measured. Obtained results are compared with results of sensor with regular, symmetrical construction without any additional layers. It has been proved that presence of auxiliary layer influenced on sensor response. Based on performed experiments it is hard to judge if $Bi_8Nb_2O_{17}$ improves sensor properties. Further studies are necessary.

Acknowledgements

This work was partially supported by the Polish Ministry of Science and Higher Education under grant No. N N515 243437 and State Budget Funds assigned for statutory activity.

References

[1] J. W. Fergus, Materials for high temperature electrochemical NO_x gas sensors., Sens. Actuators B 121 (2007) 652-663.
[2] E.L. Shoemaker, M.C. Vogt, F.J. Dudek, T. Turner, Gas microsensors using cyclic voltammetry with a cermet electrochemical cell, Sens. Actuators B 42 (1997) 1-9.
[3] P. Jasiński, A. Nowakowski, Simultaneous detection of sulphur dioxide and nitrogen dioxide by Nasicon sensor with platinum electrodes, Ionics 6 (2000) 230-234.
[4] G. Jasiński, P. Jasiński, B. Chachulski, A. Nowakowski, Electrocatalytic gas sensors based on Nasicon and Lisicon, Mater. Sci.-Poland 24 (2006) 261-268.
[5] H.-Y. Dang, X.-M. Guo, Characteristics and performance of NASICON-based CO_2 sensor using $Bi_8Nb_2O_{17}$ plus Pt as solid-reference electrode, Sens. Actuators B 178 (2013) 163-168.
[6] Y. Shimizu, Y. Azuma, S. Michishita, Sol-gel synthesis of NASICON discs from aqueous solutions, J. Mater. Chem. 7 (1997) 1487-1490.