Solid-state electrochemical gas sensors

P. JASIŃSKI[*]

Department of Biomedical Engineering, Gdańsk University of Technology,
ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

Various types of solid-state electrochemical gas sensors are presented. The sensing mechanism and examples of potentiometric, amperometric and electrocatalytic sensors are described. The possibility of multi-gas detection in the case of amperometric and electrocatalytic sensors is characterized. The principle of operation of the wide-band oxygen sensor, combining the potentiometric and amperometric modes, is presented.

Key words: *electrochemical gas sensor; solid electrolyte; air monitoring*

1. Introduction

A lot of recent work focuses on the development of solid-state gas sensors [1]. Especially interesting are electrochemical sensors, because they can be compact, robust, and cost effective in large-scale production. Solid electrolytes are key components of electrochemical gas sensors. They usually operate at elevated temperatures because most solid electrolytes have low conductivity at room temperature. A higher temperature of operation is an advantage, because electrode reactions proceed much faster and the sensor can work in demanding environments (e.g. exhaust gases). Depending on the mode of operation, electrochemical sensors are divided into potentiometric, amperometric and electrocatalytic ones. In the potentiometric mode, the measured signal is an electromotive force, while in the amperometric mode an electric current is recorded. In the case of electrocatalytic sensors, the current–voltage plot should be analysed.

2. Potentiometric sensors

Galvanic cells consisting of a solid electrolyte and two electronically conducting electrodes, reversible against mobile or immobile ions of the electrolyte, are used for potentiometric measurements. The electrodes are often called the reference electrode

_____

[*]E-mail: pijas@eti.pg.gda.pl

(R) and working (sensing) electrode (W). Chemical potentials are formed at the electrode–electrolyte interfaces due to equilibria of electrochemical reactions. Namely, chemical potentials are created at the electrolyte-reference electrode interface and at the electrolyte-sensing electrode interface, where an equilibrium with the ambient gas is established. The gradient of chemical potential across the electrolyte results in an electrical potential drop, which can be measured as an electromotive force (EMF) of the galvanic cell. The EMF is related to the gas partial pressure through the Nernst equation:

$$\text{EMF} = E_0 + \frac{RT}{nF} \ln \frac{p_w}{p^\circ} \tag{1}$$

where, E_0 is the EMF at a standard pressure of 1 bar, R – the gas constant, F – the Faraday constant, n – the number of electrons involved in the electrochemical reaction of the gas molecule, T – the absolute temperature, p_w is the gas partial pressure at the working electrode and p° is the standard pressure (1 bar).

The essential requirement for a reference electrode is its independence of the investigated gas. Usually, the chemical potential at the reference electrode–electrolyte interface is fixed by an electrochemically reversible reference gas or a solid solution. In the former case, the sensor consists of two gas chambers separated by an electrolyte. One chamber is filled or exposed to a reference gas, while the other is exposed to the gas whose concentration is to be determined [2]. In the latter case, the solid solution which can electrochemically equilibrate with the electrolyte, is in contact with the electrolyte. Any reaction with the surrounding gas is not acceptable, because the reaction products might influence the chemical potential. Therefore, the reference electrode is often sealed [3]. Sealing is usually a difficult technological process, because of different temperature expansion coefficients of the sealant, electrolyte and reference electrodes, different sintering temperatures of sensor components, and possible high reactivity of the reference electrode.

The best-known potentiometric sensor is the Lambda sensor, used in stoichiometric-burn engines to control the air-fuel ratio. The classical construction of the Lambda sensor is presented in Figure 1 [4]. It consists of platinum electrodes and a thimble-shaped oxygen-ion electrolyte which is typically made of doped zirconium oxide. The interior of the thimble is exposed to atmospheric air, while the outside to the exhaust gas. Oxygen molecules equilibrate at the interface of the electrolyte and platinum electrode, in accordance with the following electrochemical reaction:

$$O_2\,(\text{gas}) + 4e^-\,(\text{electrode}) \rightarrow 2O^{2-}\,(\text{electrolyte}) \tag{2}$$
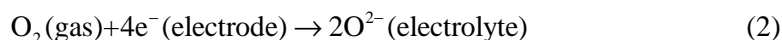
When the air-to-fuel mixture is rich, the EMF of the sensor is about 0.9 V, while in the lean mixture about 0.1 V is observed (Fig. 2). At the stoichiometric point, when an air-to-fuel mass ratio of 14.7:1 is reached, the EMF is 0.45 V. The Lambda sensor is suitable for controlling the air-fuel mixture at the stoichiometric point, while it is

unsuitable for determining the air-to-fuel ratio in lean or rich regimes. Therefore, other types of sensors (e.g., wide-band oxygen sensor) are used to control lean-burn or rich-burn engines.
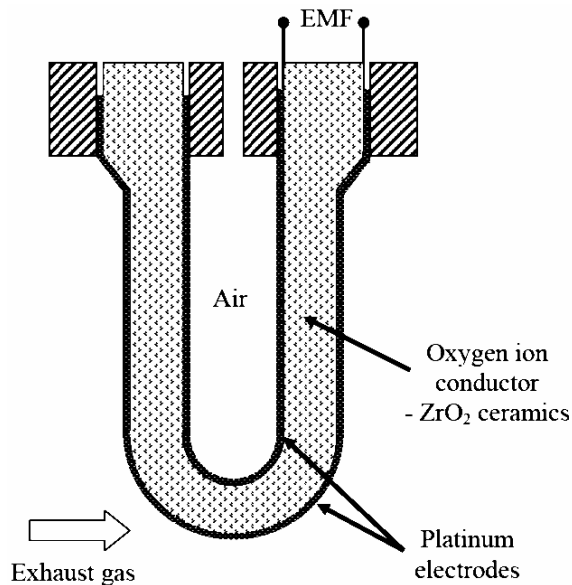

Fig. 1. Simplified schematic diagram of an unheated thimble-type oxygen sensor
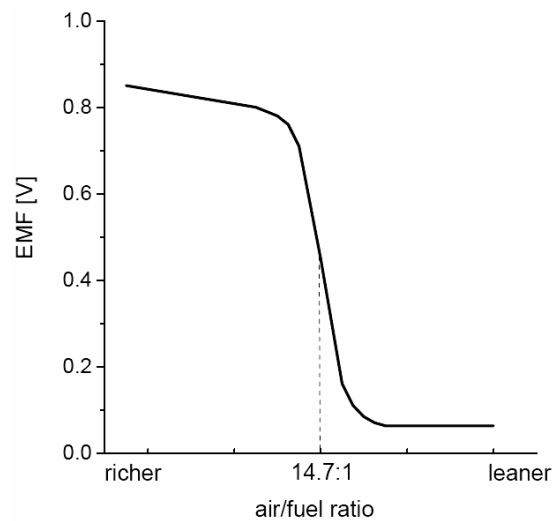(reprinted from [4] with the permission from Elsevier)

Fig. 2. Dependence of an air-to-fuel mixture on EMF of the sensor

An example of a carbon dioxide sensor with a sealed solid reference electrode is a cell with its reference electrode constructed of Na_xCoO_2, Na-β alumina electrolyte,

and Na_2CO_3 sensing electrode [5]. In this case, however, EMF of the sensor depends on both CO_2 and O_2 partial pressures. This is characteristic of a sensor with a sealed reference electrode and is caused by the fact that both carbon dioxide and oxygen influence the chemical potential of the sensing electrode. In contrast to sensors with sealed reference electrodes, this sensor can be insensitive to oxygen partial pressure when a proper material is used for the unsealed reference electrode. Such a sensor is often called a sensor with an open reference electrode. An example of a carbon dioxide sensor with an open reference electrode is a cell with a reference electrode constructed from a mixture of $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$, an Na-β'' alumina electrolyte, and Na_2CO_3 sensing electrode [6]. Such a sensor is only sensitive to carbon dioxide because changes in oxygen partial pressure affect the chemical potential of the sensing and reference electrodes in the same way. Therefore, variations in oxygen concentration do not influence the EMF of the sensor. In contrast, variations in carbon dioxide concentration affect only the chemical potential of the sensing electrode, because of the high chemical stability of the reference electrode material towards carbon dioxide [7].

3. Amperometric sensors

Amperometric sensors, in contrast to potentiometric ones, feature a linear dependence of the electric signal on gas concentration, small temperature sensitivity, and lack of any reference electrode. The later significantly simplifies sensor construction. Due to their detection range, sensitivity and high temperature operation, amperometric sensors are widely used in controlling the operation of lean-burn engines [8]. A typical structure of an amperometric oxygen sensor with a hole as the diffusion barrier is presented in Figure 3. When external voltage is applied across the galvanic cell, the following electrochemical reaction occurs at the cathode (negative terminal):

$$O_2(gas) + 4e^-(electrode) \longrightarrow 2O^{2-}(electrolyte) \tag{3}$$
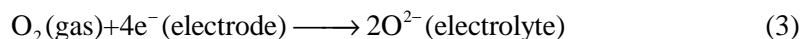
Generated oxygen ions move across the electrolyte to the anode (positive terminal), where they recombine to give oxygen molecules in an ambient gas:

$$2O^{2-}(electrolyte) \longrightarrow O_2(gas) + 4e^-(electrode) \tag{4}$$
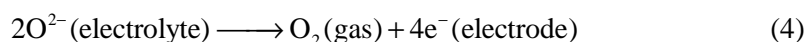
In other words, oxygen molecules reduce to oxygen ions at the cathode, and then are transported across the electrolyte to the anode, where their re-oxidation to oxygen molecule occurs. The limiting current is related to geometrical parameters of the diffusion barrier and oxygen concentration, as defined by Fick's first law of diffusion, the ideal gas equation, and Faraday's law [9]:

$$I_{\text{lim}} = -\frac{nFD_{O_2}AP}{RTL}\ln(1 - x_{O_2}) \tag{5}$$

where I_{lim} is the limiting current, n is the number of electrons involved in the reaction, F is the Faraday constant, D_{O_2} is the diffusion coefficient of gaseous O_2, A is the area of the diffusion hole, P is barometric pressure, R is the gas constant, T is the operating temperature, L – the length of the diffusion hole, and x_{O_2} – the oxygen mole fraction. For small values of oxygen mole fraction (below 10% [10]), the logarithm becomes linear and I_{lim} can be approximated by:

$$I_{\text{lim}} = -\frac{nFD_{O_2}Ac_{O_2}}{L} \tag{6}$$

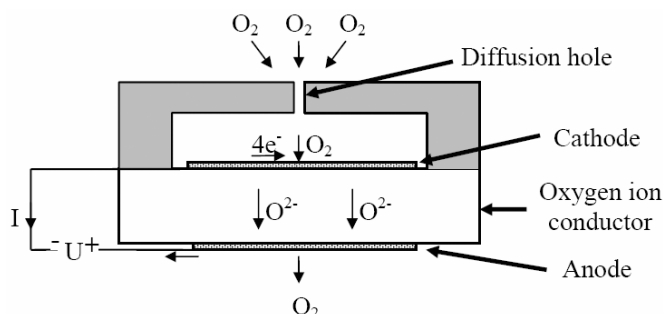where c_{O_2} is the oxygen concentration.

Fig. 3. Design and sensing mechanism of an amperometric
oxygen sensor with a hole as the diffusion barrier

In general, the principle of operation of the solid-state amperometric gas sensor is very similar to the polarographic method known from liquid electrochemistry. In this case, however, the diffusion barrier is not applied, because diffusion in liquids proceeds much slower than in gases. For example, the diffusion coefficient of oxygen in water at 25 °C is 2.4×10^{-5} cm^2/s, while in nitrogen at 20 °C it is 0.16 cm^2/s. At 700 °C, the diffusion coefficient of oxygen in nitrogen reaches 1.5 cm^2/s. Therefore, in order to obtain similar limiting currents, the electrode area of a solid state amperometric sensor should be several orders of magnitude smaller than that used in liquid polarography. This demand cannot be fulfilled, and the diffusion barrier must be introduced in order to obtain limiting currents [11].

The determination of oxygen requires the application of an oxygen ion conducting electrolyte, since it is necessary to transport reduced oxygen across the electrolyte. The same mechanism may be used for determining other gases. The number of electrolytes conducting different kinds of ions is limited, however, which restricts the number of determined gases. Nevertheless, some other gases can be detected using an

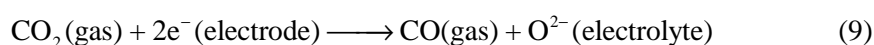indirect amperometric mechanism, based on electrodissociation or chemical oxidation/reduction reactions.

The electrodissociation of a gas molecule (e.g. CO_2 or H_2O) at the cathode electrode may occur when a sufficiently high voltage is applied to the sensor. The electrodissociation voltage for each reaction at a given temperature can be determined from Gibbs' free energy of reaction:

$$E_D = \frac{\Delta G}{nF} \tag{7}$$

It is known that water vapour electrodissociates at voltages higher than 1.2 V at 800 °C [9, 12]:

$$H_2O(gas) + 2e^-(electrode) \longrightarrow H_2(gas) + O^{2-}(electrolyte) \tag{8}$$
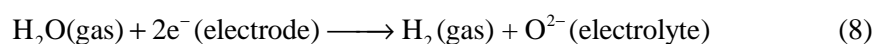
while carbon dioxide at the voltages higher than 1.6 V [9, 12]:

$$CO_2(gas) + 2e^-(electrode) \longrightarrow CO(gas) + O^{2-}(electrolyte) \tag{9}$$

This opens a possibility for sequential detection of few gases using the same sensor structure, by periodically varying the applied voltage.
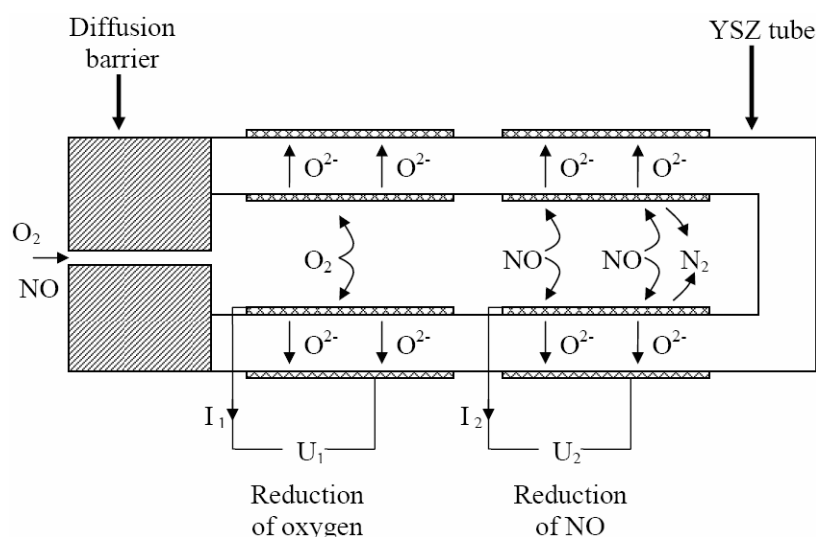

Fig. 4. Design and sensing mechanism of an amperometric sensor for simultaneous determination of nitrogen oxide and oxygen (reprinted from [13] with the permission from Elsevier)

When the sensor structure is modified, the amperometric sensing mechanism can be employed not only for sequential, but also for simultaneous measurements of multi-gas mixtures. In this case, the sensor structure is supplemented with an additional pair of electrodes. Various gases after diffusion through the barrier are conse-

quently electrodissociated at the electrodes polarized with selected voltages. This principle of operation was used in a sensor design for the simultaneous determination of nitrogen oxide and oxygen (Fig. 4) [10, 13, 14]. The voltage of 300 mV was used for the reduction and measurement of oxygen at the first pair of electrodes, while 550 mV for the reduction and measurement of nitrogen monoxide at the second pair of electrodes. A similar sensor configuration was used for the simultaneous determination of hydrocarbons and oxygen [15, 16].

4. Advanced sensor design

Recently, oxygen sensors combining potentiometric and amperometric modes have been developed for automotive applications. The so-called wide-band oxygen sensor and universal air-to-fuel ratio exhaust gas oxygen (UEGO) sensors are used in engines operating in the lean regime (air-to-fuel ratio (20–25):1)) or in special conditions (e.g., to obtain the maximum power of a gasoline engine, an air-to-fuel ratio of 12.6:1 is necessary) [17]. A schematic diagram of the Bosch LSU 4 version of the UEGO sensor is presented in Figure 5 [8]. The sensor structure, which is based on doped zirconium oxide ceramics, consists of a Lambda sensor and oxygen pump. One side of
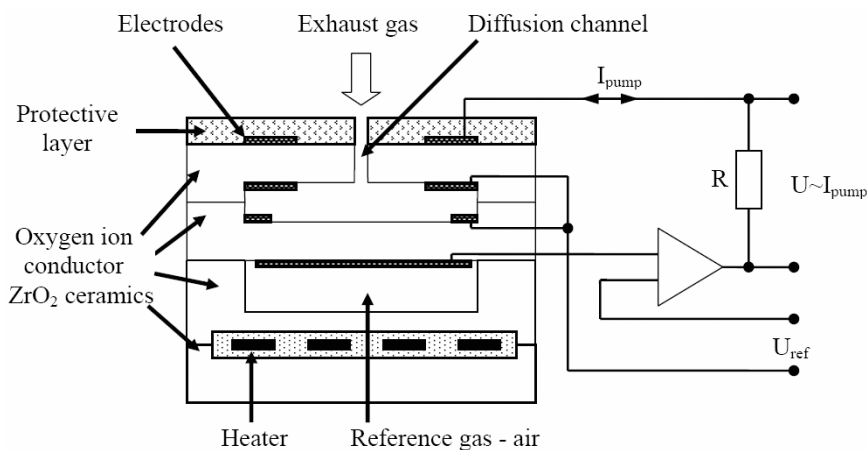

Fig. 5. Schematic diagram of Bosch LSU 4 wide-band oxygen sensor
(reprinted from [8] with permission from Elsevier)

the oxygen pump is exposed to the exhaust gas, while one side of the Lambda sensor is exposed to atmospheric air. The other electrode of the oxygen pump and Lambda sensor are buried in the diffusion gap, exposed to exhaust gas through the diffusion barrier. The electrodes of both structures are wired in such a way that the oxygen level in the diffusion gap is balanced by the current flowing through the oxygen pump. The measurement of this current allows a precise determination of the air-to-fuel ratio from 10:1 to pure

air. A built-in heater maintains a constant sensor temperature of about 750 °C, which can be obtained from a cold start within 15 s.

5. Electrocatalytic sensors

A deviation of kinetic processes from thermodynamic equilibrium due to voltage or current excitation is used in electrocatalytic gas sensors. This type of sensor may potentially provide more information than conventional potentiometric or amperometric electrochemical sensors. Its principle of operation is based on the excitation of a galvanic cell with a periodic signal, whose amplitude is so large that the sensor responds non-linearly. Usually, a triangular voltage is used as the excitation signal, while an electric current is recorded. The positions and heights of peaks in the current–voltage plot obtained in this way depend on the gas type and concentration. The working principle is similar to cyclic voltammetry, which is used in liquid electrochemistry for, e.g., detecting traces of heavy metals in water [18].
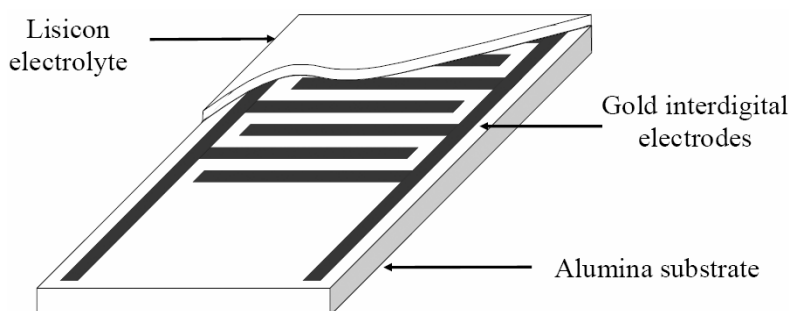

Fig. 6. Structure of the electrocatalytic gas sensor
based on Lisicon solid electrolyte [25]

The concept of the electrocatalytic sensor has been investigated using various solid electrolytes [19–24] and is based on the growth and decomposition of the gas-sensitive layer and the reactivity of this layer with the surrounding gas. Figure 6 presents the structure of an electrocatalytic sensor based on Lisicon solid electrolyte [25]. When a voltage ramp is applied to the sensor, Li^+ ions in the electrolyte migrate away from the positively polarized electrode towards the negative electrode. This activates the formation of the gas-sensitive layer at the negatively polarized electrode, while at the positively polarized electrode the decomposition of the existing gas sensitive layer proceeds correspondingly. When the voltage is reversed, the formation and decomposition occur at the opposite electrodes.

Figure 7 shows the current–voltage plot of the sensor exposed to synthetic air, 100 ppm of NO_2 and 100 ppm of SO_2 at 450 °C [25]. The existence of nitrogen dioxide in air is manifested by "positive" and "negative" peaks at about ±2.2 V, while sulphur

dioxide at about ±4 V. The heights of these peaks depend on the toxic gas concentrations. It might be expected that there is an opportunity for the simultaneous determination of various gases. The current–voltage plot of the sensor, however, when is exposed to a mixture of NO_2 and SO_2 in air, shows only one pair of peaks. It is still possible to detect NO_2 and SO_2 in air when the temperature of the sensor is altered. It can be shown that above 500 °C the Lisicon sensor is insensitive to NO_2, while below 300 °C it is over two order of magnitude more sensitive to SO_2 than to NO_2.
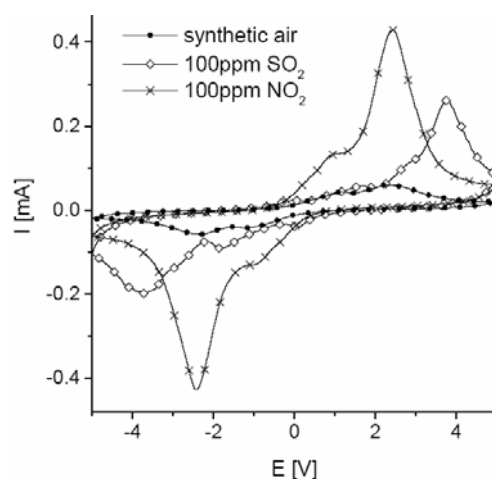

Fig. 7. Response of the Lisicon electrocatalytic gas sensor at 450 ºC [25]

6. Summary

An overview of electrochemical solid-state sensors was presented. Sensors were categorized and described based on their principle of operation. The overview covered potentiometric, amperometric and electrocatalytic sensors. A special attention was drawn to multi-gas detection and the design of the amperometric sensor for sequential and simultaneous multi-gas detection. The response of Lisicon electrocatalytic gas sensors was analysed. It was concluded that, at the current stage of the electrocatalytic sensor development, the current–voltage response must be analysed and the temperature of operation of the sensor must be altered in order to measure multi-gas mixtures.

References

[1] LEE D.-D., LEE D.-S., IEEE Sensors, 1 (2001), 214.
[2] YAMAZOE N., MIURA N., IEEE Trans. Compon. Pack. A, 18 (1995), 252.
[3] PARK C.O., AKBAR S.A., WEPPNER W., J. Mater. Sci., 38 (2003), 4639.
[4] GIBSON R.W., KUMAR R.V., FRAY D.J., Solid State Ionics, 121 (1999), 43.

[5] SCHETTLER H., LIU J., WEPPNER W., HUGGINS R.A., Appl. Phys., A57 (1993), 31.

[6] HOLZINGER M., MAIER J., SITTE W., Solid State Ionics, 86–88 (1996), 1055.

[7] HOLZINGER M., MAIER J., SITTE W., Solid State Ionics, 94 (1997), 217.

[8] IVERS-TIFFEE E., HARDTL K.H., MENESKLOU W., RIEGEL J., Electrochim. Acta, 47 (2001), 807.

[9] MASKELL W.C., PAGE J.A., Sens. Actuators, B 57 (1999), 99.

[10] SOMOV S. I., REINHARDT G., GUTH U., GOPEL W., Sens. Actuators, B 35–36 (1996), 409.

[11] DIETZ H., Solid State Ionics, 6 (1982), 175.

[12] LOGOTHETIS E.M., VISSER J.H., SOLTIS R.E., RIMAI L., Sens. Actuators, B 9 (1992), 183.

[13] SOMOV S.I., REINHARDT G., GUTH U., GOPEL W., Sens. Actuators, B 65 (2000), 68.

[14] SCHMIDT-ZHANG P., SANDOW K.-P., ADOLF F., GOPEL W., GUTH U., Sens. Actuators, B 70 (2000), 25.

[15] MAGORI E., REINHARDT G., FLEISCHER M., MAYER R., MEIXNER H., Sens. Actuators, B 95 (2003), 162.

[16] SOMOV S. I., GUTH U., Sens. Actuators, B 47 (1998), 131.

[17] RIEGEL J., NEUMANN H., WIEDENMANN H.-M., Solid State Ionics, 152–153 (2002), 783.

[18] BARD A.J., FAULKNER L.R., *Electrochemical Methods. Fundamentals and Applications*, Wiley, New York, 2001.

[19] LIU J., WEPPNER W., Appl. Phys., A 55 (1992), 250.

[20] SHOEMAKER E.L., VOGT M.C., DUDEK F.J., Solid State Ionics, (1996), 92, 285.

[21] SHOEMAKER E.L., VOGT M.C., DUDEK F.J., TURNER T., Sens. Actuators, B 42 (1997), 1.

[22] VOGT M.C., SHOEMAKE E.L., TURNER T., Sens. Actuators, B 36 (1996), 370.

[23] JASINSKI P., NOWAKOWSKI A., Ionics, 6 (2000), 230.

[24] JASINSKI P., NOWAKOWSKI A., WEPPNER W., Sensor Mater., 12 (2000), 89.

[25] JASIŃSKI G., JASIŃSKI P., NOWAKOWSKI A., CHACHULSKI B., Proc. 28th Internat. Conf. IMAPS -Poland Chapter 2004, Wrocław, 2004, p. 269.