
CONSTRUCTION AND INVESTIGATION OF SO₂ AMPEROMETRIC SENSOR WITH A SOLID POLYMER ELECTROLYTE MEMBRANE*

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Abstract: In this paper a sensor for detection of the sulphur dioxide based on three electrode cell configuration with a liquid electrolyte, a mercury sulphate reference electrode and a solid polymer electrolyte working electrode is presented. Working electrode was obtained by using Takenaka-Torikai chemical deposition method by precipitation of Au particles into the pores of the Nafion membrane.

Sensors characteristics measurements were performed in dynamic conditions during the gas flow. Responses of the sensor for the different concentration of SO₂ and NO₂ are presented. Sensitivity and selectivity of the sensor have been determined.

1. Introduction

Determination of the toxic gases concentration in air by the usage of electrochemical sensors is fast, convenient and relatively cheap. Among number of sensors' types an amperometric one are characterised by the high sensitivity and good dynamic properties. Amperometric sensors with a solid polymer electrolyte (SPE) membrane have evolved from Clark electrode for dissolved oxygen (Clark et al., 1953). Working electrode (WE) of the sensors with SPE membrane is in the form of a porous metal layer placed on a conductive polymer membrane. WE can be obtained with several methods, such as chemical deposition, metal vapour deposition, electrochemical deposition or painting. The main advantage of layers fabricated with chemical deposition is their stability during contact with water. There are two types of chemical deposition procedures. First of them is a impregnation-reduction (I-R) method which can be applied to the deposition of the layer from cationic metal precursor (e.g. [Pt(NH₃)₄]Cl₂, [Pd(NH₃)₄]Cl₂) (Schiavon et al., 1991). Second is Takenaka-Torikai (T-T) method.

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In this method anionic metal precursors (e.g. H_2PtCl_6 , RuCl_3 , PdCl_2 , HAuCl_4) are used (Takenaka, 1980).

In this article the preparation of a gold working electrode and sulphur dioxide sensor structure are presented. Responses of the sensor in the atmosphere containing different concentrations of sulphur dioxide (analyte) and nitric dioxide (interfering gas) have been measured. Sensitivity and selectivity coefficients have been determined.

2. Experimental

2.1. Sensor structure

Investigated sensor housing was made from polyether ether ketone (PEEK) which is highly resistant to acids and organic solvents (Fig. 1a). In the upper part of the housing a counter electrode (CE), a reference electrode (RE) and their contacts are placed. CE is in the form of a piece of gold sheet. Mercury sulphate reference electrode (MSE) is made of pure metallic mercury and mercury(I) sulphate obtained from the mercury(II) nitrate (Zoski, 2007). Mercury/mercury sulphate system is in contact with internal electrolyte containing sulphuric acid. Between upper and middle part of the sensor housing a working electrode and its contact are placed. More details about WE preparation method are presented in the next paragraph. Contact of WE is in the form of a gold ring. In the middle part of the housing WE contact ending, gas inlet and outlet are placed. Bottom part of the sensor has reservoir for hygrostatic liquid. Solution of 5 M sulphuric acid in water was used As an electrolyte.

2.2. Preparation of working electrode

The gold layer on the surface of Nafion membrane was obtained by using chemical plating method known as Takenaka-Torikai method. Nafion[®] 350 (Sigma-Aldrich), in the form of foil, thickness 0.01 inch (0.254 mm) strengthened by Teflon net was used. Nafion foil was washed in 5% hydrogen peroxide (at 75°C), rinsed in distilled water, and then placed in solution of the perchloric acid (at 90°C) in order to remove any impurities. After these treatments membrane was washed in distilled water several times to remove the remains of perchloric acid. Circle of Nafion, diameter 21 mm was placed in the specially designed vessel between 0.02 M solution of the chloroauric acid (PPH "POCh" S.A.) and 1 M solution of sodium borohydride (PPH "POCh" S.A.) in 1 M solution of sodium hydroxide. The vessel with the membrane and solutions were placed in the water bath at the temperature of 40°C for 4 hours. After this time membrane was removed from the vessel and washed in the distilled water. As a result the gold layer on the membrane (11 mm diameter) was obtained (Fig. 1b). The diameter of the round shaped electrode having contact with measured gas was ca. 9 mm, therefore geometric surface of the WE used later for the calculations equals 0.636 cm².

2.3. Measurement stand

Mixtures of high purity gases, namely synthetic air, 1000 ppm NO_2 and 1000 ppm SO_2 in synthetic air, have been used. Aalborg mass flow controllers were used in order to obtain the proper gas composition. All measurements were performed at room temperature.

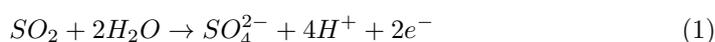


Voltammetric and potentiometric sensor responses were acquired by using electrochemical interface SI1287 and PC computer with suitable software (Corrware, Scribner Associates, Inc.). During the voltammetric measurements the linearly changing voltage with sweep rate of 5 mV/s was used for all results presented in the study. Constant gas flow of 100 millilitres per minute was maintained.

3. Results and discussion

3.1. Cyclic voltammetry measurements

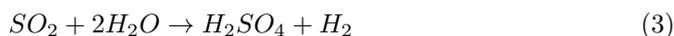
The reaction that occurred on the WE when a sulphur dioxide was present in the sensor surrounding and when a strong acid was used on internal electrolytes has the form:



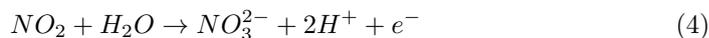
Simultaneously on the CE hydrogen ions are reduced according to equation:



Considering above the following reaction takes places in the sensor:



When in the sensor surrounding nitric oxide was present another reaction took place on the WE:



In Fig. 2 cyclic voltammograms recorded in synthetic air, 1000 ppm NO_2 and 1000 ppm SO_2 are presented. Electrochemical window (range of potentials limited by potentials of hydrogen and oxygen formation) for this sensor is from -0.2 V to 1.3 V. In the anodic (upper) part of the voltammogram oxidation processes are visible. The oxidation of SO_2 (1) occurs at potentials higher than 0.6 V. In range of potentials between 0.65 and 0.82 V a plateau region is observed for all presented curves. In this region measured current obtained for synthetic air, SO_2 and NO_2 differ significantly. As a consequence the potential in this range could be selected for the measurements at constant voltage.

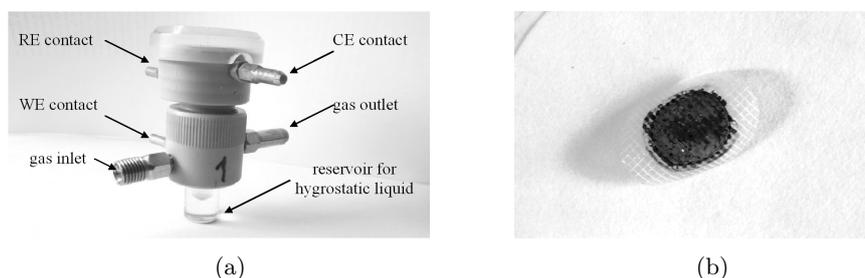


Fig. 1: Sensor (a) and Nafion membrane with layer of gold (b)



3.2. Potentiostatic measurements

In Fig. 3a response of the sensor recorded at the constant potential of 0.81 V *vs.* MSE for different concentrations of SO₂ is shown. For amperometric sensor the relationship between signal and concentration of measured gas should be linear. Fig. 3b shows data based on the measurement results from Fig. 3a. Obtained values of the current for concentration in range from 0 ppm to 400 ppm are in a good alignment with the linear relation. The linear fit for this results was performed (the linear regression coefficient $R^2=0.9981$). Sensitivity was determined from the slope of this line with a value 0.2263 mA/ppm (considering geometric electrode area - 0.3557 mA/(ppm·cm²)). For concentrations greater than 400 ppm effect of saturation can be observed and sensitivity decreases. Unfortunately, obtained value of sensitivity is approximately 2 times lower than results obtained by Gebicki (2007). It could be a result of a lower roughness and as a result lower real surface area of the electrode. Additional tests to determine real surface area of the electrode are needed. The modification of WE preparation procedure to obtain membrane with larger real surface area or modification of electrolyte composition is planned to improve the sensor sensitivity.

In Fig. 4a response of the sensor in atmosphere containing nitric dioxide is presented. The nitric dioxide could be treated as the interfering gas. Fig. 4b presents calibration plot for NO₂. The linearity of the plotted data can be seen in the concentration range from 200 to 800 ppm. The sensitivity of NO₂ calculated based on linear regression is 0.0355 mA/ppm (0.0558 mA/(ppm·cm²)). In this case the gas the saturation is not observed. The sensitivity is more than six times lower than is case of SO₂.

3.3. Selectivity

Sensor presented in this article was designed to detect of SO₂. However, other gases could also influence the response of the sensor. The influence of the interfering agent

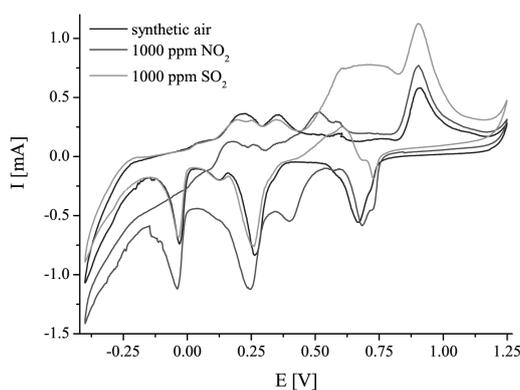


Fig. 2: Cyclic voltammograms measured in presence of synthetic air, 1000 ppm of NO₂ in synthetic air and 1000 ppm SO₂ in synthetic air



to the sensor signal can be presented as a selectivity coefficient (R). The selectivity coefficient has been calculated according to formula (Chachulski and Gebicki, 2005):

$$R = \frac{I_{NO_2}}{I_{SO_2}} \quad (5)$$

I_{NO_2} , I_{SO_2} - sensor response obtained for given concentration of NO_2 and SO_2

Selectivity coefficients were calculated based on the measured values for the concentration range 200-800 ppm (Tab. 1). For all concentrations calculated selectivity coefficients have similar value. Obtained values are comparable with results presented by Gebicki, who obtained selectivity that equals 0.18 for the concentration of

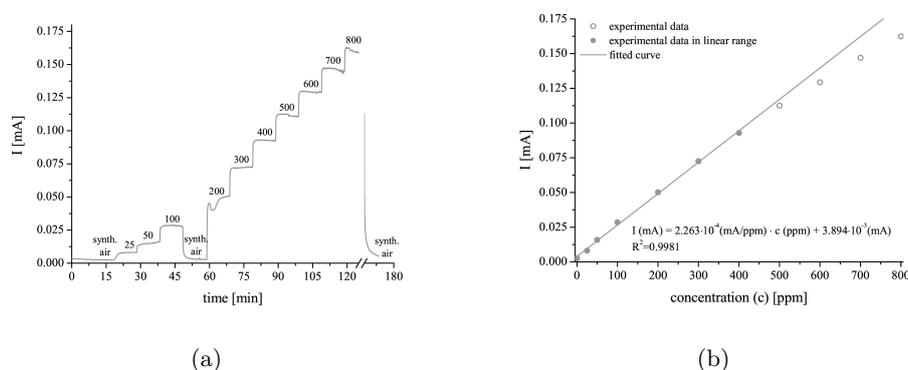


Fig. 3: Current vs. time response recorded in different concentration of SO_2 in air. Applied potential 0.81 V vs. MSE, room temperature (a). Calibration curve for SO_2 (b).

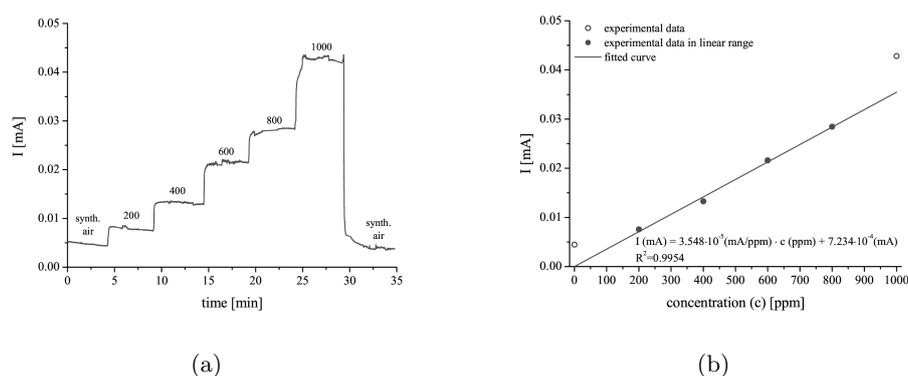


Fig. 4: Current vs. time response recorded in different concentration of NO_2 in air. Applied potential 0.81V vs. MSE, room temperature (a). Calibration curve for NO_2 (b).

Tab. 1: Values of R

concentration [ppm]	I_{SO_2} [A]	I_{NO_2} [A]	R [A/A]
200	$5.016 \cdot 10^{-5}$	$7,581 \cdot 10^{-6}$	0.1511
400	$9.284 \cdot 10^{-5}$	$1.328 \cdot 10^{-5}$	0.1431
600	$1.293 \cdot 10^{-4}$	$2.160 \cdot 10^{-5}$	0.1670
800	$1.625 \cdot 10^{-4}$	$2.846 \cdot 10^{-5}$	0.1752

200 ppm NO_2 for similar sensor construction (Gebicki, 2007). By using the sulphuric acid with lower concentration (Jacquinot et al., 2001) or addition of aprotic solvent as an internal electrolyte, the improvement of the selectivity coefficient can be obtained (Gebicki, 2007).

4. Conclusions

Construction of the sulphur dioxide amperometric sensor with the gold WE was presented and investigated. Response of the sensor in the atmosphere containing SO_2 for the different concentration was measured. Calculated sensitivity coefficient for sensor is 0.0558 mA/(ppm·cm²). Influence of interfering gas namely nitric dioxide was examined.

Acknowledgements

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References

- Chachulski, B. and J. Gebicki (2005), 'Influence of aprotic solvent on selectivity of an amperometric sensor with nafion membrane', *Electroanalysis* pp. 433–439.
- Clark, L. C., R. Wolf, D. Granger and Z. Taylor (1953), 'Continuous recording of blood oxygen tensions by polarography', *J. Appl. Physiol.* pp. 189–193.
- Gebicki, J (2007), *Praca Doktorska: Konstrukcja i parametry metrologiczne amperometrycznego czujnika ditlenku siarki zawierajacego dodatek rozpuszczalnika aprotycznego*, Gdansk.
- Jacquinot, P., A. W. E. Hodgson and P. C. Hauser (2001), 'Amperometric detection of no and no2 in the ppb range with solid polymer electrolyte membrane supported noble metal electrodes', *Anal. Chim. Acta* pp. 53–61.
- Schiavon, G., G. Zotti, R. Toniolo and G. Bontempelli (1991), 'Amperometric monitoring of sulphur dioxide in liquid and air samples of low conductivity by electrodes supported on ion-exchange membranes', *Analyst.* pp. 797–801.
- Takenaka, H. T. E. (1980), *Production of an ion-exchange membrane-catalytic electrode bonded material for electrolytic cells*, Tokyo, Japan. Japan Patent No. 55-38934.
- Zoski, C. (2007), *Handbook of electrochemistry*, Elsevier.