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Investigation of solid polymer electrolyte gas sensor with different electrochemical techniques

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Abstract. In this work solid polymer electrolyte (SPE) amperometric sulphur dioxide sensor is investigated. Nafion was used as a membrane electrode and *1M* sulphuric acid as an internal electrolyte. Sensor response to sulphur dioxide was measured. Besides traditional constant voltage amperometry also different electrochemical techniques were used. Results obtained by these methods are compared.

1. Introduction

Amperometric sensors due to high sensitivity and good dynamic properties are frequently used in toxic gas concentration monitoring [1]. Most of such sensors are based on liquid electrolytes. Up to now usage of solid polymer electrolyte (SPE) membrane with layer of porous, metal electrode in construction of amperometric sensors is the most successful approach [2]. Main advantages of this type of sensors are a very high active area of the working electrode (WE) and a short response time [3].

In this work performance of SO_2 amperometric sensor with SPE is investigated. The main goal of this work is to verify if usage of different electrochemical methods can improve sensor properties. Sensor responses were measured with constant potential amperometry (CPA), pulsed amperometry (PA), cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. Obtained results are compared.

These techniques are used with different sensors in the determination of different compounds. For example, PA technique was used with the glucose enzyme sensor [4]. CV method is commonly used in liquid solution electrochemistry and also with electrocatalytic gas sensors based on solid state electrolytes [5-9]. SWV technique can be used in the determination of volatile organic compounds [10]. In contrast with CPA, when only single value of the current is obtained, in case of the CV or SWV methods a response in a form of a curve with more information for a given gas mixture is obtained and analysed. These additional information obtained from CV and CWV response can be used to improve sensor properties. In order to analyse such responses a various methods of data analysis can be used [11]. To our knowledge, the PA and SWV techniques have not been used so far for the measurements of SPE sensors responses. For such sensors, a cyclic voltammetry technique is frequently used, however only to perform preliminary investigation in order to determine working potential. The CV is not employed for the determination of gas concentration and additional information contained in measured responses can not be used.

2. Experimental

2.1. Sensor structure

Housing of investigated sensor was made from polyether ether ketone (PEEK) which is highly resistant to acids and organic solvents. 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. 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. 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 *1M* sulphuric acid in water was used as an electrolyte.

Nafion® 350 (Sigma-Aldrich), in the form of foil, thickness 0.01 inch (0.254 mm) strengthened by Teflon net was used. Layer of gold was prepared by using chemical plating method known as Takenaka-Torikai method [12]. Details of this process was described elsewhere [13]. Geometric surface of the WE is 0.636 cm^2.

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

Voltammetric and amperometric sensor responses were acquired by using electrochemical interfaces Gamry Interface 1000 and VersaSTAT 3 controlled by computer with suitable software. Constant gas flow rate of 50 millilitres per minute was maintained. For CPA measurements, working potentials 0.5 V and 0.7 V have been used. In case of the PA, a base potential (E_b) was 0.2 V and a measurement potential (E_m) was 0.5 V. Pulses of the same duration (τ = 1s) and a constant amplitude ($\Delta E = E_m - E_b = 0.3$ V) were applied. The intervals between pulses was also 1s. For the cyclic voltammetry measurements a linearly changing voltage (range -0.3 – 1.2 V) was used. The voltage sweep rate was 20 mV/s. In case of square wave voltammetry step size was 2 mV and the frequency was 10 Hz, what corresponds to the sweep rate of 20 mV/s. Pulse size has been fixed at 50 mV and the voltage range was the same as for CV.

3. Results

3.1. Constant potential amperometry

Results of CPA measurement for working potential of 0.5 V and of 0.7 V are presented in Figure 1 and Figure 2, respectively. In these figures an increase of current with increasing sulphur dioxide concentration is clearly visible.

Based on data showed in Figure 1 and Figure 2 calibration curves have been calculated (Figure 3). In case of amperometric sensor a measured response should linearly depend on the measured gas concentration. Experimental results obtained in particular concentration of SO_2 are presented in the Figure 3 (points). Effect of fitting experimental data to straight lines is presented in the same figure (lines). Sensor sensitivity at fixed potentials is the slope of these curves. In case of the Figure 3, the following linear equations were obtained (for working potential of 0.5 V and of 0.7 V the equations (1) and (2), respectively):

$$I[mA] = 1.15 \cdot 10^{-4}[mA/ppm] \cdot c[ppm] + 0.01065[mA] \quad (1)$$

$$I[mA] = 5.27 \cdot 10^{-4}[mA/ppm] \cdot c[ppm] + 0.07593[mA] \quad (2)$$

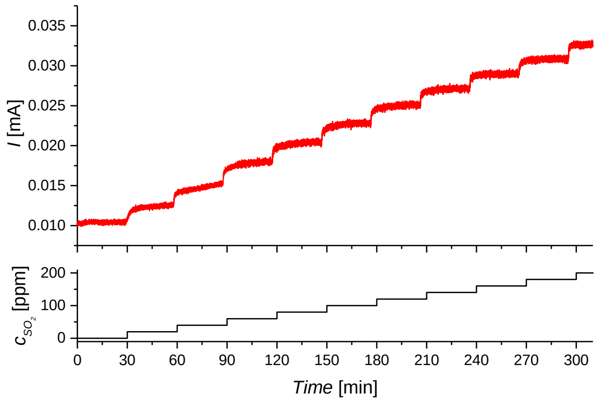

Figure 1. Current vs. time response of the sensor measured by the CPA technique at potential of 0.5 V (upper part of figure) and change of SO_2 concentration during the CPA measurement (lower part of figure).

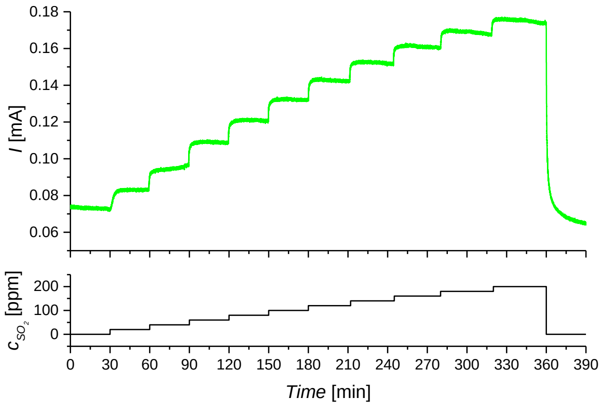

Figure 2. Current vs. time response of the sensor measured by the CPA technique at potential of 0.7 V (upper part of figure) and change of SO_2 concentration during the CPA measurement (lower part of figure).

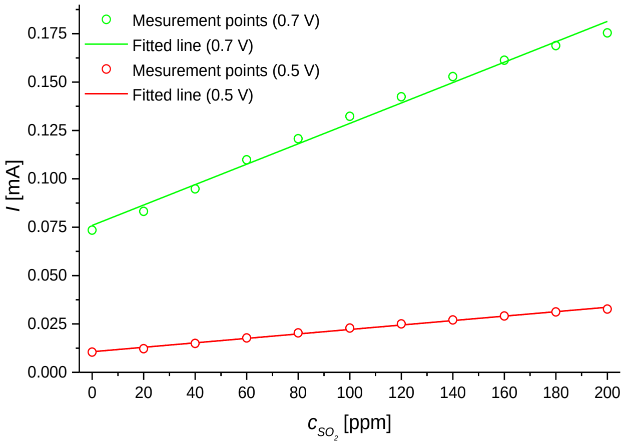

Figure 3. Calibration curves for measurement at 0.5 V and at 0.7 V made by the CPA technique.

The equations (1) and (2) shows that sensitivity at working potential of 0.7 V is almost 5 times higher than for the working potential of 0.5 V. Unfortunately value of the current registered for pure synthetic air (0 ppm SO_2) at potential 0.7 V is also much higher. This can have a negative influence on the sensor detection limit. In case of interfering gases present, a lower potential will be more desired, because for higher potentials more interfering gas components can be oxidized.

3.2. Pulsed amperometry

Pulsed amperometry is an enhancement of the constant potential amperometry technique. Shape of used excitation signal is presented in Figure 4. In case of the presented results, the measurement potential was 0.5 V. When potential was increasing to the 0.5 V, the oxidation reactions occurred on the WE surface, on the other hand, while potential was decreasing the reduction processes occurred. As a result, a surface of the sensor electrode was cleaned and refreshed before each measurement pulse. The current response of the sensor was measured 4 times per second. Namely, during each measurement, current of the pulse was measured 4 times at points A, B, C and D (as it is visible in the Figure 4). Next stairs-shaped characteristics were plotted. Current vs. time sensor response for two last measurement points C and D are presented in the Figure 5. Based on this data, the calibration curves were plotted similarly like in the case of the CPA measurements (results showed in the Figure 6).

Equations showing current-concentration relationship are presented below (equation (3) for point A, equation (4) for point B, equation (5) for point C and equation (6) for point D).

$$I[mA] = 3.2 \cdot 10^{-4}[mA/\,ppm] \cdot c[ppm] + 0.535[mA] \tag{3}$$

$$I[mA] = 3.11 \cdot 10^{-4}[mA/\,ppm] \cdot c[ppm] + 0.197[mA] \tag{4}$$

$$I[mA] = 3.45 \cdot 10^{-4}[mA/\,ppm] \cdot c[ppm] + 0.112[mA] \tag{5}$$

$$I[mA] = 3.46 \cdot 10^{-4}[mA/\,ppm] \cdot c[ppm] + 0.079[mA] \tag{6}$$

Coefficients of determinations (R^2) of these equation were 0.966 (equation 3), 0.994 (equation 4), 0.996 (equation (5)) and 0.997 (equation (6)). The current has the greatest value for points registered immediately after voltage increase (point A). It is because current increase immediately after the voltage disruption and decrease during duration of the voltage pulse. The capacitive current (unrelated to gas concentration) decrease slower than the faradic current (related to gas concentration). For this reason values of current registered for further points decrease. Value of sensitivity is the smallest for measurement made immediately after the voltage disruption and increase for further points. The best results are obtained for measurement made just before decreasing of the voltage (point D). The obtained sensitivity is in case of the PA sensitivity 3 times higher then for the CPA at the same working potential of 0.5 V.

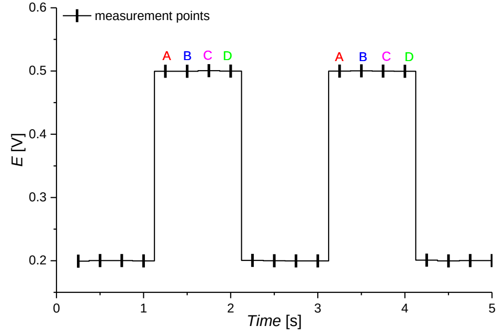

Figure 4. Shape of the voltage excitation signal used for the pulsed amperometry measurements.

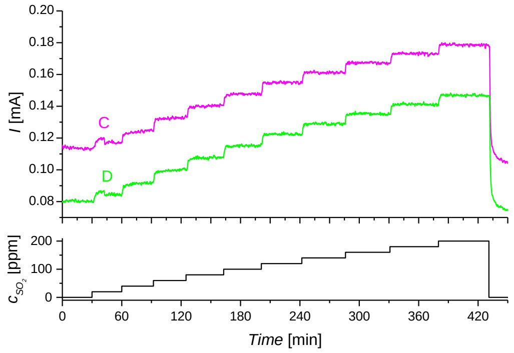

Figure 5. Current vs. time response of the sensor measured by the PA technique (upper part of figure) and change of SO_2 concentration during the PA measurement (lower part of figure).

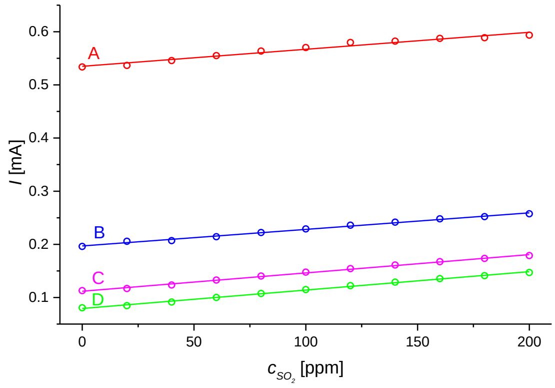

Figure 6. Calibration curves for measurement made by the PA technique.

3.3. Cyclic voltammetry

Another technique which can be used for determination of gas concentration of the SPE sensor is cyclic voltammetry. In Figure 7 two curves measured in the atmosphere of synthetic air and mixture of 1000 ppm SO_2 in synthetic air are presented. Usually, in case of the SPE sensor this type of measurement is used for determination of the working potential used later in the CPA measurements. Cyclic voltammetry plots can be analysed with different multivariate signal processing methods [14, 15]. However, while the main goal of this article is only comparison of results obtained by different measurement techniques, so in this work only a sensitivity S was used as a representation of sensor response defined as:

$$S[mA/pm]=\frac{(I_{SO_2}-I_{sa})[mA]}{c_{SO_2}[ppm]} \tag{6}$$

where I_{SO_2} and I_{sa} are currents, obtained by the measurement in atmosphere of 1000 ppm SO_2 in synthetic air and synthetic air at the same voltage during anodic sweep, c_{SO_2} is concentration of SO_2 (1000 ppm). The sensitivity calculated for these measurements is about $6\cdot10^{-4}$ mA/ppm in the voltage range of 0.5-0.8 V.

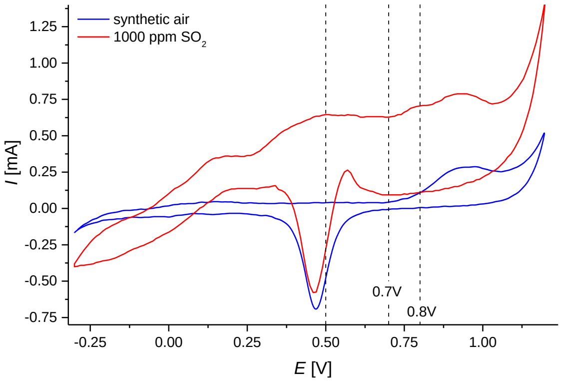

Figure 7. Current-voltage plots for synthetic air and 1000 ppm SO_2.

3.4. Square wave votlammetry

Parameters of the SWV measurements are presented in the experimental section. Plots obtained from measurements results are presented in Figure 8 and Figure 9. In the Figure 8 potential dependence of current forward (I_{fwd}) is presented. This is the current measured at the end of potential pulse. In the Figure 9 potential dependence of current difference is presented. This current is the value of difference between I_{fdw} and I_{rev}. The I_{rev} (current reverse) is the value of current measured just before the potential pulse. Usage of difference between I_{fdw} and I_{rev} allows to reduce capacitive current influence on the value of total current. Based on this data calibration curves were plotted (Figure 10).

In case of the I_{fdw} for presentation in the calibration curve, a voltage of 0.8 V was chosen as an optimal while in case of the I_{dif} value of 0.75 V was chosen. Following equations have been obtained (equation (7) for I_{fdw}, equation (8) for I_{dif}):

$$I[mA]=1.59\cdot10^{-3}[mA/ppm]\cdot c[ppm]+1.164[mA] \tag{7}$$

$$I[mA]=6.57\cdot10^{-4}[mA/ppm]\cdot c[ppm]+1.506[mA] \tag{8}$$

Coefficients of determinations (R^2) of these equation were 0.9996 and 0.9972 for equation (8) and equation (7), respectively. Sensitivity (slope of the curve) obtained for the I_{fdw} is almost 2.5 times higher than sensitivity obtained from I_{dif}. Both values of sensitivity calculated from results of SWV technique are higher than sensitivity obtained by CV technique.

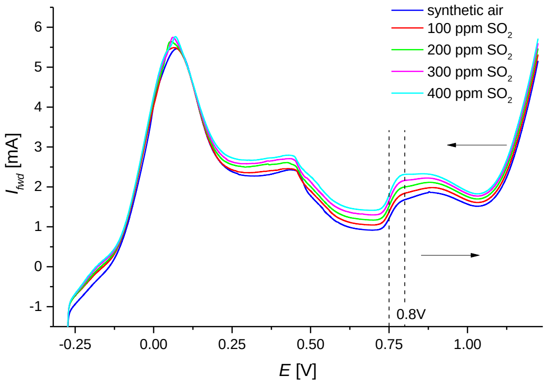

Figure 8. Current forward-voltage plots for different concentration of SO_2.

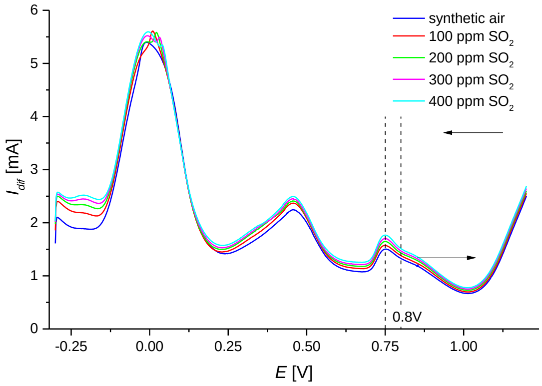

Figure 9. Current difference-voltage plots for different concentration of SO_2.

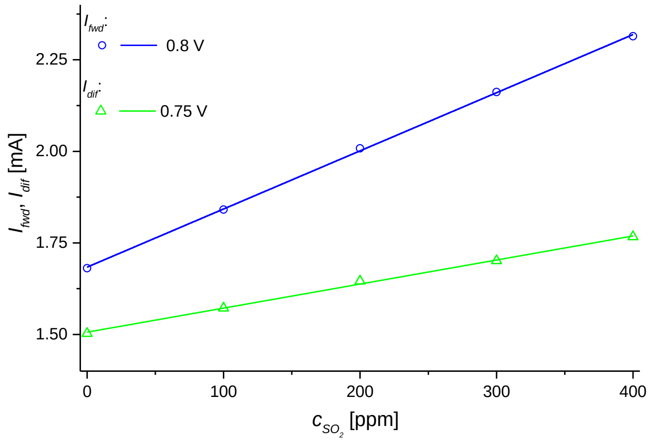

Figure 10. Calibration plots for SWV. Results obtained for the I_{fwd} and I_{dif}.

Table 1. Sensitivity of the SPE amperometric sensor obtained in measurements made by different electrochemical techniques.

Technique	Potential [V]	Sensitivity [mA/ppm]	R^2	Sensitivity [mA/(ppm · cm^2)]
CPA	0.5	$1.15 \cdot 10^{-4}$	0.9945	$1.81 \cdot 10^{-4}$
	0.7	$5.27 \cdot 10^{-4}$	0.9903	$8.29 \cdot 10^{-4}$
PA	0.5	$3.46 \cdot 10^{-4}$	0.997	$5.44 \cdot 10^{-4}$
CV	0.5	$6.05 \cdot 10^{-4}$	N.A.	$9.51 \cdot 10^{-4}$
	0.7	$5.85 \cdot 10^{-4}$	N.A.	$9.20 \cdot 10^{-4}$
	0.8	$5.98 \cdot 10^{-4}$	N.A.	$9.40 \cdot 10^{-4}$
SWV (I_{fwd})	0.8	$1.59 \cdot 10^{-3}$	0.9996	$2.50 \cdot 10^{-3}$
SWV (I_{dif})	0.75	$6.57 \cdot 10^{-4}$	0.9972	$1.03 \cdot 10^{-3}$

For a better comparison, all sensitivities of the SPE amperometric sensor obtained with different electrochemical techniques were summarised in Table 1. These results clearly shows, that usage of the PA improve sensitivity in comparison with the CPA, when the same voltage is used. Further improvement is obtained by usage of the CV, but the best sensitivity can be obtained, when SWV is used.

4. Conclusions

In this article experimental results of the SPE sensor investigation are presented. Sensor response to sulphur dioxide was measured. It was proven that measurements of a gas concentration by this kind of sensor can be realised by other techniques, than constant potential amperometry which is usually used. Measurements with more sophisticated techniques, such as pulsed amperometry, cyclic amperometry and square wave amperometry were made and their results were presented. Sensitivity was calculated from all results. It can be concluded that proper choice of measurement method can improve sensor sensitivity without modification of its construction.

5. References

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