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INVESTIGATION OF OXYGEN SENSOR BASED ON RUTHENIUM COMPOUNDS

Summary. Ruthenium is a chemical compound which is characterized by the luminescence phenomenon in the presence of oxygen and at a suitable excitation light having a wavelength corresponding to blue. This paper presents the construction of a planar oxygen sensor based on ruthenium compounds and preliminary oxygen concentration measurements using a constructed sensor. The work included determination of the composition of mixture reacting to changes in oxygen concentration and construction of the planar sensor. The measurement part consisted of implementation of the appropriate measuring chamber and measurements of the concentration. The initial research shows that sensor is characterized by high sensitivity and is selective.

Keywords: ruthenium, oxygen sensor, luminescence, planar sensors

BADANIA CZUJNIKA TLENU OPARTEGO NA ZWIĄZKACH RUTENU

Streszczenie. Ruten jest pierwiastkiem chemicznym, który cechuje się występowaniem zjawiska luminescencji w obecności tlenu i przy odpowiednim pobudzeniu światłem o długościach fal odpowiadających barwie niebieskiej. W publikacji przedstawiono budowę planarnego czujnika tlenu opartego o związki rutenu oraz wstępne pomiary stężenia tlenu z wykorzystaniem zbudowanego czujnika. Praca obejmowała ustalenie składu mieszanki reagującej na zmiany stężenia tlenu oraz wykonanie planarnego czujnika. Część pomiarowa składała się z wykonania odpowiedniej komory pomiarowej oraz przeprowadzenia pomiarów stężenia. Ze wstępnych badań wynika, że czujnik cechuje się dużą czułością i jest selektywny.

Słowa kluczowe: ruten, czujnik tlenu, luminescencja, czujniki planarne

1. INTRODUCTION

During last years the progress in metrology of non-electrical quantities has been closely allied to development of modern industry and vice versa – development in industry has been determined by advancement in industrial and R&D metrology. This is a branch of metrology dealing with measurements of physical and chemical parameters which are indispensable in

managing complex technological processes as well as scientific research. With manufacturing processes becoming more complex and with growing stress on supreme quality of end product, complete and more precise information on the process itself is required. Quite often the promptness in getting information on time-varying parameters is a key element in quick and effective response to the stimulus. This is in particular important in medicine, where patient's life is at stake [1].

Modern measurement systems carry out following tasks:

- They provide data on current values of controlled parameters to staff servicing a given device or system,
- They record measurement results,
- They generate signals for control circuit in accordance with requirements set by this circuit.
- They process and sort measurement results,
- They calculate average values and indicate deviations from required values of specified parameters.

Current work has been dictated by growing demand for light, sensitive and easy to assembly/disassembly devices used in detection of a given substance and determination of its concentration in tested environment.

Oxygen is without doubt the most important gas from the viewpoint of humans and other living organisms. It is a colourless and odourless gas slightly heavier than air. Under increased pressure and at temperature *c.* -183°C oxygen liquefies into a pale-blue liquid. For animals oxygen is a crucial factor oxidizing organic compounds in the breathing process. Breathing entails lung processes of bonding oxygen by haemoglobin present in blood and then flushing out reaction products such as carbon dioxide CO_2 and steam. Energy produced in different respiration cycles is used to sustain living processes. Oxygen is only weakly soluble in water, still this is sufficient to ensure respiration in fishes and other marine organisms. That is why the necessity for measuring oxygen concentration in any environment is so important.

One of the most often used elements in oxygen sensors is ruthenium Ru (it acts as indicator). This element does not form its own minerals and may usually be found in platinum ore. It is a weakly reactive metal characterised by its great resistance to acids. It is not easily fusible, it is hard and brittle. It can absorb gases such as hydrogen or oxygen; this particular property is used in sensor design. Ruthenium is most important in manufacture of semiconductor devices such as ruthenium layers, conductors, electrical contacts, electrodes, capacitors, transistors and diodes. Besides, ruthenium is used for many other purposes such as e.g. material for resists and mirror coatings applied in order to get a surface appropriate for catalysis. Ruthenium may also be planted by evaporation techniques on other elements. Such layers are characterised by very good anti-corrosive properties [1, 2].

A particular property utilized by oxygen sensor is oxygen quenching of fluorescence produced by ruthenium layer. Chemical compound called tris (2, 2' – bipyridyl) dichloro – ruthenium (II) hexahydrate (chemical formula $C_{30}H_{24}Cl_2N_6Ru$) is usually used in research.

2. CHEMO-OPTICAL SENSORS – MEASUREMENT BASICS

2.1. Chemo-optical sensors

Development of analytical chemistry is accompanied by progress in diverse measurement techniques providing information on a given environment or other samples. So far, the most advanced measurement procedures used spectrophotometers. This however requires delivering samples of tested material to expert laboratory. Application of optical fibres has made it possible to carry out measurements on site.

Fibre-optic chemical sensor is a device which supplies light energy to tested chemical environment or intermediate environment and converts data of measured chemical quantity into proportional optical signal [3]. Use of chemical sensors apart from standard sensors (which do not utilise optical effects) enhances greatly possibilities of measurement systems.

Conversion of chemical signal into measurable electrical signal is based upon effects occurring in so-called interfaces (chemo-optical and optoelectronic). Tested analyte (i.e. gas or chemical solution) is delivered to measurement head (chemo-optical interface). There chemical signal is converted into proportional optical signal [3] by utilizing e.g. change in absorption, fluorescence or another physical phenomenon. Signal produced by chemo-optical interface is transmitted via optical fibre to optoelectronic interface; there it is converted into corresponding electrical signal, amplified and it may be also subjected to other processing in accordance with applied measurement method. This signal is then input to PC via data acquisition board and it may be recorded in real time, parameter course may be displayed in computer screen. The whole process is sketched in Fig.1.

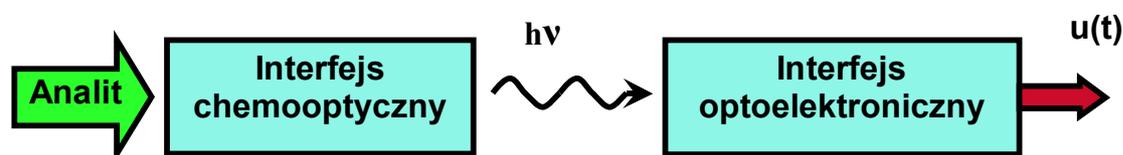


Fig. 1. Steps of signal processing in fibre-optic chemical sensor

Rys. 1. Etapy przetwarzania sygnału w światłowodowym czujniku chemicznym

The tested analyte may react with chemo-optical interface in different ways. Direct measurement is easiest; there the sample changes its optical properties or directly affects optical fibre parameters. However, this technique is not always possible, therefore so-called

indicators are used (dyes, reacting substances) as go-betweens in transmitting information from sample to optical fibre, changing chemical signal into optical one. Hence chemical sensors may be classified into either indicatorless or those using indicators [1].

The basic problem is how to choose an appropriate indicator, since a very limited number of analytes displays spectrum properties which might be used in construction of fibre-optic sensors. Design and process technology of the sensor is substantially affected by choice of reacting substance. The form of reacting substance (liquid, powder, granules) is important, since it influences the method of joining reagent to matrix. Indicator must not:

- leak out,
- be liberated from optrode,
- get decomposed,
- become photodegraded.

Depending on reagent type, changes in absorption, reflectance, luminescence or other physical effects are monitored.

Selection of proper polymer is also important; this is a matrix which distinctly affects sensor reaction time (which is determined by the diffusivity of analyte across membrane). When polymer is chosen, different factors must be taken into account, i.e.:

- polymer permeability for a tested analyte,
- stability of polymer spectral parameters,
- porosity rate of constructed membrane, it must ensure the easiest possible contact between optrode and analyte,
- time stability and market availability,
- compatibility with other materials used in optrode manufacturing process,
- compatibility with tested environment,
- biocompatibility and possibility of sterilising the constructed measurement head,
- possibility of providing optical isolation between head and tested sample.

Membranes are made of natural or synthetic materials. Cellulose is often used (it is a natural polymer); synthetic polymers are teflon, polyvinyl chloride (PVC), polyvinyl alcohol (PVAL), polymethyl methacrylate (PMMA), polystyren (PS) and silicones [3].

The main task of the membrane is to immobilise reagent and connect the reagent layer to optical fibre or any other waveguide layer. Immobilisation methods used are classified as surface ones (when indicator molecules are joined to polymer film) and volume ones (then the reagent is built into membrane during membrane manufacturing process).

2.2. Luminescence

Luminescence is any kind of radiation where Kirchhoff's Law is not applied and radiation energy is not due to other kinds of energy than thermal. Kirchhoff's Law states that

if a body at a given temperature emits radiation of a specified wavelength, then it must also absorb radiation of identical wavelength [4].

Luminescence may be observed when excited particle releases energy in the form of light wave [3]. Such particles, atoms or ions are called luminescent centres, since under the influence of some factor they attain triggered state. Luminescent centres are located at places where crystalline structure of a given material is disturbed. Atoms disturbing the structure are called activators. Luminescence may be classified as fluorescence, that is radiation which is quickly extinguished when triggering factor is off or phosphorescence, that is a more lasting light phenomenon. Illustration of luminescence effects is given in Fig.2. Electron triggered up to F level may pass directly to basic level; that is when fluorescence takes place. When electron goes into metastable state M, it will remain there until energy needed for re-entry into F state is obtained. The photon emitted then is delayed in relation to fluorescence. Fluorescence and phosphorescence are characterised by at least three parameters: excitation wavelength, emission wavelength and radiation decay time or intensity of emitted radiation. Sensors using fluorescence or phosphorescence are considered to be more selective than sensors operating on the basis of absorption changes. According to another classification, fluorescence is a kind of radiation occurring at one or several spontaneous transitions, while phosphorescence occurs in centres only and thermal energy of the medium takes part in its emission [4].

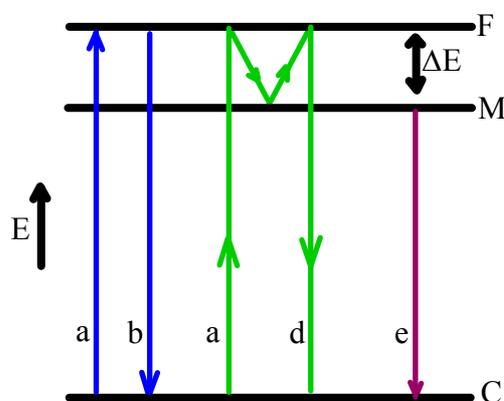


Fig. 2. Luminescence phenomenon: C - basic level, F - level triggered, M - metastable level, a - absorption, b - fluorescence, d - phosphorescence, e - long-lived fluorescence

Rys. 2. Schemat zjawisk luminescencyjnych: C – poziom podstawowy, F – poziom wzbudzony, M – poziom metatrwały, a – absorpcja, b – fluorescencja, d – fosforescencja, e – fluorescencja długożyciowa

In phosphorescent material, the persistence (i.e. lifetime) depends on temperature; for fluorescence lifetime does not depend on temperature. Under frozen conditions, transitions from metastable to basic level take place, this weak glow is called long-lived fluorescence (e).

2.3. Fundamentals of oxygen concentration measurements

Measurements of oxygen (or any other gas) concentration with sensor utilizing the effect of dye fluorescence due to impact of tested substance's concentration may be carried out applying different measurement techniques based generally on Stern-Volmer relationship. Radiation intensity or its decay time may be measured. Different intensity, phase and frequency-type methods are based on those principles. We shall now discuss different measurement methods together with their pros and cons.

Oxygen concentration measurements are based on changes in fluorescence intensity or decay time of fluorophore radiation. Fluorescence intensity of indicator in the interval ranging from wavelength λ_1 to wavelength λ_2 is expressed as [5]:

$$I_{\lambda_{1,2}} = I_{abs,A} \eta_A \Gamma \int_{\lambda_2}^{\lambda_1} f_{em,A}(\lambda) d\lambda \quad (1)$$

and:

$$I_{abs,A} = \int_{\lambda} f_{abs,A}(\lambda) I_{ex}(\lambda) d\lambda \quad (2)$$

where:

η_A – fluorescence efficiency,

$f_{em,A}(\lambda)$ – fluorescence spectrum,

$f_{abs,A}(\lambda)$ – spectrum of A factor absorbance,

$I_{ex}(\lambda)$ – spectrum of light source intensity,

Γ – geometric factor.

Any change in fluorescence efficiency may be used to determine the impact of analyte concentration on indicator's fluorescence intensity. Oxygen is a gas which dynamically quenches (extinguishes) fluorescence and therefore it may be investigated with previously known methods of fluorescence monitoring (Bergman, 1968; Kautsky, 1935).

In ideal case the ratio of quenched (η) to unquenched (η_0) fluorescence efficiency is expressed as [5]:

$$\frac{\eta_0}{\eta} = \frac{1}{1 + K_{SV} [O_2]} \quad (3)$$

Thus, intensities and lifetimes of quenched and unquenched molecules may be described as:

$$\frac{I_0}{I} - 1 = \frac{\tau_0}{\tau} - 1 = K_{SV} [O_2] \quad (4)$$

This equation provides a linear relationship between oxygen concentration and radiation intensity in homogenous environments; K_{SV} is Stern – Volmer constant, while $[O_2]$ is tested

oxygen concentration. S-V constant corresponds to sensitivity of oxygen sensor. It may also be stated that:

$$K_{SV} = k\tau_0 \quad (5)$$

where:

τ_0 – lifetime of luminophore in excited state,

k – bimolecular rate quenching constant equal to:

$$k = 4\pi gRN_A D \quad (6)$$

g – statistical factor related to quenching of triplet state of ruthenium compound by oxygen,

D – coefficient of oxygen diffusion via membrane,

R – effective oxygen diffusion path,

N_A – Avogadro number.

Significance of triplet and singlet states and related concepts of fluorescence and phosphorescence are presented by so-called Jablonski diagram. Photoluminescence takes place when some molecules are excited by the light to a higher energy level. When excited molecule goes back to basic level, it emits light with a greater wavelength than light which caused the excitation (Stokes shift). If this transition takes place between two singlet states, this radiation is short-lived and we call it fluorescence; transition from triplet state to basic level requires change of electron's spin, hence probability of such transition is less. This radiation is long-lived and we call it phosphorescence. Both types of radiation may be described with Stern – Volmer relationship [17]. Finally:

$$\frac{I_0}{I} = 1 + \tau_0 k [O_2]. \quad (7)$$

In practice these formulas may prove to be more complex, because of non-ideal performance of immobilised indicator.

Tests of radiation intensity have been thoroughly described in many publications (Wolfbeis, 1988; McDonagh, 1998; McEvoy, 1996). Measurement technique is easy and data may be acquired with no trouble, the ratio of signal to noise is high. However, many drawbacks are also present, such as high sensitivity to light source, detector drift and change of conditions in optical circuit path. The measurement is also impaired by drift due to degradation of used dye.

3. PRACTICAL DESIGN OF SENSOR AND MEASUREMENT CIRCUIT

Our investigation has included placing indicators in polymer matrix with the help of different solvents; ruthenium compounds have been used as indicators. Finally layers of different thickness have been created at the surface of glass plates chamfered at 90° and 45°. Phenomena taking place in this type of sensor are shown in Fig.3.

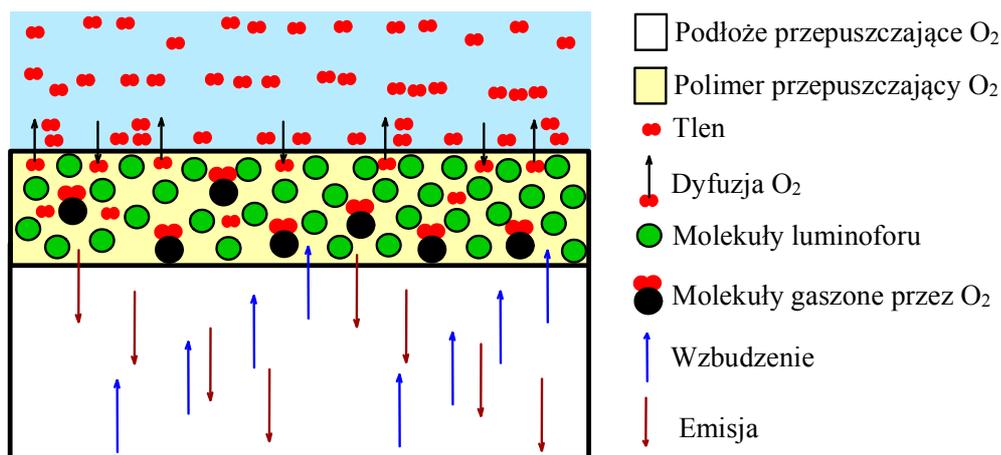


Fig. 3. Physical phenomena in the oxygen sensor measuring head
 Rys. 3. Zjawiska zachodzące w głowicy pomiarowej czujnika tlenu

When luminophore is excited with blue light, radiation emission starts from the sensor; wavelength is equal to c . 580 nm. Oxygen molecules from surrounding environment start to diffuse through polymer layer and they quench luminescent radiation, i.e. cause decrease of radiation intensity [6, 7].

The measurements have consisted of periodic changes of atmosphere in measurement chamber (from nitrogen or air to pure oxygen content). Data has been recorded using PC data acquisition board and voltage measurement software. Measurements of light intensity have been supplemented with temperature measurements.

3.1. Chemical compounds used

Our task was to create membrane composition such that final compound would consist of a homogeneous mixture of dissolved matrix and indicator. During research we investigated performance of polystyrene (PS) and polymethyl methacrylate (PMMA) in the roles of polymer matrices [1].

In order to prepare compound No.1 we added 6.6 ml of chloroform to 10 mg of ruthenium, this mixture was subjected to 60 minute mixing at 20°C; then solvent was added (30 ml) and vessel was placed again in ultrasonic washer for 30 minutes. Then a proportional amount of matrix material was added to indicator; undissolved polystyrene (7g) was used. A homogenous and transparent mixture was obtained after blending. The prepared compound was then centrifuged on clean glass plates chamfered at 45°. Each subsequent layer was dried at 40°C for 60 minutes and only then next layer could be applied. Plates containing 2, 4 and 7 layers have been constructed. It was not feasible to use a greater number of layers, since adhesion of polystyrene to glass surfaces has not been adequate and this has resulted in coatings dropping off the glass [7, 8].

In second case 2 ml of acetonitrile (CAN) was poured on 3 mg of ruthenium and this was subjected to mixing in ultrasonic washer for 10 minutes at room temperature. After obtaining a homogenous liquid, 200 g of PMMA was put into the solution, next mixing was applied for 90 minutes at 20°C.

The final solution is transparent and homogenous, at $c.40^{\circ}\text{C}$ it resembles oil. When the compound is cooled, it alters its properties: it becomes opaque and densifies. During tests we centrifuged 3 layers at the glass base. After application of each subsequent layer, the glass was put into furnace at 80°C for 30 minutes. This temperature was selected on account of physicochemical properties of the solvent (acetonitrile) and, to be more precise, by its boiling point. The produced layers are opaque, their structure is rough and non-homogenous. Notwithstanding this fact, during investigation of membrane spectrum we have observed that fluorescence intensity is much higher than that of other sensor plates.

3.2. Test stand

Test stand for measuring oxygen concentration consists of three basic parts: the first one is responsible for uniform pumping of nitrogen and oxygen to the second compartment (which holds the sensors). Radiation recording takes place in the third part of the stand (containing PC). The set-up of measurement stand is shown in Fig.4.

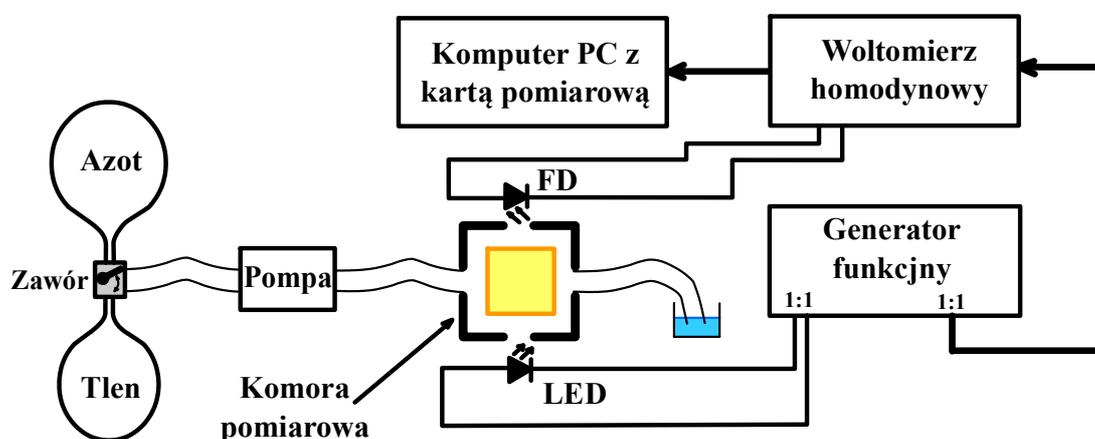


Fig. 4. Measurement set-up

Rys. 4. Budowa stanowiska pomiarowego

Section which pumps gases holds a peristaltic pump. Due to appropriate settings, it pumps gas at the rate of 75 ml/min via a hydraulic hose of 3 mm diameter. Directional control valve is situated at the end of the hose, so that it is possible to open or close the gas path manually; nitrogen tank is connected to one input and oxygen tank to the other. Gas outlet from the chamber is made up of a hose immersed in beaker full of water, so that gas flow may be

visually controlled. This design makes it possible to react at once to any interruption in gas supply caused by break in the circulation or loosening of ducts in the pump.

Housing of test chamber is made of oxidized aluminium walls, which are bolted together in such a way, that it is possible to replace tested samples. The chamber is also equipped with gas inlet and outlet, located in the lower wall. Sample is put into the chamber with indicator layer facing down; this is due to location of gas inlet, gas should get directly to sensor layer and not to the entire plate.

Two optical filters are built into chamber walls. The upper window is the transmitting one; it is fitted with a blue filter. Electroluminescent diode (OSUB 5111A-RS) is placed above this window and supplied from function generator. It emits a wave of 470 nm wavelength. The side window is equipped with orange filter, which allows transmission of light resulting from fluorescence phenomenon only. This window is placed directly across one of the edges of waveguide layer. Outside the chamber and behind the receiver window we have placed a photodiode BPYP44, which records intensity of signal produced by the sensor. The output signal from photodetector is input to homodyne nanovoltmeter [1, 2].

Devices supplying photodiode and LED as well as measurement data recorders belong to third part of the measurement set-up.

G911 generator produces square-wave signal at 0.95 kHz. This waveform is directly input to blue diode instigating luminophore glow. Generator's 1:1 input is connected to reference input of homodyne voltmeter; this helps to make the measurement independent of changes in external lighting. Voltmeter's output signal is input to data acquisition board of the PC, this is used to measure voltage. The obtained data is visualised on computer screen. Acquired glow intensity is recorded into text file; then it may be processed in e.g. spreadsheet.

Cross-section of the chamber presented in Fig.5 shows location of filters, sensor plate and other elements described in the text.

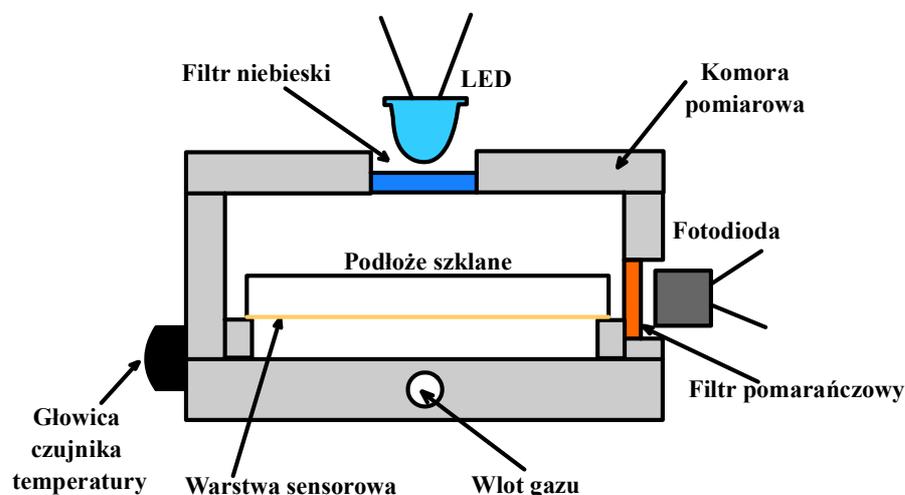


Fig. 5. Cross section of measurement chamber

Rys. 5. Przekrój poprzeczny komory pomiarowej

Temperature sensor is the fourth and additional element of measurement set-up. It is not indispensable to sensor operation. Sensor head has been fixed to side wall of the chamber (*cf.* Fig.5). Temperature has been recorded simultaneously with fluorescence intensity. Temperature measurements have been run in order to clarify the origin of drift present in signal originated in oxygen-sensitive layer.

Measurement method is important in the prepared measurement system. Voltage measurement software makes it possible to measure fluorescence intensity at determined time intervals. However, on account of certain limitations of temperature sensor, measurements of temperature and glow intensity have been performed every two seconds. The entire measurement process for a given sample has been run long enough to determine its usability in oxygen detection and to verify the temperature dependency of a given layer.

When sample is placed in the chamber and chamber is sealed, nitrogen dosage is started and then measurements may commence. When obtained signal is stabilized, pumping of oxygen can be started. When signal attains minimum, type of input gas is changed. This process is repeated as long as necessary to obtain confirmation as to repeatability of measurements; dosage of gases may be changed at approximately constant time intervals dependent on the rate of stabilisation of measured signal. Stabilisation time depends on sample thickness. When thickness is increased, then gas diffusion in the layer is slower, so that reaction of sensor to input gas takes longer.

4. MEASUREMENTS

Comparisons of constructed membranes have been run on the basis of calculations of specific parameters vital for each sensor. These are:

- percentage change in the signal present at sensor S output, when input gas is changed from nitrogen to oxygen. It is calculated as:

$$\frac{S_{azot} - S_{ilen}}{S_{azot}} \cdot 100\% \quad (8)$$

- layer reaction time to oxygen as decay time constant of exponential function τ :

$$y = ae^{-\frac{t}{\tau}} \quad (9)$$

This function has been fitted into section of the curve, which corresponds to oxygen or synthetic air injection into previously dosed nitrogen.

Measurement results from sensitive membrane covered with two layers of the prepared compound on polystyrene base are shown in Fig.6.

Change of signal when nitrogen is replaced with oxygen is 3.2%, while sensor reaction time is *c.* 6 s. Sample does not exhibit significant drift, since temperature during tests was

more or less stable. Measurement results for sample consisting of 7 layers (same chemical composition) are shown in Fig.7.

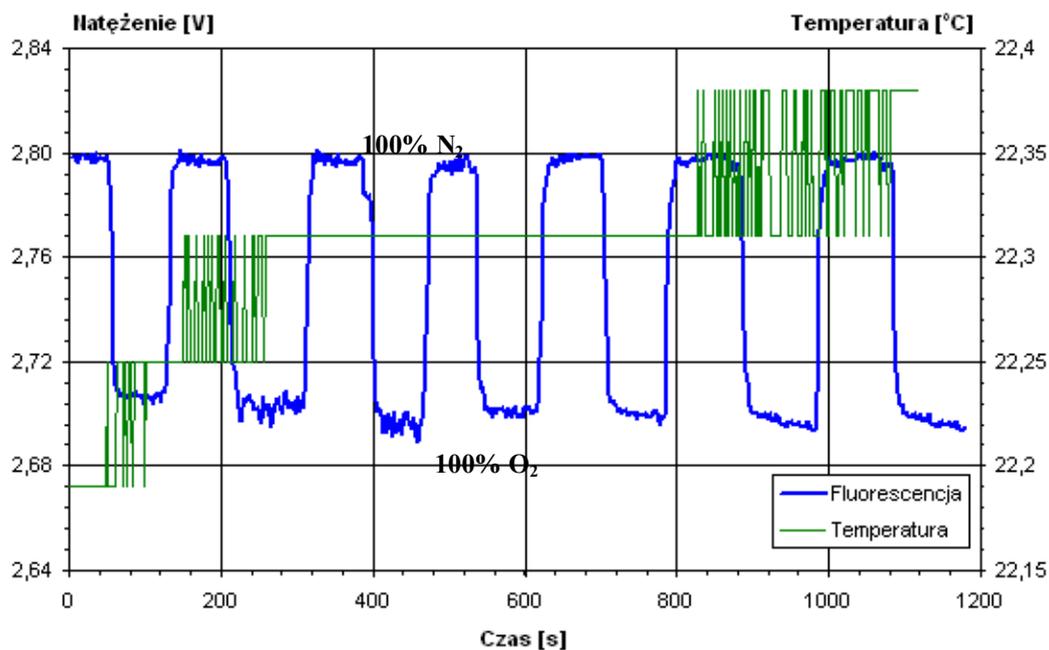


Fig. 6. Intensity of fluorescence of two-layer sample Ru + PS + CHCl₃
Rys. 6. Natężenie fluorescencji próbki: Ru + PS + CHCl₃ o 2 warstwach

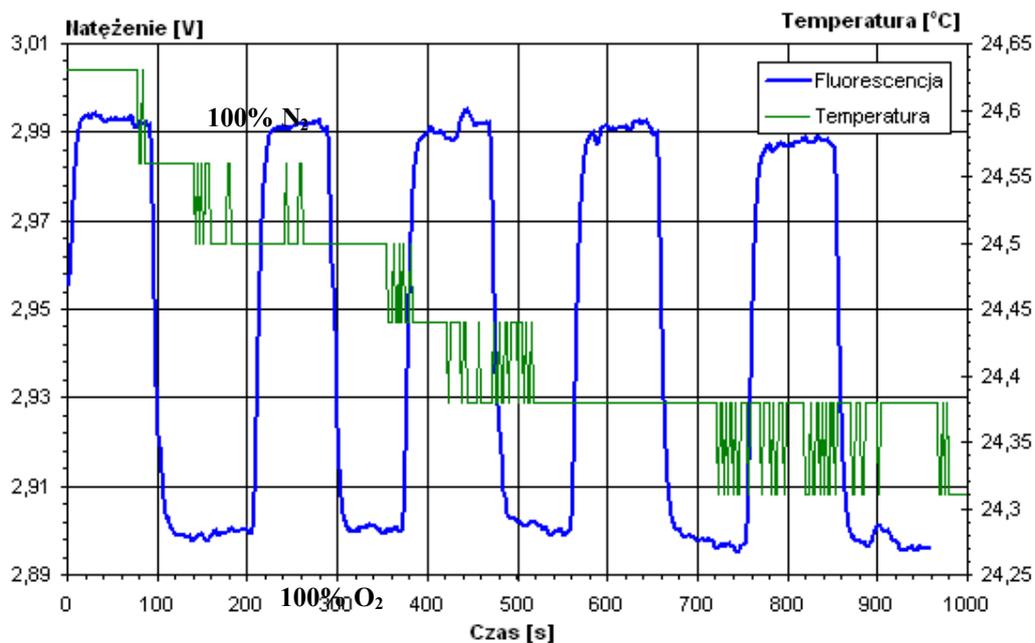


Fig. 7. Intensity of fluorescence of 7 layer sample Ru + PS + CHCl₃
Rys. 7. Natężenie fluorescencji próbki: Ru + PS + CHCl₃ o 7-warstwach

In case of sample containing 7 polystyrene layers, 3% signal change in reaction to oxygen injection has been noted together with extension of reaction time by 3 seconds. It may be observed that reaction time corresponds to membrane thickness. This effect is due to time required by oxygen molecules for diffusing into the layer in order to quench the fluorescence. This relationship will be present for each membrane type.

Polystyrene-based layers perform best in measurements in spite of their bad adhesion to base (coatings become loose in case of greater number of layers, edges are rough and uneven). Such sensors are characterized by small temperature drift, short response time and high repeatability of obtained results. Another advantage is low consumption of indicator solution. Results of measurements for second mixture based on PMMA are shown in Fig.8.

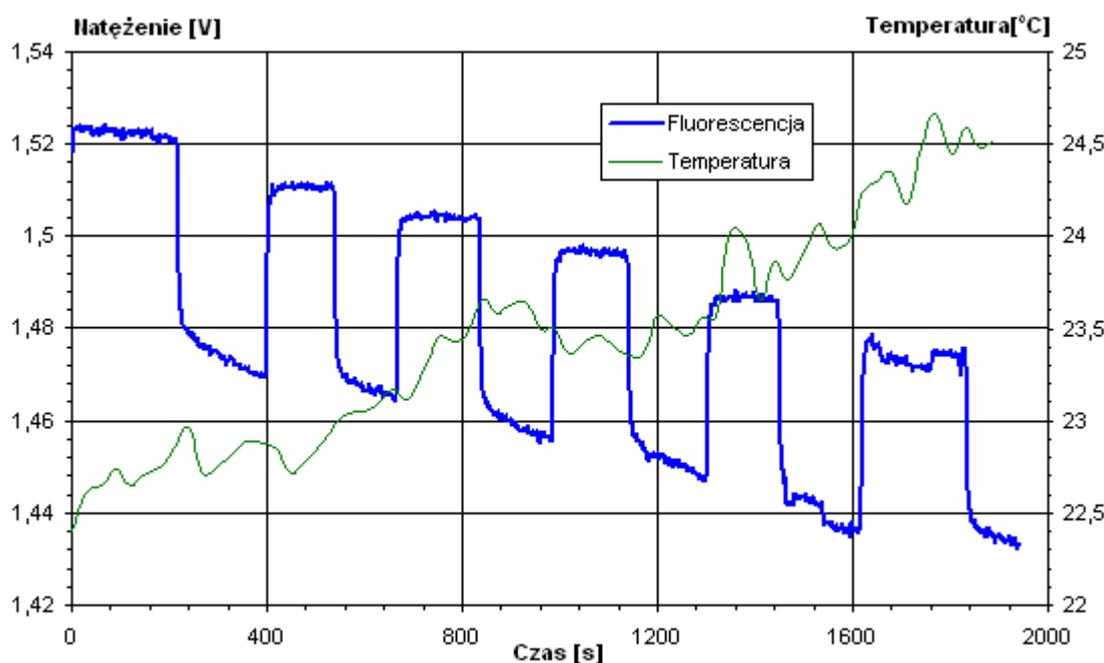


Fig. 8. Intensity of fluorescence of three layer sample Ru + PMMA + ACN
Rys. 8. Natężenie fluorescencji próbki: Ru + PMMA + ACN o 3-warstwach

Compound created in accordance with second composition, based on PMMA and acetonitrile, is strongly temperature-dependent. It has been perceived that when solution is heated to *c.* 50°C, it is transparent and fluid, but when solution is cooled, its properties are lost. Taking this issue into account, layers have been applied after previous heating of mixture in ultrasonic washer. In spite of these measures, the coating is not homogeneous on account of fast solidification of solution into dense and opaque structure. Sensor's reaction to oxygen is not significant and measurement is hampered by strong temperature drift. Advantage of this design is that fluorescence exhibits strong intensity (only with 3 layers), which makes it possible to reduce number of electronic devices (amplifiers mostly) needed for proper signal detection. This is of some practical significance, because measurement set-up may be somewhat miniaturised.

5. CONCLUSIONS

The obvious conclusion which may be drawn from conducted measurements is the dependence of fluorescence intensity on indicator concentration. When concentration goes up, colour of obtained compound becomes more intensive; hence number of layers needed to achieve light intensity required for detection and subsequent processing may be less. This result is of great economic importance, because lower number of layers means that we may produce a greater number of sensors with identical parameters.

The obtained results are set out in Table 1. It contains a list of all membranes used together with their most significant parameters, i.e. percentage alteration of signal in response to gas change from nitrogen to oxygen or from nitrogen to synthetic air, sensor reaction time and ruthenium concentration in each membrane.

Table 1.

Parameter comparison of constructed sensor membranes

| Sample | Signal change N – O ₂ [%] | Reaction time N – O ₂ [s] | Dye concentration [%] |
|-------------------------------------|---|--|-----------------------------|
| Ru+PS+CHCl ₃ 2 layers | 3.2 | 6.26 | 0.018 |
| Ru+PS+CHCl ₃ 4 layers | 4.60 | 8.35 | |
| Ru+PS+CHCl ₃ 7 layers | 3.13 | 11.15 | |
| Ru+PA-09+ACN 2 layers | 2.45 | 6.31 | 0.178 |
| Ru+PA-09+ACN 1 layer (1mm) | 5.40 | 140.80 | |
| Ru+PMMA+ACN 3 layers | 2.13 | 50.30 | 0.077 |

Presented measurement results are subordinated to some drift, which is caused by temperature. That is why each conducted test was accompanied by temperature measurement. During measurements it was noticed that each sample was characterised by different properties. Some samples react faster to changes in gas, some exhibit much higher sensitiveness. The technological process of manufacturing a given layer should be adequately fast (2-3 hours) and should produce repeatable results. In general, it may be stated that each sample exhibits some advantages together with some drawbacks. The choice of sample for a future sensor depends on proposed sensor application. Still, further research is necessary in order to work out a sensor characterised by better parameters, in particular mechanical ones.

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