A low-cost pH sensor based on RuO_2 resistor material

Libu Manjakkal[1, a], Katarina Cvejin [1, b], Jan Kulawik [1, c], Krzysztof Zaraska [1, d], and Dorota Szwagierczak[1, e]

[1]Institute of Electron Technology, Cracow Division, 30-701, Krakow, Zablocie 39, Poland
[a]lmanjakkal@ite.waw.pl, [b]kcvejin@ite.waw.pl, [c]jkulawik@ite.waw.pl,
[d]kzaraska@ite.waw.pl, [e]dszwagi@ite.waw.pl

Keywords: pH sensor, screen printing, Nernstian response, sensitivity.

Abstract. Fresh water deficiency caused by climate change calls for employing novel measures to ensure safety of drinking water supply. Wireless sensor networks can be used for monitoring hydrological conditions across wide area, allowing flow forecasting and early detection of pollutants. While there are no fundamental technological obstacles to implementation of large area sensor networks, their feasibility is constrained by unit cost of sensing nodes. This paper describes a low-cost pH sensor, intended for use in fresh water monitoring. The sensor was fabricated in a standard thick film process, and an off-the-shelf resistive paste is used as a sensing material. For the fabrication of sensor, RuO_2 resistive paste was screen printed on the alumina substrate with silver conducting layer. Test solutions with pH ranging from 2 to 10 were prepared from HCl or KOH solutions. The potential difference between reference and sensing electrode (electromotive force emf of an electrochemical cell) should be proportional to the pH of a solution according to the Nernst equation. The fabricated sensor exhibits Nernstian response to pH. Influence of storage conditions on sensing performance was also investigated.

1. Introduction

Water pollution is a one of the major issue in global environmental system. Water quality monitoring demands the determination of water quality parameters like pH, dissolved oxygen, conductivity, turbidity, temperature, content of ammonia, metal ions, etc. [1-5]. The determination of pH being the measure of acidity or basicity of a solution is important in many chemical and biological reactions [6-8]. Major method employed for monitoring of water quality is collecting samples and their analysis in laboratory. This traditional method shows a number of drawbacks. The data for sampling are collected from a small area and the time gap between sampling and analysis will influence the result for some kind of contaminations. In addition, the glass electrode which has been widely adopted for pH measuring due to its high sensitivity, wide pH available measurement range, excellent stability, good response close to Nernstian behavior and long lifetime [9-11], exhibits many disadvantages. These are mechanical fragility, difficulty of miniaturization, chemical instability in corrosive systems and response dependence on pressure and temperature. Researchers have been trying for a long time to overcome these problems and develop a new pH measurement system which could be also helpful for making a new generation of wireless pH sensors for online monitoring of water quality [1, 2, 12].

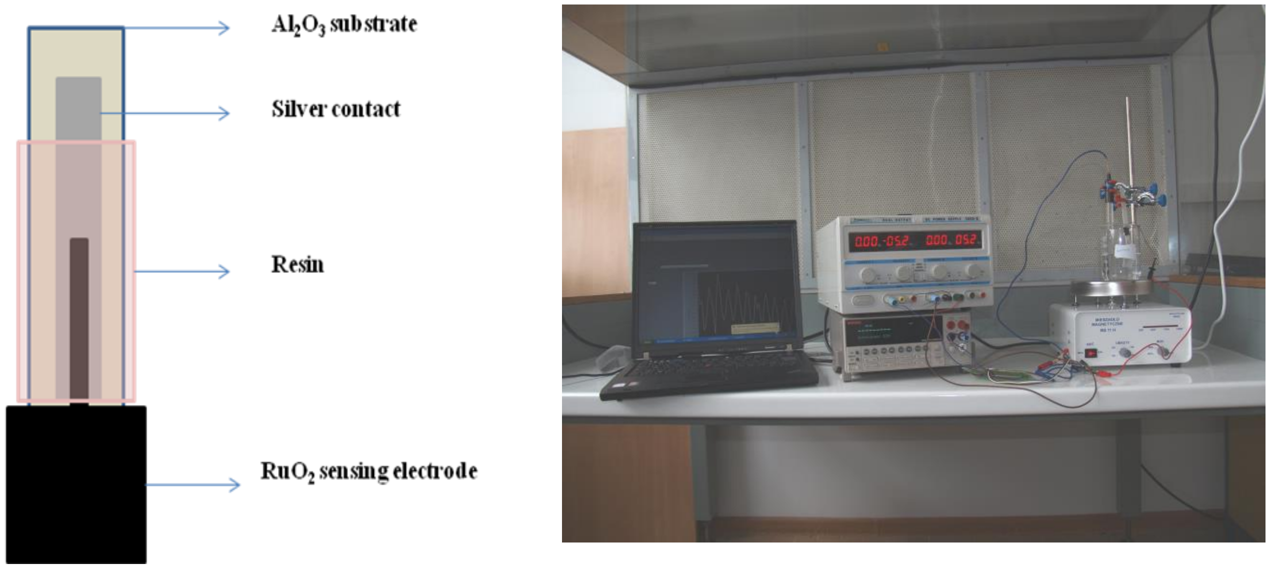
Semiconductor sensing metal oxide materials are useful for fabricating accurate, inexpensive and reliable wireless pH sensors for online monitoring of pH of a solution. So far, there has been much work done in the area of metal oxide based thin and thick film pH sensors [13-20]. A few of them reported on RuO_2 based [4, 21-25] pH sensors for online monitoring of pH of water. As compared to other pH sensitive solid state materials, RuO_2 exhibits excellent sensitivity, close to the Nernstain response in a wide pH range. It is considered as a promising material for fabricating pH and dissolved oxygen sensors. Ruthenium dioxide is a stable, electronically conductive oxide of the rutile structure which is widely applied in electrocatalysis, ultracapacitors, thick film resistors.

This paper describes the fabrication of pH sensor by screen printing technology. The surface and a cross-sectional view of the sensor were studied using optical and scanning electron microscopes. The sensitivity of the sensor stored in water for a long time was compared with that of the sensor stored in air. Also, we reported that the fabricated sensor shows the pH value of water very close to the result obtained by a glass electrode.

2. Experimental

In this work, the pH sensor was fabricated by using thick film screen printing technology. The layout of the pH sensor is shown in Fig. 1(a) [22]. The Ag conducting layer (Ag/Pd ESL 9695 paste) was printed onto the alumina substrate and fired in a belt VI-zone furnace at a maximum temperature of 850°C. RuO_2 based resistor paste (ESL 3914, 10 kΩ/sq.) intended for a sensitive layer was then printed. The screen printed layer was dried at 120°C and fired according to a standard profile in a BTU belt VI-zone furnace. Typically, a total cycle time of 45 minutes and a peak temperature of 850°C held for 10 minutes were applied. An insulating layer (polyurethane resin) was painted on the surface of the sensor, except the sensitive area which contacts with a solution and the pad for electrical contact. This layer functions as a protective layer for the sensor.

Desired pH values of a test solution (in the range of 2-10) were attained and varied by the drop-wise addition of 1 mol % solution of HCl or KOH into the distilled water. A calibrated glass pH-meter (ELMEIRON, CPC-411) was also applied to control pH of a solution. Buffer solutions with pH of 4, 7 and 9 were used for calibration of this instrument. Electromotive force emf of the electrochemical cell consisting of RuO_2 sensing electrode and reference electrode (Ag┃AgCl┃KCl) was measured as a function of pH of a solution by using a Keithley 2002 multimeter, which was connected to a PC. The experimental setup used for pH measurement is shown in Fig. 1(b). In order to establish proper pH measurement procedure, various storage conditions of the sensing electrode were investigated. These are storage in deionized water and storage in air. Digital microscope (KH 7700, HIROX, Japan) was applied to obtain the surface image of the RuO_2 thick film. Microstructure of fractured cross-sections of the thick film sensor was studied using a scanning electron microscope (FEI Company Nova Nano SEM 200, USA). The compositions of the layers were analyzed by Energy Dispersive Spectroscopy (EDS) method (EDAX EDS System Genesis Software).



(a)

(b)

Fig. 1. (a) Layout of screen printed RuO_2 based pH sensor. (b) Experimental setup for pH measurement system

3. Results and Discussion

3.1. **General mechanisms for pH sensing of RuO_2 layers.** RuO_2 is a promising material used for making pH sensors due to its chemical stability and high conductivity which inhibits the space charge accumulation. According to Fog and Buck [13], there are two main reasons for pH response in RuO_2 metal oxide, (i) 'oxygen intercalation' and (ii) ion exchange in a surface layer containing –OH groups. The general mechanism was explained as [24, 25]:

(i) For oxygen intercalation $RuO_2 + 2H^+ + 2\bar{e} \Leftrightarrow RuO + H_2O$ (1)

where RuO_2 and RuO are higher and lower metal oxide. Then the electrode potential is given by Nernst equation:

$$E = \frac{RT}{F}\ln a_{H^+}^{1} + \frac{RT}{2F}\ln a_0^{s} + \text{Constant} \tag{2}$$

where $a_{H^+}^{1}$ is the proton activity in the liquid phase, a_0^{s} is the oxygen activity in the solid phase and F is the Faraday's constant.

(ii) For proton exchange $RuO_x(OH)_y + \delta H^+ + \delta\bar{e} \Leftrightarrow RuO_{x-\delta}(OH)_{y+\delta}$. (3)

The electrode potential is then given by [24, 25]:

$$E = \frac{RT}{F}\ln\left[H^{+}\right] + \frac{RT}{\delta F}\ln\left[\frac{RuO_{x}(OH)_{y}}{RuO_{x-\delta}(OH)_{y+\delta}}\right] + \text{Constant} \tag{4}$$

The magnitude of this potential is proportional to the pH of a solution according to the Nernst equation.

$$E = E_0 - \frac{2.303RT}{nF}\,pH = E_0 - \frac{59.12mV}{n}\,pH \tag{5}$$

where E - emf of electrochemical cell, E_0 - standard potential, R - universal gas constant, T – absolute temperature, n - number of electrons and F – Faraday's constant. At temperature T equal to 25°C the slope factor must be 59.12mV/pH.

3.2. Microstructure of RuO_2 thick films: An optical microscope image of the surface of RuO_2 based thick film screen printed on the alumina substrate is shown in Fig. 2. The layer is very dense, without any pores or cracks. Darker regions with irregular shapes which can be attributed to RuO_2 rich phase are surrounded by glassy matrix.

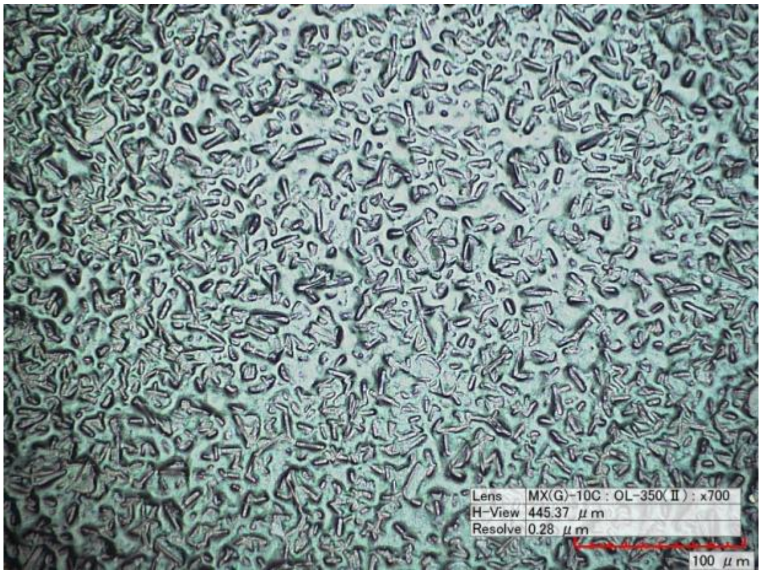
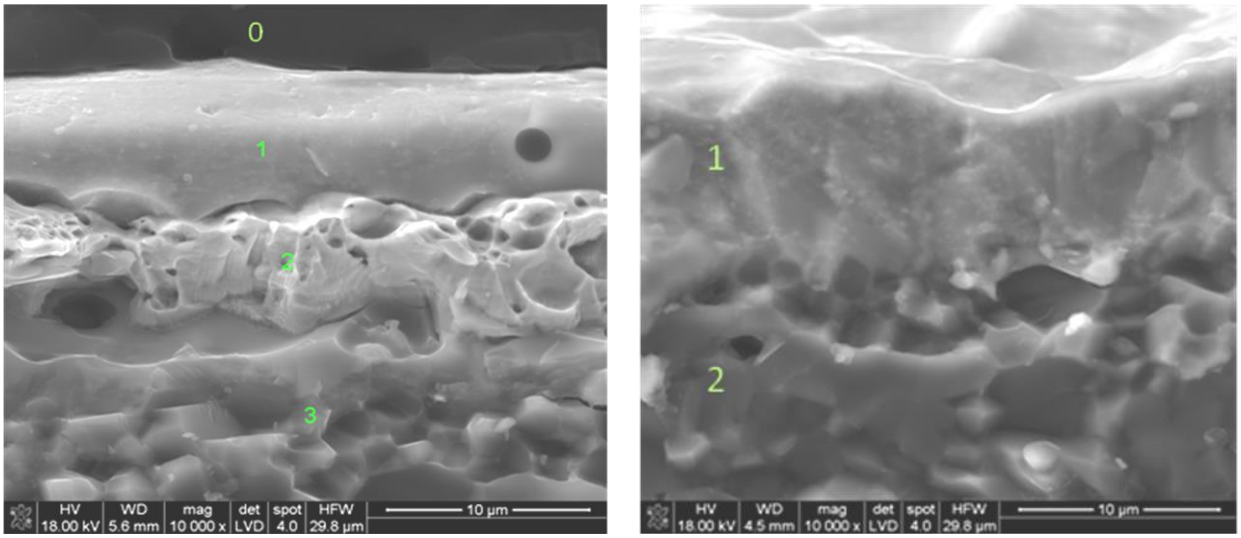


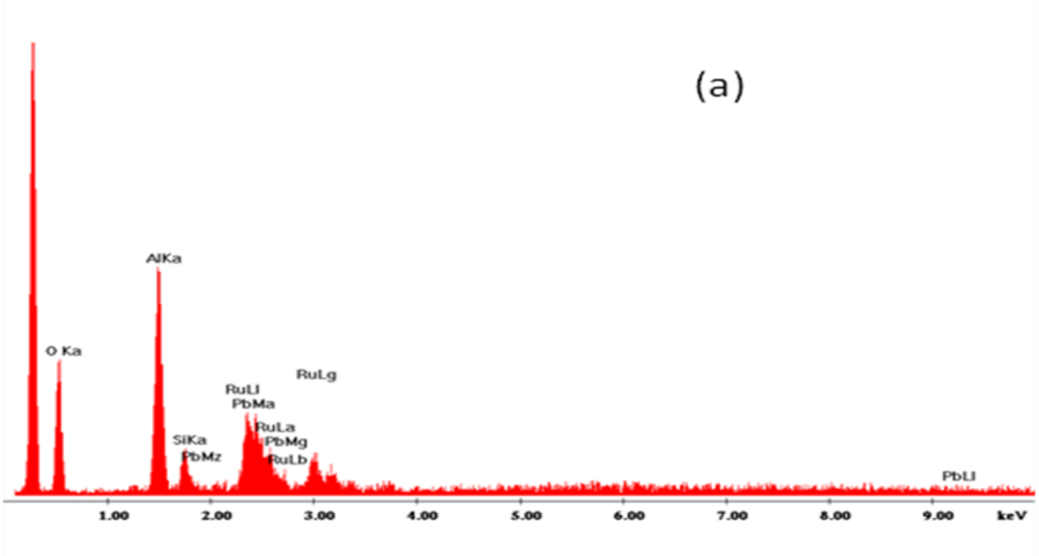
Fig. 2. Optical microscopic image of RuO_2 thick film

In Fig. 3, SEM micrographs of a fractured cross-section of the fabricated sensor are presented. Fig. 3a illustrates microstructure of all layers applied in the sensor - Ag conductive layer screen printed on alumina substrate, RuO_2-based sensitive thick film and protective polyurethane resin layer. It can be stated that the cooperation between all the layers is good. The EDS analysis indicates that the main component of the sensitive layer is ruthenium and that the glass in the applied commercial paste contains lead, aluminum and silicon (Fig. 4). The thickness of the both screen printed layers is about 7 µm. The view of the cross-section in the region of the sensing electrode (Fig. 3b) reveals very dense microstructure of RuO_2 based layer and its excellent adhesion to the alumina substrate.



(a) (b)

Fig. 3. (a) SEM images of a fractured cross-section of RuO_2 based sensor (0) resin layer/ (1) RuO_2 thick film/ (2) Ag thick film/ (3) alumina substrate. (b) (1) RuO_2 thick film/ (2) Alumina substrate.



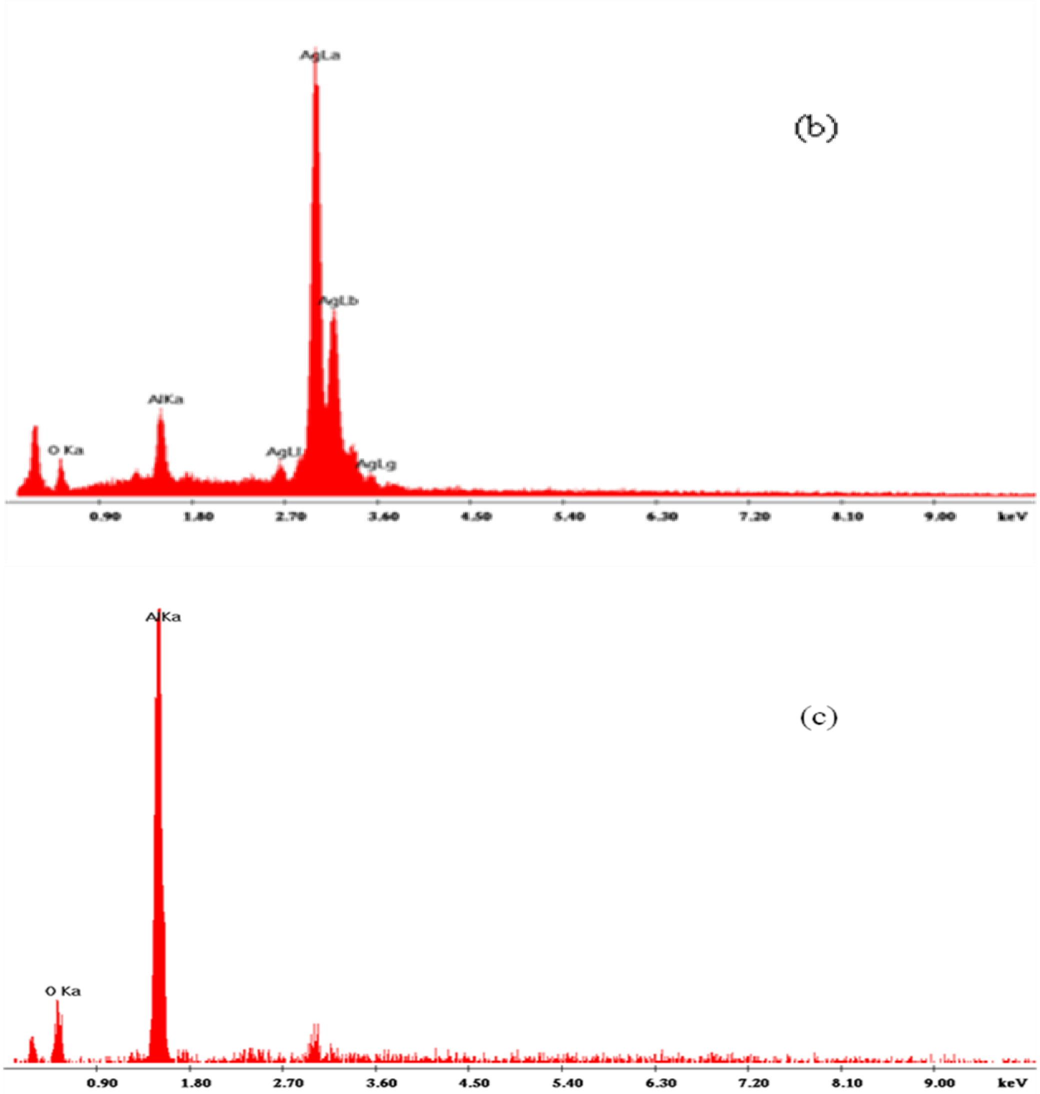
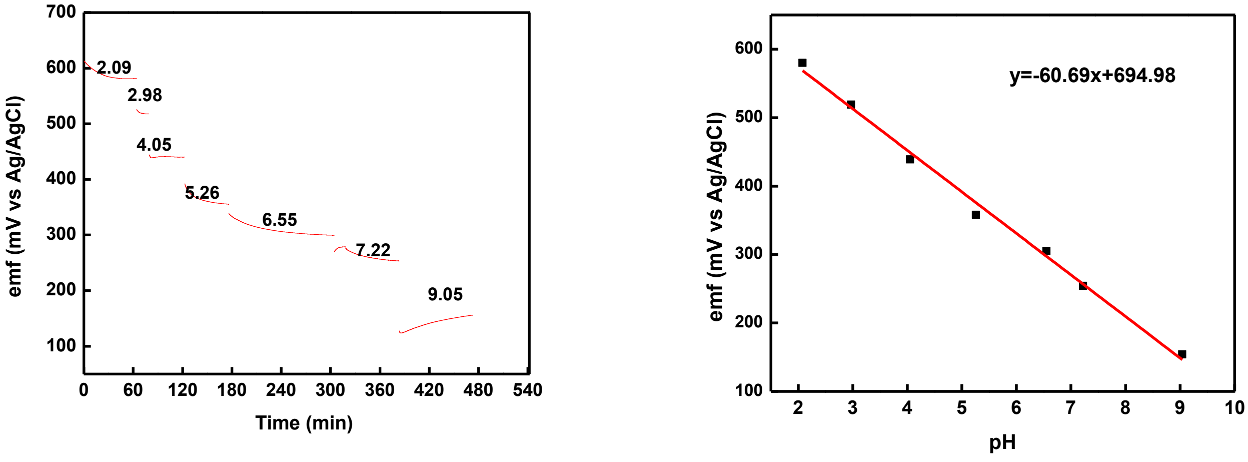


Fig. 4. EDS spectra for sensor: (a) RuO_2 layer, (b) Ag conducting layer and (c) alumina substrate

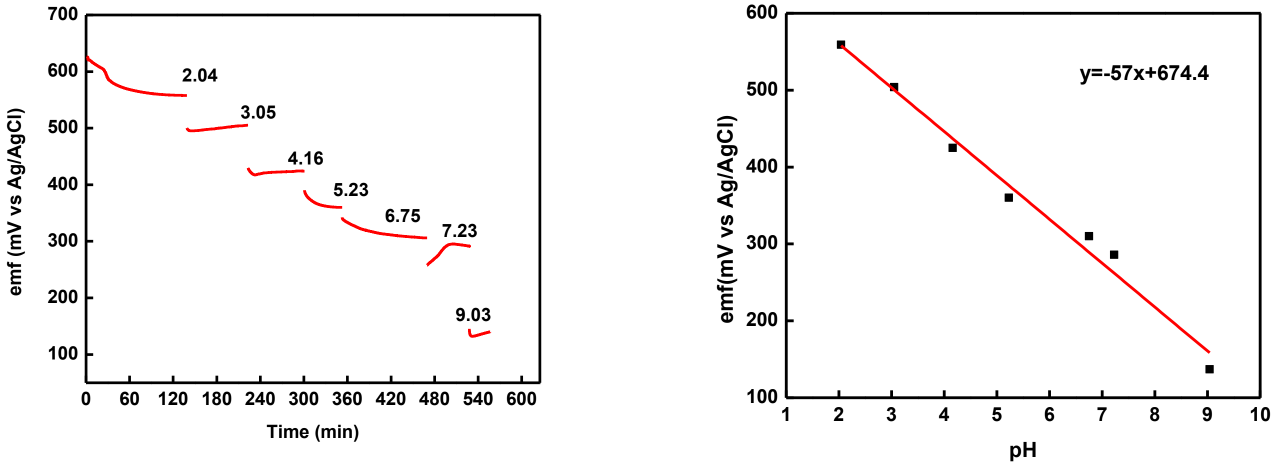
3.3. pH response of RuO_2 sensors: The sensing behavior of the RuO_2 electrode was evaluated by treating the sensor with different pH solutions. The response of the sensor stored in deionized water for a long time was compared with that of the sensor stored in air. Prior to the measurements the sensor was stored in deionized water for 25 days and then used for pH measurements. Fig. 5(a) shows the dynamic response of the sensor in different pH solutions. The variation of potential versus Ag/AgCl reference electrode was monitored by changing the pH of a solution. The electrode was rinsed with water and dried with tissue paper before changing from one to another solution with a different pH, in order to reduce the contamination by a previously used solution. All the experiments were carried out at temperature of 20°C. The emf variation of RuO_2 sensor versus pH is shown in Fig. 5(b). The slope of this plot reflects the sensitivity of the fabricated electrode. The sensor shows a sensitivity of -60.69mV/pH with a standard potential of 694.98 mV.



(a) (b)

Fig. 5. (a) Dynamic characteristics of the sensor stored in water (b) the measured emf versus pH of a solution

It was found that the sensor stored in air at the room temperature showed some fluctuations of emf for solutions of different pH at the beginning of the measurement and it took a long time to get stabilization. After several tests the sensor showed a stabilized emf value for each pH. Fig. 6(a) shows the dynamic response of the sensor for different pH of a solution. The change of the electromotive force with pH is depicted in Fig. 6(b). The sensor exhibits a slope factor of -57mV/pH with a standard emf of 674.40 mV.



(a) (b)

Fig. 6. (a) Dynamics of pH response of RuO_2 sensor stored in air and (b) emf of the sensor as a function of pH of a solution

A comparison between the sensors stored in water and in air at room temperature is shown in table 2. The potential of the sensor stored in water was stabilized very fast as compared to the sensor stored in air at room temperature. The soaking of the sensor in water has strong influence on the behavior of the sensor [2, 24]. The sensor stored in air shows some drift in voltage at the initial period of analysis which may be due to the diffusion of hydrogen ions through the RuO_2 sensing layer [2]. The mean pH sensitivity of the sensors for both storage procedures was close to the theoretical Nernstian factor for a single electron reaction (59.12 mV/pH).

Table 1: Comparison between the sensors stored in water and in air at room temperature

Storage conditions	Stored in air at room temperature	Stored in water for 25 days
Slope factor (mV/pH)	-57	-60.69
Standard electrode potential E_0 (mV) vs Ag/AgCl	674.40	694.98

The result of the measurement of the potential difference between the reference electrode Ag/AgCl and the screen printed RuO_2 electrode carried out for water as a test solution is shown in Fig. 7. After the substitution of this potential into the equation determined previously from the Nernstian response obtained for the RuO_2 sensor stored in water (y=-60.69x+694.98), the pH of deionized water was calculated as 7.08. This pH value is very close to that obtained using a commercial pH-meter (pH of deionized water =7.11).

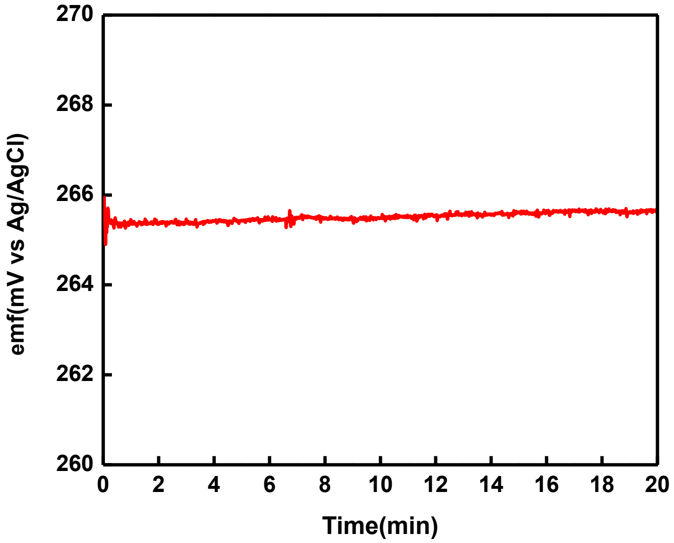


Fig. 7. Response of RuO_2 thick film sensor in water

Conclusion

The pH sensor was fabricated in a standard thick film process, and an off-the-shelf resistive paste based on RuO_2 was used as a sensing material. Sensing electrode and Ag conducting paths were screen printed onto alumina substrate and fired at 850°C. The electromotive force of a cell consisting of the fabricated RuO_2 sensing electrode and the reference electrode Ag/AgCl was measured as a function of pH of test solutions. The storage conditions were found to influence significantly the time necessary for stabilization of a measurement. The potential of the sensor stored in water is stabilized very fast as compared to that of the sensor stored in air at room temperature. The sensor without keeping in water shows a drift in potential during initial measurement. The slopes of the Nernst plots are 60.69mV/pH and 57 mV/pH for the sensors stored in water and in air, respectively, both values being close to the theoretical value of 59.12 mV/pH. The emf measurements confirm the applicability of the fabricated sensor for measuring of pH of water.

Acknowledgements

We gratefully acknowledged Institute of Electron Technology, Kraków, Poland for supporting the research work. The work is financially supported by European Commission in the framework of the FP7 project SENSEIVER, grant number 289481.

References

[1] R. Martınez-Manez, J. Soto, E. Garc-Breijo, L. Gil, J. Ibnez, E Gadea, A multisensor in thick-film technology for water quality control, Sens. Actuators A 120 (2005) 589–595.
[2] S. Zhuiykov, Solid-state sensors monitoring parameters of water quality for the next generation of wireless sensor networks, Sens. Actuators B 161 (2012) 1– 20.
[3] S. Zhuiykov, D. O'Brien, M. Best, Water quality assessment by an integrated multi-sensor based on semiconductor RuO_2 nanostructures, Meas. Sci. Technol. 20 (2009) 095201.
[4] S. Zhuiykov, Development of ceramic electrochemical sensor based on $Bi_2Ru_2O_{7+x}$ _ RuO_2 sub-micron oxide sensing electrode for water quality monitoring, Ceram Int. 36 (2010) 2407–2413.
[5] J.K. Atkinson, A.W.J. Cranny, W.V. Glasspool, J.A. Mihell, An investigation of the performance characteristics and operational lifetimes of multi-element thick film sensor arrays used in the determination of water quality parameters, Sens. Actuators B 54 (1999) 215–231.
[6] V. M. Stippl, A. Delgado, T. M. Becker, Development of a method for the optical in-situ determination of pH value during high-pressure treatment of fluid food, Innov. Food. Sci. Emerg, 5(2004) 285–292.
[7] E. Kress-Rogers, Solid-state pH sensors for food applications, Trends Food Sci. & Tech. 2 (1991) 320–324.
[8] P. Kahrilas, Gastroesophageal reflux disease, New Engl. J. Med.359 (2008) 1700–1707.
[9] P. Kurzweil, Metal Oxides and Ion-Exchanging Surfaces as pH Sensors in Liquids: State-of-the-Art and Outlook, Sensors 9 (2009) 4955-4985.
[10] W. Vonau , U. Guth, pH Monitoring: a review, J. Solid State Electrochem. 10 (2006) 746–752.
[11] G. Eisenmann, Glass electrodes for hydrogen and other cations, Marcel Dekker, New York, 1967.

[12] B. E. Horton, S. Schweitzer, A. J. De Rouin, and K. Ghee Ong, A Varactor-Based, Inductively Coupled Wireless pH Sensor, IEEE Sensors Journal, 11 (2011), 1061-1066.
[13] A. Fog, R. P. Buck, Electronic Semiconducting Oxides as pH sensors, Sens.Actuators 5 (1984) 137-146.
[14] M. Yuqinga, G. Jianguo, C. Jianrong, Ion sensitive field effect transducer-based biosensors, Biotechnology Advances 21 (2003) 527–534.
[15] M. Wang, S. Yao, M. Madou, A long term stable iridium oxide pH electrode, Sen. Actuators B 81 (2002) 313-315.
[16] K. Paztorby A. Sekiguchi, N. Shimo, N. Kitamura, H. Masuharaay, Iridium oxide-based microelectrochemical transistors for pH sensing, Sens. Actuators B, 12 (1993) 225-230.
[17] Y.L. Chin, J.C. Chou, T.P. Sun, W.Y. Chung, S.K. Hsiung, A novel pH sensitive ISFET with on chip temperature sensing using CMOS standard process, Sens. Actuators B 76 (2001) 582-593.
[18] C.W. Pan, J.C. Chou, T. P. Sun, S.K. Hsiung, Development of the real-time pH sensing system for array sensors, Sens. Actuators B 108 (2005) 870–876.
[19] W.D. Zhang , B. Xu, A solid-state pH sensor based on WO_3-modified vertically aligned multiwalled carbon nanotubes, Electrochemistry Communications 11 (2009) 1038–1041
[20] M.J. Natan, T.E. Mallouk, M. S. Wighton, pH-Sensitive WO_3-Based Microeiectrochemicai Transistors, J. Phys. Chem. 91 (1987) 648-654.
[21] R. Koncki, M. Mascini, Screen-printed ruthenium dioxide electrodes for pH measurements, Anal. Chim. Acta 351 (1997) 143-149.
[22] S. Zhuiykov, Morphology and sensing characteristics of nanostructured RuO_2 electrodes for integrated water quality monitoring sensors, Electrochem. Commun. 10 (2008) 839–843.
[23] H. N. McMurray, P. Douglas, D. Abbot, Novel thick film pH sensor based on Ruthenium dioxide glass composites, Sens. Actuators B 28 (1995) 9-15.
[24] J.A. Mihell, J.K. Atkinson, Planar thick-film pH electrodes based on ruthenium dioxide Hydrate, Sens. Actuators B 48 (1998) 505–511.
[25] Y.H. Liao, J.C. Chou, Preparation and characteristics of ruthenium dioxide for pH array sensors with real-time measurement system, Sens. Actuators B 128 (2008) 603–612.