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CORRELATION OF THE SURFACE STRUCTURE OF THE RuO_2/Ti AND TiO_2 /Ti FILMS WITH ELECTROCHEMICAL IMPEDANCE DATA

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The surface structure and nature of the capacitance formation of RuO_2/Ti and TiO_2/Ti films are discussed. The factors affecting the reversibility of the adsorption-desorption processes of oxygen on the surface of RuO_2/Ti and TiO_2 /Ti films are described. The influence of the geometry of the pore, ruthenium content, thickness of the films, and the capacitance value of oxide films was studied using electron microscopy and electrochemical impedance spectroscopy. The changes in pore content and their geometry depending on Ru concentration are fixed by electron microscopy. The changing capacitance and capacitance dispersion in a wide frequency range was used to obtain 3D images of the film's surface. A scheme of the adsorption-absorption ratio changing in relation to the pore's structure of the films was proposed.

Keywords: ruthenium, titanium, surface film, pore geometry, capacitance, sensitivity.

INTRODUCTION. The increasing concern in the detection of combustion gases calls for the development of highly sensitive sensor devices as well as for the understanding and determination of simplified models of such sensor operation mechanisms. For many years the main interest has been focused on wide bandgap semiconducting metal oxides such as SnO_2, ZnO, and TiO_2, which suffer changes in conductance when oxidizing or reducing species in the air, which have the ability to chemisorbing onto the oxide particle or film surface [1, 2]. However, sensors based on TiO2 systems require more effort in order to improve the selectivity, stability, and response times at high temperatures (300 °C–600 °C) [3,]. One of the suggested methods for improving the performance of such sensors is doping TiO_2-based systems with variable valence elements such as Pt, Ru, Cr, etc. [5–7] or semi-conductive oxides [8—10]. The simplicity and high sensitivity of these devices are based on the high surface area, high porosity, and effective surface modulation of the oxides [11]. In the presence of the stoichiometric RuO_2 (110) surface is terminated by bridge-coordinated oxygen atoms (O_β) and by coordinatively unsaturated Ru (Ru_{cus}) atoms. The exposure to gaseous O_2 leads to the formation of two additional surface species: a molecularly chemisorbed state (O_σ) bridging two neighboring Ru_{cus} atoms and weakly held O atoms (O_γ) in a terminal position above the Ru_{cus} atoms [12—14]. Based on such properties a new thick film oxygen potentiometric sensors have been developed. Moreover, TiO_2-coated RuO_2 electrodes showed a linear response as a function of the logarithm of the dissolved oxygen concentration in the 0.5–8 ppm range (log [O_2], −4.82 to −3.60; concentration of O_2 in mol dm^{-3}). The electrode displays a Nernstian slope of 59.4 mV per decade at 25 °C. The value of this slope suggests the presence of a reaction involving one electron per oxygen molecule which was tentatively attributed to the formation of super-oxide ions at the electrode surface [15]. So, it has many questions about the formation of sensitive properties of TiO_2/ RuO_2 films. But there is no systematic study of the correlation between surface pore configuration and electrochemical behavior of the films. The present study focuses on understanding the role of the thickness and component composition of TiO_2/ RuO_2 films in the electrochemical behavior of sensors.

EXPERIMENT AND DISCUSSIONS OF THE RESULTS. Synthesis of Undoped and Doped TiO_2 films was realized by three various methods: pyrolysis, spray - pyrolysis and sol-gel precipitation.

Pyrolysis. Catalytically active titanium based coatings were obtained by thermal decomposition of the corresponding metal salts. To do this, a calculated amount of metal salt was dissolved in water, added to the titanium powder and dried under a lamp reflector in a porcelain bowl, after which the composition was subject to calcination in a muffle furnace in a titanium crucible at a certain temperature. In order to avoid catalyst losses, decomposition was carried out in a muffle furnace in the presence of porous ceramic soaked in water. All powders were stored in closed containers.

The reaction of the pyrolysis in the presence of water ends with the formation of oxide:

$$RuOHCl_3 + H_2O = RuO_2 + 3HCl\uparrow$$

$$TiCl_4 + 2\,H_2O \rightarrow TiO_2 + 4HCl\uparrow.$$

Spray- pyrolysis: the production of TiO_2 films is based on the thermal decomposition of aerosol salt solutions on hot substrates. Aerosol phase was obtained by pneumatic method. The experimental setup consisted of elements such as a compressor, an atomizer, a substrate holder, a reaction chamber, an oven, a measuring tank for spray. The furnace used for pyrolysis was of a cylindrical type: 0.1 m in diameter and 0.2 meter in length. The sprayer had an outlet with a diameter of ~ $2.5x10^{-4}$ m. The gas was purified air under a pressure of 1.3—2.5 atm. A water-alcohol solution of titanium chloride was used as a precursor. The initial concentration of the solution was 0.2 M. This concentration is optimal for the deposition time of the film, which affects the cooling of the substrate during the deposition process and the ability to control the thickness and growth rate of the TiO_2 film. The solution was sprayed onto heated titanium substrates. The substrate temperature was in the range of T = 400—450 ° C (the optimum temperature range for the manufacture of gas sensors). Films deposited at the indicated temperatures have maximum porosity. The flow rate of the solution during deposition was ~ 0.1 ml / s.

Sol-Gel: The method included several main technological phases. Initially, water or organic solutions of the initial substances were obtained. To obtain a sol we used hydrolysis of salts of weak bases or alcohols. After that the sol was transformed into a gel by removing a part of water from it using heating and subsequent extraction with the appropriate solvent. Obtained gel was used directly for the manufacturing of films and monolithic products. Aerogels or xerogels (fragile microporous powder) were obtained after drying of the gel. Such powders were used for catalytically active indicator electrode formation. Samples of TiO_2, RuO_2 were made by the sol-gel method with drying at T = 320 °C for 50–60 minutes and further temperature processing at T = 400-450 °C during 20 minutes.

The surface morphology of TiO_2 and TiO_2/RuO_2 films was analyzed by SEM (JEOL JSM-6060 LA) operated at 30 kV. A scanning electron microscope (SEM) (Ultra 55 from ZEISS) equipped with an Energy Dispersive X-ray (EDX) analyzer was employed for the investigation of the obtained morphology including the diameter and length of the nano-tubular layer and changes in morphology, which may occur in the case of doping and/or heat treatment. A detailed investigation of the morphology and composition of the doped layers was carried out by transmission electron microscopy (TEM). In addition, TEM investigations by means of bright/dark field were employed to determine the phase conditions of Ru doped TiO_2.

Impedance spectra were recorded from 0.001 to 1 MHz with no bias and limited voltage (10 mV) as air was contacting with sensor samples. The impedance spectra were taken in a two-electrode cell using an Autolab30 electrochemical modular block (PGSTAT302N Metrohm Autolab) equipped with a FRA (Frequency Response Analyzer) assembly unit within the range from 10–2 to 106 Hz. The modular block was controlled by Autolab 4.9 according to the standard procedure. The spectral analysis, the equivalent circuit (EC) and the simulation of the EC were done with the software ZView 2,0 of Scribner Assoc.

According to elemental analyses of samples, the growth of the thickness of RuO_2 surface films increased the Ru amount in the coating by linear law (tab.1). So, it could be assumed that Ru plays the main role in the formation of the surface properties of obtained films. And the subsequent electrochemical studies of such systems showed the impact of film thickness on their electrochemical properties.

Table 1. Elemental composition and thickness of the surface films.

№	Ti, mass %	Ru, mass %	Thickness of films, nm
1	100	0	–
2	99,97	0,017	0,5
3	99,89	0,098	5
4	99,15	0,836	95

The simulation of the film's EIS spectrum determined that pure TiO_2 had another equivalent circuit than TiO_2/RuO_2 systems. Such circuits are typical of the systems with separate bulk layers present between $Ti/TiO_{2.}$ In such case a double electrical layer (DEL) on the TiO_2 surface is formed by the adsorption of oxygen, and the presence of oxygen created an additional inductance element in the equivalent circuit [16, 17]. So, the presence of paramagnetic properties of adsorbed oxygen molecules formed an image of spectra (all spectra occurred in the positive part of the Nyquist plot) (fig. 1).

Calculation of capacitance demonstrated linear dependence between the capacitance and thickness of RuO_2 coatings. The maximum value of capacitance is exhibited by the sample with minimal thickness of the RuO_2 film. During growth of thickness, capacitance decreases. Minimum value was demonstrated by pure TiO_2 film (table 2).

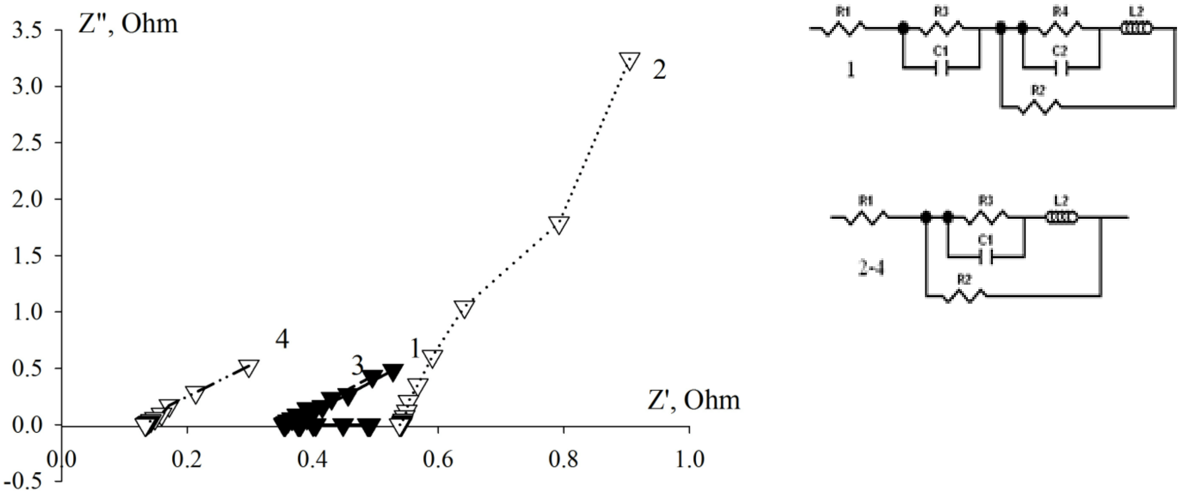


Fig. 1 EIS spectra in Nyquist plots and equivalent circuits of the electrode samples: 1 – TiO_2, 2—4 - TiO_2/RuO_2 with different thickness of coatings: 2 — 0,5 nm, 3 — 5 nm, 4 — 95 nm.

Table 2 Relationship between the capacitance and thickness of RuO_2 coatings

№	Thickness of films, nm	Capacitance (C), F
1	–	1,21
2	0,5	6,58
3	5	4,65
4	95	3,89

It is well known that equivalent circuit for the adsorption control of hydrogen in solutions [18] consists of CD- double-layer capacitance $R_{ad}H$, $C_{ad}H$- resistance and capacitance of hydrogen adsorption Re-solution resistance (Fig. 2).

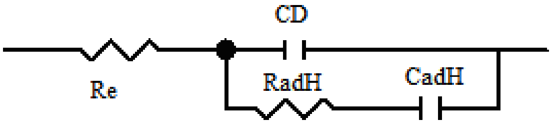


Fig. 2. Equivalent circuit for adsorption control [18].

The same equivalent circuit was obtained for Ti/TiO_2 sample. But for Ti/TiO_2 and TiO_2/RuO_2, samples in the presence of oxygen equivalent circuit transformed into another circuit with inductance and without second capacitance (fig1). The appearance of inductance in the equivalent circuits could be connected with adsorption of paramagnetic species, such as O_2. So, the large frequency range of inductance indicates a big amount of adsorbed oxygen and large area of the electrode surface, which takes part in adsorption. Such behavior could be realized only in the presence of sufficient quantity of pores on the electrode surface. Moreover, the images of impedance spectrum according to [19] like images of porous electrodes with V-shaped pores (fig. 3).

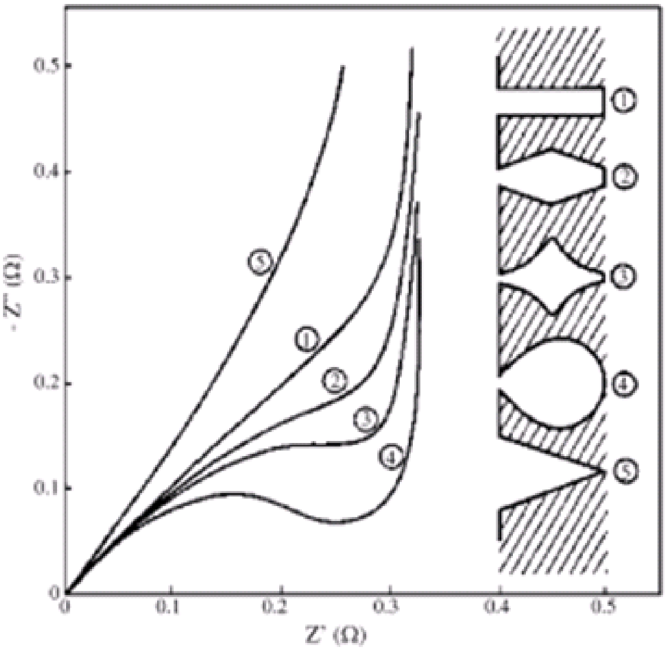


Fig. 3. Modes of porous electrode impedance spectrum with various forms of porous after Kaiser et al. [19].

It is well known that porous electrode is not ideal polarized electrode and has a tendency to dispersion of capacitance [20].

$$C(\omega) = ([(Z\omega) - Z(\omega \to \infty)]\omega) \qquad (1)$$

Such dispersion is the main characteristic of the surface morphology of an electrode. On the another hand, capacitance according to Kirchhoff’s circuit laws [19, 21] is the function of the currents in the electrical circuit nodes:

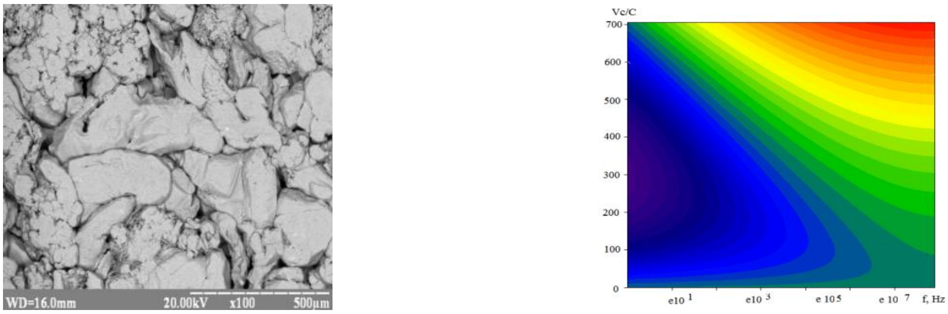
$$\frac{du_C}{dt} = \frac{1}{C}(-i_2 + i_1 + J) = \frac{1}{C}(-\frac{u_C}{R_2} + i_1 + J) \qquad (2)$$

So, the capacitance at fixed frequency could be used as second parameter for recognizing pore image.

Moreover, by changing the frequency of alternating electric current it would be possible to obtain 3D fiber form of surface films (fig. 4—7).

a b

Fig. 4. SEM and EIS images for Ti/TiO$_2$: a – SEM images; b – EIS images.



a b

Fig. 5. SEM and EIS images for TiO$_2$/RuO$_2$ (0,5 nм): a – SEM images; b – EIS images.

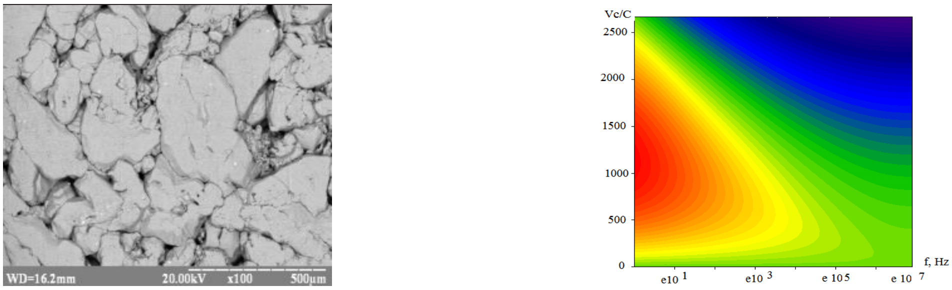


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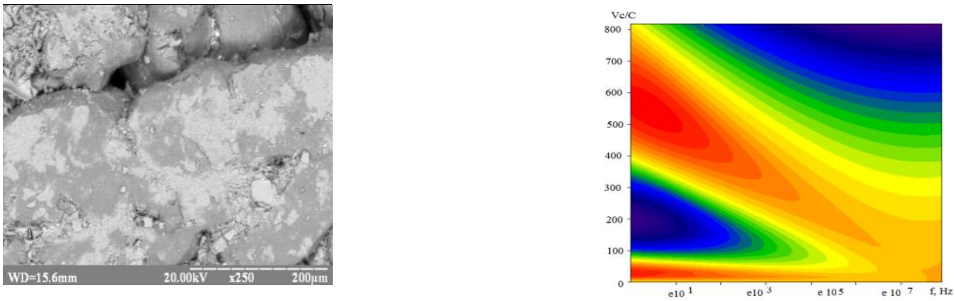
Fig. 6. SEM and EIS images for TiO$_2$/RuO$_2$ (5 nм): a – SEM images; b – EIS images.



a b

Fig. 7. SEM and EIS images for TiO$_2$/RuO$_2$ (95 nм): a – SEM images; b – EIS images.

The obtained images (fig. 4—7) showed that Ti/TiO$_2$ sample has rectangular-shaped pores with small amount of V-shaped pores on the top piece of surface (fig. 4 b). On the another hand, all the TiO$_2$/RuO$_2$ samples have the different levels of surface volume (fig. 5—7, b). The number of V-shaped pores on the top piece of surface increases during growth of RuO$_2$ film thickness and has a maximum at maximum thickness and Ru concentration (fig 7.b).

Matching the value of capacitance and the presence of rectangular-shaped and V-shaped pores on the boundary of titanium base and oxide film the following dependence of capacitance decrease was shown: large V-shaped pores on the boundary of titanium base and oxide film and on the surface of film > small V-shaped pores on the boundary of titanium base and oxide film, and large pores on the surface of film > rectangular-shaped pores on the boundary of titanium base and oxide film and small V-shaped pores on the surface of film. So, the decrease in of capacitance would be connected with increase in the absorption of oxygen due to the presence of various types of pores and their organization and a decrease in adsorption (fig. 8). In this case, reversible adsorption-absorption processes on the surface are retarded the electrode could lose sensitivity and considerably increase the time of sensor relaxation. Thus by selection of the film's content, it could be possible to regulate the technical data of sensors by changing properties of the adsorption component (properly sensor) [1] and absorption component (microgenerator) [22].

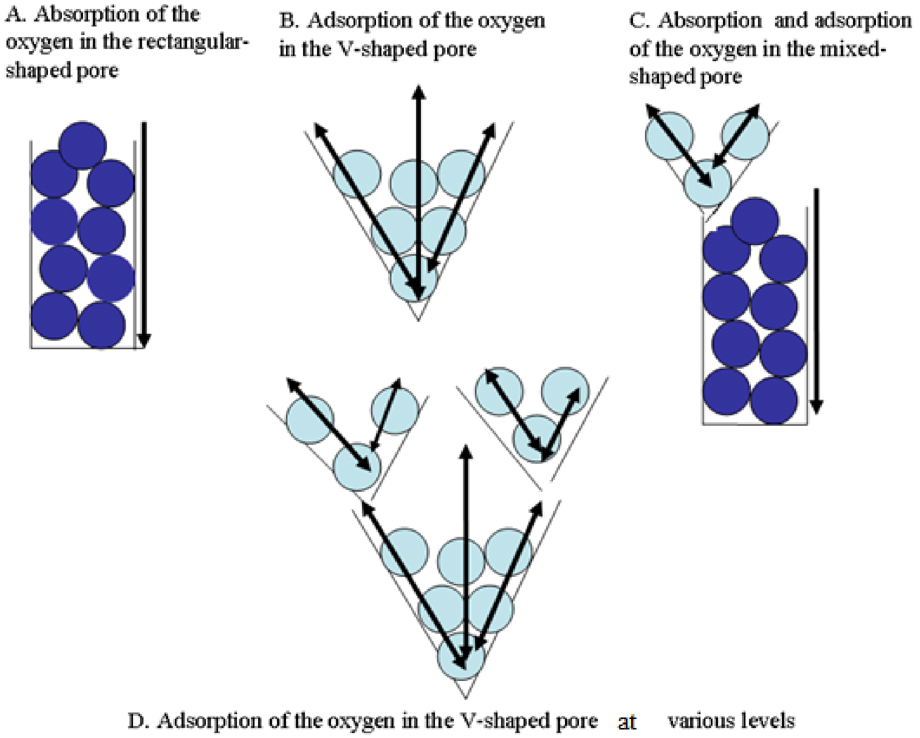


Fig. 8. Scheme of the adsorption - absorption ratio changing in relation to the film pore's structure.

CONCLUSIONS. The study of the composition, morphological structure and electrochemical behaviour of RuO_2/Ti and TiO_2 /Ti films determined the impact of the pore shape of surface films on the adsorption-absorption ratio of oxygen, which regulated technical data of sensors. By changing the capacitance and capacitance dispersion in a wide frequency range, it was proposed to obtain 3D images of the surface. It was found that decrease of DEL capacitance has following relationships: large V-shaped pores on the boundary of titanium base and oxide film and on the surface of film > small V-shaped pores on the boundary of titanium base and oxide film, and large pores on the surface of film > rectangular-shaped pores on the boundary of titanium base and oxide film and small V-shaped pores on the surface of film. The formation of the pore geometry and surface structure is dependent on the ration of ruthenium and the thickness of films. So, it is possible to change the morphological and electrochemical properties of sensors by the regulation of ruthenium content.

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КОРЕЛЯЦІЯ МІЖ ПОВЕРХНЕВОЮ СТРУКТУРОЮ ПЛІВОК RuO_2/Ti І TiO_2/Ti З ДАНИМИ ЕЛЕКТРОХІМІЧНОГО ІМПЕДАНСУ

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Обговорено структуру поверхні та характер формування ємності плівок RuO2/Ti та TiO2/Ti. Описано фактори, що впливають на оборотність процесів адсорбції-абсорбції кисню на поверхні плівок RuO2/Ti та TiO2/Ti. Вплив геометрії пор, вмісту рутенію, товщини плівок і величини ємності оксидних плівок досліджували за допомогою електронної мікроскопії та спектроскопії електрохімічного імпедансу. За допомогою електронної мікроскопії фіксували зміни вмісту пор та їхні геометрії залежно від концентрації Ru. Зміну ємності та дисперсію ємності в широкому діапазоні частот було використано для отримання 3D-зображень поверхні плівки. Запропоновано схему зміни співвідношення адсорбції-абсорбції кисню залежно від структури пор плівок.

Ключові слова: рутеній, титан, поверхнева плівка, геометрія пор, ємність, чутливість.

REFERENCES

1. Neri G. First fifty years of chemoresistive gas sensors. *Chemosensors*. *3*(1): 1—20.
2. Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M. ... & Mohamad D. Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-micro letters*. 2015. *7*(3): 219—242.
3. Cheng S., Liu H., Hu S., Zhang D., & Ning, H. A survey on gas sensing technology Xiao Liu. *Sensors*. 2012. *12*: 9635—9665.
4. Zhang J., Hu J. Q., Zhu F. R., Gong H. & O'shea S. J. Quartz crystal microbalance coated with sol-gel-derived thin films as gas sensor for no detection. *Sensors*, 2003. *3* (10): 404—414.
5. Wisitsoraat A., Tuantranont A., Comini E., Sberveglieri G. & Wlodarski W. (2009). Characterization of n-type and p-type semiconductor gas sensors based on NiOx doped TiO2 thin films. *Thin Solid Films*. *517*(8): 2775—2780.
6. Yamazoe N., & Shimanoe K. Theory of power laws for semiconductor gas sensors. *Sensors and Actuators B: Chemical*. 2008. *128*(2): 566—573.
7. Maskell, W. C. Inorganic solid state chemically sensitive devices: electrochemical oxygen gas sensors. *Journal of Physics E: Scientific Instruments*. 1987. *20*(10). 1156.
8. Sardarinejad A., Maurya D. K. & Alameh K. The pH sensing properties of RF sputtered RuO2 thin-film prepared using different Ar/O_2 flow ratio. *Materials*. 2015. *8*(6): 3352—3363.
9. Fine G. F., Cavanagh L. M., Afonja A. & Binions R. Metal oxide semi-conductor gas sensors in environmental monitoring. *Sensors*. 2010. *10*(6): 5469—5502.
10. Wang H., Chen L., Wang J., Sun Q. & Zhao Y. A micro oxygen sensor based on a nano sol-gel TiO2 thin film. *Sensors*, *14*(9). 2014. 16423—16433.
11. Francioso L., Presicce D. S., Siciliano P. & Ficarella A. Combustion conditions discrimination properties of Pt-doped TiO2 thin film oxygen sensor. *Sensors and Actuators B: Chemical*. 2007. *123*(1): 516—521.
12. Kim Y. D., Seitsonen A. P., Wendt S., Wang J., Fan C., Jacobi K. … & Ertl G. Characterization of various oxygen species on an oxide surface: RuO2 (110). *The Journal of Physical Chemistry B*. 2001. *105*(18): 3752—3758.
13. Over Y. D., Kim A. P., Seitsonen S. W. & Wendt S. E. Lundgren, M. Schmid, P. Varga, A. Morgante and G. Ertl. *Science*. 2000. *287*(54—57). 1474.
14. Jakob P. & Schlapka A. CO adsorption on epitaxially grown Pt layers on Ru (0 0 0 1). *Surface science*. 2007. *601*(17): 3556—3568.
15. Martínez-Máñez R., Soto J., Lizondo-Sabater J., García-Breijo E., Gil L., Ibáñez J. ... & Alvarez S. New potentiomentric dissolved oxygen sensors in thick film technology. *Sensors and Actuators B: Chemical*. 2004. *101*(3): 295—301.
16. Harrington D. A. & Den Driessche V. P. Mechanism and equivalent circuits in electrochemical impedance spectroscopy. *Electrochimica Acta*. 2011. *56*. 8005—8013.
17. Riabokin O. L., Boichuk A. V. & Pershina K. D. Control of the State of Primary Alkaline Zn–MnO2 Cells Using the Electrochemical Impedance Spectroscopy Method. *Surface Engineering and Applied Electrochemistry*. 2018. *54*(6): 614—622.
18. Oelgeklaus R., Rose J. & Baltruschat H. On the rate of hydrogen and iodine adsorption on polycrystalline Pt and Pt (111). *Journal of Electroanalytical Chemistry*. 1994. *376*(1—2): 127—133.
19. Macdonald, D. D. Reflections on the history of electrochemical impedance spectroscopy. *Electrochimica Acta*. 2006. *51*(8—9):1376—1388.
20. Kerner Z. & Pajkossy T. On the origin of capacitance dispersion of rough electrodes. *Electrochimica Acta*. 2000. *46*(2—3): 207—211.
21. JGabelli J., Feve G., Berroir J. M., Plaçais B., Cavanna A., Etienne B. & Hill R. E. al, Y. Jin, and DC Glattli. *Science*. 2006. *313*. 499.
22. Sobieszuk P., Pohorecki R., Cygański P. & Grzelka J. Determination of the interfacial area and mass transfer coefficients in the Taylor gas–liquid flow in a microchannel. *Chemical engineering science*. 2011. *66*(23): 6048—6056.

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