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**MODELING THE IMPEDANCE PARAMETERS OF BARIUM- STRONTIUM
TITANATE-BASED ELECTROLYTE CONDUCTIVITY SENSOR:
TWO- ELECTRODE CONFIGURATION**

A contactless electrolyte conductivity (EC) sensor with Pt interdigitated electrode equivalent circuit, for the two-electrode configuration are developed and examined. As a covering insulator material (protective layer) on Pt metallic electrodes in EC sensor, (Ba,Sr) TiO_3 nano-films were used. The theoretically calculated parameters of equivalent circuits are compared with the experimental results and good conformity is obtained.

Keywords: contactless, electrolyte conductivity, perovskite-oxide film, interdigitated electrode.

Introduction. Perovskite oxides have aroused increasing attention as catalytically active multifunctional materials in the field of (bio-)chemical sensors. One of the most popular and intensively studied multifunctional perovskite-oxide materials is the barium - strontium titanate [1,2]. Some of such virgin application frontiers for perovskite oxides of different compositions include, for instance, pH sensing [3-5], hydrogen peroxide [6,7] and hydrocarbon detection [8]. In previous experiments, the BST films have been applied for the detection of humidity [9], hydrogen [10], ammonia gas [11], etc.

In recent years, due to micro- and nanotechnology developments, great attention has been paid to biosensors, including contactless measuring sensors based on thin-film interdigitated electrodes which are compatible with the modern microelectronic technologies [12-18]. The use of a contactless electrochemical detection mode offers some advantages over faradic electrochemical methods [13,16]. But this method has a disadvantage: the parasitic capacitance of the structure is large [19,20]. Another way to control the influence of the electrode impedance is covering the electrode surface with a special insulator layer [21-24] which allows to fix the electrode impedance and prevent its dependence on electrolyte concentration (Fig.1). The main disadvantage of the contactless EC measuring system is attributed to its lower sensitivity when compared to other electrochemical modes of detection.

The motivation and description of the operation principle of a new type of contactless electrolyte conductivity sensor based on Pt electrodes covered with high k perovskite-oxide (BST-Barium- Strontium Titanate) nano-films has been examined by us earlier [5, 23,24].

The aim of this work is to develop an exact and adequate equivalent circuit of the BST protective layer based two-electrode EC sensor and to systematically analyze the impedance spectra characteristics, as well as compare it with the experimental results.

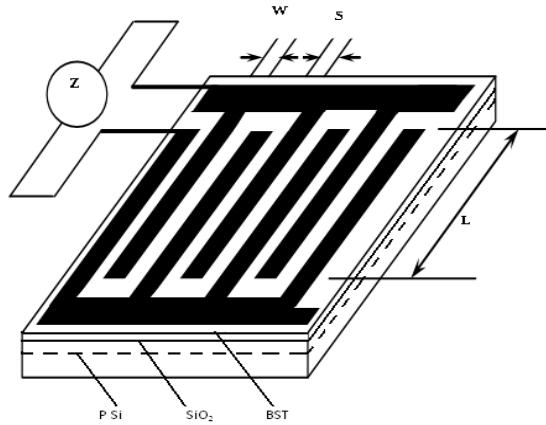


Fig.1. Impression of an interdigitated electrode pair, W , L , S —are the electrode width, their length and the interelectrode space, respectively. The device is on a p-Si substrate with SiO_2 on top of which metallic (Pt) electrodes are deposited. The whole device is covered with an insulating $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film [5,23,24]

1. The equivalent circuit of a two-electrode sensor. The two-electrode conductivity sensor equivalent circuit is presented in Fig.2, where C_{dl} is the electrical double layer capacitance; C_f - the ferroelectric film based protective layer capacitance; R_e - the electrolyte conductance; C_c - the cell capacitance; C_{ox} - the oxide (SiO_2 layer) capacitance; R_s - the substrate active resistance; R_L - the common parasitic resistance of the measuring system.

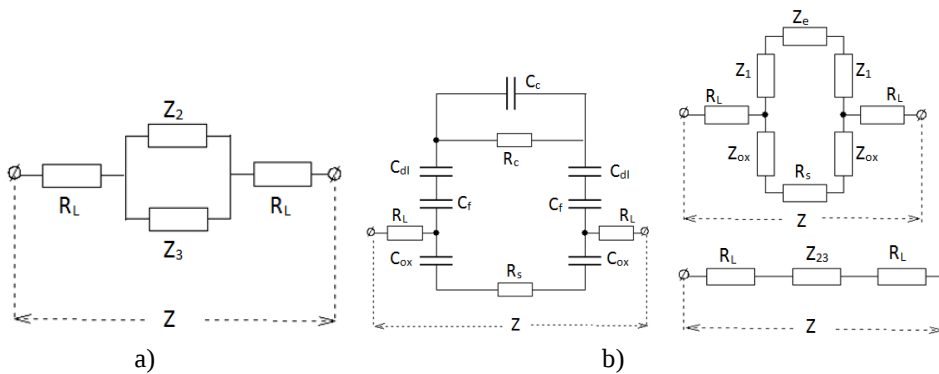


Fig. 2. The equivalent circuit of a two electrode sensor (a) and its with transformation (b)

$$\text{Where: } Z_1 = \frac{(C_{dl} + C_t)}{j\omega(C_{dl} \cdot C_t)} = \frac{\alpha}{j\omega}, \quad Z_e = \frac{R_e}{1 + j\omega R_e C_{cel}}, \quad Z_{ox} = \frac{1}{j\omega C_{ox}},$$

$$Z_2 = 2Z_1 + Z_e, \quad Z_3 = R_s + 2Z_{ox}, \quad Z = \frac{Z_2 Z_3}{Z_2 + Z_3} + 2R_L, \quad \alpha = \frac{C_{dl} + C_f}{C_{dl} \cdot C_f},$$

ω is the measuring signal angular frequency.

Neglecting the substrate resistance, R_s , in respect to the other active resistances (R_L , R_e), [12,15,21-24], for the measuring system impedance, we obtain:

$$Z_1 = \frac{\alpha}{j\omega}, \quad Z_2 = 2Z_1 + \frac{R_e}{1 + j\omega R_e C_{cel}} = \frac{2\alpha + j\omega\gamma_1}{\omega^2\gamma_2 + j\omega^2}, \quad Z_3 = \frac{2}{j\omega C_{ox}},$$

$$\gamma_1 = R_e(1 + 2\alpha C_{cel}), \quad \gamma_2 = -R_e C_{cel}, \quad Z_2 \cdot Z_3 = \frac{4\alpha + 2j\omega\gamma_1}{-\omega^2 C_{ox} + j\omega^3 C_{ox}\gamma_2},$$

$$Z_2 + Z_3 = \frac{2j\omega(1 + \alpha C_{ox}) + \omega^2(2\gamma_2 - C_{ox}\gamma_1)}{-\omega^2 C_{ox} + j\omega^3\gamma_2 C_{ox}},$$

$$Z = \frac{Z_2 Z_3}{Z_2 + Z_3} = \frac{4\alpha + 2j\omega\gamma_1}{2j\omega(1 + \alpha C_{ox}) + \omega^2(2\gamma_2 - C_{ox}\gamma_1)} + 2R_L,$$

$$Z = 2R_L + \frac{(4\alpha + 2j\omega\gamma_1)(\omega^2 - j\omega\gamma_4)}{\omega^4\gamma_3^2 + \omega^2\gamma_4^2},$$

$$\gamma_3 = 2\gamma_2 - C_{ox}\gamma_1, \quad \gamma_4 = 2(1 + \alpha C_{ox}),$$

$$Z = 2R_L + \frac{4\alpha\gamma_3 + 2\gamma_1\gamma_4}{\omega^2\gamma_3^2 + \gamma_4^2} + j \frac{(2\omega^2\gamma_1\gamma_3 - 4\alpha\gamma_4)}{\omega^3\gamma_3^2 + \gamma_4^2\omega},$$

$$Z = R_\Sigma + jX_\Sigma, \quad R_\Sigma = 2R_L + \frac{4\alpha\gamma_3 + 2\gamma_1\gamma_4}{\omega^2\gamma_3^2 + \gamma_4^2}, \quad X_\Sigma = \frac{2\omega^2\gamma_1\gamma_3 - 4\alpha\gamma_4}{\omega^3\gamma_3^2 + \gamma_4^2\omega},$$

$$|Z| = \sqrt{R_\Sigma^2 + X_\Sigma^2}. \quad (1)$$

At lower frequencies, the impedance will be dominated by the concentration dependent double layer capacitance, C_{dl} , until the impedance of this capacitor becomes lower than the resistance of the electrolyte and the sensor impedance becomes frequency independent. The low frequency point where the impedance of the measuring system changes from the capacitance character and becomes almost

non-dependent of the frequency active resistance, we can define via these conditions. $|Z| \approx X_\Sigma \geq R_\Sigma$ or:

$$\frac{2\omega^3\gamma_1\gamma_3 - 4\alpha\omega\gamma_4}{\omega^4\gamma_3^2 + \omega^2\gamma_4^2} \geq \frac{4\alpha\omega^2\gamma_3 + 2\omega^2\gamma_1\gamma_4}{\omega^4\gamma_3^2 + \omega^2\gamma_4^2} \quad (2)$$

which yields to $\omega^2 - b\omega - c \geq 0$, where $b = \frac{(2\alpha\gamma_3 + \gamma_1\gamma_4)}{\gamma_1\gamma_3}$.

The solution of (2) for the two possible cases, namely:

$$\frac{4c}{b^2} \leq 1 \text{ (} f_{lo1} \text{) and } \frac{4c}{b^2} \geq 1 \text{ (} f_{lo2} \text{)}, \text{ are: } f_{lo1} \cong \frac{1}{\pi R_e (C_{dl} + 2C_{cel})},$$

$$f_{lo2} \cong \frac{1}{2\sqrt{2}\pi R_e C_{dl}}, \quad (3)$$

which both $f_{lo1,2}$ indicate that at lower frequencies, the impedance will be dominated by the concentration dependent double layer capacitance, C_{dl} , until the impedance of this capacitor becomes lower than the resistance of the electrolyte and the sensor impedance becomes frequency independent.

The high frequency point where the impedance of the C_{cell} becomes lower than the R_{elec} and the impedance decrease again with increasing frequency, showing the pure “capacitance” character, we can define via these conditions: if R_Σ is admitted as the electrolyte solution active resistance, R_e , then from the $|Z| \leq R_\Sigma$, or

$$R_\Sigma \rightarrow 0 \text{ requirement } R_e = 2R_L + \frac{4\alpha\gamma_3 + 2\gamma_1\gamma_4}{\omega^2\gamma_3^2 + \gamma_4^2} \rightarrow 0 \text{ (if the measuring system}$$

wires, bonding pads, etc parasitic resistance, R_L , is less than R_e), for the ω , one can obtain:

$$\begin{aligned} \omega^2 R_e \gamma_3^2 + R_e \gamma_4^2 &\cong 4\alpha\gamma_3 + 2\gamma_1\gamma_4, \\ \omega &\cong \frac{2\alpha C_{ox}}{2R_e C_{cel} + C_{ox} R_e (1 + 2\alpha C_{cel})} \cong \frac{2\alpha C_{ox}}{R_e [2C_{cel} + C_{ox} + 2\alpha C_{ox} C_{cel}]}, \\ f_{hi1,2} &\cong \frac{2\alpha C_{ox}}{\pi R_e [2C_{cel} + C_{ox} + 2\alpha C_{ox} C_{cel}]}. \end{aligned}$$

Taking into account that $C_{dl} \gg C_{ox}$, $C_f \gg C_{ox}$, $C_{dl} \gg C_f$, $\alpha = \frac{C_{dt} + C_f}{C_{dt} \cdot C_f} \approx \frac{1}{C_f}$,

$$f_{hi} \cong \frac{\alpha C_{ox}}{\pi R_e C_{ox} (1 + 2\alpha C_{cel})} \cong \frac{\alpha}{\pi R_e (1 + 2\alpha C_{cel})} \cong \frac{1}{\pi R_e (C_f + 2C_{cel})}, \quad (4)$$

indicates that the high cut-off frequency is a function of the electrolyte resistance and the cell capacitance, C_{cel} .

The width of the frequency band can be expressed as:

$$\Delta f \cong \log \frac{f_{hi}}{f_{lo}} \approx \log \frac{C_{dl}}{(C_f + 2C_{cel})}. \quad (5)$$

From expression Δf (5), it follows that the presence of the high dielectric permittivity protective layer ($Ba_xSr_{1-x}TiO_3$) which originated (conditioned) high capacitance, C_f , for certain conditions may be alert on frequency range of measure, particularly shift the cut-off frequency to a lower frequency range, as well as influence the measurable value of the electrolyte resistance, R_e , and thus the sensor sensitivity.

This f_{hi} will also decrease for lower concentration through the increase in electrolyte resistance.

It is worth to note that expressions (2) and (4) are in conformity with the results of other authors [18,21,22].

2. Modeling results. Based on the impedance equation of the equivalent circuit shown in Fig. 2, the impedance can be calculated as a function of the now known values of the components and the frequency. The theoretical simulations of the impedance spectra of the above described EC sensor has been carried out

according to Eqs. (1) - (4), assume, that the cell constant $\kappa_{cell} = R_e \sigma = \frac{\varepsilon_0 \varepsilon_s}{C_{cel}}$,

$\kappa_{cell} \cong 1,25$ [23,24], where σ is the specific conductance of the electrolyte and R_e is the measured resistance, ε_0 , ε_s are the dielectric constant of the free space and electrolyte solution respectively.

The theoretical simulation shows that impedance becomes frequency independent for the experimentally measured different conductivity values between 0.3 mS/cm and 50 mS/cm (see Fig. 2) when C_{dl} varies in the range $(200000 \div 15000) \text{ pF}$, C_f varies in the range of $(4678.62 \div 7478.99) \text{ pF}$, and C_{cel} varies in the

range $(2808.31 \div 3000)pF$, indicating the fact that the double layer capacitance decreased with the increase of solution conductivity, as well as that, at the same time, the ferroelectric protective layer capacitance increases and C_{cel} decreases with the increase of the solution conductivity.

All these changes of parameters are agree with our theoretical predictions, conditioned by electrochemical processes which take place on the surface of insulator-electrolyte solutions [9-10,13,18, 21-24].

In Fig.3, the experimentally measured and calculatedBode plot of a two-electrode EC sensor is presented.

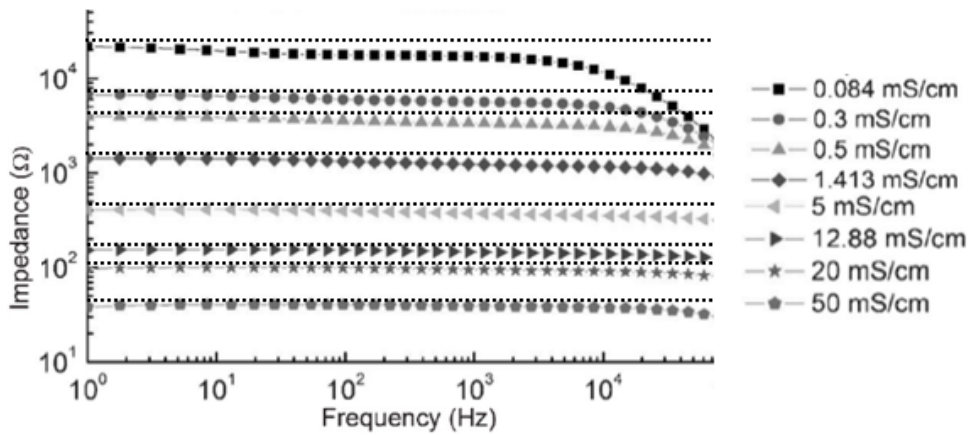


Fig.3. The Bode plot of the modulus of impedance of a two electrode EC sensor with 485 nm BST as protective layer recorded in various conductivity standard solutions [5, 23,24] and calculating value of impedance module(dashed lines)

Conclusions. As it follows from Fig.3, there is good agreement between experiments and theoretical calculations, which in turn indicates the high adequateness of the developed equivalent scheme of the examined sensors. The low frequency threshold value of the BST containing sensor starts, for example, from $f \cong 1 Hz$ and for the Ta_2O_5 protective layered sensors - from $f \cong 100 Hz$ [18,21,22] for the same conditions, which are critical for the other type isolation protective layer application cases.

Thus, the existence of high dielectric permittivity BST protective layer leads to the shift of the threshold value of the low frequency (see Eq.(5) , where the impedance of the system becomes purely active, to lower frequency range of measures for all other equal conditions. The double layer capacitance decreases significantly with decreasing the electrolyte concentration and, as a result, the role of capacitance of the protective layer becomes dominating. The observed difference between the measured and calculated impedance modules can be caused

by a simplifications and approximations in the electrical equivalent model of the sensor which we have done. Using a high dielectric permittivity BST nanofilm as a noble metal - covered protective layer in the examined IDE EC sensors will help to solve problems associated with contact-mode EC detection techniques, such as bubble formation due to electrolysis, the effect of redox processes. The contamination and fouling of electrodes during continuous use can be eliminated or at least minimized.

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National Polytechnic University of Armenia. The material is received 11.10.2016.

Ա. Լ. ՄԱՆՈՒԿՅԱՆ

**ԲԱՐԻՈՒՄ-ՍՏՐՈՆՑԻՈՒՄ ՏԻՏԱՆԱՏԻ ՀԻՄՔՈՎ ԷԼԵԿՏՐՈԼԻՏԻ
ՀԱՂՈՐԴԱԿԱՆՈՒԹՅԱՆ ԵՐԿԷԼԵԿՏՐՈՂԱՅԻՆ ԿԱՌՈՒՑՎԱԾՔՈՎ ՏՎԻԶԻ
ԻՄՊԵՐԱՆՍԱՅԻՆ ՊԱՐԱՄԵՏՐԵՐԻ ՄՈՂԵԼԱՎՈՐՈՒՄԸ**

Մշակվել և ուսումնասիրվել է Pt-ե միկրոշերտավոր երկէլեկտրոդային կառուցվածքով էլեկտրոդիտների հաղորդականության (ԷՀ) ոչ կոնտակտային չափման տվիչ: Որպես մետաղական էլեկտրոդները ծածկող մեկուսիչ շերտ օգտագործվել են $(\text{Ba,Sr})\text{TiO}_3$ պերովսկիտ-օքսիդային նանոթաղանթները: Համարժեք սխեմայի պարամետրերի տեսական հաշվարկների արդյունքները համեմատվել են փորձական արդյունքների հետ, և ցույց է տրվել դրանց համապատասխանությունը:

Առանցքային բաներ. ոչ կոնտակտային, էլեկտրոդիտի հաղորդականություն, միկրոշերտային էլեկտրոդ:

А.Л. МАНУКЯН

**МОДЕЛИРОВАНИЕ ИМПЕДАНСНЫХ ПАРАМЕТРОВ ДАТЧИКА
ПРОВОДИМОСТИ ЭЛЕКТРОЛИТОВ НА ОСНОВЕ БАРИУМ-СТРОНЦИУМ
ТИТАНАТА: ДВУХЭЛЕКТРОДНАЯ КОНФИГУРАЦИЯ**

Разработан и исследован датчик бесконтактного измерения проводимости электролитов с Pt-штыревыми электродами для конфигурации из двух электродов. В качестве диэлектрического слоя, покрывающего металлические (Pt) электроды, использованы $(\text{Ba,Sr})\text{TiO}_3$ перовскит-оксидные нанопленки. Сравнение теоретических и экспериментальных результатов показало их хорошее соответствие.

Ключевые слова: бесконтактный, проводимость электролита, микрополосковый электрод.