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EQUIVALENT CIRCUIT AND OPTIMIZATION OF IMPEDANCE CHARACTERISTICS OF AN ELECTROLYTE CONDUCTIVITY SENSOR

V.V. Buniatyan[1], C.A. Huck[2], A.S. Poghossian [2], M.J. Schoening[2], L.G. Rustamyan[1], H.H. Hovnikyan[1]

[1] *State Engineering University of Armenia (SEUA)*
[2] *FH Aachen, University of Applied Sciences, Institute of Nano- and Biotechnologies, Campus Jülich*

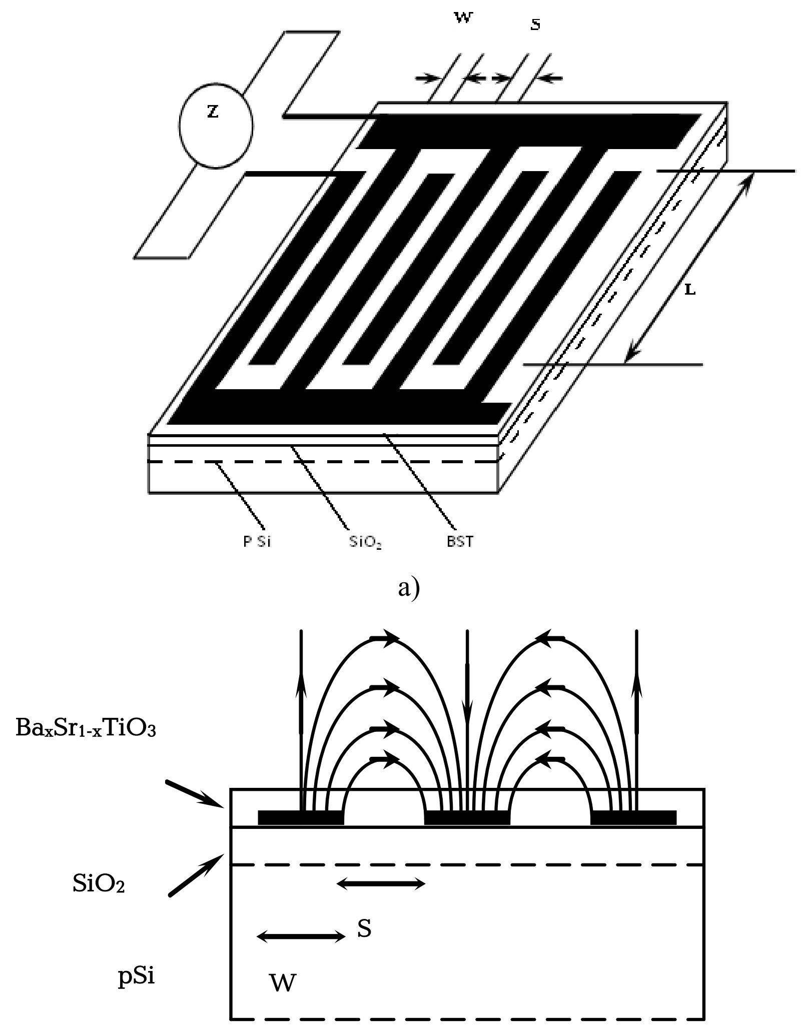
A new construction of a miniaturised contactless electrolyte conductivity sensor based on Pt interdigitated electrodes is proposed. High dielectric permittivity perovskite-oxide films of different composition have been first used as a covering insulator material on metallic electrodes. An equivalent circuit of the sensor is composed and the impedance characteristics are theoretically calculated and experimentally investigated. The operation frequency range and the sensor parameter bilateral dependencies where the sensor exhibits pure active resistance is obtained and evaluated analytically.

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

Introduction. The motivation and description of a new type of contactless electrolyte conductivity (EC) sensor operation principle based on Pt interdigitated electrodes covered with high dielectric permittivity perovskite-oxide (BST- Barium Strontium Titanate) nano-films have been examined by us earlier [1].

Taking into account the factors mentioned in [1,2], the aim of the present paper is to study and investigate the equivalent circuit of the structure proposed (Fig. 1), as well as to establish the bilateral dependencies between the sensor impedance components and the frequency range of operation in order to optimize the sensor characteristics in the future.

Modeling and experiments. By using conventional Si-and thin-film technology, p – Si – SiO_2 – Pt (interdigitated electrodes)-BST structures with different thicknesses of BST have been fabricated (Fig. 2). As the processes in the electrochemical cell with a conductometric interdigitated transducers are mostly simulated by equivalent schemes and experimentally studied by the impedance–spectroscopy method [3-10], we have composed a structure corresponding to the equivalent scheme for the transducers proposed.



a)

b)

Fig. 1. (a) Impression of an interdigitated electrode pair, W, L, S –are the electrode width, their length and the interelectrode space, respectively. (b) Cross section of the device on p-Si substrate with SiO_2 *on top of which metallic (Pt) electrodes are deposited. The whole device is covered with an insulating* $Ba_xSr_{1-x}TiO_3$ *film*

The structures have been tested* as an EC sensor by using the impedance–spectroscopy measurement method (using an impedance analyzer Zahner Elektrik-IM 5d and Zahner-3). The measurement conditions are:

- all conductivity measurements are performed at 25 °C in standard conductivity solutions,

- the sensor is rinsed with distillated water and dried with N_2 before being used.

Potentiostat: Open circuit potential (OCP), 20 mV in a frequency range of 1 *Hz* – 1 *MHz*.

The results of measurements are shown in Fig. 3.

#sensor	BST	electrodes
#10136-C1*	50 *nm*	2 elec
#10135-C2*	100 *nm*	2 elec
#10134-C3*	150 *nm*	2 elec

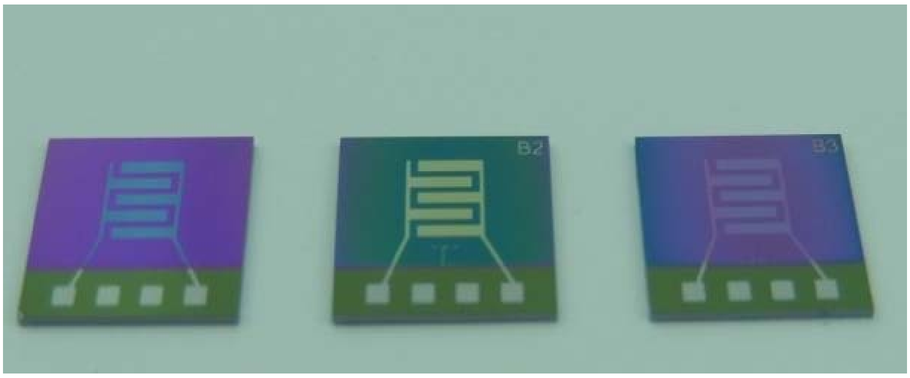


Fig. 2. An EC sensor configuration with different BST thicknesses

An electrical model of the proposed sensor structure is shown in Fig. 4. The metal (Pt) electrodes are covered with an insulating ferroelectric layer (BST). This insulating layer behaves electrically as a capacitor C_f, whose value depends on its thickness and the area of the covered metal electrode. The double layer (conditioned by Stern layer and a diffusive layer according to Gouy-Chapman model [8-10]) adds an extra capacitor C_{dl} in the series with an insulating layer capacitor.

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[*] Measurements have been carried out at the Institute of Nano- and Biotechnologies (Aachen University of Applied Sciences, Germany).

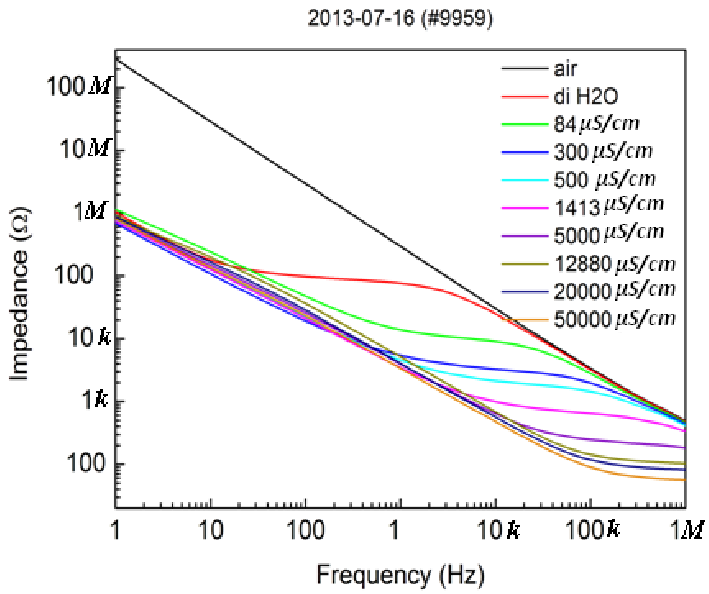
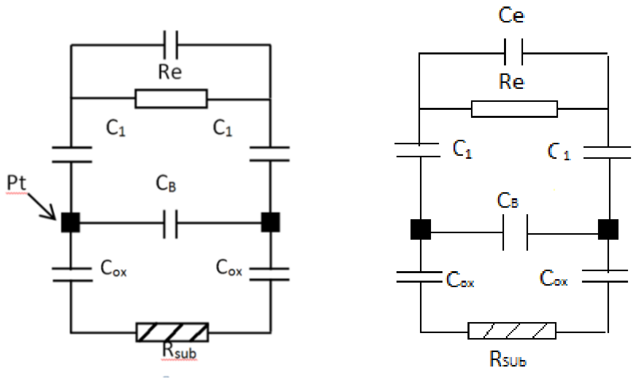


Fig. 3. Impedance-frequency characteristics of an EC sensor for different concentrations of electrolyte (NaCl)

These two capacitors form the "electrode impedance". The conductive and dielectric contribution of the liquid is represented by resistor R_e and capacitor C_e (placed in parallel), respectively. Their values are linked to the spacing between the metal electrodes, the area of the electrodes and their geometry. At low measurement frequencies, the dielectric contribution of the liquid is negligible. The SiO_2 insulator layer conditioned capacitance and p - Si-substrate active resistance are denoted as C_{ox} and R_{sub} respectively. The parasitic capacitance between the two Pt electrodes is C_B.



a) ***b)***

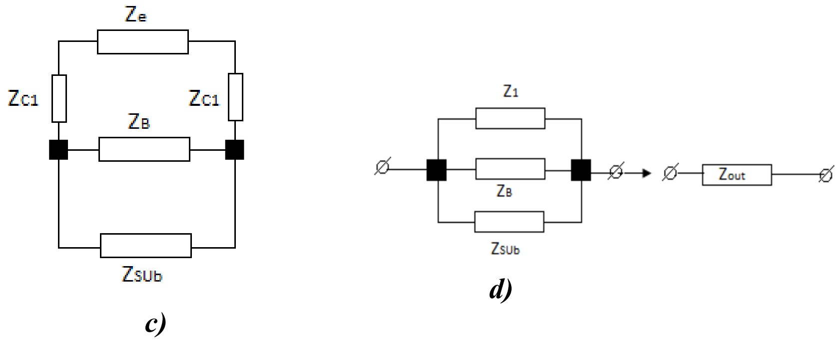


Fig. 4. An electrical model of the contactless two electrode detector, including the respective measurement setup: (Pt) metal electrode (C_{ox}, C_f, C_B, C_{dl}, C_e, and R_e are the capacitance of the insulating layer, the ferroelectric film capacitance, the lateral capacitance between Pt electrodes, the double-layer capacitance, the capacitance of the liquid, and the resistance of the liquid, respectively (a) and the simplified equivalent circuits (b,c,d)

In Fig.4:

$$C_1 = \frac{C_f C_{dl}}{C_f + C_{dl}}, \quad Z_e = \frac{R_e}{1 + j\omega\tau_e} = \frac{R_e}{1 + (\omega\tau_e)^2} - j\frac{\omega R_e \tau_e}{1 + (\omega\tau_e)^2},$$

$$\tau_e = R_e C_e ,$$

$$Z_1 = Z_e + 2Z_{C1}\ , \ Z_{C1} = \frac{1}{j\omega C_1}, \quad Z_B = \frac{1}{j\omega C_e},$$

$$Z_{sub} = R_{sub} + \frac{2}{j\omega C_{ox}}\ , \ Z_{out} = \frac{Z_1 Z_B Z_{sub}}{Z_B Z_{sub} + Z_1 Z_{sub} + Z_1 Z_B}\ , \ Z_{out} = R_{out} + jX_{out}\ ,$$

$$Z_1 = \frac{1}{\beta}\left\{R_e - j\omega\left[\frac{2\beta + R_e\omega^2 C_1}{\omega^2 C_1}\right]\right\},$$

$$\beta = 1 + (\omega\tau_e)^2$$

$$Z_{out} = \frac{\{\omega^2(R_S\beta_{1.}C_{ox} + 2R_eC_1) + j\omega(\gamma_2 R_e R_S - 2\beta_1)\}}{\{\omega^2 a_2 + j\omega b_2\}},$$

ω is the angular frequency, $a_1 = \omega(R_S\beta_1 C_{ox} + 2R_eC_1)$, $b_1 = (\gamma_2 R_e R_S - 2\beta_1)$,

$a_2 = \omega[2\beta C_1 + \beta_1 C_{ox} + C_B(2\beta_1 - \gamma_2 R_e R_S)]$, $b_2 = [R_S\beta\gamma_2 + R_e\gamma_2 + {} + \omega^2 C_B(\beta_1 R_S C_{ox} + 2R_eC_1)]$,

$\beta_1 = 2\beta + \omega^2 R_e C_1 \tau_e$, $\gamma_1 = \omega^2 C_B \beta$, $\gamma_2 = \omega^2 C_{0X} C_1$.

The output impedance is introduced in the form:

$$Z_{out} = \frac{a_1+jb_1}{a_2+jb_2} = \frac{(a_1+jb_1)(a_2-jb_2)}{a_2^2+b_2^2} = \frac{(a_1a_2+b_1b_2)}{a_2^2+b_2^2} + j\,\frac{(b_1a_2-a_1b_2)}{a_2^2+b_2^2} = R_{out} + +jX_{out}\,, \qquad (1)$$

$$Z_{out} = \frac{a_1+jb_1}{a_2+jb_2} = \frac{a_1a_2+b_1b_2}{a_2^2+b_2^2} + j\,\frac{b_1a_2-a_1b_2}{a_2^2+b_2^2}\,,$$

$$R_{out} = \frac{a_1a_2+b_1b_2}{a_2^2+b_2^2}\,, \qquad X_{out} = \frac{b_1a_2-a_1b_2}{a_2^2+b_2^2}\,. \qquad (2)$$

As the impedance spectroscopy (Bode plot) measurements of the EC sensor have a schematic view presented in Fig. 3 and Fig. 5, we can admit that in the frequency range of $0 < f < f_1$, $|X_{out}|$→has a capacitance character and is larger than that of R_{out}, which corresponds to f_{min}. In the frequency range of $f_1 < f < f_2$, the sensor mainly exhibits an active resistance which is an important precondition for designing electrolyte conductivity sensors. The frequency range (band) where impedance has mainly a resistive character corresponds to the regime of $Z_{out} \equiv R_{out}$.

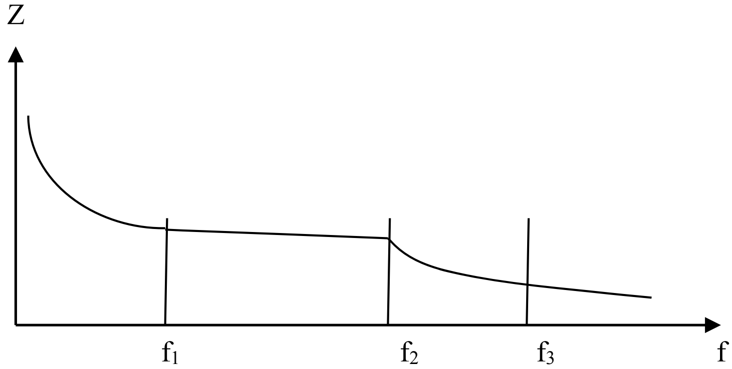


Fig. 5. A scheme of Z-f dependence

In this regime

$$R_{out}\Bigg|_{\substack{C_{0x}\to 0\\ R\,S\to 0\\ C_B\to 0}} \Rightarrow \frac{a_1}{a_2} \Rightarrow \frac{2\omega R_eC_1}{2\omega C_1(1+\omega^2{\tau_e}^2)} = \frac{R_e}{(1+\omega^2{\tau_e}^2)} \Rightarrow$$

$$\Rightarrow \frac{R_e}{1+\frac{2{\tau_e}^2}{R_eC_1\tau_e-2{\tau_e}^2}} \Rightarrow \frac{R_e}{1+\frac{2\tau_e}{R_eC_1-2\tau_e}}\left(|X_{out}| \to \frac{b_1}{a_2} \to 0\right)$$

and, neglecting the R_S, C_B, C_{ox} and after substituting the corresponding parameters for (Eq.2), one can obtain a quadratic equation in respect of ω:

$$\omega^2 - \omega\left(\frac{2\tau_f}{4\tau_e^2+2\tau_f\tau_e}\right) + \frac{4}{(4\tau_e^2+2\tau_f\tau_e)} = 0, \qquad (3)$$

where $\tau_f = C_1R_e$, $\tau_e = R_eC_e$, and

$$\omega_{1,2} = \frac{\tau_f}{2(2\tau_e^2+\tau_f\tau_e)}\left\{1 \pm \sqrt{1-\frac{2[2\tau_e^2+\tau_f\tau_e]}{\tau_f^2}}\right\},$$

or $$f_{1,2} \cong \frac{\tau_f}{4\pi R_e C_e(2\tau_e+\tau_f)}\left\{1 \pm \sqrt{1-\frac{2\tau_e}{\tau_f^2}(2\tau_e+\tau_f)}\right\}. \tag{4}$$

If:

a) $\tau_f \gg 2\tau_e$, $f_1 \cong \frac{1}{2\pi R_e C_e}$, which coincides with the results, obtained in [2], and when

b) $f_2 \cong \frac{\tau_f}{4\pi R_e C_e(\tau_f+2\tau_e)}$ and, as $\tau_f \gg \tau_e, C_1 \gg C_e$, $f_2 \cong \frac{1}{4\pi R_e C_e}$.

In the common case, from equations: $Z_{out} \equiv R_{out}$, $|X_{out} \to 0\,|$, $(C_{ox} \to 0,$ $C_B \to 0,\ R_S \to 0,\ \ \gamma_2 \to 0)$
for ω we can obtain:

$$\omega_{op} \cong \frac{2C_1\beta + C_{0X}[2R_e^2C_1^2+\beta]}{C_1 C_{0X}\beta R_{cl}} \quad \text{or} \quad \omega = \left\{\frac{1}{4(R_eC_1-2\tau_e)\tau_e}\right\}. \tag{5}$$

We can present the frequency dependence on the sensor parameters as:

$$f_{|z\to R_e|} \cong \frac{1}{4\pi R_e C_e\sqrt{\frac{C_f}{C_f+C_e}}} \cong \frac{1}{4\pi R_e C_{de}\sqrt{\frac{C_f}{C_f+C_{de}}}}. \tag{6}$$

Conclusions. As it is known [2] that the double layer capacitance decreases significantly with decreasing electrolyte concentration, we have assumed that for low electrolyte concentrations and any certain conditions and frequencies, C_f can be higher than C_{dl} and C , and hence the existence of C_f can shift the frequency band to a lower frequency range, where the impedance of the sensor shows dominantly an active resistive character.

The above mentioned relationship comes also from equation (6).

If we neglect the ferroelectric film capacitance, the value of the frequency corresponding to an active resistance origin [see (4), (6)] coincides with the results obtained in [2]. Thus, by varying the composition and geometry of ferroelectric films (that is C_f), it is possible to control the frequency band and sensitivity of sensor where the impedance of the structure becomes active. Due to the use of the chip technology, portability, simplicity and low costs, in the future, such devices can successfully be implemented in drug and food industry, in medical practices (blood conductivity, capillary electrophoresis).

We predict that the high dielectric permittivity, low dielectric losses, low leakage current, tunable features, good electrical, thermal and mechanical stability and high corrosion-resistant properties of perovskite-oxide thin-films will lead to a decrease in the electrode-electrolyte impedance at certain measuring frequencies resulting in a more precise and accurate measurement of electrolyte conductivity in a wide range of electrolyte concentrations.

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ԷԼԵԿՏՐՈԼԻՏՆԵՐԻ ՀԱՂՈՐԴԱԿԱՆՈՒԹՅԱՆ ՏՎԻՉԻ ՀԱՄԱԺԵՔ ՍԽԵՄԱՆ ԵՎ ԻՄՊԵԴԱՆՍԱՅԻՆ ԲՆՈՒԹԱԳՐԵՐԻ ՕՊՏԻՄԱԼԱՑՈՒՄԸ

Վ.Վ. Բունիաթյան, Ք.Ա. Հուկ, Ա.Ս. Պողոսյան, Մ.Ջ. Շյոենինգ,
Լ.Գ. Ռուստամյան, Հ.Հ. Հովնիկյան

Առաջարկվել է էլեկտրոլիտների հաղորդականության ոչ հպումային չափման՝ Pt-ե սանրաձև էլեկտրոդներով տվիչի նոր միկրոմանրակերտ կառուցվածք: Որպես մետաղական էլեկտրոդները ծածկող մեկուսիչ շերտ առաջին անգամ օգտագործվում են տարբեր բաղադրությամբ, մեծ դիէլեկտրիկ թափանցելիությամբ պերովսկիտ-օքսիդային նանոթաղանթները: Մշակվել է տվիչի համարժեք սխեման, և տեսականորեն հաշվարկվել ու փորձնականորեն հետազոտվել են իմպեդանսային բնութագրերը: Անալիտիկորեն ստացվել և գնահատվել են տվիչի աշխատանքային հաճախությունների միջակայքը և պարամետրերի փոխադարձ կախվածությունները, որտեղ դրսևորվում է նրա ակտիվ դիմադրության վարքը:

Առանցքային բառեր. ոչ հպումային չափում, էլեկտրոլիտի հաղորդականություն, պերովսկիտ - օքսիդային նանոթաղանթ, միկրոշերտային էլեկտրոդ:

ЭКВИВАЛЕНТНАЯ СХЕМА ДАТЧИКА ПРОВОДИМОСТИ ЭЛЕКТРОЛИТОВ И ОПТИМИЗАЦИЯ ИМПЕДАНСНЫХ ХАРАКТЕРИСТИК

В.В. Буниатян, К.А. Хук, А.С. Погосян, М.Дж. Шоенинг,
Л.Г. Рустамян, Г.Г. Овникян

Предложена новая микроминиатюрная структура датчика с гребенчатыми *Pt-ми* микрополосковыми электродами для бесконтактного измерения проводимости электролитов. В качестве диэлектрического слоя, покрывающего металлические (Pt) электроды, впервые использованы перовскит-оксидные нанопленки различного состава с большой диэлектрической проницаемостью. Разработана эквивалентная схема датчика, проведены теоретические расчеты и экспериментально исследованы ее импедансные характеристики. Аналитически получены и оценены рабочий частотный интервал и взаимосвязь параметров датчика, где проявляется его активный резистивный характер.

Ключевые слова: бесконтактный, проводимость электролита, перовскит-оксиднàя нанопленка, микрополосковый электрод.