

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY CHARACTERIZATION OF A SOLID-STATE ELECTRODE WITH POTENTIAL APPLICATION IN Pb^{2+} IONS DETECTION

CARACTERIZACIÓN POR ESPECTROSCOPIA DE IMPEDANCIA ELECTROQUÍMICA DE UN ELECTRODO DE ESTADO SÓLIDO CON POTENCIAL APLICACIÓN EN LA DETECCIÓN DE IONES Pb^{2+}

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In this work, the characterization of a solid-state ion-selective electrode (SS-ISE) by electrochemical impedance spectroscopy (EIS) was performed for potential detection of Pb^{2+} ions. This electrode is based on a PVC-membrane with an aroylthiourea derivative as ionophore. The solid transducer was prepared using an epoxy-graphite-graphene composite. The impedance analysis (from 20 Hz – 1 MHz) allows to describe the electrochemical response of the electrode in terms of the electrical processes in the membrane instead of the circuitual elements related to the charge-transfer process at the transducer/membrane interface. The Pb^{2+} ions concentration was determined with this SS-ISE in aqueous solution by EIS using the electrical resistance of the membrane. The limit of detection reached by this approach was in the concentration range from 10^{-7} – 10^{-6} mol/L, one order of magnitude lower than the obtained by classical potentiometry. This analysis could be applied to the implementation of analytical determinations by EIS using SS-ISE.

En este trabajo se realizó la caracterización de un electrodo selectivo a iones de estado sólido (ESI-ES) por espectroscopía de impedancia electroquímica (EIS) para la detección potencial de iones Pb^{2+} . Este electrodo se basa en una membrana de PVC con un derivado de aroylthiourea como ionóforo. El transductor sólido se preparó con un compuesto epoxi-grafito-grafeno. El análisis de impedancia (20 Hz – 1 MHz), permite describir la respuesta electroquímica del electrodo en términos de los procesos eléctricos en la membrana en lugar de los elementos circuitales relacionados con el proceso de transferencia de carga en la interfaz transductor/membrana. Se determinó la concentración de iones Pb^{2+} con este electrodo en solución acuosa mediante EIS utilizando la resistencia eléctrica de la membrana. El límite de detección alcanzado por este enfoque se encuentra en el rango de concentración de 10^{-7} – 10^{-6} mol/L, un orden de magnitud inferior que el obtenido por potenciometría clásica. Este análisis podría aplicarse en la implementación de determinaciones analíticas mediante EIS con ESI-ES.

PACS: Electrochemical sensors (sensores electroquímicos), 82.47.Rs; Applied electrochemistry (electroquímica aplicada), 82.47.-a; Measurements in electric variables (including voltage, current, resistance, capacitance, inductance, impedance, and admittance, etc.) (Medidas en variables eléctricas [incluyendo voltaje, corriente, resistencia, capacitancia, inductancia, impedancia y admitancia, etc.]), 84.37.+q.

I. INTRODUCTION

Pollution is one of the most serious and important environmental problems for today's society. Heavy metals, as Pb, Cd and Hg, are among the chemical pollutants of water resources, soils and living organisms due to their toxicity and potential to form complex compounds with the organic matter [1]. The main contamination sources of these toxic metals are the release of untreated household and industrial wastewaters from mining, metallurgy, pharmaceuticals, paintings, plastics, organic chemicals, pesticides, and so forth [2]. Heavy metals are persistent in the environment and non-degradable, they can bioaccumulate in the tissues of minor organisms and reach humans and animals causing serious diseases in multiple systems and even death.

Detection and quantification of heavy metals, as well as its control under certain permissible limits in water, soils, air, and food media has become a major priority to several countries and international organizations due to the harmfulness of these elements. This has involved the development of a wide variety of analytical methods based on optic and electronic instrumentations. Spectroscopic techniques have become the most used as standard methods in the multi-element and trace-level determination of heavy metals. Atomic absorption spectrometry, inductively coupled plasma mass spectrometry, X-ray fluorescence and neutron activation analysis have been applied with high sensitivity and low detection limits reaching ppb concentrations [3]. These methods require transportation and treatment of samples, long determination times, specialized trained personnel and high costs.

In parallel, more simple devices have been developed for real-time detection in contaminated areas such as Solid-State Ion-Selective Electrodes (SS-ISEs). These sensors are very appropriate for this purpose due to their robustness, easy fabrication and manipulation, quick responses, small sample volumes and low costs. Hence, their development and application has spread to many areas and currently, there are a large number of selective electrodes for heavy metals cations determination [4,5].

Lead is one of the most used heavy metals in industry. Therefore, the application of selective electrodes for detection of Pb^{2+} ions has been extensively investigated. In recent years, most of the potentiometric sensors developed for this cation use liquid membranes with ion exchange sites [6]. Many ionophores (ligands) have been studied for determination and quantification of Pb^{2+} ion such as crown ethers, calixarenes derivatives, amides, thioamides, 9,10-anthraquinone and thiourea derivatives, among others [7]. In general, under optimized conditions, SS-ISEs to Pb^{2+} ions show low detection limits (down to 10^{-9} mol/L), wide linear dynamic range, long lifetime and suitable selectivity with respect to alkaline, alkaline earth and other heavy metals [7,8].

Since the 90s of the last century, acyl and aroylthiourea derivatives have been used as ionophores for Pb^{2+} and other ions, but there are just a few examples reported [9–12,14].

Di-substituted aroylthioureas were described for detection of Pb^{2+} ions by Lazo-Fraga in 2015 [14]. Despite the satisfactory analytical characteristics of the sensors based on aroylthioureas, there are still some parameters to be improved such as the reproducibility, the stability in the response signal and the optimization of the ion-to-electron transduction process in order to achieve a response with lower detection limits [5]. In this way, the introduction of nanostructured carbon materials, conductive polymers and others, as solid-contact transducer materials, have exhibited an improvement in the performance characteristics of this type of ISEs in several studies [15]. Also, the combination of selective electrodes with other electrochemical techniques as chronoamperometry, dynamic control techniques (e.g. constant-current chronopotentiometry) [16], and electrochemical impedance spectroscopy (EIS) have been conducted to characterize theoretical and experimental response of solid-state electrodes.

EIS is applied to study ion-selective electrodes since the 1980s [17]. This technique allows to describe the interfacial and bulk properties of various selective electrodes based on PVC membranes and other electrochemical sensors in terms of reaction rates, electric double layer capacitances, diffusion impedances, charge transfer resistances and solution resistances. Also, it has been employed for detecting and quantify target species with selective electrodes based on the charge transfer processes that occur at the interface between the solid transducer and the selective membrane at low frequencies ranges [15–19].

In a previous work, different methods have been described to modify with graphene the transducer of a solid-state electrode based on a conductive material composed of epoxy-graphite.

These transducers were studied and characterized by cyclic voltammetry, and for the first time, by using impedance spectroscopy in solids [20].

Now, a potential solid-state Pb^{2+} -ion selective electrode was prepared based on a 3-disubstituted aroylthiourea. This sensor incorporates the obtained graphene-modified transducer with better electrochemical properties according to previous results. The analysis by EIS was carried out to obtain information about the electrochemical response of the ion-selective membrane and the sensor functionality due to the potentialities of this technique regarding potentiometry. An analytical characterization by potentiometry including response time, optimum pH range, lifetime and selectivity in the presence of interfering ions can be found in [14].

II. EXPERIMENTAL

II.1. Reagents

Graphite powder (99.9%, Merck), epoxy resin was prepared with Araldite® M (Ciba-Geigy) and Hardener HY 5162 (Ciba-Geigy), tributylphosphate TBP (Fluka), tetrahydrofuran THF (Merck), poly(vinylchloride) PVC (Aldrich) and $Pb(NO_3)_2$ (Aldrich). All reagents with analytical-reagent grade. Bidistilled water (conductivity $\leq 1.5 \mu S/cm$) was obtained from an Aquatron model A4D apparatus.

The ionophore 1-benzoyl-3,3-diethylthiourea (BDET), used in the PVC based membrane, was synthesized and characterized in the Laboratory of Organic Synthesis at the Faculty of Chemistry, University of Havana. The graphene material was obtained by an electrochemical exfoliation method as described in [21] and subsequently characterized.

II.2. Preparation of all-solid-state Pb^{2+} -ion selective electrodes

Electrodes transducers were constructed according to the procedure reported in previous work [20]. The electrode body is formed by a poly(methacrylate) tube (\varnothing : 8 mm, length: 10 cm), the electric contact was established by an electric wire connected at one end of the tube to a copper sheet (99.9%, Merck) and supported with a PVC ring (i.d.: 8 mm, length: 1 mm) leaving 2 mm from the surface to fill with the conductive composite. The composite material was made by the mixture of the epoxy resin (araldite and hardener), graphite powder and graphene. The mixture was introduced into the poly(methacrylate) tube filling the 2 mm of thickness to the copper sheet. The electrode is dried at 60 °C for 12 h for the cure of the composite. Then the surface was polished with sand paper and alumina (5 μm).

The PVC membrane was deposited on the surface of the electrode body in a 5 mm cavity created in the conductive filler inside the tube during the polish process. The resultant geometric area for the electrodes was 0.50 cm².

The composition of the membrane cocktail was: ionophore BDET (5 wt. %), PVC (33 wt. %) and TBP (62 wt. %). This mixture was dissolved in 3 mL of THF and dropped manually

over the electrode surface in additions of 50 μL at intervals of 10 min, to assure the evaporation of the solvent until the entire cavity was cover. After 24 h, the electrodes were activated in a solution of $\text{Pb}(\text{NO}_3)_2$ (10 – 2 mol/L) during 48 h.

II.3. Apparatus and measurement

Electrochemical impedance measurements (EIS) were carried out using the solid electrodes with and without sensing membrane. A two-electrode system was used: Pt as a counter electrode and the constructed electrodes as working electrodes. Volumes of 25 μL of standard solutions of $\text{Pb}(\text{NO}_3)_2$ (10^{-4} – 1 mol/L) were added on 25 mL of bidistilled water. The electric impedance measurements were performed in Keysight technologies E4990A Impedance Analyzer, in a frequency range between 20 Hz to 1 MHz, with a 250 mV sinusoidal perturbation and zero bias potential was applied. This relatively high amplitude guarantees an optimal signal/noise ratio and a linear regime. Zview software was used for the impedance data analysis. The Kramers-Kronig verification was successful in the range 60 Hz to 1 MHz.

Potentiometric measurements were performed using a Crison Basic20 pH-meter with a Ag/AgCl reference electrode (Thermo model Orion 900200), saturated with an AgCl reference solution of 0.1 mol/L; the outer compartment uses a 10% KNO_3 reference solution. Calibrations with Pb^{2+} ions were made by the IUPAC recommendations [22]. All experiments were performed at room temperature (laboratory temperature of 25.0 ± 0.5 °C).

III. RESULTS AND DISCUSSION

III.1. Electrochemical impedance measurements

The EIS study carried out in distilled water ($c(\text{Pb}^{2+}) = 0$ mol/L) is presented at the Nyquist plot in Fig. 1. The measurements were carried out using the electrodes with the ion-selective membrane (e.g. **E1M**) and without membrane (e.g. **E1**). The Nyquist plot is the representation of the imaginary component (Z'') versus the real component (Z') of the complex impedance ($Z^* = Z' + jZ''$). For the electrode **E1M**, it can be observed one depressed and slightly deform arc, which suggest the overlapping of two signals: one principal arc at lower frequencies (LF) and a second arc, overlapped with the principal one, at higher frequencies (HF). In the inset of Fig. 1, corresponding to the electrode **E1**, only one arc can be appreciated.

It is well known that in the Nyquist diagram an arc represents a process, whose electrical nature is simultaneously resistive (R, charge conduction mechanism) and capacitive (C, polarization or charges separation mechanism), with an associated time constant ($\tau = RC$). Hence, the impedance response of **E1M** has the contribution of two mechanisms with different time constants.

The existence of mechanisms with different time constants can be better observed from the representation of the imaginary part of the Complex Modulus with frequency (M''):

$$M^* = M' + jM'' = (j2\pi f C_0) Z^* \quad (1)$$

being C_0 the geometric capacitance.

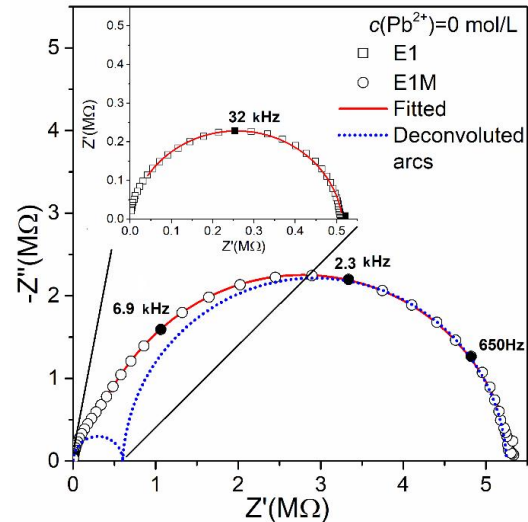


Figure 1. Nyquist plots for the electrodes **E1** (inset) and **E1M** in aqueous solution. Frequency range: 20 Hz – 1 MHz.

In this plot, the frequency (f) at which appears the maximum of M'' is related to the response time of the mechanism according to $\tau = 1/2\pi f$. The plot of M'' vs $\log(f)$ for the studied electrodes in distilled water is presented in Fig. 2. It can be observed the difference in the impedance response between the electrodes: only one time constant for **E1** (without membrane) and two time constants for **E1M** (with membrane) in the entire frequency range studied.

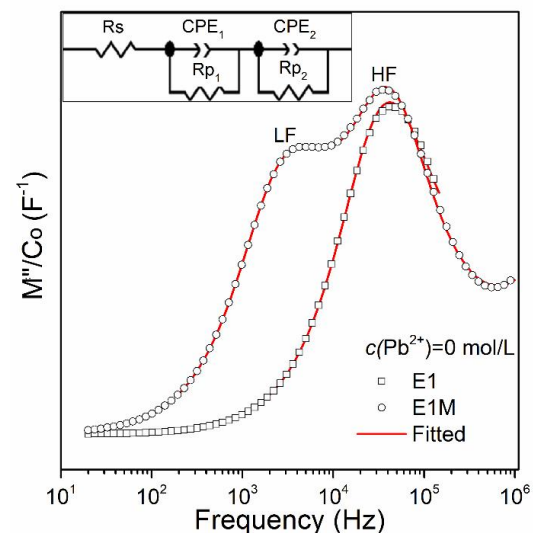


Figure 2. Modulus plots for the electrodes **E1** and **E1M** in aqueous solution. (Inset: electrical equivalent circuit proposed for the electrode **E1M** by EIS).

The HF mechanism is present in both electrodes, **E1** and **E1M**, around the same frequency value (see Fig. 2). Hence, this response could be related to various combined contributions: 1-the resistance and capacitance of the electrode transducer, 2- the solution resistance and 3- the geometric capacitance of the electrochemical cell configuration.

This statement can be supported due to the drastic shift of the HF response to higher frequencies with the increasing of

Pb²⁺ ions concentration in the medium (See inset in Fig. 3). According to $\tau=1/2\pi f=RC$, a decrease in R due to an increase in the Pb²⁺ ions concentration in the solution would lead to a decrease in the time constant and therefore to an increase in f . On the other hand, the LF mechanism slightly affected by the rise of Pb²⁺ ions concentration (see inset in Fig. 4), is only present in the **E1M** plot, so it must be related to the response of the bulk membrane or the electrode/membrane interface.

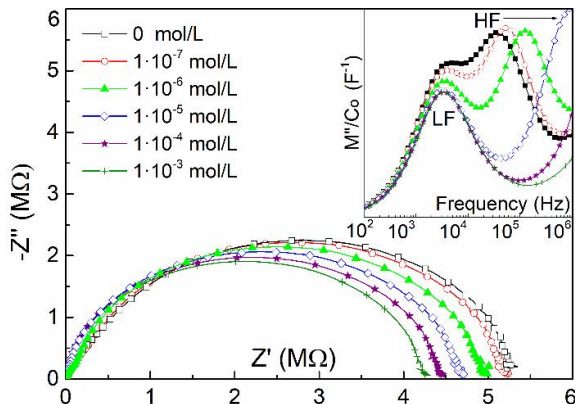


Figure 3. Nyquist plot for the electrode **E1M** for different Pb²⁺ ions concentrations (Inset: Modulus vs frequency plots).

For SS-ISEs based on PVC membranes, such as the electrode **E1M** presented in this work, the ion-to-electron transduction mechanism is the result of an electrical double layer formation at the membrane/transducer interface [5]. This interface can be schematically described as an asymmetric electrical capacitor. From one side, the charges are in the form of ions (cations and anions in the selective membrane) and on the other side the charges are electrical (electrons or holes in the solid transducer material). For ion-selective electrodes, the processes that take place in this membrane/transducer interface are known as charge transfer processes and occur through very slow mechanisms generally accompanied by a slow Warburg diffusion process (observed around 10⁻¹–10⁻³ Hz in a Bode type plot) [23]. The Warburg contribution, observed as a straight line in the low-frequency region of the Nyquist plot, is not present in our measurements due to the use of a relatively high frequency range. Hence, taking into account the slow nature of interfacial mechanisms, the non-observation of Warburg diffusion processes and the fact that the LF maximum in **E1M** is observed above 103 Hz, the chance is that the LF contribution is related to the response of the bulk membrane rather than the electrode/membrane interface. Interesting, in the Nyquist plot of Fig. 3 it can be observed a complete low frequency arc, whose diameter changes with increasing concentration, accompanied by an incomplete arc (shoulder) at higher frequencies. Hence, the diameter of the low frequency arc could be related to the resistive response of the membrane and its change with Pb²⁺ ions concentration could be used as a sensing mechanism.

Based on the above discussion, the equivalent circuit model in the inset of Fig. 2 is proposed for the electrochemical impedance response of the electrodes coated with a Pb²⁺-ion selective membrane (e.g. **E1M**). In this circuit, R and CPE are resistive and capacitive elements, being the latest, an empirical constant phase element that accounts for non-ideal

resistive or capacitive behavior. The CPE impedance follows the relationship:

$$Z_{CPE} = T^{-1}(j2\pi f)^{-\alpha} \quad (2)$$

being T (expressed in $F \cdot s^{\alpha-1}$) and α ($0 < \alpha < 1$) fitting parameters [24]. The first branch of the circuit (R_s , CPE_1 and Rp_1) represents the combined contributions of the solution resistance (R_s) coupled with the elements associated to the solid transducer: electrical resistance (Rp_1) and geometrical capacitance (CPE_1). The cell configuration can also contribute to this branch. While, the second branch (CPE_2 and Rp_2) represents the polarization (CPE_2) and bulk resistance (Rp_2) of the selective membrane.

The solid red lines in Fig. 1 and 2 are the fitted curves obtained by using the proposed equivalent circuit. Only the first branch was used to fit the electrical response of the electrode **E1**. As can be observed, a good agreement between the proposed model and the experimental measurements were reached both in the Nyquist and Modulus representations. Similar results were obtained for the different electrode units. In Table ?? appears summarized for **E1M** the fitting parameters, the equivalent (or effective) capacitance of a parallel R_p —CPE configuration and the frequency ($f = 1/2\pi\tau$) as a function of $c(\text{Pb}^{2+})$. Since that a semicircle is clear observable in the complex impedance plane and that it has been demonstrated that for coatings and films the effective capacitance, related to CPE element, is in agreement with Hsu and Mansfeld [25] instead of Brug [26] formula, the former is used in the present work [24–27]:

$$C_{eq} = R_{p2}^{-1}(R_{p2}T_2)^{1/\alpha} \quad (3)$$

Only the parameters of the second branch of the equivalent circuit are shown in Table ?? because they represent the physical-chemical response of the Pb²⁺-ion selective membrane. The difference in the values of the fitting parameters obtained for the different constructed units are a direct consequence of the inhomogeneous thickness of the membrane related to the manual electrode preparation.

Table 1. Fitting parameters for **E1M** electrode as a function of $c(\text{Pb}^{2+})$

$c(\text{Pb}^{2+})$ (mol/L)	Parameters			
	R_{p2} (M ω /cm ²)	CPE ₂		$C_{eq} \cdot 10^{-11}$ (F/cm ²)
		$T_2 \cdot 10^{-11}$ (F \cdot s ^{$\alpha-1$})	α_2	
0	13.2 ± 0.1	1.70 ± 0.01	0.95 ± 0.01	2.05 ± 0.01
5·10 ⁻⁸	13.1 ± 0.1	1.70 ± 0.01	0.95 ± 0.01	2.06 ± 0.01
1·10 ⁻⁷	13.0 ± 0.1	1.69 ± 0.02	0.95 ± 0.01	2.07 ± 0.01
1·10 ⁻⁶	12.6 ± 0.2	1.73 ± 0.04	0.95 ± 0.01	2.09 ± 0.01
1·10 ⁻⁵	12.2 ± 0.1	1.69 ± 0.03	0.95 ± 0.01	2.12 ± 0.01
1·10 ⁻⁴	11.8 ± 0.2	1.60 ± 0.04	0.96 ± 0.01	2.12 ± 0.01

The values of the equivalent capacitances ($C_{eq} \sim 10^{-11}$ F/cm²) are far below than the reported for typical interfacial charge-transfer processes ($\sim 10^{-8} - 10^{-6}$ F/cm²) [28]. Considering that, the dielectric constant values for plasticized PVC-based membranes are in the range of 20-50 [29], we can make a rough estimation of the thickness (h) for the planar capacitor formed at the sensing membrane through the equation:

$$C = \epsilon_r \epsilon_0 A / h \quad (4)$$

being ϵ_r : the dielectric constant, ϵ_0 : the vacuum dielectric constant and A : the geometric area of the electrode.

The obtained thickness ranging from 0.45 – 0.9 mm is in correspondence with the thickness of the membrane and well above the nanometric length expected for the depletion zone in the electrode-membrane interface [28]. In fact, the values of Rp_2 and Ceq_2 obtained are in agreement with previous reports for plasticized PVC-based ion-selective membranes [30].

The above discussion is a confirmation that we are actually measuring, in the selected frequency range, the resistive-capacitive response of the bulk membrane instead of the double-layer interface response. Hence, the resistance Rp_2 and the capacitance Ceq_2 are the electrical equivalent parameters that characterize the physical-chemical processes that take place inside the membrane (e.g. formation of Pb_{2+} -aroylthiourea complex species due to the coupling of Pb_{2+} ions to the active sites in the membrane and charges redistribution, etc).

In Fig. 4 is presented Rp_2 as a function of the logarithm of Pb_{2+} ions concentration for E1M and an empirical relationship was found between these parameters and the classical potentiometric calibration plot for ion selective electrodes [22]. The error bars accounts for the deviation resulting from the measurement of different electrode units. Two well-differentiated zones can be observed. In the first zone, at lower values of $\log c(Pb_{2+})$, Rp_2 are practically constant, suggesting that in this range, the electrical processes in the membrane are insensitive to the changes of Pb_{2+} ions concentration in the solution. In the second zone, at higher values of the $\log c(Pb_{2+})$, Rp_2 decreases linearly as $c(Pb_{2+})$ increases. As in the case of potentiometric calibration, the intersection of the straight lines of regions with different behaviors of Rp_2 suggest that a limit of detection for Pb_{2+} ions can be estimated by EIS.

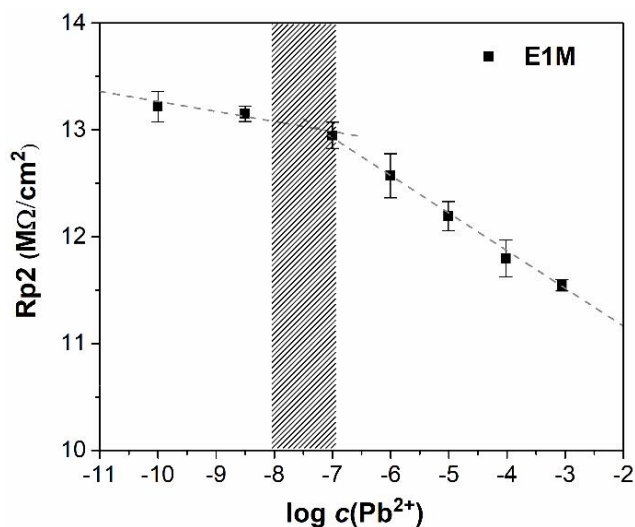


Figure 4. Dependence of Rp_2 with the $\log c(Pb_{2+})$ for different electrode units.

In the proposed circuit (see Fig. 2), Rp_2 is the resistance associated with the processes that take place inside the selective membrane. The decrease of this parameter with the increment of the ionic concentration can be related

to the increase in the number of charge carriers in the membrane, associated with the formation of the complex specie Pb_{2+} -aroylthiourea between the ionophore molecules confined in the membrane and the ions that are incorporated from the solution.

The potentiometric calibration of the constructed electrode shows a typical Nernstian response (See Fig. 5). The sensitivity values are close to the theoretical sensitivity of 29.58 mV/dec for a divalent cation at 298.15 K. The limit of detection (LD) is in the order of 10^{-6} mol/L and was calculated as the intersection of the Nernstian and not-Nernstian slope lines [22]. It can be observed that, the limit of detection reached by EIS is almost two orders of magnitude lower (between 10^{-8} – 10^{-7} mol/L) than the obtained by the corresponding potentiometric calibration (Fig. 5) for the same electrode (between 10^{-6} – 10^{-5} mol/L). The potentiometric calibration was used as proof of the electrodes correct functionality to perform the impedance spectroscopy experiments.

This better sensibility of the EIS experiment respect to potentiometric technique has been previously reported in [19]. The improvement in the limit of detection could be related to the fact that impedance spectroscopy takes into account the contribution of all-mobile charges and not only of those with long range movement as the potentiometry does.

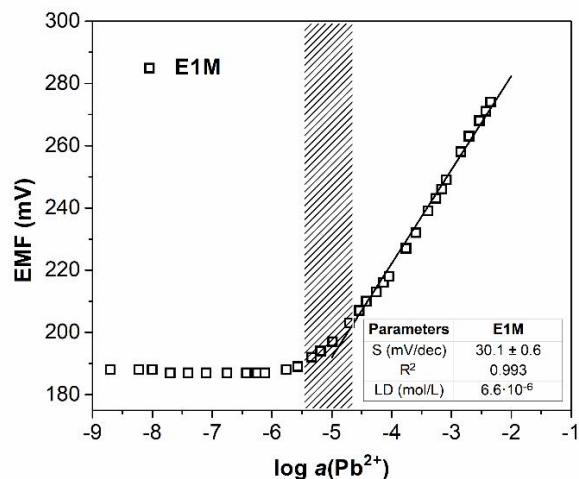


Figure 5. Potentiometric calibration curves for the constructed electrode.

It should be noted that contrasting with previous reports [19, 31–33], in which the electrochemical response used to determine the analyte concentration is that related to processes that take place only in the membrane/transducer interface (i.e. charge transfer resistance and double layer capacitance), with this work we are proposing the use of the electrochemical response of the bulk membrane. The use of equivalent elements, such as the resistance (Rp_2), associated with the membrane processes for quantify the concentration of Pb_{2+} ions by EIS, constitutes a novel approach and, to the best of our knowledge, has not been reported previously for this kind of electrochemical sensors. Since, electrochemical processes that take place in the membrane present shorter relaxation times than the charge transfer processes at the transducer/membrane interface, faster determinations can be made by using electrochemical impedance spectroscopy in

the studied frequency range with ISEs based on similar PVC membranes or other metal cations.

IV. CONCLUSIONS

Potential Pb^{2+} ion-selective electrodes can be analyzed using EIS at high frequencies by the characterization of the electrochemical response of the selective membrane. Pb^{2+} ions concentrations were detected in one order of magnitude lower than that obtained by classical potentiometry. With this approach, faster analytical studies can be conducted by the combination of EIS and Pb^{2+} -ISEs using electrical response parameters related to the selective membrane instead of the widespread transducer/membrane interface charge transference processes, which involve large determination times. The studies confirm EIS as a useful and effective tool for the characterization and possible application of electrochemical sensors.

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REFERENCES

- [1] B. Bansod, T. Kumar, R. Thakur, S. Rana, I. Singh, *Biosens. Bioelectron.* **94**, 443 (2017).
- [2] K.H. Vardhan, P.S. Kumar, R.C. Panda, *J. Mol. Liq.* **290**, 111197 (2019).
- [3] R.K. Soodan, Y.B. Pakade, A. Nagpal, J.K. Katnoria, *Talanta* **125**, 405 (2014).
- [4] A. Michalska, *Electroanalysis* **24**, 1253 (2012).
- [5] J. Hu, A. Stein, P. Bühlmann, *TrAC Trends Anal. Chem.* **76**, 102 (2016).
- [6] V.K. Gupta, M.R. Ganjali, P. Norouzi, H. Khani, A. Nayak, S. Agarwal, *Crit. Rev. Anal. Chem.* **41**, 282 (2011).
- [7] M. Guziński, G. Lisak, J. Kupis, A. Jasiński, M. Bocheńska, *Anal. Chim. Acta* **791**, 1 (2013).
- [8] A. Jasiński, M. Guziński, G. Lisak, J. Bobacka, M. Bocheńska, *Sens. Actuators, B* **218**, 25 (2015).
- [9] L. Perez Marín, Y. Martínez Rubi, O. Arias De Fuentes, O. Fonseca Ortíz, E. Otazo Sánchez, O.L. Estévez, Y. Fajardo, J. Alonso Chamorro, J. Casabó, *Afinidad* **55**, 130 (1998).
- [10] L. Perez-Marín, G. Ortíz, P. Ávila, E. Otazo, H. López, J. Alonso, O. Estévez, *Afinidad* **56**, 397 (1999).
- [11] D. Wilson, M. de los Ángeles Arada, S. Alegret, M. del Valle, *J. Hazard. Mater.* **181**, 140 (2010).
- [12] S. Firouzabadi, I. Razavipanah, R. Zhiani, M. Ghanei-Motlagh, M.R. Salavati, *Monatsh Chem.* **144**, 113 (2013).
- [13] K.S. Ying, L.Y. Heng, N.I. Hassan, S.A. Hasbullah, in *The 2017 UKM FST Postgraduate Colloquium*, edited by AIP Publishing LLC (AIP Conference Proceedings, American Institute of Physics, 2018).
- [14] A.R. Lazo-Fraga, A. Vasconcelos-Pacheco, A. Díaz-García, M. Bustamante-Sánchez, O. Estévez-Hernández, *Rev. Cubana Quim.* **27**, 262 (2015).
- [15] Y. Shao, Y. Ying, J. Ping, *Chem. Soc. Rev.* **49**, 4405 (2020).
- [16] T. Han, U. Mattinen, J. Bobacka, *ACS Sens.* **4**, 900 (2019).
- [17] B. Pejic, R. De Marco, *Electrochim. Acta* **51**, 6217 (2006).
- [18] T. Yin, D. Pan, W. Qin, *J. Solid State Electrochem.* **16**, 499 (2012).
- [19] Z.A.Y. Jahromi, M. Mazloum-Ardakani, H. Reza, *Anal. Bioanal. Electrochem.* **9**, 562 (2017).
- [20] M.V. Portales, A.R.L. Fraga, A.M.D. García, O. García-Zaldívar, A.P. Barranco, M.A.A. Frutis, *J. Solid State Electrochem.* **22**, 471 (2018).
- [21] C.Y. Su, A.Y. Lu, Y. Xu, F.R. Chen, A.N. Khlobystov, L.J. Li, *ACS Nano* **5**, 2332 (2011).
- [22] R.P. Buck, E. Lindner, *Pure Appl. Chem.* **66**, 2527 (1994).
- [23] P. Tamiasso Martinhon, J. Carreño, C.R. Sousa, O.E. Barcia, O.R. Mattos, *Electrochim. Acta* **51**, 3022 (2006).
- [24] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, *Electrochim. Acta* **55**, 6218 (2010).
- [25] C.H. Hsu, F. Mansfeld, *Corrosion* **57**, 747 (2001).
- [26] G.J. Brug, A.L.G. Van Den Eeden, M. Sluyters-Rehbach, J.H. Sluyters, *J. Electroanal. Chem.* **176**, 275 (1984).
- [27] A. Lasia, *Electrochemical impedance spectroscopy and its applications*, 1st Ed. (Springer, New York, 2014), pp. 176-183.
- [28] T. Ghosh, H.J. Chung, J. Rieger, *Sensors* **17**, 2536 (2017).
- [29] R.D. Armstrong, G. Horvai, *Electrochim. Acta* **35**, 1 (1990).
- [30] J. Bobacka, *Anal. Chem.* **71**, 4932 (1999).
- [31] A. Rouis, M. Echabaane, N. Sakly, I. Dumazet-Bonnamour, H.B. Ouada, *Synth. Met.* **164**, 78 (2013).
- [32] S.G.R. Avuthu, B.B. Narakathu, A. Eshkeiti, S. Emamian, B.J. Bazuin, M. Joyce, M.Z. Atashbar, in *IEEE SENSORS Conference*, edited by IEEE (Institute of Electrical and Electronics Engineers, Valencia, 2014).
- [33] S. Liu, M. Kang, F. Yan, D. Peng, Y. Yang, L. He, M. Wang, S. Fang, Z. Zhang, *Electrochim. Acta* **160**, 64 (2015).

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