

Role of anion size in the electrochemical performance of a Poly(thionine) redox conductive polymer using electrochemical impedance spectroscopy

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ABSTRACT

Thionine is one of the most studied monomers for the synthesis of conductive polymer films by electropolymerization. Poly(thionine) film has interesting properties that can be applied in different areas, such as energy storage, photoelectronic devices, and electrochemical sensors. During electropolymerization, the anion in the solution plays a crucial role in polymer synthesis, which can result in changes in the (electro)chemical behavior. Thus, the present study evaluated the influence of the supporting electrolyte anion size used during the electropolymerization of poly(thionine) on the electrochemical behavior. Poly(thionine)Cl, poly(thionine)NO₃, poly(thionine)H₂PO₄ and poly(thionine)HSO₄ films were electrosynthesized using HCl, HNO₃, H₃PO₄, and H₂SO₄ inorganic acids, respectively. Electrochemical impedance spectroscopy (EIS) shows a linear relationship between anion size and interfacial physicochemistry phenomenon due to the charge transfer resistance of the polymer and capacitance of the electrical double layer. This behavior originates from both a decrease in the mobility of the anions with increasing anion size and a decrease in the porosity. This result can help design strategies for building polymeric thionine films for (bio)sensors or charge storage applications.

1. Introduction

Since their accidental discovery in the early 1970s, conducting polymers have revolutionized many areas of science due to their interesting properties [1,2]. Devices based on conductive polymers offer advantages due to the possibility of building flexible and wearable structures [3,4]. These properties are essential to meet the current demands of electronic devices [5]. Hence, conductive polymers have been intensively investigated due to their wide ranging and promising application in electronic devices, electrochromic displays, bio-electrochemistry, photoelectrochemistry, (bio)sensors, organic electrochemistry and energy storage [1,2,4,6–9].

There are different routes to obtain conductive polymer films, and the most common is radical polymerization in solution or the vapor phase [10–12]. Electropolymerization stands out for enabling an effective way to form thin conducting polymeric films with the possibility of modulating their properties [13–15]. This modulation is easily controlled through parameters such as the applied potential range, which can controllably generate radical and/or radical dications in solution, depending on the type of chemical bond desired in the polymer.

Additionally, by varying the number of applied potential cycles, it is possible to control the amount of material synthesized. Thus, features such as electronic conductivity and charge storage capacity can be increased, expanded or decreased depending on the application of the conductive polymer [16,17]. In addition to the applied electrochemical parameters, the composition of the electropolymerization solution is also a key factor in forming and obtaining conductive polymer films. In this sense, the supporting electrolyte plays a crucial role since it performs the counter balance for charge during the formation of the polymer chain and strongly influences its structure and properties [17].

Phenothiazine monomers have received considerable attention for study in the field of electropolymerization due to their huge variety of applications in the construction of chemical and biochemical sensors, electrocatalysis and energy conversion devices [18,19]. Thionine monomers are one of the most popular representatives of the phenothiazine group. Cyclic voltammetry electropolymerization of thionine by N-aromatic coupling from its primary amino groups is satisfactorily related to the growth of its polymeric chain for deposition on conductive substrates. Whether poly(thionine) (polyTH) is obtained in accordance with its electroactive characteristics is determined by the maintenance

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of its delocalized π -electronic system and favoring charge accumulation by polymeric extension [20,21]. Therefore, interruptions arising from defects, as well as the generation of unconjugated oligomers or copolymers, have a significant impact on the electrochemical response of the polymer generated during its synthesis.

The electronic conductivity of conducting polymeric films is directly linked to the movement of counterions within the polymeric film [22, 23]. Anions play a central role during the formation of conducting polymeric films in the electropolymerization technique via the application of an anodic potential. The anions present in the solution act to counterbalance the charge. Depending on the anion used during anodic electropolymerization, there is a change in electrochemical and morphological characteristics, such as an increase or decrease in the porosity of the film, as well as a direct influence on the electronic transport ability.

The use of electrochemical impedance spectroscopy (EIS) for the characterization of conducting polymers has intensified in recent decades [24,25]. EIS is a powerful electrochemical tool for investigating charge transfer and charge transport processes [26,27]. In addition, it has advantages over traditional electrochemical techniques in that only a small sinewave is applied, which keeps the system close to equilibrium. Thus, the present work aims to present a study of the influence of different inorganic acids on the formation and electrochemical performance of poly(thionine) films, as well as a systematic analysis based on electrochemical impedance spectroscopy. The spectra obtained by EIS were analyzed by an equivalent circuit model, and parameters such as charge transfer resistance and electrochemical capacitance were compared. Additionally, an investigation of the influence of the applied potential on the behavior of the poly(thionine) film was carried out to further contribute to existing investigations of this interesting class of conducting polymers.

2. Experimental

Reagents: thionine acetate salt, hydrochloric acid (36.5–38%), sulfuric acid (95.0–98%), nitric acid (70%), phosphoric acid (85%), and potassium chloride. All reagents used are from Sigma-Aldrich. The solutions were prepared using deionized water. All measurements were performed in a conventional electrochemical cell with three electrodes: a saturated calomel electrode (SCE) as the reference electrode; a platinum wire as the counter electrode and a fluoride-doped tin oxide (FTO) electrode coated with different poly(thionine) films as the working electrode (geometrical area of 1.0 cm²). All electrochemical measurements were performed with Palsens3 interfaced PSTrace 5.8 software.

Before the electropolymerization, the FTO electrodes were cleaned by sonication in acetone solution for 10 min. Afterward, the electrodes were washed abundantly in distilled water and dried at room temperature. The poly(thionine) film was prepared on the FTO surface by potential cycling between -0.30 and $+1.60$ V (vs. SCE) for 30-cycle scans at a scan rate of 20 mV s⁻¹ in a deaerated solution (N₂) containing 10 mmol L⁻¹ thionine acetate in 0.10 mol L⁻¹ HCl, HNO₃, H₂SO₄, or H₃PO₄ medium. After electropolymerization, the modified electrodes were washed abundantly with distilled water and dried in room temperature. All pH values for the solutions were measured with a Metrohm 781 pH meter.

The EIS measurements were performed using a sine wave with an amplitude of 10 mV applied in a frequency range of 50 kHz to 0.1 Hz with 10 step/dec in deaerated solution (N₂) 0.50 mol L⁻¹ KCl pH 2.0 (the pH value was achieved using conc. HCl). All spectra were recorded at 25 °C in a N₂ atmosphere. The mathematical adjustments for the equivalent circuit models were performed using ZPlot 2.4 software.

3. Results and discussion

3.1. Poly(thionine) film electropolymerization

The electropolymerization technique is widely used in polymer electrosynthesis, as it enables great control over the coating of the surface of conductive substrates by polymer films [11,20,28]. To evaluate the influence of the anion on the formation of a conductive polymer film based on a thionine monomer (TH) on an FTO electrode, HCl, HNO₃, H₂SO₄ and H₃PO₄ acids were used as supporting electrolytes at a concentration of 0.10 mol L⁻¹ to obtain Cl⁻, NO₃⁻, HSO₄⁻ and H₂PO₄⁻ anions in solution. It is important to highlight that although H₂SO₄ and H₃PO₄ are polyprotic acids, they formed the monovalent species (HSO₄⁻ and H₂PO₄⁻) as the predominant chemical species in solution because the pH of the electropolymerization solution was kept between ~ 1.0 and 1.6 . Thus, it is possible to comparatively analyze the influence of the size of anions (hydrated radius - d_{hyd}) on the formation of the poly(thionine) film.

Fig. 1 shows the cyclic voltammograms for the electropolymerization of films with different inorganic acids. All films show similar behavior, where during the first scan, a first redox oxidation peak ($E_{\text{ap-thio}}$) for the thionine monomer in solution is observed [20,21,29]. Additionally, during the first cycle, forward with the anodic scan, two other peaks are verified and assigned for irreversible oxidation processes related to the formation of the radical cation (TH^{•+}) and radical dication (TH^{2•+}) [30]. The formation of radical species initiates the formation of the conductive polymeric film from C–N bonds (head-to-tail bonding) [19]. The poly(thionine) formation mechanism has a great influence on anions in solution, playing a role both in the stabilization and mobility of the radical and radical dication formed, directly influencing the structural formation of the polymer chain as well as its electrochemical characteristics [18,31]. The values for the radical cation formation potentials are similar for poly(thionine)Cl (1.09 V) and poly(thionine)NO₃ (1.10 V), and lower values for poly(thionine)HSO₄ (1.04 V) and poly(thionine)H₂PO₄ (1.02 V) are obtained, showing better stabilization of radical species by larger anions.

From the other cycling of applied potentials, the Cl⁻, NO₃⁻ and HSO₄⁻ films show an increase in the current magnitude in the region of the formation of radical cations and dications with a subsequent decrease in this current and an overlapping of the peaks. The decrease in current in the region of radical cation formation is typical behavior of the phenothiazine group and occurs because of the decrease in the exposure of the TH monomer to the surface area of the FTO electrode due to its coating by the poly(thionine) polymer [18,32].

The formation of poly(thionine) polymeric films is indicated by an increase in current, which is related to the polymeric redox pair $E_{\text{ap-poly(thio)}}$ and $E_{\text{cp-poly(thio)}}$ during successive potential cycling (eq. 4) [11,20,29]. For Cl⁻ and NO₃⁻, the increase is accompanied by a negligible shift in the peak potential values. The HSO₄⁻ and H₂PO₄⁻ films show more complex behavior during electropolymerization. For the poly(thionine)HSO₄ film, the current is increased until the 11th cycle, where a decrease in current magnitude occurs as well as a significant shift in peak potentials. For the poly(thionine)H₂PO₄ film, immediately after the first applied potential cycle, the current is decreased. Afterward, a displacement and an increase in the current up to the 10th cycle is observed (with reference to the anodic current) followed by a new decrease in the current values. The behavior observed for poly(thionine)HSO₄ and poly(thionine)H₂PO₄ films is indicative of system saturation and increased difficulty in directing the reaction, requiring a greater overpotential [33,34]. The explanation for this behavior is based on the size of the anions H₂PO₄⁻ and HSO₄⁻. Recent studies indicate that larger anions have a lower mobility and are commonly trapped in the polymer matrix, reducing the electronic transport capacity of the polymer [22,23].

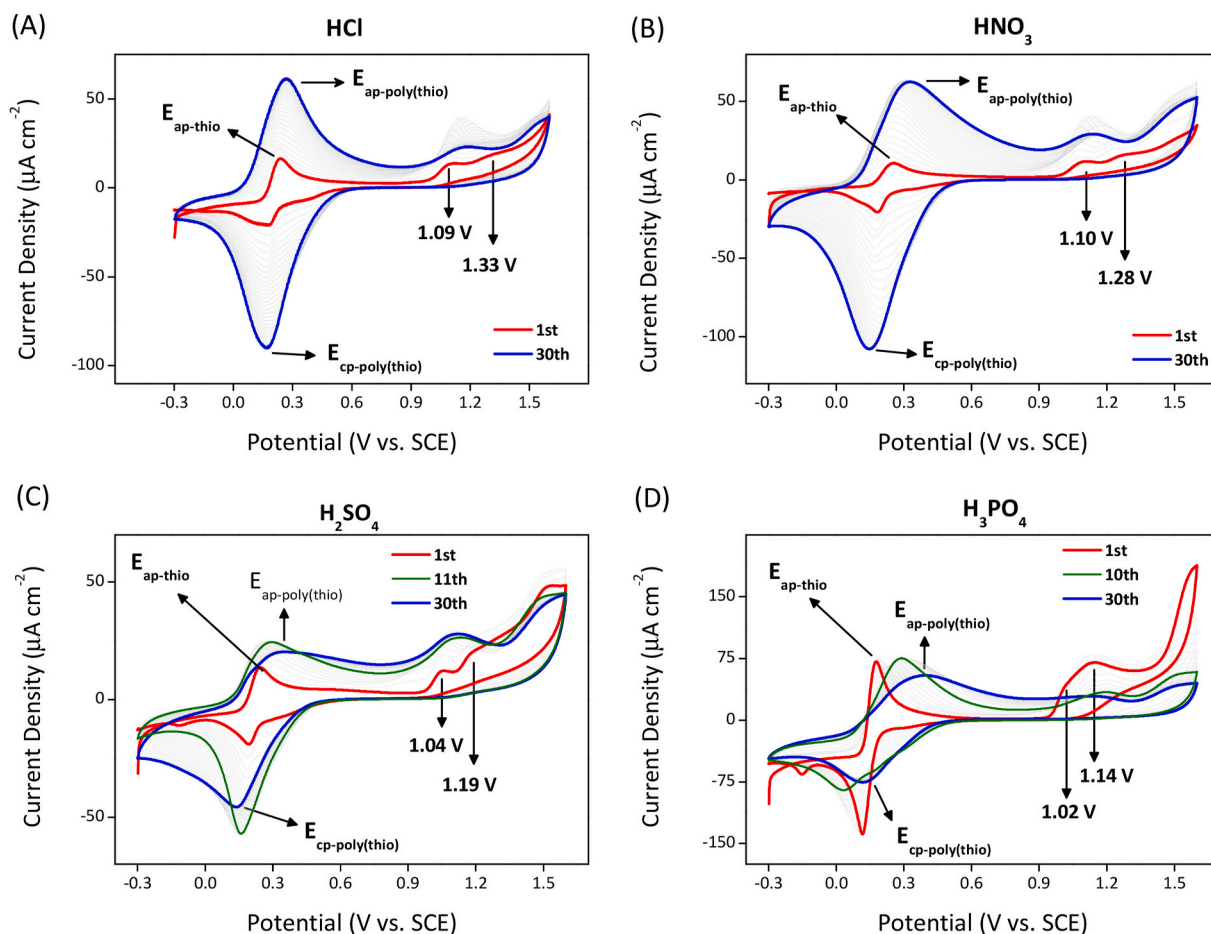


Fig. 1. Cyclic voltammogram for poly(thionine) film electropolymerization with 30 cycles at a scan rate of 10 mV s^{-1} in 1.0 mmol L^{-1} of the thionine monomer in 0.10 mol L^{-1} of HCl (A), HNO_3 (B), H_2SO_4 (C) and H_3PO_4 (D) under a N_2 atmosphere at 25°C .

3.2. Electrochemical impedance spectroscopy evaluation

3.2.1. Equivalent circuit model

The data obtained by EIS for the different films formed with different counteranions were analyzed using equivalent circuit models represented by Fig. 2. The same equivalent circuit model was found to be satisfactory for performing the mathematical adjustments for the spectra

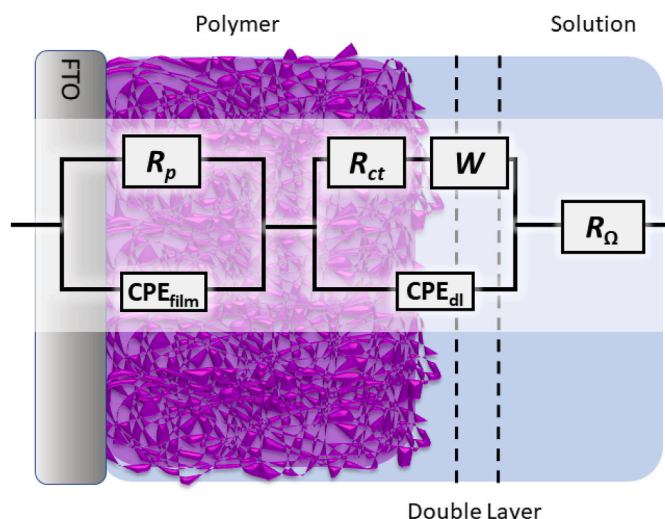


Fig. 2. Equivalent circuit model used for poly(thionine) fitting.

obtained at different applied potentials (-0.40 to $+0.60 \text{ V vs. SCE}$) for the four poly(thionine) films built with different inorganic acids.

The equivalent circuit model proposed for poly(thionine) films (Fig. 2) is similar to that presented in previous studies for conducting polymers containing redox sites [18,35]. For the present model, the capacitive elements were replaced by constant phase elements (CPEs). CPE is commonly used in electrochemical systems because it represents nonideal capacitive elements, such as the electrical double layer for modified electrodes [36,37]. The nonideality of the element is visualized through the dispersion parameter α . If $\alpha = 1$, the CPE is an ideal capacitor. As the value of α moves away from 1, one moves away from ideality. Thus, for $\alpha = 0.5$, CPE takes the form of a Warburg element, and where $\alpha = 0$, CPE takes the form of a resistance element [36,38].

Thus, the ECM for poly(thionine) films has a solution resistance ($R_\Omega = 14.0 \Omega$) in series with two parallels. The first parallel contemplates the high frequency region, presenting a charge transfer resistance related to the resistance of the protons within the polymeric film (R_p) and the CPE related to the pseudo-redox-capacitance of the poly(thionine) film (CPE_{film}) [39]. The second parallel, for the low frequency region, presents a charge transfer resistance for the polymeric film redox reaction (R_{ct}) in series with a Warburg element (W) related to the counterion mass transport [38]. In parallel to the R_{ct} - W set, there exists a capacitance of the electrical double layer (CPE_{dl}).

3.2.2. Influence of the counter-anion on film formation

The electrochemical performance of films constructed with different inorganic acids was evaluated in 0.50 mol L^{-1} ($\text{pH } 2.0$) KCl solution by EIS. For analysis, an applied potential of $+0.20 \text{ V}$ was used as a reference

point for the comparative investigation, corresponding to the formal potential (see Fig. 6). The formal potential is the potential at which the formed polymers present a higher conductivity (lower resistance) and higher capacitance for the film.

Fig. 3 presents the spectra for poly(thionine) films formed with different counter-anions. The Nyquist plot (Fig. 3A) shows a small incomplete semicircle in the high frequency region due to the relaxation time of the interfacial phenomenon being much lower than 1 [40]. For the medium-low frequency region, semi-circumference followed by linearity related to the mass transport phenomenon is verified. There is a clear change in the behavior of the films due to the change in the magnitude of the capacitive arc of the spectrum, resulting in an increase in the system impedance in the sequence of $\text{Cl}^- < \text{NO}_3^- < \text{H}_2\text{PO}_4^- < \text{HSO}_4^-$.

Fig. 3B verifies that the anion used in the construction of the film influences the magnitude of the phase angle values, as well as the peak frequency values (f_1 and f_2). As long as the phase angle value is directed toward 90° , the greater the amount of current that is directed to the capacitive elements of the system, in other words, towards the charge accumulation [41]. Thus, the poly(thionine) HSO_4 film shows greater trends in capacitive behavior (in the f_2 frequency region) than the other films studied. Despite this, the values are relatively low compared to those expected for a pure capacitor ($\sim 90^\circ$) [39,42,43]. The recorded phase angle magnitudes are in agreement with the behavior typically verified for supercapacitors with pseudo capacitance [42].

To further explore the influence of anion size on the electrochemical response of the poly(thionine) film, the resistance and capacitance values for the interfacial elements were evaluated as a function of anion size. They were obtained by mathematical adjustments of the spectra for the equivalent circuit model discussed above.

Fig. 4 shows the behavior of the different interfacial elements versus the hydrated radius of each anion [44]. For the case of NO_3^- , two d_{hyd} values are verified due to its molecular geometry [44]. In this case, for the present work, we chose to use the average value for its two hydrated radii. Analysis of the resistance values for the polymer/FTO interface (R_p) reveals a linear relationship between the resistance of the poly(thionine) film as a function of the hydrated radius of the anion used in the formation of the polymeric film. For the resistance of the polymer/solution interface (R_{ct}), an increase in the resistance with increasing anion radius is also verified. However, this behavior is nonlinear. This increase in film resistance (decrease in conductivity) is expected for conductive polymers dependent on the effect of ion migration during the doping and dedoping process [22].

Similar behavior was verified for PANI films (polyaniline), where the

conductivity is higher for the Cl^- anion than for the SO_4^{2-} anion [22]. As discussed earlier, conducting polymeric films constructed with large anions tend to be immobile and end up becoming “trapped” in the polymeric network during their synthesis, becoming cation-directed [23]. Therefore, the ionic mobility within the polymer is decreased, which leads to a decreased conductivity, and, consequently, increased resistance value.

This argument becomes clearer when comparing the coefficient values obtained for active species (Γ) on the electrode surface (Fig. 4F). The active species coefficient (Γ) was calculated based on the relationship $\Gamma = Q/nFA$, where Q is the charge obtained through the integral of the area of the anodic current values as a function of the scan time with baseline correction (C) (data not shown here), n is the number of electrons involved ($n = 2e^-$), F is Faraday's constant ($96485.3399\text{C mol/e}^-$), and A is the electrode area (1.0 cm^2). The decrease in the number of active species is clearly due to the increase in the hydrated radius of the acid anion due to the occupation of these sites by anions trapped in the polymer matrix. Additionally, the proximity of the Γ values for the Cl^- and NO_3^- anions is remarkable. The use of HCl and HNO_3 acids as electrolytes to obtain poly(thionine) films with high conductivity is equally effective.

Furthermore, the double layer capacitance and the pseudocapacitance of the polymeric film are dependent on the number of active species, resulting in a decrease of the film charge capacity as a function of an increase in the size of the anion (Fig. 4B and D) [45,46].

Finally, conductive polymers can be described by Warburg (W) elements, which is attributed to the diffusion of ions into the polymer matrix (Fig. 4E) [47]. For the poly(thionine) film, a decrease in the diffusion resistance with an increase in the anion dimension was verified. This result agrees with the “size memory effect”, where the polymer porosity is dependent on anion size [48]. Large anions make large pores, which can be accessed by other anions with small sizes but not for anions with large sizes. Thus, the chloride used in this study as a supporting electrolyte in aqueous solution can access the interior of the poly(thionine) HSO_4 with less difficulty than poly(thionine)Cl.

3.3. Behavior as a function of applied potential

3.3.1. Mott-Schottky study

Redox conducting polymers are organic semiconductors that can be characterized according to the Mott-Schottky model. The Mott-Schottky model is widely used as a tool in the investigation of conductivity and in the understanding of ion and electron transfer processes at the electrode-electrolyte interface [49–51]. This is done by varying the potential

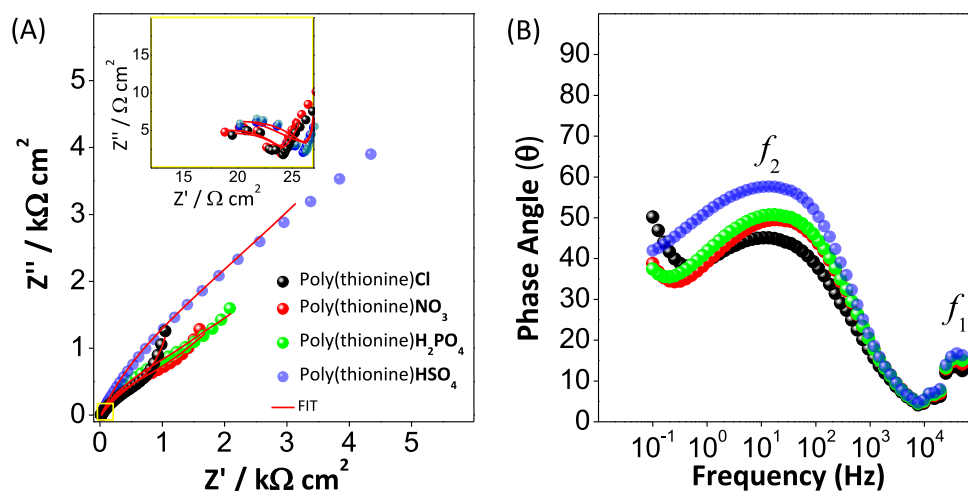


Fig. 3. Nyquist (A) and BODE (B) plots for films constructed with different inorganic acids. A potential of $+0.20\text{ V vs. SCE}$ was applied in $\text{KCl } 0.50\text{ mol L}^{-1}$ ($\text{pH} = 2.0$). N_2 atm. at 25°C .

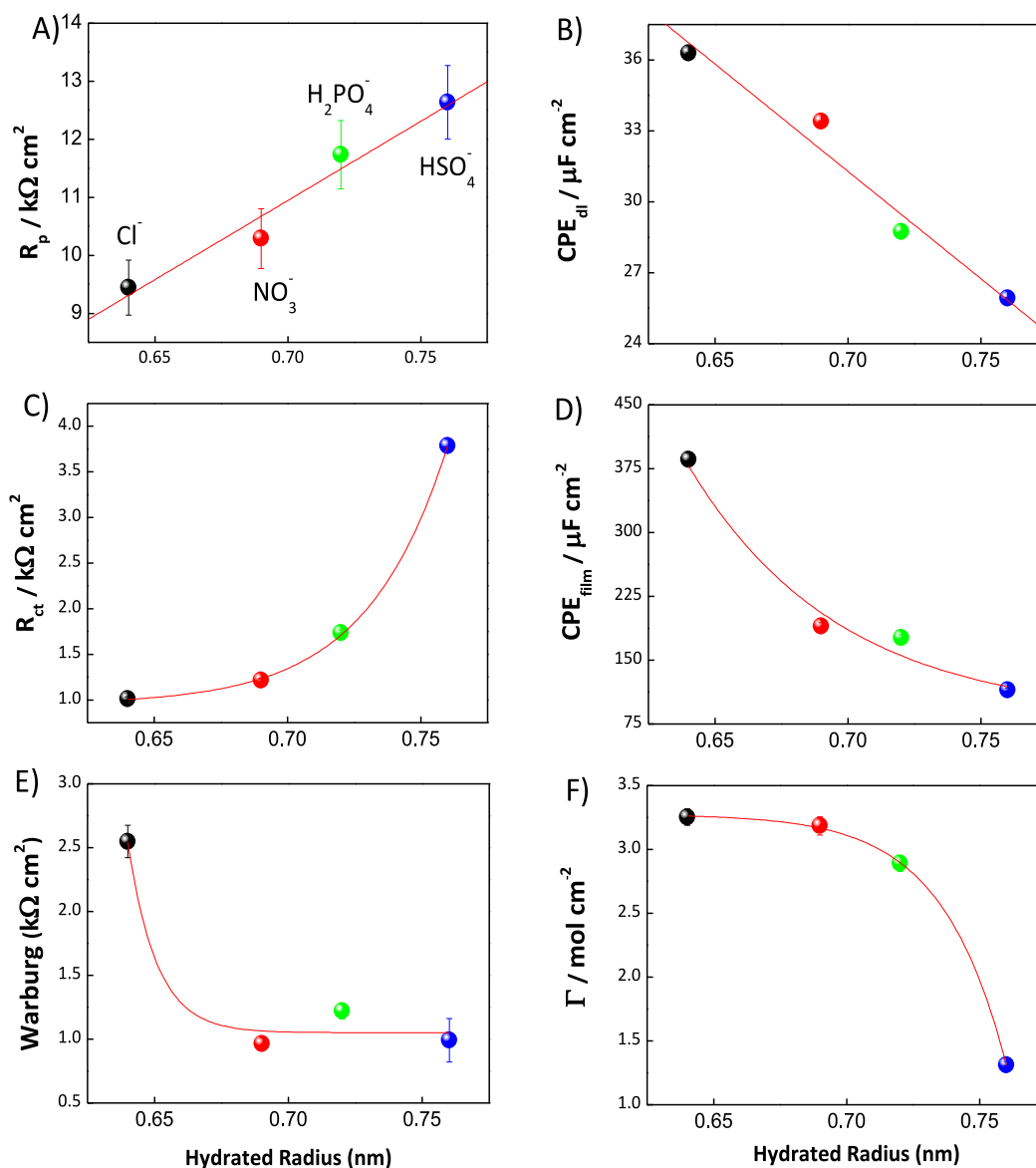


Fig. 4. Interfacial parameter values versus hydrated radius of the anion used during the electropolymerization step. A) Resistance of the polymer/FTO interface (R_p), B) double layer capacitance (CPE_{dl}), C) charge transfer resistance for the polymer/solution interface (R_{ct}), D) film capacitance (CPE_{film}) and E) ion diffusion (W). F) Calculated active surface area. The different colors represent different anions: chloride (**black**), nitrate (red), dihydrogenphosphate (green) and hydrogen sulfate (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

applied to the electrochemical cell, making it possible to measure the charge-space capacitance [35,51,52]. As in previous studies, measurements were performed in a 0.50 mol L^{-1} KCl solution (pH 2.0). Fig. 5 presents the MS graph for the different poly(thionine) films.

The linear behavior observed with a negative slope reveals that poly(thionine) semiconductor polymeric films are p-type [51,53]. The linear curves in the Mott-Schottky plot can be used to determine the charge carrier concentration (N_A) and flatband potential (V_{FB}) using Equation (1):

$$\frac{1}{C^2} = \frac{2}{(e\epsilon_0\epsilon_r N_A)} (V_{app} - V_{FB} - RT/F) \quad (5)$$

where C is the capacitance (F cm^{-2}), e is the electron charge ($1.602 \times 10^{-19} \text{ C}$), ϵ_0 is the permittivity of the vacuum ($8.854 \times 10^{-14} \text{ C V}^{-1} \text{ cm}^{-1}$), ϵ_r is the dielectric constant of the material, RT/F is the temperature-dependent term (0.026 V at 298 K), and V_{app} is the applied

potential. Thus, the N_A values can be obtained from the slope (Eq. 2):

$$\frac{d(C^{-2})}{dV_{app}} = \frac{2}{(e\epsilon_0\epsilon_r N_A)} \quad (6)$$

Commonly, semiconductor materials exhibit better electronic conductivity performances due to a higher concentration of acceptors (or donors in the case of n-type semiconductors). Nevertheless, for the thionine polymer, the film with the lowest concentration of charge carriers (higher slope) shows the best conductivity performance. This phenomenon is a result of advancing the concentration of charges beyond the optimal value. Paulsen and collaborators [50] verified, in a study with poly(3-hexylthiophene), that conductive polymers present a maximum peak in the conductivity gain behavior that is proportional to the increase in the concentration of charge carriers. After reaching the optimum value, conductive polymers tend to show a decrease in conductivity with increasing charge carrier concentration. This is due (for the case of p-type semiconductors) to the total emptying of the

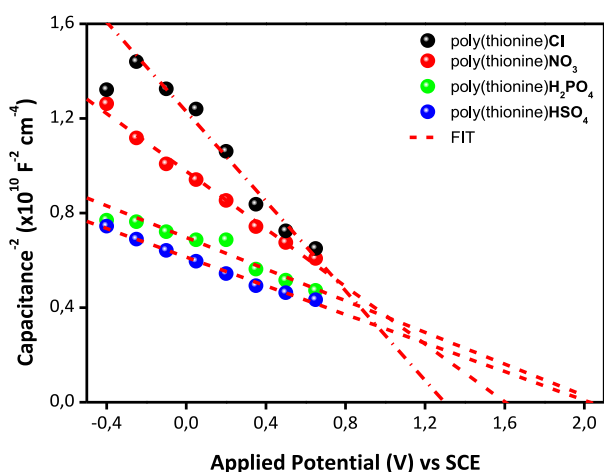


Fig. 5. Mott-Schottky plot for poly(thionine) films at an applied frequency of 10 kHz.

polymer's HOMO orbital, and, thus, not having an adequate number of empty states to meet the needs of the electronic transport mechanisms. Thus, for poly(thionine), the acid used during the synthesis of the polymeric film exerts not only a doping effect in the sense of cavity dimension or anion diffusion capacity through the polymeric structure but also effects the filling rate of the HOMO-orbital polymer, which ultimately interferes with the electronic transport mechanism.

3.3.2. EIS applied potential variation study

The influence of the applied potential variation on the poly(thionine) films was also investigated using EIS. The electrochemical behavior of poly(thionine) films was investigated by EIS in a potential window from -0.25 to $+0.60$ V (Fig. 6), comprising the entire interval where the poly(thionine) redox reaction occurs, as verified by cyclic voltammetry. Special attention was given to the medium-low frequency elements, as they represent the charge transfer phenomena for the redox reaction and the pseudocapacitance of the film. Therefore, the R_p and CPE_{dl} values are not discussed here.

Fig. 7A presents the R_{ct} values as a function of the applied potential. Based on the polymer structure, it is possible to understand the

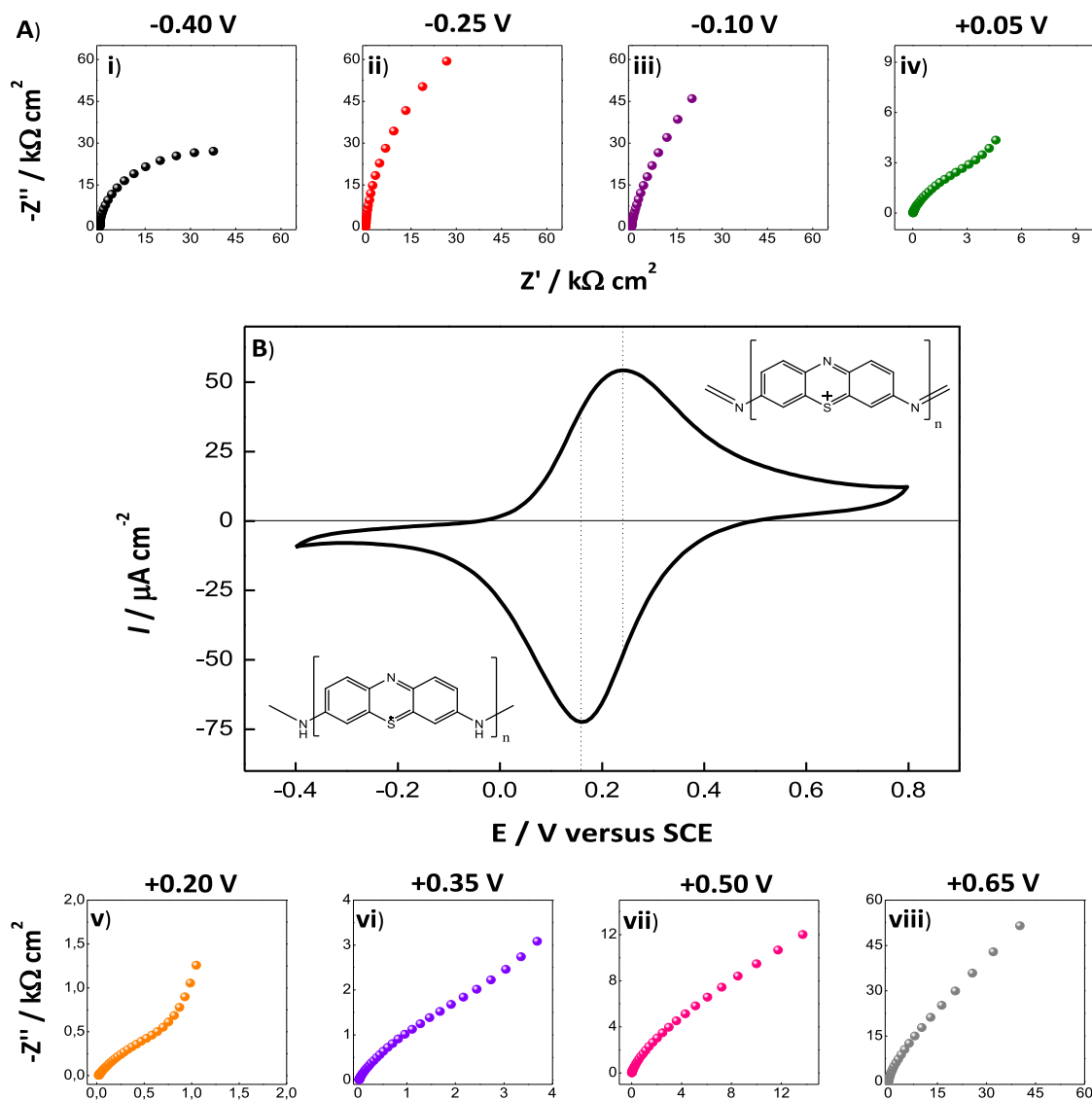


Fig. 6. Poly(thionine)Cl film electrochemical response at 0.50 mol L^{-1} KCl (pH 2.0) in a N_2 atmosphere. A) Nyquist plots for an applied potential ranging from -0.40 V to $+0.65$ V vs. SCE (i to viii). B) Cyclic voltammetry at 25 mV s^{-1} . Inset: poly(thionine) in its oxidized and reduced forms.

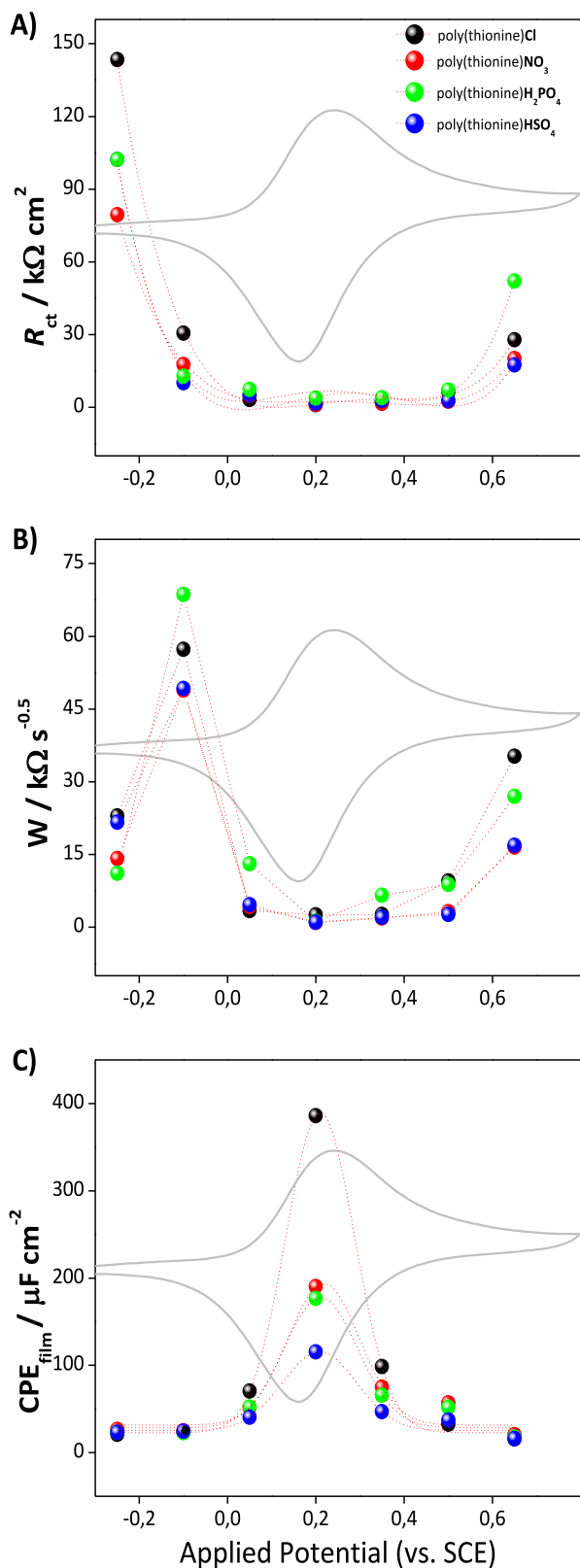


Fig. 7. Charge transfer resistance- R_{ct} (A), Warburg- W (B) and capacitance-CPE (C) versus applied potential. The element values were obtained by mathematical adjustment using the equivalent circuit model shown in Fig. 2. Inset: cyclic voltammogram recorded for poly(thionine)Cl at 25 mV s⁻¹.

conduction behavior by dividing the graph into two regions: The first region is called the low conductivity region, comprising the potential range from -0.25 to -0.2 V vs. SCE. In this region, poly(thionine) is in its fully reduced form [20,30]. In this conformation, poly(thionine) presents its lowest electronic conduction ability (greater resistance), probably due to the interruption of its pi-conjugation as well as the extinction of the delocalized positive charge due to the reduction of the molecule. The second region, comprising the potential range from -0.10 to +0.50 V, presents the lowest R_{ct} values. In this region, the film is in its conjugated form and has a positive formal charge that can suffer relocation [30]. The large change in the polymer conductivity, still at a value of -0.10 V demonstrates that the film conductivity is strongly influenced not only by the presence of pi-conjugation for its polymer chain but also by the movement of counterions in its structure, which act as dopants, as discussed earlier (Fig. 7B). Before reaching the potential of -0.035 V (onset potential of the polymer oxidation reaction), the only ion movement due to electrostatic attractions is caused by the variation in the electrode potential. After the onset potential, an electrode polarity change is observed, going to the anode potentials and consequently changing the counterion of the electrode/solution interface. In addition, the polymeric film oxidation begins with the incorporation of Cl⁻ ions in the polymeric structure. Thus, the value of W decreases due to the ion exchange process, maintaining a certain stability up to a potential of +0.35 V (after the oxidation peak). Advancing to +0.35 V, there is an exponential increase in the Warburg value due to the limitation of current values due to the diffusion mechanism for Cl⁻ ions, which now find it more difficult to diffuse inside the already oxidized film.

The CPE_{film} value shows a symmetrical increase and decrease behavior, reaching a maximum value exactly over the formal potential of +0.20 V. This behavior is typical of supercapacitor polymers and has been previously reported for polypyrrole conductive polymer films [54]. The symmetric behavior of the capacitance increase over the formal potential is indicative of conductivity control by ion transport. That is, the electronic transport mechanism is slow in relation to counterion transport [54]. This fact again reinforces the influence of the counterion on the formation and electrochemical response of the poly(thionine) film.

4. Conclusion

In the present study, the influence of the counteranion on the electropolymerization of poly(thionine) polymer film was investigated. The electropolymerization was carried out through cyclic voltammetry, which enables us to follow the development of polymeric film electroformation. Through the electropolymerization voltammogram, it is shown that large anions favor the formation of radical cations at lower applied potentials. However, with a larger anion size, a decrease in mobility occurs, impairing film formation and resulting in a decrease in the current magnitude for the polymer as well as in the displacement of the peak potentials.

The decrease in performance observed when using larger anions is well shown through an electrochemical impedance spectroscopy study in aqueous solution. Using mathematical adjustments for an equivalent circuit model, the resistive and capacitive interfacial elements are obtained, compared, and organized as a function of the hydrated radius of the anions used during the electropolymerization step. This analysis shows interesting correlations. One of them is that an increase in the size of the anion used for the formation of the poly(thionine) film leads to an increase in the film strength. This increase in resistance arises from the trapping of larger cations, making the polymer cation-directed, which means that a smaller amount of chloride ions can access the polymer matrix for doping during the oxidation phase due to the presence of trapped anions. The trapping of larger anions in the polymeric matrix is evidenced by Mott-Schottky analysis, where a higher concentration of acceptors in the interchange space is verified. Finally, a study of the

variation of the applied potential on the polymeric film shows that the poly(thionine) polymer presents a maximum conductivity and capacitance at a potential of +0.20 V, which is precisely the equilibrium potential. This study also shows that the polymer formation is anion dependent. That is, the redox behavior of the polymer is limited by the movement of anions in its polymer matrix.

CRedit authorship contribution statement

André Olean-Oliveira: Visualization, Discussion, Writing – original draft. **Gilberto A. Oliveira Brito:** Visualization, Discussion, Funding acquisition. **Celso Xavier Cardoso:** Visualization, Discussion, Funding acquisition. **Marcos F.S. Teixeira:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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