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Technical Report

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Abstract

In this work we have analyzed the effect of thiourea concentration in the acid zinc deposition process. For these purpose, we have used the electrochemical techniques (cathodic voltammetry and Electrochemistry Impedance Spectroscopy, EIS). It allows determining the optimal concentration thiourea additive. In this range, we have obtained better finishes, more refined and decoratives layers. We have found in voltammetric studies that the electroreduction of Zn^{2+} in the presence of thiourea is accelerated. The EIS studies has shown the "electrodeposition resistance" decrease in the presence of thiourea. The addition of more thiourea in the solution, in the optimum concentration, the electrodeposition resistance to the electrodeposition process is increased. The main contribution of this research and its scientific contribution is the use of electrochemical techniques for determining the optimal concentration of thiourea additive in the zinc electroplating solution in chloride acid media.

Keywords: *zinc; electroplating; additives; control; EIS.*

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1. Introduction:

It is well known that small quantities of the additive change the nature of the metallic deposit and changes the properties and surface finishing. The effect of organic additives on the process of electrochemical metal deposition has been extensively studied by many authors [1-10, 14]. Thiourea is an example of an organic substance that in aqueous solution accelerates several electrode process including the Zn^{2+} reduction. Organic additives produce a compact, finely crystalline adherent electrodeposits [2-4, 9]. The additives are generally organic substances that are added to the electroplating solution because they modified the growth of the first crystals, also change the structure of electrodeposits and, therefore, the quality of metallic finishes. Additives are used for improving the physical-mechanical properties of the coatings promoting the reduction of dendritic formations, pitting corrosion and stress. The additive concentrations differ between 10^{-7} M and 10^{-2} M in the electroplating solution. The additive formula and its functional groups can modify the mechanism of action during the electrodeposition and protect the base metal used as substrate [1, 2, 5]. In the bibliography, generally there are no reports among functional groups of additives (alcohol, acid and ester) and its direct action mechanisms (adsorption, complexation) and the effect on the coatings (levelling, brighteners, hardeners).

T.C. Franklin [2] in a review has postulated that “The additives affects the rate of deposition of metals. The mechanisms of action of additives in electrodeposition process include 1-blocking the surface, 2-changes in Helmholtz potential, 3- complex formation including induced adsorption and ion bridging, 4- ion pairing, 5- changes in interfacial tension and filming of the electrode, 6-hydrogen evolution effects, 7- hydrogen absorption, 8- anomalous codeposition, 9- the effect of intermediates. The organic additives in other fields such as corrosion inhibition and catalytic poising are also generally treated as acting by the dirt mechanism. The opinion about whether additive adsorption is on active sites, geometrical protrusions or specific crystallographic faces and whether the influence is on diffusion or deposition, but there is general agreement that the additive is essentially acting only as dirt (leveling and brightening) depended on the size of molecule, its basic or acid nature and the available number of electron pairs in the molecule. The last two criteria relate to its ability to adsorb. This type of additive only causes a decrease in the rate of electrode reactions. Additives in other fields, such as corrosion inhibition and catalytic poisoning, are also generally treated as acting by the “dirt mechanism” [2].

L. Oniciu and L. Muresan [5] give a review about some fundamental aspects of levelling and brightening on the deposit, the grain refinement of the deposit, polarization of the cathode, incorporation of additive in the deposits, the change of the orientation of crystals and the synergism (3,10) of additives in metal electrodeposition, and others additives changes the surface tension. Cyanides [8] are used in plating solutions, can be considered as additives, and acts by the mechanism of complexation of metal cation being deposited by altering the kinetics of deposition for metals of Group 1B, 2B and 3A of the periodic table.

Some additives act by the "additive complexing mechanism with the cation of the metal being deposited". Thus, the additives control all the electrodeposition process, the transport of the metal from the solution to the external surface, the charge transfer from the cathode to the partially desolvated and uncomplexed ions, with the formation of adatoms on the cathode surface, lateral diffusion on the metal surface until their incorporation into the crystal lattice" [5]. "A dentrite free, levelled, compact and adherent deposit requires such values of overpotentials as to provide a sufficiently high nucleation rate, a moderate charge transfer rate and a sufficiently high crystallization overpotential"[5,6].The additives prevent unwanted dendritic growths with isolated nuclei at the initial stages of the electrodeposition. So, with additives added to plating solutions, the growth of grains is layer by layer and the coatings obtained are of better quality [6,7,8]".

Additives brighteners works by means of a non-difusional mechanism called electroadsorption [8, 9]. For zinc in acid medium on the steel, the electroadsorption mechanism of the thiourea is proposed [10, 16]. "An interesting case is that of thiourea and other additives used as levelling and brightening agent [5, 20, 22] in a Watts type nickel plating bath, they shown that in the presence of thiourea decreases cathode polarization at concentrations less than 0,001 M and increases it considerably at higher concentration". The reduction in surface roughness vs thickness to show the Levelling power of bright copper deposited in a presence of a proprietary additive [14].

It was found that the grains were smaller in the presence of thiourea and the electrodeposits were more refined and bright [2, 5, 8, 10, 11, 12, 13, 14].

Furthermore, considering the surface which is constituted by peaks and valleys additives called "levelling" act by inhibiting deposition on the peaks [15]. The metal is deposited on the valleys and not on the peaks. Then, the massive deposition occurs in the valleys and go on to level the coating, so the coatings obtained are more refined and more level. Radioactive tracer techniques, have been particularly effective for studying the behavior of thiourea as levelling and brightening agent in nickel electroplating [7, 14, 15]. The additives are generally organic substances that are added to the electroplating solution because they alter the growth of the first crystals, also change the structure and the texture [8, 9, 19] of electrodeposits and the quality of metallic finishes. Additives are used to improve the physical-mechanical properties of the coatings promoting the reduction of dendritic formations and pitting corrosion, stress and increase the brightness and leveling [14, 15, 20, 22].

The additive concentrations vary between 10^{-7} M and 10^{-2} M for the electroplating solution. The additive formula and its functional groups can modify the mechanism of action during the electrodeposition and have effect in the base metal used as substrate [2, 5, 14].

The additives for zinc, in an acidic media as dextrose, dextrin, glucose, beta naphthol, vegetable gum, gelatin and naphthalene- disulfonate are mentioned [16].

Therefore, the deposition overpotential moves the potential to more positive or negative depending on the additive in question and its concentration in the solution [2, 5, 10, 14, 16]. The inhibitory effect of thiourea, in the initial stages of growth of Zn on the surface by the additive occurs, both in acid medium and in alkaline medium [1, 8, 9, 10, 11, 15 ,17, 18, 19, 21] was studied. B. Marckzewska [1] has demonstrated that the mechanism of the acceleration effect of adsorbed non electroactive thiourea on the electrochemical reduccion of Zn^{2+} in aqueous solution as expressed by the increase in standard rate constants, by EIS studies.

J. Bressan and R. Wiart [16] Pedro De Lima Neto [18] and Z. Mahmud [20] have reported the use of impedance measurements for the control of additives in electrodeposited Zn [18] ZnNi [10, 20, 22] and ZnCo(18).

The coatings in the presence of additives improve the functional properties of the coatings as in the case of zinc plating [9,19] galvanized (hot dip) or hard chrome that produce increasing of the hardness, mechanical strength, electrical conductivity, wear resistance and corrosion resistance [14, 18, 20, 22].

2. Experimental

Measurements were performed in a conventional three compartment cell. Low carbon steel (AISI 1010) embedded in epoxy resin was use as working electrode ($A = 0.2\ cm^2$). Prior to each experiment the electrode was mechanically polished with 600 grade emery paper and rinsed with tap and distilled water. Finally, the electrode was dried with tissue paper. Immediately immersed in the electroplating solution 0.3 M $ZnCl_2$ + 4.2 M NH_4Cl ≅ (pH 3.5 and ionic strength I = 5.1 M) to which thiourea was added at a concentration of 10^{-5} M to 10^{-3} M.

A large area sheet counter electrode and a saturated calomel reference electrode (E = - 0.240 V vs. SHE) were used. All potentials in the text are referred to this electrode. Before each electrochemical measurement, a potential $E_i \cong 5$ mV more positive than the open circuit potential E_{oc} was applied to a constant current density of 100 µA cm^{-2} (for 300 s). The electrodeposition of Zn was carried out, using single linear potential sweep between the chosen $E_{i\ measured} \cong -0.65$ V and $E_f = -1.5$ V at the potential scan rate, $v = 0.010\ Vs^{-1}$.

Electrochemical Impedance measurements (EIS), were carried out at different electrodeposition potentials in the frequency range $0.005 Hz \leq f \leq 10^5 Hz$, with $f = \omega/2\pi$. The measurements were performed with a potentiostat-galvanostat EGG Princeton Applied Research & Par 273 and 273 A.

3. Results and Discussion

3.1 Cathodic zinc deposition

The zinc electroplating voltammetry in an acidic medium depends of the applied potential. Figure 1 shows five potential regions that are associated with different processes that are identified by the letter "Z":

The initial potential value, Ei determines the characteristics of the steel surface and then the quality of zinc electrodeposited.

1. potential zone of "Z_1 peak" is observed in potential more positive than the reversible potential before starting the deposition.
2. potential zone of nucleation of zinc is called "Z_2".
3. potential zone "Z_3" presents characteristic of deposition with activated control.
4. Potential zone of "Z_4 peak" present characteristics of deposition with diffusion mass controlled.
5. Potential zone of "Z_5" "limiting current trend" where the limiting deposition process is control by mass transport in boundary conditions as discussed below.

In the zinc deposition zone due to the high applied potential, Z_5, involves hydrogen-evolution with zinc deposition.

Figure 1 shows the deposition Voltammetry

obtained in the presence and absence of additive.

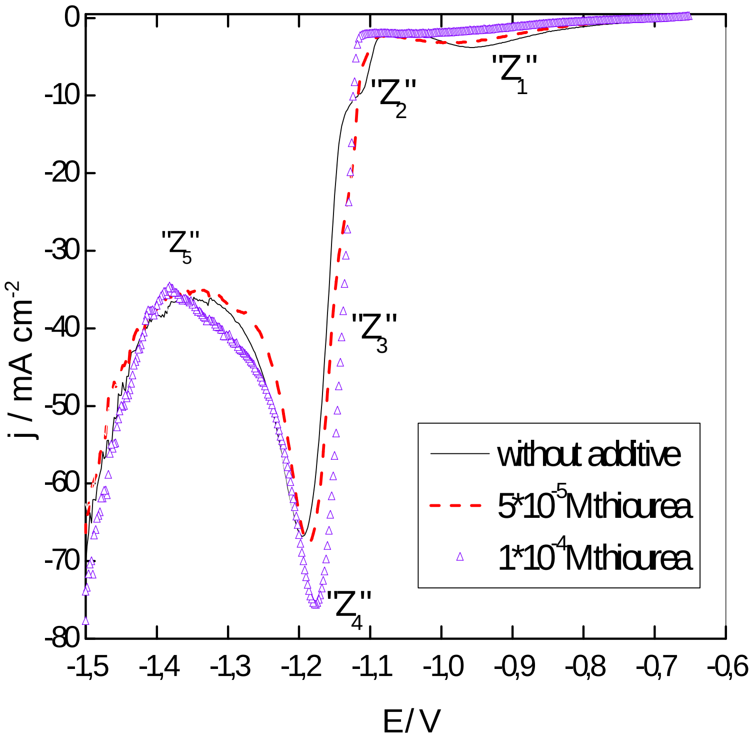

Figure 1. Deposition voltagram at v = 10mVs^{-1}. Black without additive, red 5 * 10^{-5} M, purple 1 x 10^{-4} M.

If thiourea is added in small concentration to the solution, the plateau seen in Figure 1 practically disappears at an approximate concentration of 10^{-4} M.

It is possible to observe that in the presence of thiourea, the “Z_1“ zone flattens when it increases the concentration of the additive, and the nucleation zone "Z_2" is modified. This fact would indicate that adsorption of thiourea produces a change in the kinetics of nucleation reaction at the start of the electrodeposition.

During the nucleation process, diffusional fields on the nucleus are generated. Nucleation is a different process when adding or no thiourea to the plating solution.

When the concentration of thiourea at the plating solution is very low (compared with the optimum) or there is no additive in the solution at the start of nucleation process, the diffusional fields occur such that the metal (Zn^{2+}) arrives uncontrollably at the nucleus. In that case, on the first zinc cores high currents occur and result in the phenomenon known as "concentration polarization”.

Diffusional fields that are always generated on the nuclei collide with "soft collisions”.

Therefore, the arrival of Zn^{2+} zinc cations from the solution to the surface between nucleus becomes more difficult because the surface diffusional fields collide with "soft collision" surrounding nearby nuclei.

This fact causes porous deposits and therefore lower quality. This nucleation process is shown in the voltammogram in the area called "Z_2".

In the presence of thiourea, contained in the electrodeposition solution, the mass transfer of the solution to the electrode is slow. Therefore, the currents that reach the nucleus j_0 are low and the kinetic constant of reaction of electrodeposition is low too, being ($j_o = K * CZn^{2+}$). By decreasing the kinetic constant K of the reaction, the deposition is more controlled.

In the presence of additives in solution, as a result of thiourea addition, the nucleus collide against each other with "hard collision". This is due to the fact that additives alter the way in which material comes from the solution to the electrode surface. Therefore, the formation of deposit is facilitated until it forms a continuous layer and then layer by layer formation of the coating.
The coating is different depending on the constant of complexation of metal and pH solution. The electrodeposition process depends strongly on the metal complexation constant and the chemistry of the solution (in the presence or absence of additive). That is, the availability and Zn^{2+} ion transfer and speed of arrival of the metal at the surface. In this case a complex is formed: $ZnCl_4^{2-}$ pH= 4 and thiourea significantly changes the coating characteristics (morphology, grain size). In this case, the process is slow and controlled by the concentration of the thiourea additive, deposits are more refined, smooth and levelled.

The peak current in "Z_4" is increased when the thiourea is present in the solution, in the zone of massive deposition and the potentials values are more anodic values. While in the potential "Z_5" so-called "limiting current trend", there is a major change in the current density with the concentration of thiourea to 10^{-4} M. Thus, the addition of thiourea, additive improves the characteristics of the electroplated surfaces.

3.2 Potenciostatic curves at different cathodic potentials in the voltammetry.

The potenciostatic studies were made to be sure that the system is in stationary state during the measure by EIS at each potential.

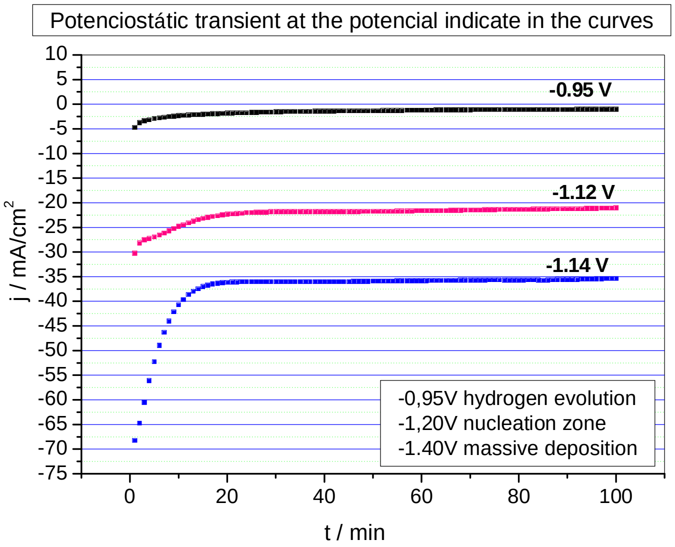

Figure 2. Potenciostatic Deposition salts. Black -0.95V, red -1.12V, blue –1.14V.

The Figure 2 shows that the system is stationary by long times at all deposition potentials. Then, at these potentials it is possible measure the spectrum by EIS.

3.3 EIS Electrochemistry Impedance Spectroscopy

3.3.1 EIS at hydrogen evolution -0.95V, in the nucleation potential -1,12V and in massive deposition at - 1.14 V.

The Figure 3 shows the Nyquist plots at different potentials without thiourea.

The complexe plane exhibits a slightly capacitive circles at high frequencies and a second time constant at medium and low frequencies, probably associated with a diffusion process. When potentials studied are more negative the impedance values decrease (Figure 3).

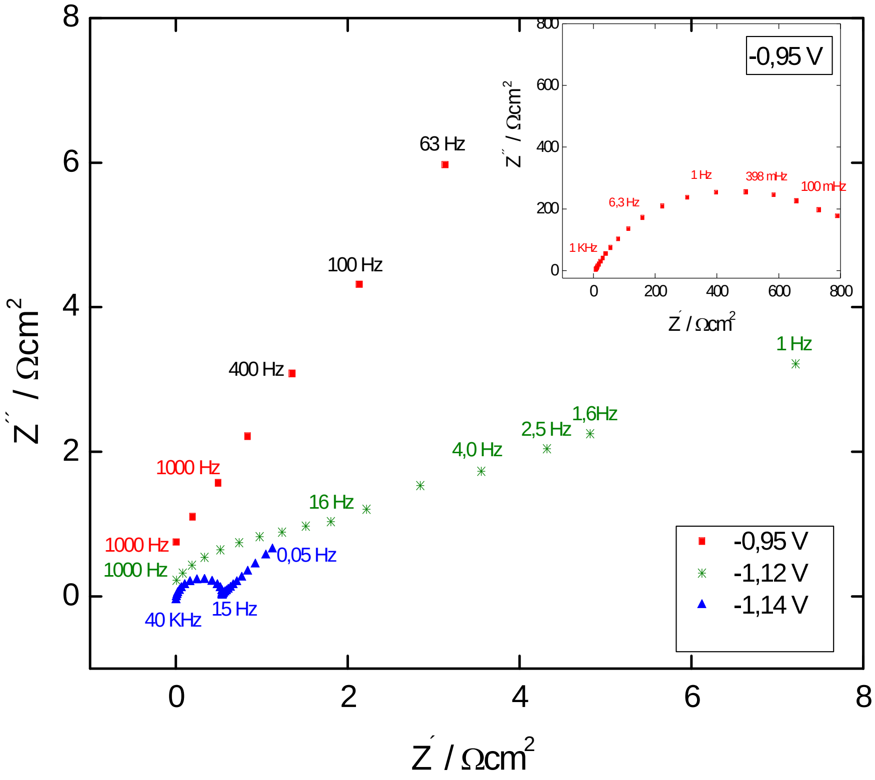

Figure 3. Nyquist plots at different potentials shown in Figure 1. Electrodeposition solution without additive.

3.3.2 EIS at the nucleation potential at -1.12 V in the presence of thiourea.

Impedance plots are modified by the addition of thiourea (Figure 4).

It is observed that in the presence of thiourea additive, the impedance values are modified. When increasing the thiourea concentrations the impedance values decrease.

A -1.12 V in the whole range of frequencies, at a concentration of thiourea in the solution of up to 5 x 10^{-5} M there are two time constants a capacitive loop at high frequencies and a diffusional contribution at low frequencies.

Whereas for concentrations of 5 x 10^{-4} M the diffusional process disappears and only the capacitive process remains with one time constant and higher values of impedance that in a concentration of 5 x 10^{-5} M.

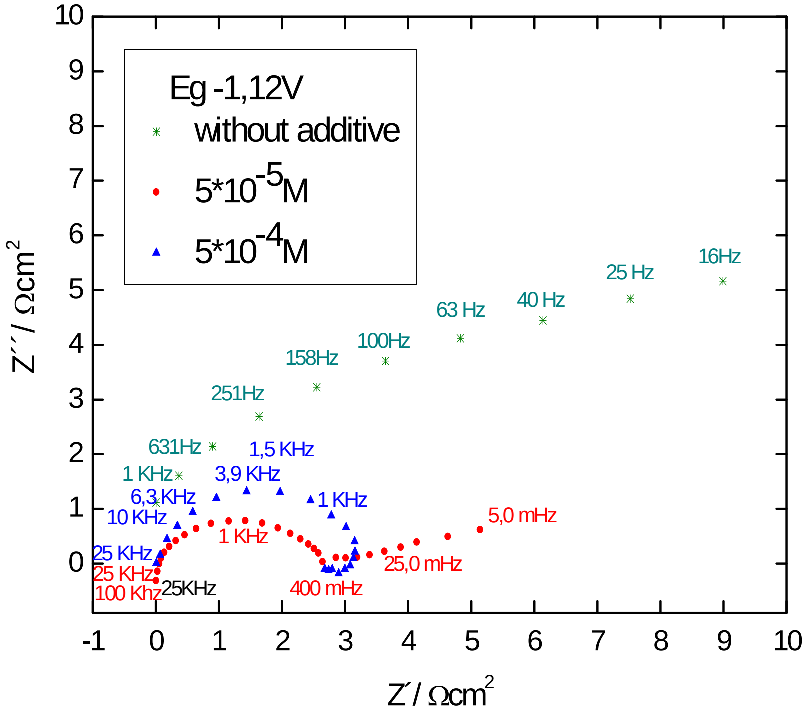

Figure 4. Nyquist plot to -1.12 V, electroplating solution with and without additive.

The phenomenon can be explained by a modification of the nucleation and growth process at the beginning of the electrodeposition process that causes diffusional process to disappear, resulting in a better deposit because there is no "concentration polarization". A greater Impedance value Z, implies that the charge transfer resistance R_{tc}, is great. Then the value of $R_{tc} = cte / j_o$ is great, then j_o is low, and the kinetic parameter called exchange current density j_0 decreases. A lower value of j_0 indicates that the rate constant of reaction k decreases being $j_0 = k * C$.

A low value of k decreases the rate constant of kinetics reaction during the nucleation.

Thus, the deposition rate at the beginning is lower and more controlled.

- **Microstructure of the coatings obtained at constant E = -1.12 V in the presence of thiourea**

The thiourea produces grain refinement and the metal coatings are brighter and more uniforms (Figure 5).

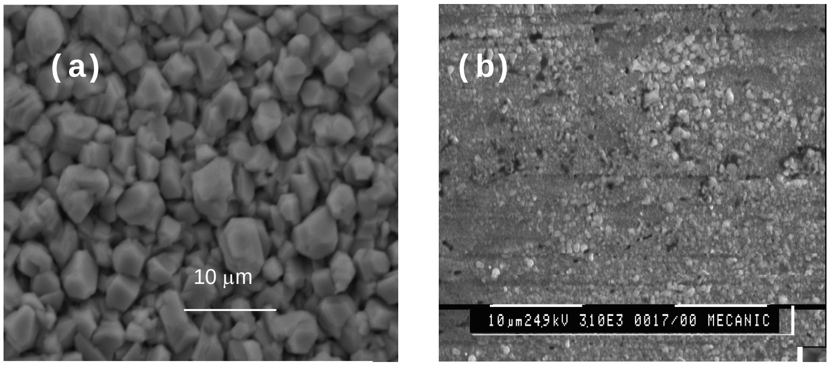

Figure 5. Photomicrographs by SEM. of zinc deposits a) without additive and b) with thiourea 510^{-5}M. Deposits were grown in the nucleation potential Eg = -1.12 V until a charge Q = 0.2 Ccm^{-2}.

3.3.3 EIS at the in massive deposition potential at - 1.14 V in the presence of thiourea.

In Figure 6 a plot of impedance to -1.14 V, that presents with higher concentrations of thiourea.

Figure 6 shows that adding low concentrations of thiourea to the electroplating solution 5 10^{-5} M the value of the real component of the impedance decreases.

When thiourea is added to the solution, above a concentration of 10^{-4} M, the charge transfer resistance R_{ct}, at high frequencies increases and, therefore, j_0 decreases, which involves a more controlled deposition, because as explained above, when decreases j_0, the reaction rate constant, k decreases, as $j_0 = k * C$ where C is the concentration of the species being deposited, in this case Zn.

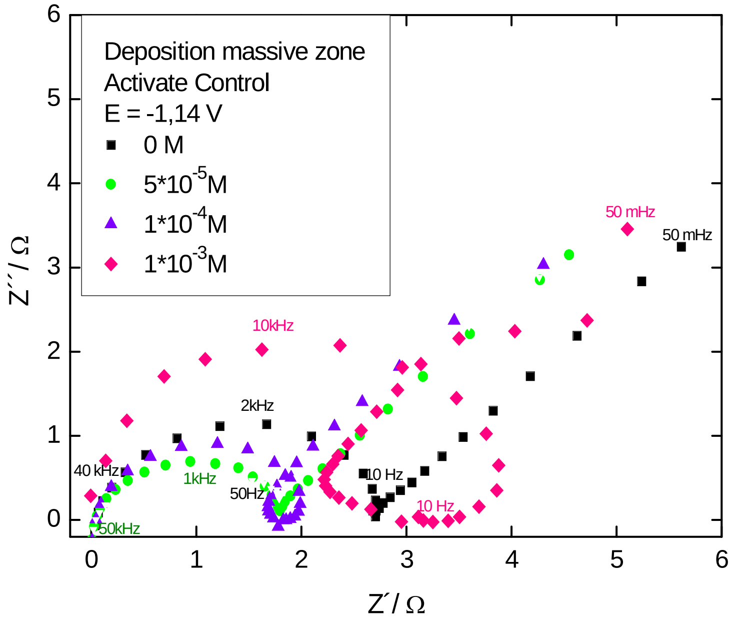

Figure 6. Nyquist plot to -1.14 V, without additive and with the addition of various concentrations of thiourea.

The additive concentration from 10^{-4} M is optimal, because j_0 is lower from the value at minor concentrations.

• Microstructure of the coatings in the presence of thiourea at -1.14 V

In the photomicrographs of Figure 7, the electrodeposited layers at a potential of E = -1.14 V in the absence and presence of thiourea are observed.

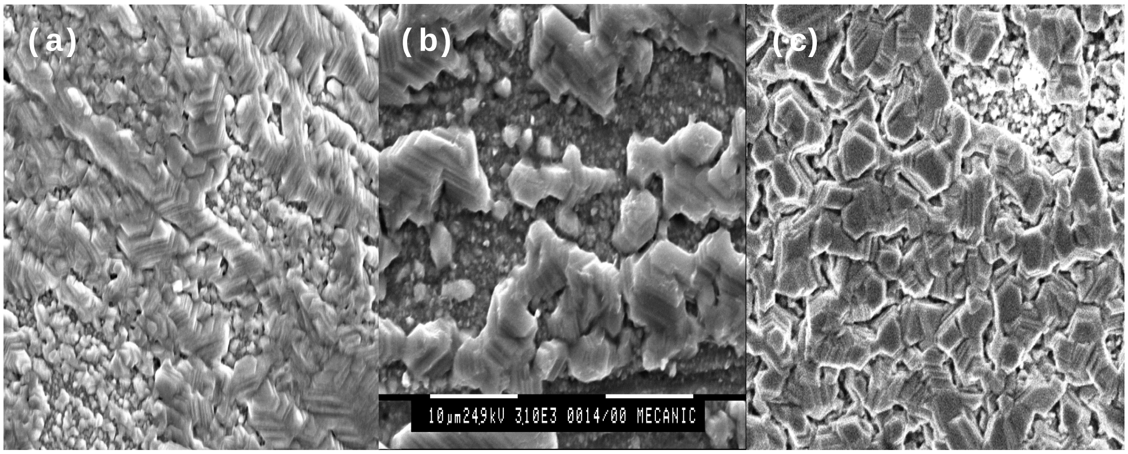

Figure 7. Photomicrographs obtained by SEM. The electrochemical technique used is voltammetric (a $100 mVs^{-1}$ from the initial potential Ei until deposition potential to -1.14 V) and then the potentiostatic to E constant at -1.14 V, electrodeposition solution $ZnCl_2 + NH_4Cl$: a) no additive, b) with $3x10^{-5}$ M thiourea c) 10^{-4} M thiourea.

3.3.4 EIS in the massive deposition potential at - 1.19 V (in diffusional current density) in the presence of thiourea.

Figure 8 shows the Nyquist plots in the mass deposition zone with control by transport at -1.19 V. In this range of potentials, it can be seen that the optimum additive concentration is 2.5 10^{-4} M thiourea because at that concentration increases the Rct and, in that concentration, the reaction rate constant of deposition is lower and, therefore, more controlled. Additive concentration is greater in this case because mass deposition occurs with control by transport and parallel reaction of water decomposition takes place.

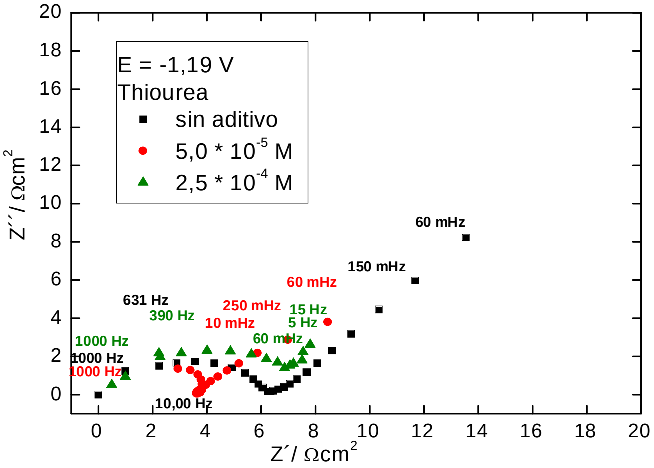

Figure 8. Effect on the Nyquist plot at -1.19 V. The electroplating solution with different concentrations of thiourea.

4 Impedance results were adjusted through the following transfer function:

The transference function and the electrical equivalent circuit corresponds to the physicochemical system in which there are in series the solution resistance Rs, and RC circuit (Zp is the RC impedance). R is the sum of (Rct: the charge transfer resistance and W: the Warburg resistance), both in parallel with a capacitor where the total impedance, Z, of the electrochemical system is given by the sum of Rs and Zp equations (1) and (2):

$$Z = Rs + Zp = Rs + \left(\frac{1}{Zp}\right)^{1} = Rs + \left(\frac{1}{Z_2} + \frac{1}{Z_3}\right)^{-1} = Rs + (Z_2 + Z_3 / Z_2 * Z_3)^{-1} \quad (1)$$

$$Z = Rs + \frac{(R_{ct} + W)\ (-1/\omega\, C_{dl})\, j}{(R_{ct} + W) - (1\ /\ \omega\, C_{dl})\, j} \quad (2)$$

The table 1 presents data obtained by simulation using an electric circuit by Theory of Bouckamp as described.

Table I. Fit parameters to the thiourea concentration at the potential zone of the voltammetry.

Tiourea (Conc. Molar)	**Potencial**	**FIT PARAMETERS**		
	E / V	Rs / Ω cm2	Rtc / Ω cm^2	C µF cm^{-2}
0	-0,95	7,23	107	250
0	-1,12	5,61	6,44	170
5x10-5M	-1,12	2,20	2,56	92
5x10-4M	-1,12	2,50	3,20	40
0	-1,14	2,20	2,7	30
5x10-5M	-1,14	2,10	1,78	56
1x10-4M	-1,14	2,81	1,50	140
5x10-4M	-1,14	2,34	1,30	140
1x10-3M	-1,14	3,20	2,00	52
0	-1,19	1,00	7,35	15
5x10-4M	-1,19	1,00	3,00	10
2,5x10-4M	-1,19	4,78	9,30	39

In Figure 9, the diagram shows data measured and adjusted at nucleation potential and they are in good accord with equivalent circuit chosen.

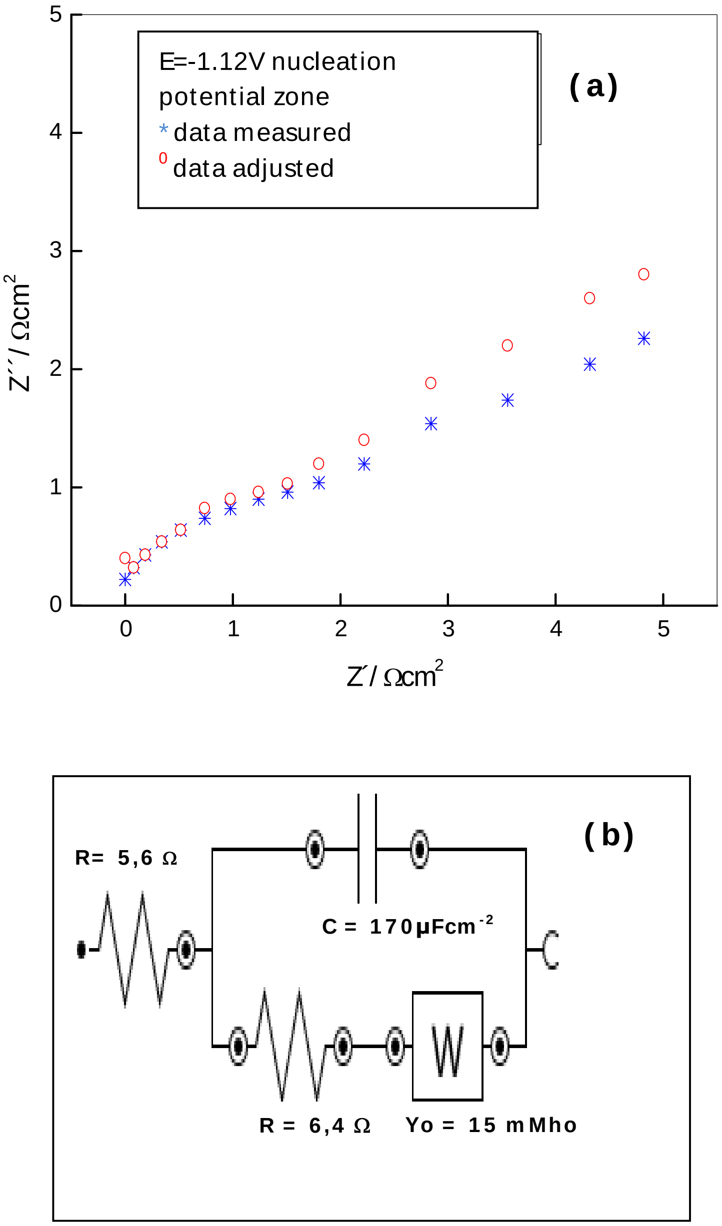

Figure 9. a) EIS electrochemical impedance spectroscopy. Values measured and adjusted to the transference equation. b) equivalent electrical circuit.

W in the electric circuit is the Warburg diffusional resistance R=66,6 Ω.

4. Conclusions

- The main contribution of this work is the use of electrochemical techniques for determining the optimal concentration of thiourea additive in the zinc electroplating solution, in chloride acid media.

- At the same time we have found that at the appropriate concentration of the additive, the inhibition properties and kinetics of electrodeposition of zinc with additive are regulated.

- At the nucleation potential of -1.12 V and in the massive deposition at -1.14 V, the equivalent circuit representing the total system impedance is given by R(C[RW]) and with the use of thiourea (when certain concentration of thiourea is added) occurs the change of the circuit to another circuit R (RC), which is different in each case.

- The optimum amount of additive to achieve a quality deposit depends on the zone of potential studied, since in each case, occurs change in the control.

- The optimum value of the additive concentration is reached when the value increases charge transfer resistance.

Acknowledgements

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