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Research Article

ELECTROCHEMICAL STUDIES OF ZINC DEPOSITION CONDITIONS

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ABSTRACT

Zinc films are deposited on steel from sulphate bath using electrodeposition process. Cyclic voltammetry and chronoamperometry are used to study the effect of pH on zinc electrodeposition process and nucleation model respectively. Furthermore, potentiodynamic polarisation and electrochemical impedance spectroscopyare used to study corrosion behaviour of zinc films.The pH of the bath was controlled at 4, for decreasinghydrogen evolution reaction,and increasing current efficiency of the Zn deposition. The study of the influence of deposition potential on corrosion behaviour in 3.5% NaCl, solution indicated that Zn film obtained at -1.26V presented less corrosion current and bestcorrosion resistance.

Keywords: Zinc films, electrodeposition, deposition potential, corrosion resistance.

1. INTRODUCTION

Zinc electrodeposits are widely used for corrosion protection ofsteel. Electrodeposited zinc coatings have long been recognized as effective barrier and sacrificial coatings for ferrous substratesCantwell et *al*(2009). Zinc electrodeposition is performed in cyanide baths, in alkaline cyanide-free baths, in acid chloride zinc baths, sulphate baths and in ionic liquids Boiadjieva et *al* (2009); Krishnan et *al* (1992); Ramesh et *al* (1998); Liu et *al* (2013); Salles et *al* (2011); Ibrahim et *al* (2016).Otani et *al* (2016), Marcos et *al* (2013).

Study based on pH value of the bath, proposed a reaction model based on the competition between the inhibition of adsorbed H^+ and the autocatalytic discharge of Zn^{2+},as well as a reversible adsorption of the anion specific for the electrolyte Epelboin et *al*(1975a), Epelboin et *al* (1975b).In addition, the interfacial pH changes when the hydrogen reduction occurs, the chemical equilibrium of the species present in solution is also modified. It was shown that H^+ reduction is inhibited by the presence ofZn^{2+} ions in solution Gomes et *al* (2006). Research showed that in acid sulphate bath,the hydrogen evolution reaction start at early stage potential whichthe decrease of the current efficiency of zinc deposition. In later works Cachet et *al* (1990); Cachetet *al* (1994).it was suggested that the discharge of Zn^{2+} is inhibited by the hydrogen adsorption in highly acid sulphate solutions. In the other hand, the results on the effect of pH on the zinc electrodeposition, indicate that the high current efficiently of Zn

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electrodeposition occurs in the region of potential (-1.2 V /-1.34 V), this behaviour indicates an activation of this process with increasing pH Salles et *al* (2011).

The Electrodeposition conditions such as bath composition, current density, presence of additives; also have a profound effect on the electrochemical properties of zinc deposits and on corrosion behaviour. Recently, study on the influence of the deposition mode show that deposits obtained by pulse current provide better protection against corrosion Nitin et *al* (2015).

In the present paper, Zn films were electrodeposited on steel substrate from sulphate bath. The influence of deposition conditions; pH, time and potential, on electrochemical behavior were studied. The cyclic voltammetry was used to study the influence of pH on the electrodeposition process. The potentiodynamic polarization and the electrochemical impedance spectroscopy were used to study the corrosion resistance of Zn films in 3.5% NaCl solution.

2. EXPERIMENTAL

Zn films were prepared by electrodeposition under potentiostatic conditions from a sulphate plating bath, containing 0.2M Zn $SO_4 \cdot 7H_2O$, 0.4 M H_3BO_3, 1M Na_2SO_4 at room temperature. Electrochemical experiments were carried out in a conventional three-electrode cell using a VoltaLab 40 potentiostat/galvanostat controlled by a PC. The counter electrode was a platinum plaque electrode, the reference electrode a saturated calomel electrode (SCE) and the working electrode was steel pies. Before the deposition, the steel substrates were cleaned in nitric acid and then rinsed with distilled water. The exposed free surface plated was 0.4 cm^2. The Zn films obtained are rinsed with distilled water and used as working electrodefor corrosion measurements in 3.5% NaCl solution, in which deposits were immersed for 1 hour before corrosion study.Electrochemical behavior was carried out by cyclic voltammetry for different pH values 2, 2.5, 3 and 4 to determine the appropriate deposition potential. The chronoamperometry methode is applied for the deposition of zinc films. Corrosion measurements are carried out by potentidynamic polarization experiments performed in potential range from -1.2 V to 1 V, at a scan rate of 2mV.s-1. The corrosion current densities (i_{corr}) and corrosion potential (E_{corr}) were determined from extrapolation of Tafel plots(E (Potential) vs. log$i$ (current density)).The electrochemical impedance spectroscopy measurements were obtained at open circuit potential (OCP) in a frequency range from 50 kHz to 10 mHz with an applied amplitude sinusoidal voltage of 10 mV. Charge transfer resistance (R_{ct}) was extracted from impedance curves.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry(CV)

All voltammogramsare carried in a potential range of -0.2 Vto -1.4 V / SCE at a scan rate 20 mV / s. The reduction of H^+ ions is a secondary and inevitable during the electrodeposition process. So it is interesting to characterize the evolution of this reaction in the supporting electrolyte, without the metal cations (Zn^{2+}), which allows us to highlight the contribution of this phenomenon on the development of Zn films. The electrochemical behavior of substrate (steel) has been studied by cyclic voltammetry in an electrolytic bath containing 1 M Na_2SO_4 and 0.4 M H_3BO_3, in the absence of Zn^{2+}(Fig1.a). The curve shows that he current density increases from -0.94 V / SCE. This is related to the reductionof H^+ ions as follows:

$$2H^+ + 2\,e^- \rightarrow H_2$$

This indicates the presence of a competing reaction in the electrodeposition of metals in aqueous solution Bockris et *al* (1993). A limiting current density is observed about -11.72 mA.cm^{-2}. It is also noted the total absence of the anodic current. In presence of Zn^{2+} ions (Fig1.b), the voltammogram shows that the Zn^{2+}reduction reaction is started at about -1.20 V,and followed by theappearance of a loop at about -1.3V indicating of the zinc nucleation process. In the reverse potential, pure zinc oxidation peak was found at about −0.91 V, in agreement with the results obtained in chloride media by other authors Elkhatabi et *al* (1996).

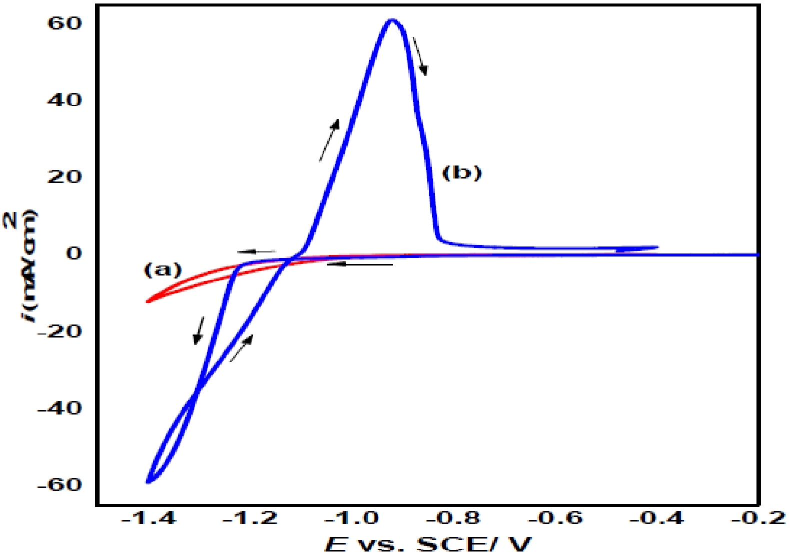


Figure 1. Cyclic voltammograms of steel substrate : a) 1 mol.L^{-1} Na_2SO_4,0.4 H_3BO_3, b) 1 mol.L^{-1} Na_2SO_4, 0.4 H_3BO_3 and 0.2 mol.L^{-1} $ZnSO_4{\cdot}7H_2O$, scan rate 20 mV/s, pH= 4.

In order to study the influence of hydrogen evolution reaction, on zinc electrdeposition process and determine the appropriate pH of the bulk, the voltammograms for different pH values are realized (Fig2). The comparison of cyclic voltammograms showed that with increasing pH,the current density of part C decreases from 15.32 to 0.89 mA.cm^{-2}.This indicates a decrease in the evolution of hydrogen on the substrate. It can be concluded that electrodeposition process is significantly dependent on the pH of the solution and a strict control of the pH is necessary to reachhigh current efficiency for zinc electrodeposition.

3.2. Chronoamperometry (CA)

Zinc films are deposited under potentiostatic conditions on steel substrate. Fig.3 illustrate current- transientof zinc deposition obtained at potential deposition -1.3V for 3mn.The curve is characterized by a rising current due to the formation and growth of Zn nuclei until a current maximum, i_m, is reached at a time, tm, the Zn nuclei begin to overlap, then followed by a decaying portion, converging to a limiting current corresponding to linear diffusion of the electroactive ions to electrode surface.

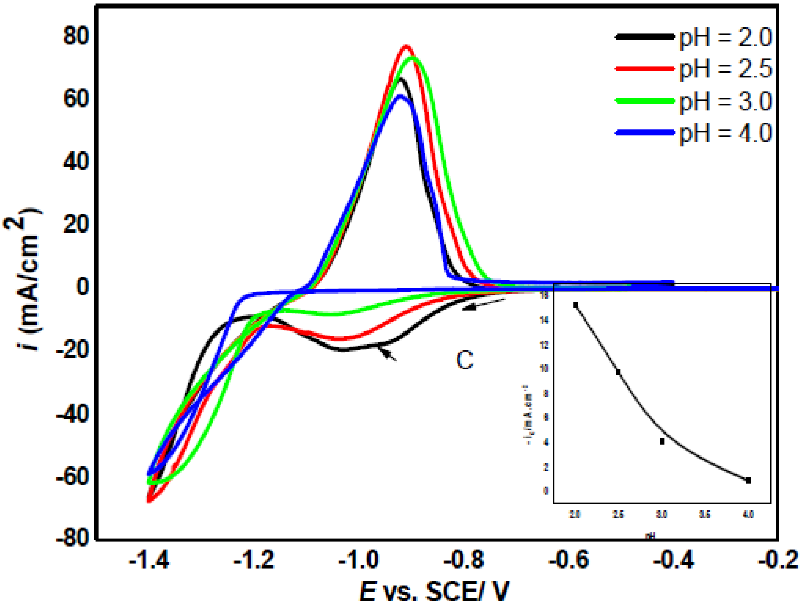


Figure 2. Cyclic voltammograms of steel substrate in 1 mol.L^{-1} Na_2SO_4, 0.4 H_3BO_3 and 0.2 mol.L^{-1} $ZnSO_4 \cdot 7H_2O$ at different pH values, scan rate 20 mV/s.

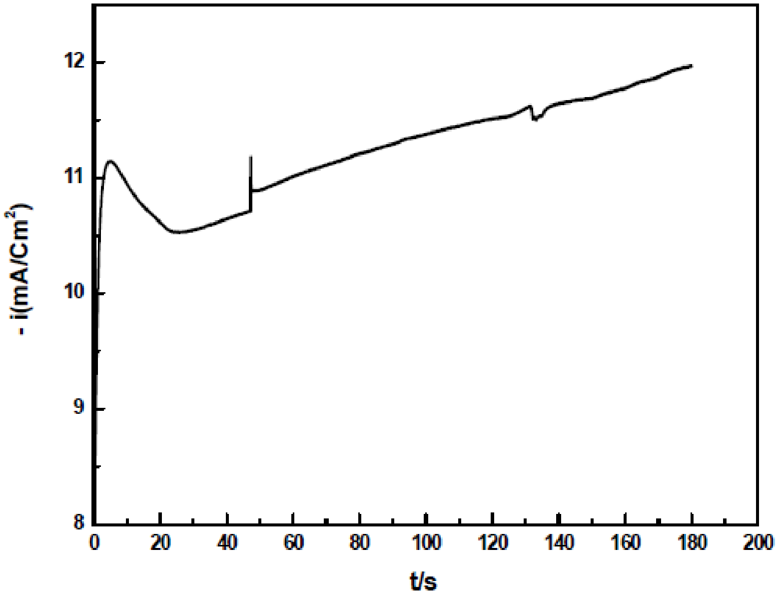


Figure 3. Current-time transient for Zn electrodeposited on steel, at -1.30V.

Nucleation and the growth kinetics were investigated by comparing the experimental results to the theoretical model normalized in terms of the maximum current, i_{max}, and the time atwith the current density reached its maximum value, t_{max} Scharifker et *al* (1983); Gunawardena et *al* (1982).Fig 4 shows the experimental current transients plotted in current-time coordinates, along with the lines for instantaneous and progressive nucleation. According to Fig4, it is apparent that Zn follows an instantaneous nucleation mode. A similar behavior was reported for zinc electrodeposition Songet *al* (2017); Song et *al* (2018) and Xu et *al* (2018).it is a mechanism whereby a large number of Zn nuclei form instantaneously and grow at the same rate, resulting in a homogeneous distribution of crystallite sizes Abbott et *al* (2011a, b).

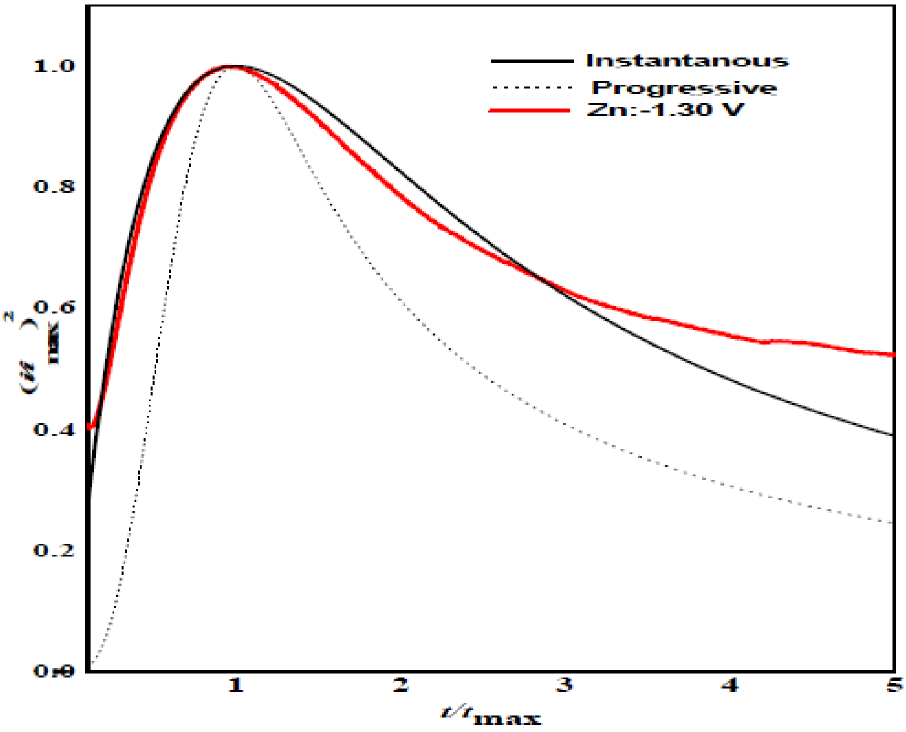


Figure 4. Comparison of experimental data obtained from current-time transients with instantaneous and progressive nucleation models in 1 mol.L^{-1} Na_2SO_4,0.4 mol.L^{-1} H_3BO_3 and 0.2 mol.L^{-1} $ZnSO_4 \cdot 7H_2O$.

4. CORROSION MEASUREMENTS

Corrosion measurementsare carried out in 3.5% NaCl solution, using potentiodynamic polarisation, Tafel plots and electrochemical impedance spectroscopy. Zinc films obtained at different deposition potential are immersed 1hour in test solution.

4.1. Potentiodynamicpolarisation

The potentiodynamic polarization curves obtained for Zn films deposited at different deposition times, immersed for 1 hour in 3.5 wt.% NaCl solution are shown in Fig5.the polarization curves represent the three part of a typical curve for a metal surface in an aggressive environment which are immunity passivation and transpassivity. The potential at which the current density increases sharply is defined as the pitting potential, E_{pit}. For deposition time of 15mn, the passive region is large (-0.320V to 0.124V) and the pitting potential, E_{p} (0.124V) in comparison with films obtained for deposition time of 20mn, the passive region is (-0.20V to -0.0165V) and the pitting potential, E_{p} (-0.0165V).It can be seen that pitting potential of deposit obtained for 15mn was less noble than E_{p} of deposit obtained for 20 mn. This may be attributed to hydrogen evolution for a longer time, which affects on the Zn depositionby the accumulation in the substrate sites.

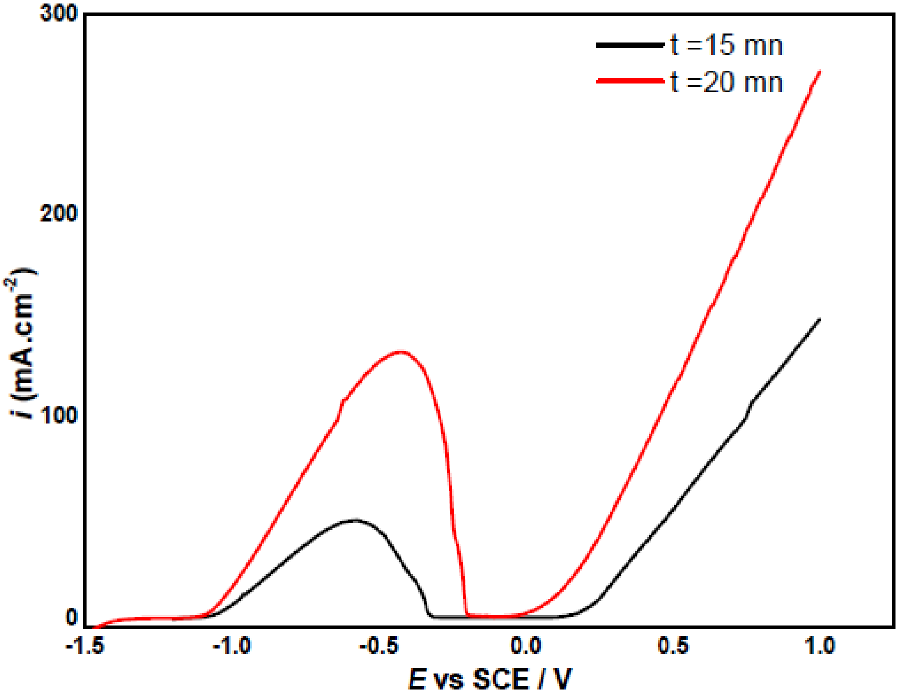


Figure 5. Anodic polarization profile of Zn electrodeposits at different time.

Fig 6illustrates potentiodynamic polarisation curves for Zn films obtained at different deposition potentials for 15 mn, after immersion for 1 hour in 3.5 wt.% NaCl solution. The curves show that Zn film obtained at -1.26 V presentless dissolution in comparison to zinc film obtained at -1.3 V. Furthermore the pitting potential for deposit obtained at -1.26V, shifts slightly to positive direction, so it provide best corrosion resistance.

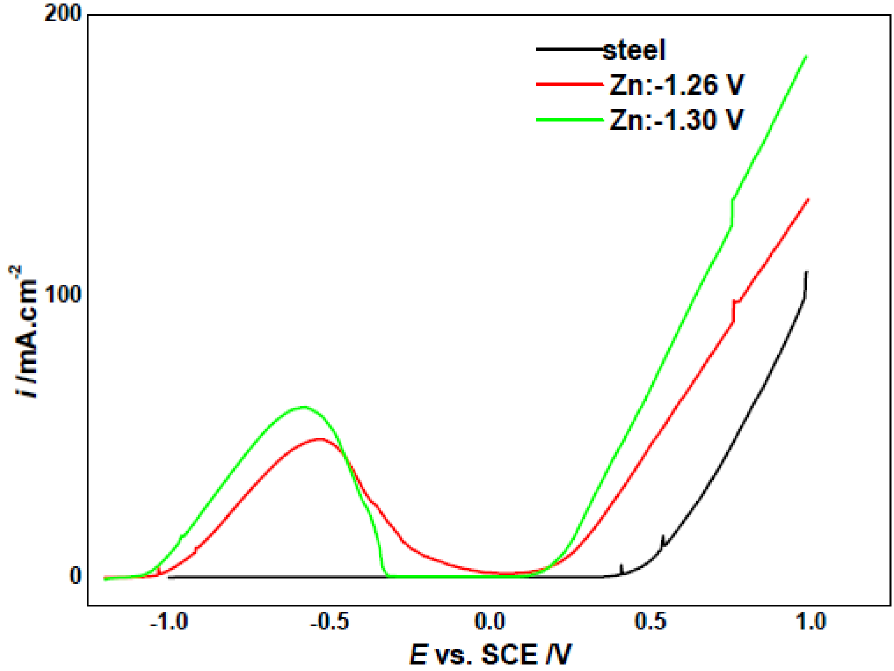
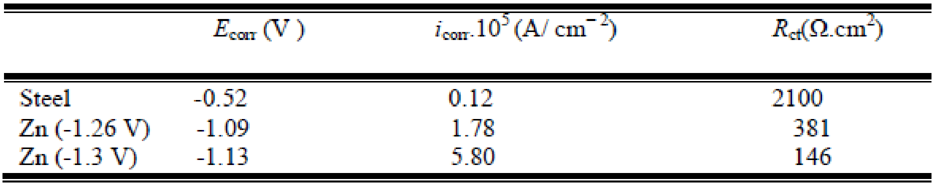


Figure 6. Anodic polarization profile of Zn deposits at different deposition potential.

4.2. Tafel curves

Tafel curves recorded in 3.5% NaCl solution for steel and Zn electrodeposits at different deposition potentials are presented in Fig7. Electrochemical parameters; corrosion current density i_{corr} (corrosion rate) and corrosion potential E_{corr}, of Zn films are summarized in Table 1. It is clear that steel exhibit more noble corrosion potential(-0.52 V) in comparison with zinc films.The shift of corrosion potential to more negative direction, indicatethe sacrificially protect ofzinc films to steel. In the other hand, corrosion current density of the film obtained at -1.26V is lower thanthat of the film obtained at -1.3V.

Table 1. Electrochemical data of steel and Zn films extracted from potentiodynamic polarization curves and electrochemical impedance measurements



	E_{corr} (V)	$i_{corr}.10^5$ (A/ cm^{-2})	R_{ct}(Ω.cm^2)
Steel	-0.52	0.12	2100
Zn (-1.26 V)	-1.09	1.78	381
Zn (-1.3 V)	-1.13	5.80	146

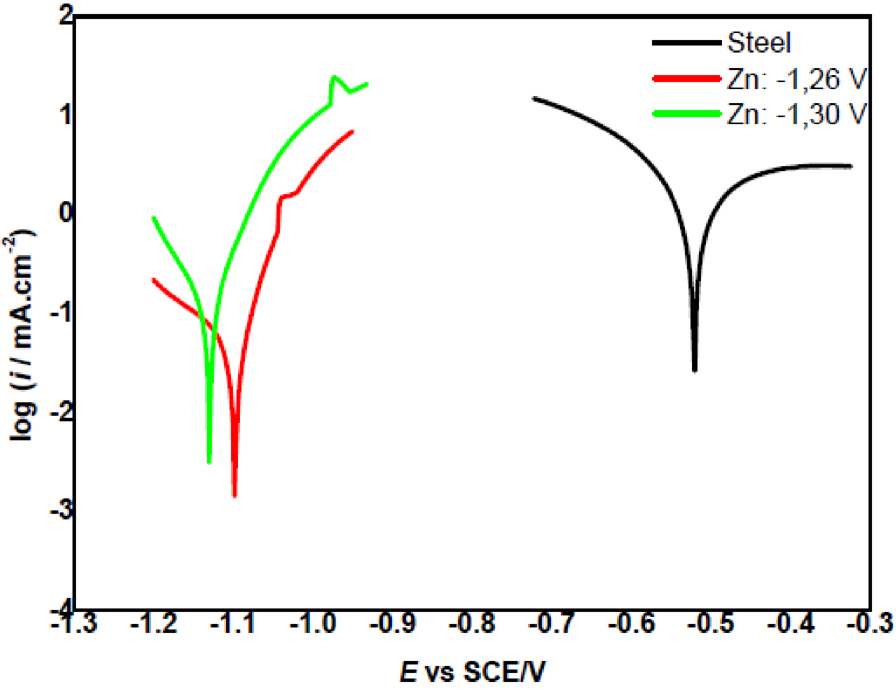


Figure 7. The potentiodynamic polarization curves of Zn deposits at different deposition potentials.

4.3. Electrochemical impedance spectroscopy (EIS)

The impedance diagrams were displayed as Nyquist plots are presented in Fig8.The spectra were obtained at the open circuit potential during exposure 1 hour to NaCl solution. All curves show semicircle at high frequencies, attributed to the charge transfer process. The diameter of the semicircle corresponds to a charge-transfer resistance (R_{ct}).It is clear that the diameter change with deposition potential, thus deposit obtained at -1.26 V showed a superior resistance R_{ct} (Table1)indicating a high corrosion resistance. These results are in accordance to those obtained by potentiodynamic polarization (Fig 6) and Tafel plots (Fig 7).

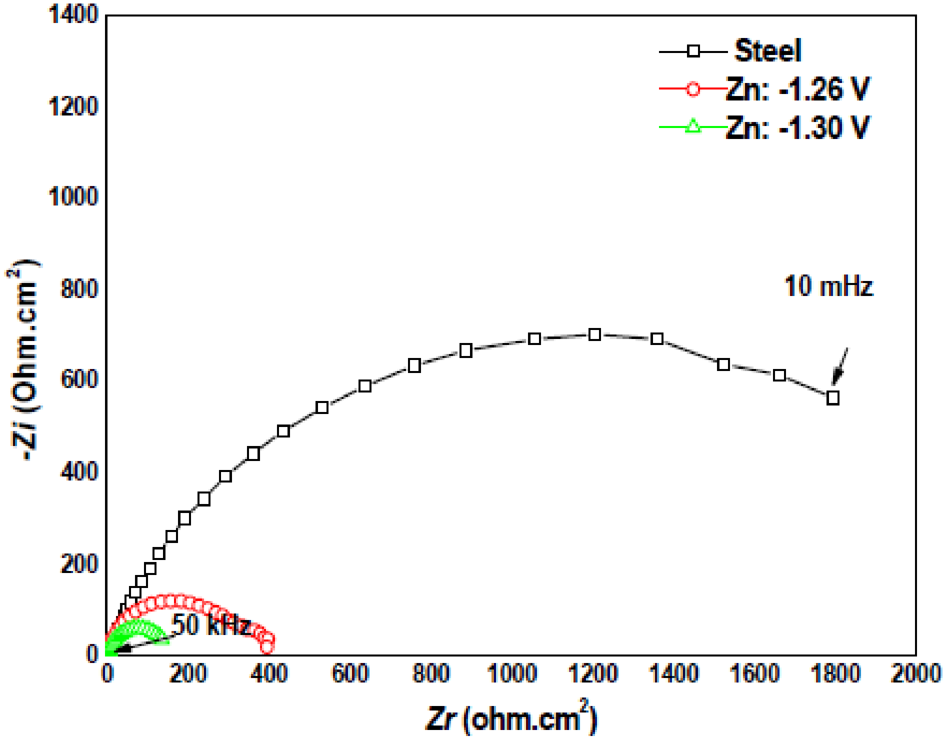


Figure 8. Nyquist impedance obtained for Zn depositsat different deposition potentials.

5. CONCLUSION

Zinc films are electrodepositedfrom sulphate bath on steel, at different deposition potential. Cyclic voltammograms show that a strict control of the pH is crucial parameter for current efficiency for zinc electrodeposition.

Nucleation and the growth kinetics display that Zn follows an instantaneous nucleation mode. Corrosion measurements carried out in 3.5% of NaCl solution obtained by Tafel plots, and electrochemical impedance spectroscopy show that corrosion potential and charge transfer resistance are dependent on deposition potential.

The shift of corrosion potential to more negative direction, indicate the sacrificially protect of zinc films to steel, zinc film obtained at -1.26 V present highresistance, which improve better protection to steel.

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