Electrochemical Impedance Spectroscopy study of Zinc electrodeposition

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Introduction

Zn coatings are widely used for steel protection against corrosion in many fields; electrochemical energy converters, automobile industry, aeronautic industry, batteries applications, food industry…. Zn coatings are extensively used not only because Zn is anodic to steel and thus act as a barrier on the steel surface and sacrificially protect the substrate but also owing to its low cost and natural abundance [1]. The metal can be applied by a variety of techniques including hot dipping, metal spraying, cementation, cladding and electrodeposition [2]. Among them, electrodeposition offer a unique combination of superior properties such as high efficiency, corrosion resistance and low cost [1, 3]. The corrosion characteristics are strongly determined by the texture and microstructure obtained that, in turn, depend on the electrochemical deposition parameters employed, such as current density, temperature, pH, substrate surface preparation and bath composition [4].

The aim of this study is to investigate the effect of current density and pH on the corrosion resistance of Zn deposited coatings from a free additives bath. Electrochemical Impedance Spectroscopy was mainly used for the corrosion study in 3,5% NaCl solution.

Electrochemical Impedance Spectroscopy

Effect of current density

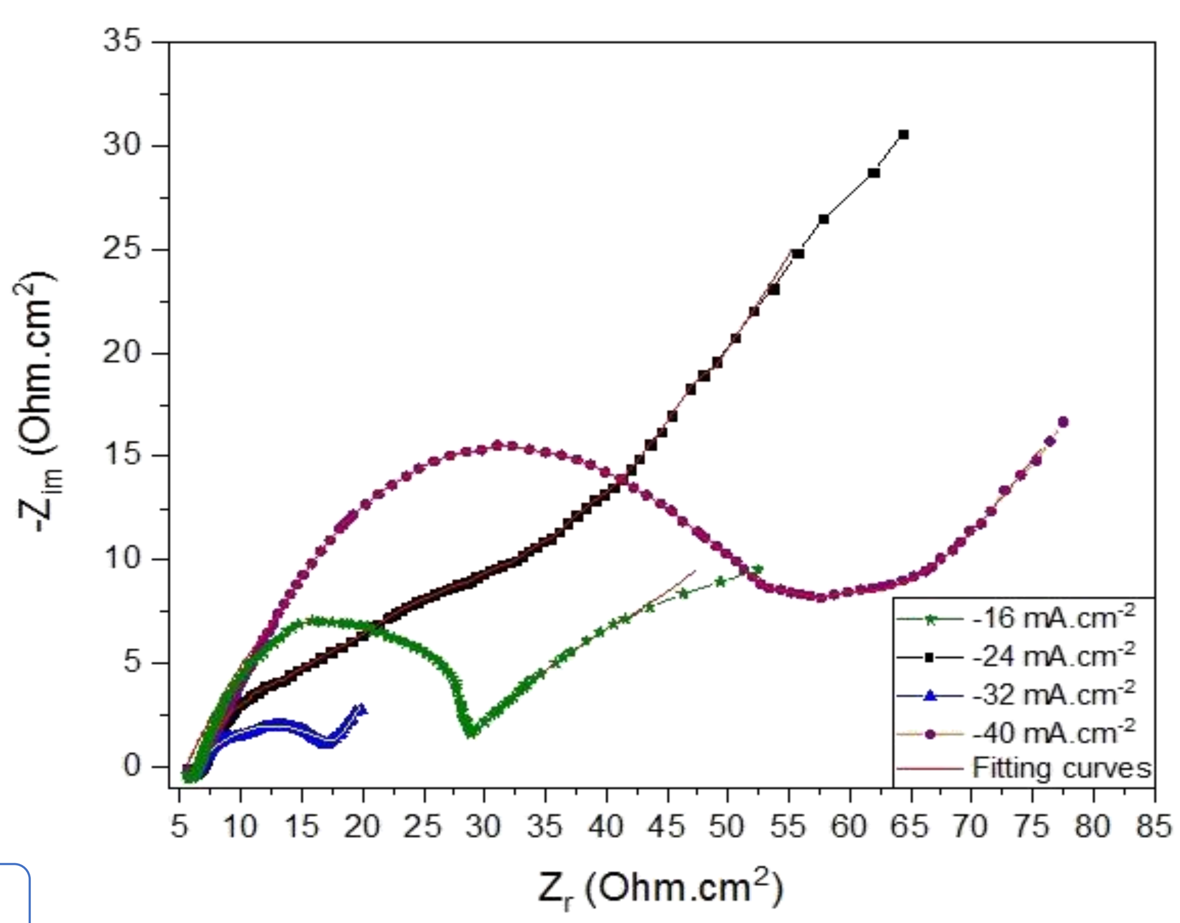

Figure 1 : Nyquist plots of impedance response obtained in 3.5% NaCl solution with different current densities

- A semi-circle aspect is first observed in the Nyquist plot, followed by a straight line whose tangent to the real axis is 45°, which is related to a Warburg diffusion process [5],
- In this case, Warburg impedance represents the diffusion of oxygen from the electrolyte to the pores of zinc [6],

Effect of pH

- At pH = 1.4, we are in the presence of a phenomena of diffusion through a film.
- With increasing the pH value to 3 and 4.5, the coating is more uniform and the Warburg impedance represents the diffusion of oxygen.
- At a pH of 5.5, we note the presence of two loops, related to charge transfer resistance, the double layer capacitance, and oxygen diffusion into the coating. .

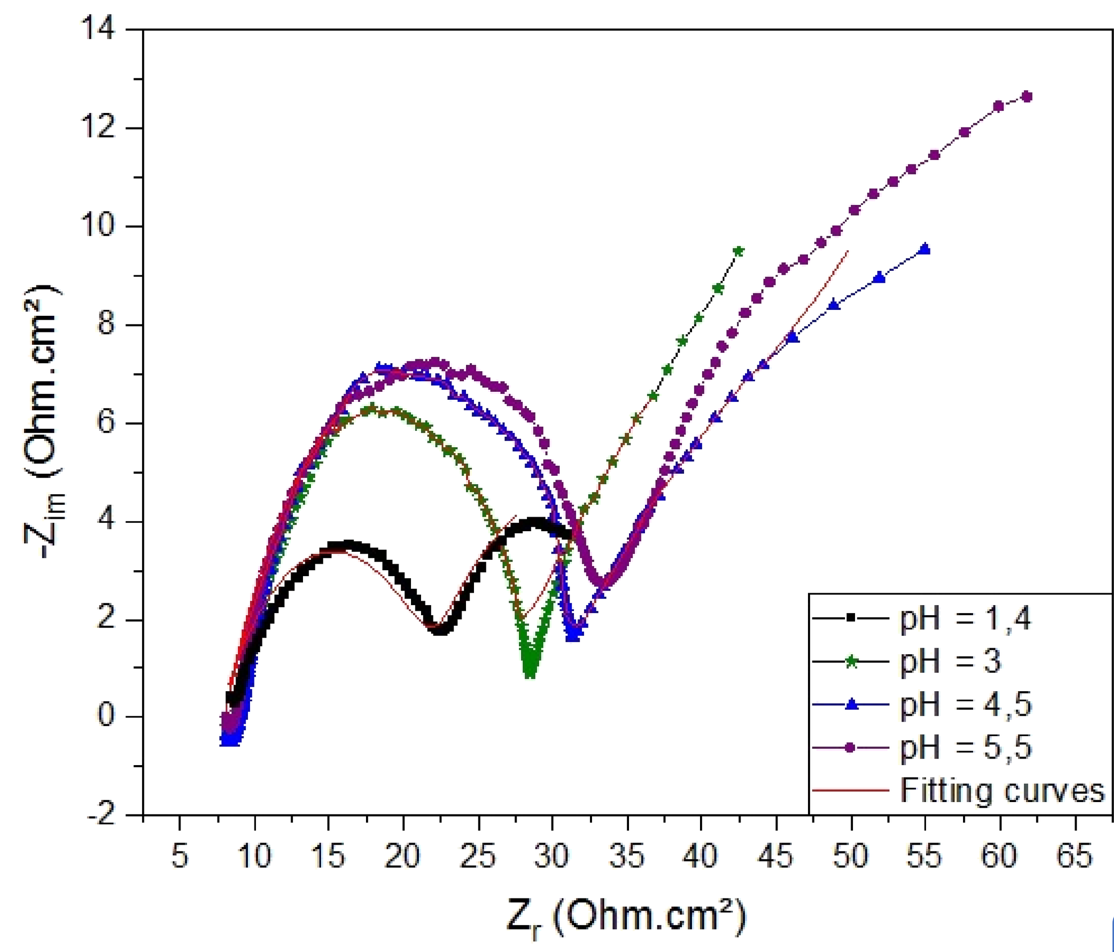

Figure 3 : Nyquist plots of impedance response obtained in 3.5% NaCl solution with different pH values

Results

Equivalent circuit

- The decrease in charge transfer resistance Rct could be associated to the dissolution of new and unstable corroded surface areas, while for a current density of -40 mA.cm-2, the increase in Rct value indicates that the active area became totally covered by precipitated corrosion products
- The increase in Qdl indicates a less compact and less stable layer.
- The polarization resistance Rp showed that the best corrosion resistance is realized with a current density of 40 mA.cm-2 followed by 16 mA.cm-2

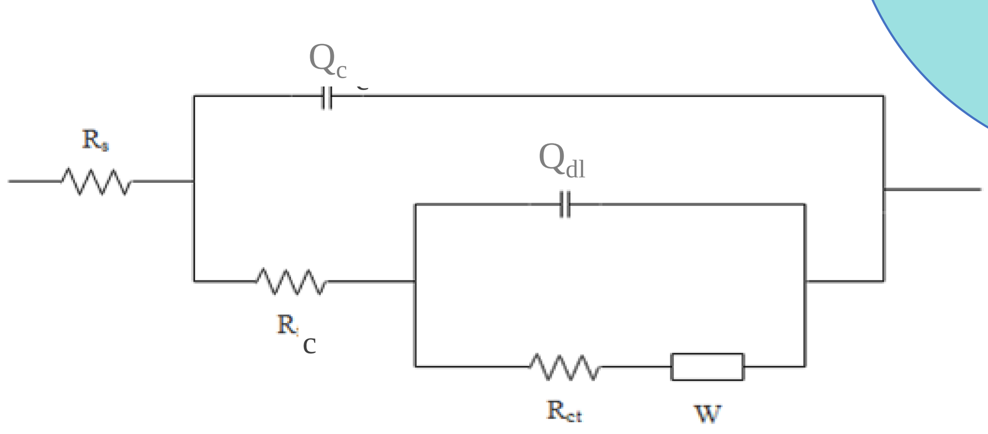

Figure 2 : EC for electrodeposited Zn coatings in 3.5% NaCl at various current densities

Table 1 : Equivalent circuit parameters of Zn coatings with different current densities

j (mA.cm⁻²)	R_s Ω.cm²	Q_c µF.cm²	n_c	R_c Ω.cm²	Q_{dl} µF.cm²	n_{ct}	R_{ct} Ω.cm²	W Ω. $s^{-1/2}$	R_p Ω.cm²
-16	10.75	1.45	0.61	30.05	7.65	0.47	6.75	1.53	36.80
-24	6.49	1.04	0.62	13.96	0.01	0.73	14.91	8.59	28.87
-32	6.05	0.01	0.37	13.24	5.62	0.97	4.68	0.79	17.92
-40	7.49	3.05	0.59	54.73	0.18	0.47	19.53	14.3	74.26

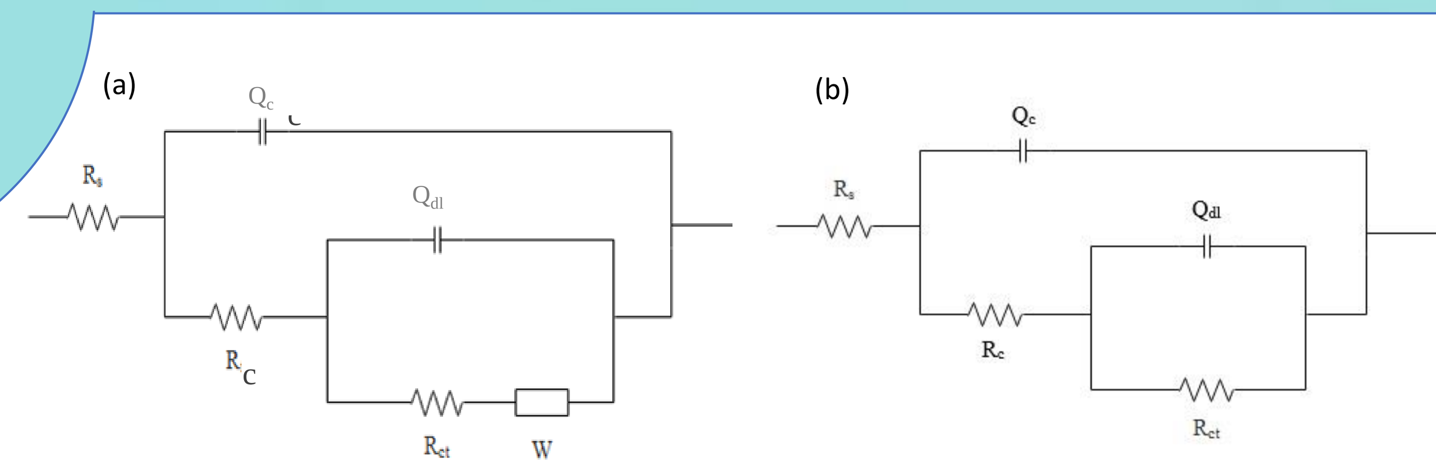

Figure 4 : EC for electrodeposited Zn coatings in 3.5% NaCl at various pH values (a) 1.4, (b) 3, 4.5 and 5.5

- The value of the polarization resistance (Rp) is higher for zinc electrodeposited at pH 5.5 than at pH 1.4, because of the formation of a resistive layer of ZnO,
- The deposit developed at a pH of 4.5 is the one that contains the least impurities, the highest Zn content and provides a good corrosion resistance,

Table 2 : Equivalent circuit parameters of Zn coatings with different pH values

pH	R_s Ω.cm²	Q_c F.S.n⁻¹	n_c	R_c Ω.cm²	Q_{dl} F.S.n⁻¹	n_{ct}	R_{ct} Ω.cm²	W Ω. $s^{-1/2}$	R_p Ω.cm²
1.4	5.175	1.17	0.53	15.12	0.08	0.72	9.25	1.95	24.37
3	11.13	1.10	0.61	20.36	0.37	0.55	12.42	2.4	32.78
4.5	10.75	1.45	0.61	30.05	7.65	0.47	6.75	1.53	36.80
5.5	8.2	0.74	0.59	32.24	4.1	0.49	6.42	4.9	38.66

Conclusion

- The inspection of the effect of the current density on the deposition of Zn on steel substrate showed that the corrosion rate increases with increasing the current density, because of the intensive HER. However, at higher current densities, a local increase in the pH leads to the formation of a passivation layer of oxide/hydroxide zinc products, causing an improvement in the corrosion resistance.
- The corrosion study revealed an increase in the polarization resistance with increasing pH, because of the formation of oxide/hydroxide zinc products with higher pH values. Nevertheless, it was found that the deposit realized at pH 4.5 contains the least impurities, the highest Zn content and provides a good corrosion resistance.

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