



Performance of magnesium-based sacrificial anode for cathodic protection of steel in simulated saline solution

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ABSTRACT

Magnesium is widely used as a sacrificial anode for protecting steel from corrosion. In this paper, the electrochemical behaviour of magnesium sacrificial anodes has been studied using electrochemical impedance spectroscopy (EIS) and polarisation curves, completed by Evans' diagrams (under galvanic conditions) and SEM observations. The impedance diagrams are composed of two capacitive loops at the high and middle frequencies; the first one is related to the charge transfer resistance in parallel to the double layer capacity, the other one is attributed to the magnesium ion concentration. An inductive loop at low frequencies appeared as due to the formation, adsorption and desorption of the corrosion products, on the surface of the anodes. The intensiostatic curves permit the evaluation of the anodes efficiency as a function of the current flow. The obtained Evans' diagrams are discussed taking into account the polarization effects at the electrodes for different experimental conditions.

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Introduction

Corrosion is a phenomenon in which metals tend under the influence of various environmental factors, to return to their native state: oxides, sulfides, carbonates, etc., which are thermodynamically more stable regarding the considered medium. In such aggressive environments, metals undergo a deterioration of their chemical and physical properties [1-4]. Several methods are used for the protection of metals against corrosion [5-8]. One of them is the cathodic protection in which sacrificial anodes, a highly active metals, are used to minimize the corrosion of steel in seawater. Sacrificial anodes have a more negative electrochemical potential than the metal to be protected and hence they will be consumed instead of the metal, which lead to the designation "sacrificial" anode [9-11]. Magnesium is widely used to protect steel because it is more electronegative than it and hence it is capable to supply electrons to the more electropositive steel, providing cathodic protection of this metal surface [12-15].

In the present work, we investigate the electrochemical cor-

rosion behavior of a commercial magnesium anode used as a sacrificial anode for steel. Electrochemical tests, potentiodynamic-potentiostatic polarization and electrochemical impedance spectroscopy (EIS), are conducted in 3% NaCl solution to simulate saline waters. The Mg anode is also characterized by Raman spectroscopy, SEM and EDX techniques.

Experimental procedures

The material used is a sacrificial anode based on magnesium standard type of composition: Mg-6Al-3Zn-2Mn. The samples are polished before use, using abrasive paper polishing of decreasing particle size up to 1000, then they are rinsed with distilled water, degreased with acetone and dried in hot air. The experimental device used for the plot of potentiodynamic and potentiostatic polarization curves is an EGG M.173 chain coupled to an M.175 driver. The equipment used to carry out electrochemical impedance measurements is the PGZ 301 potentiostat/galvanostat assembly associated with the "Volta Master 4" software.

The potentiodynamic polarization curves are obtained with a scanning rate of 30mV/min. This speed allowed us to work in a quasi-stationary conditions and to have a good reproducibility of the results. The plot of the polarization curves in potentiostatic regime aims to study the behavior of our anode in

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the domains delimited by the characteristic potential values: Ecorrosion and Epassivation. The impedance measurements are carried out at 25°C after each polarization in the chloride medium, the amplitude of the sinusoidal voltage applied to the dropout potential is 10 mV peak-to-peak at frequencies between 50 kHz and 10 mHz, with 5 points per decade. For all the tests carried out, a three-electrode cell is used. The auxiliary electrode is a platinum electrode and the reference electrode is a silver chloride electrode saturated with KCl. The working electrode is in form of disc with a surface 5 cm².

Results and discussions

Composition of magnesium anode

To confirm the purity of the material used, a characterization of the commercial sacrificial magnesium anode surface was performed by SEM coupled to EDX. The micrograph and the composition obtained are shown in Fig. 1.

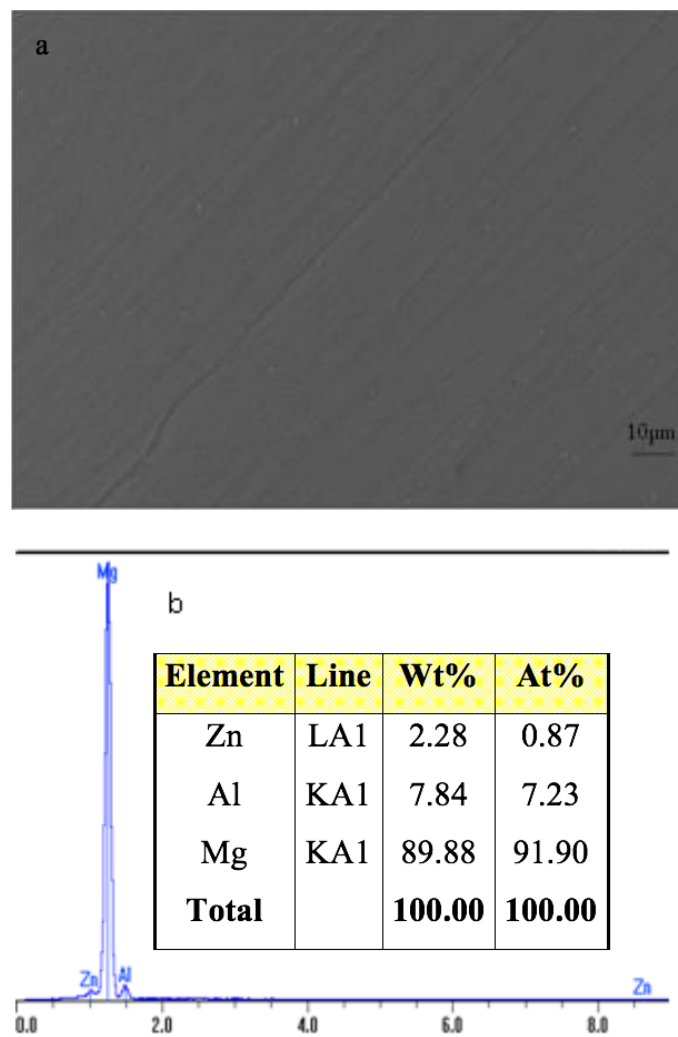


Fig 1. (a) SEM observation, (b) EDX analysis, of the magnesium anode surface before immersion in the corrosive medium.

Open circuit potential measurement

In order to obtain information on the material surface modification, we chose to carry out the electrochemical analyses in a corrosive medium containing 32 g/L NaCl at different immersion time. The open circuit potential evolution of magnesium anode at room temperature is presented in Fig. 2.

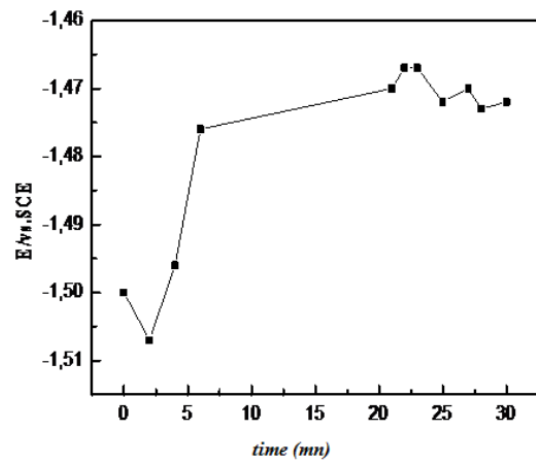


Fig. 2. The open circuit potential of magnesium sacrificial anode in the test solution (3% NaCl).

A slight decrease is observed in the potential towards a stable quasi-stationary limit value. This pattern is characteristic of the stable and active surface of magnesium as shown by SEM observations (Fig. 3) of the surface morphology of the retrieved samples.

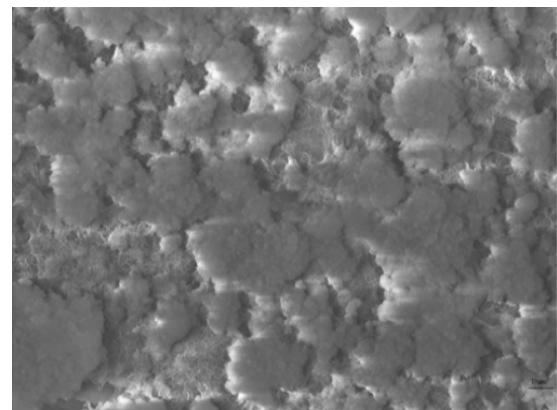


Fig. 3. SEM micrograph of the magnesium anode surface after immersion in 3% NaCl after 30 min.

Polarization curves intensity-potential

Polarization measurements give informations about the behavior and kinetics of the cathodic and anodic reactions. The polarization curves were conducted at various time immersions in NaCl solution.

Fig. 4 depicts typical potentiodynamic polarization curves of steel susceptible to homogeneous corrosion.

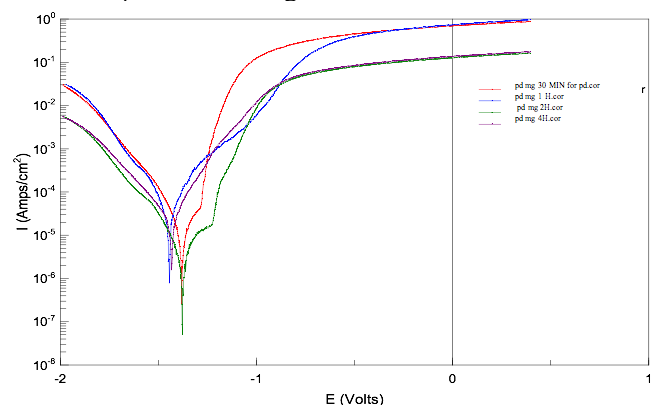


Fig. 4. Potentiodynamic polarization curves of Magnesium anode in NaCl at different immersion time.

Fig. 5 represents the micrograph of Mg anode after 5 days of exposure to the aggressive environment. The SEM observations allow us to confirm the homogeneity of the general attack. The surface roughness and the presence of craters observed are attributed to the intense formation of hydrogen as a result of the depolarization cathodic reaction.

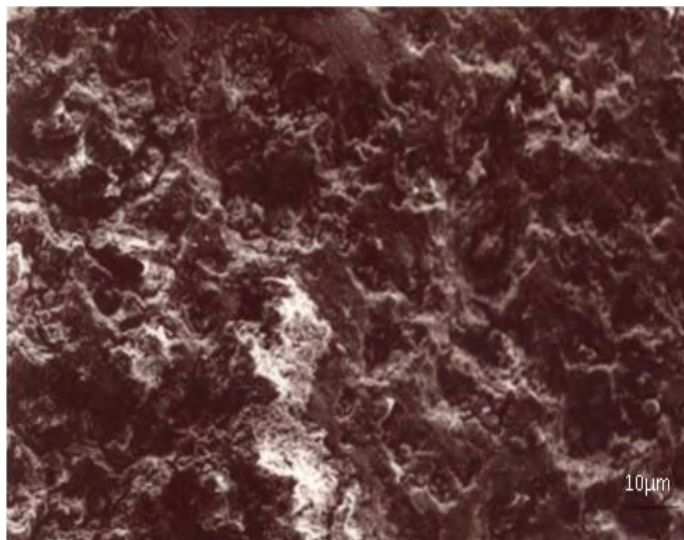


Fig. 5. SEM image of Mg anode at corrosion potential.

Intentiostatic tests

The intiostatic tests are designed to simulate the service operating conditions of sacrificial magnesium anodes. In general, the potential evolution as a function of time at different imposed currents values recorded in each case is sufficiently negative (Fig. 6). It is always lower than the theoretical protection potential of steel (-850 mV) for all values of the imposed current. The potential values differed slightly, but only at the beginning of the tests. Moreover, the anodes working at low current density need a longer time to achieve a steady state, but the other ones reached a stable level faster. The stability of the potential corresponds to the homogeneous corrosion of Mg surface.

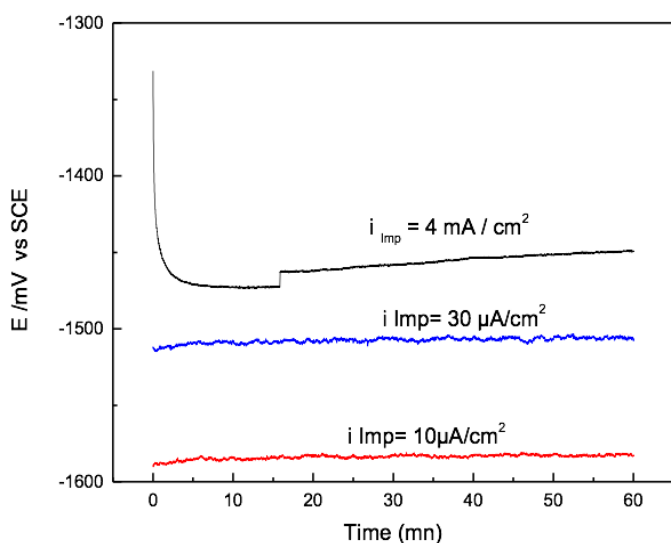


Fig. 6. Potential stabilization on time of Mg anode in 3% NaCl.

Electrochemical impedance tests

The corrosion behavior of Mg anode was investigated by electrochemical impedance spectroscopy (EIS) at different imposed current density in the same solution and the same experimental conditions. EIS data were plotted in the form of Nyquist diagrams (complex versus real components of the impedance) as reported in Fig. 7 and 8.

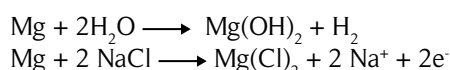
Nyquist representation of magnesium anode showed two capacitive semicircles in high and medium frequencies and an inductive semicircle in low frequencies. In general, the first capacitive semicircle is attributed to the electrochemical double-layer capacity and the second corresponds to the Mg^+ relaxation [16]. The inductive component is attributed to a semi-protector deposit at the electrode surface [17]. The intiostatic polarisation tests have allowed to vary the state of surface recovery by corrosion products. When the recovery is total (high current intensities), the inductive behavior doesn't appear. A partial surface recovery was obtained at the corrosion potential and at the end of an anodic polarization (low current intensity), an inductive arc was observed.

In order to describe the corrosion resistance of the system from EIS data, the equivalent circuit (EC) in Figure 9 was considered. The RC components correspond to the double layer capacity and to the relaxation of the Mg^+ species, let us conclude that the first loop corresponds to the recovery rate of a semi-protective deposit. The second inductive loop can be attributed to the relaxation of the hydrogen recovery rate or to the presence of a second magnesium hydride deposit. Under these conditions, the second inductive component would be related to the relaxation of the adsorbed hydrogen Hads.

Characterization by Raman spectroscopy and EDX

The SEM micrographs (Fig. 10) of Mg surface exposed to the aggressive solution for five days exhibited the cauliflower morphology that is associated with the presence of O-H group as highlighted by Raman spectroscopy. This allows to suggest that deposit composition is of $\text{Mg}(\text{OH})_2$ type. This deposit of the powdery constitution is not protective.

The EDX results of magnesium after immersion in 3% NaCl (figure 11) show that oxygen and chlore amounts are increased. This indicates that $\text{Mg}(\text{OH})_2$ and MgCl_2 are formed at the electrode surface according to the following reactions:



The Raman spectrum of magnesium anode is presented in figure 12 where two different zones are observed. In the low-wavenumber range, there is a Raman peak at 542-545 cm^{-1} with lower wavenumber values (443-459 cm^{-1}). One of the possible corrosion products on the magnesium anode is $\text{Mg}(\text{OH})_2$ or MgO . Indeed, the Raman bands at 279 cm^{-1} and 443 cm^{-1} are characteristic of $\text{Mg}(\text{OH})_2$ and MgO . For high wavenumber values, less intense Raman peaks were recorded at 3649 and 3718 cm^{-1} , suggesting that the presence of OH-ion groups in the form of water is most likely derived from $\text{Mg}(\text{OH})_2$. In several areas of the magnesium anode, a peak was observed at 1088-1089 cm^{-1} . This intense peak corres-

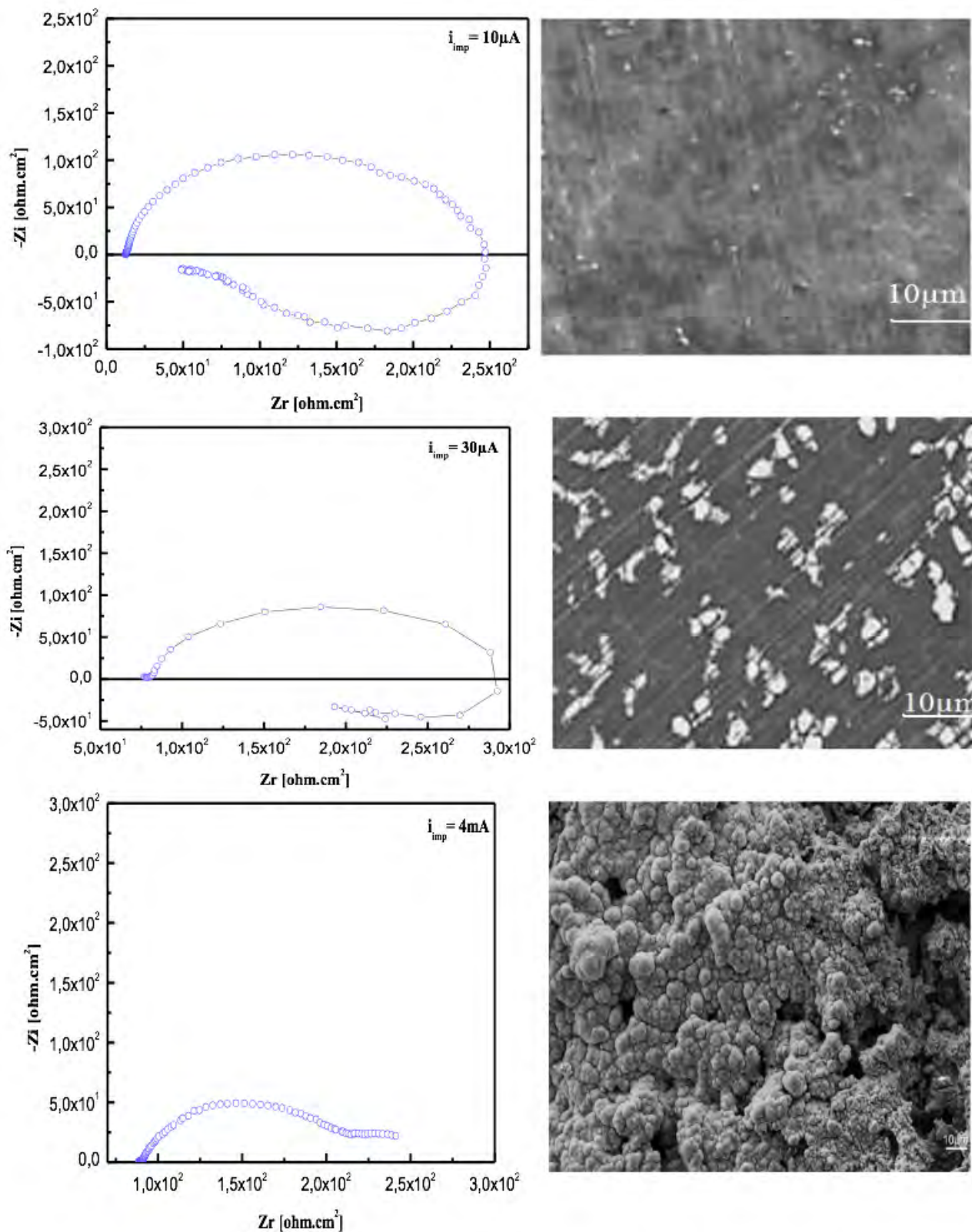


Fig. 7. Measured impedance spectra of magnesium at different imposed current in 3% NaCl.

ponds to the Cl-Mg group indicating the presence of $MgCl_2$. The EDX analysis of the magnesium anode reveals that the magnesium content decreases, while the amount of chlorine and oxygen decreases.

Conclusion

In this paper, electrochemical behavior of Mg sacrificial anode and its microstructure in the chloride-containing

aqueous solution have been studied by using EIS, potentiodynamic polarization and open circuit potential measurements, SEM-EDX microscopy and Raman spectroscopy. The Results show that when Mg anode is exposed to the corrosive medium, macroscopical corrosion damage initiates. Polarization behavior of blank Mg anode makes significant changes including the shift of corrosion potential E_{corr} towards a nobler values, aggravation of E_{corr} fluctuation, an extension of the apparent inducing period for pitting, increments of both ano-

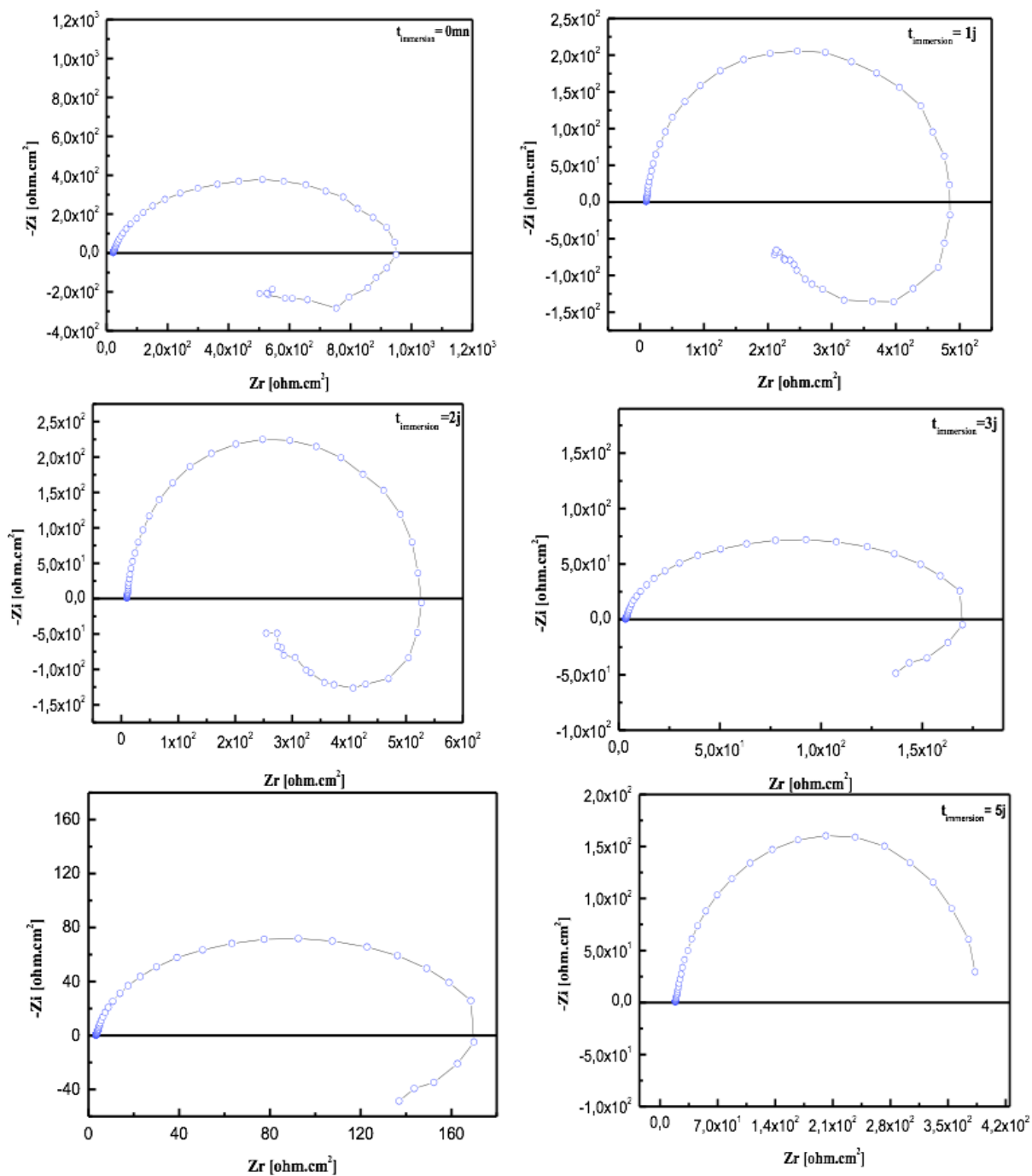


Fig. 8. Measured impedance spectra of magnesium at different time immersion in 3% NaCl.

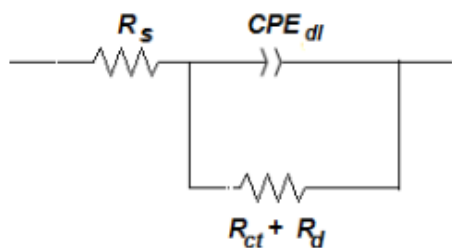


Fig. 9. Equivalent circuit (EC) used to model the impedance data.

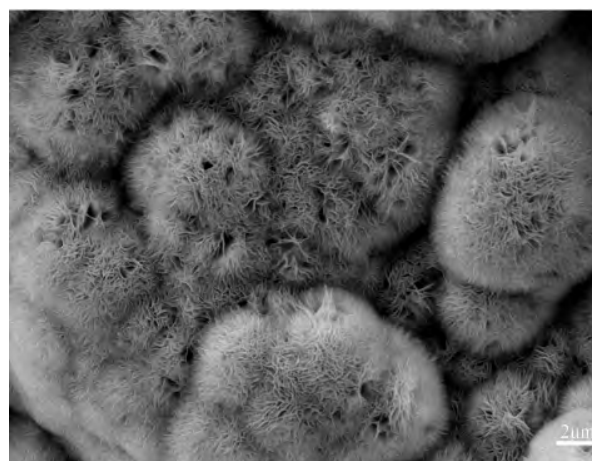


Fig. 10. Cauliflower morphology of the deposits formed on magnesium surface.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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