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Aqueous extract of *Rosmarinus officinalis* L. as inhibitor of Al–Mg alloy corrosion in chloride solution*

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Abstract

The first neutral phenol subfraction of the aqueous extract of rosemary leaves was studied as corrosion inhibitor for the Al–2.5Mg alloy in a 3% NaCl solution at 25 °C. Experiments were carried out over a wide range of concentrations. The results show that the additive adsorbs on the alloy according to the Freundlich isotherm. The polarization curves show that the first neutral subfraction acts as a cathodic-type inhibitor. The impedance spectrum obtained was interpreted in terms of change in characteristics of the natural oxide film at the surface of the alloy. Equivalent circuits, which represent the system, are proposed and individual circuit elements are defined.

1. Introduction

Due to the various industrial applications and economic importance of aluminium and its alloys, its protection against corrosion has attracted much attention [1–10]. Most aluminium alloys have good corrosion resistance towards natural atmospheres and other environments, because aluminium alloy surfaces are covered with a natural oxide film of thickness about 5 nm. This oxide film is stable over the pH range 4 to 9. However, in the presence of aggressive ions, like chloride, the protective layer can be locally destroyed and corrosive attack takes place [11].

One of the methods to protect metals or alloys against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate [12]. Unfortunately, many of the inhibitors used are inorganic salts or organic compounds with toxic properties or limited solubility. Increasing awareness of health and ecological risks has drawn attention to finding more suitable inhibitors, which are nontoxic.

The importance and wide application of alloys of aluminium with magnesium (i.e. in shipbuilding, chemical and food-processing industry) have provided an incentive for research into the possibility of inhibition of corrosion of unprotected Al–2.5Mg alloy in a 3% NaCl solution by means of natural antioxidant from rosemary leaves. Rosemary (*Rosmarinus officinalis* L.) is an aromatic plant of Mediterranean origin with outstanding antioxidant [13] and antimicrobial [14] properties.

2. Experimental details

The experiments were carried out with the Al–2.5Mg alloy. Prior to each measurement the electrode was polished mechanically and degreased in alcohol. A new electrode surface was used for each run. The immersion time was 30 min and the measurements were performed at least twice. The electrochemical glass cell was of the usual type with provision for purging with purified nitrogen and thermostatting (25 °C). A large platinum sheet as a counter electrode and a saturated calomel electrode (SCE) in contact with the working electrode via Luggin capillary were used. The basic solution was 3% NaCl to which the additives were added in varying concentrations (from 1×10^{-7} to 1×10^{-3} M). Potentiodynamic polarization curves were produced using a potentiostat (PAR M273) with scanning rate of 2 mV s^{-1}. Anodic and cathodic branches of the polarization curves were recorded and joined by a computer into a Tafel diagram. The least squares method was used to extrapolate Tafel straight lines and to determine the electrochemical parameters. When performing impedance measurements a lock-in amplifier (PAR M5210), was also used. Impedance measurement were carried out at the open circuit potential (OCP) 30 min after the electrode had been immersed in the test solution. The a.c. signal was 10 mV

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peak-to-peak with five data points per decade. The frequency range studied was 50 kHz to 30 mHz.

The rosemary leaves dried in air for seven days. The polyphenolic constituents were extracted from the plant material with water (maceration 6 h, room temperature). The raw extract was purified by means of diethyl ether. Fractionation into acidic and neutral phenolic compounds was carried out on Sep Pak C18 cartridges (Waters Associates, Milford, MA, USA). The HPLC–RP (high-pressure liquid chromatography of the reverse phase) separation in the neutral phenolic fraction, using gradient elution, was described previously [15]. The catechin monomer: (+)-catechin was identified by its retention time, using the external standard method. The HPCL system used was from Varian, with a 9010 pump, a u.v.–vis. 9050 detector, and a 4400 integrator standard of (+)-catechin, purchased from Aldrich (USA). All solvents were obtained from Merck (Germany). The HPLC-grade water was prepared by redestillation. In this work the first neutral phenol subfraction was used for further investigation.

3. Results and discussion

The analysis of composition of the first neutral subfraction by means of HPLC–RP technique has confirmed the presence of a natural polyphenolic compound -monomer (+)-catechin, as can be seen in the chromatogram shown (Figure 1). This subfraction may therefore be called the 'catechin fraction'.

3.1. *OCP measurements*

The OCP against time plots in quiescent and deaerated 3% NaCl without and with addition of catechin fraction and commercial (+)-catechin are shown in Figure 2. The time needed to reach a stable OCP values was less than 30 min. The values of the open circuit potential in the presence of additives were shifted by approximately 35 mV in the negative direction relative to the pure 3% NaCl solution.

3.2. *Polarization measurements*

Figure 3 shows the potentiodynamic polarization curves for the Al–2.5Mg alloy in a 3% NaCl solution both with and without the catechin fraction in different concentrations.

Figure 3 indicates that the addition of the catechin fraction reduces the cathodic current density without affecting active anodic dissolution. Since the measurements were carried out in deaerated solutions, the only cathodic reaction possible was hydrogen evolution, which takes place very slowly by dissociation of water molecules catalysed by the Al_2O_3 film:

$$2\,H_2O \rightarrow H_3O^+ + OH^- \tag{1}$$

$$2\,H_3O^+ + 2\,e^- \leftrightarrow H_2 + 2\,H_2O \tag{2}$$

The catechin fraction affects the cathodic hydrogen evolution, its effect weakening with the decrease in concentration. The form of anodic polarization curves in the presence of the catechin fraction resembles the curve obtained in a pure NaCl solution. This means that this fraction does not affect anodic metal dissolution through the naturally formed oxide film. For comparison, the same potentiodynamic measurements were carried out with the commercial (+)-catechin, whose effect on the cathodic current density is shown in Figure 4.

The inhibition efficiency of additives, E, and surface coverage, Θ, for the catechin fraction and the commercial (+)-catechin were determined from the corrosion current density obtained by intersection of cathodic and anodic Tafel lines, according to the equation:

$$E = \Theta \times 100 = \frac{i_{\mathrm{cor}} - (i_{\mathrm{cor}})_{\mathrm{inh}}}{i_{\mathrm{cor}}} \times 100 \tag{3}$$

were i_{cor} is the corrosion current density of the uninhibited solution, and $(i_{\mathrm{cor}})_{\mathrm{inh}}$ the corrosion current density of the inhibited solution. Table 1 lists the values obtained. Equation 3 can be used only on the basis that

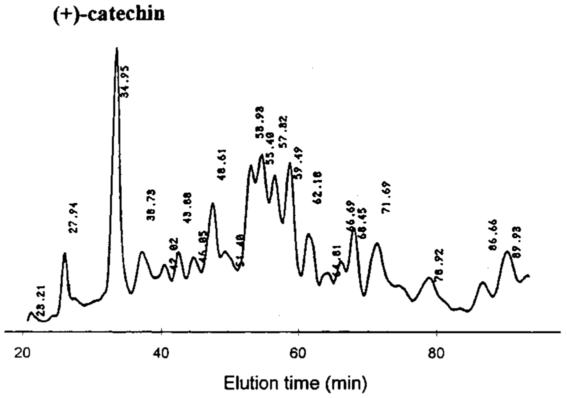

Fig. 1. The HPLC–RP chromatograph of the neutral phenolic fraction of the aqueous extract of rosemary leaves.

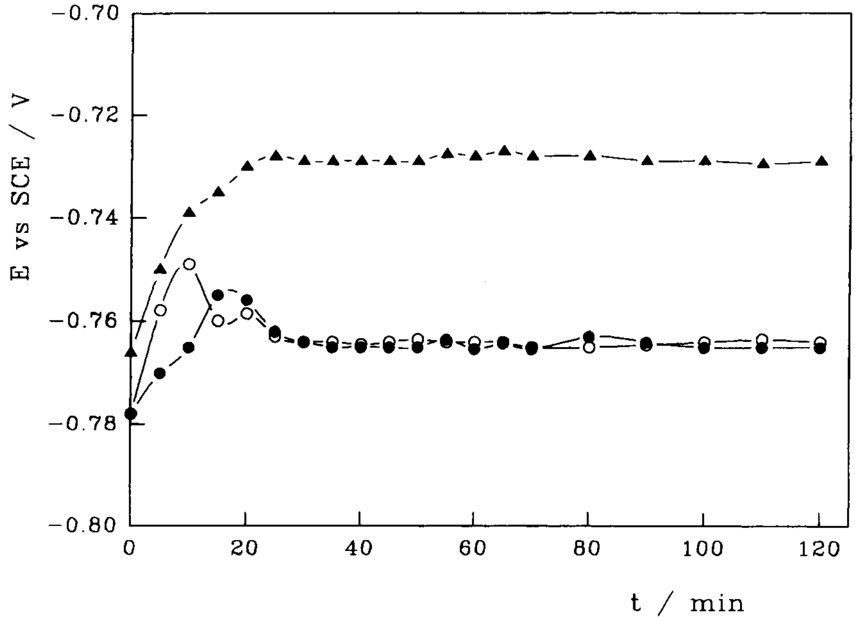

Fig. 2. Open circuit potential (OCP) against time curves in quiescent and deaerated 3% NaCl solution without (▲) and with 1 × 10^{-7} M catechin fraction (●) and commercial (+)-catechin (○).

adsorbed molecules of the substance mechanically screen the coated part of the electrode surface and, therefore, protect it from the action of the corrosive medium [16].

The observed changes in Θ are shown in Figure 5 as functions of concentration of the examined catechin fraction and the commercial (+)-catechin in a 3% NaCl solution. The Freundlich adsorption isotherm [17] is

$$\Theta = KC^n \quad (4)$$

where $0 < n < 1$, or

$$\ln \Theta = \ln K + n \ln C \quad (5)$$

K and *C* represent the equilibrium constants of adsorption and the additive concentration, respectively. A plot of ln Θ against ln *C* would give a straight line of intercept ln *K* if Equation 5 is applicable. These plots are shown for both additives in Figure 5, and are linear, which suggests that the Freundlich adsorption isotherm is obeyed.

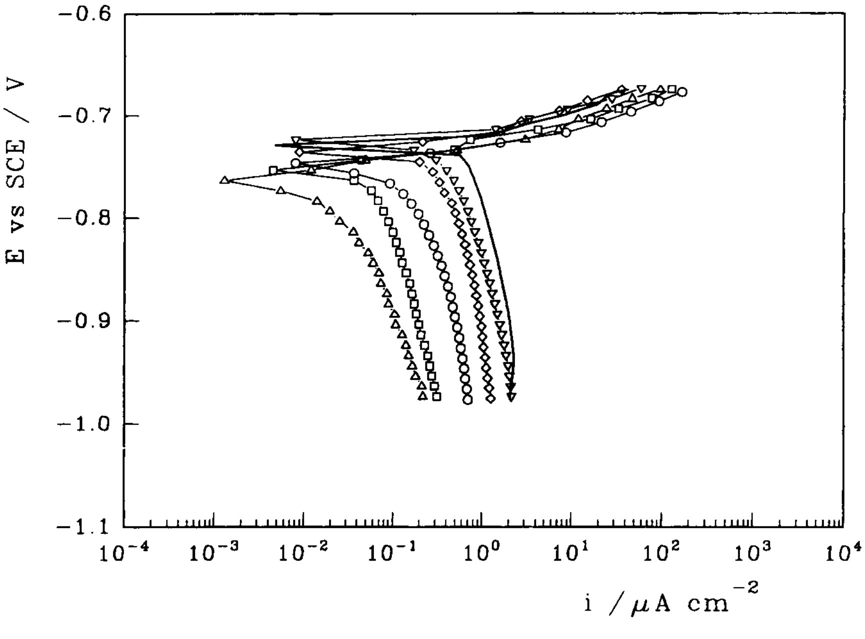

Fig. 3. Potentiodynamic polarization curves for the Al–2.5Mg alloy in 3% NaCl in the absence (——) and in the presence of the catechin fraction with varied concentrations of (+)-catechin. Concentrations: (△) 1 × 10^{-3}, (□) 1 × 10^{-4}, (○) 1 × 10^{-5}, (◇) 1 × 10^{-6} and (▽) 1 × 10^{-7} M.

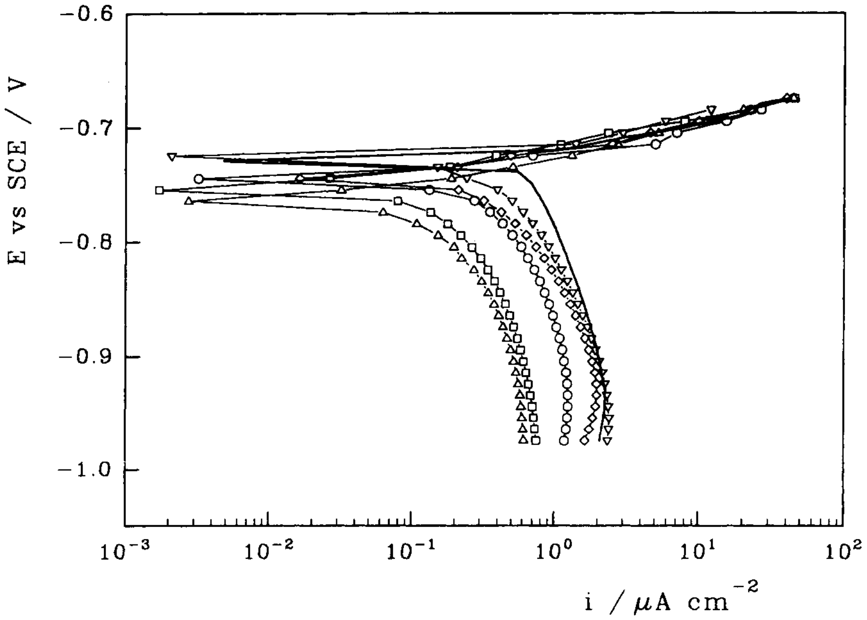

Fig. 4. Potentiodynamic polarization curves for the Al–2.5Mg alloy in 3% NaCl in the absence (——) and in the presence of the commercial catechin in varied concentrations. Concentrations: (△) 1×10^{-3}, (□) 1×10^{-4}, (○) 1×10^{-5}, (◇) 1×10^{-6} and (▽) 1×10^{-7} M.

The equilibrium constant of adsorption, K, is related to the standard free energy of adsorption, $\Delta G^{\circ}_{\text{ads}}$ by

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{\text{ads}}}{RT}\right) \tag{6}$$

The value 55.5 in the above equation is the concentration of water in the solution (M). Table 2 lists the thermodynamic data obtained from the adsorption isotherms. The values obtained indicate physical adsorption of organic matter on the surface of the metal. A comparison of results obtained shows similarity in behavior, which confirms that (+)-catechin is responsible for the inhibitory action of the catechin fraction of the aqueous rosemary extract. Some differences are due to synergetic action of some substances whose probable presence is due to the impossibility of ideal extraction.

The literature indicates that natural polyphenolic compounds containing a catechol group in their B-ring (vicinal hydroxyl groups) readily form complexes with di- and trivalent metal ions [18, 19]. The inhibitory action of the compounds considered could therefore be explained by the formation of complexes in the form of chelates with aluminium ions in the solution (Figure 6), and subsequent precipitation of the complex formed at the surface of the alloy in places where the oxide film has been destroyed. The thin layer formed presents a physical barrier preventing electrolyte action on the metal surface.

Table 1. Density of corrosion currents and surface coverage for the Al–2.5Mg alloy in 3% NaCl solution in the absence and in the presence of varied concentrations of the catechin fraction and commercial (+)-catechin

C/M	0	1×10^{-7}	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}
catechin fraction						
i_{cor}/μA cm^{-2}	0.720	0.340	0.295	0.230	0.118	0.044
θ	–	0.528	0.590	0.681	0.836	0.938
(+)-*catechin*						
i_{cor}/μA cm^{-2}	0.720	0.350	0.306	0.274	0.192	0.131
θ	–	0.514	0.575	0.619	0.733	0.818

3.3. *Impedance measurement*

Figure 7 shows the Nyquist plot for the Al–2.5Mg alloy in a 3% NaCl solution at OCP. The Bode plot leads to no indication of hidden features at high frequencies. As can be seen, two loops were observed in the Nyquist diagram: (a) the capacitive loop at high frequencies; (b) the inductive loop at low frequencies. The capacitive time constant at high frequencies is attributed to the reactions involved in formation of the oxide layer [20, 21] or to the oxide layer itself [22–24]. An oxide film is usually considered to be a parallel circuit of resistance due to ionic conduction in the oxide, and a capacitance due to dielectric properties of the oxide. The inductive loop at low frequencies can be attributed to the observed localized process at the oxide/electrolyte interface [23] which defines the faradaic processes in the system examined.

The effect of the catechin fraction on the impedance spectra of the Al–2.5Mg alloy in a 3% NaCl solution at OCP is shown in Figure 8. The spectra show that the impedance changes rapidly with inhibitor concentration. The changes are observed by the abrupt growth of diameter and size of the capacitive semicircle, which probably reflects physical blocking of the alloy surface. Furthermore, at a catechin fraction concentration $\geq 10^{-6}$ M the inductive loop in the Nyquist complex plane completely disappears, which indicates prevention

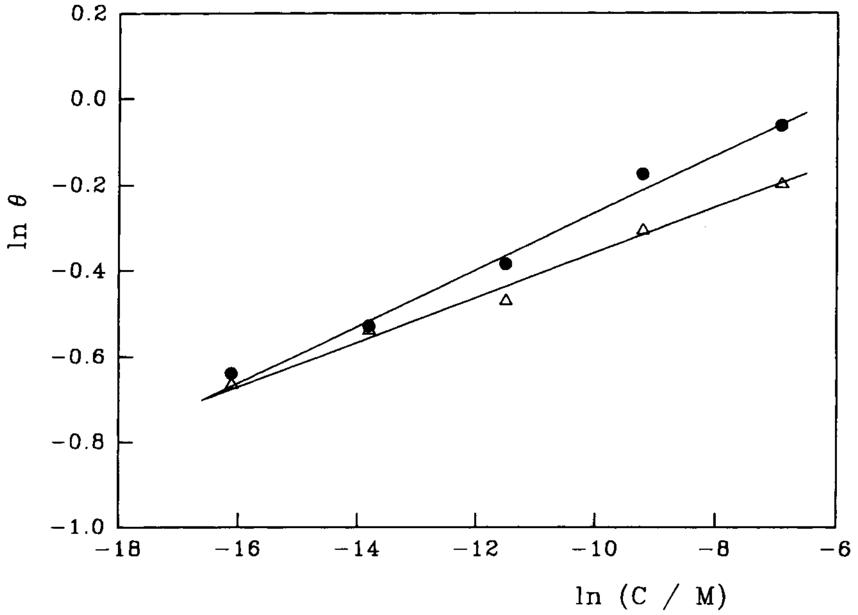

Fig. 5. Adsorption isotherms for the catechin fraction (●) and commercial catechin (Δ) on the Al–2.5Mg alloy in 3% NaCl at 25 °C.

of local corrosion. The capacitive properties of systems considered in the presence of the catechin fraction are attributable to the dielectric properties of the surface (metal–oxide–inhibitor) adsorption layer.

In mathematical analysis of impedance diagrams the constant phase element, CPE, was used instead of an 'Ideal' capacitor to account for the deviations observed as capacitive loops are depressed. The impedance, Z_{CPE}, of CPE is described by the expression [25, 26]:

$$Z_{\mathrm{CPE}} = Q^{-1}(i\omega)^{-n} \tag{7}$$

with Q and n constants, that can be used in data fitting when interpreting frequency dispersions. When the value of n is close to 1, the CPE behaves like an ideal capacitance. The constant phase element, with the impedance defined by Equation 7, may represent either a single CPE or a sum of two or more CPEs of different physical origin, becoming dominant in the same frequency range.

Figure 9(a) shows the equivalent circuit used to fit the experimental data. It consists of a CPE (substituting for capacity in the equivalent circuit $n \approx 1$ and $Q \approx C$) in parallel to the series resistors R_1 and R_2 and an inductance L in parallel to R_2. R_{el} corresponds to the electrolyte resistance and was found to be of order $4\ \Omega\ \mathrm{cm}^2$. The impedance corresponding to the equivalent circuit consisting of R_1, R_2, C and L may be considered as a general term, including faradaic impedance effects. The characteristic values of Z_{f} are the charge transfer resistance, R_{ct}, and the polarization resistance, R_{p} [22]. The charge transfer corresponds to the sum of R_1 and R_2 and the polarization resistance, R_1.

The parameters of the equivalent circuit R_{el}, R_1, Q, R_2 and L were evaluated using a simple least squares fit procedure and are presented in Table 3. From the Table it can be seen that, when the catechin fraction concen-

Table 2. Adsorption equilibrium constant and standard free adsorption energy for the Al–2.5Mg alloy in a 3% NaCl solution in the presence of the catechin fraction and the commercial (+)-catechin

	K/M^{-1}	$\Delta G^{\circ}_{\mathrm{ads}}/\mathrm{kJ\ mol}^{-1}$
catechin fraction	1.48	−10.9
(+)-catechin	1.16	−10.3

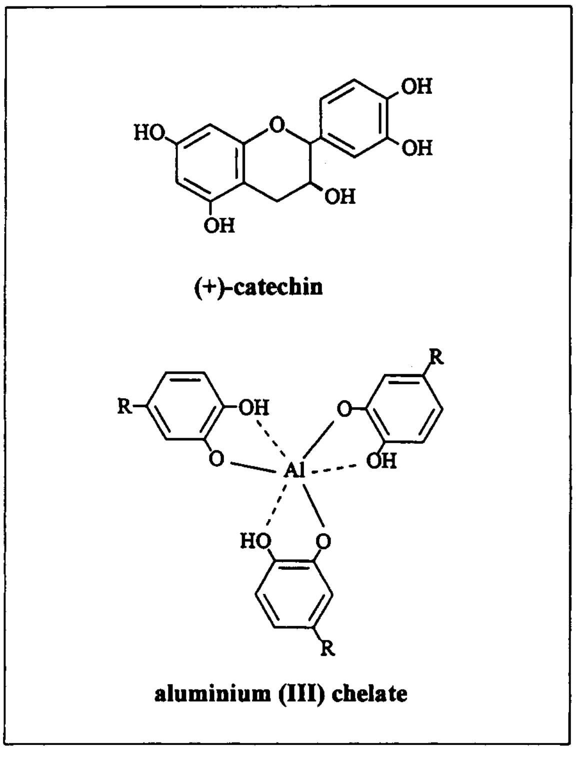

Fig. 6. Molecular structures of the (+)-catechin and aluminium(III) chelate.

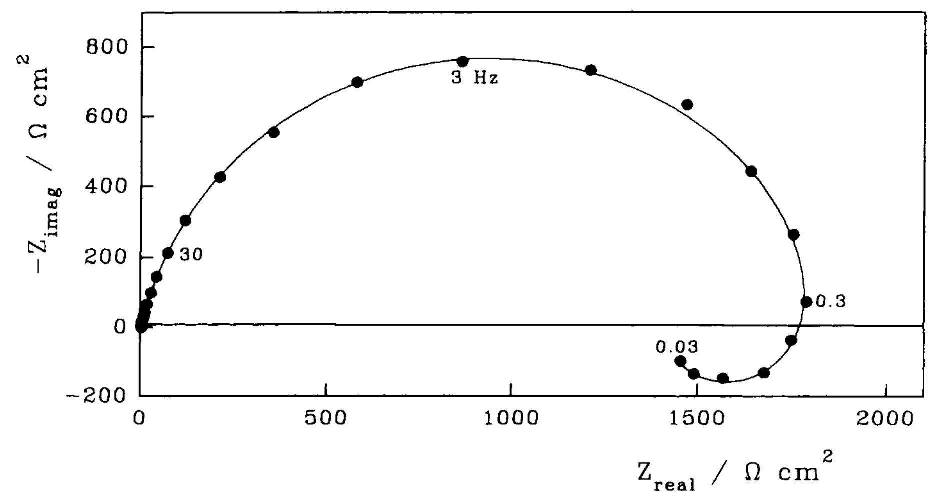

Fig. 7. The Nyquist plot of the Al–2.5Mg alloy in 3% NaCl at open circuit potential.

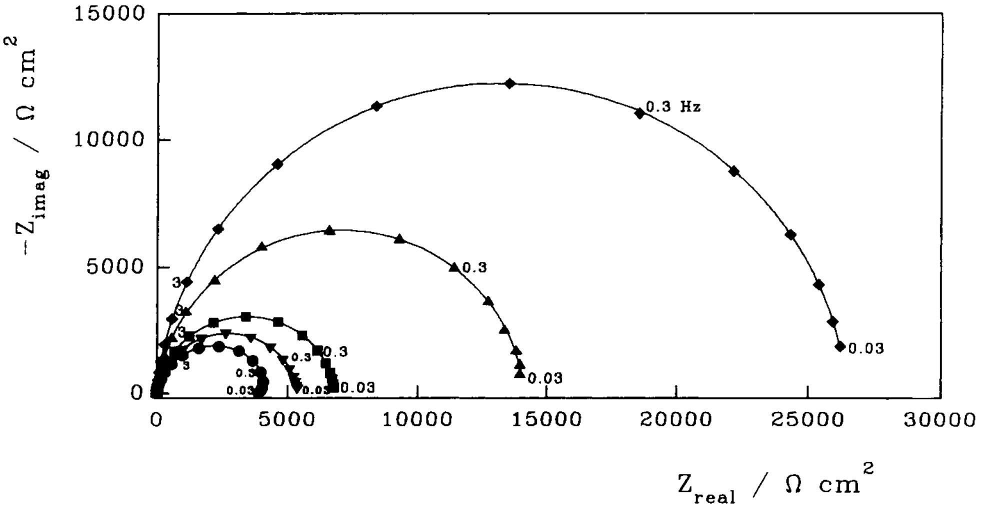

Fig. 8. Nyquist plots of the Al–2.5Mg alloy in 3% NaCl at open circuit potential in the presence of (●) 1 × 10^{-7}, (▼) 1 × 10^{-6}, (■) 1 × 10^{-5}, (▲) 1 × 10^{-4} and (◆) 1 × 10^{-3} M catechin fraction.

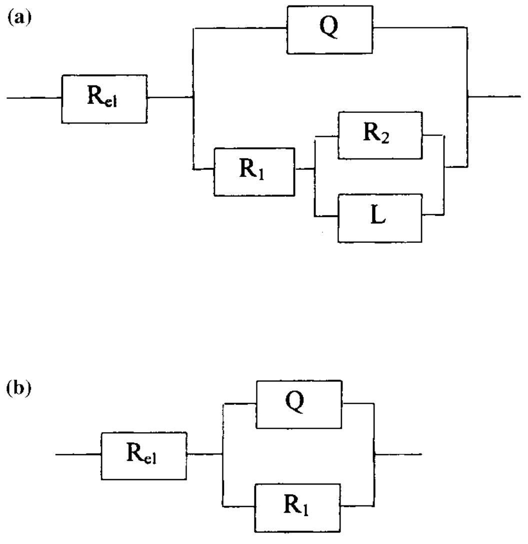

Fig. 9. Equivalent circuits for modeling impedance data of the Al–2.5Mg alloy.

Table 3. Impedance parameters for the Al–2.5Mg alloy in 3% NaCl in the absence and in the presence of varied concentrations of the catechin fraction at open circuit potential

C/M	$Q \times 10^6$ /Ω^{-1} s^n cm^{-2}	n	R_1 /kΩ cm^2	L /kH cm^{-2}	R_2 /kΩ cm^2
0	45.06	0.87	1.41	0.69	0.46
1 × 10^{-7}	35.07	0.89	3.91	0.54	0.52
1 × 10^{-6}	30.63	0.91	5.40	–	–
1 × 10^{-5}	23.14	0.92	6.83	–	–
1 × 10^{-4}	17.68	0.94	14.12	–	–
1 × 10^{-3}	13.08	0.95	26.45	–	–

tration increases from 10^{-7} to 10^{-3} M the impedance of the system increases from 4.43 to 26.45 kΩ cm^2. The value of Q decreases from 35.07 to 13.08 × 10^{-6} Ω^{-1} s^n cm^{-2}, while the parameter n increases from 0.89 to 0.95. This decrease in Q can be associated with the defectivity change in the oxide film. Namely, the

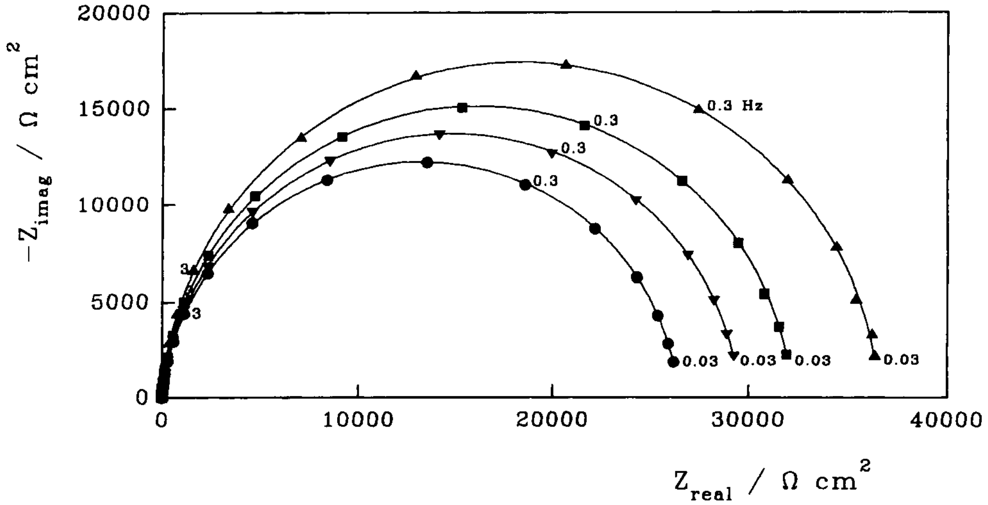

Fig. 10. The Nyquist plot of the Al–2.5Mg alloy at open circuit potential in 3% NaCl + 1 × 10^{-3} M catechin fraction after (●) 30, (▼) 60, (■) 120 and (▲)180 min.

catechin fraction adsorbs at the surface of the alloy, or more precisely, at defective sites in the oxide film already existing at the surface, resulting in its healing and strengthening.

Figure 10 shows the effect of the time component on the impedance spectrum in the presence of the catechin fraction $C = 1 \times 10^{-3}$ M at the open circuit potential. The response of the system in the Nyquist complex plane is a semicircle whose diameter increases with immersion time in inhibitor-containing solution. Values for electrode impedance listed in Table 4 were determined by computer adjustment of measured impedance relative to frequency with the theoretical function of impedance for a simple equivalent circuit consisting of a parallel *RQ* combination connected in series with the electrolyte resistance (Figure 9(b)). The results presented in Table 4 indicate that with an increase in stabilization time up to 3 h the value of the resistance R_1 increases (from 26.45 to 36.53 kΩ cm^2) and the value of constant phase element decreases (from 13.08 to 8.28 × 10^{-6} Ω^{-1} s^n cm^{-2}) indicating better protective properties of the (Al–oxide–inhibitor) adsorption layer.

The experimental observations show that the catechin fraction does not alter the electrochemical reactions responsible for corrosion. It inhibits corrosion primarily through its adsorption on the alloy surface. If the catechin fraction concentration is $\geq 10^{-6}$ M, a compact and coherent oxide-inhibitor layer is formed at the surface of the alloy, acting as a physical barrier to impede the attack of the medium.

Table 4. Impedance parameters for the Al–2.5Mg alloy after varied immersion duration at open circuit potential in 3% NaCl + 1 × 10^{-3} M catechin fraction

t/min	$Q \times 10^6$ /Ω^{-1} s^n cm^{-2}	n	R_1 /kΩ cm^2
30	13.08	0.95	26.45
60	12.56	0.95	29.56
120	11.43	0.96	32.20
180	8.28	0.97	36.53

4. Conclusion

The results of polarization measurements have indicated that the catechin fraction of the aqueous rosemary leaves extract acts as a cathodic inhibitor of corrosion of the Al–2.5Mg alloy in a 3% NaCl solution. The HPLC–RP technique has confirmed the (+)-catechin to be the active substance in that fraction.

The adsorption behavior of the catechin fraction and the commercial catechin can be described by the Freundlich adsorption isotherm. The values determined for standard free adsorption energies correspond to physical adsorption of an organic substance at the surface.

The impedance measurements performed at OCP without inhibitor are characterized by a high-frequency capacitive loop related to the dielectric properties of the oxide film and a low-frequency inductive loop which was determined by the faradaic process and attributed to the localized corrosion. The increase in the catechin fraction concentration increases the resistance and decreases the capacitance of systems considered, while the catechin fraction in the concentrations $\geq 10^{-6}$ M completely prevents localized corrosion attacks. Capacitive properties of systems considered in the presence of the catechin fraction are attributed to dielectric properties of the surface (metal–oxide–inhibitor) adsorption layer which shows increasingly better protection properties with increase in immersion duration.

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