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A novel method for determination of diffusion coefficient of corrosive species in organic coatings by EIS

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The diffusion coefficients of water and Cl^- ion in epoxy coatings on aluminum alloys LY12 were investigated by electrochemical impedance spectroscopy (EIS). The key task in the present work remained in the model fitting of EIS data, from which coating capacitance was derived and was used to calculate water diffusion coefficient by the commonly used "capacitance method". Moreover, by the fitting analysis of EIS, appropriate equivalent electrical circuits (EEC) were proposed for different immersion stage. After that the initiation time for the appearance of each EEC was known. These times were correlated to the required times for penetrants arrival through the coating at metal interface. Then the diffusion coefficient was calculated from these characteristic required times in the case of Fickian diffusion. This novel method is defined as "required time method" in this work. It was shown that comparative values were obtained by using both the capacitance and required time methods for the water diffusion coefficient. Even more, the diffusion coefficient of Cl^- ion calculated by required time method was very close to that reported in the literature (measured by nuclear magnetic resonance (NMR) technique).

1. Introduction

The diffusion behavior of water through polymer films has been extensively investigated by electrochemical impedance spectroscopy (EIS) [1–3], from which the film capacitance is obtained and used to derive the water sorption curves. In the case of Fickian diffusion, the water diffusion coefficient can be calculated from the sorption curves. This conventional capacitance method has become a successful tool for determination of water diffusion coefficient [4, 5]. Unfortunately, the coating capacitance is almost independent of ions (Na^+, Cl^-, etc.) uptake, therefore the capacitance method cannot be used to measure the amount of ions uptake and thereby the ions sorption kinetics. Due to the slower process of ions permeation compared to that of water [6, 7], it is also difficult to use the gravimetric method. Up to the now, the measurements of ions uptake were limited to physical methods, e.g. the nuclear magnetic resonance (NMR) technique as normally used to measure the concentration profiles of metal ions and other anions [8–10]. For these reasons, to explore new and convenient methods for ions uptake characterization is of particular interest in the coating-metal field.

The aim of this work is to introduce a simple novel method for the determination of diffusion coefficient of penetrants in organic coatings. In addition, the water diffusion coefficient obtained from this method should be compared with that from capacitance method.

2. Theoretical background

2.1. Capacitance method for water uptake

If (i) there is a linear relationship between the permittivity of the polymer-water system and those of the pure components, (ii) a random distribution of water, and (iii) a linear relationship between permittivity and capacitance, the amount of water, $M(t)$, taken up by the coating can be calculated from the capacitance values using the following relationship [11]:

$$M(t) = \frac{LS\rho_w}{\ln \varepsilon_w} \ln \frac{C(t)}{C_d} \tag{1}$$

where $C(t)$ and C_d are the coating capacitance at time t and zero, respectively, S is the surface area of the polymer, L is the coating thickness, ρ_w is the density of water absorbed into the polymer, and ε_w is the dielectric constant of pure water (equal to 78.5 at 25°C). This equation is usually employed in a normalized form as follows:

$$\frac{(\ln C(t) - \ln C_d)}{(\ln C_\infty - \ln C_d)} = \frac{M(t)}{M_\infty} \tag{2}$$

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where C_∞ is the capacitance of the coating fully saturated with water, and M_∞ the amount of absorbed water at equilibrium.

For a Fickian behavior with a constant diffusion coefficient D, the sorption data should follow the equation [12]

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{\mathrm{n}=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left(\frac{-(2n+1)^2 D\pi^2}{L^2}t\right) \quad (3)$$

By combining Equations 2 and 3, and by a series expansion of Equation 3 with a short time approximation, one obtains

$$\frac{(\ln C(t) - \ln C_\mathrm{d})}{(\ln C_\infty - \ln C_\mathrm{d})} = \frac{2\sqrt{D}}{\mathrm{L}\sqrt{\pi}}\sqrt{t} \quad (4)$$

Thus the water diffusion coefficient can be derived from curves of $\ln C(t)$ versus $t^{0.5}$.

2.2. Required time method for penetrants diffusion

Generally, for a Fickian diffusion the sorption processes of water, oxygen and other species follow the first and second Fickian laws:

$$J = -D\frac{\partial\gamma(x,t)}{\partial x} \quad (5)$$

$$\frac{\partial\gamma(x,t)}{\partial t} = D\frac{\partial^2\gamma(x,t)}{\partial x^2} \quad (6)$$

where J is the solute flux over a distance x, $\gamma(x,t)$ the concentration and D is the diffusion coefficient of either the water, the oxygen or other ions diffusion coefficients. The initial and boundary conditions for solving Equation 6 are respectively at

$$t = 0, x \geq 0 : \gamma(x,0) = 0 \quad (7)$$

$$t \geq 0, x = 0 : \gamma(0,t) = \gamma_0 \quad (8)$$

γ_0 is the concentration on coating surface. When water and (or) oxygen arrive at metal/coating interface, electrochemical sites are generated where water and oxygen are cathodically consumed. At first, sufficient reaction of oxygen and water at the coated metal interface is assumed, which leads to a low concentration of these species being maintained at the interface. If we take a condition where the permeation flux at the coated metal interface is one tenth of the final steady-state permeation flux (J_∞) as the determination for initial permeation of each species onto the metal/coating interface, i.e.

$$t = t_\mathrm{init}, x = L\colon J(L, t_\mathrm{init}) = J_\infty/10 \quad (9)$$

as the other boundary condition for Equation 6, then the required time, t_init, for diffusion of permeation species through the coating to metal interface is given by the following equation [13]

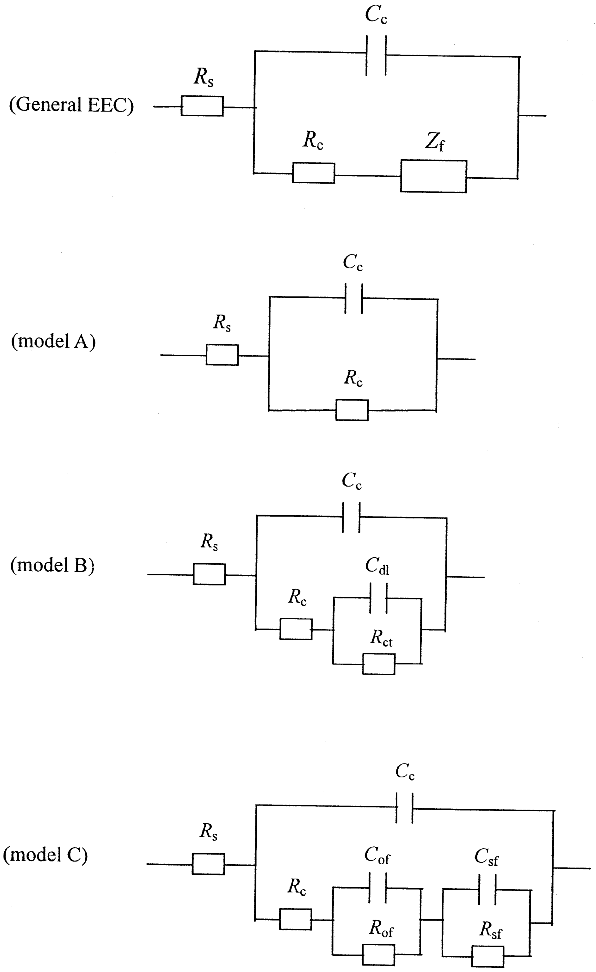

Figure 1 General equivalent electrical circuit (EEC) and three typical impedance models for organic coated aluminum electrodes immersed in NaCl solution.

$$t_\mathrm{init} = 0.0653 \cdot (L)^2/D \quad (10)$$

D can be thereby derived from the above equation. The question remaining is how to obtain the value of t_init, that is to detect the arrival of penetrants at coating/metal interface.

Organic coated metals usually present a general equivalent electrical circuit (EEC) as displayed in Fig. 1 [1]. R_s refers to electrolyte resistance, C_c the coating capacitance, R_c the coating or pore resistance and element Z_f represents the electrochemical process at the metal interface. For a dry coating (before immersion) R_c and Z_f tend to be big enough, and the total impedance is simplified as $R_\mathrm{s}C_\mathrm{c}$. Prolonging the immersion leads to a declining of R_c as a result of water penetration through the coating, thus the EEC becomes $R_\mathrm{s}(R_\mathrm{c}C_\mathrm{c})$ (model A, as shown in Fig. 1). When water and oxygen molecules arrive at the metal surface, the electrochemical element Z_f appears. In the case of oxygen de-polarization being coupled with water participation, Z_f usually consists of double-layer capacitance, C_dl, in parallel to the charge transfer resistance of electrochemical corrosion process, R_ct. The EEC changes to $R_\mathrm{s}(C_\mathrm{c}(R_\mathrm{c}(R_\mathrm{ct}C_\mathrm{dl})))$ (model B, as shown in Fig. 1). When aggressive ions (such as Cl^-, SO_4^{2-}, etc.) reach the metal/coating interface and participate in electrochemical reactions, the characteristic element(s) are expected to appear in the EEC. For instance, for a bare aluminum immersed in sodium chloride solution, a second capacitive loop related to Cl^- ion-incorporated layer formation reaction on metal oxide surface has been clearly detected in impedance spectra [14–16]. The EEC for bare Al metal in NaCl solution could be represented as $Rs(R_{of}C_{of})(R_{sf}C_{sf})$. R_{of} and C_{of} are resistance and capacitance of the inner oxide film formed on metal surface, and R_{sf} and C_{sf} are resistance and capacitance of the Cl^- Ion-incorporated outer film (salt film) respectively. If therefore concerning the participation of Cl^- ion in the interface electrochemical reactions, the possible EEC for coated Al (alloys) immersed in NaCl solution after the Cl^- ions have arrived at the metal surface might be $R_s(C_c(R_c(R_{of}C_{of})(R_{sf}C_{sf})))$ (model C, as shown in Fig. 1).

Thus the required time for water diffusion through coating to metal interface can be obtained from the initial time of the appearance of model (B), and that for Cl^- ion from the onset of the model (C).

3. Experimentals

Polished (200 grit) LY12 aluminum alloys were prepared. The coating used in this study was a commercial epoxy (E-44 from Xuelian Resin Factory, Wujiang, China). The curing agent was polyamide (type 650 from Yongzai Chemical Engineering, Pujiang, China). The weight ratio of polyamide and epoxy resin was kept at 80%. Samples with two thicknesses (~74 μm and ~100 μm) were prepared. The paints were cured at 25°C for 10 h and then stored in a desiccator at room temperature for 30 days. Five parallel samples were used to ensure the experimental data were reliable.

EIS measurements were performed using a PAR 273 potentiostat and a PAR 5210 lock-in amplifier. The measurements were carried out over a frequency range of 100 kHz to 10 mHz using a 20 mV amplitude sinusoidal voltage. The coated samples were immersed in 3.5%

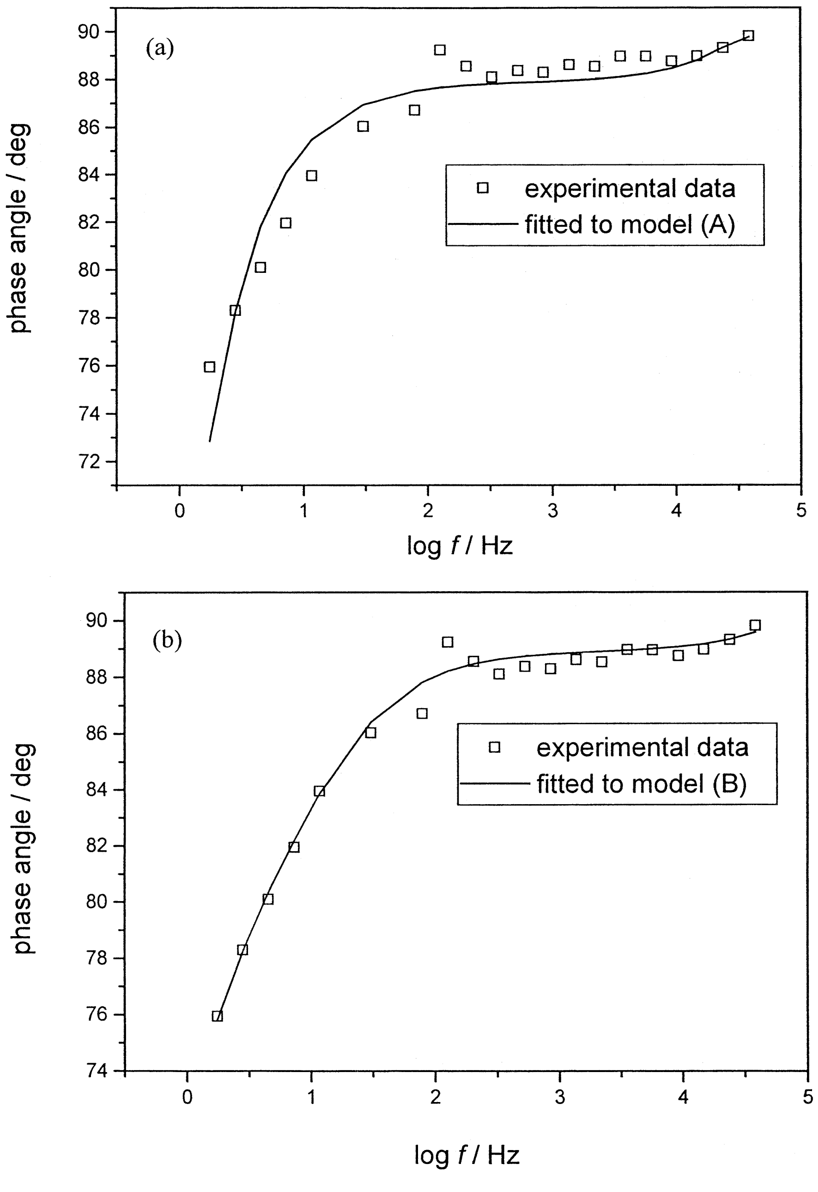

Figure 2 Bode plots for epoxy coated (74 μm) LY12 Al alloys immersed in NaCl solution for 32 min. Scatters-experimental data, lines-simulated results.

NaCl in distilled water at 25°C. A three-electrode cell arrangement was used in the experiments. A perspex cylinder was attached to the surface of a coated substrate in order to create a vessel to hold the electrolyte. The coated aluminum panel was the working electrode. The counter electrode was a stainless steel disk. The reference electrode was a saturated calomel electrode (SCE). The whole tested area of working electrode was $\sim$13 cm^2. All the measurements were performed at the open-circuit potential (OCP) at room temperature (25 ± 1°C). The impedance spectra were analyzed using Boukamp's EQUIVCRT fitting program.

4. Results and discussion

It is found that the ageing behavior of impedance model for the different thick coatings are basically similar. Therefore, only the fit to the results of EIS data for 74 μm thick coating samples are presented in this work. In the initial immersion stage, the coatings exhibit an EEC composed of a coating resistance parallel to a coating capacitance (model A). The experimental data after immersing for 32 min, however, does not fit well to model (A). Concerning the possibility of arrival of water and (or) oxygen at the metal surface through the organic coatings, the electrochemical reaction-sites may appear on metal surface, and the EEC becomes model (B). The validity of the selected impedance model can be verified by comparing the fitness using two different circuits as shown in Fig. 2. To display more clear information about impedance patterns, phase angle Bode plots are used. It can be seen that the simulation using the model (A) no longer matches the experimental data (Fig. 2a), while the model (B) provides a good fit to the results (Fig. 2b), indicating the initiation of base attack by the penetration of water and oxygen.

Prolonging the exposure time does not result in obvious variation in the shape of impedance patterns. EIS data before 216 h immersion can be successfully fitted to model (B), however it seems that after this time this model does not work well. Fig. 3a displays the complex plane with immersion for 216 h. The simulation results show that, the model (B) cannot provide a satisfactory fitness in the low and intermediate frequency region as shown in Fig. 3b. By using the model containing the contribution of salt film formation (model C), the Bode plot can be well fitted well over the whole frequency region (see Fig. 3c), indicating that Cl$^-$ penetrates onto the substrate surface.

By using Equation 4, the $\ln C_c \sim t^{0.5}$ curve is plotted in Fig. 4. The value of C_c is obtained from the simulation results of EIS data by selecting appropriate EEC in different immersion stage. The figure consists of two distinguishable sorption stages with an initially fast and then slow process. The inserted curve in Fig. 4 shows an enlarged plot for the first stage, indicating a linear relationship of $\ln C_c$ against $t^{1/2}$ for small values of t. Thus, the diffusion coefficient of water, $D(H_2O)$, across the epoxy coating can be calculated to be 2.13×10^{-9} cm^2 s^{-1} by Equation 4 from the first sorption stage. This value is in good agreement with the literature [17, 18] in which an order of magnitude of 10^{-9} cm^2 s^{-1} of water diffusion coefficient in epoxy coatings has been reported.

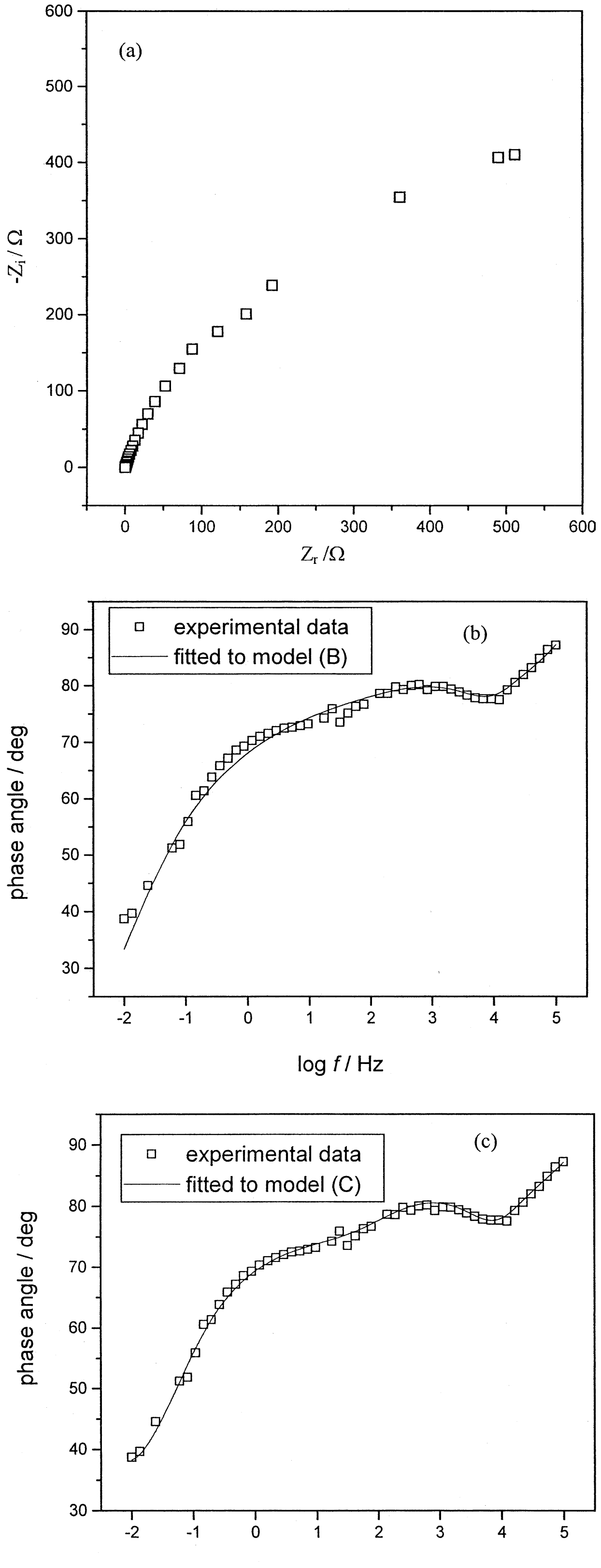

Figure 3 Complex plane (a) and Bode plots (b and c) for epoxy coated (74 μm) LY12 Al alloys immersed in NaCl solution for 216 h. Fitting is conducted by two possible circuits (models B and C).

Diffusion coefficient of penetrants can also be obtained by "required time" method. From the impedance analysis by EEC simulation, one can find the t_{init} for

TABLE I Diffusion coefficients of water and Cl$^-$ ion in epoxy paints with different thickness

	Water diffusion coefficient/10^{-9} cm^2 s^{-1}		Cl$^-$ ion diffusion coefficient/10^{-12} cm^2 s^{-1}	
Thickness	Capacitance method	Required time method	Required time method	NMR method
74 μm	2.13	1.86	4.60	
100 μm	2.44	2.18	4.68	
				4.67[a]

[a]Measured by NMR technique [6].

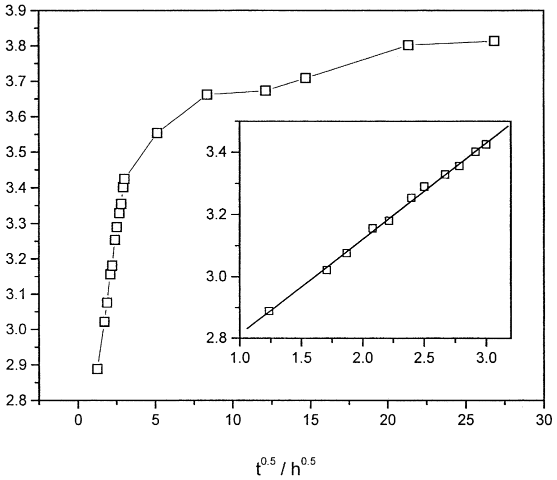

Figure 4 ln $C_c \sim t^{0.5}$ relationship of epoxy coated (74 μm) LY12 Al alloys immersed in NaCl solution. Insert displays an enlarged linear region of the curve.

water permeates onto the aluminum surface is ~32 min, and that for Cl$^-$ ion corresponds to ~216 h. For 100 μm thick films, the t_{init} of water is ~50 min and that of Cl$^-$ ion ~388 h. By substituting the time and coating thickness values into Equation 10, the diffusion coefficients of water and Cl$^-$ ion in epoxy paints can be calculatedly.

Table I summarizes the evolved values of diffusion coefficients for water and Cl$^-$ ion in epoxy paints with 74 μm and 100 μm in thickness by capacitance and required time methods, respectively. The results show that both the methods are in good agreement for the water diffusion coefficient. Furthermore, one can find from the table that, the diffusion coefficient of Cl$^-$ ion derived from the required time method is in almost exact agreement with the values reported in the literature as measured by NMR technique [6].

5. Conclusions

In addition to the capacitance method, the diffusion coefficient of water in organic coatings is investigated by using a novel "required time" method. It was shown that both methods give comparative results. These two techniques are based on the fitting of measured EIS data, to appropriate EECs. From the "required time" for the appearance of Cl$^-$ ion-incorporated film formation impedance, diffusion coefficient of Cl$^-$ ion in epoxy films was calculated to be between 4.60 and 4.68 × 10^{-12} cm^2 s^{-1}. These values are very close to that reported in the literature as measured by NMR technique.

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