JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 1277–1281

Evaluation of thin defect-free epoxy coatings using electrochemical impedance spectroscopy

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Received 16 March 1998; accepted in revised form 9 June 1998

The water sorption of thin defect free epoxy films and coatings on aluminium electrodes was studied using the gravimetric method and electrochemical impedance spectroscopy. The results show that the double layer capacitance of the wetted surface of the aluminium electrode under the epoxy film is considerably smaller than that of a bare aluminium electrode, except in the early period of immersion. The resistivity of the solution absorbed in the epoxy coating is much higher than that of the bulk solution. A method for approximately determining the equilibrium water sorption of the epoxy coatings on the metal surface from the double layer capacitance is reported.

Keywords: *electrochemical impedance spectroscopy*, *epoxy coating*, *water sorption*, *coating resistance*, *double layer capacitance*

List of symbols

A_{cs}	cross-sectional area of water passage
A_C	A_{cs} obtained from C_{dl}
A_R	A_{cs} obtained from R_f
C_{dl}	double layer capacitance
C_{dl}^0	specific value corresponding to C_{dl}
d	thickness of the epoxy film
D	diffusion coefficient of water
M_t	fractional mass of water sorption at time t (wt%)
M_∞	fractional mass of equilibrium water sorption (wt %)
R_f	coating resistance
R_f^0	specific value corresponding to R_f
t	immersion time
V_∞	fractional volume of equilibrium water sorption (vol %)

Greek symbols

ρ	resistivity of the solution in the water passages
ρ^0	resistivity of bulk solution

1. Introduction

Epoxy resins are used extensively as coating materials [1, 2]. Water sorption can greatly weaken the adhesion and protection ability of the coating to the substrate. To evaluate the effect of water sorption on the protection offered by coatings, electrochemical impedance spectroscopy (EIS) is a useful technique [3–15].

Haruyama *et al.* [8, 9] proposed equations for evaluating coating performance:

$$A_R = R_f^0/R_f \qquad (1)$$

$$A_C = C_{dl}/C_{dl}^0 \qquad (2)$$

where R_f is the coating resistance, C_{dl} is the double layer capacitance of the coating–metal interface, R_f^0 and C_{dl}^0 are the specific values corresponding to R_f and C_{dl}, and A_R and A_C are the wetted area on the substrate metal surface obtained from R_f and C_{dl}, respectively.

For coatings with macroscopic physical defects [7] or artificial holes [11] in which the concentration and the mass transport properties of the solution are the same as those of bulk solution, $R_f^0 = \rho^0 d$, where ρ^0 is the resistivity of bulk solution, and d is the thickness of the coating. For the same case, the C_{dl} per unit area of the bare metal/bulk solution interface can be taken as C_{dl}^0 [6–11].

If the defects and the artificial holes can be simplified as cylindrical holes [11, 12], A_R equals A_C before delamination of the coating occurs. However, experimental results show that large discrepancies always exist between A_R and A_C. This discrepancy has provoked discussion. Armstrong *et al.* [10] pointed out that A_C is truly the wetted area on the substrate metal surface while A_R is, in fact, the cross-sectional area of the defects in the coating. When water reaches the coating/metal interface, it can cause rapid delamination of the coating. This rapid de-

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lamination causes A_C to be thousands of times larger than A_R. Armstrong *et al.* ascribed the large discrepancy between A_R and A_C to their different physical meanings and delamination of the coating; Mansfeld [12], however, did not agree with this explanation. He postulated that the resistivity of the solution absorbed by the coating (ρ) may be much higher than ρ^0; thus the value of A_R obtained using ρ^0 is by far too low. Due to the effect of the coating on the distribution of current and transport of corrosive species, C_{dl}^0 under the coating may be very different from that obtained from the bare metal/bulk solution interface. However, Mansfeld gave no method for obtaining R_f^0 and C_{dl}^0.

In this work, a method for obtaining C_{dl}^0 is reported and reasons for the discrepancy between A_R and A_C are discussed. A method for approximately determining the equilibrium water sorption of thin coatings on the metal surface is reported.

2. Experimental details

2.1. *Materials*

Epoxy resin: YDCN-702 p epoxy *o*-cresol novolac resin (ECN), from Tohto Kasei, Japan. Hardener: H-1 phenol novolac resin (NOV), from Sumitomo, Japan; phenol novolac acetate resin (NOVA), synthesized in our laboratory [16]. Curing accelerator: 2-methyl-imidazole (2MI), from Wuhan Pharmaceutical Co., China.

2.2. *Preparation of epoxy films*

Two types of epoxy films were used, one cured with NOV (EP), and the other cured with NOVA (EPA). EP was prepared from 66.3 wt % ECN, 33.2 wt % NOV and 0.5 wt % 2MI. EPA was prepared from 57.5 wt % ECN, 42.0 wt % NOVA, and 0.5 wt % 2MI. The mixture of raw materials was dissolved in acetone.

The epoxy coating was made on the surface of the aluminium working electrode by a dipping method with the acetone solution, left in the air at room temperature for one day and then cured in a vacuum drier at 45 °C (15 min), 80 °C (15 min), 120 °C (3 h), 150 °C (2 h) and 180 °C (1 h), and finally cooled slowly to room temperature.

The thin epoxy film was made by smearing the acetone solution on a piece of aluminium foil, then treating as above and peeling off for use.

The thickness of the cured epoxy sample was measured by a Coatest-1000 (UK) nonferrous digital coating thickness gauge.

2.3. *EIS measurement*

A three-electrode cell containing 0.5 mol dm^{-3} NaCl solution was used. An epoxy film coated aluminium disc embedded in an epoxy electrode holder with an exposed area of 7.07 cm^2 was used as working electrode. A platinum electrode and a saturated calomel electrode served as counter electrode and reference electrode, respectively.

EIS measurements were carried out at open circuit potential using an EG&G PARC M378 electrochemical impedance system (USA) [13–15]. Analysis of the impedance spectra was performed using an EG&G PARC EQUIVCRT impedance modelling software. The equivalent circuit generally reported in the literature for polymer-coated electrodes as shown in Fig. 1(a) of [6] is used in the present work.

For measuring C_{dl}^0, a special electrode was made as depicted in Fig. 1. Prior to experiment, the surface of the aluminium disc was wetted with 0.5 mol dm^{-3} NaCl solution (30 °C) and covered with an epoxy film of 6.4 μm in thickness. A silicon rubber O ring was put on the film and then the electrode was screwed in place.

All electrochemical measurements were conducted at 30 ± 0.1 °C in a water bath.

2.4. *Gravimetric measurement*

The water sorption (M_t) as a function of immersion time (t) was measured using a microbalance.

3. Results and discussion

3.1. *Chemical structures of the cured resins*

Scheme 1 represents the chemical structures of the cured epoxy resins. From the scheme it is seen that no hydroxyl groups, but rather acetoxy groups, are left in the EPA resin [16].

3.2. *Evaluation of coating quality*

The M_t/M_∞ against $t^{1/2}\ d^{-1}$ relationship obtained by the gravimetric method is shown in Fig. 2. The diffusion coefficient (D) of water can be obtained using

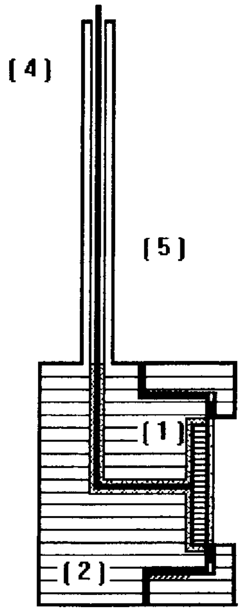
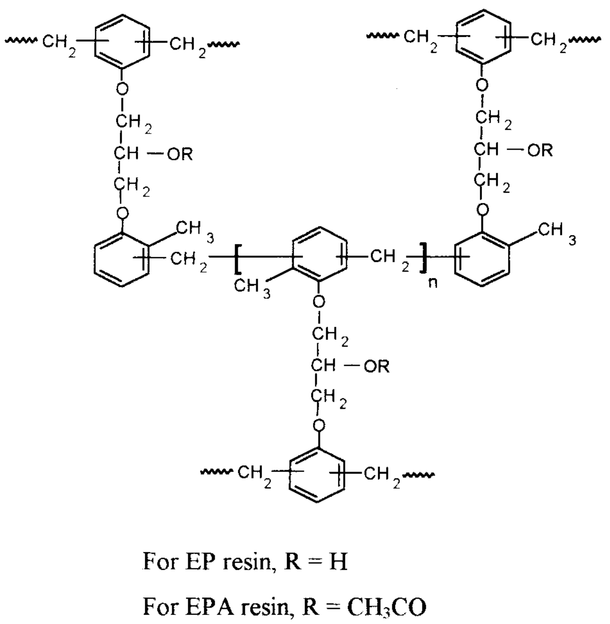


Fig. 1. Electrode for measuring C_{dl}^0. Key: (1) Al disc, (2) Plexiglass electrode holder, (3) O-cover, (4) lead, (5) Plexiglass tube.



Scheme 1

Equation 3 [2, 17] from the slope of the straight line in the early period of immersion as shown in Fig. 2. Thus for the EP film, D is $2.7\times10^{-9}\,\mathrm{cm^2\,s^{-1}}$, while for the EPA film, D is $1.2\times10^{-8}\,\mathrm{cm^2\,s^{-1}}$ at 30 °C.

$$M_t/M_\infty = 4(D/\pi)^{1/2}t^{1/2}d^{-1} \qquad (3)$$

where M_∞ is the equilibrium water sorption and d is the thickness of the film.

If the water passages in the film are of macroscopic size, the transport property of water in the water passages should be the same as that in bulk solution [6, 10]. However, the self-diffusion coefficient of the water in bulk water is about $3\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at 30 °C [18], which is far larger than that in the water passages of the films. This indicates that diffusion of water in the water passage is seriously retarded. For the EP film, two reasons may account for this retardation, one is that the water passages in the film are of molecular size and the other is that water molecules can form hydrogen bonds with hydroxyl groups in the film. However, for the EPA film, this must solely be due to the small size of the water passage [15, 19–23].

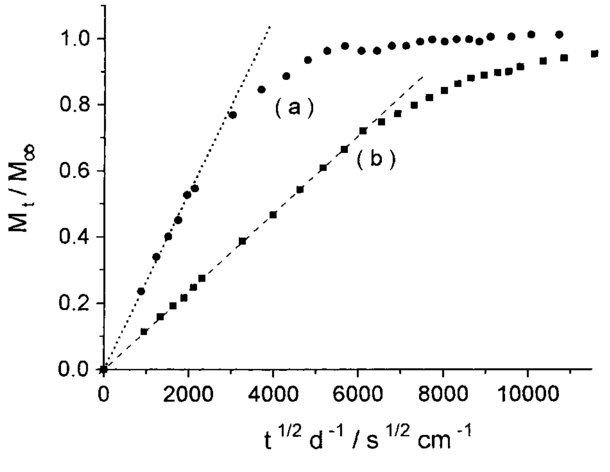


Fig. 2. M_t/M_∞ against $t^{1/2}\,d^{-1}$ plot for the EPA film (a) and the EP film (b) immersed in water at 30 °C.

The D value for the EPA film is more than 4.4 times larger than that for the EP film. This can be attributed to the weak interaction between water molecules and acetoxy groups.

Table 1 lists the M_∞ values of the films immersed in deionized water at different temperatures. It can be seen that, as immersion temperature increases, M_∞ of the EP film decreases while that of EPA film increases.

The water sorption process of the cured resin can be expressed as

$$\text{Resin} + x\,H_2O\,(\text{bulk}) \overset{\text{sorption}}{\rightleftharpoons} \text{Resin} + x\,H_2O\,(\text{in resin})$$
$$- Q_1 \overset{\text{interaction}}{\rightleftharpoons} \text{Resin}\cdot x\,H_2O + Q_2 \qquad (4)$$

That is, diffusion of water into the resin is an endothermic process while the interaction of water molecules with hydroxyl groups on the polymer chains is exothermic [24].

For the EPA film, because the interaction between water molecules and acetoxy groups is weak, the whole process of water sorption is endothermic. As temperature increases, the water sorption equilibrium shifts to the right; hence the M_∞ of the film increases. But for the EP film, the thermal effect of interaction between water molecules and hydroxyl groups is large and the whole process is exothermic; the equilibrium shifts to the left with increasing temperature and hence M_∞ of the film decreases.

From the above discussion it can be concluded that the water passages in the present films are of molecular size and the films are defect free. The water transport properties of the solution in the defect free films may be very different from those in bulk solution [12].

3.3. *EIS measurements*

A typical Nyquist plot is shown in Fig. 3. The simulated plot fits the experiment plot well, just as the other Nyquist plots in this work.

3.4. *Determination of C_{dl}^0*

The C_{dl} against $t^{1/2}$ plot for a bare aluminium electrode and a prewetted aluminium electrode covered with a thin epoxy film immersed in $0.5\,\mathrm{mol\,dm^{-3}}$ NaCl (30 °C) are presented in Fig. 4. By extrapolating the linear parts of the curves in the early periods to $t = 0$, it is found that C_{dl} of the bare aluminium

Table 1. M_∞ (wt %) of the resins at different immersion temperatures

T/°C	*20*	*30*	*40*	*50*
EP	2.54	2.32	2.27	2.20
EPA	0.76	0.77	0.84	0.86

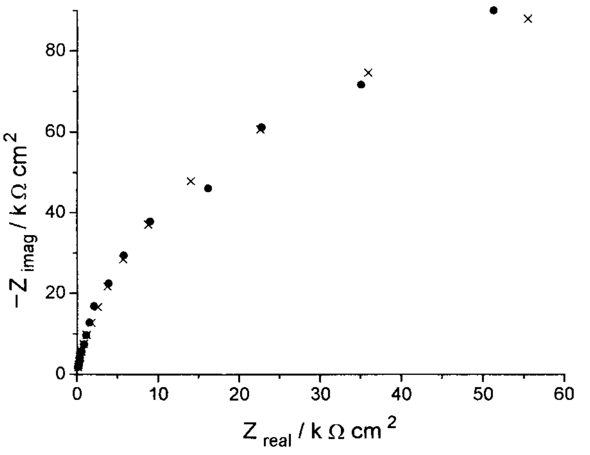


Fig. 3. Nyquist plot of an EP coating immersed in 0.5 mol dm^{-3} NaCl solution at 30 °C for 10 min measured at the open circuit potential, frequency range: $10^3 \sim 10^5$ Hz. Key: (●) measurement; (×) simulation.

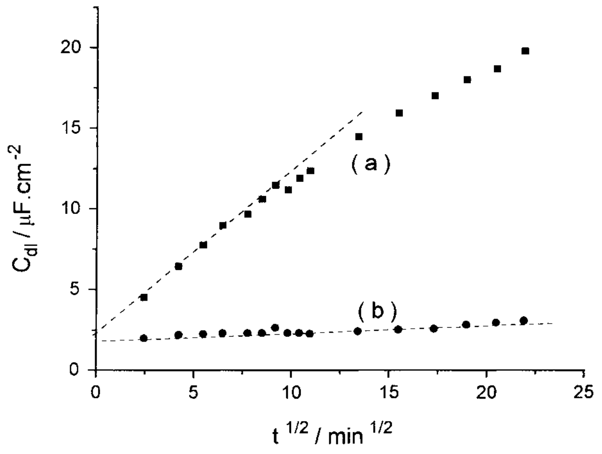


Fig. 4. C_{dl} against $t^{1/2}$ plots for a bare aluminium electrode (a) and a prewetted aluminium electrode covered with an epoxy film ($d = 6.4\,\mu$m) (b) in 0.5 mol dm^{-3} NaCl solution at 30 °C.

electrode ($C_{dl,b}$) and the prewetted aluminium electrode covered with an epoxy film ($C_{dl,f}$) are nearly the same at the beginning. But $C_{dl,b}$ changes much more rapidly, so that after 8 h, the value of $C_{dl,b}$ is about six times larger than that of $C_{dl,f}$. The slight change of $C_{dl,f}$ may be attributed to the low values of D of water and corrosive species in the water passages. Thus the corrosion of the aluminium electrode under the epoxy film develops to a lesser extent [12]. Since the interface for measuring $C_{dl,f}$ is similar to that of the aluminium/epoxy coating, the values of $C_{dl,f}$ are adopted as C^0_{dl} in the present work. This approach is promising as will be demonstrated later.

3.5. *Determination of A_R, A_C and V_∞*

Table 2 lists the values of A_R and A_C in an EP coating (4.2 μm in thickness) using EIS.

According to the above discussion, R^0_f for the defect free coatings may be much larger than the $\rho^0 d$ product, but until now we have not found a practical method for measuring ρ. In this work, we still adopt $R^0_f = \rho^0 d = 20 \times 4.2 \times 10^{-4} = 8.4 \times 10^{-3}\,\Omega\,\text{cm}^2$ [25] and compare the value of A_R thus obtained with that of A_C so as to estimate the value of ρ [6, 10, 20].

According to Table 2, after 480 min of immersion, the water sorption in the coating was complete. If the water passages in the coating can be taken as cylindrical holes [10, 11], before delamination of the coating occurs, A_C under equilibrium conditions can be taken as the cross-sectional area of the water passage (A_{cs}) and the value of A_C can be also taken as the volume fraction of the equilibrium water sorption (V_∞) of the coating, that is, 1.85 vol %. The M_∞ of the EP film is 2.32 wt % which can be converted to $V_\infty =$ 2.77 vol %. For conversion, the densities of epoxy resin (1.2 g cm^{-3}) and water (1.0 g cm^{-3}) are used. Therefore the result obtained from EIS is close to that obtained by the gravimetric method. However, if we calculate V_∞ using A_R, we obtain a value for V_∞ of only 1.01×10^{-3} vol %. This suggests that A_R is much smaller than the virtual A_{cs}. The small value of A_R can be ascribed to the poor transport property of the solution in the epoxy film, that is, ρ is thousands of times larger than ρ^0.

Figure 5 shows the V_∞ against d relationship of the epoxy films measured by the gravimetric method and by EIS. It can be concluded that V_∞ of the EP film is independent of d, while V_∞ of the EPA film varies considerably with d for films less than 100 μm thick.

For an EPA film 4.2 μm thick, the water sorption is too small to be measured by the gravimetric method, and we can only estimate its V_∞ by extrapolating the linear part of the curve in Fig. 5(b). V_∞ thus obtained is 0.090 vol%. But the R_f and C_{dl} of an aluminium electrode coated with EPA coating 4.2 μm thick under equilibrium conditions can be measured easily using EIS to be 21.4 kΩ cm^2 and 1.99 nF cm^{-2} respectively. Then, we obtain A_C of 0.065 vol%, which is close to the result obtained by the gravimetric method. This further demonstrates that the

Table 2. Values of A_R and A_C calculated from R_f and C_{dl}, respectively

t/min	*10*	*20*	*30*	*60*	*120*	*250*	*360*	*480*
R_f/kΩ cm^2	2.60	2.00	1.79	1.51	1.28	0.952	0.863	0.832
C_{dl}/nF cm^{-2}	8.00	14.8	19.3	26.1	31.5	44.4	51.6	56.8
C^0_{dl}/ μF cm^{-2}	2.00	2.22	2.27	2.30	2.27	2.53	2.83	3.07
$10^6 \times A_R$	3.23	4.20	4.69	5.56	6.56	8.82	9.73	10.1
$10^3 \times A_C$	4.00	6.67	8.50	11.3	13.9	17.5	18.2	18.5
$10^{-3} \times (A_C/A_R)$	1.23	1.59	1.81	2.04	2.11	1.99	1.87	1.83

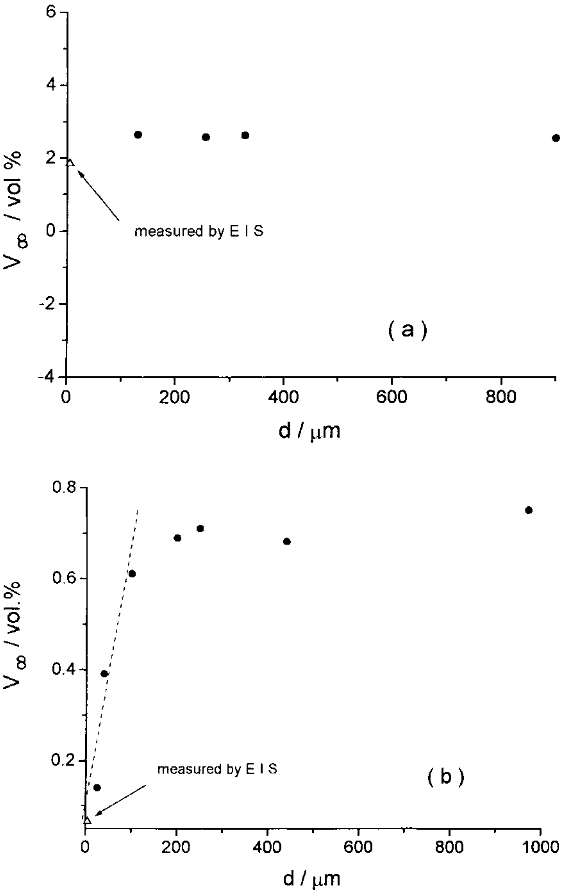


Fig. 5. V_∞ against d plots for EP film (a) and EPA film (b) using the gravimetric method and EIS (indicated in the Figures).

present EIS method can be used to approximately determine V_∞ of thin coatings on metal surfaces. However, V_∞ of the EPA film obtained from A_R is 3.9×10^{-5} vol%, which is still much less than that from the gravimetric result.

3.6. *Delamination of the coating*

Delamination of coating may cause a large value of A_C/A_R. However, for the present EP coating, the value of A_C/A_R attains a value of 1230 only after 10 min of immersion (cf., Table 2). Such a serious coating delamination in so short a period is obviously impossible. Moreover, the fair agreement of V_∞ obtained from the present EIS method with that from the gravimetric method as reported above suggests that A_C is close to the virtual A_{cs} in the coating. This cannot be explained satisfactorily by delamination.

From the above discussion we can attribute the large discrepancy between A_R and A_C mainly to the misuse of ρ^0 for ρ.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China.

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