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LETTER

Comments on the article 'Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coatings' by F. Mansfeld

A. T. A. JENKINS, R. D. ARMSTRONG

Chemistry Department, University of Newcastle, Newcastle upon Tyne, NE1 7RU, Great Britain

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Mansfeld in his recent article [1] on the use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coatings presents a method of calculating the delaminated area under defective polymer protective coatings which is correct only in special circumstances. We show that use of Mansfeld's Equation 1 for the calculation of delaminated area A_d (based on high frequency impedance information relating to the coating impedance) does not generally give the true delaminated area. We use some of our own experimental data to show that the value of A_d calculated from Equation 1 may be several orders of magnitude smaller than what would be calculated from Equations 2 and 3 and that the quantity which should be calculated from the high frequency impedance data is the coating porosity, P.

Mansfeld [1] claims that the (same) delaminated area of a polymer coated metal can be calculated from any of the three relationships:

$$R_{po} = \frac{R_{po}^0}{A_d} = \frac{\rho d}{A_d} \tag{1}$$

$$R_p = \frac{R_p^0}{A_d} \tag{2}$$

$$C_{dl} = C_{dl}^0 A_d \tag{3}$$

where R_{po} is the pore resistance, C_{dl} the double layer capacitance of the exposed metal, and R_p the polarization resistance of the metal. A_d is the delaminated area (expressed as a dimensionless quantity). R_{po}^0 and C_{dl}^0 are the corresponding quantities for the bare metal, while ρ is the resistivity solution in the pore and d is the film thickness.

Equation 1 is only correct if the area of corroding metal at the bottom of pores is the same area as the pore itself, i.e., there is no delamination. However, Equations 2 and 3 measure directly the corroding area at the bottom of pores in the coating, irrespective of the area of the pores as they determine quantities proportional to the corroding area (or wetted metal area, W) while Equation 1 does not. Therefore, Equations 2 and 3 will, in general, lead to very large values for A_d compared with those obtained from Equation 1. Figure 1(a) shows a polymer pore which would be correctly described by Equations 1–3, where the area of A_d is equal to the cross-sectional area of the pore and where $P = W$. Figure 1(b) shows a more general polymer pore which gives rise to different values for the coating porosity (P) and the wetted metal area (W).

Impedance measurements were made on a u.v. damaged polyester coated steel using a Solartron 1255 FRA at frequencies between 10 kHz and 100 mHz. 0.1 M hydrochloric acid electrolyte was used and experiments were performed at the rest potential of the bare steel. The Boukamp analysis program was used to analyse the resultant data. All resistance and capacitance values are given for an electrode area of 4.9 cm^2 unless stated otherwise.

The results of the impedance analysis of this coating is shown in both Bode and Nyquist type (complex plane) format in Figs 2 and 3(a) and (b). These results are representative of many similar experiments carried out on these systems [2]. The high frequency impedance data were fitted as a resistance and capacitance in parallel. The resultant values of pore resistance, R_{po} and coating capacitance, C_g are shown:

$$R_{po} = 2.41\ \text{M}\Omega$$

$$C_g = 421.8\ \text{pF}$$

Using Equation 1 the delaminated area (A_d) can, in principle, be calculated, as the value R_{po}^0 can be calculated from a knowledge of the conductivity of the electrolyte, as shown by Skerry and Eden [3] and Armstrong and Wright [4]. This is based on assuming

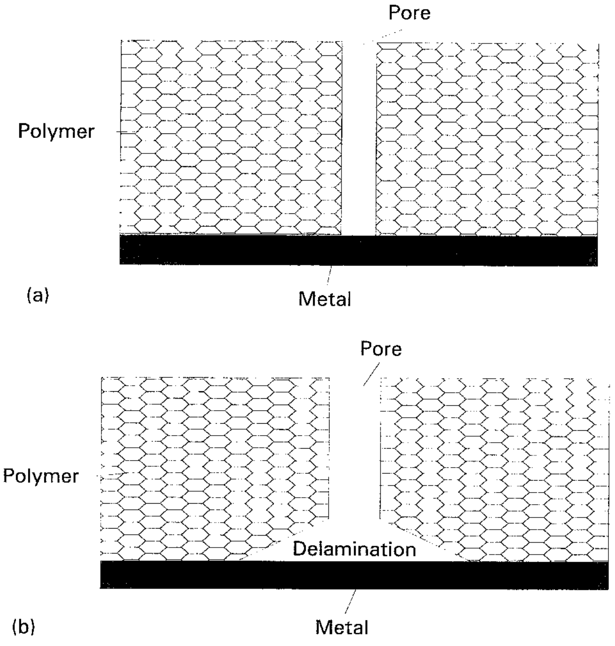

Fig. 1. (a) Model of a polymer pore where porosity and wetted metal area are the same. (b) Model of a polymer pore where wetted metal area exceeds porosity.

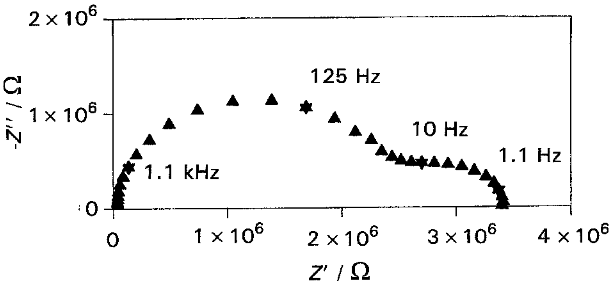

Fig. 2. Nyquist (complex plane) plot of degraded polyester on steel.

that R^0_{po} is the resistance of a theoretical coating containing 100% porosity. So,

$$R^0_{po} \frac{d}{\kappa A}$$

Here κ is the conductivity of the electrolyte, d the coating 'thickness' and A the electrode area. For the work carried out on the u.v. degraded polyester R^0_{po} was calculated as 0.026 Ω, for an electrode of 4.9 cm^2 area with a coating 53 μm thick and 0.1 M HCl with a conductivity of 0.042 $\Omega^{-1}\,\mathrm{cm}^{-1}$. Using Equation 1 to calculate A_d gives a value of

$$A_d = 1.08 \times 10^{-8}$$

Expressed as a 'real' area this gives $5.29 \times 10^{-8}\,\mathrm{cm}^2$.

Using Equations 2 and 3 should, according to Mansfeld, then give roughly similar values of A_d, within experimental error.

The values of the polarization resistance, R_p, the bare metal polarization resistance, R^0_p, the double layer capacitance, C_{dl}, and bare metal double layer capacitance, C^0_{dl}, were calculated from fitting a semicircle to the low frequency impedance data. Using these values in Equations 2 and 3 gives values of A_d very different from the value of A_d calculated from Equation 1:

$$R_p = 874\,\mathrm{k\Omega} \quad R^0_p = 75\,\Omega$$

$$C_{dl} = 36\,\mathrm{nF} \quad C^0_{dl} = 210\,\mu\mathrm{F}$$

and, from Equation 2:

$$R_p = \frac{R^0_p}{A_d} \quad A_d = 8.6 \times 10^{-5}$$

Expressed as a 'real' area this gives $4.2 \times 10^{-4}\,\mathrm{cm}^2$, and, from Equation 3:

$$C_{dl} = C^0_{dl} A_d \quad A_d = 1.71 \times 10^{-4}$$

Expressed as a 'real' area this gives $8.4 \times 10^{-4}\,\mathrm{cm}^2$.

It can be observed that while Equations 2 and 3 give approximately the same value for A_d, Equation 1 underestimates A_d by a factor of about 10^4 as it fails to take into account delamination under the coating. In fact it is the coating porosity P which is obtained from Equation 1, not A_d (= W). While the data shown in this communication is only from one experiment it is representative of many similar measurements.

One further point is worth making. Mansfeld [1] claims that Bode plots are better at showing coating breakdown than Nyquist type (complex plane) plots. We have found the opposite to be the case in most situations. Figure 3(a) and (b) shows the Bode plot for the impedance data presented here. Figure 2 shows the Nyquist type (complex plane) plot for the same data. It can be seen that the low frequency impedance characteristics are clearly observed and can be easily measured on the Nyquist type (complex plane) plot, but are virtually undetectable on the Bode plot.

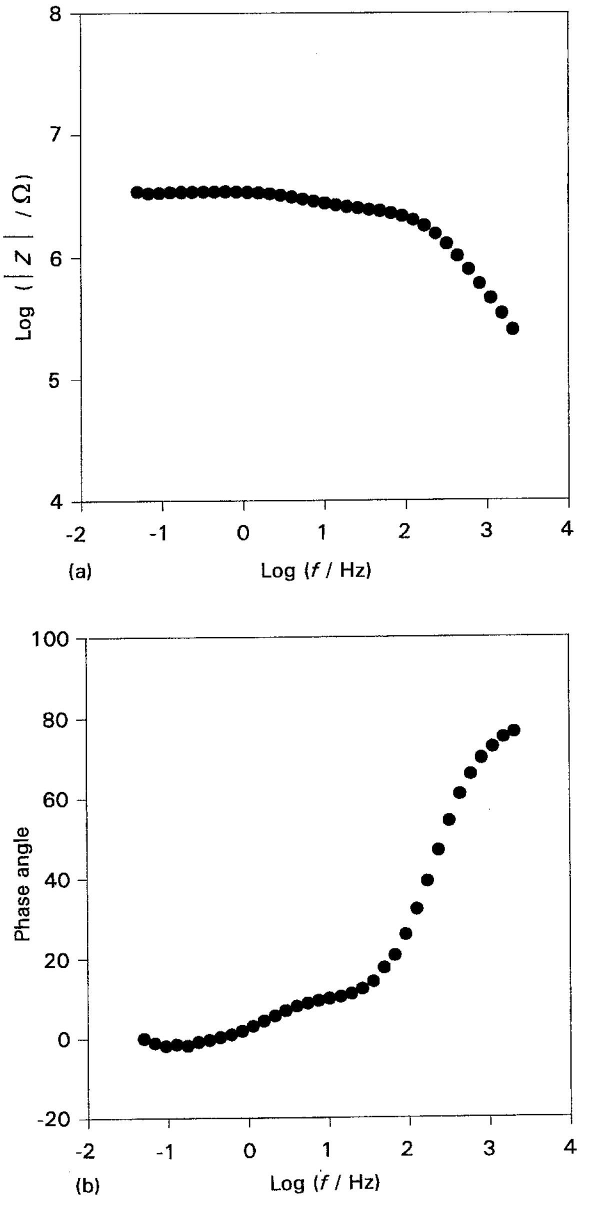

Fig. 3. (a) Bode plot of degraded polyester on steel; (b) Bode plot of degraded polyester on steel.

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