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The influence of electrode polarization on corrosion beneath paint

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ABSTRACT

A Zn–Fe bi-electrode coated with different clear lacquers was exposed to NaCl solution, so that a well-defined galvanic cell was established with the current directly measured by a zero-resistance ammeter (ZRA). Electrochemical impedance spectroscopy (EIS) was periodically used to monitor the two coated electrodes individually or coupled together. Transient potentiostatic current measurements were also made after applying potential steps of different amplitudes to the individual metals, from which polarization curves were plotted. The ohmic potential drop in the paint was corrected using film resistance values determined by EIS. Evans diagrams were thus plotted from the *iR*-corrected polarization curves to make the first experimental determination of Evans diagrams as used by Mayne[1] to illustrate his resistance inhibition model.

1. Introduction

It has long been recognized that paints with high ionic resistance when applied to metals confer good protection [1]. Mayne rationalized this as "resistance inhibition", using an electrochemical model of corrosion with anodes and cathodes created at different locations so that corrosion currents need to pass through the paint between anodes and cathodes and are inhibited by high coating resistance [2]. These ideas underpin our use of EIS in assessing protective coatings. Our aim here as been to establish a well-defined galvanic cell between iron and zinc, so that the galvanic current can be measured directly by zero-resistance-ammetry, providing a well-characterised model analogue of such a corrosion cell. The sample also simulates the behaviour of a zinc coating on galvanized steel damaged in processing and subsequently painted. Such a direct measurement is not possible in normal tests on coated metal panels.

In a separate set of measurements changes in the coating above anode and cathode were assessed by EIS, and the anodic polarization of the zinc and cathodic polarization of the steel were measured potentiostatically, using a potential step method.

By combining these measurements we have been able to plot Evans diagrams (as used by Mayne to illustrate resistance inhibition) from real data for the first time, with correction of the overpotential for ohmic potential (*iR*) drop in the paint. Results for polyvinyl butyral (PVB), epoxy-amine and a vinyl-hydrocarbon coating are obtained.

2. Experimental

2.1. Sample preparation

Bi-metallic specimens were prepared as described previously [3]. The electrodes (7 mm × 10 mm) were made from mild steel (Q panel) and 99.99% pure zinc foil (Advent Research Materials Ltd.) hot-mounted side-by-side in acrylic resin (ClaroFast, Struers). The electrodes were separated by a narrow gap (~0.5 mm) and each was connected to a wire for electrical measurements. The front surface was ground flat with P800 grit metallographic paper, cleaned with ethanol, and dried in air, before applying the coating.

A poly-vinyl butyral (PVB) solution was prepared by dissolving 100 g of PVB powder (Aldrich: average molecular weight 70,000–100,000) in 600 g of ethanol. Unpigmented epoxy resin was prepared by mixing un-pigmented epoxy resin and a proprietary phenalkamine curing agent (International Paint). The one-pack vinyl coating system was based on a proprietary blend of resins: Laroflex MP45 (BASF), a PVC copolymer, a specifically developed proprietary hydrocarbon resin, and DER331, a bis-A epoxy resin (Dow Chemicals) and was supplied as a solution in xylene/methyl isobutyl ketone (9:1 by wt) by International Paint. Coatings were applied to the specimen by draw down using a glass rod with PVC insulation tape as a thickness guide. The dry film thicknesses (measured with an Elcometer SS.1200 thickness gauge) were PVB 69 μm (at its thinnest part), epoxy resin 54 μm and vinyl resin

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[1] J.E.O. Mayne, Chem. Ind. (London, UK), 293 (1951).

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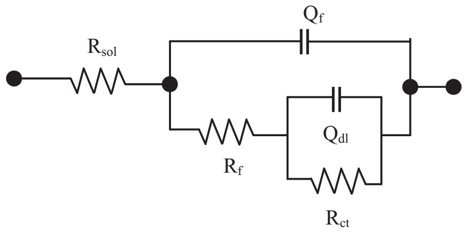

Fig. 1. Equivalent circuit for a coated metal.

40 μm. Finally, the edges of the specimen were sealed with hot 4:1 beeswax/colophony mixture to avoid any attack at edges.

After curing for an average of 3 weeks, the two metals were connected together to create a galvanic corrosion cell and exposed to 1% (w/v) NaCl solution.

2.2. Experimental measurements

2.2.1. Electrochemical impedance spectroscopy (EIS)

Measurements were taken after different periods of exposure using a Gill AC Potentiostat with a high-impedance paint buffer (ACM Instruments) to provide sufficient input impedance. A saturated calomel electrode (SCE) was used as the reference electrode and platinised titanium as the counter electrode. The impedance was measured separately for each electrode at the potential of the coupled electrodes, or with the electrodes connected together. The frequency range was 30 kHz to 0.1 Hz and the excitation signal 20 mV. The EIS data were fitted using *ZSimpWin* 2.0. software to the model circuit $R(Q(R(QR)))$ (Fig. 1): R_{sol} is the solution resistance, Q_f is the non-ideal coating capacitance (constant-phase element), R_f is the coating resistance, Q_{dl} is the double-layer capacitance (CPE with $n \approx 1$) and R_{ct} is the charge transfer resistance.

2.2.2. Zero-resistance ammeter (ZRA)

With the zinc and steel connected via the ZRA (Gill AC Potentiostat) current was measured continuously after different periods of immersion in NaCl solution. The potentiostat maintains zero potential difference between the two sample leads (as if they were connected) and records the current supplied to achieve this.

2.3. Potentiostatic measurements

A series of potential steps from the measured rest potential (normally 100–400 mV) were applied to the working electrode under potentiostatic control. The resulting current transient was measured at intervals of 0.02 s and the value after a fixed delay of 180 s (to allow current to stabilize) was recorded as the steady current. The sample was returned to its rest potential until current become steady before applying another step. The potential step causes fast charging of the coating capacitance so that interfacial response can be more readily observed [4]. It avoids error from charging current that would interfere with a potentiodynamic test.

3. Results

3.1. PVB coating

Fig. 2(a)–(c) shows Nyquist plots after 6 d exposure for the steel electrode alone, the zinc electrode alone, and the coupled pair. All show well-defined high-frequency semi-circles, with the diameter being much larger in the case of zinc. The diameter of the high frequency semi-circle gives the coating resistance, R_f. It is clear that the EIS plot of the coupled electrodes is very similar to that of the steel electrode, because the low impedance of the coated steel is placed in parallel with the higher impedance of the coated zinc electrode. The parameter values obtained from the first semi-circles are listed in Table 1.

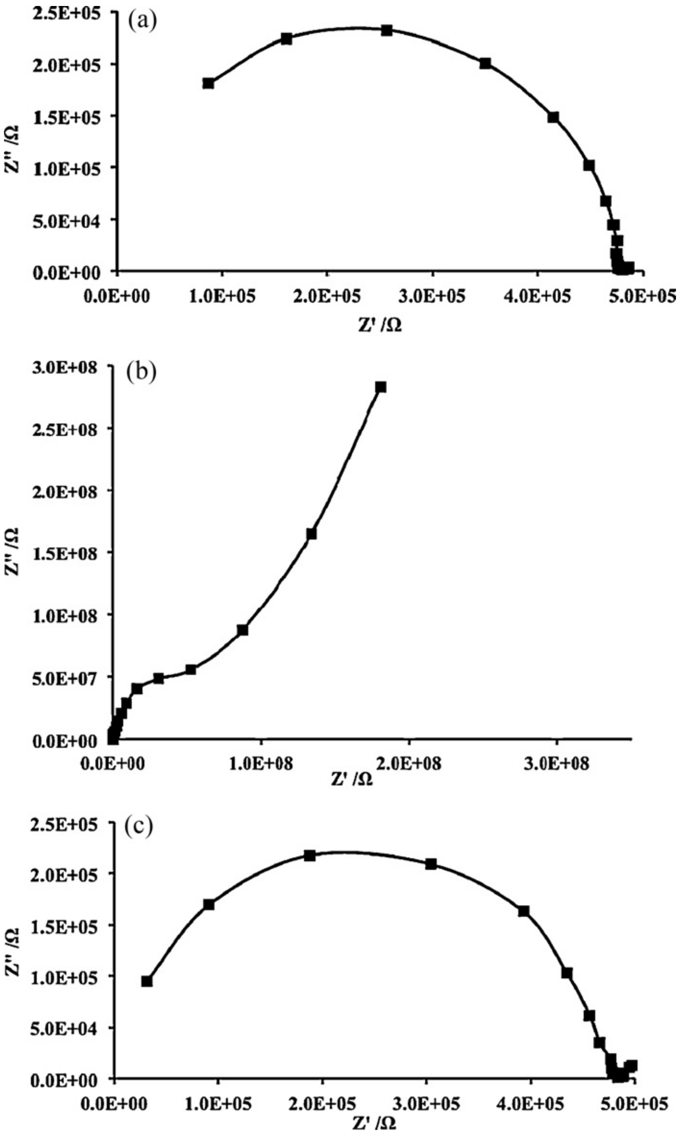

Fig. 2. EIS data (Nyquist plots) of PVB-coated steel (a), zinc (b) and coupled (c) electrodes (after 6 d in 1% NaCl solution).

The coating resistance above the zinc electrode is 10^7–$10^8\ \Omega$ throughout the measuring period, while the coating resistance above the steel is only in the 10^5–$10^6\ \Omega$ range. The coating resistances fall as the film deteriorates, but coating capacitances change little over time. The measurement for samples coupled together shows only the lower resistance on the steel and gives no

Table 1
Parameters for PVB film from fitting of EIS results.

	Time (d)	Q_f (nF)	n	R_f (MΩ)
Zinc	6	0.124	0.94	127
	13	0.109	0.96	83.6
	20	0.146	0.93	50.6
Steel	6	0.101	0.97	0.478
	13	0.100	0.98	0.349
	20	0.113	0.97	0.405
Coupled	6	0.178	0.98	0.469
	13	0.183	0.98	0.333
	20	0.203	0.97	0.397