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SHORT COMMUNICATION

A simple nondestructive electrochemical method to test the barrier resistance of organic coatings

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1. Introduction

Organic coatings on metallic substrates are widely used to prevent metal corrosion especially in the case of iron alloys. The quality of these protective coatings is generally very good, thus making it difficult to apply classical electrochemical corrosion measurements, (i.e., current potential curves performed at low potential, such as the Tafel method). Even electrochemical impedance measurements require the use of specially designed high impedance potentiostats [1]. Consequently, these methods are mostly used during destructive accelerated corrosion tests [2].

Another difficulty is the fact that corrosion often occurs at point defects on the coatings, which may be either intrinsic (as a result of the coating method itself) or extrinsic (due to accidental scratching of the paint): in this last case extrapolation from laboratory tests to real size pieces is hazardous.

The high potential, fast electrochemical scanning method presented here may overcome some of those problems, as this method is very sensitive, nondestructive, and usable on real, large area coatings. This method can be used to measure the barrier resistance and capacitance of the coating itself. These are more or less independent of the substrate behaviour, the knowledge of which is generally not essential for practical tests.

As is well known, a perfect coating in contact with an electrolytic solution should behave in a purely capacitative manner [3]. However, defects lead to ohmic behaviour due to the presence of mobile ions in the coating [4]. We consider here that these ions are provided by water present in the porosity.

2. Experimental details

A coated sample A ($30\,\mathrm{cm}^2$), acting as working electrode, constituted one side of the electrochemical cell (Fig. 1). This side was separated by a rubber joint C from the other side B, made of polymethyl methacrylate. A platinum wire D acted as both counter and reference electrodes. The electrolyte E was generally a dilute (0.5 M) NaCl solution. The cell was connected (Fig. 2) to a high voltage Tacussel potentiostat (PRT 100–1 X), driven by an analogue programmer Tacussel 'Servovit' (some problems may occur with digital programmers, giving 1 mV increments). The potentiostat was used in a two electrode potential amplifier mode (i.e., like a programmed power supply). To avoid current loss through the $1\,\mathrm{M\Omega}$ input resistance of the analogue X–Y plotter (Kipp and Zonen), the potential was directly recorded from the programmer signal. The current flowing in the cell was recorded across the $1\,\mathrm{M\Omega}$ serial resistance R_m. This current was calculated taking into account the $1\,\mathrm{M\Omega}$ internal potential divider of the recorder (i.e., 1 V recorded on the 'I' channel was read as $2\,\mu\mathrm{A}$). This $0.5\,\mathrm{M\Omega}$ resistance was negligible compared to the measured ones.

3. Results and discussion

Figure 3 shows a typical voltammetric curve. The potential E was scanned at $20\,\mathrm{V\,min^{-1}}$ towards negative potentials. The curve can be primarily seen, under steady state conditions, as the superposition of a capacitative charging current i_c and an ohmic one i_o. According to Fig. 4, where R_tc and R_tw are transfer resistances at the counter and at the working electrodes, the capacitance C_c of the cell is easily calculated as

$$C_\mathrm{c} = \frac{i_\mathrm{c}}{\mathrm{d}E/\mathrm{d}t}$$

and the barrier resistance R_b (provided $R_\mathrm{m} + R_\mathrm{tc} + R_\mathrm{tw} \ll R_\mathrm{b}$) as

$$R_\mathrm{b} = E/i_\mathrm{o}$$

C_c is typically of the order of a few nanofarads and R_b of a few gigaohms. These entities, normalized to one square centimetre, are written R_b ($\Omega\,\mathrm{cm}^2$) and C_c ($\mathrm{F\,cm^{-2}}$). Then the permittivity ε is given by

$$\varepsilon = c_\mathrm{c}\delta/\varepsilon_0$$

where ε_0 is the vacuum permittivity ($8.85 \times 10^{-14}\,\mathrm{F\,cm^{-1}}$) and δ is the coating thickness. More thorough information may be extracted from the part of the curve where the voltage sweep is reversed: here the curve looks like an exponential which may be written as

$$i = i_\mathrm{o} \exp(-t/\tau)$$

The calculated time constant τ is typically of the order of a few seconds. Taking into account the serial $0.5\,\mathrm{M\Omega}$ measuring resistance, a capacitance of a few microfarads may be derived. This result disagrees with the previously calculated coating capacitance (a few nanofarads). No definitive explanation is given for this problem. It is possible that the counter electrode transfer resistance, R_tc, may become large

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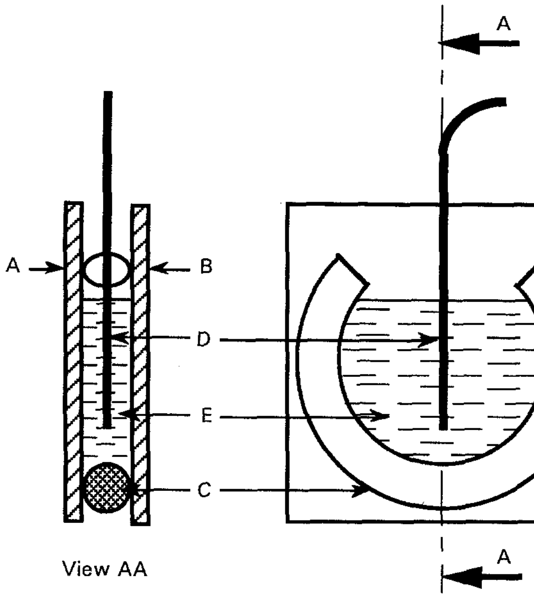

Fig. 1. Cell configuration: coated sample (A), Pt counter electrode (D), NaCl electrolytic solution (E), polymethyl methacrylate wall (B), rubber joint (C).

enough (1 GΩ) to explain the observed time constant value when the potential sweep is reversed (i.e., the current sweeps locally from anodic to cathodic). This electrode, a platinum wire with an area about 20 mm^2, is where oxygen or hydrogen evolves.

Finally, one may try to calculate the damage induced by the experiment itself, that is, by charge transfer at the substrate–electrolyte interface under the coating, noting that the current remains there cathodic. The duration of a cycle is typically 2 min, with an average faradaic current of 1 nA (i.e., 120 nC or 1.2×10^{-12} faraday) corresponding theoretically to the evolution of 0.6×10^{-12} mole of hydrogen (i.e., 1.5×10^{-8} cm^3) over a mean area of 30 cm^2: this is really negligible. Indeed the parameters (higher potential and scanning speed) must be adapted to each coating quality to obtain significant results without damaging the sample. Accidental scratches may lead to catastrophic localised currents with hydrogen evolution.

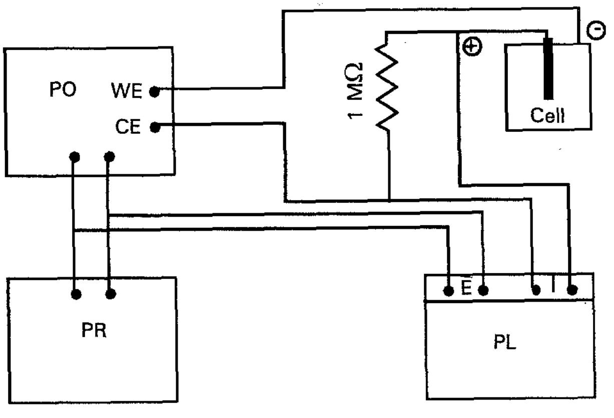

Fig. 2. Electrical setup: potentiostat (PO, used as a power supply), programmer (PR), X-Y plotter (PL).

4. Examples of practical tests

Four series of identical phosphated steel plates were painted using two different procedures (cataphoresic or electrostatic paints). The results are reported in Table 1. For each series, ten plates were tested. The reported results are averaged values, after eliminating the anomalous results (low R_b) which were attributed to accidental damage of the plates.

It appears that the barrier resistances, R_b, are always high, and roughly linked to the thicknesses of the coatings, the resistivities of which remain relatively constant, at least for cataphoresic painting. The capacitances appear to vary as the inverse of the thicknesses, leading to relatively constant permittivities, ε. The high values obtained for ε may be due to residual water in the coating. This hypothesis may also explain why the resistivities, ρ, are always lower than their intrinsic values for the polymer. This interpretation is confirmed by the following experiments:

(i) Heating (at 200 °C for 15 min) of some plates with low R_b values ($< 3 \times 10^{11}$ Ω cm^2) and high ε values ($\varepsilon > 12$) leads to the enhancement of R_b (6×10^{11} Ω cm^2) and the lowering of ε (7.9).
(ii) Measurement using Hg instead of aqueous solutions also gives high R_b and low ε values.

Here arises the fundamental question of the validity of R_b for measuring the coating quality as it depends not only on the porosity but also on the resistivity of the water solution inside this porosity. Measurements of NaCl diffusion from the outside solution clearly require slow and destructive assays. This question is general and also occurs for a.c. impedance measurements. However, the initial values of R_b do have some significance.

Finally, the product R_b C_c appears relatively constant for a given type of paint.

5. Conclusion

The simple and inexpensive method presented here is nondestructive, as successive tests on the same plate give similar results, if the plate has been extracted from the solution between the tests. However, prolonged contact with the saline solution progressively damages the plates.

Testing of the same plates under salt spray has not allowed differentiation between series 1 and 2, which showed different R_b values. These destructive tests are probably more sensitive to the adherence quality than to the barrier behaviour of the coatings. A more thorough analysis of these results, correlated with new experiments, should clarify the meaning of the time constant observed at the current inversions. Nevertheless, the two calculated parameters R_b and C_c seem to be sufficiently significant for practical use, considering a coating choice. Moreover, they are often the only data extracted from more sophisticated a.c. impedance measurements [5].

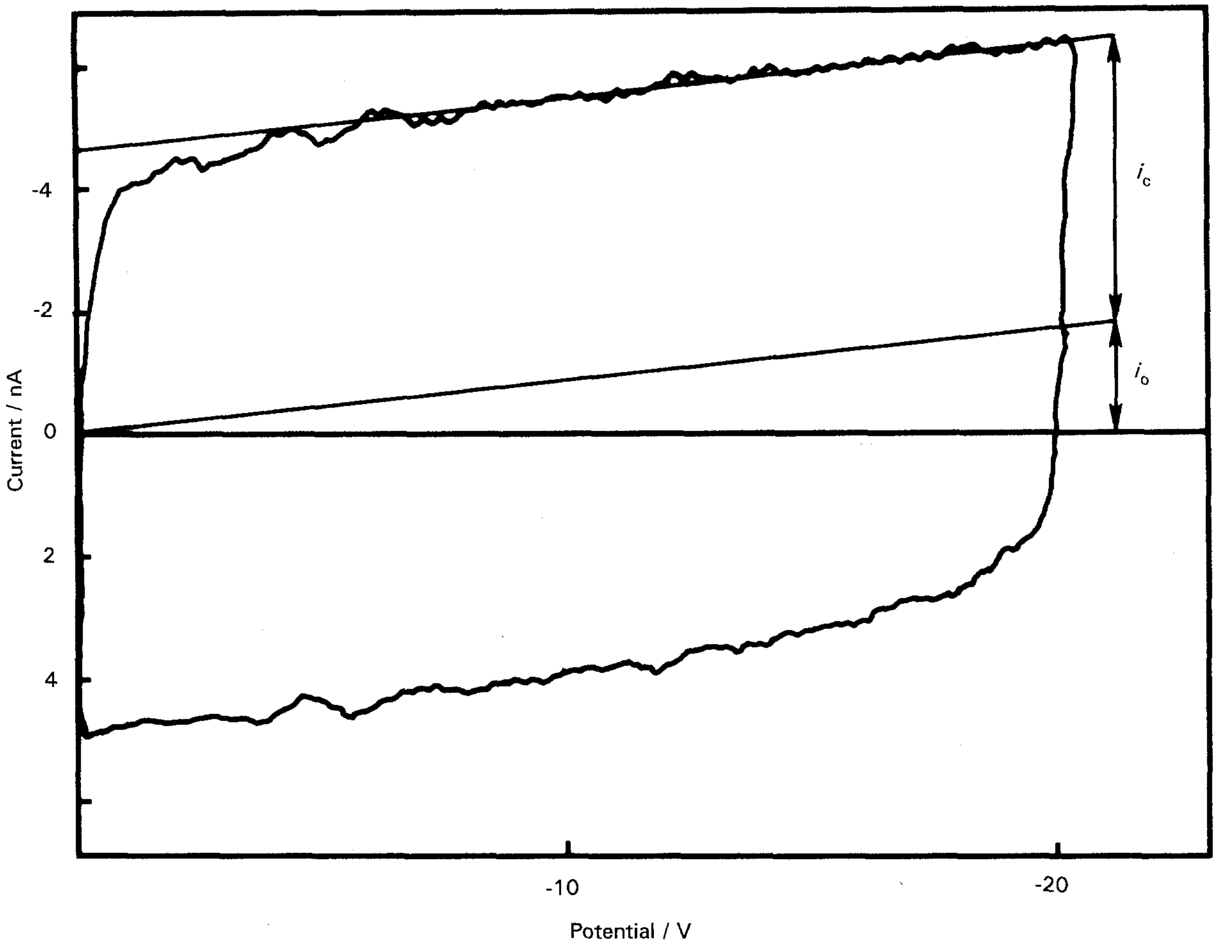

Fig. 3. Example of a recorded voltammetric curve ($dE/dt = 20\,\mathrm{V\,min^{-1}}$): capacitive current ($i_c$), ohmic current ($i_o$).

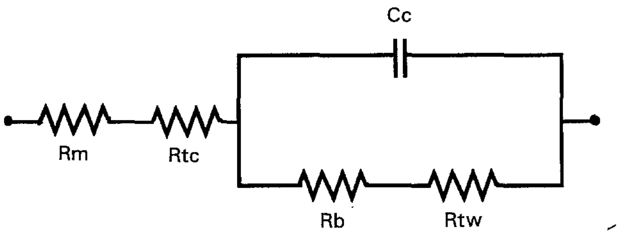

Fig. 4. Model used to define the characteristics of a coated sample. C_c; coating capacitance, R_b: barrier resistance, R_m: 1 MΩ measure resistance, R_{tw}: transfer resistance at the working electrode, R_{tc}: transfer resistance at the counter electrode.

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Table 1. Comparison of the results obtained on four series of painted steel plates

Lot	*th* μm	R_b /GΩ cm^2	ρ /TΩ cm	C_c /pF cm^{-2}	ε	R_bC_c /s
1*	28–29	480	170	260	8.3	125
2*	14–15	320	210	370	6.2	118
3*	17–19	330	190	330	6.9	109
4†	110–190	780	50	65	9–18	51

* Cataphoresic paintings
† Electrostatic paintings

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