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Impedance studies into the corrosion protective performance of a commercial epoxy acrylic coating formed upon tin plated steel

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The behaviour of epoxy acrylic coatings (on tin plated steel) when contacted with aqueous solutions of hydrochloric acid and a citrate buffer solution has been examined. The behaviour can be explained by assuming that the coatings contain defects which allow the solutions to penetrate them and contact the underlying metal.

1. Introduction

Organic polymeric coatings have been widely used in the corrosion protection of metals in many different environments. One such application is the interior of food cans. A typical food can may consist of two or three pieces of tin plated steel coated with an organic coating such as an epoxy acrylic.

The corrosion performance of polymer coated metals has received much attention in the literature [1–4]. Since corrosion is essentially an electrochemical process, the electrochemical properties of a system are of particular importance. As well as d.c. measurements an increasingly popular method for characterizing organic coatings is electrochemical impedance spectroscopy [5–14], which has the advantage of being a small signal perturbation technique. This allows the system to be studied at potentials close to the corrosion potential, thus avoiding irreversible changes to the system caused by potentials different from the corrosion potential.

A perfect protective coating would have:

- No free ions present in it
- No oxygen or water present in it
- Zero mobility for ions
- Zero diffusion coefficients for oxygen and water

Such a protective coating would prevent either atmospheric or electrochemical corrosion of the underlying metal. The impedance for such a coated metal when in contact with, for example, 0.1 M HCl would be entirely capacitive with the capacity, C_g, given by

$$C_g = \varepsilon_0 \varepsilon_r A/d \qquad (1)$$

where A is the surface area of the coated metal, d is the polymer thickness and ε_r is the dielectric constant of the film (assumed frequency independent). In principle there is a resistance, R_0, in series with C_g due to the electrolyte solution between the protective coating and the reference electrode, which may be evident at high frequencies. If a real coating gives a capacitive impedance over the available frequency range this does not necessarily mean that it is a perfect coating but only that the concentration and mobility of ions in it is too small to be measured. There is no information concerning the concentration and diffusion coefficients of oxygen and water in the coating from impedance spectroscopy. However, corrosion of the underlying metal, which occurs solely as a result of the diffusion of molecular oxygen and/or molecular water through the coating without any ion movement in the coating, may be evident from impedance spectroscopy if a low conductivity oxide/hydroxide is formed between the metal and the polymer.

Real protective coatings generally have a finite ionic conductivity equivalent to a resistance R_b which appears to be a bulk property of the film. This is due either to defects in the coating which contains aqueous solution, or to true ionic conductivity in the bulk of the coating. In the case of defects, where these are of near uniform cross section in nature and run orthogonal to the polymer film, we can write

$$R_b = d/aN\kappa \qquad (2)$$

where N is the number of defects per unit area, a is the average area of a single defect and κ is the conductivity of the aqueous solution. Therefore, one way of characterizing defective coatings of this type is to measure R_b and calculate the apparent value of aN.

The geometric capacity, C_g, of a real coating in contact with an aqueous electrolyte is likely to be different from that due to the coating in the dry condition as a result of the presence of water molecules and water droplets. The presence of a high dielectric material like water in the coating would be expected to cause the value of C_g to increase as a result of an increase in the dielectric constant. One complication

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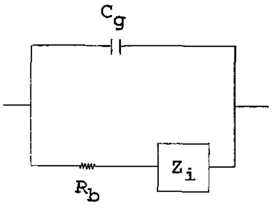

Fig. 1. The equivalent electrical circuit of a coated metal exposed to an electrolyte.

here is the fact that, in polymeric materials, the dielectric constant is generally frequency dependent as a result of restricted molecular motion in the polymer. Nevertheless changes in C_g can be used as some measure of the extent of water uptake. For example a coating which is essentially nothing but water would be expected to have a dielectric constant close to 80.

The complete equivalent circuit for the impedance of a coated electrode with pores which allow electrolyte penetration to the metal surface has been considered by numerous authors [3, 4, 8, 10, 11, 12, 24] and the generally accepted circuit is that shown in Fig. 1, where Z_i is the interfacial impedance due to the pore ends nearest the metal surface. In the simplest case Z_i is made up of a double layer capacity, C_{dl}, in parallel with a charge transfer resistance, R_{ct}. If the metal is potentiostatically controlled in a deaerated solution so that the only process occurring is hydrogen evolution the measured R_{ct} refers to this process alone; similarly, if the potential is held anodically to the corrosion potential the R_{ct} observed is due to the metal dissolution process only (provided that the metal is in the region of active dissolution). On open circuit, however, both processes occur at the same rate, hence the R_{ct} measured arises from both the anodic and cathodic reactions. Therefore, the R_{ct} measured on open circuit can be used as a measure of the corrosion rate. If diffusional processes are involved at the metal/solution interface Z_i may have contributions from Warburg type impedances. C_{dl} (measured in $\mathrm{F\,cm^{-2}}$) would be expected to be very much smaller than the corresponding C_{dl} value for the bare metal surface in contact with aqueous solution, C_{dlo}, because of the very much smaller contact area between the metal and the aqueous solution in the film covered case. In fact C_{dl}/C_{dlo} should correspond to the ratio of wetted surfaces in the two cases. Likewise, if R_{cto} is the R_{ct} value for the bare metal R_{cto}/R_{ct} should also give the ratio of wetted surfaces, provided that both are measured at an identical potential. This means that in a favourable case it is possible to compare two dimensionless ratios for protective coatings with defects running through them: one corresponding to the number of defects running through the bulk of the film (aN) and one corresponding to the extent of wetted metal in the presence of the film (R_{cto}/R_{ct}).

Measurements of interfacial impedances are generally made at the open circuit corrosion potential, in which case the R_{ct} values are identical to the corrosion polarization resistance values, normally designated R_p. However, this is not the case if measurements are made at potentials different from the corrosion potential.

There are many more complex possibilities for Z_i, particularly if the coating has begun to delaminate, since, in this case, distributed impedances may be present. There is also the possibility that the charge transfer processes on the bare metal may be diffusion controlled, in which case the processes on the coated metal is probably also diffusion controlled. In the present investigation, in order to effectively study the processes occurring at the polymer/metal interface, it was considered necessary to also investigate the electrochemical properties of the uncovered tin surface. This was performed using impedance spectroscopy and a rotating disc electrode.

An alternative method of measuring the corrosion current in the presence of a coating, and from this estimating the wetted metal surface area, is to perform a potential sweep through the corrosion potential, and to use a Tafel plot to determine the corrosion current. The corrosion current is measured on the bare substrate ($i_{cor(bare)}$) and on the coated samples ($i_{cor(coated)}$). Because the corrosion current is directly proportional to the surface area of the metal exposed to the electrolyte the extent of wetted metal in the coated sample is expected to be equal to the ratio ($i_{cor(coated)}/i_{cor(bare)}$).

One of the most relevant impedance studies of the behaviour of coated tinplate is that of Drazić *et al.* [16] where, in the case of an epoxy-phenolic lacquer, evidence was found for pre-existing pores which rapidly filled with the aqueous contacting solution. The delaminated area (or wetted area) was found to be as high as 1 part in 500 of the total coated surface. Although Drazić [16] characterized the corrosion properties of lacquered tinplate by a.c. and d.c. methods, the difference between the porosity of the coating and the wetted surface area beneath the coating was not stressed. Work by Montanari *et al.* [17] on lacquered tinplate also found evidence in some coatings for pre-existing pores which filled with electrolyte, and Tait [18] proposed the use of the charge transfer resistance to determine the suitability of a coating for a given application.

Some older studies [19, 20, 21] have proposed the use of d.c. polarization measurements in the evaluation of lacquered tinplate. They were particularly directed at evaluating the mean corrosion current. A critical review by Walter [23] of d.c. measurements of painted metals is available.

There are many references in the literature for characterization and lifetime prediction of organic coatings on metals, especially coated steels. Previous impedance work has suggested the use of the charge transfer resistance and the double layer capacitance of the coated and bare samples to determine the wetted metal surface area beneath the coating [8, 11, 13, 25]. The porosity of an organic coating has been previously estimated from its bulk resistance [24].

The principal objective of the present study was the determination of the relationship between the porosity of the coating on the one hand and the wetted surface area beneath the coating on the other, since this relationship has not previously been addressed. We have used i_{cor}/i_{coro} as the measure of wetted metal area since, in the present case, the interfacial impedance at the bottom of pores is complicated by the diffusion of Sn^{2+}. Although Haruyama *et al.* [25] performed similar measurements on polymer coated steel they did not stress the difference between wetted metal area beneath the film and the porosity of the sample.

2. Experimental details

The coatings under study were formed on tin plated steel, the surface of which was prepared by degreasing with acetone followed by immersion in 0.1 M HCl for 2 min. The tin plate (4 cm × 4 cm) was then dipped into the emulsion, and placed in a pre-cure oven (100° C) for 10 min before being transferred to the curing oven (200° C) for 2 min (film thickness 60 μm). Double coated samples were prepared by repeating the above procedure on a single coated sample.

Two electrolytes were used in this work, 0.1 M hydrochloric acid and a citrate buffer solution containing 0.5 M citric acid, 0.5 M sodium citrate and 0.1 M sodium sulphate. The citrate buffer solution is similar to the environment to which a real can lacquer may be exposed and 0.1 M HCl was chosen as a medium in which any corrosion products are likely to be soluble. All solutions were prepared using thrice distilled water, and all measurements were made at room temperature (23 ± 2° C).

The coated samples were examined using a specially designed three electrode cell which contained a stainless steel auxiliary electrode, a saturated calomel reference electrode and an exposed area of coated metal (working electrode) of 5.32 cm^2. The atmosphere above the cell was either nitrogen or oxygen. All impedance spectra were obtained using a Solartron 1255 frequency response analyser in conjunction with a Solartron 1186 electrochemical interface. The input impedance of the 1186 was greater than 10 GΩ, enabling impedances of 1 GΩ to be measured to an accuracy of 10%. The spectra were recorded at the corrosion potential and any change in the impedance spectrum was monitored with time.

The corrosion rate of the coated samples was measured by performing a potential sweep from 0 to −200 mV with respect to the corrosion potential at a rate of 25 mV min^{-1} (the anodic part of the sweep was omitted to minimize undercutting of the metal). The data was plotted as a Tafel curve, and the corrosion current was taken from the intercept of the corrosion potential with the extrapolated linear region curve. If the measured current was below the limit of the potentiostat used (0.1 nA) the cell was switched to a low current unit (resolution 0.1 pA) operating in a two electrode mode (Ag/AgCl auxiliary and reference) contained in a Faraday cage.

The ionic conductivity of the coating in its initial unwetted form was measured using a specially adapted two electrode micrometer cell, which consisted of two parallel stainless steel electrodes [22]. The change in capacitance of a sample was measured after exposure to a 75% humid atmosphere and agian after contact with deionized water. In the last case excess water was removed using a clean filter paper.

The bare substrate (tin plated steel) was characterized in the same way as the coated samples using the three electrode cell and measuring the impedance and current–potential relationships.

The electrochemical behaviour of pure tin was characterized in deaerated 0.1 M hydrochloric acid. This was performed using a rotating disc electrode (of surface area 0.196 cm^2) and sweeping the potential from −0.7 to 0.5 V with respect to the corrosion potential at a rate of 25 mV min^{-1} and a rotation speed of 5000 r.p.m.

To observe the rotation speed dependence of the current at a particular potential the current was monitored at four rotation speeds. This was performed at two potentials, 50 mV positive to the rest potential and 600 mV negative.

In order to obtain reproducible results for the rotating tin disc electrode it was necessary to follow a standard routine of electrode preparation. This consisted of an acetone wash followed by polishing with aluminium oxide powder (3 μm), rinsing with deionized water and polishing with a finer powder (0.3 μm) before a final wash with deionized water. The tin was then held 50 mV positive to the rest potential for 5 min to corrode the tin to a fresh surface and remove embedded polishing material.

The FTIR spectra of coated samples were recorded using a Digilab Qualimatic QS 100 (QC REV 2.51) spectrometer over a frequency range 4500–600 cm^{-1}. The reflectance spectra of an uncoated substrate, a coated untreated sample and samples which had been treated with 0.1 M hydrochloric acid and the citrate buffer solution for one week, were recorded at an indicent angle of 50°.

3. Results and discussion

When a coated sample was initially exposed to either 0.1 M hydrochloric acid or the citrate buffer solution, the coating was capacitive down to 10^{-2} Hz. After a short period of time (2–3 h) the coated sample became measurably conductive giving an R_b value which fell with time, becoming time independent after several days. A series of impedance runs performed in deaerated 0.1 M HCl are illustrated at Nyquist plots in Fig. 2, where the fall in the bulk resistance with time can be clearly seen. The results from a similar series of runs involving contact with HCl and the citrate buffer are shown in Fig. 3, the R_b value of the coating in contact with the 0.1 M HCl at long times being lower than that for the citrate buffer.

A sample which had been in contact with 0.1 M HCl was then contacted with 1 M HCl. The bulk resistance of the coating rapidly dropped by a factor of ten (Fig. 4).

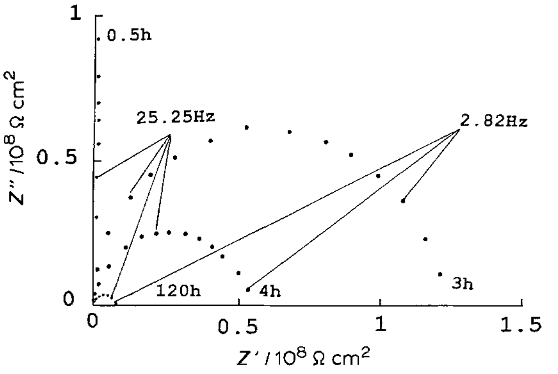

Fig. 2. A series of Nyquist plots illustrating the fall of the bulk resistance with time of a coating contacted with 0.1 M HCl under nitrogen (measured at the corrosion potential).

The change from an initially capacitive spectrum to a conductive spectrum on exposure to an electrolyte indicated the short circuiting of the polymer dielectric by the formation of ionically conducting pathways through the polymer. The fact that the R_b value fell and then became stable, and that this stable value was sensitive to the concentration of the electrolyte, can be explained if it is assumed that there are channels in the polymer which allow penetration of the aqueous solution to, or almost to, the metal surface. The behaviour of the double coated samples support this view since they remained capacitive over several weeks, which can be explained on the assumption that any defects in the first coating do not align with any in the second. Therefore it is reasonable to have some confidence in the dimensionless ratio aN, which is a measure of the extent to which the film has defects filled with aqueous electrolyte running through it and which, for these films, typically lies between 1×10^{-8} and 1×10^{-11}, i.e. for a geometric area of 1 cm^2 the area of defects which penetrate the coating lies between 1×10^{-8} and 1×10^{-11} cm^2. A film consisting entirely of defects would have an aN value of 1.

Capacitance measurements were performed in the micrometer cell on a coated sample which was (i) exposed to 75% humid atmosphere and (ii) contacted with deionized water followed by drying with a clean filter paper. The capacitance increased slightly with exposure to moist air and further increased with contact with liquid water (Table 1). These changes are consistent with incorporation of water into the polymer as water molecules. The increase in the dielectric constant on contact with liquid water is within the experimental error expected with 100% humidity. Therefore the incorporation of liquid water into the film cannot be detected over the effect of the incorporation of water molecules. The dielectric constant of the film increased from 3.11 to 3.78 for the dry film subsequently contacted with liquid water.

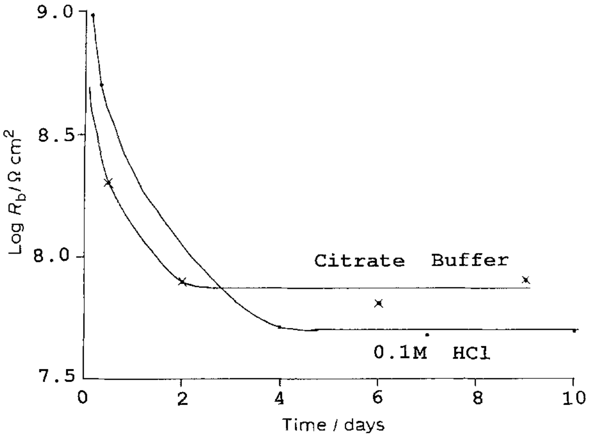

Fig. 3. Log R_b against time curves for two coated samples in contact with 0.1 M HCl and the citrate buffer.

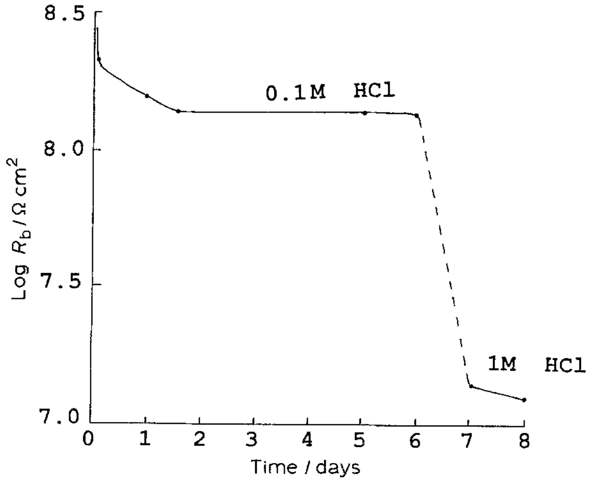

Fig. 4. Log R_b against time curve for a coated sample illustrating the effect of a ten fold increase in the concentration of the electrolyte (0.1 M HCl to 1 M HCl).

To study the corrosion processes occurring at the surface of the coated metal sample from the impedance measurements it is necessary to resolve the charge transfer resistance in the low frequency part of the Nyquist plot. This was impossible, as can be seen from Fig. 5, which illustrates how the bulk resistance was so high that the charge transfer resistance was unresolvable. Therefore the corrosion processes were investigated instead by recording the current–potential relationships for coated samples by slow linear sweep. Calculations of the ohmic potential drop within the pores of the film showed that it had a negligible effect on the i–E measurements.

The impedance spectrum of pure (uncoated) tin in contact with deaerated hydrochloric acid was recorded. The scatter of points around the high frequency part of the plot indicates that the charge transfer resistance is small i.e. the tin corrosion is very fast. At lower frequencies the spectrum exhibits a Warburg impedance, which suggests the corrosion of

Table 1. Capacitance measurements of a single coated sample after various treatments measured at 938 Hz

Treatment	*Capacitance /pF cm^{-2}*
Dry coating	69.0
75% humidity for 1 week	78.5
Deionized water dried with filter paper	83.7

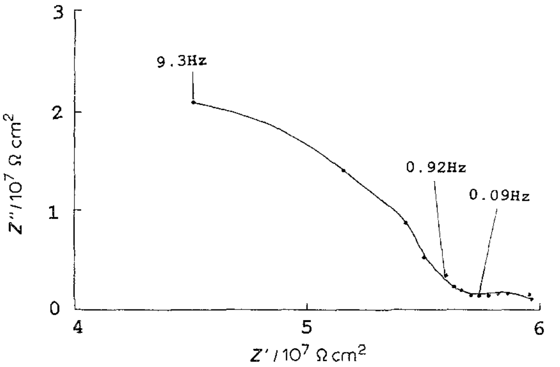

Fig. 5. Low frequency part of Nyquist plot of a coated sample measured at the corrosion potential, illustrating how the R_{ct} is unresolvable.

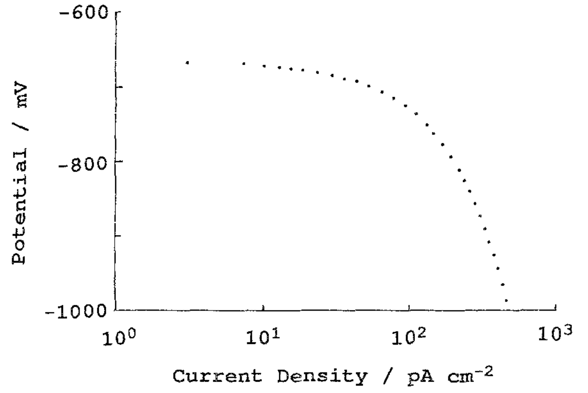

Fig. 7. Tafel plot of a coated sample (measured cathodic to the corrosion potential to avoid undercutting).

tin is a diffusion controlled process, probably involving diffusion of Sn^{2+} away from the surface. This is illustrated in Fig. 6. If diffusion of the Sn^{2+} is the rate controlling factor then the current observed at a fixed potential on the tin dissolution line will be dependent on the rotation speed of the electrode.

A series of potential sweeps were performed on pure tin and tin plate (both coated and uncoated). For the measurements on pure tin a rotating disc electrode was used. Typical Tafel plots of the tin plated steel are shown in Figs 7 and 8 for coated and uncoated samples. It is important to note the similar corrosion potentials of the coated and uncoated samples. The Tafel slopes of the curves for the uncoated sample are consistent with a diffusion controlled anodic process (b_a = 30 mV dec^{-1}) and a slow charge transfer cathodic process (b_c = 120 mV dec^{-1}). The apparent Tafel slope for the cathodic line on the coated sample was typically between 120 and 500 mV dec^{-1}. This led to an ambiguity in the determination of the corrosion, current. There was therefore, an uncertainty of a factor of ten in the value calculated for the wetted surface area. For the coated samples it was decided to perform the cathodic part of the sweep only, to minimize any undercutting of the metal. The corrosion current was taken as the intercept of the cathodic line with the corrosion potential. From these measurements if the corrosion current for a coated sample is taken to be proportional to the wetted area, for every 1 cm^2 geometric area the wetted metal area lies between 10^{-3} and 10^{-5} cm^2.

A potential was chosen on the tin dissolution (−0.533 V) line and the current was measured at four rotation speeds (Fig. 9), and a similar experiment was performed on the hydrogen evolution line (−1.115 V) as shown in Fig. 10. It can be seen that the cathodic current is independent of rotation speed unlike the anodic current. This rotation speed dependence of the anodic currents again suggests the tin dissolution process is governed by the diffusion of Sn^{2+} away from the surface.

The FTIR spectra of samples which had been exposed to the citrate buffer did not give evidence for any significant reaction, although in the HCl case there was some slight evidence for a new C–Cl stretch (690 cm^{-1}) after exposure to the electrolyte.

4. Conclusions

There are three main conclusions which can be drawn from this work:

1. The epoxy acrylic coating does not provide complete corrosion protection when applied to tin plated steel as described in the text. There are defects inherent in the coating which penetrate from the aqueous solution to, or close to, the substrate. In terms of earlier classifications of defects [26] these are D-type defects. The impedance measurements show that in 1 cm^2 geometric area of the coating there are defects equivalent to an area of between 1×10^{-8} and 1×10^{-11} cm^2. These defects may arise from residual

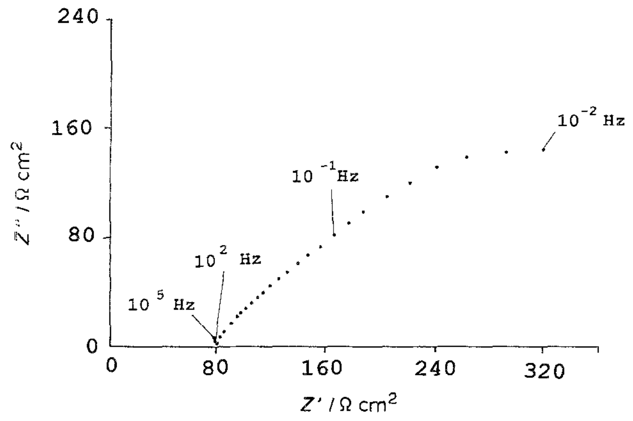

Fig. 6. Nyquist plot of the impedance of bare tin plate measured at the corrosion potential.

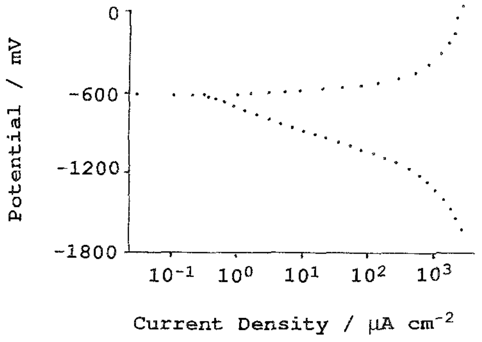

Fig. 8. Tafel plot of bare tin plated steel (−600–300 mV at 25 mV min^{-1}).

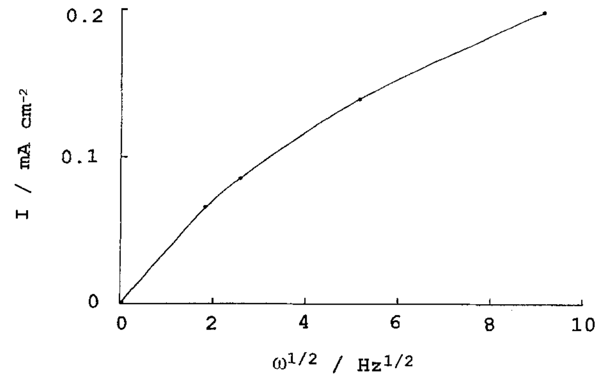

Fig. 9. Rotation speed dependence of current on the tin dissolution line (−533 mV).

solvent beneath the coating, or from small particles of dirt or grease on the substrate.

2. When a coated metal sample is exposed to an acidic medium (i.e. 0.1 M HCl or the citrate buffer) the solution penetrates these defects, forming conducting pathways through the coating. The electrolyte exhibits very little reaction with the coating, but when it reaches the tin surface corrosion occurs. The wetted area of the metal beneath the coating is typically between 10^{-3} and $10^{-5}\,\mathrm{cm^2}$ per $\mathrm{cm^2}$ of geometric area.

3. There is a surprising difference between the porosity of the film and the wetted surface area beneath it. For a particular sample values of $10^{-11}\,\mathrm{cm^2}$ porosity in the bulk of the film compared to $10^{-5}\,\mathrm{cm^2}$ wetted metal for every 1 $\mathrm{cm^2}$ geometric area, suggests that the coating has very few pores, but that when the electrolyte reaches the interface it rapidly spreads ($10^{-5}\,\mathrm{cm^2}$ wetted area). This may be due to the corrosion of the tin causing undercutting of the coating or, possibly, the poor adhesion of the film to the surface.

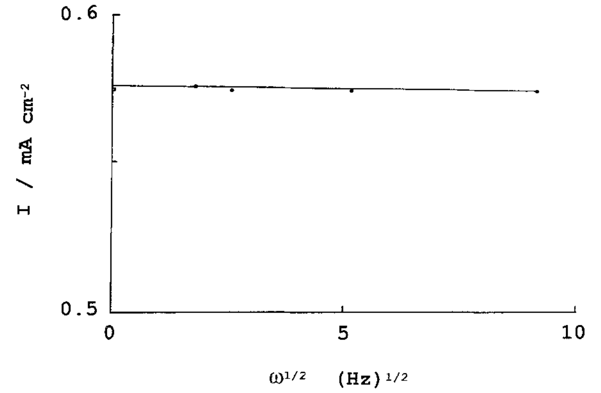

Fig. 10. Rotation speed dependence of current on the hydrogen evolution line (−1115 mV).

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