Wire beam electrode: A new tool for studying localised corrosion and other heterogeneous electrochemical processes

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Abstract

Heterogeneous electrochemical processes are very common in industry and are important, but difficult topics in electrochemical and corrosion science studies. Traditional electrochemical techniques which employ a conventional one-piece electrode have major limitations in studying heterogeneous electrochemical processes since the one-piece electrode has major difficulties in measuring electrochemical parameters from local areas of the electrode surface. In order to overcome this problem, a multi-piece electrode, namely the wire beam electrode, has been developed. This new electrode enables the measurement of electrochemical parameters from local areas over a working electrode surface and thus it can be used to study heterogeneous electrochemical processes. This paper describes how this new electrode was applied in studying several typical heterogeneous electrochemical processes including water-drop corrosion, corrosion under non-uniform organic films and cathodic protection. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A metal surface exposed to an electrolyte is often electrochemically non-uniform due to factors such as localised chemical environment over the metal surface, the structural inhomogeneity of the metal surface, localised defects in a protective film which covers the metal surface, and a polarisation voltage which non-uniformly polarises the metal surface. When a metal surface is electrochemically non-uniform, heterogeneous electrochemical processes occur over the metal surface.

Heterogeneous electrochemical processes are very common in practice. The most

common and probably the most important heterogeneous electrochemical process is localised corrosion such as pitting corrosion and crevice corrosion. When localised corrosion occurs, there is a distinct separation of the anodic and cathodic areas on the metal surface and different electrochemical reactions occur on the anodic and cathodic areas. Electrons continuously travel from the anode areas to the cathode areas through the electrode body and at the same time ions travel between anode and cathode areas through the electrolyte, resulting in the most destructive form of corrosion, localised corrosion. Another important heterogeneous electrochemical processes is cathodic protection of metals. In the case of cathodic protection of a metal structure using a sacrificial anode, protection current (galvanic current) is often not uniformly distributed over the metal structure surface. For instance, locations that are far away from the sacrificial anode site often have lower protection current density and thus may not be effectively protected. This is a major problem that has to be addressed when a cathodic protection system is designed. Another example of heterogeneous electrochemical processes is the electroplating of a complexly shaped work-piece (an electrode). Electrochemical reaction rates, which are determined by the density of applied electroplating currents, can vary significantly over the surface of the work-piece. This can result in an electroplated layer of non-uniform thickness. Similar situations occur in almost all electrochemical industries such as electrotyping, electrometallurgy, electrowinning, electro-machining etc.

To characterise a heterogeneous electrochemical process, electrochemical parameters at local areas of a working electrode surface, such as local electrochemical reaction current, have to be determined. However, conventional electrochemical techniques have major difficulties in doing this. This is mainly because conventional electrochemical techniques use a one-piece electrode, an electrode which is constructed by a single piece of metal or other electrically conductive material of various sizes. When such a one-piece electrode is used, normally only mixed and averaged electrochemical parameters, for instance a mixed potential, over the whole electrode surface are measurable. These measured electrochemical parameters are neither related to the anodic zone nor the cathodic zone of the heterogeneous electrode surface. With a one-piece electrode, it is impossible to measure the galvanic currents that flow in the electrode body between localised anodic and cathodic sites since an ammeter is not able to be inserted between anodic and cathodic sites which are located on a single piece of metal surface. For these reasons, the conventional, one-piece electrode has major limitations in measuring and studying heterogeneous electrochemical processes. Although techniques such as the scanning reference electrode technique and the scanning vibrating electrode technique have been developed to detect localised electrochemical parameters by detecting ionic current flows in the electrolyte phase over a one-piece electrode surface, they only measure the currents in solution phase and not exactly at the surface of the metal. The scanning results from these techniques do not delineate clearly the areas of cathodes and anodes [1]. Indeed, the distribution of ionic current in the electrolyte is normally very complex and is very difficult to accurately detect.

On the other hand, conventional electrochemical techniques have major limitations in determining the kinetics of heterogeneous electrode processes. The fundamental

formulation describing the electrochemical kinetics over a metal surface, the Butler–Volmer equation, is based on a uniform electrochemical corrosion mechanism. Traditional electrochemical techniques which are based on the Butler–Volmer equation such as the Tafel polarisation method, the linear polarisation method and the AC impedance spectroscopy, in principle, are applicable only to measure the electrochemical kinetics of a uniform electrode surface [2].

To overcome some of the difficulties associated with conventional electrochemical techniques. A multi-piece electrode, namely the wire beam electrode (WBE), has been developed [3]. The WBE is fabricated from a metallic wire bundle embedded in insulating materials. The metal wire bundle is constructed from many electrically insulated metal wire sensors which are made from metal wires of identical, dissimilar, galvanised, heat-treated or stressed metal materials with the terminals of the wire bundle connected together. The surface shape of a WBE simulates the surface shape of a practical work-piece. A schematic diagram showing the conceptual design of a WBE is in Fig. 1.

Each wire in a WBE is an individual electrochemical sensor. This enables a WBE to measure electrochemical parameters from local areas of the electrode surface by means of wires located at those areas. Another important characteristic of the WBE is that the surface area of each wire in the WBE is much smaller than the total working electrode area, thus corrosion and electrochemical processes on each wire surface can be assumed to be uniform even if the whole electrode surface is electrochemically non-uniform. This assumption allows electrochemical techniques and theories of describing uniform electrochemical processes to be applied to each wire in a WBE, i.e. traditional electrochemical theories and techniques are extended to study localised corrosion and other heterogeneous electrochemical processes. Based on this assump-
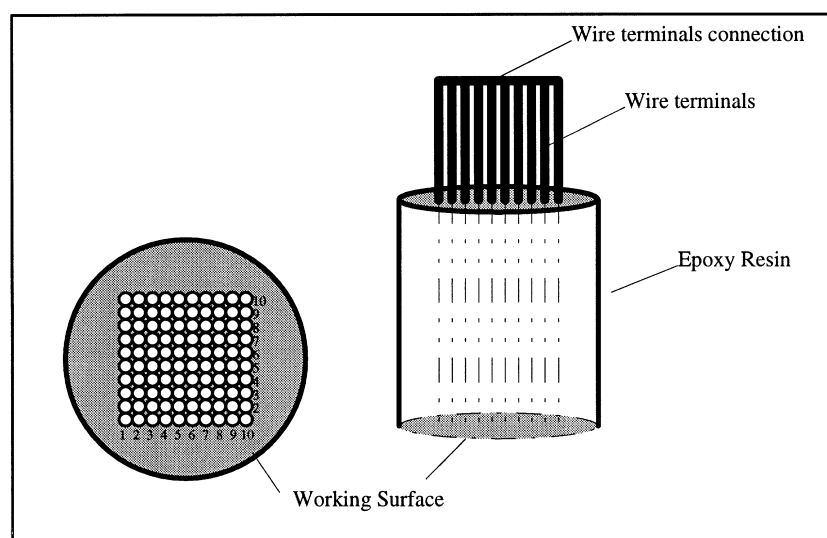

Fig. 1. A schematic diagram showing the conceptual design of a WBE.

tion and the Butler–Volmer equation, new equations describing the electrochemical kinetics of each individual wire have been derived and applied to study the kinetics of localised corrosion processes [2].

The WBE was initially developed and used to detect local defects in organic coating films [3–6] and in anti-rust oil films [7]. Its application has been extended to the study of crevice corrosion [8] and the classical water-line corrosion processes [2]. These studies have already shown that the WBE is a very promising method for studying localised electrode processes. The working surface of a WBE (with all wire terminals connected) can effectively simulate the electrochemical corrosion processes occurring on a one-piece electrode surface with an acceptable accuracy [2]. Similar corrosion patterns were experimentally observed over a WBE and a large area one-piece electrode surface when both electrodes were exposed to an identical localised corrosion environment. This experimental result has been explained theoretically [2].

Based on those previous findings, this present work was designed to further explore the capability of the WBE to simulate and monitor various types of complicated heterogeneous electrochemical and corrosion processes.

2. Experimental

Water-drop corrosion [9] is a classical experiment of localised corrosion which illustrates the establishment of local anodes and cathodes due to the formation of oxygen concentration cells. This experiment is traditionally carried out by visual observation of colour changes in the water drop. Only recently the potential distribution in the water drop was measured by Chen and Mansfeld using a Kelvin probe [10]. Water-drop corrosion also occurs in practical atmospheric corrosion conditions. This present work is designed to elucidate the processes of water-drop corrosion and its cathodic protection by measuring electrochemical parameters such as corrosion potential, coupling (galvanic corrosion) current and their distributions, directly from water drop corrosion areas using a WBE.

2.1. Water-drop corrosion and its cathodic protection

Figure 2 shows an experimental design for investigating water-drop corrosion using a WBE. The WBE used in this work was made of 100 mild steel wires Fig. 1. These wires were embedded in an epoxy resin, insulated from each other with a very thin epoxy layer. Each wire had a diameter of 0.18 cm and acted both as a mini-electrode (sensor) and as a corrosion substrate. The working area (the area occupied by the wire beam) was approximately 3.2 cm^2 (1.8 cm × 1.8 cm). The distribution of these mini-electrodes in the working surface of the WBE is shown in Fig. 1. The working surface of the WBE was polished with 800 and 1200 grit silicon carbide paper and cleaned with ethanol and isopropanol. The working surface was exposed to the corrosive environment (a drop of 0.05 N NaCl solution) under static conditions at about 20°C to allow corrosion to occur. During exposure periods, all the wire terminals of a WBE were connected together to allow electrons to move freely between
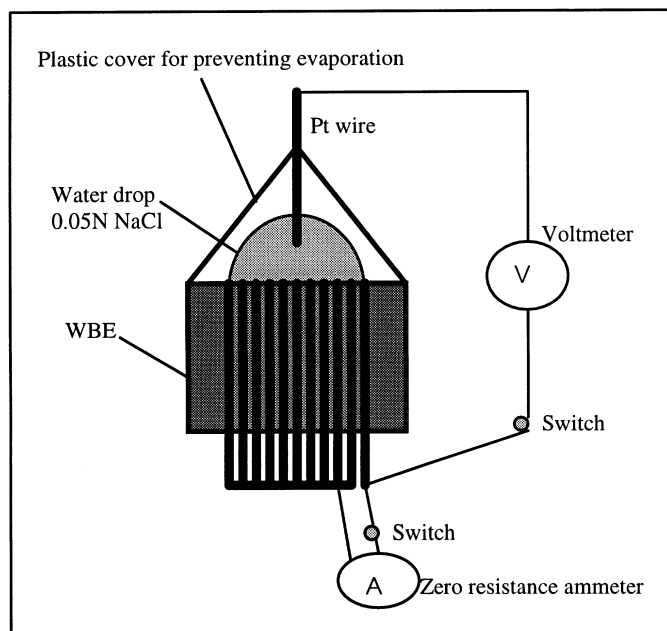
Fig. 2. A schematic diagram showing a water-drop corrosion experiment designed for measuring galvanic corrosion current distribution and the system corrosion potential.

wires, in a similar way as would be the case with mild steel electrodes/plates with a larger surface area. A platinum wire was used as a reference electrode for corrosion potential measurements since a platinum wire is more convenient in this experiment than other conventional reference electrodes. An Automatic Zero Resistance Ammeter (AutoZRA, ACM Instruments, England) was used to record corrosion potential of each wire and to measure galvanic current flowing between each wire and the remaining wires of the whole wire bundle. The AutoZRA enables current (325 mA to 10 pA) and voltage to be measured accurately and to be recorded automatically. Its data logging software runs in the Microsoft Windows (Microsoft Corporation, USA) environment complete with a real time Excel link. Thus the potential and current data analysis and plotting can be performed with Microsoft Excel.

The measurements of galvanic currents (I_{gk} for the wire 'k' of the wire bundle) flowing between each individual wire and the system were carried out by using an experimental design shown in Fig. 2. An AutoZRA performed the measurement on an individual wire terminal in sequence using an automatic switch. The system corrosion potential (E_{sys}) was also measured using this experimental design by employing a voltage meter against a platinum reference electrode. The corrosion potential of each individual wire (E_k for the wire 'k' of the wire bundle) was measured using an experimental design shown in Fig. 3. When measuring the corrosion potential of the wire 'k' against the platinum reference electrode, the terminal of the selected wire was temporarily disconnected from the wire system and was connected to the AutoZRA.
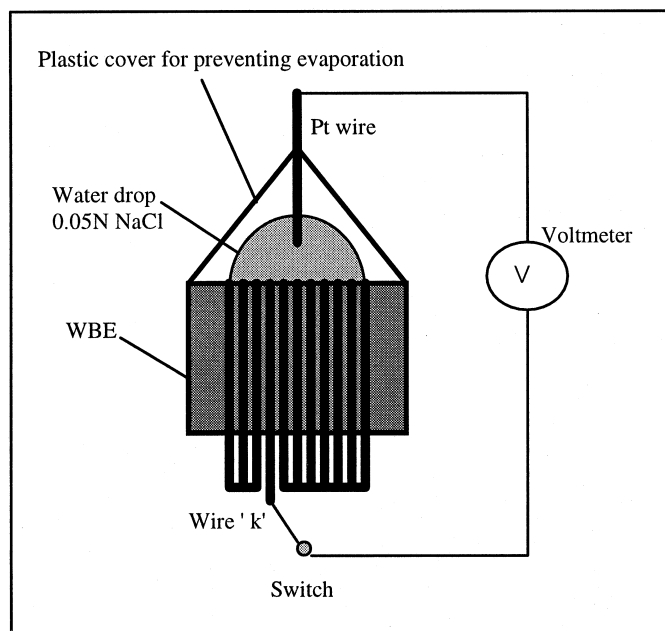
Fig. 3. A schematic diagram showing a water-drop corrosion experiment designed for measuring corrosion potential distribution.

There is an interval of 10 seconds between the measurement of successive wires. The measurements were repeated regularly during the experimental period. Visual observations were made at different stages of the exposure period.

At the end of the water-drop corrosion experiment, a zinc wire was introduced into the water drop, replacing the position of wire '1' in the WBE (Figure 4). This zinc wire behaved as a sacrificial anode to prevent further water-drop corrosion. Protection current distribution was measured using an experimental design shown in Fig. 4.

2.2. Corrosion under non-uniform organic films and its cathodic protection

This experiment is designed to study the non-uniform corrosion of an electrode covered with a rustproof oil film under water-drop exposure conditions. Water-drop exposure condition is common in atmospheric corrosion of coated metal. Water drops with various sizes often form on coated metal surface and that causes localised corrosion damage.

This experiment used similar experimental designs to those shown in Figs. 2–3 and Fig. 4. The only difference is that an organic film was pre-painted on the working surface of the WBE before it was exposed to water-drop corrosion conditions [Fig. 5(a)]. Two rustproof oil films were used in this work. The first was a thin film of a very widely used rustproof oil WD-40 (WD-40 Company Pty Ltd., New South Wales, Australia) and the second was a thin film of an engine oil SAE 20W-50 (Mobil
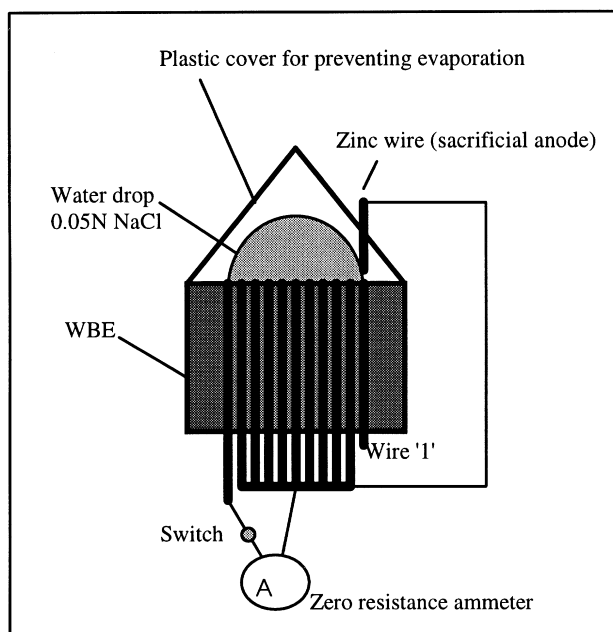
Fig. 4. A schematic diagram showing cathodic protection of water-drop corrosion.

Oil Australia Limited, Melbourne, Australia). The thickness of the oil films were approximately 10 µm. Same experimental methods as described in Section 2.1 of this paper were adopted in this investigation.

In industry, cathodic protection is often used in conjunction with organic coatings to prevent localised corrosion at weak areas in the coating films. To study this process, at the end of the water-drop exposure experiment, a zinc wire was introduced into the water drop, replacing the position of wire '1' in the WBE [Fig. 5(b)]. This zinc wire behaved as a sacrificial anode to prevent localised corrosion at weak areas of the rustproof oil film. Protection current distribution was measured using an experimental design shown in Fig. 5(b).

3. Results and discussions

3.1. Corrosion under water drops of various sizes

Water-drop corrosion was first reported by Evans in 1926 [9]. It has been discussed in almost every textbook on corrosion as one of the classic experiments in corrosion science. A drop of NaCl solution with small additions of phenolphthalein and potassium ferricyanide was placed on a horizontal steel sheet. After a period of exposure, a large anode in the center of the drop surrounded by a ring of rust and a large cathode were observed based on the colour changes of the solution. Chen and Mansfeld for
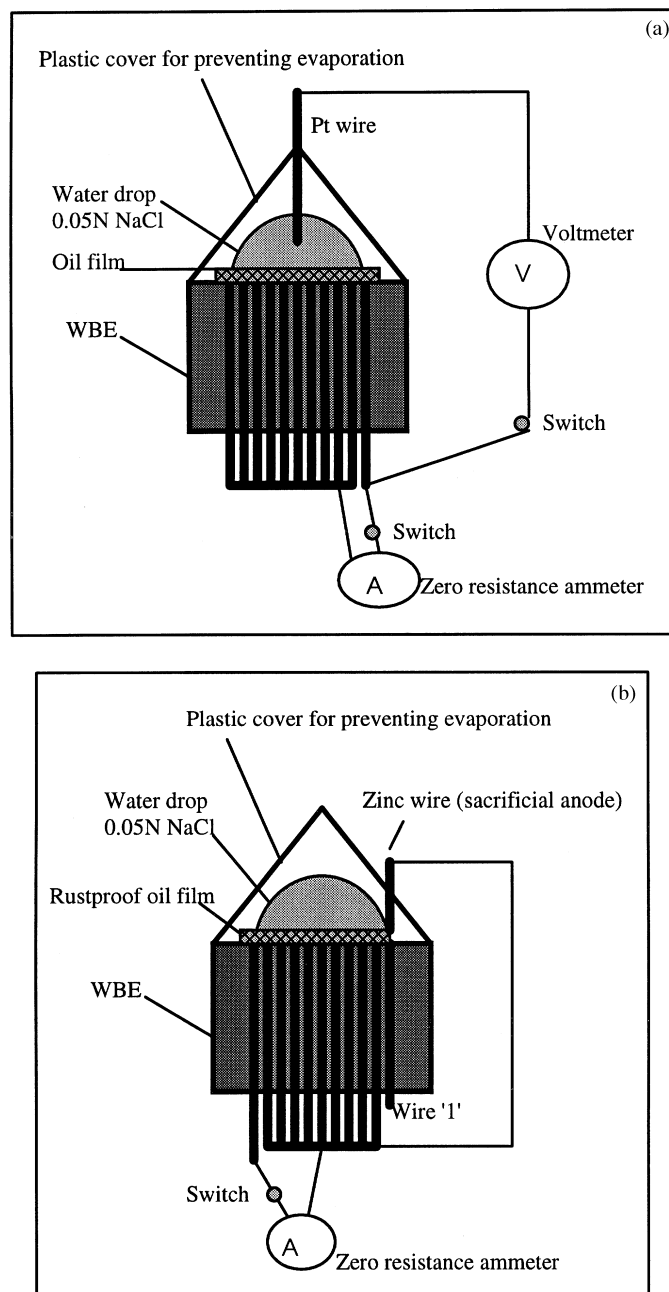
Fig. 5. A schematic diagram showing measurements of galvanic corrosion current and cathodic protection current of a filmed WBE under water-drop exposure conditions. (a) measuring galvanic corrosion current distribution, (b) measuring cathodic protection current distribution.

the first time measured the potential distribution in the water drop using a Kelvin probe [10]. However, details of the corrosion process and galvanic current distribution in the water drop have not been studied.

Using experimental designs shown in Figs. 2–3, galvanic current and potential distributions in the water drop were measured. Measurements were repeated at various stages of the exposure period in order to study the processes of the water-drop corrosion.

When a small water drop (approximately 7 mm in diameter) was used, as shown in Fig. 6(a), similar potential distribution to that reported by Chen and Mansfeld [10] was recorded. The lowest potential values occurred in the center of the water drop and correspondingly positive galvanic currents occurred in the center of the drop [Fig. 6(b)]. These results clearly indicate that in the center of the droplet, the steel wires become anodic and near the edge of the droplet, where the diffusion path of oxygen was the shortest, the steel wires become cathodic. Visual observations of the WBE working surface corresponded well with those reported in the literature [9, 10].

However, when the size of the water drop was increased, the distributions of galvanic current and potential in the water drop changed significantly. Figure 7 shows the galvanic current distributions recorded from a larger water drop (approximately 12 mm in diameter) at various stages of exposure period. At the beginning of the exposure, as shown in Fig. 7(a), only a few isolated anodic sites, indicated by the positive galvanic currents, appeared among a large number of cathodic sites. In later stages [Fig. 7(b), Fig. 7(c)], some of the anodic sites merged together forming a localised corrosion 'ring' around the center of the water drop, unlike corrosion in the smaller water drop [Fig. 6], where corrosion was concentrated in the center of the water drop. There was very good agreement between visual observations and galvanic current distribution (Figure 8).

This result could be related to the change in water drop shape when the water drop size was increased. Change in water drop shape resulted in more complex diffusion path of oxygen and more complex distribution of cathodic and anodic zones. Indeed, as the size of the water-drop was increased further, a very different corrosion pattern was measured and observed (Figure 9). One side of the large drop became cathodic (negative current and less negative potential) while the remaining areas became anodic zones. It is interesting to note that the galvanic corrosion currents were distributed non-uniformly over the anodic zones. The areas close to the cathodic zone recorded higher anodic currents and thus more rapid corrosion. This is in agreement with visual observation [Fig. 9(c)].

3.2. Cathodic protection of water-drop corrosion

At the end of the water-drop corrosion experiment as shown in Figs. 7–8, a zinc wire with a surface area of approximately $0.015 \, cm^2$ was introduced into the water drop, replacing the position of wire '1'. An experimental design, shown in Fig. 4, was employed to measure galvanic current distribution in this system.

The zinc wire behaved as a sacrificial anode in this system and worked to prevent further water-drop corrosion. As shown in Fig. 10, the zinc wire became the only
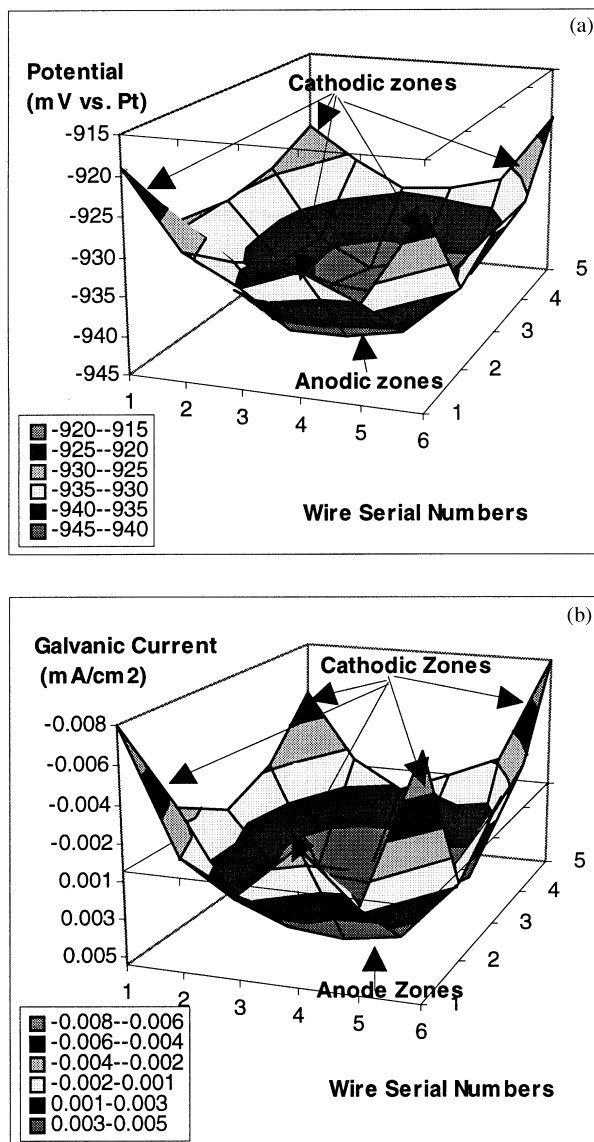
Fig. 6. Corrosion potential (a) and galvanic current (b) distributions in a drop of 0.05 N NaCl solution (approximately 7 mm in diameter).

anode in the WBE system and produced a large protection current (7.6 mA/cm^2) to prevent other mild steel wires in the water drop from further corrosion.

It is interesting to note that the protection currents were not uniformly distributed. As shown in Fig. 10, larger protection currents appeared in a ring shape area that previously was a cathodic zone in Fig. 7(c). This is understandable since this ring
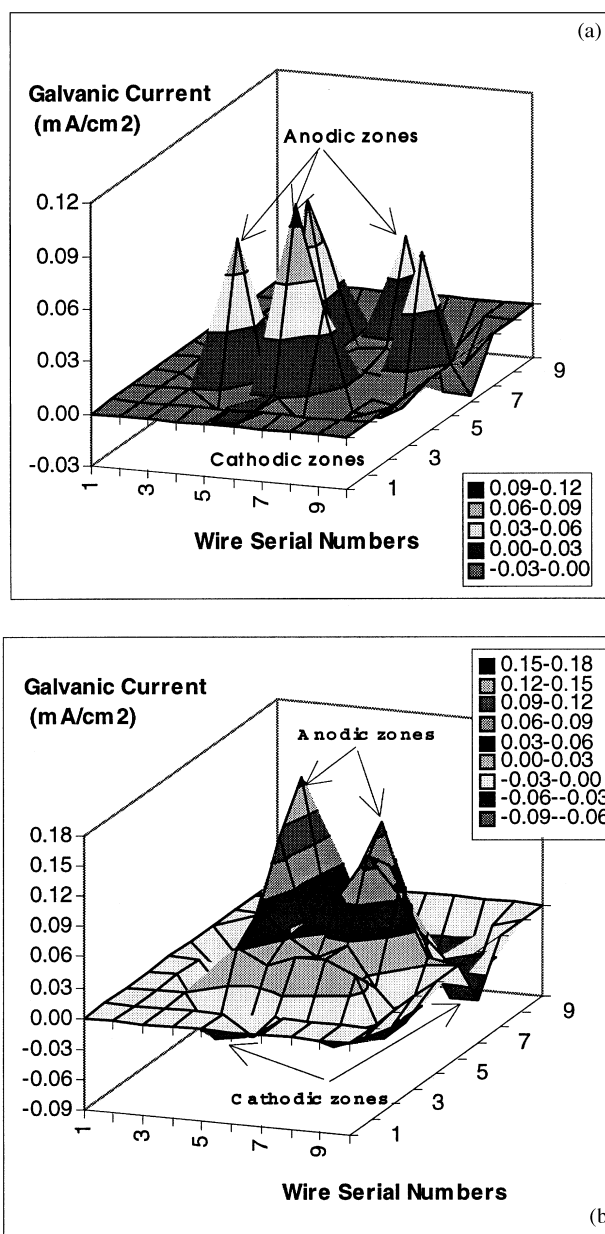
Fig. 7. Galvanic current distributions of a WBE exposed to a drop of 0.05 N NaCl solution (approximately 12 mm in diameter). (a) After 10 minutes exposure, (b) After 30 minutes exposure, (c) After 15 hours exposure.
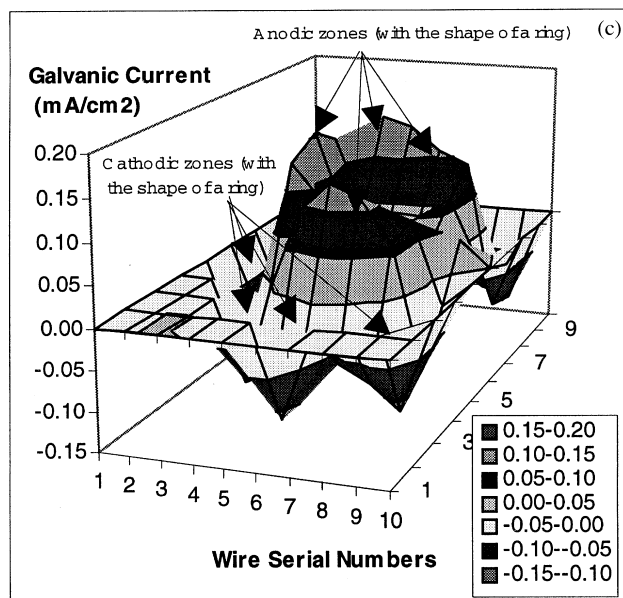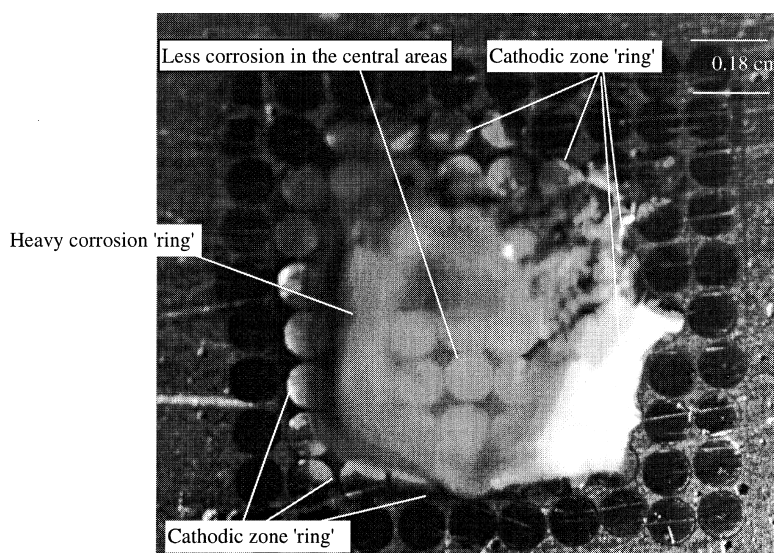
Fig. 7 (continued)

Fig. 8. Visual observation of a WBE after exposed to a drop of 0.05 N NaCl solution (approximately 12 mm in diameter) for 17 hours.

shape area was close to the edges of the water drop where the diffusion path of oxygen was the shortest. Sufficient supply of oxygen supported rapid cathodic reactions. This
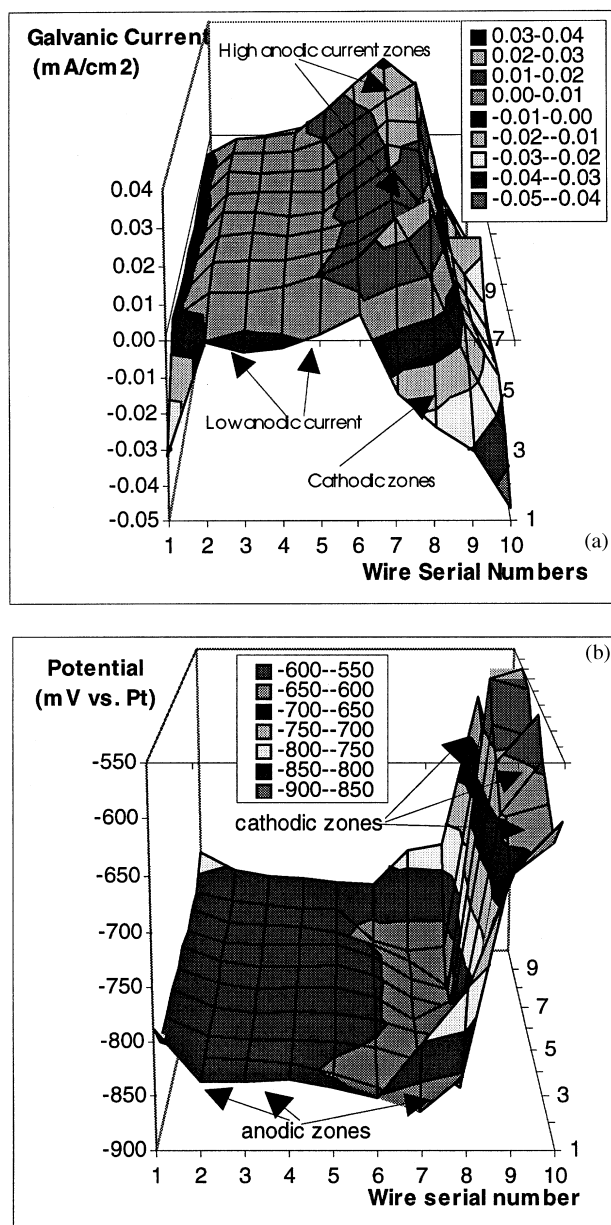
Fig. 9. Galvanic current (a), potential (b) distributions and visual observation (c) of a WBE exposed to a drop of 0.05 N NaCl solution (approximately 19 mm in diameter) for 19 hours.
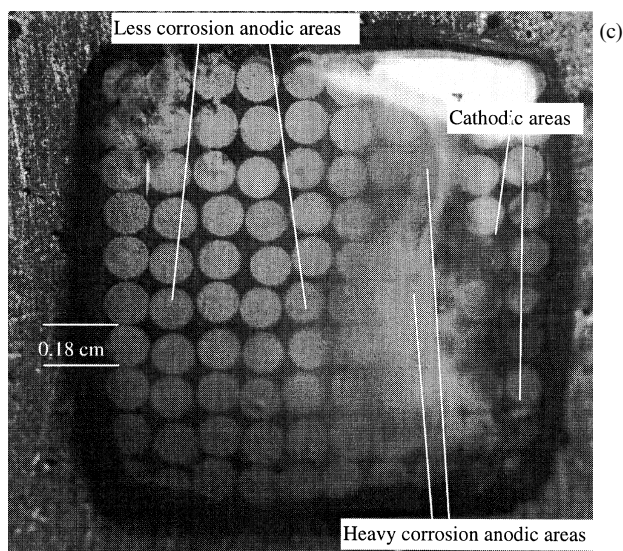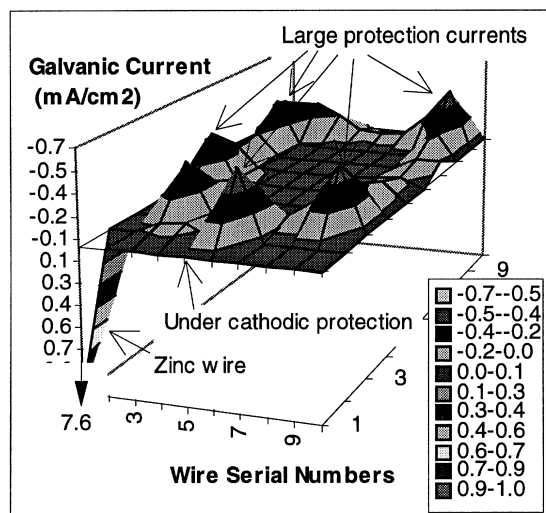
Fig. 9 (*continued*)

Fig. 10. Cathodic protection current distributions over a WBE surface exposed to a drop of 0.05 N NaCl solution (approximately 12 mm in diameter).

result suggests that the distribution of protection currents depends not only on the geometry of a metal structure and the conductivity of corrosion environments, it depends also on factors such as the electrochemical heterogeneity of metal surface. These factors need to be considered when a cathodic protection system is modelled and calculated mathematically. However, this mathematic modeling and calculation

can be very difficult, especially when a protected metal structure has a complex shape and the corrosion environment is complicated. The use of a WBE could be a much better method for characterising a cathodic protection system.

3.3. Corrosion of a filmed electrode under a drop of water

Organic coating films and organic inhibitor films are inhomogenous in nature [3–5, 7] and this inhomogeneity can significantly affect the reproducibility and reliability of conventional electrochemical measurement of corrosion under organic coatings [3, 4]. This problem can be overcome if a WBE, instead of a conventional one-piece electrode, is used [4] since the WBE is able to measure local electrochemical parameters [3, 4]. Indeed, the WBE enables evaluation of organic coatings statistically and this statistical analysis has improved the reliability and reproducibility of coating evaluation and has avoided serious influences from occasional factors such as pores in a coating film on electrochemical evaluation of organic coatings [4]. Wu and co-workers [7] also measured the electrochemical inhomogeneity of electrodes with rustproof oil films and found that the distributions of corrosion potential and d.c. resistance over an electrode surface were non-uniform and were subjected to change when corrosion inhibitors were added. However, the corrosion processes under a rustproof film has not yet been studied. This present work is designed to further explore the application of the WBE in studying the corrosion processes under organic coating films.

Using an experimental design shown in Fig. 5(a), galvanic current distributions over a WBE surface, filmed with a thin layer of rustproof oil WD-40 (approximately 10 µm in thickness), were measured at various stages of the exposure period. At the beginning of the exposure, as shown in Fig. 11(a), there was a small area which exhibited a large anodic current peak ($0.046 \, mA/cm^2$). This peak may correspond to a weak area in the oil film. However, when exposure is extended, this large anodic current peak disappeared and was replaced with much smaller anodic peaks [Fig. 11(b) and (c)]. This phenomenon may be related to the self-repair processes of this rustproof oil film, although the exact reason is not clear. Generally only very small galvanic currents were recorded in this system although there was a clear separation of anodic and cathodic zones under the rustproof oil film. This corresponds well with the good rustproof ability of this widely used rustproof oil.

Using the same experimental design, galvanic current distributions over a WBE surface, filmed with a thin layer of less protective engine oil (Mobil SAE 20W-50, approximately 10 µm in thickness), were measured at various stages of the exposure period. At the beginning of the exposure, as shown in Fig. 12(a), a large anodic current peak ($0.016 \, mA/cm^2$) was recorded from a small electrode area, similar to the galvanic current behaviour in Fig. 11(a). This anodic current peak, however, did not disappear with the extension of exposure, instead, it increased with exposure time [Fig. 12(b) and (c)]. At the end of this exposure test, brown corrosion products were observed at the anodic current peak location, which obviously corresponded to a weak area in the oil film. This oil film was not able to self-repair this weak area. This result correlated well with the less rustproof ability of this engine oil.

A zinc wire was then introduced to the system, as shown in Fig. 5(b), replacing the wire '1'. Cathodic protection was thus applied with the zinc wire behaving as a sacrificial anode. As shown in Fig. 13, the zinc wire became the only anode in the WBE system and produced a large protection current (0.50 mA/cm²) to prevent other mild steel wires, especially those located at the weak areas of the oil film, in the water drop from further corrosion.
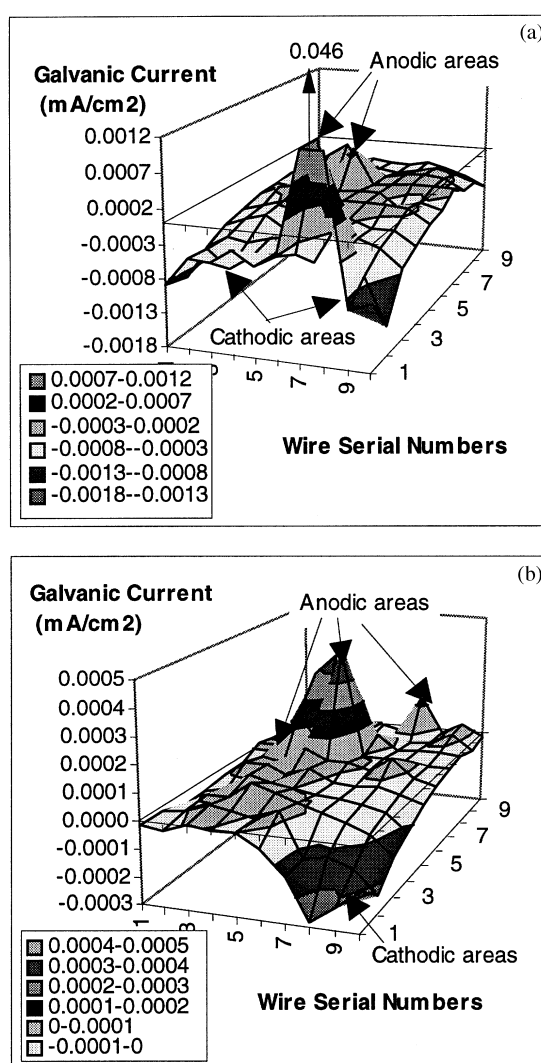

Fig. 11. Galvanic corrosion current distributions over a WBE surface, with a thin layer of rustproof oil WD-40, exposed to a drop of 0.05 N NaCl solution. (a) After 2 hours exposure (b) After 4 hours exposure (c) After 28 hours exposure (approximately 12 mm in diameter).
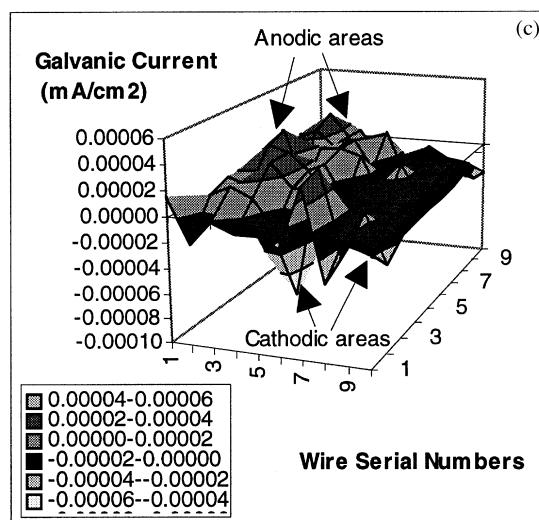
Fig. 11   (*continued*)

4. Conclusions

1. The wire beam electrode was used to study heterogeneous electrochemical corrosion processes occurring under a drop of water. Electrochemical parameters
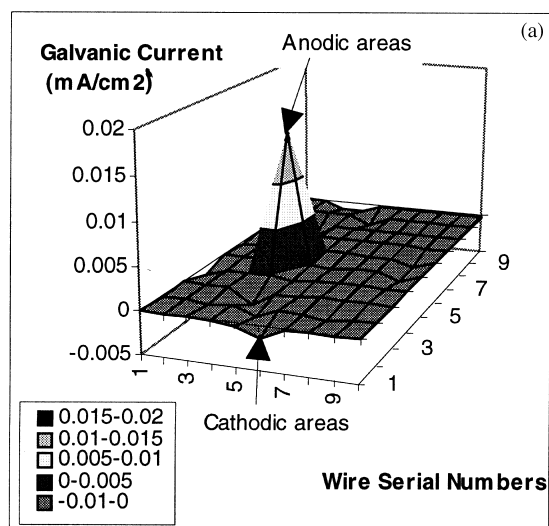

Fig. 12. Galvanic corrosion current distributions over a WBE surface, with a thin layer of engine oil, exposed to a drop of 0.05 N NaCl solution (approximately 12 mm in diameter). (a) After 2 hours exposure (b) After 4 hours exposure.
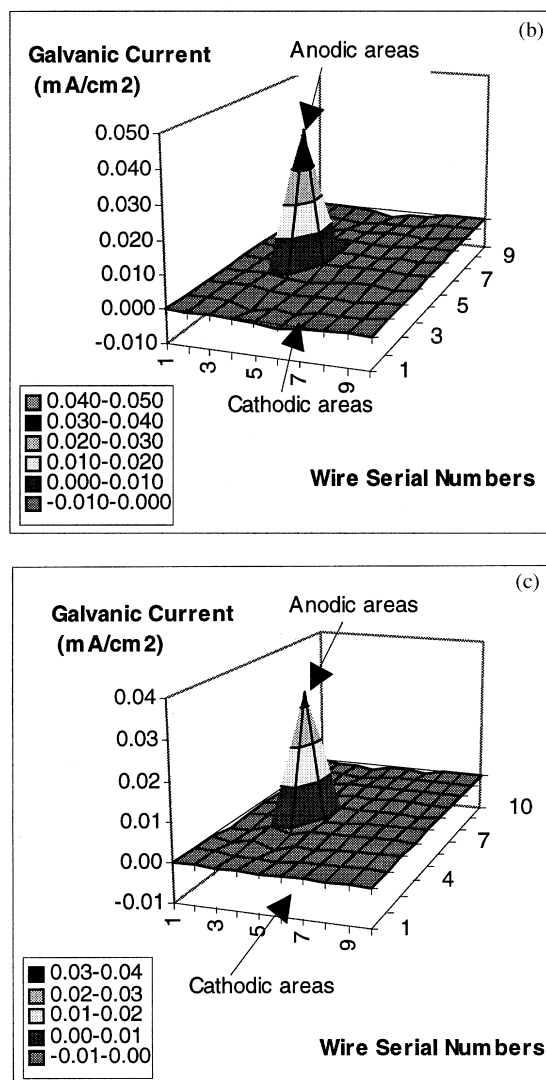
Fig. 12   (*continued*)

including galvanic corrosion current and corrosion potential and their distributions were measured directly from various local areas of the WBE surface, exposed to water drop corrosion conditions.

2. The WBE was used to measure electrochemical parameters from local areas under an organic protective film. These electrochemical parameters were used to study and evaluate the corrosion protective ability of rustproof oil films.

3. The WBE was used to determine the exact distribution of cathodic protection currents over a protected surface experimentally. This technique can provide
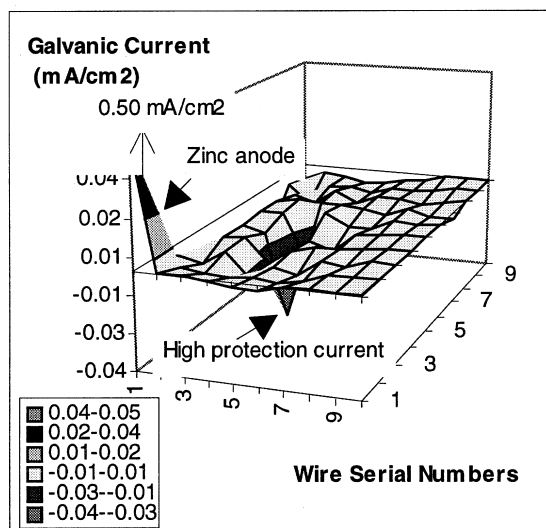
Fig. 13. Cathodic protection current distributions over a WBE surface, filmed with a thin layer of engine oil, exposed to a drop of 0.05 N NaCl solution. (approximately 12 mm in diameter).

important parameters for designing effective cathodic protection systems in order to avoid over-protection or under-protection of some sections of a metal structure.

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