



Investigating the separation of anodic and cathodic defects in organic coatings applied on metal substrates. An experimental contribution



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ABSTRACT

When artificial defects are produced on organic coatings applied to metals it is common to observe a separation of anodic and cathodic defects. An investigation is presented in which real defects are imitated by two disk electrodes of the same metal, embedded in insulating matrix and electrically connected. A variety of measurements was performed to characterise the corrosion of this twin electrodes set-up: SVET, micro-distributions of pH and dissolved O₂, polarisation curves, galvanic current and video monitoring. The tendency for anodic and cathodic processes to proceed in separated electrodes was observed. It became clear that a strong increase in local pH on the cathode renders it passive to metal oxidation while the other electrode corrodes. It is possible to explain the maintenance of the separation in time but what triggers the separation at the beginning of immersion remains unidentified.

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1. Introduction

It is common to produce artificial defects when using localized techniques to investigate the corrosion and protection of coatings applied on metals. In general, a clear separation of anodic and cathodic defects is observed. Examples are a 20 μm thick epoxy coil coating applied on hot dip galvanised steel with two defects down to the ferrous substrate analysed by SVET (Scanning Vibrating Electrode Technique) and Zn²⁺-ISME (ion selective microelectrode) [1] or a 2 μm hybrid organic-inorganic sol-gel film applied on aluminium alloy 2024-T3 with two defects analysed by SVET, pH and O₂ microelectrodes [2]. In these two examples one defect became anodic and the other cathodic. In another example [3] five defects were produced in a similar sol-gel film applied on magnesium alloy AZ31B and the corrosion was analysed by SVET, pH-ISME and Mg²⁺-ISME. Three defects became anodic, one cathodic and one showed both anodic and cathodic activities. In all examples the separation was maintained over time and no interchange was observed. The reason for this behaviour is unclear and puzzles those working in the field.

The separation of anodic and cathodic areas beneath organic coatings is known at least since 1949 [4] when Mayne, working

with intact unpigmented polystyrene lacquers applied on mild steel and immersed in sodium chloride solutions, observed that corrosion took place under the film with special separation of anodic and cathodic areas. Cathodic reactions led to blisters filled with sodium hydroxide solution and the anodic reaction was iron oxidation. Ions were thought to migrate between the anodic and cathodic areas beneath the film and across it, through regions where ionic conduction was easier. The separation of anodic and cathodic regions was also recognised in the corrosion pattern of steel plate in sodium chloride solutions investigated in the 1930s by Evans, being the number and size of regions dependent on the NaCl concentration. An account of these studies can be found in the 1960 Evan's book [5].

The present work investigates the separation of anodic and cathodic processes at defects of painted metals. Due to the localised character of the subject, microelectrode techniques were employed: the SVET measured ionic currents in solution, a potentiometric microelectrode analysed the local pH and an amperometric boron doped diamond microelectrode sensed the distribution of dissolved O₂ in solution. Two types of samples were studied: epoxy coated iron sheet with two artificial defects and electrochemical cells comprising two wires of pure iron embedded in insulating matrix and electrically connected. The polished surface of the wires represented two metal disks with the same size as the defects of the coated iron sheet. This type of electrochemical cell imitated the real problem and allowed measuring the galvanic

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current flowing between the two electrodes and record independent polarisation curves of each electrode.

2. Experimental

2.1. Materials and samples

The metal used in this work was iron in the form of 1 mm thick sheet (99.5% pure) and 250 μm or 1 mm diameter wires (99.99+% pure) purchased from Goodfellow (UK). The sheet was coated with unpigmented epoxy paint and two round shaped defects were manually produced with a needle. To imitate these defects pure iron wires (250 μm or 1 mm diameter) were embedded in epoxy moulds (EpoKwick, Buehler, USA). After abrasion the samples depict only two metallic disks in an insulating surface, exactly what is found in painted metals with two defects at the beginning of immersion. The wires can be electrically connected from the back or left uncoupled. A $5 \times 5 \text{ mm}^2$ iron plate was also embedded in epoxy mould. To prevent crevice some wires were coated with a varnish (Lacomit, Agar Scientific, UK) before embedding in the moulds.

The painted iron sheet was glued to plastic holders and the edges isolated with epoxy cement. The epoxy moulds with embedded twin wires and the iron sheet were abraded with 1200 grade SiC paper and washed in distilled water followed by pure ethanol. Adhesive tape around the plastic holders and epoxy moulds served as solution reservoir. The testing media was aqueous 0.05 M NaCl prepared with distilled water and p.a. grade reagent. In one experiment the pH was adjusted to 10 with drops of 0.01 M NaOH solution.

2.2. Electrochemical methods

2.2.1. SVET

The SVET equipment was manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET 2.0 program developed by Sciencewares (USA). The SVET probe was a polymer insulated Pt–Ir microelectrode with 20 μm diameter platinum black sphere at the tip, vibrating in the direction normal to the surface with 10 μm amplitude and 162 Hz frequency. The measured potential differences were converted to ionic currents after a calibration routine performed with a point current source [6,7].

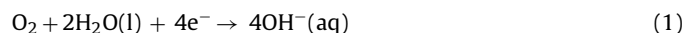
In this work the probe scanned 100 μm above the surface and maps comprised 50×50 points (24 min of scanning time). In each measurement point the probe waited 0.2 s and then averaged for 0.2 s. Along with the maps the SVET system collected optical images of the sample.

2.2.2. Micro-potentiometric measurement of pH

The pH microprobes were made in the laboratory and consisted of silanised borosilicate glass capillaries with one end thinned to 2 μm . The capillaries were front-filled with 30 μm column of hydrogen I cocktail B ionophore (Fluka, Ref. 95293) and back-filled with an internal solution of 0.1 M KCl + 0.01 M KH_2PO_4 . A silver chloride coated silver wire inside the micropipette served as internal reference electrode and a homemade Ag|AgCl|0.05 M NaCl electrode worked as external reference electrode. The pH microelectrode was connected to a pre-amplifier (input resistance $> 10^{15} \Omega$) which was mounted in the same 3D positioning system used for SVET and connected to an IPA2 amplifier (Applicable Electronics Inc, USA) in potentiometric mode (input resistance $> 10^{12} \Omega$). The ASET program controlled the measurements and recorded the data. The microelectrodes were calibrated with commercial pH buffers (Riedel-de Haen), giving a linear response in the 5 to 13 pH range [2].

2.2.3. Micro-amperometric measurement of dissolved O_2

The measurement of dissolved O_2 in solution was based on the reaction



and was performed in a two electrode arrangement with a Ag|AgCl electrode and a homemade boron doped nanocrystalline diamond microelectrode polarised at -1.2 V vs Ag|AgCl [8]. At this potential the oxygen reduction is controlled by diffusion and the measured current is proportional to the concentration of O_2 . The electrodes were connected to a pre-amplifier which was mounted in the same 3D positioning system used for SVET and connected to the IPA2 amplifier in the amperometric mode.

2.2.4. Polarisation curves and galvanic current

The polarisation curves were performed with a Ivium Compact-Stat (The Netherlands) in a three-electrode arrangement, using a homemade Ag|AgCl, 0.05 M NaCl electrode as reference, a platinum counter electrode and each embedded wire as working electrode. The sweep rate was 1 mVs^{-1} . In some cases, the SVET probe was placed above one or the other electrode to measure the local current while the potential was being swept. The galvanic current was obtained in an amperometric measurement for zero potential with one electrode connected to the working electrode terminal and the other to the counter and reference terminals.

3. Results

3.1. Epoxy coated iron sheet with two artificial round shaped defects

Fig. 1 shows an iron substrate coated with a clear epoxy coating and two round shaped defects produced with a needle immersed in aqueous 0.05 M NaCl. The SVET maps were obtained in a plane 100 μm above the coating and revealed that one defect was anodic and the other was cathodic. This suggests that the defects are not working independently rather they are galvanically coupled. Reduction of dissolved O_2 (equation 1) predominated in the cathodic defect while oxidation of iron,



dominated in the anodic defect. An electronic path between anode and cathode was established in the metal sheet and the electric circuit was closed by ionic fluxes in solution. SVET measures these ionic currents. It must be noted that SVET maps show the net current in each point of measurement, being thus possible that in each defect both reactions occur but one at a much smaller rate. Thanks to the absence of pigmentation, the optical pictures show that after 12 h, corrosion was already taking place beneath the coating in the vicinity of the anodic defect. A number of small brown spots are visible and seem to coincide with regions of imperfect adhesion, where solution was able to penetrate. Interestingly the corroded spots were restricted to the area close to the “anodic” defect. After 12 h of immersion the two defects still displayed the separation of anodic and cathodic processes and no signs of corrosion existed in the cathodic defect or its immediate surroundings.

3.2. Twin electrode cell to mimic the two defects

The separation of processes can be due to heterogeneities in the surface conditions, or differences in depth, size, or aeration, which are generally associated to the onset of local corrosion cells. This seems unlikely to occur in the studied systems but can't be excluded. A way to simulate the separation avoiding these effects is by using two electrodes of the same metal in an insulating layer

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