Application of the scanning electrochemical microscope to the examination of organic coatings on metallic substrates

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Abstract

The application of scanning electrochemical microscopy (SECM) for corrosion studies of organic coatings on reactive metals is presented. In this work, the SECM was used to monitor the electrochemical processes at painted galvanized steel substrates immersed in 0.1 M NaCl aqueous solution. The coatings were investigated both as obtained and scribed, to simulate a defect across the coating, down to the metal-substrate surface. The SECM was operated under either the feedback or a variation of the sample generation/tip collection modes. In the first case the variations in the feedback current measured at the SECM-tip when scanned at constant height over the sample allowed imaging of the topography of the coated surface with high local resolution. In the second case, chemical species participating in the corrosion reactions at the sample are detected at the SECM-tip by applying appropriate potential values to the microelectrode. Local concentration variations could be assessed in this way.

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1. Introduction

Coating metals with a polymeric film is the most widely employed protection procedure against the corrosion of metallic materials [1,2]. The organic coating generates a physical barrier that retards the advancement of the corrosion processes by hindering the transport of the aggressive species present in the environment towards the metal/coating interface [3,4]. Nevertheless, all polymers are permeable to potentially corrosive species such as oxygen, water and ions [5], which eventually lead to the initiation of metal corrosion under the polymeric film. Corrosion of a polymer-coated metal requires the existence of a conductive environment containing a reactant that participates in the cathodic reaction, such as water or oxygen, and the anodic dissolution of the metallic substrate [2]. Additionally, the reaction may be accelerated by aggressive ions present in the solution phase. In fact, non-defective films applied on metals are known to delaminate after some time, which indicates that species from the environment may diffuse either through microscopic pores in the coating or even through the polymer matrix [2].

Unfortunately, the mechanisms of the corrosion processes that take place at defect-free coated metals, and of delamination in the vicinity of defects, are not yet completely known. Conventional electrochemical techniques, including electrochemical impedance spectroscopy (EIS), provide valuable information about these processes which are electrochemical in nature. But they are integral methods and thus lack spatial resolution, which is a major drawback specially in the early stages of the degradation process. To overcome such limitation, new techniques that perform local measurements are increasingly applied. In fact, very interesting
information on these systems is currently being obtained with the scanning vibrating electrode technique (SVET) [6–10], the scanning Kelvin-probe (SKP) [11–14] and localized electrochemical impedance spectroscopy (LEIS)[15,16].

Another microelectrochemical technique which may be used to study corrosion processes at coated metals is the scanning electrochemical microscopy (SECM) [17,18], a method that couples scanning probe techniques with electrochemistry. It consists of a mobile ultramicroelectrode immersed in an electrolyte solution, which is scanned in close proximity to a solid surface to characterize the topography and redox activity of the solid/liquid interface. This technique exhibits high spatial resolution, and is applicable to both insulating and conducting surfaces [19,20]. Therefore, the SECM-tip may be used to quantitatively detect the reactants and products participating in the corrosion reactions [19,21,22].

The aim of this paper is to demonstrate that the scanning electrochemical microscopy is a powerful technique for the investigation of the electrochemical reactions responsible for the delamination of polymeric coatings from metallic substrates in the presence of defects. The experimental system under investigation consisted of galvanized steel coated with an epoxy film, after a scratch was produced through the coating. The system has been tested in 0.1 M NaCl aqueous solution, open to air, at ambient temperature.

2. Experimental

2.1. Experimental details

A two-component epoxy primer containing zinc phosphate was examined. Coated samples (1 cm × 1 cm) were cut from galvanized steel panels that had been degreased and coated by immersion of the sample in the paint. The paint was used commercial, supplied by Hempel Coatings (Portugal), with a dry film thickness of 50 μm. A scratch of ca. 1 cm length and 2 mm width was produced in the coating to the metal substrate with a scalpel.

The specimens were mounted into a SECM model CHI900 (CH Instruments, TX) equipped with a 10 μm platinum tip as the probe, an Ag/AgCl/KCl (saturated) reference electrode and a stainless steel counter electrode, all set up in a cell made of polytetrafluoroethene. All potentials are referred to the Ag/AgCl/KCl (saturated) reference electrode. Specimens were mounted horizontally facing upwards. When the cell was mounted in position, the testing electrolyte was introduced into the cell. The samples were immersed in aerated 0.1 M NaCl solution at room temperature, and examined in situ with the SECM. The specimen was left unbiased at its open-circuit corrosion potential for all the work. The experiments were performed at selected heights of the microelectrode above the sample.

2.2. Experimental procedure

Two model experiments have been performed to demonstrate application possibilities of the SECM technique for the in situ investigation of the degradation processes from scratches at coated metals during their immersion in aqueous electrolytes:

• In a first model experiment, the SECM technique has been employed to image the topography of the defect-free sample while it was left unbiased, that is, at its open-circuit potential value in the environment. In this case, a feedback mode experiment was performed by using an electrochemical mediator. Local features at the surface of the substrate originate changes in the current response at the SECM-tip when scanned at a constant distance above the sample. The resolution will depend both on the size of the ultramicroelectrode that acts as SECM-tip, and on the distance the tip is located above the sample.

• In a second model experiment, the SECM-tip has been used to detect local concentrations of reactants involved in corrosion processes. A variation of the substrate generation/tip collection experiment (SG/TC) is then performed, in which the sample is also left unbiased. The variation consists in measuring the depletion of a reactant as result of an electrochemical reaction occurring at the sample.

In the measurements conducted by using an electrochemical mediator, 1 mM K4[Fe(CN)6] was added to the test solution, and the tip potential was set at +0.40 V to follow the oxidation of ferrocyanide to ferricyanide ions as described by:

\[
\text{Fe(CN)}_6^{4-} \rightarrow \text{Fe(CN)}_6^{3-} + e^{-}
\]  

The SECM-tip is made the working electrode for the diffusion-limited oxidation of the mediator species A, and the corresponding current, \(i_{x6}\), for a disc-shaped micro-electrode when it is far from any surface, is given by [23]

\[
i_{x6} = 4nF D_A C_A a
\]  

where \(D_A\) and \(C_A\) are, respectively, the diffusion coefficient and the bulk concentration of the species A in the electrolyte solution, \(n\) is the number of electrons exchanged in the redox reaction and \(a\) is the tip radius. The SECM response is based on how the current of this microelectrode is perturbed by the presence of a substrate near the tip [24]. When the tip approaches an inert non-conductive sample, such as a paint coating, the current will be smaller than the \(i_{x6}\) in the solution as given by Eq. (2) because the surface blocks the diffusive flux of A to the tip. The tip current will steadily diminish as the tip gets closer to the insulator surface, eventually becoming zero when the microelectrode touches the sample. This feedback mode experiment is illustrated schematically.
in Fig. 1 considering the reduction of the mediator A to produce the species B. The same behaviour is observed when the SECM-tip approaches a conducting substrate when its potential neither allows for A to be consumed nor to be regenerated. The resulting approach curve is then used to determine the height of the tip over the substrate. In summary, the topography of a sample can be imaged by moving the SECM-tip towards the substrate, until the tip current is perturbed by its presence. Following this approach, the tip can be rastered in a plane parallel to the surface to image any variations in the distance between the tip and the sample.

In the second model experiments, dissolved oxygen in the solution was imaged directly by the SECM-tip set at \(-0.70 \, \text{V}\), at which reduction of oxygen occurs as:

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}
\]  (3)

3. Results and discussion

3.1. Mapping of a coated sample by SECM

To image the coated sample, 1 mM ferrocyanide was added to the solution. Prior to imaging, a cyclic voltammogram was measured in the test solution (Fig. 2), which allowed selecting a potential value of +0.40 V for the diffusion-limited oxidation of ferrocyanide in this medium. One image of the sample in 0.1 M NaCl solution at the open-circuit corrosion potential is presented in Fig. 3. The mediator employed in this experiment was ferrocyanide, and the tip potential was set to +0.40 V. The map was generated with the tip at ca. 15 \(\mu\text{m}\) from the specimen surface by scanning a 200 \(\mu\text{m} \times 200 \mu\text{m}\) area. The image clearly depicts the topography of the sample, in which hills and valleys are observed as regions with distinct tip currents because of the varying extent of the blocking effect towards ferrocyanide diffusion. It must be noted that smaller currents correspond to those sites where the coating advances to the SECM-tip, that is, describing hills or bulges, which hinders in a greater extent the diffusion of the electrochemical mediator.

Fig. 3. Topographic map generated by SECM of a painted specimen immersed in 0.1 M NaCl + 1 mM K_2[Fe(CN)_6], corresponding to 200 \(\mu\text{m} \times 200 \mu\text{m}\) in X and Y directions. The vertical Z direction is calibrated in terms of current at the SECM-tip. Tip potential is +0.40 V vs. the Ag/AgCl/KCl (saturated) reference electrode. Current values expressed in amperes.
Therefore, the SECM operating in the feedback mode with a suitable redox mediator added to the electrolyte may facilitate the in situ imaging of a coated metal, and may be used to follow the evolution with time of the surface as a result of the corrosion processes occurring in the system. It must be stressed that we have recently succeeded in the visualization of the early stages of coating degradation by this technique, since any swelling or coating disbonding should result in the coating effectively advancing towards the SECM-tip, thus increasingly resulting in lower currents at the microelectrode [20].

3.2. Measurement of local concentrations of species participating in a corrosion reaction by SECM

In this experiment, the ability of the SECM-tip to measure the local concentration of a dissolved species, either a reactant or a corrosion product, was explored. The potential of the tip was set to a value at which the species under investigation undergoes a redox reaction, thus allowing for the tip current to be quantitatively correlated with the local concentration at that location [25]. In our case, electrochemical reactivity could only be found at the scratch, where both anodic and cathodic reactions must occur. As the underlying metal is the galvanized layer, the corrosion reaction involves the oxidation of zinc with the formation of soluble Zn^{2+} species, whereas the corresponding cathodic reaction is the reduction of dissolved oxygen. Thus, the species which could be considered to follow the advancement of the corrosion process with the SECM-tip are either the Zn^{2+} ions as the corrosion product or the Zn^{2+} ions as the corrosion product for the anodic half-cell reaction, or oxygen which is the reactant for the corresponding cathodic reaction. With this arrangement, Zn^{2+} ions cannot be detected at the SECM-tip through their electroreduction to Zn°, which occurs at a potential more negative than that for oxygen reduction in this medium, as zinc deposition on the surface of the Pt electrode will result in drastic changes of the electrode potential. Therefore, it was decided to investigate instead local variations of the concentration of dissolved oxygen as a result of the corrosion process.

Before studying the substrate/electrolyte interfaces, the oxygen reduction current was measured when the tip of the SECM was at sufficient large distance from the substrate for the tip-current not to be perturbed. The steady-state cyclic voltammogram measured in this case (Fig. 4) has shown that the limiting current reduction of oxygen occurs at potential values more negative than −0.40 V. Further excursion of potential to more negative values shows the onset of hydrogen evolution at potentials below −0.9 V. Therefore, the remaining experiments were conducted at a tip potential in the range between −0.4 and −0.9 V.

The applicability of the SECM-tip to detect depletion in oxygen concentration was investigated by performing the following experiment, consisting in the controlled addition of a solution containing Na_2SO_3 to the test solution. Fig. 5 shows the current transient measured at the SECM-tip polarised at −0.75 V. The initial part of the transient was collected as the potential value was applied to the tip, with the corresponding initiation of oxygen electroreduction. After approximately 20 s, a steady-state current regime was attained. Later, starting at ca. 390 s, 1 ml of the Na_2SO_3-containing solution was added into the cell. Due to oxygen consumption by sulphite anions, an abrupt decrease of the electroreduction current was promptly measured at the SECM-tip. The observations derived from this bulk experiment can be also applied to those experiments conducted by rastering the microelectrode parallel to the surface at selected tip heights. In this case, variations in oxygen concentration must originate from the corresponding corrosion reaction at the sample.

Fig. 6 shows the current at the SECM-tip corresponding to two line-scans over the surface, measured at different distances of the tip over the sample, of 100 and 1000 μm. During
Fig. 6. Line-scans measured in 0.1 M NaCl by moving the SECM-tip between two locations at the surface of the sample, one over the polymer film and the other above the scratch, as schematically shown in Fig. 7. They have been measured at two different tip heights, given in the figure. Arrows indicate the scan direction for each scan. Tip potential is $-0.70 \text{ V}$ vs. the Ag/AgCl/KCl (saturated) reference electrode.

The scan showed that the tip moved between a point in the coated area of the sample and another point located over the scratched area, as schematically shown in Fig. 7 by points A and B. The two scans showed very different results. Whereas no effect due to the scratch could be observed in the transient measured at a distance of 1000 $\mu$m, the other was close enough to the surface to detect the consumption of oxygen from the solution at the cathodic areas developed in the scratched area. That is, there is a large variation in the current measured at the SECM-tip as a result of the corrosion processes occurring in the system when the microelectrode is scanned in sufficiently close vicinity of the sample. This effect is more readily observed from the measurements depicted in Fig. 8. In this case, the current at the SECM-tip was measured as the microelectrode was vertically moved away from the sample at locations A and B. In both cases, the sample was initially located as indicated in the figure and was shifted in 1 $\mu$m steps. It must be noted that the scales for both curves do not correspond to the same heights in the solution, since the experiments have been initiated at a constant distance from the surface directly below the tip, which for location B is actually at a lower level as the coating thickness is not included this time.

From the foregoing, it can be observed that the concentration of oxygen in the solution only varies where the underlying metallic substrate is directly exposed to the electrolyte, i.e. at the scratch. Oxygen depletion is more noticeable at shorter distances from the surface, and the reducing currents increase with the distance, until it approaches the values typical in the bulk solution for distances of 1000 $\mu$m and above.

It is interesting to observe that the tip heights indicated in Figs. 6 and 8 are much larger than those usually employed in SECM experiments, typically in the range of 1–2 tip diameters (cf. Fig. 3). In this case, the microelectrode was used to follow the depletion of one of the reactants participating in the corrosion reactions occurring at the sample, which was demonstrated to extend much further than the dimensions encountered in typical SECM experiments.

4. Conclusions

The present study demonstrates that scanning electrochemical microscopy is suitable to investigate the processes involved in the degradation of coated metals. Both mapping of the surface and detection of reactants participating in the corrosion reactions are achieved by scanning the SECM-tip over the surface of the sample. This is possible because the SECM operates on both insulating (coated areas) and conducting (non-coated) surfaces and exhibits high spatial resolution. Furthermore, the SECM-tip may be used to quantitatively detect the reactants participating in
the corrosion reactions by adequately calibrating the current measured at the tip in solutions of known concentration. Further improvement of the calibration procedures will allow a quantitative determination of the species detected at the microelectrode, a task that is currently under work.

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