Use of SVET and SECM to study the galvanic corrosion of an iron–zinc cell

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Abstract

The work makes use of the scanning vibrating electrode technique (SVET) and the scanning electrochemical microscope (SECM) to investigate microscopic aspects of the electrochemical reactions that occur in an iron–zinc galvanic couple immersed in aqueous sodium chloride solution. Detection of the corrosion processes was made by sensing the phenomena occurring in solution. The SVET provided information on the distribution of ionic currents arising from the metal surface, whereas the SECM measured the concentration of chemical species relevant to the corrosion processes. The two techniques had comparable sensitivity for the corrosion of iron but significant differences were observed concerning the detection of corrosion of zinc.

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1. Introduction

Several micro-chemical and micro-electrochemical techniques have been introduced to the corrosion laboratory in recent times with the advantage of giving microscopic information on the processes occurring at the surface of corroding metals. Electrochemical noise analysis from immersed microelectrodes [1–6], localised electrochemical impedance spectroscopy [15–18], wire beam electrodes (WBE) [19–23], capillary and droplet cells [24–32] are currently used in a number of laboratories to investigate localised corrosion processes with great success. Scanning probe techniques like atomic force microscopy and scanning tunnelling microscopy are also becoming increasingly used for these investigations, although the limitations they exhibit for in situ operation in the case of complex systems such as corroding metals, tend to restrict their use to either the investigation of highly idealized systems as single crystal probes [33–35] or their later ex situ characterization under air or vacuum operation [36–40].

Special mention should be made of scanning electrochemical techniques with high spatial resolution that allow in situ measurements, as they can provide valuable information on the behaviour of the corroding system at a microscopic level. They consist basically of scanning a microelectrode over the immersed specimen, either in a static mode (scanning reference electrode technique, SRET) or in a vibrating mode (scanning vibrating electrode technique, SVET), allowing for mapping of either current or potential in the solution [41]. These techniques have been effective in monitoring the progress of many corrosion situations [42–54]. An alternative technique is the scanning electrochemical microscope (SECM) [55–58]; in the generation/collection mode, the ultramicroelectrode can work as an amperometric sensor of chemical species in solution, allowing the measurement of local differences in electrochemical reactivity on the scanned substrate. The SECM has been applied to corrosion research in various occasions [59–74].

In this paper we report the results of experiments designed to follow the corrosion processes occurring at iron and zinc samples directly exposed to an aqueous environment containing chloride ions, the metals being either isolated or electrically connected as a galvanic couple. No polarization of the samples was performed, thus allowing the systems to evolve spontaneously as it occurs in naturally driven corrosion processes. Experiments were conducted by SVET and SECM in naturally aerated electrolyte at ambient temperature.

2. Experimental

2.1. Chemicals, materials and sample preparation

Experiments were performed on 99.5% pure iron and 99.95% pure zinc, both supplied as sheet of thickness of 1 mm by Goodfellow Materials Ltd. (Cambridge, UK). The sheets were cut and mounted into an epoxy resin sleeve, so that only a square area with ca. $1 \times 1 \text{mm}^2$ formed the testing metal substrate – Fig. 1(a). For the galvanic couple experiments two electrodes were embedded in the resin and connected electrically at the back – Fig. 1(b). The mount with the samples was then polished with silicon carbide paper down to 1200 grit, washed thoroughly with Millipore deionised water, dried with acetone and finally surrounded laterally by sellotape, thus creating a small container for the electrolyte solution. The electrochemical cells for both SVET and SECM were completed with the
inclusion of their corresponding microelectrodes. Testing was carried out in aqueous 0.1 M NaCl solution made from analytical grade reagent and Millipore deionised water. The solution was naturally aerated and experiments were conducted at ambient temperature.

2.2. SVET instrumentation and experimental procedure

The SVET instrumentation was manufactured by Applicable Electronics Inc. (MA, USA) and controlled by dedicated software. Further details can be found in the literature [54,75]. The technique is based upon the measurement of small potential variations in solution, associated to the ionic fluxes that come from oxidation and reduction reactions occurring on the active surface [42,43]. The microelectrode had a platinum tip with a diameter of 20 \( \mu \text{m} \) and vibrated with an amplitude of 20 \( \mu \text{m} \), its main position being located at a distance of 200 \( \mu \text{m} \) from the sample. A calibration routine converted the measured potentials into current density at the corroding surface [41,76].

2.3. SECM instrumentation and experimental procedure

The Scanning Electrochemical Microscope consisted of model CHI900 (CH-Instruments, Texas, USA) and operated with a 10 \( \mu \text{m} \) diameter platinum disk at the tip of the probe, an Ag/AgCl/KCl (saturated) reference electrode and a stainless steel counter electrode. All potential values are referred to the Ag/AgCl/KCl (saturated) reference electrode. This technique, working in the amperometric mode, measures a faradaic current at the microdisk, while the tip is rastered over the metal sample. Provided the current is controlled by diffusion of the electroactive species to the microelectrode, for a species \( A \) in the solution, the limiting current, \( i_\infty \), is given by [56,57]

\[
i_\infty = 4nFD_A C_A a,
\]

where \( D_A \) is the diffusion coefficient of the species, \( C_A \) is its bulk concentration, \( a \) is the tip radius, \( F \) the Faraday constant and, \( n \) the number of electrons consumed or produced in
the reaction. Further details can be found in [73,74]. The currents measured are presented as current intensity at the probe.

## 3. Results

### 3.1. Iron

The main reactions responsible for corrosion of iron in NaCl solution at neutral pH are the oxidation of iron

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad (2)
\]

and the reduction of dissolved oxygen

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (3)
\]

Reaction (2) leads to an upward flow of metal cations above the anodic regions, which are detected by SVET as positive currents; conversely, in the cathodic regions an upward flow of OH\(^-\) anions emerges from the surface as a consequence or reaction (3), being detected by SVET as negative currents. As long as corrosion exists, these reactions are maintained and so are the existence of the localized positive and negative ionic flows in solution. At the same time, the amount of O\(_2\) dissolved in solution is lower near the cathodic regions since it is consumed in those regions following Eq. (3).

In Fig. 2 it is possible to observe how spontaneous corrosion of iron occurred with clear separation between a large cathode and a small anode. The anodic and cathodic activities were usually maintained at the same locations for several hours, although the location tended to change as the corrosion products started blocking the surface. The cathodic areas were more difficult to sense with the SVET, because they were less localized.

The progress of reactions (2) and (3) can be followed by selecting adequate potential values at the SECM tip. As an example, Fe\(^{2+}\) ions may be detected by setting the tip at +0.60 V. In these conditions the amperometric detection of Fe\(^{2+}\) is under the limiting current of oxidation to Fe\(^{3+}\), as confirmed by the cyclic voltammogram depicted in Fig. 3(a). A calibration curve was obtained using 0.1 M NaCl solutions with different additions of FeSO\(_4\)(NH\(_4\))\(_2\)SO\(_4\)·6H\(_2\)O. Only a small range of concentrations could be used due to experimental difficulties, but it showed a reasonably good linear correlation between the current measured and the concentration, as given in Fig. 3(b). Extrapolation of the fitted line towards zero concentration does not cross the Y-axis at zero current, which suggests that a calibration curve can lead to better estimation of concentration. Applying Eq. (1) to the measured currents leads to an average diffusion coefficient of \(4.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\), which is slightly higher than the value 0.72 \(\times 10^{-9} \text{ m}^2 \text{ s}^{-1}\) from the literature [77]. The detection of dissolved Fe\(^{2+}\) in solution above a corroding iron electrode is shown in Fig. 4(a). This detection was not easy in the freshly prepared surface but became more evident later, after scratching the layer of corrosion products. Above the scratched area, an excess of Fe\(^{2+}\) ions was measured; the resulting curves for Fe\(^{2+}\) oxidation were asymmetrical and showed narrow spikes randomly distributed upon a broad shoulder that covered the entire length of the iron surface.

The dissolved oxygen in solution, which is consumed in reaction (3) was measured in the same manner as Fe\(^{2+}\), this time by polarizing the tip at −0.70 V. Amperometric scan curves for dissolved O\(_2\) are depicted in Fig. 4(b). The curves display a well-defined
Fig. 2. Ionic current mapping (left) and video images (right) of a pure iron electrode during immersion in 0.1 M NaCl at selected exposure times: (a) ca. 5 min, (b) 1 h, and (c) 1 day. Electrode size: $1 \times 1 \text{ mm}^2$. Current scales are given in $\mu\text{A cm}^{-2}$.

Fig. 3. (a) Cyclic voltammogram measured at the SECM tip immersed in a 5 mM solution of FeSO$_4$(NH$_4$)$_2$SO$_4$. 6H$_2$O in 0.1M NaCl; scan rate: 10 mV s$^{-1}$. (b) Calibration curve for Fe$^{2+}$ measured with the SECM microelectrode set at +0.60 V.
depletion above the metal surface, resulting from the cathodic reaction occurring on it. The minimum of the curve approaches zero as the distance to the surface decreases. When the scans were made sufficiently close to the surface, a local anode was revealed in the oxygen curve by a local small peak that coincides with the highest accumulation of Fe\textsuperscript{2+}. The oxygen concentration profile was also assessed by scanning the probe vertically and plotting the current at the probe as a function of the vertical distance to the metal surface, as depicted in Fig. 5. Oxygen depletion is observed starting from 1000 \( \mu \text{m} \) from the surface.

According to Eq. (1), the measured currents can be converted into concentration values by introducing the diffusion coefficient of oxygen in the solution. The value of \( 2.01 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) for the diffusion coefficient of oxygen in water \([77]\) resulted in the determination of a bulk concentration of \( 4.38 \times 10^{-4} \text{ M} \), which is greater than the solubility of oxygen in 0.1 M NaCl of approximately \( 2.35 \times 10^{-4} \text{ M} \) referred in the literature \([78]\). This difference may be due to the simultaneous reduction of protons at the potential of \(-0.70 \text{ V}\). Further, polishing of the microelectrode was made by hand, which may result

*Fig. 4. Amperometric curves for (a) Fe\textsuperscript{2+} and (b) O\textsubscript{2} obtained above the scratched iron surface, when the tip potential was set at +0.60 and −0.70 V, respectively. Probe heights for each scan are indicated in the graphs.*

*Fig. 5. Oxygen reduction current over the iron sample obtained by approaching the probe to the iron surface with the microelectrode potential set at −0.70 V.*
either in a small tilt or in a rougher surface, and thus to an increased real area of the platinum electrode.

3.2. Zinc

The ionic flows above spontaneously corroding zinc – Fig. 6 – showed a clear definition of one cathode and one anode well before corrosion signs became visible to the naked eye. The anodic activity results from the oxidation of zinc according to

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \tag{4} \]

and the cathodic activity is described by Eq. (3). The currents measured were in the same range as those previously observed for the iron sample. The attack was very localized, with the development of one pit only above which the anodic currents continuously increased during the period of immersion. The cathodic reaction was quite localized during the first hour of immersion but became more spread over the surface after one day, when corrosion products covered the original cathode.

With the SECM, the probe scan curve for oxygen showed a minimum above the zinc electrode (Fig. 7). This minimum was sharper than on iron, due to the more localized

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Fig. 6. Ionic current mapping (left) and video images (right) of a pure zinc electrode during immersion in 0.1 M NaCl at selected exposure times: (a) ca. 5 min, (b) 1 h, and (c) 1 day. Electrode size: \( \sim 1 \times 1 \text{ mm}^2 \). Current scales are given in \( \mu \text{A cm}^{-2} \).
cathodic activity. Detection of zinc was not possible under the working conditions. Zinc becomes reduced at potentials below the reversible potential for Zn\(^{2+}/Zn\), at ca. \(-1.00\) V. The disadvantage of this method is that it involves deposition of metallic zinc on the microelectrode, with the consequent need for cleaning after the experiment. In order to confirm the sensitivity of the technique, the zinc electrode was polarized anodically (\(-0.83\) V) and the surface scanned with the microelectrode polarized at \(-1.15\) V. A distinct peak was then observed. This observation apparently contrasts with the results from Tada et al. [79], who monitored the concentration of Zn\(^{2+}\) over a zinc electrode. Their study, however, involved galvanic corrosion with a significantly larger cathode to anode area ratio, which led to an acceleration of the process comparable to the anodic polarization.

### 3.3. Iron–zinc galvanic couple

Fig. 8 shows maps of ionic currents in solution measured at different distances above the surface. The cathodic and anodic activities were well separated and located on iron and zinc, respectively, as anticipated in a galvanic couple with zinc oxidizing sacrificially and preventing the corrosion of iron. When the electrodes were connected the potential became shifted to about \(-1.040\) V, i.e., slightly more positive than the potential of zinc in the same medium (\(-1.060\) V). At that potential, iron cannot be oxidized (its potential when corroding freely is \(-0.750\) V) and the main reactions that take place are the oxidation of zinc to Zn\(^{2+}\) ions and the reduction of oxygen at the iron surface. As a result of the three-dimensional diffusion of ions from the generating surface, the ionic currents become less intense and less localized with increasing distance. This is revealed by the sharp signals measured near the surface, becoming broader and smaller for longer distances, ultimately vanishing at sufficiently high distances. The same can be observed in Fig. 9 for line scans obtained at various distances above the surface. It is interesting to note that the potential field in solution extends to approximately 1 mm from the surface. Above that, only a baseline was obtained, corresponding to the response of the bulk solution.
Fig. 10 shows currents of O$_2$ reduction measured at different heights above the iron electrode. The amount of oxygen dissolved in solution decreases when approaching the iron surface in either direction, as a result of its consumption in the cathodic reaction. The values encountered are smaller than those obtained for isolated iron and zinc, due to the enhanced cathodic activity at the iron electrode caused by galvanic coupling.

Fig. 8. Ionic current mapping of a galvanic couple (pure Fe and pure Zn) in 0.1 M NaCl obtained at various distances from the surface: (a) 100 \( \mu \)m, (b) 300 \( \mu \)m, (c) 700 \( \mu \)m and (d) 2000 \( \mu \)m.

Fig. 9. Ionic current lines obtained at different distances (indicated in \( \mu \)m) above the galvanic couple immersed in 0.1 M NaCl.

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4. Discussion

The SVET measurements showed that currents fade away with distance from the ions’ sources, as expected for processes controlled by diffusion. Fig. 11 plots the absolute peak values of both cathodic and anodic currents against probe height. The magnitudes are similar for the same distance, as anticipated for a galvanic couple where cathodic and anodic activity should cancel out. It is usually accepted that the currents detected by SVET come from the activities on the surface. However, the possibility of other ions, namely Na\(^+\) and Cl\(^-\), migrating to compensate the excess of charges in cathodic and anodic sites, thus giving an increased signal, cannot be totally discarded. In this case the values relative to OH\(^-\) and Zn\(^{2+}\) would be overestimated. Work is needed in this particular area to identify the species that are in fact giving the SVET response.

The distribution of dissolved oxygen at any height \(z\) and radial distance \(r\) from the surface of a disk-shaped cathode of radius \(b\) can be estimated [80] starting from the saturation concentration \(C_{O_2}^0\),

\[
C_{O_2} = C_{O_2}^0 \left[ 1 - \frac{2}{\pi} \sin^{-1} \left( \frac{2b}{\sqrt{(r-b)^2 + z^2} + \sqrt{(r+b)^2 + z^2}} \right) \right]
\]  

Fig. 12 shows the concentration profiles of O\(_2\) obtained using Eq. (1) for the currents measured above Fe either isolated or in the galvanic couple. Also shown is the calculated profile using Eq. (5) for the case of Fe in the galvanic couple and the saturation oxygen concentration in 0.1 M NaCl solution [78]. Since the total height of solution used in the experiments was only 4–5 mm, Eq. (5) is not totally valid because the concentration gradient extends all across the liquid layer.

A more complete approach to the corrosion process would include pH, Na\(^+\) and Cl\(^-\) (ions from the electrolyte) determination as well as improved detection of both Fe\(^{2+}\)
and Zn$^{2+}$. Ultimately, accurate determination of all these species with proper spatial resolution would lead to the establishment of a model capable of relating the distribution of the species in solution and the reactions occurring on the metal surface.

One factor that affects the measurements in both techniques is the stirring of the solution provoked by the movement of the probe. In both techniques, the maximum distance at which the corrosion process was detected was approximately 1 mm. This distance is
comparable to the total height of electrolyte used (4–5 mm) and therefore the gradients of potential and of concentration can be affected by the interface with the atmosphere.

Comparison of the results from the two techniques shows that on iron the detection of both the anodic and the cathodic activities were easily detected by both techniques. When the galvanic couple was established, however, the SVET proved to be more sensitive to the anodic currents on zinc, whereas the SECM had a lower sensitivity to the presence of Zn$^{2+}$ ions in solution. An important advantage of the SECM is the proximity of the probe to the metal surface, which allowed a very good spatial resolution, as was observed in the corrosion of the single iron electrode.

5. Conclusions

The SVET and the SECM provided consistent information on the local ionic fluxes and local concentrations of reagents and products of the electrochemical reactions that occur on the surface. The two techniques offer complementary information: ionic fluxes corresponding to cathodic and anodic reactions were measured with the SVET, though it lacked chemical discrimination to identify the nature of the ionic species involved; on the other hand, by adequately selecting the potential value at the microelectrode in the SECM, reactants and products of the corrosion reactions could be identified. Furthermore, their concentrations in the aqueous phase could be estimated, thus providing in situ information as a function of the time elapsed since immersion.

The results have shown an advantage of the SECM resulting from the proximity of the probe to the substrate, whereas the SVET proved to be more sensitive to the anodic activity of zinc.

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