Investigating corrosion processes in the micrometric range: A SVET study of the galvanic corrosion of zinc coupled with iron

R.M. Souto a,*, Y. González-García a, A.C. Bastos b, A.M. Simões c

a Departamento de Química Física, Universidad de La Laguna, E-38200 La Laguna, Tenerife, Spain
b Departamento de Engenharia de Cerâmica e do Vidro, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
c Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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Abstract

The galvanic corrosion of an iron/zinc pair immersed in aqueous 0.1 M Na₂SO₄ solution has been investigated by using the scanning vibrating electrode technique (SVET). In this way, investigations in the micrometer range of the progress of the electrochemical reactions involved in galvanic process were performed. The anodic oxidation process is observed to be initiated on the zinc sample in a localized manner, whereas the cathodic reaction involving the electroreduction of dissolved oxygen is homogeneously distributed over the iron sample. This later process is the rate determining step in the overall corrosion process, as demonstrated by the changes in the ionic and galvanic currents measured in the system when the area of the iron specimen is varied relative to that of zinc. The occurrence of coupled chemical reactions in the solution phase involving the products of the corrosion reactions could also be deduced from the integration of the ionic currents measured for each half-reaction during a SVET scan. Thus, the corrosion processes involved in the galvanic coupling of iron and zinc have been further understood by using this microelectrochemical technique appropriately, helping to better interpret large scale measurements.

Keywords: A. Iron; A. Zinc; B. SVET; C. Galvanic couple

* Corresponding author. Tel.: +34 922318067; fax: +34 922318002.
E-mail address: rsouto@ull.es (R.M. Souto).
1. Introduction

Though metals remain stable for very long periods in vacuum, they corrode when exposed to the atmosphere or aqueous environments without protection. The surface becomes oxidized and electrochemical reactions take place in the interface between the metal and the environment. Localized anodes and cathodes are developed on the metallic surface, resulting in the formation of local microcells. The metal is oxidized at the anodes, whereas the corrosion process is maintained by the reduction of some species from the environment at the cathodes (namely oxygen in neutral and moderately alkaline media, or protons in acidic solutions). Generalized corrosion arises from continuous modifications in the local distribution of anodes and cathodes on the metal surface, allowing for the metal to be corroded to a similar extent at all points. Galvanic corrosion, also called bimetallic corrosion, is a form of corrosion that occurs when two different metals are coupled or in electrical contact. Preferential corrosion of the most active metal occurs, whereas the most noble metal usually remains protected. Galvanic corrosion can be simulated by separating the components of the galvanic cell and measuring the currents flowing when they are connected externally.

Corrosion processes are usually monitored by using conventional electrochemical techniques, which allow both the evaluation of corrosion rates and the identification of corrosion mechanisms. As they average the electrochemical behaviour of the total surface, the information obtained relates to the global properties of the corroding system. This is a major limitation in the investigation of localized corrosion processes such as passivity breakdown, pitting corrosion and the breakdown of coated systems. In these cases, the appearance of corrosion symptoms through these techniques are often related to the final stages of a complex and dynamic mechanism that started at a microscopic level. But even simple corrosion systems such as those experiencing galvanic corrosion can involve complexities at a microscopic level due to the local distribution of microanodes and microcathodes on the surface of the coupled metals. Local variations in electrochemical reactivity on the metallic materials can only be investigated in situ by employing techniques with enhanced spatial resolution.

In recent years several techniques with spatial resolution have been developed, with the capability of determining distribution maps of quantities such as current densities [1–4], Volta potential [5–8], and ion concentrations (such as H\(^+\) and released metal ions) [2,9–13]. These techniques are typically based not on the working electrode itself, but upon sensing species, or parameters, that are in some way correlated with the corrosion activity. We have used two of those techniques, the scanning vibrating electrode technique (SVET) [14–16] and the scanning electrochemical microscope (SECM) [17–20], 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 [13,21,22]. Consistent information regarding the local ionic fluxes and local concentrations of reagents and products of the electrochemical reactions that occur on the metal surfaces were thus obtained.

The present study presents the results of experiments designed to investigate the effects of solution composition and of metal surface ratios on the galvanic corrosion of the iron–zinc galvanic couple immersed in an aqueous environment containing sulphate ions. We show that SVET provides information about the corrosion process and its nature in a localized manner. Surface current mapping gives information such as the location of anodes and cathodes responsible for galvanic corrosion.
2. Experimental

This work was carried out on 99.5% purity iron and 99.95% purity zinc surfaces. These metals were supplied as sheets of thickness 1 mm by Goodfellow Materials Ltd. (Cambridge, UK). The sheets were cut into square specimens of 1 mm $\times$ 1 mm dimensions, and mounted into an epoxy resin sleeve, such that only a square end surface formed the testing metal substrates (cf. Fig. 1). Samples were then polished with silicon carbide paper to 1200 grit and washed thoroughly in double-distilled water and acetone.

Testing was carried out in aqueous 0.1 M Na$_2$SO$_4$ base solution, and its pH was adjusted within the range $4.8 \leq \text{pH} \leq 9.1$ through the addition of dilute amounts of either H$_2$SO$_4$ or NaOH. Solutions were made from analytical grade reagent and double-distilled water. The experiments were conducted at ambient temperature in the naturally aerated solutions.

The electrochemical cells for SVET experiments were produced as it follows. The epoxy-sleeved metal specimen (diameter of ca. 4 cm), once polished and cleaned, was taken as the base for the electrochemical cell by placing it horizontally with the polished surface facing upwards. Then the specimen was surrounded laterally by tape, thus allowing a volume for the electrolyte to be filled in.

The scanning vibrating electrode instrumentation used was manufactured by Applicable Electronics Inc. (Forestdale, MA, USA). A Micro Probe PI200101F microelectrode, which consisted of Pt/Ir (80%/20%) wires insulated with paralene C$^\circledR$ and arced at the tip to expose the metal, was employed. The microelectrode was platinized in order to produce a spherical platinum black deposit of 10–20 $\mu$m diameter. The measurements were made with the electrode tip vibrating in a plane perpendicular to the sample, at an amplitude of 20 $\mu$m and with frequencies in the order of 200–400 Hz. The mean distance between the microelectrode and the sample surface was 200 $\mu$m. A reference measurement with the microelectrode away from the active area was subtracted from the values measured during the scan. The electrochemical cell was completed by using a Pt-black wire as reference electrode. All such experiments were carried out at the free mixed-corrosion potential.

The ionic current maps are composed by 4000 data points, resulting from a 20 $\times$ 20 points matrix in $X$ and $Y$ directions. The sample area imaged in each experiment was

Fig. 1. Photographs of lateral and top views of the iron and zinc samples embedded in an epoxy sleeve. The electrical connection for the galvanic couple was made at the rear of the mould.
4 mm$^2$ approximately, whereas the time needed to complete each map amounted to ca. 10 min. The experiments were followed during 90 min, thus allowing for six ionic current maps to be determined consecutively.

The total current flowing in the system due to galvanic coupling was monitored by introducing a zero resistance ammeter in the electrical connection between the two metals at the rear of the electrochemical cell.

3. Results and discussion

An example of the local current density maps which arise from galvanic coupling zinc and iron in 0.1 M Na$_2$SO$_4$ solution is shown in Fig. 2. Electrochemical information is

Fig. 2. (a) Ionic current mapping. (b) Ionic current profiles determined above the galvanic couple immersed in 0.1 M Na$_2$SO$_4$. 
sensed by the SVET as small potential variations in solution which are associated to the ionic fluxes due to the oxidation and reduction reactions occurring on the active surface.

Two regions of different electrochemical activity are distinguished above the locations of the two metal wires, namely a flux of positive currents is observed over the zinc sample and negative currents over iron. The positive currents are due to the flux of Zn\(^{2+}\) ions released from the zinc surface during the oxidation of the metal according to:

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad (1)
\]

Analogously, the negative currents measured over the iron sample arise from the flux of hydroxide ions generated at the metal surface from the reduction of dissolved oxygen:

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

As long as corrosion exists, these reactions are maintained and so is 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. (2).

It may be also observed from the inspection of Fig. 2 that the current distributions around the anodic and cathodic areas do not exhibit the same characteristics. In fact, the electrochemical activity at the iron sample is quite homogeneously distributed over the whole exposed area, whereas a location of higher activity can be observed at the zinc sample giving rise to a well-defined peak in the corresponding current profile (see Fig. 2b).

The evolution of the electrochemical activity with exposure time can be followed from the inspection of consecutive ionic current maps, as depicted in Fig. 3. In all cases the ionic fluxes measured from consecutive scans initially exhibited an increase for both the anodic and the cathodic regions when passing from the first to the second maps, but subsequently showed a rather smooth decay with time for the remaining scans. No significant changes in the spatial distribution of the ionic currents over each metal with time were observed, with the anodic process exhibiting a rather localized pattern at all times.

The influence of solution pH on the galvanic corrosion process was next investigated. Measurements were performed in the 4.7 \(\leq \) pH \(\leq\) 9.2 range, thus allowing to cover conditions ranging from the active regime for both metals (i.e., at the lowest pH value under consideration), to that in which both of them are in the passive regime, according to the corresponding Pourbaix diagrams of iron and zinc [23]. The SVET images obtained at selected pH values are depicted in Fig. 4. The ionic fluxes are observed to diminish steadily as the pH is increased in the range under study, an effect that becomes more important as the solution becomes alkaline. The location of the anodic process on a portion of the zinc surface is also more noticeable in the alkaline medium, whereas a very homogeneous distribution is observed over the iron wire.

The overall currents flowing in either the anodic or the cathodic regions in the SVET map could also be determined by integration. The integrated values obtained from such calculation for the experiments given in Fig. 4 are reported in Tables 1–3, as well as those determined from subsequent scans. The data obtained in the near-neutral solution deliver practically identical values for the currents in both regions (see Table 1). This result is consistent with equal charges been carried by the zinc ions released through the anodic reaction (1), and by the hydroxide ions formed in the cathodic reaction (2). On the other hand, the integrated currents for both half-reactions are different in the case of the experiments conducted in either acidic or alkaline media, as can be observed from the data (Tables 2
Fig. 3. Ionic current maps determined above the galvanic couple immersed in 0.1 M Na₂SO₄. The recording of the maps was initiated after: (a) 11 min, (b) 41 min, and (c) 96 min since immersion of the sample in the test electrolyte.
Fig. 4. Influence of pH on the ionic current maps determined above the galvanic couple immersed in 0.1 M Na₂SO₄ base electrolyte; pH values: (a) 4.7, (b) 5.5, and (c) 8.2.
and 3). In the acidic media, the values are found to be systematically higher for the anodic process than for the corresponding cathodic, as shown in Table 2. Though differences arising from the finite time employed to obtain each map for a dynamic surface as the corroding metal cannot be completely discarded, they are expected to play a somewhat minor role as the ionic currents measured are similar in range to those measured in the near neutral solution. Then, this effect is attributed to the composition of the solution, because a portion of the electroformed \( \text{OH}^- / \text{CO}_2 \) ions must be neutralized by the protons in excess in the acidic medium, and they are not available to diffuse into the solution. In this way, significantly smaller values should be obtained for the cathodic currents compared to those related to the anodic process, where the dissolution of zinc ions can be monitored from the corresponding integrated currents. Thus, in acidic media the ionic fluxes measured by the vibrating electrode, operating at a distance of 200\( \mu \)m from the surface, must be regarded not to characterize quantitatively the cathodic process.

Significantly smaller currents are determined in alkaline media for both the anodic and cathodic reactions compared to those measured at lower pH values (cf. Table 3). In this environment the surfaces of the metals tend to become passive, and a smaller current is used to maintain the galvanic corrosion process. Furthermore, the integrated currents from the anodic region are smaller compared to those originated from the cathodic reaction, as it could be expected from the precipitation of zinc hydroxide species in the alkaline

### Table 1
Integrated ionic currents for the cathodic and anodic half-reactions measured for an 1:1 iron/zinc system immersed in 0.1 M \( \text{Na}_2\text{SO}_4 \) (pH 5.5)

<table>
<thead>
<tr>
<th>Immersion time (min)</th>
<th>Anodic current (( \mu )A)</th>
<th>Cathodic current (( \mu )A)</th>
</tr>
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<tbody>
<tr>
<td>11</td>
<td>3260.2</td>
<td>-3478.1</td>
</tr>
<tr>
<td>23</td>
<td>2243.7</td>
<td>-2556.1</td>
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<tr>
<td>41</td>
<td>2643.5</td>
<td>-2560.9</td>
</tr>
<tr>
<td>66</td>
<td>3178.7</td>
<td>-3095.3</td>
</tr>
</tbody>
</table>

### Table 2
Integrated ionic currents for the cathodic and anodic half-reactions measured for an 1:1 iron/zinc system immersed in 0.1 M \( \text{Na}_2\text{SO}_4 \) adjusted at pH 4.7

<table>
<thead>
<tr>
<th>Immersion time (min)</th>
<th>Anodic current (( \mu )A)</th>
<th>Cathodic current (( \mu )A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2377.7</td>
<td>-1781.71</td>
</tr>
<tr>
<td>20</td>
<td>3173.6</td>
<td>-2072.1</td>
</tr>
<tr>
<td>32</td>
<td>2713.7</td>
<td>-2500.1</td>
</tr>
<tr>
<td>65</td>
<td>2509.4</td>
<td>-2139.0</td>
</tr>
</tbody>
</table>

### Table 3
Integrated ionic currents for the cathodic and anodic half-reactions measured for an 1:1 iron/zinc system immersed in 0.1 M \( \text{Na}_2\text{SO}_4 \) adjusted at pH 8.2

<table>
<thead>
<tr>
<th>Immersion time (min)</th>
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</tr>
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<tbody>
<tr>
<td>7</td>
<td>1432.1</td>
<td>-1885.4</td>
</tr>
<tr>
<td>21</td>
<td>1242.9</td>
<td>-1930.5</td>
</tr>
<tr>
<td>35</td>
<td>1364.8</td>
<td>-1916.5</td>
</tr>
<tr>
<td>48</td>
<td>1369.6</td>
<td>-2125.6</td>
</tr>
</tbody>
</table>
environment. In this case, the ionic currents measured for the anodic process do not quantitatively account for the extent of zinc corrosion in the galvanic process.

The different extent of the galvanic corrosion reaction at the diverse pH values tested is additionally confirmed by inspecting the time courses of the total current measured with the zero resistance ammeter in Fig. 5. The highest currents are measured in the acidic solution at all exposure times, a result consistent with the thermodynamic prediction that both metals are located in their active regime, and conversely, the smallest currents occurred in the alkaline environment.

Finally, the influence of the relative areas of the two metals was also investigated with the SVET. In addition to the 1:1 iron/zinc areas ratio considered up to now, two other ratios were considered, either zinc or iron presenting half the area than the other metal. Those surface ratios were produced by covering with paraffin wax half of the area exposed to the environment of either metal. Fig. 6 shows a comparison of the typical current density maps obtained for the three relative surface ratios. In general, they exhibit the characteristic features regarding ionic current distributions over the metal surfaces previously observed in Fig. 2, that is, a rather homogenous distribution of the ionic fluxes over the iron and a more localized distribution over the zinc. These features are observed also for longer exposure times.

The total currents flowing in both the anodic and the cathodic regions during each scan were also determined by integration. The integrated values obtained from such calculation are given in Tables 4 and 5 for the various relative surface ratios and for different exposure times. From the comparison of these data, a number of observations regarding the effect of the relative surface area of the two metals on the galvanic corrosion process can be deduced. Though the total currents measured for the anodic and the cathodic regions were the same within experimental error when iron and zinc exposed the same surface to the environment (cf. Table 1), the reduction of the area of any metal relative to the other, results in the subsequent depletion of the integrated ionic current determined for the smallest sample. Accordingly, the integrated ionic currents measured for the largest sample also decrease to some extent, as should be expected since the electrical circuit is constituted by the combination of the two metals. Nevertheless, this reduction is more pronounced when

![Fig. 5. Time evolution of the galvanic currents flowing between the coupled metals exposed to 0.1 M Na₂SO₄ base electrolyte; pH values: (□) 4.7, (○) 5.5, and (△) 8.2.](image-url)
Fig. 6. Ionic current maps determined above the galvanic iron/zinc couple immersed in 0.1 M Na₂SO₄ for different relative areas of the metals. Relative iron:zinc surface ratios: (a) 1:1, (b) 1:2, and (c) 2:1.
the iron surface is smaller than that of zinc. This fact is also evident from the inspection of the galvanic currents measured with the zero resistance ammeter, which are plotted in Fig. 7. That is, whereas the galvanic current is almost the same when the areas of the metals is about the same, and when the area of iron is larger than that of zinc, the reduction of the iron surface by half results in the galvanic currents for the galvanic pair effectively reduced by half as well. The observed changes in the galvanic currents and in the SVET maps with the variation in the relative surface areas suggest that it is effectively the area of the iron sample that determines the extent of the galvanic process. This is an indication that the rate determining process is the reduction of oxygen on the iron sample, which is facilitated by a large surface of the exposed metal. Conversely, variations in the area of zinc exposed to the environment have a negligible effect on the overall current flowing in the system.

Table 4
Integrated ionic currents for the cathodic and anodic half-reactions measured for an 2:1 iron/zinc system immersed in 0.1 M Na₂SO₄ (pH 5.5)

<table>
<thead>
<tr>
<th>Immersion time (min)</th>
<th>Anodic current (μA)</th>
<th>Cathodic current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2057.6</td>
<td>−1633.5</td>
</tr>
<tr>
<td>52</td>
<td>1859.7</td>
<td>−1106.9</td>
</tr>
<tr>
<td>74</td>
<td>2327.8</td>
<td>−1510.6</td>
</tr>
<tr>
<td>94</td>
<td>1967.8</td>
<td>−1206.5</td>
</tr>
</tbody>
</table>

Table 5
Integrated ionic currents for the cathodic and anodic half-reactions measured for an 1:2 iron/zinc system immersed in 0.1 M Na₂SO₄ (pH 5.5)

<table>
<thead>
<tr>
<th>Immersion time (min)</th>
<th>Anodic current (μA)</th>
<th>Cathodic current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1114.8</td>
<td>−2248.2</td>
</tr>
<tr>
<td>26</td>
<td>1028.9</td>
<td>−1883.2</td>
</tr>
<tr>
<td>50</td>
<td>1269.8</td>
<td>−2079.3</td>
</tr>
<tr>
<td>82</td>
<td>1345.8</td>
<td>−1912.2</td>
</tr>
</tbody>
</table>

Fig. 7. Time courses of the galvanic currents flowing between the coupled metals exposed to 0.1 M Na₂SO₄ base electrolyte; relative iron:zinc surface ratios: (□) 2:1, (○) 1:1, and (△) 1:2.
4. Conclusions

1. The scanning vibrating electrode technique (SVET) has been used to study the galvanic corrosion of the iron/zinc system when exposed to 0.1 M Na₂SO₄ aqueous solution at ambient temperature. The SVET results clearly demonstrate that it is possible to get complimentary data supporting the physical interpretations of the galvanic corrosion processes based on the application of classical electrochemical techniques.

2. The technique provides excellent spatial resolution. In this way, it has been possible to observe that zinc oxidation started in localized regions, regardless the experimental conditions employed in this work. Conversely, the oxygen reduction reaction occurring on the iron samples has been observed to distribute fairly homogeneously on the electrode surface.

3. Care must be taken in interpreting SVET data from the integration of the ionic current maps. What must be investigated is whether all the species produced in the corrosion reactions are transported into the electrolyte phase, or they may be (partially) consumed in coupled chemical reactions, as it has been observed to occur for the neutralization of hydroxide ions in acidic environments, and for metal ions precipitation in alkaline media.

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References