Introduction

Scanning electrochemical microscopy (SECM) is gaining increasing application in corrosion science for the in situ investigation of localized corrosion processes with high spatial resolution.[1–3] SECM is a scanning probe microscopy (SPM) technique that is based on the amperometric signal generated at a microelectrode by redox-active species in solution, which can perform quantitative local electrochemical experiments at interfaces to gather information on the topography or reactivity of substrates. This is often achieved by applying a variety of electrochemical waveforms at the probe or at the substrate, or even by coupling SECM with other SPM techniques, particularly atomic force microscopy (AFM).[4,5] The SECM probe is often a platinum or gold microelectrode, and by rastering the probe in close proximity to the surface of the sample, a map is made of the substrate properties. In general, image maps formed by SECM are based on an amperometric signal as a function of the tip position. SECM imaging experiments can be performed by either feedback or generation–collection (G–C) mode.[6] SECM has been applied successfully to a great variety of corrosion processes including the visualization of anodic and cathodic areas,[7,8] the identification of precursor sites for pitting corrosion,[9–12] the detection of metastable pit nucleation,[13] the generation of single pits on passive metals,[14–18] the dissolution of inclusions in alloys,[19–21] the water uptake and blister formation at organic-coated metals,[22–24] the degradation of organic coatings from metal–coating interfaces,[25–28] the permeation of hydrogen through metals,[29] and the characterization of chemical inertness of ceramic coatings on metals.[30,31] In most instances, the corrosion process is followed through the detection of the metal ion released in the aqueous phase from the corresponding corroding metal or metal alloy.[25] However, a number of technologically interesting metal materials, such as zinc, cannot be investigated in this way because their corresponding redox potentials are in the range of hydrogen evolution (at about −1.00 V versus Ag/AgCl/KCl sat). Interferences can also arise from oxygen reduction, which, for instance, at a Pt-disk microelectrode, produces a single four-electron wave due to the reduction of the oxygen to hydroxide ions at about −0.60 V versus Ag/AgCl/KCl sat.[32] Thus, if the redox process to be monitored at the tip occurs at high negative potentials, hydrogen generation or oxygen reduction would hide the signal due to the reduction of the ion species. Another drawback that can be encountered in corrosion investigations performed by
SECM coupled to the use of solid microelectrode tips is the circumstance that, for some dissolved metal ions, the only redox process available for detection is the electroreduction to the zero oxidation state. In this case, nucleation and growth of metals on the microelectrode tip leads, in turn, to the continuous modification of the active surface area of the electrode during the measurements. Zinc is an interesting material because metallic structures made of this metal are widely employed in our technological society for a variety of applications, for instance, batteries, die casting, and brass metallurgy, in addition to its common use as galvanized layers for the protection of steel objects. Unfortunately, soluble zinc species cannot be monitored using platinum or other solid microelectrodes in naturally aerated aqueous solutions because their reduction processes are affected by all the aforementioned interferences. This was our motivation for exploring alternate electrode materials to detect zinc ions by SECM during the corrosion process of the metal. To this purpose, an electrode material that possesses useful properties is mercury. In fact, mercury displays high hydrogen overvoltage and forms amalgams with numerous metals. Mercury-coated metal microelectrodes\(^{[36]}\) have been extensively used for anodic stripping voltammetry (ASV) of trace metal ions in aqueous solutions.\(^{[4,6,9]}\) More recently, mercury microelectrodes have also been successfully employed as SECM tips to approach solid/solution interfaces to monitor various metal ions, including \(\text{Zn}^{2+}\), \(\text{Cd}^{2+}\), \(\text{Pb}^{2+}\), \(\text{Cu}^{2+}\), \(\text{Mn}^{2+}\), and \(\text{Ti}^{4+}\).\(^{[41–47]}\) Moreover, the functions to predict diffusion-controlled steady-state currents\(^{[48]}\) and approach curves at sphere-cap tips for both negative and positive feedback conditions are available.\(^{[49]}\) Mercury sphere-cap microelectrodes can be fabricated onto microdisks of platinum by electrodeposition from mercury-ion solutions; the deposits adopt sphere-cap geometry.\(^{[50]}\) Such protruding tips provide a larger electrode area than the basal disks onto which they are fabricated, yet they allow the sample surface to be approached more closely.\(^{[51]}\) All these properties make sphere-cap SECM tips very useful for corrosion investigations. However, to the best of our knowledge, only a few papers exist in the literature that deal with the application of Hg-coated Pt SECM tips for investigating the open-circuit release of Cd, Pb, and Bi ions from thin films of the corresponding metals.\(^{[47,50]}\) In this paper, we present a study of the corrosion of zinc samples to illustrate the potential of coupling mercury tips and SECM in corrosion science under typical metal-corroding conditions. Naturally aerated aqueous chloride-containing solutions have been employed as the test environment.

**Results and Discussion**

**Monitoring \(\text{Zn}^{2+}\) ions at mercury microelectrodes:** Firstly, the potential ranges for the reduction and the oxidation of zinc species at a mercury microelectrode were tested by cyclic voltammetry in an aerated \(\text{Zn(NO}_3)_2\) (2 mmol L\(^{-1}\)) + NaCl (0.1 m) solution. As seen in Figure 1A, in the forward scan, a series of cathodic processes are evident in the potential range that extends from \(-1.20\) to \(-1.70\) V versus Ag/AgCl/KCl\(_{\text{sat}}\) with a main peak that occurs at \(-1.50\) V versus Ag/AgCl/KCl\(_{\text{sat}}\). Over this potential range, the reduction of \(\text{Zn}^{2+}\) species to \(\text{Zn}^0\) occurs, as is confirmed by the presence of the anodic peak centered at about \(-0.80\) V versus Ag/AgCl/KCl\(_{\text{sat}}\) upon potential reversal. The observation of various peaks during the cathodic scan in the CV can be related to the stepwise reduction of oxygen to hydrogen peroxide [Eq. (1)], the subsequent reduction of hydrogen peroxide to hydroxide anions [Eq. (2)],\(^{[51]}\) and the reduction of \(\text{Zn}^{2+}\) species, the process of which is complicated by the formation of sparingly soluble zinc hydroxide or oxide species at the electrode surface.\(^{[52]}\) This is due to the high local hydroxide ion concentration induced by the following reactions:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad (1)
\]

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

The formation of sparingly soluble compounds at the electrode surface would explain the presence of a reduction peak instead of a wave, as expected for microelectrodes that work on an experimental timescale in which hemispherical diffusion prevails.\(^{[53]}\) To confirm this scenario, CV measurements were performed either in a NaCl (0.1 m) aerated solution in the absence of \(\text{Zn}^{2+}\) ions (Figure 1B) or in a deoxygenated \(\text{Zn(NO}_3)_2\) (2 mmol L\(^{-1}\)) + NaCl (0.1 m) solution (Figure 1C). As is evident from Figure 1B, in the aerated solution two well-defined waves that correspond to Equations (1) and (2)\(^{[46]}\) are observed. This supports the idea that \(\text{Zn}^{2+}\) ions are actually reduced in a locally basic medium. On the other hand, as is shown in Figure 1C, the shape of the...
CV is simpler when the experiment was performed in the same electrolyte solution (as in Figure 1A) after purging with nitrogen. In fact, when dissolved oxygen molecules had been removed from the electrolyte, the expected sigmoidal reduction wave in the cathodic scan (characterized by a half-wave potential of $-1.10 \, \text{V} \text{ versus Ag/AgCl/KCl}_{\text{sat}}$) and the stripping peak due to oxidation of metallic Zn is observed. Measurements carried out in the bulk Zn$^{2+}$-containing solution after purging with nitrogen for different times so as to vary the amount of oxygen present in the medium provided CVs of a shape that varied between those of Figure 1A and C, which move from high to low oxygen content. These preliminary experiments therefore suggested that: 1) oxygen could be monitored in a CV scan that corresponded to the first wave in Figure 1B with no interference from Zn$^{2+}$ ions, and 2) Zn$^{2+}$ ions could be monitored at more negative potentials through either the plateau current in the negative scan (if the amount of oxygen locally present is low) or from the stripping peak in the reverse potential scan for low zinc-ion concentration or in solutions that contain relatively high oxygen concentration.

**Zinc metal-corrosion processes during exposure to aqueous chloride solution:** The possibility of monitoring independently the release of zinc(II) species during the corrosion of the metal and the simultaneous oxygen depletion by the use of the mercury microelectrode as an SECM tip was next investigated through the exposure of a pure zinc sample to naturally aerated NaCl (0.1 m) solutions. The zinc sample was kept unbiased throughout the experiments. Figure 2 contrasts typical approach curves recorded either on the insulating material that surrounded the zinc surface or that performed at the sample surface by setting the tip potential at $-0.70 \, \text{V} \text{ versus Ag/AgCl/KCl}_{\text{sat}}$, where only the reduction of oxygen occurred through Equation (1). Above the insulating substrate, negative feedback is observed, which reflects the decrease in the normalized current with the decrease of the tip–substrate distance due to the partial blockage of oxygen diffusion to the microelectrode.$^{[6,43]}$ Above the zinc surface, negative feedback is also recorded. However, in the latter case, oxygen depletion starts at higher tip–substrate distances. This clearly reflects the consumption of oxygen at the zinc surface during the corrosion, and it represents the oxygen diffusion layer thus established. The generation of Zn$^{2+}$ ions was recorded by using a different procedure. The experiments consisted of recording a series of CVs at 50 mV s$^{-1}$ over the potential range from 0 to $-1.60 \, \text{V} \text{ versus Ag/AgCl/KCl}_{\text{sat}}$ by placing the mercury microelectrode tip at varying distances from the spontaneously corroding metal. It was observed that far away from the substrate the CVs closely resembled that displayed in Figure 1B for oxygen reduction alone. On the other hand, when moving the tip towards the substrate, the CV shapes transitioned from that shown in Figure 1A to that displayed in Figure 1C at relatively small tip–substrate distances. Whenever possible, plateau currents were then determined from each voltammogram, and the values were plotted as a function of the tip–sample distance as is shown in Figure 3A. It is observed that the values of the limiting current greatly increase as the microelectrode approaches the metal surface, this effect being noticeable for tip–sample distances smaller than 400 µm, as should be expected for a corroding metal that acts as the source of the zinc ions. On the other hand, when the tip is located far away from the zinc sample (that is, for tip–sample distances greater than 500 µm under the

![Figure 2](image-url)  
**Figure 2.** Approach curves recorded with the Hg microelectrode immersed in NaCl (0.1m) aerated solution above the insulating surface (c) or above the zinc sample (c). Tip potential: $-0.70 \, \text{V} \text{ versus Ag/AgCl/KCl}_{\text{sat}}$; scan rate: 10 µm s$^{-1}$. (---) Theoretical approach curve calculated for negative feedback condition at a sphere-cap microelectrode with $H=1$ and $RG=5$.

![Figure 3](image-url)  
**Figure 3.** A) Diffusion-limiting current at the hemispherical mercury microelectrode as a function of the tip–sample distance. The values were obtained from the linear voltammetric curves measured by placing the microelectrode at various distances from the sample. B) Calibration plot for Zn$^{2+}$ ions measured with the Hg microelectrode in NaCl (0.1 m) solution containing different amounts of Zn(NO$_3$)$_2$. C) Concentration profile of the dissolving Zn$^{2+}$ species expressed as a function of the distance between the mercury microelectrode and the zinc sample.
employed experimental conditions), the limiting currents determined from the voltammograms never became zero. A value of about \((20 \pm 2)\) nA was always found regardless of the distance of the tip from the corroding sample. This non-zero current arose from the reduction of the dissolved oxygen in the electrolyte, which thus constitutes a background current that adds to the Faradaic signal detected at the tip during the CV measurements for \(\text{Zn}^{2+}\) reduction. This signal must be subtracted from the total current if the actual contribution of metal ions to the current measured at the tip is to be determined. As an approximate method, the limiting current measured at the SECM probe in the CVs was related to the concentration of \(\text{Zn}^{2+}\) by using an external calibration plot performed in a deoxygenated NaCl (0.1 M) solution. As is shown in Figure 3B, the plateau current was found to depend linearly on the concentration of \(\text{Zn}^{2+}\) over the range \(0.05-0.8 \text{ mm}\), which was wide enough to establish the amount of \(\text{Zn}^{2+}\) generated during the corrosion process. Thus, after the background current in the current values of Figure 3A was subtracted, a relationship between the concentrations of dissolved \(\text{Zn}^{2+}\) ions as a function of the tip-sample distance could be estimated as shown in Figure 3C.

It must be remarked that the approach curves recorded either for oxygen or zinc ions (with the above procedures) depended on the actual position of the tip above the substrate as well as on the time the substrate had been left immersed in the aerated solution, as the corrosion process starts as soon as the sample comes into contact with the aerated solution. The latter circumstances explain the reasons why in the above experiments the distances at which oxygen depletion started to occur or zinc ions could be detected were different.

**SECM mapping of zinc metal-corrosion processes:** The corrosion of zinc metal during immersion in an aqueous solution that contained chloride anions led to the release of \(\text{Zn}^{2+}\) ions as a result of the anodic process, whereas the dissolved oxygen is reduced in the cathodic process (see Scheme 1). The metal ions or molecular oxygen can be detected by using the mercury microelectrode tip as shown in the previous section. In this way, SECM scans performed across the sample can visualize the distribution of anodic and cathodic sites distributed on the metal exposed to the corrosive environment. The operating tip-sample distance for SECM operation was established after recording approach curves of the microelectrode tip towards the insulating epoxy sleeve that surrounded the metal specimen. The potential of the tip was set at \(-0.70 \text{ V versus Ag/AgCl/KCl}_{\text{sat}}\) to use oxygen electroreduction as redox mediator,\(^{[54]}\) and a negative feedback effect resulted as the microelectrode approached the sample. After the tip was retracted to a height of 50 \(\mu\)m, which was considered a suitable distance to avoid tip damage, either SECM line scans or two-dimensional scans were registered above the zinc specimen. From the cyclic voltammograms displayed in Figure 1, a suitable potential for the reduction of zinc ions to \(\text{Zn(Hg)}\) was established. We adopted a tip potential value of \(-1.20 \text{ V versus Ag/AgCl/KCl}_{\text{sat}}\). At this potential, in the absence of \(\text{Zn}^{2+}\) ion species the reduction of oxygen that corresponded to the first wave could be monitored as well. Figure 4 shows the steady-state currents monitored at the microelectrode during a line scan taken through the center of the zinc specimen (the metal is located between 250 and 1250 \(\mu\)m). It is evident that when the microelectrode reaches the X value of 250 \(\mu\)m (that is, the border of the metal surface), the current measured at the tip starts to increase over the background current values. A rather symmetric current peak is defined as the tip is displaced further over the zinc specimen; then the tip Faradaic current falls below even the background currents to describe another current peak that extends over longer distances than the previous ones. The first current peak, which presents the greatest values of the cathodic current, is conceivably due to the electroreduction of \(\text{Zn}^{2+}\) ions released by the corroding metal at the anodic sites. That is, the SECM tip was actually monitoring the flow of \(\text{Zn}^{2+}\) species from the dissolving surface of zinc towards the bulk solution. Supplementary evidence for this hypothesis is gathered from inspection of the cyclic voltammogram shown in Figure 5, which was recorded after placing the microelectrode tip above the place on the surface of the metal, at
which point a current peak was observed during the line scan shown in Figure 4, while keeping it at the same height. The characteristic wave during the negative scan and the anodic peak after scan reversal can be observed, as expected for the Zn$^{II}$/Zn$^{0}$ reduction/oxidation at the Hg microelectrode. As for the second peak observed in the line scan recorded in Figure 4, the following considerations can be made. If zinc were homogeneously corroding, the tip would have recorded bigger cathodic currents than the background values as long as the tip passed above the metal surface. Instead there is a region over the zinc sample at which a depletion of cathodic current is observed. This result indicates that two zones with different electrochemical behaviors were found while the tip was rastering the surface of the metal. The development of areas on the zinc sample for which the microelectrode tip polarized at $-1.20\, \text{V versus Ag/AgCl/KCl}_{\text{sat}}$ recorded smaller cathodic values than the background current is related to the cathodic half-reaction in the corrosion process. Indeed, two different redox reactions can simultaneously occur at the tip at this potential, namely: 1) the reduction of the Zn$^{II}$ to Zn, and 2) the reduction of the oxygen (see the cyclic voltammogram of oxygen using the Hg electrode given in Figure 1B). Therefore, the observed decrease in current during the line scan could arise from local areas at the metal surface in which oxygen was consumed during the cathodic reaction. The tip would thus detect lower amounts of dissolved oxygen in the solution in the proximity of the cathodic sites. Additional support for this interpretation is given by Figure 6. It depicts the line scan recorded when the potential at the tip, set at $-0.7\, \text{V versus Ag/AgCl/KCl}_{\text{sat}}$, was passing above the same line of the sample covered in Figure 4. In this case, only the area of depleted currents below the background was observed. This agrees well with the expectation that the only redox process that could occur at the microelectrode at this potential is the reduction of oxygen. It is also interesting to notice that the depletion of the current in Figure 6 occurred precisely above the same region of the zinc sample in which depleted currents were recorded at the microelectrode biased at $-1.20\, \text{V versus Ag/AgCl/KCl}_{\text{sat}}$ previously shown in Figure 4. The extent and location of the different active areas on the zinc sample during its exposure to the test solution could be imaged by acquiring a two-dimensional scan of the metal surface with the tip polarized at $-1.20\, \text{V versus Ag/AgCl/KCl}$. The resulting 3D image is shown in Figure 7. A narrow peak that exhibits rather high negative currents is clearly displayed, and this is due to the electroreduction of the dissolving Zn$^{II}$ ions from the sample. Next, a rather extended area with depleted currents is found in the proximity of the anodic peak, an indirect observation of the cathodic reaction contribution to the overall corrosion reaction. In this way, mercury microelectrodes polarized at $-1.20\, \text{V versus Ag/AgCl/KCl}_{\text{sat}}$ allow for the detection of both anodic and cathodic sites from the observation of larger and smaller reduction currents at the tip than the background values measured over the insulator. This procedure was employed to monitor the temporal evolution of the electrochemical activity on the zinc substrate by recording a sequence of SECM images as shown in Figure 8. It is observed that anodic activity changes location and intensity over time due to the progressive blockage of the initial anode by corrosion products. This situation eventually leads to the formation of a new anode at a different location on the metal surface to support the oxidation of the metal. Anodic activity always occurs in a highly localized manner on the metal surface, that is, the area of the anodes is small. Conversely, the cathodic reaction extends over most of the surface of the exposed specimen.

**Conclusion**

The use of hemispherical mercury microelectrodes as the scanning probe in SECM can be used to detect the Zn(II) ions released in the corrosion of zinc specimens immersed in
Detection of Metal Dissolution

**Experimental Section**

**Solutions and samples:** All chemicals employed were of analytical reagent grade and used as received. NaCl, KCl, and ruthenium(III) hexaammonium trichloro complex were purchased from Aldrich; Hg(NO₃)₂ and KNO₃ were purchased from Fluka. Triton X-100 detergent was purchased from Sigma-Aldrich. All aqueous solutions were prepared with Milli-Q water. The solutions were naturally aerated, and experiments were performed on 99.95% pure zinc supplied as sheets of thickness 1 mm by Goodfellow Materials Ltd (Cambridge, UK). The experiments were performed on 99.95% pure zinc supplied as sheets of thickness 1 mm by Goodfellow Materials Ltd (Cambridge, UK).

**Electrodes and instrumentation:** The platinum microdisks, which served as the substrate for mercury deposition, were prepared by sealing wires 25 μm in diameter into glass capillaries. The electrode tips were then lathe-ground with silicon carbide paper down to 1200 grit, washed thoroughly with Millipore deionized water, dried with acetone, and finally polished with SiC papers of different sizes. They were characterized by cyclic voltammetry at low scan rates in deaerated solution for hindered diffusion to a microsphere cap [42] characterized by parameters $H=1$ and $RG=5$. A home-built SECML apparatus (previously described in ref. [42]) was employed. Cyclic voltammetry (CV) and chronoamperometry were performed with a PAR 283 potentiosstat/galvanostat controlled with a personal computer and the M270 PAR software.

**Conclusions:** The results presented here demonstrate that nanoamperometry is a powerful tool for the investigation of localized corrosion processes. The ability to detect and quantify the corrosion currents at the microelectrode tip allows for a better understanding of the corrosion mechanisms and can be used to optimize corrosion inhibition strategies.
All measurements were carried out in a classical three-electrode cell arrangement located in a Faraday cage.

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**References**


**Scanning Electrochemical Microscopy**


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