



Resolution of the apparent experimental discrepancies observed between SVET and SECM for the characterization of galvanic corrosion reactions

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ABSTRACT

A new approach for studying the local distribution of anodic and cathodic sites in a corroding system using the scanning vibrating electrode technique (SVET) and scanning electrochemical microscopy (SECM) is presented. When zinc is coupled to iron, dissolution of the active metal occurs in a localized manner (e.g., pitting corrosion), allowing for cathodic sites to be developed on zinc. Local alkalization and oxygen consumption related to cathodic activity are detected above portions of the zinc surface using SECM. Anionic fluxes related to the generation of OH⁻ ions could be measured on the zinc surface outside the corroding pit by rastering the SVET probe closer to the substrate.

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1. Introduction

Application of scanning microelectrochemical techniques in Corrosion Science has contributed to a major advancement in the understanding of corrosion reactions because earlier stages of these processes have become available. Despite the differences in operating principles employed, their outcomes are usually complementary helping to gain new insights with spatial and electrochemical resolution [1,2]. Among them, the Scanning Vibrating Electrode Technique (SVET) is widely employed in corrosion laboratories [1], whereas scanning electrochemical microscopy (SECM) is gaining interest because of its chemical selectivity [2].

SVET has been applied to the zinc–iron galvanic pair to investigate the effect of ambient parameters on the galvanic process [3], to screen the efficiency of corrosion inhibitors [4], and to characterize delamination effects from cut edges [5] or defects on coated galvanized steels [6]. Additionally, most of the SECM-based operation modes that are available for the characterization of corrosion processes have been validated using this model system, namely determination of concentration distributions from amperometric generation-collection operation [7], monitoring of oxygen with the redox competition mode [8], quantitative metal dissolution determination using tip modification and stripping voltammetry [9], and local pH and ion-selective detection under potentiometric operation [10,11]. Though good agreement

between the information provided by SVET and the new operation modes in SECM used to be the rule, some discrepancies have been discovered recently. They originate from the localized nature of the dissolution process occurring on zinc, and the new evidences of an extension of the cathodic activity to this metal.

In this work we report evidences of local cathodic activity on the more active metal within the zinc–iron galvanic couple detected using the new operation modes of SECM. The same features were monitored by SVET when operation conditions ensured greater spatial resolution.

2. Experimental

99.5% purity iron and 99.95% purity zinc cut into square specimens of 1 × 1 mm² dimensions were mounted into an epoxy resin sleeve (dia. 4 cm). The separation between the metals was ca. 1 mm, and electric connection was made at the rear of the mount. The front side of the mounts was ground with silicon carbide paper down to 4000 grit and subsequently polished with 0.3 μm alumina. The resulting surface was rinsed with Millipore deionized water and allowed to dry in air. The front side of the mount was placed upwards and surrounded laterally by Sellotape, thus creating a small container for the electrolyte solution (electrolyte volume: 3.5 mL). The sample itself was immersed under 5 mm of solution thereby ensuring no enhanced oxygen supply due to thin film overlayers [12]. The solubility of oxygen in these conditions is approximately 2.4 · 10⁻⁴ M [13,14]. The electrochemical cells for SVET and SECM were completed with the inclusion of their corresponding microelectrodes. Testing was

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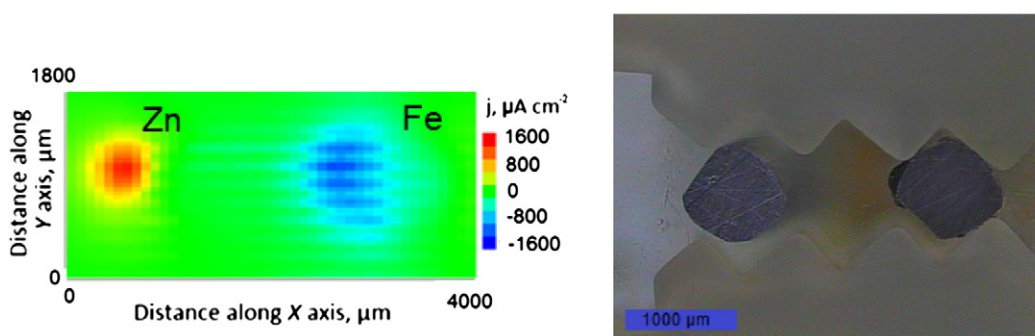


Fig. 1. Ionic current map (left) and video image (right) of a zinc–iron galvanic pair immersed in 0.01 M NaCl. Tip–substrate distance: 150 μm . Scan rate: 350 $\mu\text{m/s}$.

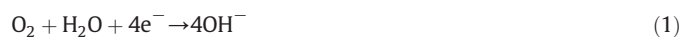
carried out in aqueous 0.01 M NaCl solution made from analytical grade reagent and Millipore deionized water. The solution was naturally aerated and experiments were conducted at ambient temperature.

The SVET instrument used in this work was manufactured by Applicable Electronics (New Haven, CT, USA). The vibrating probe was prepared from a Pt/Ir (80%/20%) wire insulated with paralene C® and arced at the tip to expose the metal. The microelectrode was platinized in order to produce a spherical platinum black deposit of 20 μm diameter. The measurements were made with the electrode tip vibrating at 75 Hz in a plane perpendicular to the sample with 20 μm amplitude. The scans were carried out over the bimetallic system at a height of 80 and 150 μm . For each point along the scan, the current was averaged during 0.5 s.

A home-built SECM system was employed [15]. For the potentiometric operation, a $10^{12} \Omega$ input impedance operational amplifier was introduced in the measuring circuit [11]. An antimony tip [10] was employed both as amperometric tip and pH sensor, having a 25 μm diameter active disk surface and an RG value of about 5. ($\text{RG} = \text{Rg}/a$, where a is the radius of the Pt disk, and Rg is the radius of the insulating glass surrounding the metal in the tip). It exhibits a linear relationship between the potential and the solution pH in the $3 < \text{pH} \leq 11.5$ range, with slope 46.1 mV/pH unit. The SECM cell was completed with an Ag/AgCl/KCl 3 M reference electrode, and a Pt wire as counter electrode for the amperometric measurements. The scans were carried out over the bimetallic system at a height of 25 μm at scan rates of 10–15 $\mu\text{m/s}$.

3. Results and discussion

Fig. 1 shows the ionic current flows over a zinc/iron couple measured by SVET, closely matching previous reports [3]. 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. The ionic flows related to cathodic activity emerge from a large cathode that covers the complete surface of iron. They correspond to an upward flow of OH^- anions produced in the reduction of dissolved oxygen:



Accordingly, the amount of O_2 in solution should be lower near this cathodic region, simultaneously to local alkalization of the electrolyte. Next, a small anode was observed on the zinc wire related to the development of one corrosion pit. Anodic currents were detected only above the pit corresponding to the flow of cations produced during the oxidation of zinc:



pH changes also occur due to the hydrolysis of the metal ions:



leading to weak acidification in the solution around the anodic sites [16].

The consumption of dissolved oxygen related to cathodic activity can be imaged in situ using the amperometric mode of the SECM, provided that a sufficiently negative potential is applied to the antimony microelectrode (namely $-0.65 \text{ V vs. Ag/AgCl/3 M KCl}$) [10]. Fig. 2 displays a series of scan lines measured with the tip traveling above the center of the two metals for different times. The first line recorded after 28 min depicts a region of depleted oxygen concentration extending over the dimensions of the iron sample, and the concentration steadily tends to the values in the bulk electrolyte when the tip is placed over the resin sleeve at both sides of the iron strip independently of the location of the zinc anode. That is, the lowest concentrations of oxygen are found over the iron strip, indicating that oxygen is consumed in the cathodic half reaction and diffusion from the bulk electrolyte is not sufficient to renew the oxygen content above this metal. Therefore, smaller amounts of oxygen are available for electroreduction at the microelectrode tip when it scans above the cathodic sites. Further excursion of the antimony tip above the zinc strip reveals another region of depleted oxygen concentration in the solution. With the elapse of time, the tip currents were even smaller, indicating that oxygen was consumed on both metals and it became

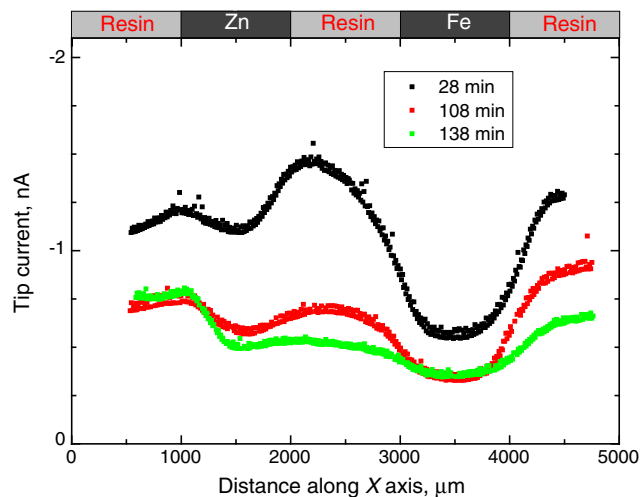


Fig. 2. Distribution of oxygen concentration above the zinc–iron galvanic couple in 0.01 M NaCl measured by amperometric SECM using an antimony tip. $E_{\text{tip}} = -0.65 \text{ V vs. Ag/AgCl/3 M KCl}$; tip–substrate distance: 25 μm . Scan rate: 10 $\mu\text{m/s}$.

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