The effect of electric field on potentiometric Scanning Electrochemical Microscopic imaging

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ARTICLE INFO

ABSTRACT

Potentiometric Scanning Electrochemical Microscopy (SECM) is a powerful tool in corrosion science. It allows the selective imaging of a particular ionic species released at the anodic sites in a corrosion micro-cell, by using ion-selective microelectrodes (ISMEs) as scanning probes. Galvanic corrosion is a particularly often studied process. The measured potential of the ISME is thought to depend only on the activity of the primary ion. However, an electric field is also formed as a result of the potential difference between the surfaces of the galvanic pair, which has a direct influence on the potential of the sensing microelectrode; the measured potential is the sum of these two contributions. The potential difference caused by the electric field can be substantially large, exceeding that of the potential difference associated with the activity of the primary ion. In this paper, we present experimental evidence of this feature, and investigate the extent to which it influences the final chemically-resolved image.

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1. Introduction

In the past decade, potentiometric SECM has become increasingly popular among corrosion scientists [1–6]. The most extended application is the visualization of galvanic corrosion processes [7–10]. Galvanic corrosion occurs when two dissimilar metals are both connected electrically and immersed in the same electrolyte. The electric coupling originates preferential and accelerated dissolution of the less noble metal acting as the anode of the corrosion cell, while the corrosion rate of the cathode is reduced. The spatial separation of the anodic and the cathodic sites makes the complex corrosion processes readily interpretable, and due to the increased corrosion rates, conveniently shorter exposure times may be sufficient to obtain spatially-resolved images of the concentration distributions developed in the solution adjacent to the corroding sample.

Despite these beneficial circumstances, quantitative evaluation of galvanic corrosion using potentiometric SECM often fails due to — up to now — unrevealed reasons. Izquierdo et al. reported discrepant results comparing Z-approach curves towards the cathode of a Mg-Fe galvanic couple obtained by either amperometric O_2

detection or potentiometric pH measurement [11]. Local alkalinization could be detected even at 2 mm tip-substrate distance, whereas oxygen concentration already reached the bulk level at only ca. 900 μm height. This discrepancy was attributed to an (unknown) contribution of the electric field to the potentiometric signal. In other works, the concentration of Mg^{2+} that was detected using a Mg ISME above the Mg alloy disc, while galvanically coupled to iron, highly exceeded the upper limit of detection of the probe [12–14]. On the other hand, pMg values fell below the lower limit of detection of Mg ISMEs scanning above cathodically polarized magnesium strips [15].

These observations can be explained in terms of a contribution of the electric field to the measured potential. As it is well-known, the corrosion current is carried by electrons within the metallic phase, and it experiences negligible ohmic potential differences, because of the high conductivity of the material. Conversely, the ionic current flowing in the aqueous phase is associated with potential differences [16]. That is, the potential difference between the anode and the cathode surfaces causes an electric field to be formed. This phenomenon is exploited in the Scanning Reference Electrode Technique (SRET), which allows to determine corrosion currents by actually measuring the potential variation in the solution with a scanning passive reference probe [17–20]. The localized electric field SRET method has been progressively replaced by the more sensitive Scanning Vibrating Electrode Technique (SVET) in which a single vibrating probe is sensitive enough to detect smaller potential

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gradients that have arisen from ionic currents flowing in the solution [21]. In the potentiometric SECM experiments cited above conducted on galvanic couples, the ISMEs must be subjected to the same effects. Then, as suspected by the above-mentioned researchers, the local electric field may produce an undesired contribution to the potentiometric signal. The potential difference between the points where the electrodes are located is added to the potential difference associated with the primary ion activity at the tip of the measuring electrode (see Fig. 1):

$$\Delta E = E_M - E_R + (\phi_M - \phi_R) \tag{1}$$

where ΔE is the measured potential difference, E_R is the potential of the reference electrode, and ϕ_M and ϕ_R are the local potentials in the electric field at the measuring and reference electrodes, respectively. E_M is the potential of the measuring ion-selective electrode for instance Mg^{2+}:

$$E_M = S \times \lg[Mg^{2+}] + E_M^o \tag{2}$$

where S is the slope of the calibration curve of the potentiometric cell with respect to the primary ion, and E_M^o is the standard potential. Since one could expect that the potential measured by the ISME is solely determined by the activity of the primary ions, and the aim of the experiments is to obtain quantitative and reliable concentration distributions of the species of interest, the additional contributions to the analytical signal have to be revealed.

In this contribution, the effect of the electric field on the measured potential difference at an ion-selective microelectrode probe has been investigated. The galvanic corrosion between an AZ63 Mg-Al alloy and iron was used as model system.

2. Materials and methods

The preparation of solid contact Mg^{2+} selective microelectrodes was described in detail before [14]. In brief, micropipettes were pulled from borosilicate capillaries (outer diameter $\oslash = 1.5$ mm,
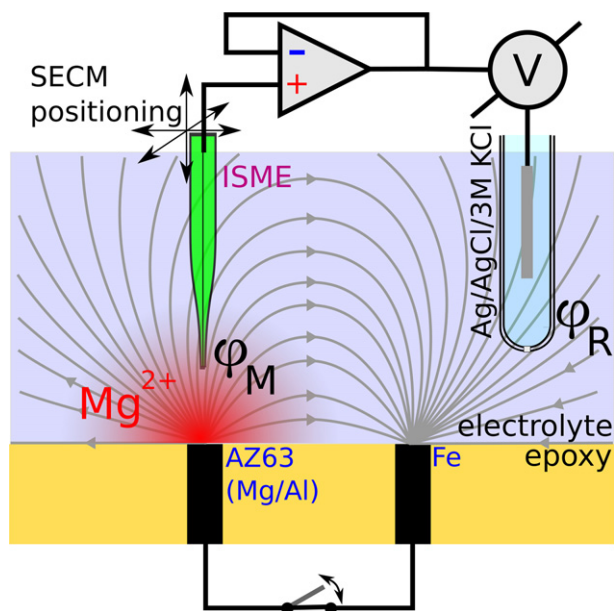

Fig. 1. An electric field is formed between the surfaces of the dissimilar metals constituting the galvanic couple. The potential difference between the measuring (ϕ_M) and reference (ϕ_R) electrodes is added to the Nernstian potential associated with the activity of the particular ion.

inner dia. $\oslash = 1.0$ mm, obtained from Hilgenberg GmbH, Malsfeld, Germany) with a Sutter Instruments P-30 type vertical capillary puller (Novato, CA, USA). The capillaries were silanized by 1 h exposition to the saturated vapor of dichloro-dimethyl-silane at 120 °C. A poly-ethylen-dioxy-thiophene (PEDOT) coated carbon fiber of 33 μm diameter (Specialty Materials, Lowell, MA, USA) served as the solid contact of the ISME. The PEDOT was electrochemically polymerized onto the carbon fiber and subsequently doped in KCl solution. The membrane components were purchased from Fluka (Buchs, Switzerland). The Mg-ISMEs were calibrated by measuring their potential against an Ag/AgCl/KCl (3 M) reference electrode in $MgCl_2$ solutions with tenfold increased concentrations between 10^{-7} and 10^{-1} M. The activities were calculated using the Debye-Hückel approach. A Nernstian relationship was observed between 10^{-1} and 10^{-5} M; the equation of the linear portion of the calibration curve is E = 29.5 mV/lg[Mg^{2+}] + 98.3 mV ($R^2 = 0.9997$). The lower limit of detection was pMg = 5.3. Detailed characterization of the ISME regarding the resistance, response time, selectivity coefficients, etc. can be found in [14,22].

The (Mg/Al)/Fe galvanic couple specimen was prepared using the AZ63 Mg/Al alloy and high purity Fe wires of 0.76 mm diameter. The wires were mounted in an epoxy resin sleeve (Struers, Ballerup, Denmark), exposing only the disk shaped surfaces at one side of the mould, and protruding at the rear side allowing to establish electric contact. Frontal surface of the mould was first ground with SiC paper up to 4000 grit, then polished with 1.0 and 0.3 μm alumina powders.

SECM experiments were carried out using a homemade instrument operated with custom software. The potential values of the Mg ISMEs were measured with respect to an Ag/AgCl (3 M KCl) reference electrode. All the measurements were performed using a high input impedance eDAQ pH ISE isoPod USB (eDAQ Pty Ltd, Australia). The testing electrolyte was 0.001 M NaCl solution throughout this work. The tip-sample distance was determined using the method described in [14]. The Z approaching curves were recorded with 10 μm step size and 33 μm/s effective scanning rate. The 2D scans were carried out with 100 μm step size in both X and Y axes, and 100 μm/s scanning rate following the widely applied meander algorithm.

3. Results and discussion

A series of consecutive Z-approach curves were recorded above the corroding AZ63 sample (as shown in Fig. 2A). The first 6 measurements were taken while the AZ63 sample was not electrically connected to the iron sample (red lines, *a-b*). As expected, Mg^{2+} activity slowly increased with time as a result of spontaneous corrosion. The overall change was about 10 mV in 5 min. Next, the two metals were connected at the rear of the mould. As a result of establishing the galvanic connection, there was an immediate rise of about 40 mV in the measured potential of the microelectrode (transition from *b* to *c*, depicted by ΔE_1 in Fig. 2A). Since the galvanic coupling was established while the scanning tip was located 1000 μm from the AZ63 sample, the reported change cannot possibly be attributed solely to an abrupt increase in Mg^{2+} activity. Indeed, such a 40 mV change would correspond to an increase of ca. 1.5 orders of magnitude in Mg^{2+} activity occurring in less than one second. Immediately after, six additional Z-approach curves were recorded during the galvanic coupling. The resulting accelerated dissolution of Mg^{2+} can be distinguished from the blue curves (*c-d*) in Fig. 2A. Intense gas evolution could be observed on the surface of the AZ63 sample, which explains the noticeably more noisy curves recorded in this case. During this period of galvanic coupling, the potential sensed at the ISME, when situated at h = 1000 μm, increased in app. 40 mV. This rise (ΔE_2) can be totally attributed to the increase in activity of the dissolving metal, i.e.: $\Delta E = 29.5$ mV $\times \Delta$lg[Mg^{2+}].