

The effect of electric field on potentiometric Scanning Electrochemical Microscopic imaging

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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 microcell, by using ion-selective microelectrodes (ISMEs) as scanning probes. An often studied process is galvanic corrosion, which involves two dissimilar metals in electrical contact, that are immersed in the same electrolyte phase. 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.

Keywords: scanning electrochemical microscopy, potentiometry, ionselective microelectrode, galvanic corrosion, electric field

1. Introduction

In the past decade, potentiometric SECM – sometimes referred to Scanning Ion Selective Electrode Technique (SIET) by the experts of this field – has become increasingly popular among corrosion scientists [1, 2, 3, 4, 5, 6]. The most extended application is the visualization of galvanic corrosion processes [7, 8, 9, 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 O₂ detection or potentiometric pH measurement [11]. Local alkalization 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 another works, the concentration of Mg²⁺ that was detected using a Mg ISME

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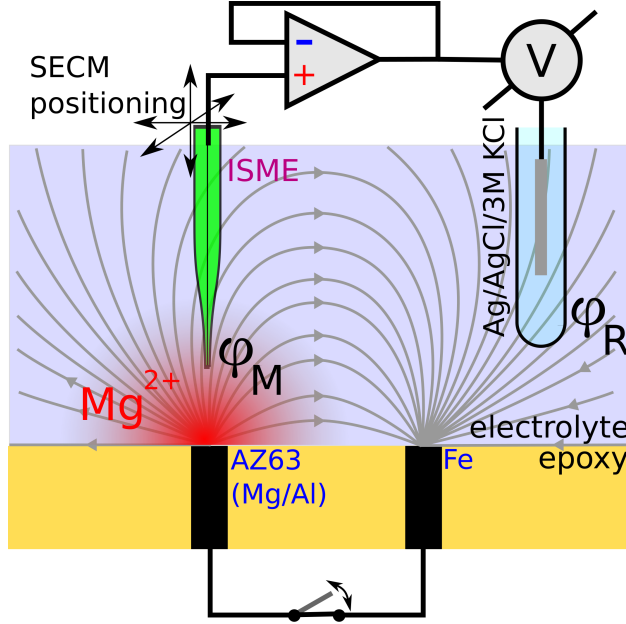


Figure 1: An electric field is formed between the surfaces of the dissimilar metals constituting the galvanic couple. The potential difference between the measuring (ϕ_M) and reference (ϕ_R) electrodes is added to the Nernstian potential associated with the activity of the particular ion.

above the Mg alloy disc, while galvanically coupled to iron, highly exceeded the upper limit of detection of the probe [12, 13, 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, 18, 19, 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 gradients 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):

$$\Delta E = E_M - E_R + (\phi_M - \phi_R) \quad (1)$$

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+} :

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

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. Material 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 $\varnothing = 1.5$ mm, inner dia. $\varnothing = 1.0$ mm, obtained from Hilgenberg GmbH, Malsfeld, Germany) with a Sutter Instruments P-30 type vertical capillary puller (Novato, CA, USA). The micropipette were soaked in 1:1 $H_2SO_4:H_2O_2$ solution and washed with twice deionized water. The capillaries were next silanized by 1 hour exposition to the saturated vapour of dichloro-dimethyl-silane in closed Petri dishes at 120 °C. A poly-ethylen-dioxy-thiophene (PEDOT) coated carbon fiber of 33 μm diameter (obtained as a generous gift from Specialty Materials, Lowell, MA, USA) served as the solid contact of the ISME. The PEDOT was electrochemically polymerized onto the carbon fiber in 0.1 M EDOT-containing BMIM- PF_6 ionic liquid solution. 10 consecutive cyclic voltammetry cycles were run in the $-0.9 \leq E \leq 1.3$ V potential range. The subsequent doping step was performed in 0.1 M KCl aqueous solution by applying 15 consecutive potential cycles in the $-0.9 \leq E \leq 0.8$ V range. The membrane components were purchased from Fluka (Buchs, Switzerland). The cocktail contains N,N'-Octamethylene-bis(N'-heptyl-N'-methyl-methylmalonamide inophore, 2-nitrophenyl-octyl ether emollient, PVC, potassium-[tetrakis-4-chlorophenyl]-borate and tetrahydrofuran. Eventually, the micropipette was front-filled with the cocktail, and the PEDOT-coated carbon fiber was inserted in the lumen of the capillary. The Mg-ISMEs were calibrated by measuring their potential against an Ag/AgCl/KCl (3M) 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 $E = 29.5 \text{ mV/decade} + 98.3 \text{ mV}$ ($R^2 = 0.9997$). The lower limit of detection was $pMg = 5.3$.

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 respect to an Ag/AgCl (3M KCl) reference electrode. All the measurements were performed using a high input impedance eDAQ pH ISE isoPod USB (eDAQ Pty Ltd, Australia).

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). As expected, Mg^{2+} activity slowly increased with time as a result of spontaneous corrosion. The overall change was about 10 mV in 5 minutes. Next, the two metals were connected at the rear of the mould. As result of establishing the galvanic connection, there was an immediate rise of about 40 mV in the measured potential of the microelectrode (that is depicted by the transition from the red to the blue curves 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

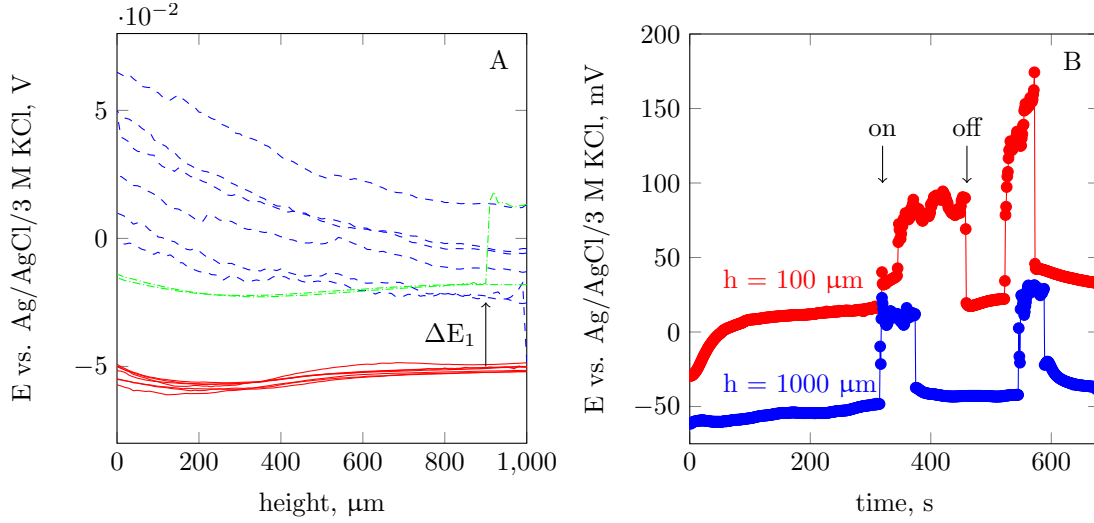


Figure 2: (A) Consecutive vertical approach curves above the center of the AZ63 target with a Mg^{2+} ISME. Step size was 10 μm . 500 ms settling time was allowed for the potentiometric cell at each points before measurements. Lines in chronological order: solid red = homogeneous corrosion, dashed blue = galvanic corrosion, dashdotted green = homogeneous corrosion. (B) Stationary recordings; red = 100 μm , blue = 1000 μm above the center of the AZ63 target. On/off notes when galvanic coupling was established or severed. Temporal resolution was 1 Hz.

Z-approach curves were recorded during the galvanic coupling. The resulting accelerated dissolution of Mg^{2+} can be distinguished from the blue curves 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 $h = 1000 \mu\text{m}$, increased in app. 40 mV. This rise can be totally attributed to the increase in activity of the dissolving metal, i.e.: $\Delta E = 29.5 \text{ mV} \times \Delta \lg[\text{Mg}^{2+}]$. Finally, when the galvanic connection was stopped, 2 additional Z-approach curves were measured (green curves in fig. 2A). A sudden jump in potential (transition from blue to green curves) can be observed, with the same magnitude as before, but opposite direction, as a result of the electric field vanishing. The shape of the curves are very similar to the first few approaching curves, only they are shifted by about 40 mV to the positive direction. This is the result of the accelerated corrosion during the second phase; Mg^{2+} activity changed by about the same factor throughout the length of the scanline. The shape of the curves recorded during the galvanic coupling are noticeably different that those recorded during the homogeneous corrosion. This is because the contribution of the electric field, just like the contribution from Mg^{2+} , is not uniform at different distances on the scanned line. The strength of the electric field is inversely proportional to the square of the distance. The shape of the function $1/z^2$ is recognizable in these curves.

Next, the potential was recorded at a constant height as a function of time, while the galvanic connection was manipulated between the two metals (fig. 2B). The tip was first positioned 100 μm above the center of the target (red curve in fig. 2B), and for about 300 s the homogeneous corrosion of the AZ63 sample was recorded. Then, the galvanic connection was established, and a sharp increase in potential of about 70 mV could be observed. This change would mean a two orders of magnitude increase of Mg^{2+} in a very short period of time. When the galvanic connection was severed, change with the same magnitude, but reversed direction could be observed. To rule out the possibility that this rise can be explained by the abrupt release of Mg^{2+} from the surface, the experiment was repeated while the tip was positioned 1000 μm above the target (blue curve in fig. 2B). A very similar sequence of potential changes could be observed. Even if one argues a change in Mg^{2+} activity of more than two orders of magnitude is possible 100 μm away the source in less then a second, it cannot be the case 1000 μm from it. The only plausible explanation is that sudden change is due to the electric field formed between the two metals.

Finally, in order to demonstrate the influence of the electric field on the SECM measurements 2D images

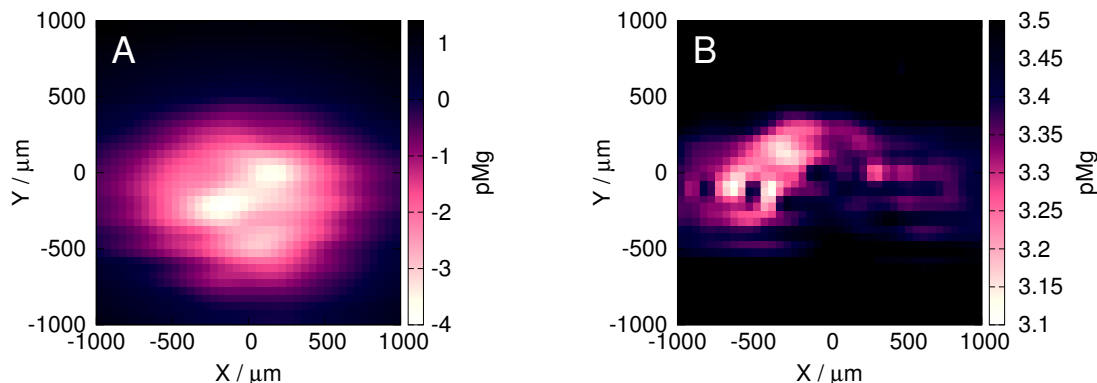


Figure 3: Caption.

were recorded at constant 100 μm tip-sample distance after 30 minutes coupling. Then the galvanic connection was severed and immediately another 2D scan was performed above the Mg disk. The two images can be seen in 3. Apparently, in case of galvanic coupling 0.1 M Mg^{2+} activity can be detected even in the bulk of the solution, whereas above the center of the disk the activity approaches the implausible 10^4 M value using the calibration curve for calculation. In fig. 3B the measured values are in the linear range of the ISME and total change is orders of magnitude less than in fig. 3A. It has to be mentioned, that during the second scan the lack of electric connection of the galvanic couple and the diffusion of the Mg^{2+} ions can introduce uncertainties in the evaluation of the image, yet does not lead to such impossible misinterpretation as fig. 3A.

4. Conclusions

Experimental evidence has been provided to confirm the suspicion experts in corrosion science has had for a while; the effect of the electric field in certain potentiometric SECM experiments – where a strong electric field is being formed – causes a significant over- or underestimation of the real primary ion activity. The reason for this is that the electric field has a direct influence on the measured potential.

Based on the results of this work, this influence should be negated by bringing the reference and measuring electrodes very close together, so the electric field „experienced” by the two is equal, therefore cancels out. Another solution might be to operate an electronic relay as a switch between the galvanic couple, and disconnect them for a very short period of time, while the measurement is performed. These two possible solutions will be subject to investigations in future work of our research group.

Acknowledgements

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