

# The effect of electric field on potentiometric Scanning Electrochemical Microscopic imaging

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## Abstract

Scanning Electrochemical Microscopy (SECM) is an invaluable tool in corrosion science. It allows the selective imaging of a particular ionic species being released at the anodic sites, using ion-selective microelectrodes (ISMEs) as scanning probes. An often studied phenomenon is galvanic corrosion, which involves two metals in electrical contact, immersed in the same electrolyte. The measured potential of the ISME is thought to depend only on the activity of 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 microelectrode; the measured potential is the sum of these two. 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, and investigate the extent to which it influences the final image.

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

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## 1. Introduction

In the past decade, potentiometric SECM – or as referred to by the experts of this field Scanning Ion Selective Electrode Technique (SIET) – has become very popular among corrosion scientists [1, 2, 3, 4, 5, 6]. The most broad spread application is the visualization of galvanic corrosion [7, 8, 9, 10]. Galvanic corrosion occurs when two dissimilar metals are connected both electrically and immersed in the same electrolyte. The electric coupling results the preferential and accelerated dissolution of the anode, while reduces corrosion rate of the cathode. The spatial separation of the anodic and the cathodic sites makes the complex corrosion processes easily interpretable and due to the increased corrosion rate conveniently short exposure times are sufficient to obtain convincing images about concentration distributions 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 vertical approaching curves towards the cathode of the Mg-Fe galvanic couple obtained by amperometric O<sub>2</sub> detection and potentiometric pH measurements [11]. Local alkalization could be detected even at 2 mm tip-substrate distance, whereas oxygen concentration reached the bulk level at ca. 900 μm height. The phenomenon was explained by the contribution of the electric field to the potentiometric signal. In another works, Mg<sup>2+</sup> above Mg alloy disc galvanically coupled to iron detected with Mg ISME highly exceeded the upper limit of detection of the probe [12, 13, 14]. On the other hand, pMg values fallen below the lower limit of detection of Mg ISMEs scanning above cathodically polarized magnesium strips [15].

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These phenomenon could be explained by a contribution of the electric field to the measured potential. As it is well-known, the corrosion current within the metallic phase carried by electrons, causes negligible ohmic potential differences, because of the high conductivity. However, the current in the aqueous phase associated with potential differences [16]. The potential difference between the surfaces of the anode and the cathode causes an electric field to be formed. This phenomenon is exploited in Scanning Reference Electrode Technique (SRET), which allows determining corrosion current by measuring the potential variation in the solution with a scanning passive reference probe [17, 18, 19, 20]. The localized electric field SRET has been slowly replaced by the more sensitive Scanning Vibrating Electrode Technique (SVET) in which a simple vibrating probe is sensitive enough to detect small potential gradients arise from ionic currents in the solution[? ]. In potentiometric SECM experiments carried out above galvanic couples the ISMEs are subjected to the same effects, therefore as suspected by the above mentioned researchers, electric field can have an unwanted contribution two 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:

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

where  $\Delta E$  is the measured potential difference,  $E_R$  is the potential of the reference electrode,  $\phi_M$  and  $\phi_R$  are the potentials in the electric field at the measuring and reference electrodes, respectively.  $E_M$  is the potential of the measuring electrode selective for e.g.  $Mg^{2+}$ :

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

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 expects that the potential measured by the ISMEs is solely determined by activity of the primary ions, and the aim of the experiments to obtain quantitatively reliably concentration distributions the additional contributions to the analytical signal have to be revealed.

The effect of the electric field on the measured potential difference has been investigated in this paper. The galvanic corrosion of the AZ63 Mg-Al alloy and iron was used as a model system.

## 2. Material and methods

The preparation of solid contact  $Mg^{2+}$  selective microelectrodes is described in details in a previous work [14]. 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 double deionized water. The capillaries were silanized by 1 hour exposition 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  $\mu m$  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 taken in  $-0.9 \leq E \leq 1.3$  V range. The 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 frontfilled 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 Ag/AgCl/KCl (3M) reference electrode in tenfold diluted  $MgCl_2$  solutions between  $10^{-7}$  and  $10^{-1}$  M concentrations. The activities were calculated using the Debye-Hückel theory. Nernstian relationship was found in between  $10^{-1}$  and  $10^{-5}$  M, the equation of the linear portion of the calibration curve is  $-29.5 \text{ mV/decade} + 98.3 \text{ mV}$  ( $R^2 = 0.9997$ ). The lower limit of detection was  $pMg = 5.3$ .

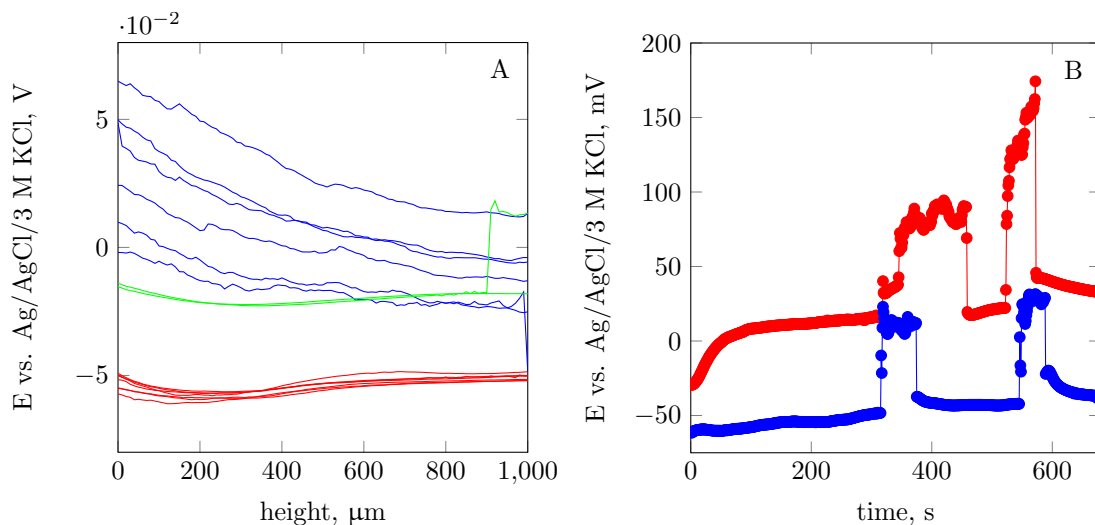


Figure 1: Caption.

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

SECM experiments were carried out using a homemade instrument operated with custom software. The sample was placed at the bottom of the electrochemical cell, while the potential values of the Mg ISMEs were measured with against a 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

First, consecutive approaching curves were recorded above the corroding AZ63 sample, while the galvanic connection with the iron sample was...

The moment the galvanic connection was established, there was an immediate rise of about 140 mV in the measured potential of the microelectrode [fig], which cannot possibly be attributed to the increase of  $Mg^{2+}$  activity that far from the source. Also, a 140 mV rise would mean an increase of about 3.5 orders of magnitude in  $Mg^{2+}$  activity in less than a second. Even if one argues it's possible 100 μm from the source, 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.

### 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.

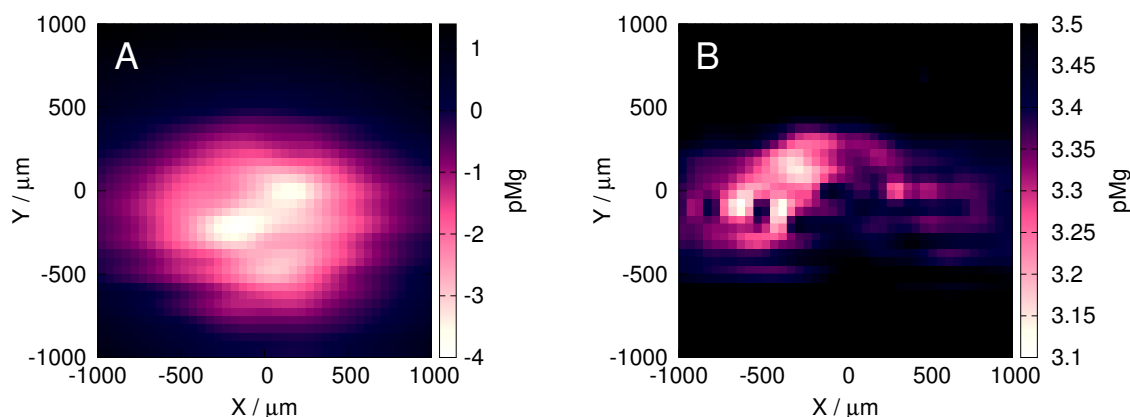


Figure 2: Caption.

## Acknowledgements

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