

The effect of electric field on potentiometric Scanning Electrochemical Microscopic images

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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. Therefore, 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, galvanic corrosion, electric field

1. Introduction

In the past decade, potentiometric SECM - or in other words used 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 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_2 detection and potentiometric pH measurements [11]. Local alkalinization 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^{2+} 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 behind lower limit of detection of Mg ISMEs scanning above cathodically polarized magnesium strips [15].

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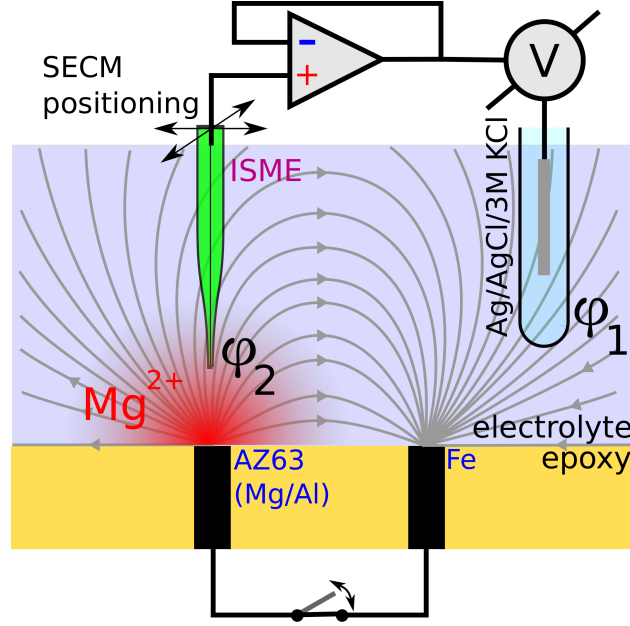


Figure 1: Caption.

2. Material and methods

The preparation of solid contact Mg^{2+} selective microelectrodes was adopted from 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 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 to 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 wre frontfilled with the coctail and the PEDOT coated carbon fiber was inserted in the lumen of the capillary.

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 then 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.

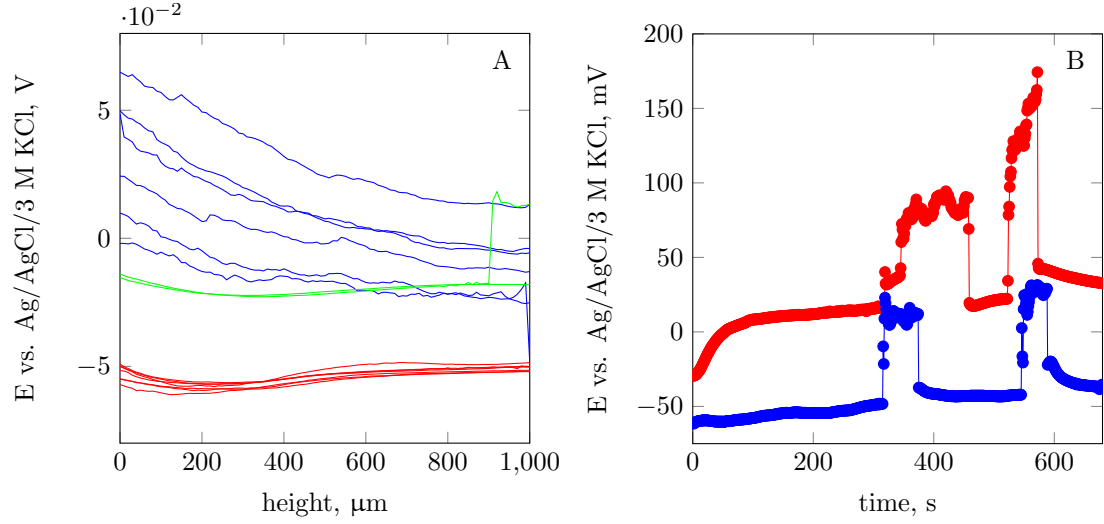


Figure 2: Transient response of the antimony microelectrode to analyte activity step. The measuring and reference electrodes were dipped into buffer solutions with $pH = 4$ before the measurements started, and $pH = 6$ at $t = 0$ s, respectively. Eq. ?? was fitted (red line) on the measurement (gray marks) from the pH step to the end of the curve when potential reaches equilibrium in the $pH = 6$ buffer.

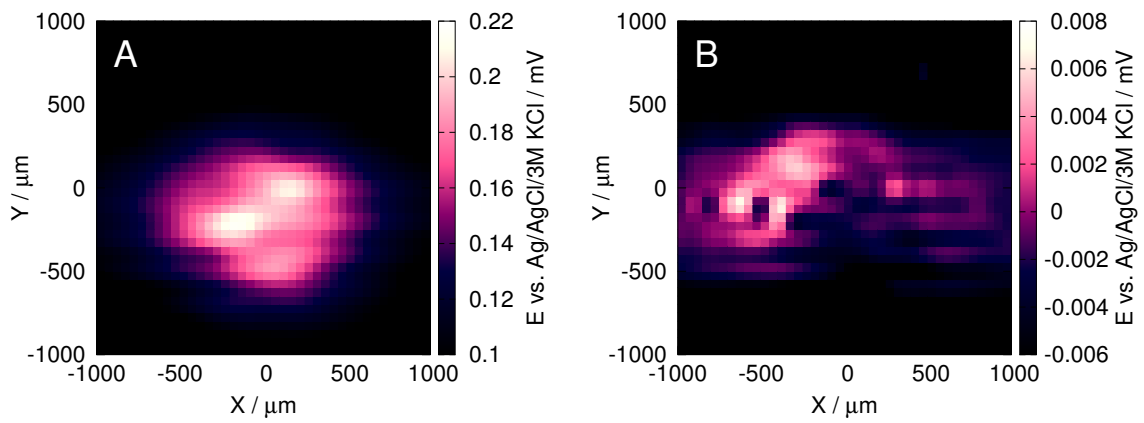


Figure 3: Caption.

4. Conclusions

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