

The effect of electric field on potentiometric Scanning Electrochemical Microscopic images

András Kiss^{1,*}, Dániel Filotás¹, Géza Nagy¹

^aDepartment of General and Physical Chemistry, Faculty of Sciences, University of Pécs, 7624 Pécs, Ifjúság útja 6, Hungary

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 ..., which has a direct influence on the potential of microelectrode. Therefore, the measured potential is the sum of these two. The potential caused by the electric field can be substantially large, exceeding that of the potential 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

Citation [1].

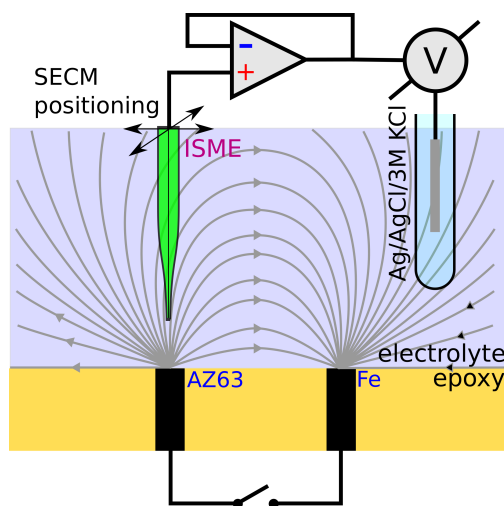


Figure 1: Caption.

*Corresponding author

Email addresses: akiss@gamma.ttk.pte.hu (András Kiss), filotasdaniel@gmail.com (Dániel Filotás), g-nagy@gamma.ttk.pte.hu (Géza Nagy)

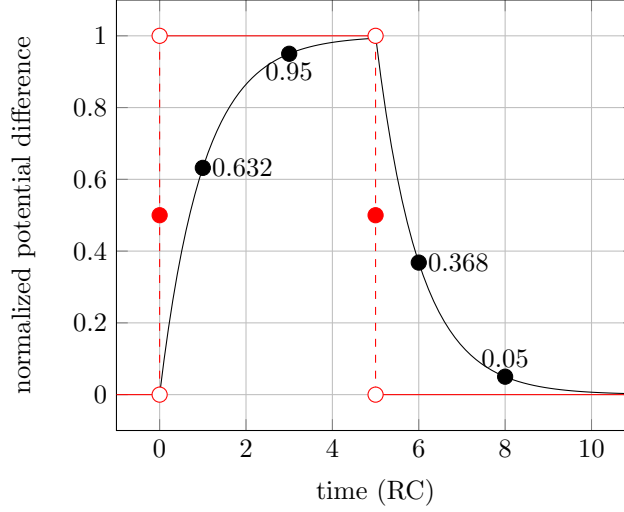


Figure 2: Charging and discharging the series RC circuit. Red: normalized input voltage (V_{in}) to the series RC circuit, two consecutive *Heaviside step functions*, the second one is inversed and shifted $5RC$ to the right. Black: normalized output voltage (V_{out}) of the series RC circuit.

Table 1: Comparison of the scanning algorithms.

Algorithm	Number of sampling points	Total scan time (s)	Mean squared error
Meander	441	440	2.75×10^{-2}
Fast comb	441	520	2.07×10^{-2}
Comb	441	881	2.75×10^{-2}
Web	110	109	9.63×10^{-3}
Arc	341	340	2.95×10^{-3}

2. Theory

Eq. 1 describes the transient cell response when the measuring electrode is brought to contact with a solution of different analyte activity.

$$E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/RC} \quad (1)$$

3. Material and methods

4. 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.

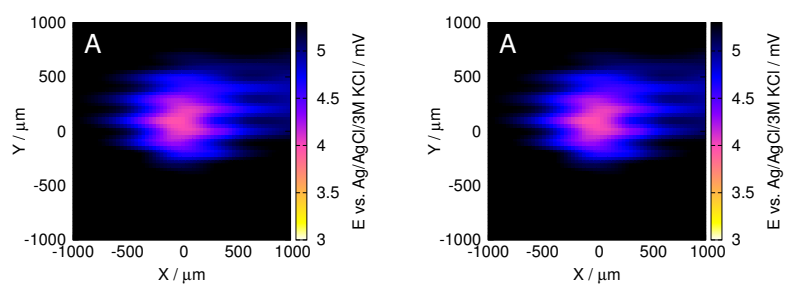


Figure 3: Caption.

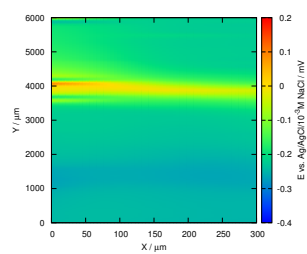


Figure 4: Caption.

5. Conclusions

Acknowledgements

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/ 2-11/1-2012-0001 'National Excellence Program' and TÁMOP-4.2.2.A-11/1/KONV-2012-0065.

References

- [1] P. J. Eaton, P. West. Atomic force microscopy. Vol. 10. Oxford: Oxford University Press, 2010.