

# 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

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## 1. Introduction

Citation [1].

## 2. Material and methods

## 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  $\mu m$  from the source, it cannot be the case 1000  $\mu m$  from it. The only plausible explanation is that sudden change is due to the electric field formed between the two metals.

## 4. Conclusions

## Acknowledgements

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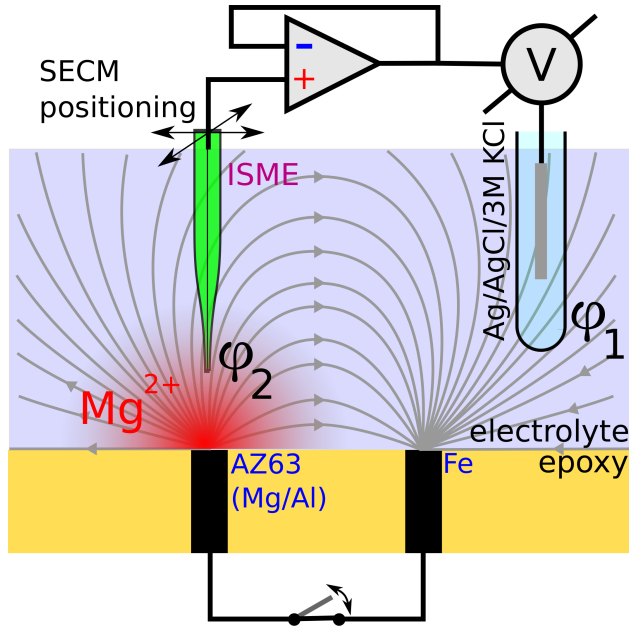


Figure 1: Caption.

Table 1: Comparison of the scanning algorithms.

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

## References

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

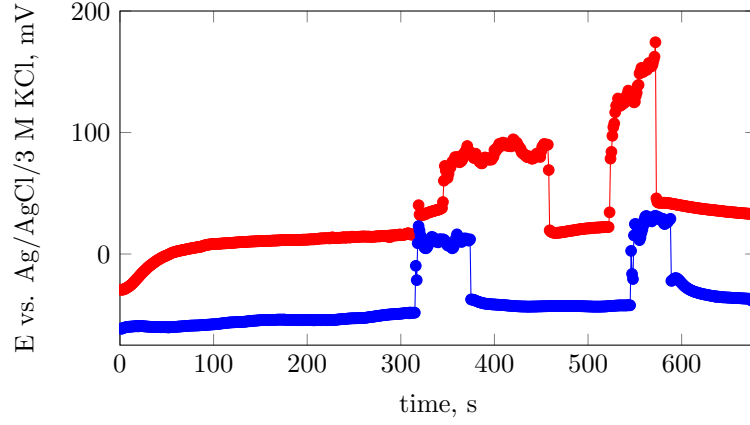


Figure 2: Transient response of the antimony microelectrode to analyte activity step. The measuring and reference electrodes were dipped into buffer solutions with  $\text{pH} = 4$  before the measurements started, and  $\text{pH} = 6$  at  $t = 0$  s, respectively. Eq. ?? was fitted (red line) on the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

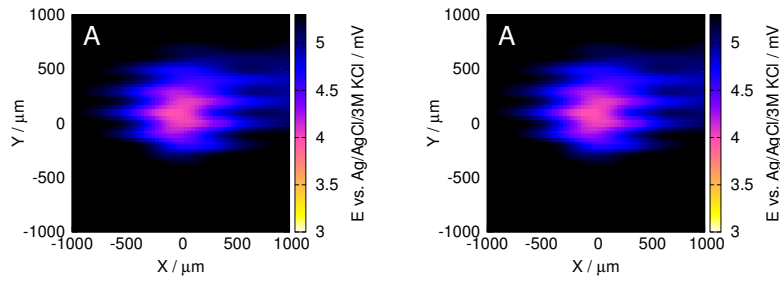


Figure 3: Caption.