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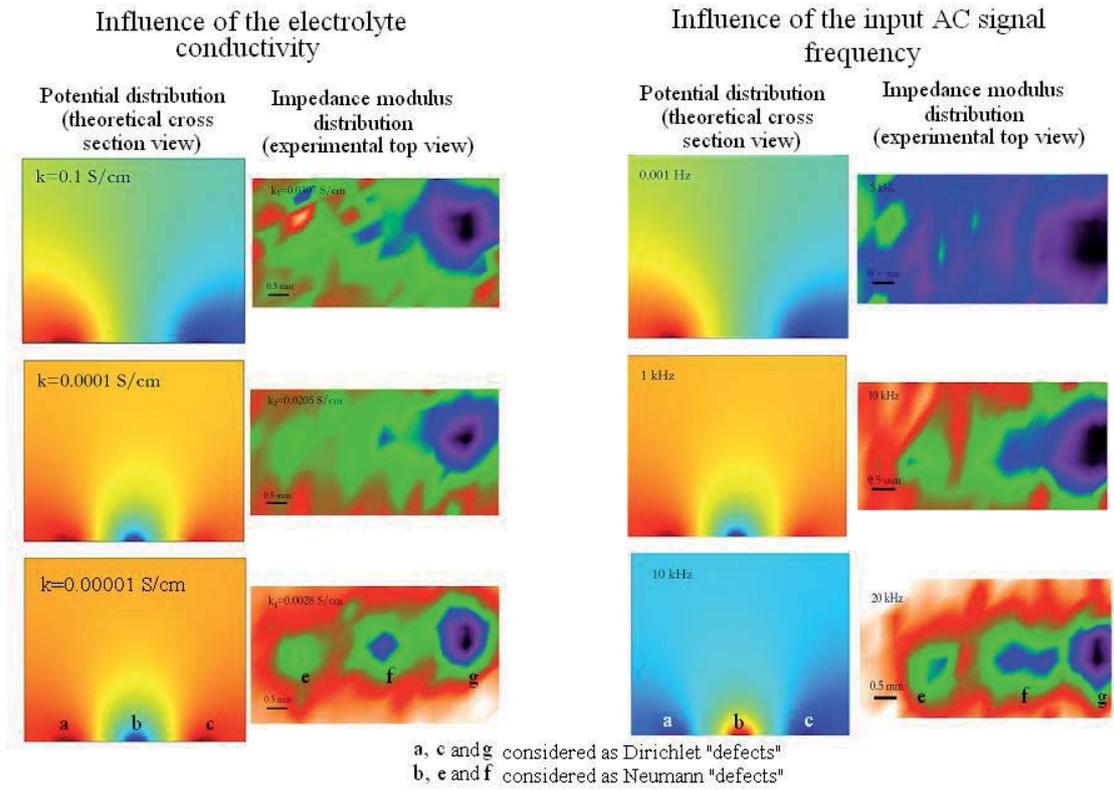
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HIGHLIGHTS

- The detection of irregularities in solid/liquid interfaces has been studied
- FEM and the Laplace equation with proper boundary conditions were used
- Adequate ranges of conductivity and input AC signal frequency should be selected
- Active borders are more affected by the above variables than fixed potential ones
- Experimental evidences obtained by LEIS mapping support the theoretical results

Effect of conductivity and frequency on detection of heterogeneities in solid/liquid interfaces using local electrochemical impedance. Theoretical and experimental study

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Abstract

This short communication demonstrates, by solving the Laplace equation with proper boundary conditions (BC) using finite element method (FEM), that it is not possible to establish a correlation between what happens in the electrolyte near an active boundary and what really occurs at the actual boundary if adequate ranges of electrolyte conductivity and input AC signal frequency are not selected, especially when inhomogeneities approximated by Neumann BC are present. Experimental evidence obtained by local electrochemical impedance mapping (LEIM) support the theoretical results.

Keywords

Finite element method; Simulation; Localized electrochemical impedance spectroscopy/mapping (LEIS/LEIM)

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1. Introduction

In the last few decades in the field of the electrochemistry many laws and fundamental governing equations (Laplace, Nernst-Einstein, etc.) have been used in order to have a better understanding of reaction mechanisms and to optimize specific parameters. Due to the complexity of the corresponding boundary value problems (BVP) and variational formulations, what is usually done is to approximate the solution using different numerical algorithms. FEM and BEM have demonstrated the greatest versatility in achieving this aim [1-4].

In a BVP the BC mathematically approximate the real physical conditions.

Dirichlet and Neumann boundary conditions are commonly used in electrochemical simulation [5]. It is possible to say that the Dirichlet type BC fix beforehand the value of the solution in some borders by means of a well-known function whereas those of the Neumann type evaluate the corresponding derivative. It means, if the solution of a BVP is the function $u(\vec{x})$, then the previous BC type are

$$u(\vec{x}) = f(\vec{x}) \text{ on } \partial\Omega$$
$$\frac{\partial u(\vec{x})}{\partial n} = g(\vec{x}) \text{ on } \partial\Omega$$

Where n and $\partial\Omega$ are the outward normal vector and the boundary respectively.

On the other hand, localized electrochemical techniques (LET) represent a field where electrochemistry has made great advances in the last few years. For example, scanning vibrating probe, scanning Kelvin probe, LEIS, are now commonly used in the study of electrochemical phenomena and processes [6-8].

In particular, LEIS-LEIM has experimented important advances in the last years in studies devoted to surfaces heterogeneities in corrosion science and electrochemistry fields. The validity of LEIS technique has been proved finding a good correlation between LEIS and EIS measurements [9].

A major challenge for electrochemical research is to develop theoretical methods for the interpretation of the results obtained with these techniques. The present paper is a contribution to these developments. Our aim has been to apply certain concepts of computational electrochemistry in order to study the influence of the electrolyte conductivity and the input AC frequency for the detection of irregularities in solid/liquid interfaces using LEIM.

2. Experimental

The experimental device consists of three platinum electrodes (diameters 0.25mm and 0.5mm, the central one being the biggest, with a separation between them of 2.5 mm)² embedded in epoxy resin, immersed in NaCl solution simulating three defects in a metal-coating electrolyte system. The corrosion potential of both the left and central electrodes was modified with an external power supply. The corrosion potential of the right electrode was only slightly modified when a frequency of 15kHz and a voltage of 0.02 V r.m.s were applied in order to measure the impedance with a Localized Electrochemical Impedance System (LEIS370, UNISCAN Instruments Ltd.).

3. Theory/calculation

² Measures long enough to avoid overlapping effects [10].

Good correlation has been found in multiple works [4,10,11] between the theoretical (solving the Laplace and Poisson equations) and the experimental results in electrochemical systems. The importance of the Poisson's equation is that it is a fundamental law in nature that relates the changes in the electric potential to the local electric charge density in an electrochemical system. The combination of Gauss' law and the electric field gives rise directly to the Poisson's equation. Sometimes, this important law is simplified and substituted by the property of electro-neutrality.

On the other hand, if the electrochemical system guarantees a uniform composition then conservation of charge implies that Laplace's equation and Ohm's law govern the equations of the electrical potential and the flux current, respectively [12].

3.1. Effect of the electrolyte conductivity on the potential distribution

As it has been studied previously, there is not easy task to identify causes of strange behavior in LEIM responses of metal-coating systems [13]. And simplifications must be done to modeling these systems.

So, considering that Figure 1a represents a 2D-cross section view of a metal coated with an ideal insulator immersed in an electrolyte and that:

- The coating has three defined defects allowing contact between the surface of the metal and the electrolyte.
- The defect located in the middle causes the activation of the metal (non homogenous Neumann condition).
- There are no concentration gradients in the electrolyte, (the current is approximated by using Ohm's law).

- The electrolyte has a uniform composition (the potential satisfies the Laplace's equation).
- There is no consideration of convection effects (fluid mechanics equations are not used).
- The lateral defects have a stable and constant potential (Dirichlet conditions).

Then its corresponding BVP is

$$-k\Delta\phi(x,y) = 0 \quad (x,y) \in \Omega \quad (1)$$

$$-k \frac{\partial\phi}{\partial n} = i = 0 \text{ on } \partial\Omega_1$$

$$-k \frac{\partial\phi}{\partial n} = i = PC \text{ on } \partial\Omega_3, \phi = \phi_0 \text{ on } \partial\Omega_2, \phi = \phi_1 \text{ on } \partial\Omega_4$$

where, PC is the function that approximates the polarization curve of a metal $\partial\Omega_3$ (magnesium in this case [14]) being in contact with the electrolyte Ω , which has an electrical conductivity k , and ϕ_0 and ϕ_1 are the potential values of the lateral defects, $\partial\Omega_2$ and $\partial\Omega_4$ respectively. BVP 1 has both Neumann and Dirichlet type BC, which together with the operator used, Laplacian, make for a problem with a unique solution, since its corresponding weak formulation has a left side that is bilinear, symmetrical, continuous and H-elliptic, while the right side is linear and continuous [4,15,16].

Although the analytical expression to obtain the potential distribution for a metallic disk in an electrolyte was already obtained [12], Mierisch *et al.* already described the limitations founded when this is used to model a finite electrochemical cell [10] and proved the advantages to use numerical methods for this issue.

In order to solve problem 1, the corresponding variational formulation is first generated. This is posed in a space of finite dimension and the FEM is ultimately applied in order to solve the numerical system obtained [4,15,16]. So, considering that the solution ϕ is approximated by the functions Φ_i in the sense

$$\phi \approx \sum_{i=1}^N a_i \Phi_i$$

where N is the number of elements in the selected mesh, the final matricial form of this problem is

$$\begin{aligned} & \begin{bmatrix} \int_{\Omega} \frac{\partial \Phi_1}{\partial x} \frac{\partial \Phi_1}{\partial x} + \frac{\partial \Phi_1}{\partial y} \frac{\partial \Phi_1}{\partial y} dX & \dots & \int_{\Omega} \frac{\partial \Phi_N}{\partial x} \frac{\partial \Phi_1}{\partial x} + \frac{\partial \Phi_N}{\partial y} \frac{\partial \Phi_1}{\partial y} dX \\ \vdots & \ddots & \vdots \\ \int_{\Omega} \frac{\partial \Phi_1}{\partial x} \frac{\partial \Phi_N}{\partial x} + \frac{\partial \Phi_1}{\partial y} \frac{\partial \Phi_N}{\partial y} dX & \dots & \int_{\Omega} \frac{\partial \Phi_N}{\partial x} \frac{\partial \Phi_N}{\partial x} + \frac{\partial \Phi_N}{\partial y} \frac{\partial \Phi_N}{\partial y} dX \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_N \end{bmatrix} \\ & = 1/k \begin{bmatrix} \int_{\partial\Omega_s} PC\Phi_1 \\ \vdots \\ \int_{\partial\Omega_s} PC\Phi_N \end{bmatrix} \end{aligned} \quad (2)$$

3.2. Effect of the frequency on the potential distribution of an electrochemical system

In order to study the effect of the frequency on the potential distribution, the system represented in Figure 1a was again considered, but in this case the impedance, and consequently the frequency, was taken in to account in the central defect. Therefore, knowing that $Z = \frac{\phi}{i}$ and $i = -k \frac{\partial \phi}{\partial n}$, the considered BVP is

$$-k\Delta\phi(x,y) = 0 \quad (x,y) \in \Omega \quad (3)$$

$$-k \frac{\partial \phi}{\partial n} = 0 \text{ on } \partial\Omega_1$$

$$-k \frac{\partial \phi}{\partial n} = \frac{\phi}{Z} \text{ on } \partial\Omega_3, \phi = \phi_0 \text{ on } \partial\Omega_2, \phi = \phi_1 \text{ on } \partial\Omega_4$$

For the purpose of calculating the corresponding impedance, a simple circuit in parallel (RC) was assumed in the central defect, [ignoring de double-layer and the charge-transfer resistance as in previous works \[17\]](#). The capacitance C and the resistance R were considered as $C=10^{-4}\text{F}$ and $R=1\text{Ohm}$. Therefore,

$$Z = \frac{\frac{1}{R} - jC\omega}{\frac{1}{R^2} + C^2\omega^2}$$

The BC of the problem 3 are then completely defined

[The mathematical computations were carried out using the software COMSOL®.](#)

4 Results

In Figure 1b the results obtained when the solution of BVP 1 is approximated by FEM are depicted in a 2D-cross section, there the critical influence of the conductivity on the potential distribution in the electrolyte can be observed. It is noteworthy to emphasize the small value of the theoretical conductivity necessary to localize the active irregularity by means of the variation of the potential in the contiguous zone of the electrolyte. At the same time, it is important to emphasize that the critical defect in these important results is the Neumann type since if only Dirichlet defects were considered then the electrolyte conductivity would not affect the results [15]. These theoretical tendencies are confirmed in the experimental results shown in Figure 1c where different 2D-top view impedance moduli distributions are depicted. As the figure

shows, both platinum disks affected by external supplies could be localized only when the electrolyte conductivity was small enough.

As is well known, a localized electrochemical mapping is directly related to the electrochemical potential distribution since the current i is approximated as

$$i = \frac{\Delta V k}{d} \quad (4)$$

k being the electrolyte conductivity, d the distance between the tip and the ring in the special bi-electrode and ΔV the potential difference in the electrolyte between the surroundings of both the ring and the tip [17-21].

It means, a biunivocal relation exists between the electrochemical potential distribution and the localized electrochemical impedance mapping, **and when one of these mappings is drawn the other can be obtained in a straightforward manner [10]. However, it must be clear that Equation 4 is a simple approximation because it considers only the perpendicular component of the current density vector and this simplification has different consequences on the real and on the imaginary parts of the impedance [22].**

The results of Figure 2a show the important effect of the frequency on the potential distribution. These results reveal that if a LET is based on the potential gradients in the electrolyte, i.e. LEIM, then under the selected conditions the imperfections of the coating will be detected only at specific frequencies, in fact only at high frequencies, as the central defect $\partial\Omega_3$ of this figure shows. These theoretical trends are confirmed in the experimental results shown in Figure 2b, where active sites, identified beforehand, cannot be localized by means of LEIM at low frequencies.

5. Discussion

Figures 1b and 1c prove theoretically that to localize a defect or irregularity of the Neumann type, by means of the perturbation that this causes in the neighbourhood of the electrolyte, can become an impossible task if a small enough conductivity is not selected. It is important to note that although this limitation is known and reported in most of the works associated with localized electrochemical techniques [17-21], whose theoretical principles are based on the potential gradients in the electrolyte, it is also true that no work refers to the fact that the effect of the conductivity is not the same **around an irregularity with constant potential as around an active irregularity.**

On the other hand, Figure 2a shows that when inhomogeneous Neumann conditions are used to simulate defects or irregularities considering its impedance, it is necessary to pay special attention in the range of the frequency used. Otherwise, detecting changes in the electrolyte which reveal the presence of electrochemical irregularities of the boundaries will be impossible as it can be verified in the experimental results shown in Figure 2b.

This means critical complications in some localized electrochemical measures depending on frequency. Because selecting a proper value – as in the case of the conductivity – of frequency solves the complications only when the LET uses a constant frequency, i.e., LEIM. Nevertheless, in techniques like LEIS where a sweeping of frequencies is necessary, experimentation becomes more complicated. Because, as Figure 2 shows: going from high to low frequencies could have as consequence moving from coherent to incoherent signals in the electrolyte. **However, some studies have been carried out in a satisfactorily way**

with this technique finding that multiples factors, as smooth changes in the distance from the tip to the working electrode, affect the measurements [22,23]. It must bear in mind that in LEIM bibliography there are simpler models, that do not consider the frequency in the mathematical calculations [10], or more sophisticated that take into account even CPE elements[22,23]. Nevertheless, the simplification presented here explains why some irregularities can be localized in wider frequency range than others.

6. Conclusions

The results obtained show that what happens at an active electrochemical boundary is not necessarily reflected in the surroundings of the electrolyte. So, a metal can be corroding aggressively and no important change will occur in the neighbourhood of the electrolyte, if adequate ranges of conductivity and frequency are not chosen. Likewise, this paper proves that the potential zones of electrolyte close to irregularities in solid/liquid interfaces are affected weakly or strongly, by both frequency and conductivity. This depends on whether these inhomogeneities have a fixed potential value while the experiment is being carried out or, on the contrary, whether the inhomogeneity is active, the current is drawn there and its potential changes during the experiment.

Acknowledgements

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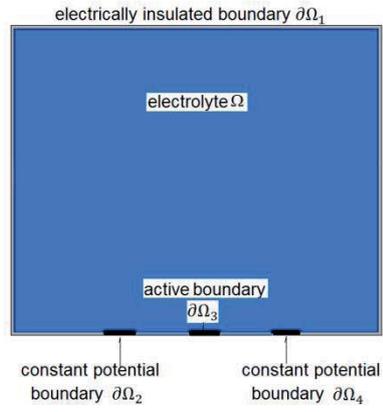
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Figure captions

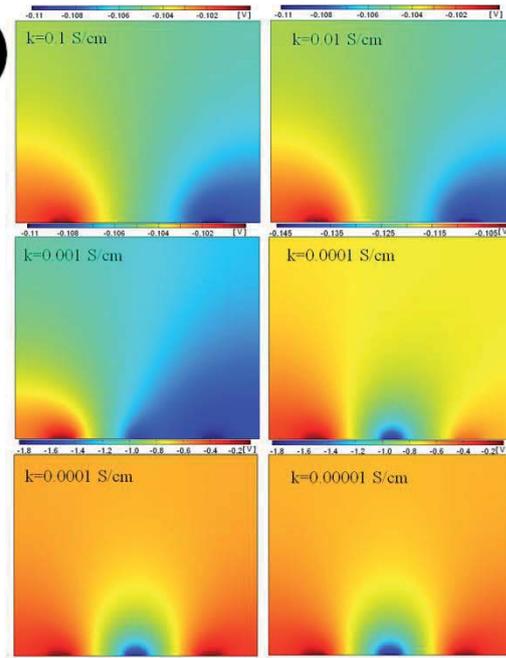
Figure 1. a) Cross section view of the geometric configuration of the system in accordance with problem 1, b) Effect of the electrical conductivity on the electrochemical potential distribution when the BVP 1 is solved by FEM (cross section), c) Effect of the electrolyte conductivity on LEIM results for three platinum electrodes embedded in epoxy resin immersed in a low conductivity electrolyte. An external polarization was applied on the left and the central defects (top view).

Figure 2. a) Effect of the current frequency on the electrochemical potential distribution in accordance with the configuration shown in Figure1a when the BVP 3 is solved by FEM (cross section), b) Effect of the frequency on LEIM results for three platinum electrodes embedded in epoxy resin immersed in a low conductivity electrolyte (top view). An external polarization was applied on the left and the central defects.

a)



b)



c)

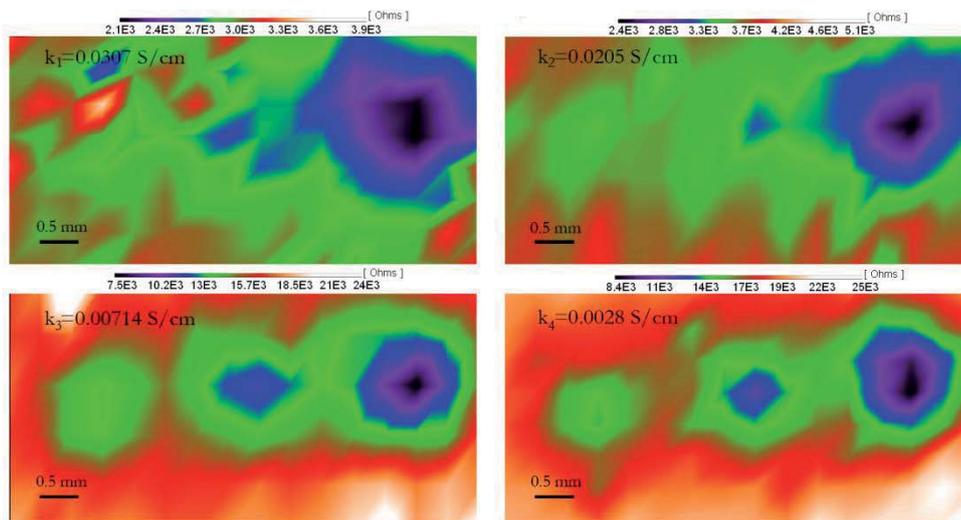


Figure 1

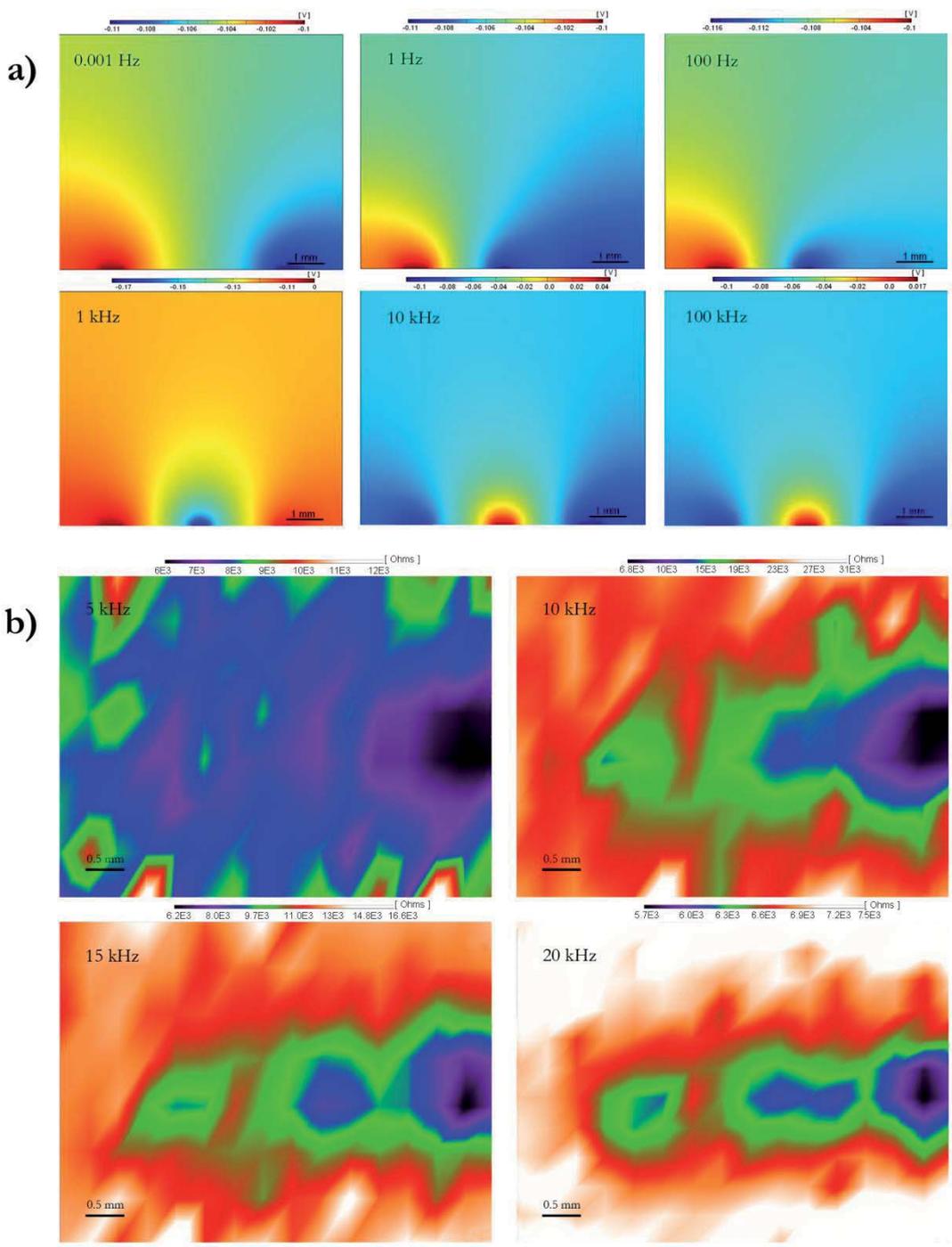


Figure 2