

# Development of solid contact micropipette Zn ion selective electrode for corrosion studies

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## Abstract

The fabrication of a new, solid contact, micropipette ion-selective electrode suitable for use as potentiometric tip in scanning electrochemical microscopy (SECM) is described. Owing to the low resistance, and long life times, these electrodes can advantageously be used in corrosion studies where the measurement of local zinc ion concentrations evolving in surface reactions can give important information about the nature of the process. Data on the properties of these Zn<sup>2+</sup> ion selective microelectrodes, namely life time, resistance and ion activity response, are shown. Preliminary findings using them in SECM imaging of zinc ion concentration profiles from a corroding sample are also given. The improvement of scanning rate achieved by lowering the tip resistance is a major advantage in potentiometric SECM.

## Introduction

As it is well known, zinc is a transition metal that has important roles in living organisms as well as in human technology. In living objects its functions involve mainly enzymatic processes and DNA replication. Additionally, the human hormone insulin contains zinc. Because of these, zinc is an important trace metal in human dietary. Interestingly human body contains a relatively high amount of zinc, as high as about 2.3 g.

Zinc is also contained in paints, batteries, pharmaceutical and other industrial products. As a result, pollutants containing zinc are commonly encountered in environmental samples. Therefore, analytical methods are needed for the assessment of zinc concentration in dietary, environmental, industrial or biological samples.

A high number of methods for the analysis of zinc in different samples is currently available, and among them, atomic spectroscopy methods seem to be the most popular.

Voltammetric methods have also been successfully employed because zinc ions can be reduced at different electrodes.

An interesting alternative for zinc analysis arises from the simplicity, and cost effective nature, of potentiometry and several attempts have been made to develop wellfunctioning ion-selective electrodes. For instance, Zamani et al. [1] have reported the preparation and application of a zinc membrane electrode, which was made of plasticized PVC membrane containing 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene(BHDE)cryptand ionophore. This electrode was used for end point detection in complexometric titration as well as in the monitoring of zinc ion occurrence in industrial wastewaters resulting from zinc electroplating processes. Alternately, Gupta and coworkers [2] employed a porfirin molecule ionophore to produce a zinc-selective electrode by. Their electrode also employed PVC matrix membrane.

Most of the schools working on the development of ion selective zinc electrodes aimed environmental, clinical or dietary analysis as potential application fields for their new, modified or further improved sensors. But due to the complexity of the matrices employed, and the low zinc concentrations in them, it has not been an easy task to find suitable ionophores, and to prepare well functioning zinc ion selective electrodes for those samples. Therefore, still further work is needed in this area in order to improve the selectivity and dynamic range of analysis properties of the resulting zinc-selective electrode.

Another potential field for the application of zinc ion selective electrodes is found in corrosion science. Zinc layers or films containing dispersed zinc particles are often used to supply cathodic protection against corrosion to metal surfaces. Therefore, the application of less complex matrices containing a higher zinc ion concentration can provide important information about the nature of the process in corrosion studies. Indeed, spatially-resolved investigations of the corrosion processes occurring when iron and zinc surfaces are put in galvanic contact have been performed by using the scanning vibrating electrode technique (SVET) and the scanning electrochemical microscope (SECM) [3]. By carrying out experiments in different ionic solutions, consistent results were obtained for the corrosion of iron, but significant differences were observed concerning the detection of zinc corrosion. It is thus expected that the use of a selective zinc concentration detecting tip could be very helpful in these corrosion studies.

Scanning electrochemical microscopy (SECM) is a powerful technique for the investigation of surface processes, among them those responsible for corrosion. It is based on the combined application of high resolution tip-positioning devices, suitable computer-

controlled measurement and data collection, and image recording and evaluation software. The SECM can provide high resolution images containing chemical information on surface processes, and about concentration profiles of different species in the liquid phase in close vicinity of interfaces.

Most SECM studies employ a voltammetric ultramicroelectrode as data collecting measuring tip while the electrochemical system operates in the amperometric mode. However, in many different studies, an ion selective electrode measuring tip and operation of the SECM in the potentiometric mode is a better choice. The local concentration of a species presenting no electroactivity in the accessible potential window can be measured with the appropriate ion selective electrode. Its selectivity, which is superior to amperometry, is also often required. During a previous collaboration with the pioneering research team of Professor A. J. Bard at the Texas University in Austin, preliminary experiments with a micropipette type zinc ion selective electrode were performed. We were able to record images displaying zinc ion concentration profiles over small size zinc ion diffusion sources as well as over electrochemical zinc ion sinks [4].

Ion selective micropipette electrodes are well known sensors and are broad scale used in experimental life sciences. Their main advantage is that they can be made with very small measurement tips. The tip diameter can be in the nm range. Their preparation procedure is quite universal, and depending on the composition of the measurement “cocktail”, several types of electrodes can be prepared by the same procedure.

Unfortunately, ion selective micropipettes are very fragile sensors, sensitive to mechanic effects and electric shocks. Their lifetime is seldom longer than a few days. They need special care during handling, and noise filtering during measurements. When considering their application in practice for SECM, one of their most annoying characteristics is their very high electric resistance. In SECM, the measuring tip travels stepwise at a given scan rate over the surface studied. At each location it measures a signal reflecting the ion activity there. The higher the resistance, the longer the time needed to achieve a steady signal at each location. This feature imposes that slower scanning rates are needed to attain reliable images when the resistance is higher. Additionally, higher resistances result in more electric noise disturbing the measurements. For the interested reader, a detailed discussion concerning the problems and difficulties of ion selective SECM can be found elsewhere [3]. Very recently, another zinc ion selective microelectrode developed and adopted for the determination of the  $Zn^{2+}$  species released in the course of corrosion processes has been described [4].

On the other hand, a novel type of micropipette ion selective electrodes has been developed in our laboratory at Pécs. In this electrode, the internal reference electrode has been replaced by a thin carbon fiber coated by a conductive polymer coated which is dipped into the ion-selective cocktail. In this way, the resistance of the electrode has been significantly decreased at the same time that its lifetime was dramatically improved [7]. In particular, the properties of the novel ammonium and potassium selective micropipettes and their application in SECM have been reported [7,8].

In the course of a new cooperation project initiated with our group at La Laguna, where they are interested in the application of the potentiometric SECM operation to corrosion studies, ion selective zinc micropipettes provided with solid contact were prepared at Pécs. In this paper we describe the preparation procedure for these electrodes, and we report the results obtained during the investigation of their properties. Preliminary data on the corrosion of zinc obtained with the SECM technique using these zinc ion selective electrode tips are also given.

## **Experimental**

### **Materials, Instruments and Methods.**

High molecular weight poly(vinylchloride), potassium tetrakis(4-chlorophenyl)borate (KTFPB), and 2-nitrophenyl octyl ether (OPOE) were purchased from Fluka, whereas tris(hydroxymethyl)-aminomethan buffer from Merck, and tetrahydrofurane from Interkemia were also used. The monomer, 3,4-ethylenedioxythiophene (EDOT) employed to coat the carbon fiber with a conductive polymer was obtained from H.C. Starck. The electropolymerization was carried out in 1-butyl-3-methyl-imidazoliumhexafluorophosphate (BMIM<sup>+</sup> PF<sub>6</sub><sup>-</sup>) ionic liquid solvent (Solvent Innovation).

The 33 μm diameter carbon fibers were a generous gift of Specialty Materials (Massachusetts, USA), and borosilicate glass capillaries (types: B100-50-10 and B200-116-10) were purchased from Sutter Instrument (Novato, CA, USA).

All chemicals were used as they were obtained. All chemicals not mentioned here were of analytical grade. The N-phenyliminodiacetic acid N', N'-dicyclohexylbisamide zinc ionophore was used in the ISME-s, it was synthesized at the Technical University of Budapest [9]. All solutions were prepared using deionized water.

A home made, battery powered voltage follower based on TL082 operational amplifier was used for all potentiometric measurements. Its output was connected to a digital

multimeter (METEX M-3630D Digital Multimeter). The cell voltage data were collected with a PC through the multimeter using the commercial program supplied for the METEX.

The scanning electrochemical microscope employed in this work was built in our laboratory [10]. It is based on a 3D step motor positioning device driven by precision step motors with 75nm minimal step size. Ag/AgCl reference electrodes in quasi-reference configuration were employed in the polymerization, potentiometric and SECM experiments, whereas a platinum wire was used as the auxiliary electrode during the preparation of the electropolymerized coating.

### Preparation of the micropipette electrodes

A scheme describing the micropipette electrodes can be seen in Figure 1. The electrodes are made of two parts. The glass pipette bearing a broader internal diameter holds the cocktail, and the thinner one is inserted into the lumen of it. The carbon fiber that provides the internal contact is sealed at the tip of the thinner pipette, whereas a thin copper wire is inserted into the lumen. Mercury or silver epoxy provides electric contact between the carbon fiber and the copper wire. The internal part of the electrode assembly is reusable. It can be inserted into a new outer part when the previously used gets damaged.

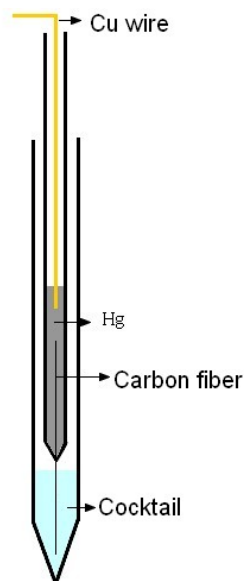


Figure 1. The structure of the micropipette electrode.

In the preparation of the micropipette electrodes, borosilicate glass capillaries of two different internal diameters (types: B100-50-10 and B200-116-10, Sutter Instruments) were selected and checked if their diameters would fit. The capillaries were soaked in “piranha solution” of concentrated sulfuric acid : hydrogen peroxide (30%). Next, they were thoroughly washed with double deionized water and ethanol, and dried in oven at 105 °C. Micropipettes were pulled from both sizes of capillaries by using a pipette puller (Sutter Instruments, type P-30, Novato, CA, USA). The 33 µm diameter carbon fiber was inserted in the lumen of the thinner capillary with the fiber reaching out for about 15 mm, and about 20 mm long in the lumen. Loctite adhesive was used for sealing. Mercury metal or Amepox silver epoxy paste (Amepox Microelectronics, Ltd. Poland), and the copper wire are then inserted into the lumen of the thin pipette as shown in Figure 1. At this point, the inner section of the electrode assembly is ready for the electropolymerization of EDOT over the portion of the carbon fiber reaching out from the tip.

Accordingly, the tip of the larger diameter pipette is supplied with a hydrophobic layer using dichlorodimethylsilan (Fluka) using a simple procedure. Namely, the tip of the micropipette is introduced into a small amount quantity of 5% solution of dichlorodimethylsilan in carbon tetrachloride, and they are subsequently kept in oven (80 °C) for about half an hour in a closed Petri dish. The finished pipettes are stored inside a Petri dish at room temperature until use. The zinc ion selective cocktail can be backfilled into the tip shortly before the assembly of the electrodes in the measuring device. In this way, a 5-10 mm long cocktail column is formed at the tip end of the pipettes.

The zinc ion selective cocktail was made having the following composition: Zink ionophore 5%, K- tetrakis (4-klorophenil) borate hydrophobic additive 1.8% , PVC matrix 13% , 2-nitrophenyl octyl ether (OPOE) plasticizer solvent 80%, Tetrahydrofurane diluting solvent 0.2%. This composition was selected after comparing the behaviour of the micropipettes built with different ratios of these components.

## **Results and Discussion**

The voltage divider method was used to measure the internal resistance ( $R_i$ ) of the cell containing the zinc micropipettes. A high ohmic resistance resistor ( $R_k$ , 100 MΩ) was selected for these studies, and the emf of the cell containing the quasi reference and the ISE zinc electrodes was recorded. Once a steady reading was obtained, the resistor  $R_k$  was switched in the measuring circuit as electric load, and the transient of the voltage drop  $\text{emf}-U_k = \Delta U$  was

recorded. Assuming that  $R_k$  and  $R_i$  are much bigger than any other resistances in the circuit, equation (1)

$$R_i = \frac{\Delta U \cdot R_k}{U_k} \quad (1)$$

can be used to calculate  $R_i$ , where  $U_k$  is the steady voltage value after switching in the resistor  $R_k$ . The average of three  $\Delta U/U_k$  data pairs were used in every case. Values in the range of 40.9 M $\Omega$ /mm were found for the resistance  $R_i$ , and they depend on the tip diameter of the electrode. As it was observed earlier with potassium [7] and ammonium [8] micropipettes, the resistance of these solid contact micropipettes is just a fraction of those exhibited by micropipettes of the same size fabricated using the “conventional” procedures. Figure 2 shows a typical recording obtained during the above described resistance measurements for an ISE electrode presenting a tip diameter of about 3 $\mu$ m. When the resistor was connected in parallel to the cell is indicated by “on” in the figure, whereas the instant when it was disconnected has been indicated by “off” accordingly.

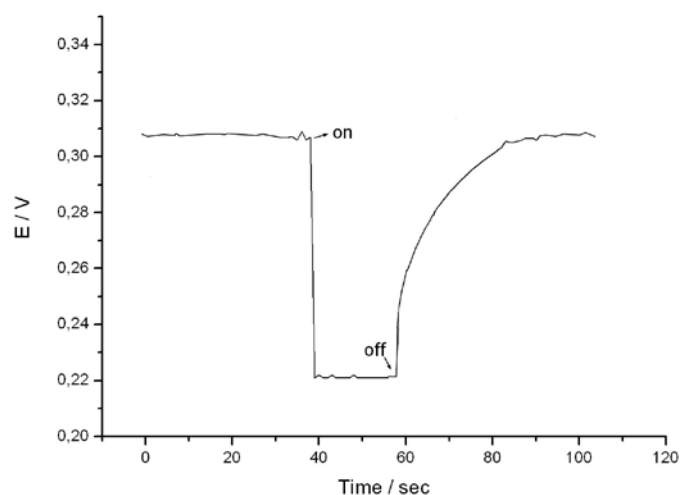


Figure 2. Cell voltage – time recording obtained during measurement of the electrode resistance.

The concentration dependence of the electrode potential was checked using solutions of different concentration. The obtained calibration curve is shown in Figure 3. As it can be seen, the response has close Nernstian slope in the concentration range of  $10^{-4}$  to  $10^{-1}$  M. In

order to study the potential stability of the zinc micropipettes, the freshly made electrodes were inserted in the measurement cell containing 0.1 M tris(hydroxymethyl)-aminomethan buffer with different zinc ion concentrations. In addition to monitoring the cell potential, the electric noise sensitivity and the potential stability were also observed. The electric noise sensitivity was checked by making measurements without using the Faraday cage. The drift was then determined as the  $\Delta E/\Delta t$  slope of the electrode potential vs. time dependence. Usually, a 0.05-0.08 mV/min drift was observed for the freshly prepared electrodes when measured after a few minutes of their introduction in the solutions for zinc concentrations between 0.1-10 mM.

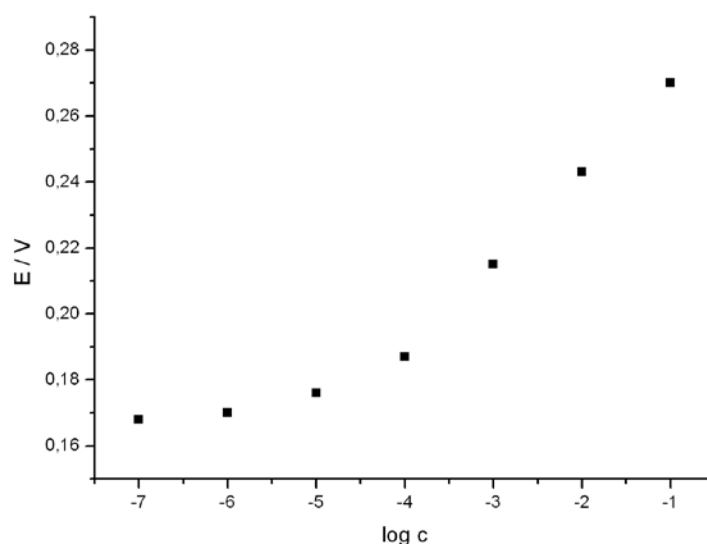


Figure 3. Plot of the electrode potential vs. log zinc concentration obtained with a solid contact zinc ion selective electrode (electrode tip diameter 70  $\mu\text{m}$ ; slope in the  $10^{-4} - 10^{-1}$  range: 27.7 mV/decade).

The applicability of the zinc micropipettes in SECM studies was checked after a small size zinc ion source was prepared and introduced through a hole in the bottom of the SECM measurement cell. This was prepared from a glass micropipette, the tip of which was closed by an agar gel plug. The pipette was filled with 0.1 M  $\text{ZnSO}_4$  solution, and the measuring cell was filled with a 0.1 M KCl supporting electrolyte solution. The zinc ion selective tip was moved vertically both outwards and towards the diffusion zinc source, as well as horizontally over this metal source, and the values of the local electrode potentials at different locations were recorded. Figure 4 displays the electrode potential – distance curve recorded above the



center of the source recorded when the tip traveled in the vertical direction outwards from the ion source. At 0  $\mu\text{m}$  distance, the tip almost touched the source plug. The electrode potential readings could be transformed into concentration values by using the previously recorded calibration curve (cf. Figure 3). The corresponding zinc ion concentration vs. distance plot is depicted in Figure 5.

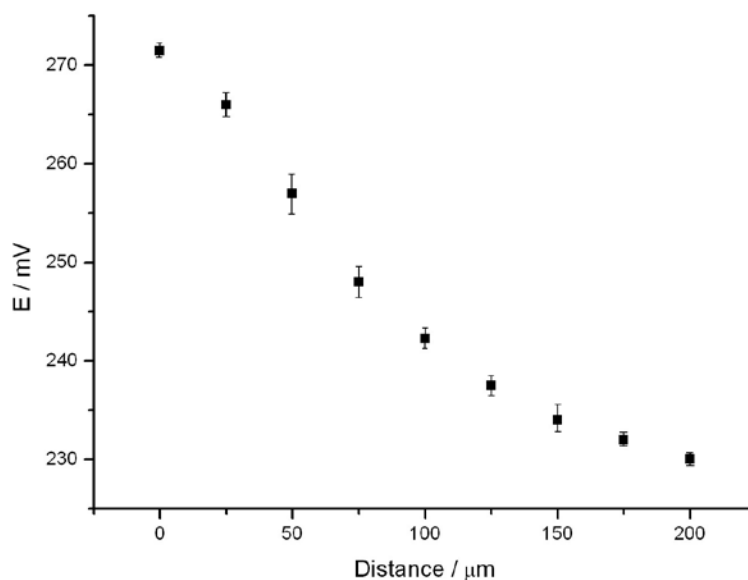


Figure 4. Electrode potential - vertical distance curve recorded with a zinc ion selective measuring tip (diameter 70  $\mu\text{m}$ ) scanned above the center of a disc-shaped diffusion zinc source.

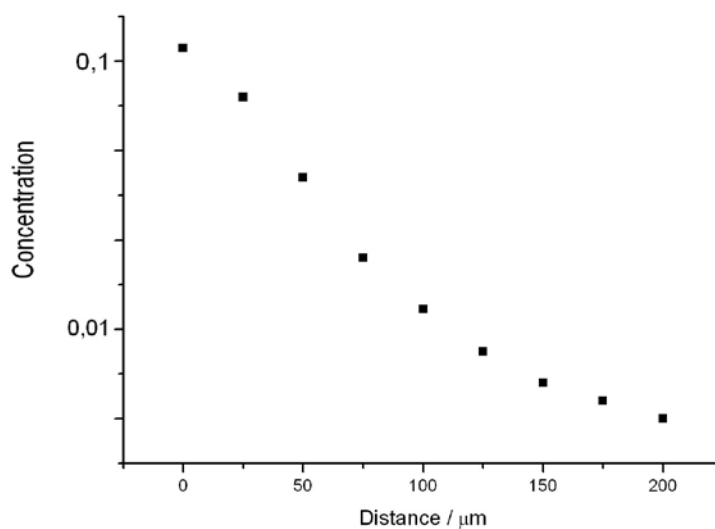


Figure 5. Concentration - vertical distance curve recorded with a zinc ion selective measuring tip (diameter  $70\mu\text{m}$ ) scanned over the center of a disc shaped diffusion zinc source.

Analogously, Figure 6 shows the electrode potential recorded when an ISE tip (about  $70\mu\text{m}$  diameter) was scanned at the constant height of  $150\mu\text{m}$  above a  $50\mu\text{m}$ -diameter source disc acting as the source for zinc ions. Though the potential curve shows some broadening beyond the limits of the ion source, which originates from the rather large distance between the measuring tip and the surface employed, the actual location of the source is satisfactorily imaged.

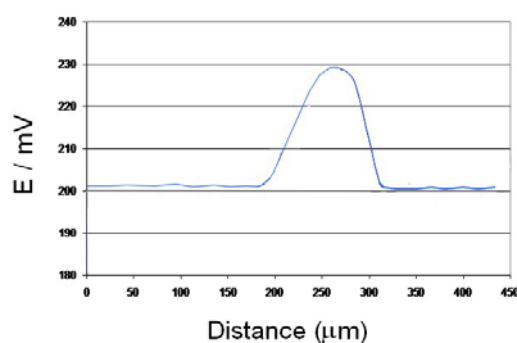


Figure 6. Electrode potential – lateral distance plot recorded with a zinc ion selective measuring tip (diameter  $70\mu\text{m}$ ) scanned over a disc shaped diffusion zinc source.

The low resistance ion selective measuring tip was developed for application in corrosion studies. Currently, experiments are in progress concerning the investigation of the galvanic corrosion of iron and zinc samples immersed in different ionic media. In those studies SECM images are recorded over electrically-connected as well as insulated iron and zinc surfaces. An early one dimension zinc electrode potential – horizontal distance image is shown in Figure 7. This figure was recorded when the ISE electrode was scanned over a flat surface containing a small size zinc disc in direct electric contact with an iron surface disc, both inserted in an epoxy resin holder. Electric contact was established at the back of the sample. The detection of Zn ionic species is clearly detected when the ISE tip passed above the zinc disc, whereas no signal could be measured either above the surrounding epoxy resin or the iron disc. The relevance of this observation towards further use of SECM in corrosion investigations can be understood when it is considered that previous studies based on the amperometric operation of the SECM only allowed for the detection of the cathodic half

reaction occurring over the iron sample measured as the local depletion of dissolved oxygen in the vicinity of the metal [3].

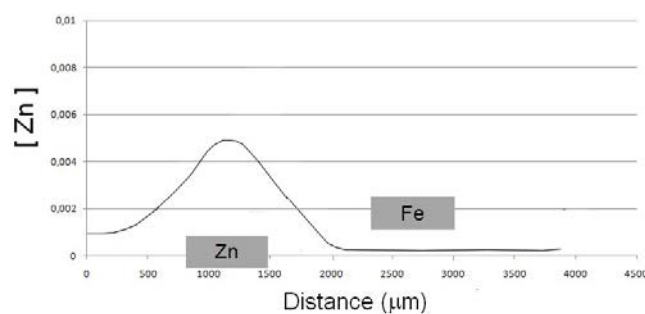


Figure 7. Line scan displaying the variation of the zinc electrode potential measured at the ISE tip when traveling above an Fe-Zn galvanic couple immersed in 0.1 M KCl.

## Conclusion

Low resistance zinc ion selective micropipette electrodes were prepared for corrosion studies. The electrodes contain electrochemically prepared PEDOT conductive polymer coated carbon fiber as solid contact. Using this design the electrode resistance could be significantly lowered, which allows faster scanning rates to be used in SECM applications. From the previous experience gained with similar potassium and ammonium selective electrodes, it is expected that the operation and storage stability of these newly developed zinc electrodes will be much longer than those made of “conventional” micropipettes. Additionally, the electrodes can be prepared with a submicron tip size. The preliminary results reported here concerning their analytical properties and SECM application proved their advantage.

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## References:

- [1] H. Ali Zamani, M. Reza Ganjali and M. Jan Pooyamanesh. 2006. Zinc(II) PVC-based membrane sensor based on 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene. *Journal of the Brazilian Chemical Society* 17(1):149-155.
- [2] Gupta V.K., Chauhan D.K., Saini V.K., Agarwal S., Antonijevic M.M. and Lang H. 2003. A porphyrin based potentiometric sensor for  $Zn^{2+}$  determination. *Sensors*. 3:223-235.
- [3] Simões A.M., Bastos A.C., Ferreira M.G., González-García Y., González S. and Souto R.M.. 2007. Use of SVET and SECM to study the galvanic corrosion of an iron–zinc cell. *Corrosion Science*. 49(2):726-739.
- [4] Wei C., Bard A.J., Nagy G. and Toth K. 1995. Scanning electrochemical microscopy. 28. Ion-selective neutral carrier-based microelectrode potentiometry. *Analytical Chemistry*. 67:1346-1356.
- [5] Denuault G., Nagy G., Toth K. 2001. Potentiometric probes. In: *Scanning Electrochemical Microscopy*, A. J. Bard and M. V. Mirkin (editors); Marcel Dekker, New York, pages 397-445.
- [6] Bastos A.C, Taryba M.G., Karavai O.V., Zheludkevich M.L., Lamaka S.V. and Ferreira M.G.S. 2010. Micropotentiometric mapping of local distributions of  $Zn^{2+}$  relevant to corrosion studies. *Electrochemistry Communications*. 12:394–397.
- [7] Gyetvai G., Sundblom S., Nagy L., Ivaska A. and Nagy G. 2007. Solid contact micropipette ion selective electrode for potentiometric SECM. *Electroanalysis*. 19 (10):1116 – 1122.
- [8] Gyetvai G., Nagy L., Ivaska A., Hernadi I. and Nagy G. 2009. Solid contact micropipette ion selective electrode for potentiometric SCEM II: Potassium electrode. *Electroanalysis*. 21(17-18):1970-1976.
- [9] Lindner, E., Horvath, M., Toth, K., Pungor, E., Bitter, I., Agai, B. and Toke, L. 1992. Zinc selective ionophores for potentiometric and optical sensors. *Analytical Letters*. 25, 453-470.
- [10] Csóka B., Kovács B. and Nagy G. 2003. Investigation of concentration profiles inside operating biocatalytic sensors with scanning electrochemical microscopy (SECM) *Biosensors and Bioelectronics*. 18:141-149.