



Micropotentiometric mapping of local distributions of Zn^{2+} relevant to corrosion studies

A.C. Bastos^{a,*}, M.G. Taryba^b, O.V. Karavai^a, M.L. Zheludkevich^a, S.V. Lamaka^b, M.G.S. Ferreira^{a,b}

^a Universidade de Aveiro, DECV/CICECO, 3810-193 Aveiro, Portugal

^b Instituto Superior Técnico, ICEMS, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

A Zn^{2+} -selective microelectrode is developed and adopted for determination of Zn^{2+} in the course of corrosion processes. Details of construction are given, together with a preliminary characterization of the electrode's properties. Successful application to examples of zinc dissolution, zinc electroplating and corrosion in defects of coated galvanised steel shows the suitability of this microelectrode for materials science and corrosion research.

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1. Introduction

Zinc is a metal of great technological importance being mostly used in galvanising of steel, batteries, brass metallurgy, die casting, as metal sheet and in chemical compounds for a broad range of industries. It also plays a significant role in a number of human metabolic processes [1]. As a consequence, the quantification of Zn^{2+} is of interest to many different areas. Potentiometry is a sensitive technique suited for many practical situations and ion-selective electrodes (ISE) for Zn^{2+} have been proposed by several authors (see [2,3] and references cited therein). Miniaturized ISE can be of great value when small volumes are to be probed or when the spatial distribution of the Zn^{2+} is to be mapped at the microscale. A microelectrode for potentiometric Zn^{2+} detection was described in reference [4]. Alternatively, an amperometric mini-sensor has been used to investigate the spatial distribution of Zn^{2+} during galvanic corrosion of a Zn/steel couple [5]. In spite of these advances, it's difficult to find published work using microelectrodes for Zn^{2+} detection, either potentiometric or amperometric.

In this paper a potentiometric Zn^{2+} -selective microelectrode (Zn^{2+} -SME) based on a new cocktail containing tetra-*n*-butyl thiuram disulfide ionophore [6] is developed and applied to corrosion studies.

2. Experimental

2.1. Microelectrode construction and potentiometric set-up

A membrane cocktail for the Zn^{2+} -SME was composed of 7 wt.% tetra-*n*-butyl thiuram disulfide, 22.8 wt.% (150 mol.% relative to ionophore) sodium-tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate and 1.4 wt.% tetrakis(4-chlorophenyl)borate tetradodecylammonium (ETH 500), dissolved in 2-nitrophenyloctyl ether (68.8 wt.%). All reagents were Selectophore grade from Fluka.

The Zn^{2+} -SMEs were made following a series of steps. In the first, borosilicate glass capillaries were pulled to micropipettes with tips of 2 μm on one side using a P97 Micropipette Puller (Sutter, USA). The glass of the micropipettes was made hydrophobic by putting them for 2 h in an oven at 200 °C after injecting 200 μL of *N,N*-dimethyltrimethylsilylamine (Fluka, Ref. 41716). The micropipettes were back-filled with 0.1 M KCl + 0.01 M KH_2PO_4 + 10^{-5} M ZnCl_2 – internal solution – to a length of 5 mm from the tip and tip-filled with a 65 ± 5 μm column of the membrane cocktail. Each micropipette was inserted in a half-cell plastic holder containing a silver/silver chloride wire.

The microelectrode was mounted in a 3D positioning system and connected to an IPA2 amplifier (input resistance $>10^{15} \Omega$) manufactured by Applicable Electronics Inc. (USA). A homemade Ag/AgCl electrode with agar–agar stabilized 0.05 M NaCl worked as external reference. The ASET program (Sciencewares, USA) con-

* Corresponding author. Tel./fax: +351 234378146.

E-mail address: acbastos@ua.pt (A.C. Bastos).

trolled the measurements and recorded the data in a Scanning Ion-selective Electrode Technique (SIET) mode.

2.2. Measurements

The Zn^{2+} -SME was calibrated using ZnCl_2 (Fluka, p.a.) solutions prepared in distilled water or in 5 mM NaCl (Fluka, p.a). The activity of Zn^{2+} in each solution was calculated using the extended Debye–Hückel equation [7]. The response time was measured according to IUPAC recommendations [8] using a “dual drop cell” described elsewhere [9]. The meaning of response time τ_{95} and τ_{lim} and calculation procedure are described in [8,9]. The selectivity coefficient to Na^+ was determined by modified separate solution method, calibrating the Zn^{2+} -SME in pure solutions of Zn^{2+} and in pure solutions of Na^+ [8,10].

The Zn^{2+} -SME was tested in two sets of experiments designed to reproduce typical cases expected to be found in practical corrosion studies. In the first, a pure zinc wire (1 mm in diameter) embedded in a non conductive polymer and polished to make a disk electrode was connected to a home built power source in a two electrode arrangement with a Pt auxiliary electrode. By this way it was possible to simulate: (a) the corrosion of zinc in 5 mM NaCl (no current passing in the circuit), (b) zinc electrodeposition (zinc wire immersed in 5 mM NaCl + 10 mM ZnCl_2 with a current of $-10 \mu\text{A}$ passing in the circuit) and (c) forced oxidation of the zinc wire (in 5 mM NaCl + 10 mM ZnCl_2 and a current of $+10 \mu\text{A}$ passing in the circuit). Maps with 30×30 points of pZn ($-\log a_{\text{Zn}^{2+}}$) were measured by SIET in solution 100 μm above the surface with an acquisition time of 3 s in each point.

A second experiment was the mapping of both pZn and ionic currents in 5 mM NaCl solution above a coil-coating sample with two round artificial defects 170 μm in diameter. The sample consisted of a carbon steel substrate with 7.5 m thick electroplated zinc layer and 20 m thick epoxy paint with TiO_2 pigmentation. The defects were made manually with a sharp needle and the size and depth were similar for both defects, confirmed by optical microscopy. The maps were acquired in two planes, one parallel (plane xy) at 100 m from the surface and another normal to the surface exactly above the defects (plane xz). The ionic currents

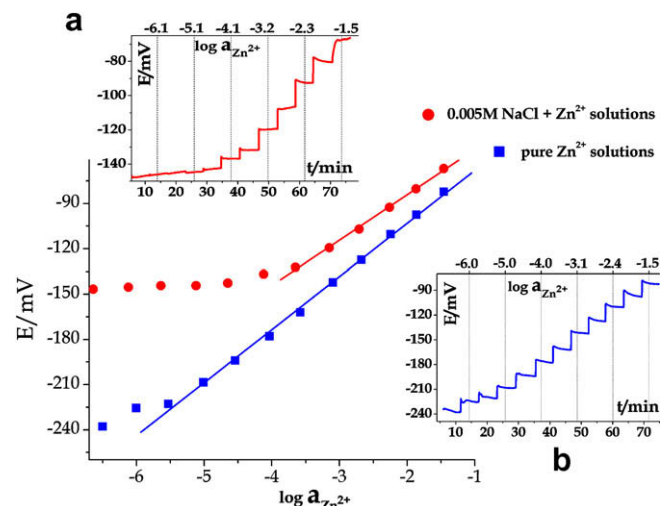


Fig. 1. Zn^{2+} -SME potentiometric response to the activity of Zn^{2+} ions (ZnCl_2) in 5 mM NaCl and in distilled water. Insets: typical dynamic calibration curves taken in solutions of Zn^{2+} with 5 mM NaCl background (a) and pure solutions of Zn^{2+} (b).

were measured with a SVET (scanning vibrating electrode technique) from Applicable Electronics (USA). This technique measures potential differences in solution which, after a calibration, can be presented as ionic currents in solution [11,12]. SVET measurements were performed as described elsewhere [13] with maps of 50×50 points and an acquisition time of 0.3 s in each point. pZn maps comprised 30×30 points with 6 s of acquisition in each point.

3. Results and discussion

Several approaches were made while trying to compose a membrane cocktail for Zn^{2+} -SME. At first, a membrane described in [6] was adopted for microelectrode by excluding the polymeric matrix, poly(vinyl chloride). However, the high selectivity claimed in [6] could not be reproduced. Moreover, the prepared microelec-

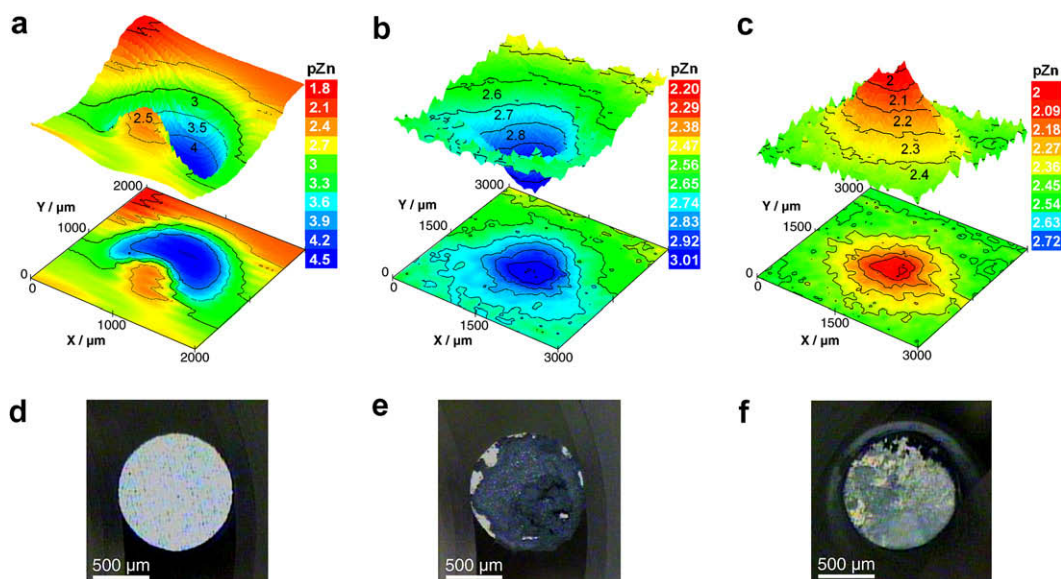


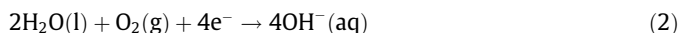
Fig. 2. Distribution of Zn^{2+} in a plane 100 μm above a polished zinc wire at different polarization conditions: zinc wire immersed in 5 mM NaCl after 6 h corroding at open circuit potential (a), zinc wire in 5 mM NaCl + 10 mM ZnCl_2 after 6 h passing a current of $-10 \mu\text{A}$ (b), zinc wire in 5 mM NaCl + 10 mM ZnCl_2 after 1 h passing a current of $+10 \mu\text{A}$ (c). Picture (d) corresponds to the wire immediately after immersion and (e) and (f) show the wire's surface after 6 h of cathodic and 1 h of anodic polarization, respectively.

trodes showed unstable potential and could not be used for localised measurements. Highly lipophilic and stable ionic sites (sodium-tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate and tetrakis(4-chlorophenyl)borate tetradodecyl-ammonium) were introduced into the membrane composition in order to increase the membrane's conductivity and stabilize the electrode's potential. The electrode's potentiometric response over a range of Zn^{2+} solutions prepared with ZnCl_2 in distilled water or in 5 mM NaCl is presented in Fig. 1. Insets show the typical time dependant calibration curves. In distilled water the response is linear from $\text{pZn} = 5.5$ to 1.5 with a slope of 34.8 mV per decade of Zn^{2+} activity while in the solutions with NaCl the response is linear from $\text{pZn} = 3.5$ –1.5 with a slope of $30.4 \text{ mV decade}^{-1}$. The time of response was $\tau_{95} = 2.6$ and $\tau_{\text{lim}} = 4.6$ s. It becomes clear from Fig. 1 that NaCl influences the electrode's response which is confirmed by the selectivity coefficient $\log K_{\text{Zn}^{2+}, \text{Na}^+}^{\text{pot}} = -1.4$.

The suitability of the developed Zn^{2+} -SME for corrosion studies was confirmed in two sets of experiments as described above. Fig. 2a shows the zinc wire corroding at open circuit potential in 5 mM NaCl. Two distinct regions can be observed. A small region of lower pZn (higher activity) is associated with a localised anodic area where zinc oxidises releasing Zn^{2+} to solution according to,



This is consistent with the accepted view that in near neutral chloride solutions zinc corrodes with the development of pitting [14,15]. A second region covers the remaining area of the wire and shows high pZn (low values of Zn^{2+} activity). This is considered to correspond to the cathodic area, where reduction of dissolved oxygen takes place by,



The low activity of Zn^{2+} in this region is interpreted as being a consequence of the precipitation of Zn^{2+} to Zn(OH)_2 due to the local high pH generated by the oxygen reduction. The local activity of Zn^{2+} is even lower compared to that in the bulk solution, which increases with time due to the corrosion of the Zn wire.

When a negative current is made to pass in the electrochemical cell, Zn^{2+} is reduced and deposited on the zinc wire via the reverse of reaction (1). The zinc wire is a sink of Zn^{2+} and the microelectrode maps a region in solution on the top of it with low Zn^{2+} activity, due to its consumption in the reduction reaction – Fig. 2b. If, on the contrary, a positive current is made to pass, the oxidation of zinc – reaction (1) – is favoured, the zinc wire becomes a source of Zn^{2+} , and its local increment in solution is detected by the Zn^{2+} -SME – Fig. 2c. The wire's surface becomes non uniform after several hours of continuous reduction or oxidation. The zinc deposit did not cover the wire evenly (Fig. 2e) and the corroded areas were located preferentially in some regions of the sample (Fig. 2f). These observations point to a non uniform distribution of Zn^{2+} near the Zn wire. The maps obtained at $100 \mu\text{m}$ height from the surface with 30×30 points were not able to resolve this local distribution. A larger number of points collected closer to the surface would be necessary for a better resolution.

Fig. 3 shows a coated sample with two artificial defects after 8 days of immersion in 5 mM NaCl. The ionic current maps obtained by SVET (Fig. 3b) show that one defect is mainly anodic (positive currents, red colour) and the other is mainly cathodic (negative currents, blue colour). Reactions (1) and (2) are considered to predominate in the anodic and cathodic defects, respectively. The ionic currents are located close to the defects with the bulk solution remaining undisturbed.

The Zn^{2+} distribution in solution measured with the Zn^{2+} -SME is depicted in Fig. 3c and shows what's to be expected after analysis of the SVET maps: higher Zn^{2+} activity in the anodic region and

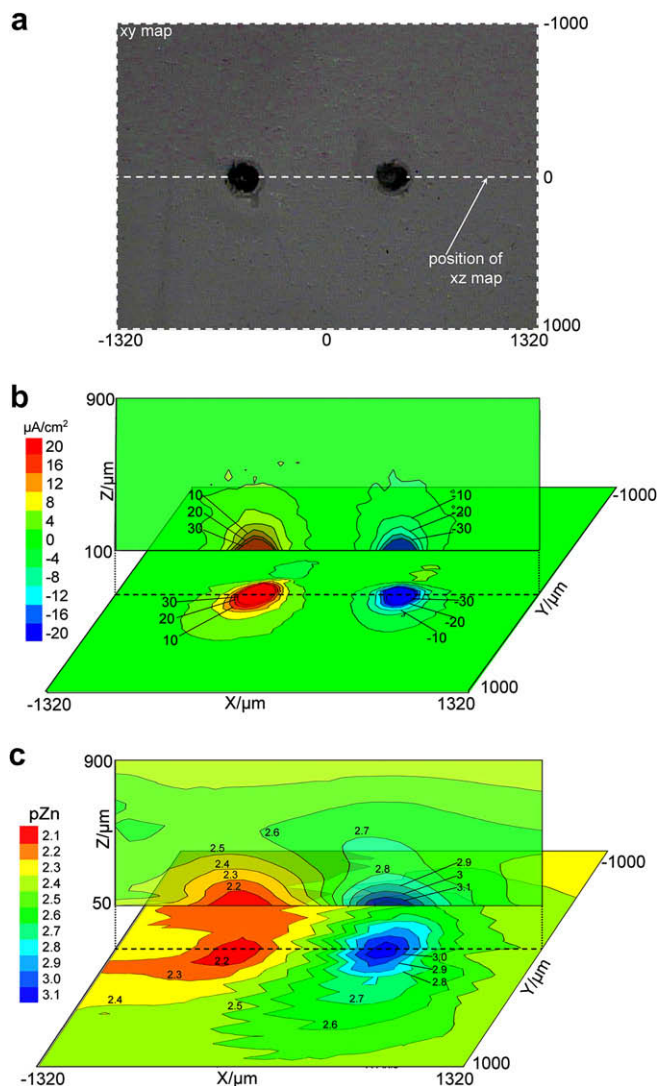


Fig. 3. Picture of painted electrogalvanised steel with two artificial defects after 8 days of exposure to 5 mM NaCl (a); SVET maps of the ionic currents in solution measured in the xz plane, normal to the surface, and in the xy plane, parallel to the surface (b); distribution of Zn^{2+} in solution obtained in the xz and in the xy planes (c). Maps in xy plane were taken at $100 \mu\text{m}$ above the surface and the scanned area corresponded to the area of figure (a).

lower activity in the cathodic site. In fact, no change in activity would be expected in the cathodic defect as neither Zn nor Zn^{2+} take place in reaction (2). However, as discussed above, due to the high pH near the cathodic defect, the zinc cations will be precipitated and the activity there will be lower compared to the surrounding solution.

The reported data shows promising results. Examples focused on corrosion research but this microelectrode can be used in other fields of application without modification. The influence of NaCl on the potentiometric response may pose some limitations. Work will continue in order to improve the selectivity and time of response of the Zn^{2+} -SME.

4. Conclusions

A Zn^{2+} -selective microelectrode was developed and successfully applied to simple but important cases in materials science and corrosion research: zinc dissolution, zinc electroplating and corrosion in defects of painted galvanised steel. The presented data show promising results but work is still needed to improve the elec-

trode's response, particularly the selectivity to Na^+ that would enable extension of the linear response in NaCl solutions.

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