Electrochemistry Communications 12 (2010) 394–397

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

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

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ARTICLE INFO

Article history:
Received 1 December 2009
Received in revised form 21 December 2009
Accepted 4 January 2010
Available online 7 January 2010

Keywords:
Corrosion
Zinc
Ion-selective microelectrode
SIET
SVET
Localised electrochemical technique

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.

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 $>10^{15}$ Ω) 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-

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doi:10.1016/j.elecom.2010.01.002

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 $-10\ \mu$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 μA passing in the circuit). Maps with 30 × 30 points of pZn ($-\log a^{2+}_{\mathrm{Zn}}$) 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 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.

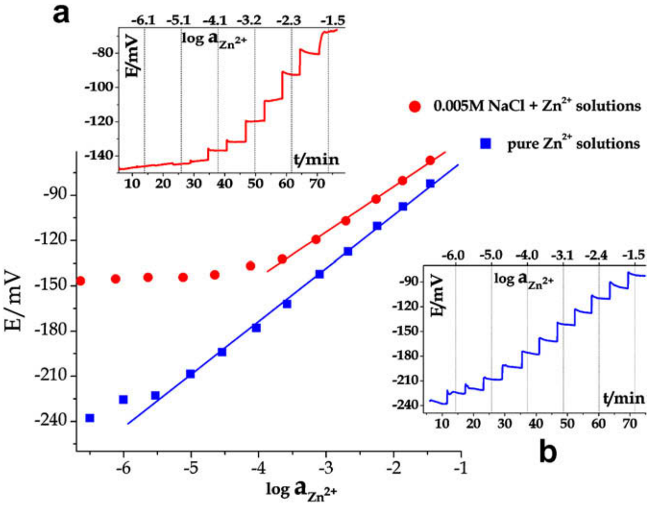

Fig. 1. Zn^{2+}-SME potentiometric response to the activity of Zn^{2+} ions (ZnCl$_2$) in 5 mM NaCl and in distilled water. Insets: typical dynamic calibration curves taken in solutions of Zn^{2+} with 5 mM NaCl background (a) and pure solutions of Zn^{2+} (b).

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-

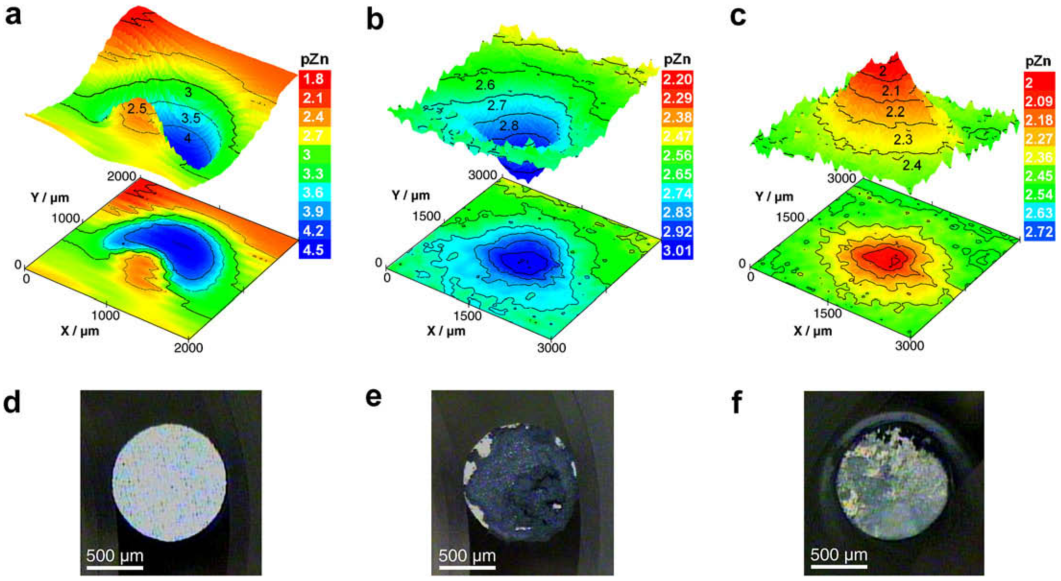

Fig. 2. Distribution of Zn^{2+} in a plane 100 μm above a polished zinc wire at different polarization conditions: zinc wire immersed in 5 mM NaCl after 6 h corroding at open circuit potential (a), zinc wire in 5 mM NaCl + 10 mM ZnCl$_2$ after 6 h passing a current of $-10\ \mu$A (b), zinc wire in 5 mM NaCl + 10 mM ZnCl$_2$ after 1 h passing a current of +10 μA (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.