Electrochemistry Communications 44 (2014) 38–41

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

Characterisation of localised corrosion processes using scanning electrochemical impedance microscopy

Volodymyr Kuznetsov [a], Artjom Maljusch [a], Ricardo M. Souto [b], Aliaksandr S. Bandarenka [c,*], Wolfgang Schuhmann [a,c,**]

[a] *Analytische Chemie — Elektroanalytik & Sensorik, Ruhr-Universität Bochum, 44780 Bochum, Germany*
[b] *University of La Laguna, Department of Chemistry, 38200 La Laguna, Tenerife, Spain*
[c] *Center for Electrochemical Sciences, Ruhr-Universität Bochum, 44780 Bochum, Germany*

ARTICLE INFO

Article history:
Received 21 March 2014
Received in revised form 11 April 2014
Accepted 16 April 2014
Available online 24 April 2014

Keywords:
Electrochemical microscopy
Impedance
EIS
Corrosion
Localised measurements

ABSTRACT

The concept of scanning electrochemical impedance microscopy (SEIM) is described for the studies of localised corrosion processes at metallic surfaces under conditions which simulate those present in the environment. SEIM is based on acquisition and comprehensive analysis (with modelling and spectra fitting) of arrays of localised impedance spectra obtained in a single area scan. This gives accurate quantitative information about important corrosion properties of non-uniform metal surfaces. It is demonstrated that SEIM-approach is advantageous in visualisation of surface domains with similar topography and morphology but different electrochemical properties as well as enables extracting parameters important in assessing local corrosion currents.

1. Introduction

Electrochemical impedance spectroscopy (EIS) measurements play a vital role in corrosion research [1–4]. EIS is informative and non-destructive method that is particularly helpful in elucidation of mechanisms of electrochemical reactions in corroding systems and in revealing important properties of passivation layers or protective films. The main pillars of the impedance analysis are (*i*) the physical modelling of the electrochemical interface and (*ii*) subsequent fitting of experimental spectra to the models in order to extract relevant physico-chemical parameters determining the properties of the electrode/electrolyte boundary. However, there is one significant issue related to this approach. Classical EIS is a “macroscopic” technique that gives only average information about the whole exposed electrode surface and, therefore, it is better suitable for characterisation of rather uniform sample surfaces.

It is well-known that corrosion of real-world metal surfaces often starts and develops at specific domains complicating the interpretation of “global” impedance data. This straightforwardly suggests that some localised impedance measurements can, in principle, provide the necessary alternative to classical EIS [5]. However, there should be several additional conditions determining the informative power of this microscopic approach. First of all, the metallic sample should always be very close or at the open circuit potential: even a very small deviation from the steady state conditions caused by alternating current (AC) probing at quasi-potentiostatic conditions can significantly influence the long-term corrosion test results. The second issue is related to the efficient visualisation of domains with different electrochemical properties in-situ, under real conditions of corrosion experiments. Ideally, this visualisation should be based on monitoring of easily interpretable parameters related to the electrode/electrolyte interface status. Finally, it is especially important to accurately quantify the critical properties of the revealed domains, e.g. in terms of the local corrosion currents.

The first two issues can be addressed by 4D-alternating current scanning electrochemical microscopy (AC-SECM) [6,7]. In this approach, the sample is not connected to any potentiostat, and the AC-perturbation is applied to the tip of significantly smaller dimensions than the substrate. By following this procedure, any eventual electrical cross-talk between the sample and the tip [8] is greatly minimised if occurring at all, and the surface status of the substrate either remains unaffected or is only minimally influenced by the probing tips. Thus, the required contrast between different domains can be adjusted by selecting impedance data taken using an appropriate AC-probing frequency (from the arrays available as a result of a single area scan). Those 4D AC-SECM datasets can be further analysed to separate the contribution of the SECM-

---

[*] Corresponding author. Tel.: +49 234 3229433.
[**] Correspondence to: W. Schuhmann, Analytische Chemie — Elektroanalytik & Sensorik, Ruhr-Universität Bochum, 44780 Bochum, Germany. Tel.: +49 234 3226200.
E-mail addresses: aliaksandr.bandarenka@rub.de (A.S. Bandarenka), wolfgang.schuhmann@rub.de (W. Schuhmann).

http://dx.doi.org/10.1016/j.elecom.2014.04.011
1388-2481/

microscope tip and the sample itself, thus visualising different surface domains using more intuitively understandable parameters, e.g. the double layer capacitance of the sample [9]. The third requirement needs special efforts, especially if the difference between the nature and composition of the surface domains is very small, and when this difference can only be revealed under specific conditions of the real-world corrosion tests.

In this contribution we describe the concept of scanning electrochemical impedance microscopy (SEIM) for the studies of localised corrosion processes at metallic surfaces in-situ. We demonstrate that this approach efficiently distinguishes domains with similar topography and morphology but different electrochemical properties, as well as gives parameters helpful in assessing local corrosion currents.

2. Experimental

Localised impedance spectra were acquired according to procedures described elsewhere in detail [6,7,9] using a setup shown schematically in Fig. 1A. The spectra were recorded using a Gamry Reference 600 Potentiostat with a FRA-module (Gamry Instruments, Inc.). The data were collected at each point during area scans in the frequency range between 150 kHz and 15 Hz using probing signal amplitudes of 35 mV. We avoided lower probing frequencies to maintain a reasonable time for data acquisition during the scans. The distance between the tip apex and a sample surface was 3 μm applying distance correction settings acquired in a preliminary tilt correction procedure. A 2 μF capacitor was connected between the reference electrode (RE) and counter electrode (CE) to minimise possible errors caused by the potentiostat at higher frequencies.

The quality of the spectra was checked using the "linear" and "logarithmic" Kramers–Kronig check procedures [10,11]. The quality of the fitting was controlled by the root-mean-square deviations and estimated individual parameter errors to ensure the validity of the model and the correctness of the fitting. The relatively high amplitude of the probing signal was the maximal allowed by the Kramers–Kronig check procedures. The impedance datasets were analysed with a home-made "EIS Data Analysis" software according to the procedure described previously [12].

All solutions were prepared using Milli-Q water, Na_2SO_4 (*pa*, Sigma Aldrich), and benzotriazole (BTAH; Avocado Research Chemicals Ltd., Ref 15423). 1 mM Na_2SO_4 was used as a working electrolyte.

Brass samples (37% Zn, 63% Cu, Goodfellow) were polished with diamond aqueous slurries (3, 1, 0.5 μm; LECO Corporation) and cleaned in an ultrasonic bath with acetone, isopropanol, and water. 1 mM inhibitor solutions were prepared by dissolving BTAH in 100 mM KCl (*pa*, Sigma Aldrich). Polished and cleaned substrates were partially immersed in the inhibitor solution for 45 min to modify the surface.

SECM-tips were made from a Pt wire ~20 μm (Fig. 1B) with the diameter of the glass shield of ~150 μm. A Pt wire and an Ag/AgCl were used as a CE and a RE, respectively.

Surface topography of the modified and non-modified samples was investigated by tapping mode AFM in air (JPK, NanoWizard 3); rms roughness was estimated to be ca. 8 nm. Combined scanning Kelvin probe force microscopy (SKPFM) experiments were performed using the frequency shift detection mode at a scan height of 50 nm.

3. Results and discussion

Fig. 1A shows a scheme of SEIM experiments. A glass shielded Pt microelectrode (tip, Fig. 1B) is positioned very close to the sample surface (1–3 μm) and plays the role of the WE. The metallic sample with two types of surfaces (non-protected brass and the areas pre-treated with the BTAH corrosion inhibitor, as shown in Fig. 1A) is not connected to the potentiostat and, therefore, is always under the open circuit

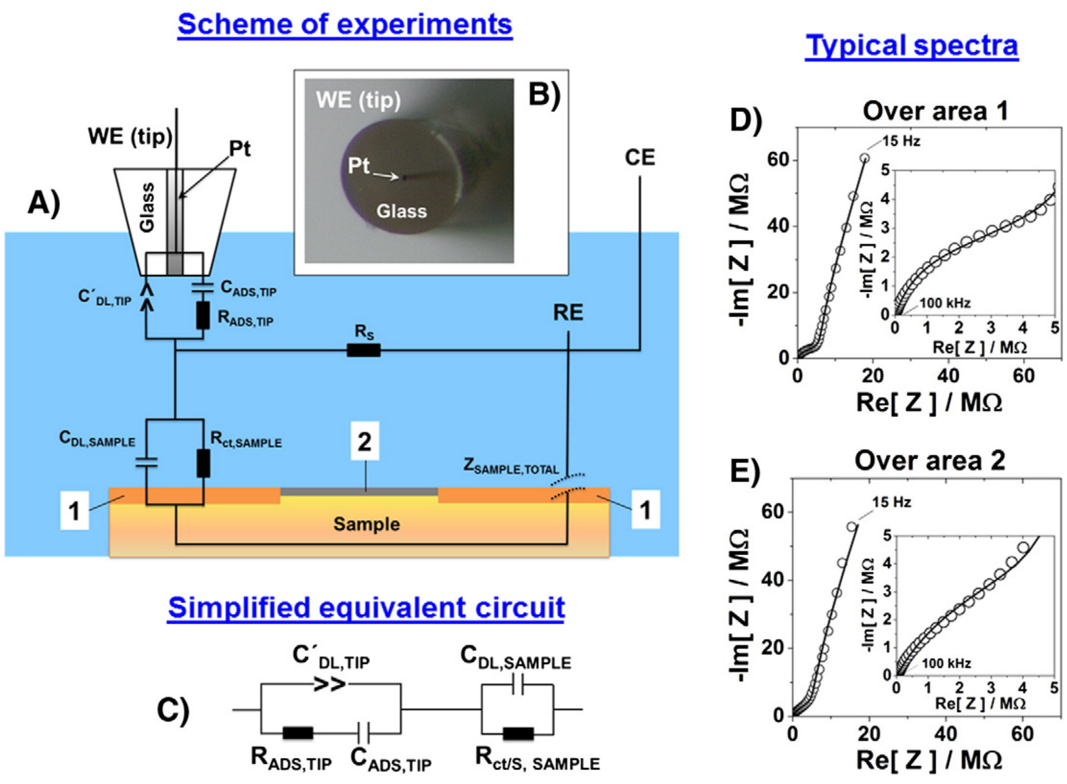

Fig. 1. (A) Schematic representation of SEIM-measurements over the metal sample where the areas 1 and 2 correspond to BTAH-modified and non-modified areas, respectively (see text). (B) Photographic image of the working part of a typical microelectrode (tip) used in SEIM experiments. (C) A simplified equivalent electric circuit elucidated from the impedance analysis. (D, E) Typical localised impedance spectra (circles) with fitting results (lines) obtained over (D) area 1 and (E) area 2 of the sample, respectively.