Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 52 (2006) 854–862
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Positive and negative AC impedance feedback observed above conductive substrates under SECM conditions

Piotr M. Diakowski, Andrzej S. Baranski *

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK, Canada S7N 5C9

Received 18 March 2006; received in revised form 20 June 2006; accepted 21 June 2006
Available online 26 July 2006

Abstract

A relationship between the tip response and the tip-to-substrate separation distance was investigated under alternating current scanning electrochemical microscopy (AC-SECM) conditions. For insulating substrates only negative AC feedback was observed. However, in the case of conductive substrates positive as well as negative AC feedback could be observed depending on experimental conditions. The theoretical model proposed in this work explains very well all observed trends and allows for qualitative predictions of the tip impedance in AC-SECM as a function of various experimental conditions (including: frequency, the supporting electrolyte concentration, the tip-to-sample separation distance and the tip diameter). In this theoretical model the double-layer capacitance of the tip and the sample is represented by a constant phase element (CPE), rather than an ideal capacitor. The paper also describes how raw experimental impedance data can be corrected for imperfections of the measuring system.

Keywords: Scanning electrochemical microscopy; AC-SECM; Constant phase element; Frequency dispersion of double-layer capacitance; Approach impedance

1. Introduction

Scanning electrochemical microscopy (SECM) [1] is a scanning probe method (SPM) [2] that is often used to visualize surface topography and surface reactivity. As in other SPMs, a minute probing tip is scanned over a sample surface usually at the tip-to-sample separation distance, *d*, comparable to the dimension of the probing tip.

Typically, SECM experiments are carried out in a DC amperometric feedback mode [3] or generation/collection mode (GC) [4], where in both cases the Faradaic current at a mobile ultramicroelectrode (UME) is measured. Also, potentiometric measurements are not uncommon [5]. In the case of feedback and generation/collection SECM, the tip current is controlled by the diffusion of electroactive species present in solution. At close separations between UME and an insulating substrate a negative feedback current is observed due to the blocking nature of the substrate. In contrast, positive feedback is observed when the tip is placed in close proximity to a conductive sample, since the redox species depleted by the tip reaction are regenerated at the conductive substrate. In the positive feedback mode the tip current is also very sensitive to the rate of electron transfer between the mediator and the substrate. Consequently the tip current is a function of the separation distance and nature of the sample surface. Usually to characterize the nature of the sample, a so called SECM approach curve is recorded, which represents the UME current dependence on the tip-to-sample separation distance, *d*.

Despite the growing popularity and increasing number of SECM applications, a review of the recent literature indicates that very little work has been devoted to carrying out SECM experiments under alternating current (AC) conditions. A successful application of the AC measurements in SECM was first reported by Horrocks et al. [6] in 1993. In this case, impedance measurements were used to control the separation distance between an ion-selective tip and a sample surface, because potentiometric probes do not produce suitable feedback signal. The application of an alternating voltage between the SECM tip and the auxiliary electrode, and continuous monitoring of the tip impedance allowed for the calibration of the distance scale.

In recent years an increase of interest in AC-SECM has occurred. Alpuche-Alviles and Wipf [7] demonstrated that AC

* Corresponding author. Tel.: +1 306 966 4701; fax: +1 306 966 4730.
E-mail address: baranski@duke.usask.ca (A.S. Baranski).

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.06.020

feedback signal can be employed to control the tip-to-sample separation distance during amperometric feedback and GC SECM experiments. Later, Schuhmann and co-workers [8–10] have shown that under AC-SECM conditions, imaging of microscopic domains of different conductivity can be carried out without a redox mediator present in the solution, which presents a major advantage over DC amperometric SECM. Moreover, a method that allows for the imaging of mixed substrates under alternating current conditions and shear-force based distance control was proposed by Etienne et al. [11]. Another group has also confirmed that SECM operated in an AC mode can be used for imaging of model sample surfaces [12]. Baur and co-workers [13] demonstrated that AC-SECM operated in the constant impedance (constant distance) mode can be used to visualize model neurons, and that imaging can be carried out directly in the cell growth media without the addition of the redox mediator, which is difficult to achieve with amperometric feedback SECM. Other important contribution was made by Ervin and White [14] who used AC-SECM to study membrane pores. It should be emphasized however, that topography can be imaged by AC-SECM only if there are no changes in local impedance or the surface properties [13]. Therefore, in the case of an unknown sample constant distance approach (for example by means of shear-force feedback) has to be used to separate topographical information from local variations in impedance signal.

However, despite a growing interest in AC-SECM, a basic relationship between the AC tip response, tip-separation distance and nature of the sample (i.e. approach curve), has not received adequate attention of researchers. It should be emphasized that knowledge of approach curves has fundamental importance for SECM applications. All the above-cited reports agree that in the case of insulating substrates, negative AC feedback is observed at close tip–substrate separations. In this case impedance of the two-electrode system (tip and auxiliary electrodes) is assumed to be similar to the impedance of an equivalent circuit consisting of a series combination of a solution resistance, R_S (that develops between the two electrodes) and the double-layer capacitance, C_{dl}, of the tip electrode. It is clear that in electrolytes of sufficiently low conductivity and/or at sufficiently high frequencies, the impedance of the system is mainly represented by the R_S, which strongly depends on the tip–sample separation distance. However, in the case of conductive substrates, the situation is somewhat less clear and the observed behavior differs from one report to another. For instance, Alpuche-Alviles and Wipf [7] indicate that the tip response shows the same general response regardless of whether insulating or conductive substrates are used, i.e. an increase in tip impedance is observed in the vicinity of the substrate surface. On the contrary, Ballesteros Katemann et al. [8] reported that a positive AC feedback was observed at small separation distances between tip and conductive samples, i.e. a decrease in tip impedance was observed. A similar behavior above conductive samples was also reported by Horrocks et al. [6] and by Gabrielli et al. [12]. Again, a negative AC feedback was observed on approach to a conductive surface by Etienne et al. [11] and the authors have made a point that similar behavior was also reported by Alpuche-Alviles and Wipf [7] (although in that work experiments were carried out at considerably higher frequencies and in the presence of the redox species).

In our earlier work [15], we demonstrated experimental evidence, that in fact, depending on the experimental conditions both positive as well as negative AC feedback can be observed on approach to conductive substrates. In that paper we also proposed a simplified equivalent circuit model corresponding to the case when the tip electrode is placed in close proximity to the large conductive substrate.

In the current report, a detailed consideration, supported by experimental evidence, is given to the phase resolved AC-SECM approach curves observed over unbiased conductive as well as insulating substrates. Experimental AC-SECM approach curves are discussed in the context of the earlier proposed equivalent circuit models [15]. The generic constant phase element (CPE) [16] is introduced as a substitute for ideal capacitors in the equivalent circuit model, and together with the readily available analytical expressions for the amperometric feedback SECM current [17], it is used to predict experimentally observed behavior.

2. Experimental

All solutions were prepared in double-distilled deionized water (Corning Mega-Pure System, MP-6A and D-2) using ACS grade chemicals. KCl used in the approach experiments was purchased from BDH Chemicals. All electrochemical measurements were carried out without the removal of dissolved oxygen.

Working ultramicroelectrodes used in this study were prepared by sealing Pt wires (Alfa-Aesar) into Corning Kovar Sealing glass tubing #7052 (World Precision Instruments) by a method described elsewhere [15]. The RG parameter (i.e. the ratio between the outer diameter of the insulating glass sheath and the diameter of the platinum wire) of a typical tip prepared by this method was between 8 and 10. The RG parameter was determined using an optical microscope equipped with a digital camera and confirmed by recording DC amperometric approach curves to an insulating substrate. The surface of the working electrode was polished with 3 and 0.3 μm aluminum oxide finishing films (TrueView Products Inc). The size of all disk electrodes used in this work is described in terms of their diameter. Approach curve experiments were carried out with a tungsten wire used as a pseudoreference electrode; however, all potentials in this paper are reported versus the standard Ag/AgCl electrode. A microscope slide and a platinum plate (Alfa-Aesar) attached to a microscope slide served as model substrates.

All experiments were carried out using the in house built SECM setup described elsewhere [15]. That setup was built around a MX760R motorized micromanipulator (SD Instruments, USA), however, in the current investigation only Z-axis motor was used to perform the approach curve experiments. The SECM setup was interfaced with a personal computer and controlled via serial port communication. The whole assembly, micromanipulator, electrochemical cell, and tip electrode was housed in a grounded Faraday cage to reduce environmental interference.

A custom-built electronic system was used to control the micromanipulator and to perform all necessary data acquisition