Electrochimica Acta 136 (2014) 121–129

Contents lists available at ScienceDirect

Electrochimica Acta

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

Development of Nano-Disc electrodes for Application as Shear Force Sensitive Electrochemical Probes

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ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 7 May 2014
Accepted 7 May 2014
Available online 22 May 2014

Keywords:
Electrochemistry
Shear Force
Nanoelectrode
scanning electrochemical microscopy (SECM)

ABSTRACT

Maintaining a well-defined tip-to-substrate separation is a critical area of development in scanning electrochemical microscopy (SECM). One technique that provides topographic data independently to the electrochemical measurement is shear force (SF) SECM. SF measurements are highly sensitive to factors including the tip-to-substrate separation, experimental solution, and probe geometry. We present a procedure for the fabrication of highly reproducible electrochemical probes with an active electrode disc with radii between 3 nm to 190 nm. A systematic study of the SF characteristics of these nano electrodes provides details on how to achieve the highest sensitivity and stability of SF signals, and maximize the number of SF sensitive frequencies. A new methodology to identify SF sensitive frequencies without needing to immerse the probes in solution or approach the surface is presented. Furthermore, we demonstrate that the greatest source of error in achieving reproducible SF behavior lies in the positioning of the piezo electric components and the piezo-nano electrode interface.

1. Introduction

Scanning electrochemical microscopy (SECM) is a well-established electroanalytical method for the characterization of substrate surfaces.[1] This method has been applied to several analytically relevant fields including bioelectrochemistry,[2,3] corrosion studies,[4] charge transport at liquid/liquid interfaces[5–7] and microfabrication.[8] In conventional SECM, a "constant height" mode is used, where, under ideal experimental conditions, the ultramicroelectrode (UME) is moved parallel to the substrate (*x*,*y* plane) with no vertical motion (*z* axis) of the UME. In this case, the UME signal depends on the local topography and electrochemical reactivity of the substrate.[9] To decouple the current contribution of topography from surface reactivity several methodologies have been proposed. For example by using impedance [10,11] or alternating current signals,[2] the topographic and surface reactivity can be determined by post-processing of the data. Alternatively, a dual electrode probe where one UME monitored a surface independent reaction to determine the topography (*e.g.* the reduction of oxygen), whilst the second UME monitored the substrate sensitive reactant has been reported.[12] The physical interaction between the tip and substrate can be used in hybrid SECM systems,[13–15] for example, tip-position modulation (TPM) algorithms,[16] intermittent-contact mode (IC),[17] voltage switching mode (VSM)[18] and SF detection which rely on the reduced damping of a vertically or laterally vibrated probe in close proximity to the substrate.[19–21] SF force distance controlled SECM is used routinely by several electrochemistry laboratories to report the topography of a variety of surfaces, including live cells,[22,23] large and complex metal samples,[24] or to monitor local activities of ions in proximity of a solid/liquid interface.[25] The method employs a feedback signal based on changes of SF tip to substrate interactions to maintain a constant probe-substrate separation. These SF interactions may be attributed to hydrodynamics forces, Van der Waals interactions, direct mechanical contact and capillary forces.[26] Several types of SF methodologies have been reported in the literature.[19,27,28] Typically, the SF method involves a UME fastened to two piezoelectric plates: dither and receiver.[19] The dither piezoelectric plate induces a sinusoidal lateral mechanical oscillation of the UME, and a receiver

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http://dx.doi.org/10.1016/j.electacta.2014.05.047
0013-4686/

plate detects the oscillation. When the UME is in close proximity to the surface, the lateral oscillation is damped due to SF interactions between the tip and the surface of the sample. As the UME is scanned laterally, a constant tip-to-substrate separation can be achieved by adjusting the *z* position of the probe to maintain a constant SF amplitude. Simultaneously, the height profile (or the topographic variation) of the surface can be constructed from the *z* motion of the probe. Early design for SF constant distance imaging suggested a constant separation mode in which the tip was maintained within the SF sensitive zone throughout all of the measurement.[19] Our system is equipped with a hopping or picking mode[29] SF amplitude controlled unit analogous to what has been described in recent work from Schuhmann.[28] This mode tends to minimize the contact between the tip and the surface by retracting the tip and performing a shear-force *z*-approach curve at each position on the *x*-*y* axes grid. When operating under conditions where the tip and substrate are not in contact, SF-SECM can be applied to substrates that are easily deformed without compromising the electrochemical and topographic data, such as a living cell. Hopping mode can also result in a faster measurement for samples with large topographical variations where the SF signal would be lost in constant distance mode.[28] The SF sensitive region is thought to extend to a few hundred nanometers above the surface,[30] depending on the nature of substrate surface, the viscosity of the liquid, and the tip size, physical properties and geometry.[25,26,30] UMEs with a small tip diameter or a small Rg exhibit shorter length of the SF signal which is very interesting for SECM imaging as it allows the measurement to be performed at a very short tip to substrate distance. [30] Pulled microelectrodes with long tapers producing flexibility reportedly exhibit improved vibrational characteristics, which implies an increased number of shear force sensitive resonance peaks.[9,31] Quartz encapsulated Pt nanoelectrodes display enhanced oscillation features.[27,32] Laser-pulled Pt/quartz disk UMEs, which possess a small diameter and long flexible taper, are suitable for SF experiments. In addition to the UME, instrumental and experimental factors are thought to affect the SF response; these include the piezo-UME interface, the choice of SF sensitive frequencies, the viscosity of the liquid or gas, surface properties of the substrate, and the probe immersion depth.[25,26]

Herein, we report a method for fabricating nano-disc Pt electrodes and the subsequent parametric optimization which provided a highly reproducible, sensitive and stable SF response for frequencies in the range of 350–550 kHz. The identification and selection of these stable SF sensitive frequencies was key to providing high stability for constant distance measurements. Furthermore, we present a fast diagnostic method that was performed entirely off sample in order to rapidly identify SF sensitive frequencies. This methodology removes the need for frequency analysis of the SF signal with the UME in contact with the substrate, significantly reducing the risk of damaging the electrode tip and the substrate during measurements.

2. Experimental

2.1. Preparation and Characterization of Nanoelectrode Probes

The nano-electrodes were fabricated using a P-2000 laser-based micropipette puller system (Sutter Instrument Company, USA) according to a previously published procedure.[33–36] Details on the fabrication procedure can be found in the supplementary information. The quality of the polishing, the radius of the electroactive surface, the platinum-glass seal and the electrochemical behavior of the UME were characterized using cyclic voltammetry in an aqueous solution of 1 mM ferrocenemethanol ($FcCH_2OH$ 97%, Sigma Aldrich, Canada) and 0.1 M potassium chloride (KCl, Fisher Scientific, USA) by linearly sweeping the potential from -100 to 450 mV at a scan rate of 10 mV s^{-1}. The radius of the glass was determined by negative and positive feedback approach curves over an insulating chlorotrifluoroethylene (CTFE) plastic puck and over a well-polished gold disk 1.6 mm (macroelectrode MF-2014 (BASi)), respectively. The speed of approach varied from 0.1 to 1 μm s^{-1} depending on the diameter of the UME. The counter electrode was a platinum wire. Potentials were recorded relative to a chloridized silver wire (in house) quasi-reference electrode.

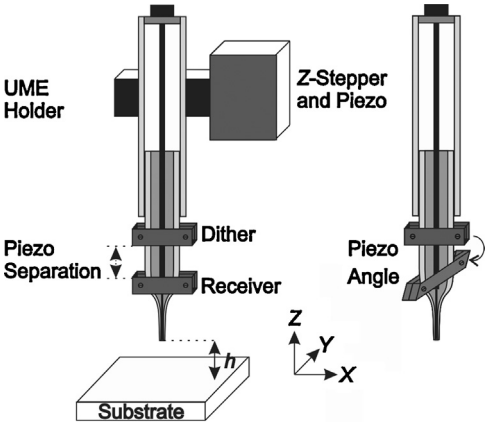

Fig. 1. Scheme of the holder by which the piezos are mechanically mounted to the capillary using four screws (2 screws per piezo). The holder is attached to the Z-stepper motor of the SECM setup.

2.2. SF-SECM Setup

SECM measurements were performed using an ElProScan 3 system (ELP 3), with POTMASTER software (version v2x66) and the ElProScan Controller ESC 3 equipped with a SF unit, SFU 3 (HEKA Elektronik, Germany). The two piezo electric plates (PIC 255, PI Ceramic GmbH, Germany) were mounted on the UME using four screws (2 screws per piezo) as shown in Fig. 1. A frequency scan range from 10 kHz to 1 MHz was performed to identify SF sensitive peaks. A stimulation amplitude of 1 mV to 10 V was applied. The duration of a frequency scan depended the number of samples recorded.

2.3. SF-SECM Measurements

The substrate surface for the SECM mapping was prepared by first cutting a blank gold CD-R into 1 cm x 1 cm chips. The CD-R was immersed in a mixture of concentrated nitric acid and sulfuric acid solution for 1 min to selectively etch the CD. The etching process removed the metallic layer of rewritable CD (Au) from the raised sections (plateaus) whilst leaving the metallic layer exposed within the trenches. Therefore the plateaus were not electrochemically active and the trenches were electrochemically active. The treated CD-R was then washed with water, dried under nitrogen. SF-SECM maps were performed in a solution containing 3.5 mM FcMeOH/0.1 M KCl (100 μL anhydrous ethyl alcohol (Commercial Alcohols, Brampton, Canada) made to 25 mL volume in water).

3. Results and Discussion

3.1. Optimization of UME Fabrication Procedure

UMEs were characterized by scanning electron microscopy (SEM), cyclic voltammetry and approach curves in both positive and negative feedback modes (Fig. 2). The optimization of the UME fabrication procedure has allowed the development of a reproducible technique leading to disk UMEs with long and flexible