



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Scanning electrochemical microscopy imaging with laser-pulled probes☆

Michelle S.M. Li, Fraser P. Filice, Zhifeng Ding*

Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7, Canada

ARTICLE INFO

Article history:

Received 2 May 2016

Received in revised form 21 June 2016

Accepted 29 June 2016

Available online xxxxx

Keywords:

Scanning electrochemical microscopy (SECM)

SECM imaging

Independently addressable microband electrodes (IAMEs)

Nanoelectrode fabrication

Redox cycling

COMSOL simulations

ABSTRACT

The fabrication of Pt nanoelectrodes (NEs) and ultramicroelectrodes (UMEs) were explored through the use of a precision laser electrode puller. As a result of the heated pull, the Pt tips of the NEs were exposed immediately during the fabrication process. Newly fabricated NEs were immediately used to observe the topographical and electrochemical characteristics of a TEM grid by scanning electrochemical microscopy (SECM) horizontal line scans. While higher spatial resolution would be offered by NEs, their use in imaging can be restricted due to sample size and instrumental limitations. To accurately characterize an independently addressable microband electrode (IAME) by SECM, a Pt UME of a known size and geometry was used. SECM depth scan and constant height images were obtained of an unbiased IAME. By utilizing a SECM probe that is similar in size to the Pt and glass microbands of the IAME (4.4 vs. 5 μm , respectively), redox cycling phenomenon was detected. From these electrochemical images, the Pt microbands appeared to be larger than their physical dimensions, while the glass microbands appeared much smaller. Since redox cycling can be affected by sample tilt, the tilt angle of the IAME was quantified through 3 different methods. The first approach was to use the traditional PAC comparison method over different locations on the sample, while the second and third approaches relied heavily on 3D finite elemental analysis simulations representative of the SECM experiments. The first of these two methods required the fitting of a tilted experimental horizontal sweep against a fixed IAME, while the second approach relied on the direct fitting of the experimental data onto tilted depth scan simulations. Each methodology delivered approximately the same tilt angle, confirming the viability of all the methodologies.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Scanning probe microscopy is a family of techniques that utilizes a physical probe to scan above a sample, characterizing its topography and physicochemical features. Scanning electrochemical microscopy (SECM) is a member of this family [1–6]. Since its emergence, SECM has been used in a wide range of applications, including but not limited to microfabrication [7,8], kinetic studies [9,10], and chemical imaging [11–15]. SECM utilizes a biased electrode ($\leq 25 \mu\text{m}$ in diameter) that is scanned over a sample submerged in an electrolyte solution (containing a redox mediator) with extreme precision [2,13,16]. The relationship between the electrode position and tip current is observed and can be represented as single line scans or multi axes current maps (images).

As a result of the potential bias, the redox mediator is converted to its oxidized or reduced form at the electrode tip in an electrochemically driven process. When the biased SECM probe is far from the sample, the resulting faradaic current will be constant, since it is still diffusion-

controlled. However, when the probe approaches a conductive sample, the current will be amplified due to the cyclic regeneration of the mediator at the sample–electrolyte interface (positive feedback). If the sample is insulating, the current will decay due to the depletion of the mediator at the electrode tip (diffusion-limited, negative feedback).

The two most common modes of SECM are constant height and constant distance [2,3,17]. As their names suggest, the constant height mode entails that the electrode is scanned across the sample at a constant height, while constant distance entails a constant tip-to-sample distance that is achieved by moving the electrode up or down to maintain a constant current at the electrode tip. Other modes have since emerged over the years, such as Schuhmann's 4D shearforce-based constant distance mode [18], where the retractions of the tip (shearforce-based) generate a comprehensive 4D data set and images, and depth scan mode (Ding Research Group), which reports the current vs. tip-to-sample distances as a single 2D image [19–21].

The electrode in depth scan mode performs multiple horizontal line scans above the sample, where with each consecutive scan, the electrode takes a downward step in the z-direction. As a result of the real-time generation of the depth scan image, we are able to monitor the electrode's approach toward the sample, avoiding collisions that can potentially harm the electrode or sample. Another advantage to this mode is that since each pixel in the SECM image is composed of both the tip

☆ Dedicated to Professor Hong-Yuan Chen for his many years of pioneering research in electrochemistry and his leadership in bioelectroanalytical chemistry in China.

* Corresponding author.

E-mail address: zfding@uwo.ca (Z. Ding).

URL: <http://publish.uwo.ca/~zfding> (Z. Ding).

current and its coordinates, a single depth scan image can provide several hundreds of probe approach curves (PACs) or horizontal line scans. Combined with finite elemental analysis simulations, PACs can allow researchers to quantitatively analyze sample traits, such as the physical properties and reaction kinetics which cannot be obtained directly from the SECM experiments [22].

Since the resolution of the SECM image is directly dependent on the electrode size, the attractiveness of nanoelectrodes (NEs) as probes are becoming increasingly popular [23]. By using NEs as opposed to ultramicroelectrodes (UMEs, micron scale) in SECM imaging, submicron size structures are no longer lost. Many research groups have developed their own NE fabrication methods [24], including laser pulling [25,26], chemical vapor deposition [27,28], and focus-ion-beam milling [29] techniques. While each method holds its own advantages and disadvantages, the laser pulling method was utilized in this report. Commonly, the conventional fabrication of these electrodes requires a final polishing step; however here, we tested the freshly pulled Pt NEs without this step.

As SECM utilizes the redox cycling principle, where the probe acts as the generator and the sample, the collector, coupling SECM with microstructure arrays, such as independently addressable microband electrodes (IAMEs) or electrode arrays [30] can lead to high amplification of the oxidative/reductive current at the electrode tip [31–35]. In the case of a reversible redox process, the amplification of the current is only dependent on the dimensions of the electrodes in the array and interdigit (glass) space between them.

The SECM probe selected to image a sample must be smaller than the individual features of the sample that require resolving (for instance, the conductive and glass microbands of the IAME). A SECM probe that is much larger than the area(s) of interest (on the sample) will average out the finer features and display either mostly conductive or insulating properties, depending on the nature of the sample. Choosing an IAME and SECM probe close in size, exploration of the redox cycling phenomena can be anticipated. Utilizing an unbiased IAME (sample), the effects of redox cycling should be noticeable when a PAC is extracted to the insulating glass between the two Pt microbands. Variation between the tip-to-sample distances can cause discrepancies in the UME tip feedback current. Therefore, the presence of a tilted IAME sample can lead to inconsistent results. Herein we also explore the use of simulation models to quantify the sample tilt in three different methods: 1) the traditional PAC extraction approach, 2) an experimentally tilted horizontal line scan against a non-tilted simulated depth scan map, and 3) simulated tilted sample depth scan maps against non-tilted experimental data.

2. Experimental section

2.1. Materials

Ferrocenemethanol (FcCH_2OH , 97%) and hexaamineruthenium(III) chloride ($\text{Ru}(\text{NH}_3)_6\cdot\text{Cl}_3$, 98%) were acquired from Sigma–Aldrich (Mississauga, ON), while potassium chloride (KCl, 99%) was obtained from Alfa Aesar (Ward Hill, MA). Stock solutions of 0.9 mM FcCH_2OH or 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ with 0.1 M KCl as the supporting electrolyte were prepared in deionized water (18 M Ω .cm, MilliQ water, Etobicoke, ON). The Pt IAME was purchased from ABTECH Scientific, Inc. (Richmond, VA). The IAME has 4 alternating independently addressable Pt and glass microbands, each 5 μm in width. The 10 nm Formvar and 1 nm carbon-coated 400 mesh Ni TEM grids were obtained from Electron Microscopy Sciences (Hatfield, PA).

2.2. Electrode fabrication

The electrodes were fabricated in-house using a procedure adapted from the Mauzeroll group [36] on a P-2000 laser-based micropipette puller system (Sutter Instrument, Novato, CA). The two modifications

from their established procedure [36] include two single-line heat settings that were used in place of their single-line setting. The first of the two is a partial quartz seal program using a line setting of heat: 580, filament: 003, velocity: 140, delay: 060, pull: 000, followed by the complete quartz seal at heat: 580, filament: 002, velocity: 140, delay: 060, pull: 000. These line settings were found to improve the integrity of the Pt wire for our experimental configuration.

Freshly pulled Pt NEs were first checked optically (under a microscope) for obvious breakage(s) in Pt wire, followed by extension of the internal electrical connections. Following successful visual inspection, these electrodes were tested for electrical connection and Pt size by the use of cyclic voltammetry (CV). Pt NEs were tested using 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ with 0.1 M KCl and these electrodes were used as pulled (unpolished). For the 4.4 μm Pt UME, the tip of the NE was removed, followed by the manual polishing of the tip surface on a home-made polishing wheel attached with abrasive alumina-coated polishing pads (3.0, 0.3, and 0.05 μm , Buehler, Whitby, ON). The size of this electrode allowed for the RG and tip geometry to be optically characterized. UMEs were electrochemically tested using 0.9 mM FcCH_2OH with 0.1 M KCl (CV).

2.3. SECM instrumentation

SECM experiments were performed on an Alpha-SNOM instrument (WITec, Ulm, Germany), specially modified to hold the electrodes. For this report, the Pt UME or NE were used as the SECM probe (working electrode) and a Ag/AgCl wire was used as a combined auxiliary/reference electrode. All electrochemical experiments were performed using a CHI 800B (electrochemical analyzer, CH Instruments, Austin, TX) with a CHI 200 Picoamp Booster (CH Instruments). The current signals were fed directly into one data acquisition channel of the Alpha-SNOM instrument. The details of this SECM instrumentation and operation procedure have been described elsewhere in great detail [20,37–39].

2.4. SECM experiments

SECM measurements were performed on the TEM grid or IAME adhered with 3M double-sided tape (conductive side exposed) onto a glass bottom Petri dish (P35G-0-20C, MatTek Corporation, Ashland, MA). The Petri dish was mounted onto the scanning stage (P-517K064, Polytec PI, Germany) of the microscope. Utilizing the Alpha-SNOM positioning system along with an inverted objective lens (Nikon objective, 50 \times lens, N.A.: 0.55 mm, W.D.: 10.1 mm), the electrode's approach to the sample was made. The biased electrodes (0.300 V for FcCH_2OH or -0.350 V for $\text{Ru}(\text{NH}_3)_6^{3+}$) approached the samples using the confocal mode setting within the WITec software, resulting in the generation of 2D SECM images (current vs. probe coordinates). Each SECM depth scan image has 256 \times 256 pixels, scan scale of 60 μm in width and 30 μm of depth, as well as an integration time of 0.05 s. The constant height SECM images have the same parameters as the depth scan images, with the following exceptions: the scan width and height were set to 60 μm each. These experiments were carried out at ambient lab conditions (23 ± 1 °C).

3. Theory and simulation

3.1. Simulation geometry

The simulation model was designed in full 3D geometry in COMSOL Multiphysics 5.2 (COMSOL, Boston, MA) to represent the true physical dimensions of the system under study (Fig. 1A and B). The UME was configured to have a Pt tip size of 4.4 μm (diameter) and an RG of 3. The IAME substrate consisted of 4 sets of alternating Pt and glass microbands of 5 μm in width on a glass plane (Fig. 1C). The plane was designed to intersect the solution domain, allowing the tilting of the

Download English Version:

<https://daneshyari.com/en/article/4908151>

Download Persian Version:

<https://daneshyari.com/article/4908151>

[Daneshyari.com](https://daneshyari.com)