Published in final edited form as:

Anal Chem. 2017 March 07; 89(5): 2687–2691. doi:10.1021/acs.analchem.7b00210.

Fabrication of Scanning Electrochemical Microscopy-Atomic Force Microscopy (SECM-AFM) Probes to Image Surface Topography and Reactivity at the Nanoscale

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Abstract

Electrocatalysts, used in energy applications, rely on the solid-liquid interface to carry out productive chemistry. This interface is generally less amenable to standard surface-science characterization methods, making the investigation of the surface activity, catalyst structure and chemical evolution at the nanoscale very challenging. Bulk measurements have been applied, but these lack sufficient resolution to identify conclusively which structures (protrusions, flat film surface, or cracks) are responsible for chemistry in these materials. In order to address these questions, we have designed and fabricated scanning probe tips for combined atomic force microscopy (AFM) and scanning electrochemical microscopy (SECM). AFM combined with SECM provides a direct correlation of topological information with the chemical surface reactivity, at a resolution defined by the probe radius. The structure/activity correlations obtained will reveal underlying reaction mechanisms that enable engineering of more active materials.

1. Introduction

Scanning electrochemical microscopy (SECM) is unique among scanning probe techniques because it images the electrochemical activity, *i.e.*, reaction rate, of surfaces.¹ Among several modes of SECM operation, feedback mode is preferred for reaction rate imaging for two reasons: 1) high spatial resolution as a result of minimal diffusional broadening and 2) high sensitivity to surface reactivity. Feedback mode SECM images are obtained by scanning an ultramicroelectrode (UME), called the SECM probe tip, above a substrate and recording the variations in the tip current (constant-height mode) or z-coordinate (constant-current mode) in a solution containing an electrochemically-active redox mediator species. The current measured at the UME is produced by reduction (or oxidation) of the mediator species, and this current is diagnostic of the electrochemical reactivity of a surface if the UME is positioned within the diffusion layer of the substrate surface. If the original redox state is regenerated at the conductive substrate surface at a diffusion-controlled rate, enhanced tip current (positive feedback) is produced. In the case of an insulating substrate, diffusion of redox species to the tip is blocked as the tip approaches the surface, so the tip

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current, i_T , decreases with decreasing separation distance, d . This case is negative feedback mode. The strong i_T versus d dependence under both positive and negative feedback conditions constitutes the basis for topographic SECM imaging. However, typical SECM measurements suffer from a lack of sufficient spatial resolution along with the convolution of topography and electrochemical response due to current-dependent positioning of the UME.

Atomic force microscopy (AFM) provides topographical surface information with high spatial resolution, *e.g.*, a few nanometers or even atomic resolution under well-controlled conditions, but it provides limited information on the chemical nature of the substrate. Merging AFM with SECM provides direct correlation of topography and surface reactivity of the substrate surface. The general requirements for the combination SECM-AFM probes are that they possess a well-defined electrode geometry and pin-hole free insulation protecting the electrode from electrolyte solution. Several methods¹³ have been reported for integrating SECM with AFM, *i.e.*, using nanoelectrodes as AFM probes. So far, probes that have been fabricated can be grouped into two categories: electrodes located directly at the apex of the AFM tip⁴⁻¹⁰ or those located at some distance from the tip apex.¹¹⁻¹⁸ Commercially available probes are shaped either as cones or spherical caps. Because of their geometries, conical and spherical tips have low SECM feedback responses, making them less suitable for feedback mode experiments. Previously demonstrated probes are in the sub-micrometer dimension range in terms of electroactive area, which limits their spatial resolution. Thus, the availability of nanoelectrodes for SECM-AFM could provide a major advance in nanoscale imaging.

SECM-AFM measurements have been conducted on model samples like microstructured patterns with conductive and insulating features.^{13,19-22} So far, combining AFM with SECM requires customized solutions as limited commercial SECM modules for AFM systems are available and, therefore, the technology only is used by a limited number of researchers. In addition, fabrication of combined probes remains challenging. First, a nanometer-sized electrode must be prepared and it must exhibit a well-defined electroactive area. Second, the insulating layer thickness must be controlled and ideally minimized to improve performance. Third, the tip must be mounted and a suitable electrical contact to the AFM tip must be established. Because of all of these requirements, it is difficult to fabricate reproducible, high quality SECM-AFM tips.

Here, we present a fabrication process of AFM-SECM probes that provide nanoscale resolution of chemical information and topography. The fabrication starts with the preparation of SECM tips using the established method of sealing a Pt metal wire into a glass capillary and pulling with a pipette puller. The probe ends are then cut polished using a focused ion beam (FIB) to expose the Pt surface. The SECM probes are subsequently cut and attached to a quartz tuning fork to complete the fabrication of the combined SECM/AFM probe. We report here on the characterization of our tips using an in-house fabricated calibration sample.

2. Materials and Methods

Commercially available ferrocenemethanol (FcMeOH) was recrystallized twice from acetone. Tetrabutylammonium perchlorate, sodium chloride (NaCl), and potassium chloride (KCl) from commercial suppliers and without further purification were used as supporting electrolytes. Aqueous solutions were prepared in deionized water with a resistivity of 18 M Ω -cm.

Our platinum test structure was prepared by direct-current sputtering 20 nm-thick Pt films onto pre-cleaned ultra-flat glass slides coated with a 5 nm-thick Ti adhesion layer. The deposition rate for Pt was $R_{Pt} \approx 0.36 \text{ nm}\cdot\text{s}^{-1}$. Pt finger patterns (ranging from 50 nm to 1 μm) were prepared by FIB milling using a dual-beam (FIB/SEM) system (Ga^+ ions, 40 pA beam current, 30 keV beam energy).

For electrochemical measurements, a two-electrode configuration was employed with a 0.25 mm diameter Ag wire coated with AgCl (Ag/AgCl) serving as a reference electrode. Electrochemical measurements were made using a commercial bipotentiostat. Evaporated Au films (100 nm) on glass were used as the conductive SECM substrate. In negative feedback mode, a bare glass slide was used as an insulating substrate. A commercial AFM equipped with a fluid cell was used for all experiments. The AFM was equipped with a scanner with a maximum scan range of 30 $\mu\text{m} \times 30 \mu\text{m}$. The AFM was placed on air table incorporating vibration isolators. Electrical connection to the SECM-AFM probe was made by means of a gold wire bonded to the tungsten needle attached to the adapter. For electrochemical imaging, either the SECM-AFM tip current or the substrate current was recorded to the auxiliary input of the AFM using a NIST-built breakout box.

2A. Probe Fabrication

Our SECM-AFM probes use quartz tuning forks (QTFs) with a resonance frequency of 32 kHz, a spring constant of 34 $\text{kN}\cdot\text{m}^{-1}$, and a Q factor of 100 000 in vacuum. As a first step of the fabrication process, the metallic cover of the resonator was removed and QTF electrode is pre-glued with an adhesive that hardens under electron beam irradiation before mounting the resonator on the SEM sample stage (Figure 1A). The FIB-polished nanoprobe was then attached to the nanomanipulator in our FIB/SEM system using adhesive. The nanoprobe was then brought close to one of the tuning fork arms, and the adhesive was hardened using a high electron beam energy (15 KeV) to attach the probe to the tuning fork (Figure 1B). The FIB was used to make a cut that separates the bulk of the nanoelectrode from the section that has been glued onto the tuning fork (Figure 1C). By employing a low current ion beam, the buried Pt was exposed and then used to make electrical contact with the tuning fork. In the vicinity of the cut, the metal line has a width of 1 μm and glass thickness of 20 μm (Figure 1D). A contact pad was created using a small segment of one of the QTF electrodes by FIB etching away part of the electrode material. A series of Pt pillars and Pt strips were made with the FIB (Figure 1E, F) to electrically connect the nanoprobe to the pad.

2B. Description of Equipment

After the nanoprobe was mounted onto the QTF, the AFM-SECM probe was integrated into a commercial AFM system with the help of a NIST-built 3D printed adapter. Figure 2 shows a schematic representation of the probe holder and electrochemical cell. The QTF probe was aligned under an optical microscope with a 10 $\times$ objective. A NIST-built custom-made electronics module was used to drive the QTF electrically to its resonance frequency. A transimpedance amplifier converted the current through the QTF into voltage with a 10⁷ V A⁻¹ gain. The current losses due to parasitic capacitance related to the contacts and cables were compensated with a matched capacitance sub-circuit. A signal was applied to drive the QTF at its resonance frequency using an integrated generator in the lock-in amplifier. The final resonance frequency after adding the extra mass of the probe was shifted and the resulting Q factor was ≈ 3000 .

A non-contact, small modulation QTF-AFM system can be used to control the distance and analyze the electrochemical properties of a substrate. Because both temperature and humidity fluctuations influence the QTF resonance frequency, we made a chamber setup that maintains the relative humidity within the experimental requirements. We used non-contact mode operation of the QTF-based AFM without jump-to-contact because of the high stiffness of the QTF.

3. Results and Discussion

After the probe fabrication, electrodes were imaged and polished in a dual FIB/SEM to check the size of the electrodes. We used a combination of SEM and cyclic voltammetry to check that the surface of a polished nanoelectrode is flat and leak free and to determine the electrode radius, a .¹ Figure 3 shows a steady-state voltammogram (Figure 3A) in solution containing 1 mmol L⁻¹ ferrocenemethanol and an SEM image (Figure 3B) obtained on the same polished Pt electrode. The tip radius, $a = 60$ nm obtained from steady state current is very well in agreement with SEM image. The voltammogram in Figure 4A is fully retracable and well-shaped, with a flat plateau and negligibly small background current. The voltammograms obtained at this electrode remained sigmoidal at sweep rates as high as 10 V·s⁻¹ (not shown). The overall success rate for this step in tip preparation is $\approx 90\%$.

The ratio of the Pt wire diameter to the overall insulating borosilicate glass diameter also was measured in the SEM images at this step because analysis of electrochemical data depends on both a and the outer radius of the quartz sheath, r_g . To evaluate the size of FIB-milled electrodes, SECM approach curves, *i.e.*, i_T plotted as a function of d , where $i_{T,\infty}$ is the tip current, were measured. The approach curves in Figure 4 were made in FcMeOH solution using a conductive gold substrate. Figure 4A shows the SEM image and SECM approach curve of a FIB-polished electrode with a radius, a of 50 nm and RG (r_g/d) of 30. For this electrode, the experimental approach curves match the theoretical curve only above the normalized distance of $0.4a$ to $0.5a$. The closest distances (25 nm) are sufficient for many SECM applications, but we improved these values by FIB-milling to reduce the diameter of the glass surrounding the Pt electrode (SEM image, Figure 4B). Figure 4B shows the SEM image and SECM approach curve for the same probe after top-milling. An approach distance range of $0.10a$ to $0.15a$ is the typically achievable, normalized distance

for our top-milled probes. The excellent smoothness of the FIB-milled tip was achieved by employing a low current gallium ion beam (7 pA at 5 keV).

We evaluated the fabricated probes to assess their SECM-AFM imaging capabilities. To evaluate the lateral resolution, a Pt test structure with strips varying in width from 50 nm to 1 μm (Figure 5A) was prepared using an FIB/SEM system. We employed a low voltage-driven amplitude to minimize the amplitude of oscillation of the SECM-AFM probe. A ratio of 0.8 was used for $A_{\text{set}}/A_{\text{free}}$, the ratio of the set point of the feedback to the maximum free amplitude at the resonance frequency. Only the probe (not the QTF) and the sample surface were immersed in the electrolyte in the liquid cell.

Figure 5A shows an SEM image of the Pt test structure. Figure 5C shows a $20\ \mu\text{m} \times 20\ \mu\text{m}$ feedback mode image of the Pt test structure that is in agreement with the SEM picture (Figure 5A). The topography image obtained with the same probe tip is in Figure 5B. The images in Figures 5B and 5C were recorded simultaneously in intermittent-contact mode AFM and feedback mode SECM, using a 50 nm-diameter probe tip and a tip potential at which ferrocene methanol oxidation occurred at a diffusion-controlled rate. An advantage of this sharp probe over a conventional SECM tip is the very small RG, which makes it easier to image surface features that are not flat without crashing the tip. The strip areas also show a higher cathodic current due to positive feedback. In areas where the Pt was removed and the SiO_2 glass substrate is exposed, a decreased cathodic current is measured due to hindered diffusion of the redox mediator towards the tip-integrated electrode. As the top-milled probe tip has a curvature close to the range of commercially-available probes for AFM, high-resolution topographical imaging is achieved.

The inset in Figure 5C shows the lateral line profile of the SECM sweep. Because of the nonlinear relationship between the tip current and the tip/substrate distance, the SECM image does not directly represent the topography of the substrate. The current map shown in Figure 5C inset was converted to the topographic image (i.e., the dependence of the tip/substrate separation distance versus the tip position).^{23a} The smallest feature that is easily resolved in current mapping (100 nm) indicates the lateral resolution of this system. Even higher spatial resolution could be attained by using a smaller SECM-AFM probe.

4. Conclusions

All the batch-fabrication approaches⁴⁻¹⁸ have often come at the cost of electrode size and imaging performance. Some high-resolution imaging was achieved by using conical probes²⁴ and by modifying commercial AFM probes using FIB and reactive ion etching (RIE).²⁴ Although thorough characterization was presented, these authors did not have control over the electrode-surface separation during the electrochemical measurement, making SECM-AFM image interpretation more challenging. We have demonstrated the fabrication of nanometer sized SECM-AFM probes with $\text{RG} < 5$ that can be used on commercially available AFM systems and used to image both surface topography and current with nanoscale separation of the electrode and substrate. The spatial resolution of the SECM-AFM is governed by the tip radius; hence our specially fabricated probes allow us to attain lateral resolution which is 3-fold improved over the recent work of Lee *et al.*²⁶ who

imaged a carbon nanotube network. Unlike previous studies, where submicrometer-sized SECM-AFM probes were employed, we imaged a solid sample with structured features, without the nanotip and the substrate colliding. This was possible because of our well-polished flat tips and decreased glass thickness. Further enhancements of the electrochemical resolution will be achieved by reducing the electrode size, by optimizing the electrode pulling process, and also by controlled milling during the polishing steps.

Acknowledgments

J. V., A. A., and S. A. acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology Award 70NANB10H193, through the University of Maryland.

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Figure 1.

SEM images showing probe attachment procedure to QTF. (A) Nanoprobe brought to resonator tip where it is pre-glued. (B) High beam exposure to harden the adhesive. (C) FIB cut to remove the bulk of the nanoelectrode. (D) Fine mill for exposing sealed Pt, (E) Pt pillar for electrical contact. (F) Pt strip contacted to pad. Scale bar is 100 μm .

Figure 2.
Schematics of SECM module for commercial AFM.

Figure 3.

(A) Steady state voltammogram of a 50 nm radius Pt electrode in 1 mmol·L⁻¹ FcMeOH and 0.1 mol L⁻¹ KCl at 50 mV s⁻¹. (B) High resolution SEM image of same electrode.

Figure 4.

Experimental (green, 1A and red, 1B) and theoretical (black)^{23a} SECM approach curves obtained with a nanoelectrode before (A) and after (B) top-milling in the FIB. The current and distance are normalized by steady state current and $a = 50$ nm, respectively. The solution contained $1 \text{ mmol}\cdot\text{L}^{-1}$ FcMeOH and 0.1 mol L^{-1} KCl. Insets show the SEM images before and after top-milling. Scale bar is 200 nm

Figure 5.

(A) SEM image of lateral resolution calibration standard (Pt on SiO₂). (B) Topography (C) electrochemistry AFM-SECM images recorded with a Pt probe (electrode size: 50 nm, tip length: 3 mm, scan speed: 0.3 line s⁻¹); inset, lateral line profile of the SECM scan where distance calibration was obtained using current-distance curve. Solution conditions: 1mmol L⁻¹ FcMeOH, tip potential = 0.4 V vs. Ag/AgCl.