

AFM-SECM USING INSULATED ELECTROCHEMICAL PROBES

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Fields as diverse as clean technology and biomedical engineering are united on a fundamental level by the electrochemical nature of their processes. These processes are often complex and heterogeneous, yet few techniques are capable of directly measuring local reaction rates or currents generated at an interface with nanoscale precision. Scanning electrochemical microscopy using an atomic force microscope (AFM-SECM) enables nanoscale mapping of chemical surface activity with correlated structural information. Here we use the Scuba Probe Technologies Electrochemical Probe (SPT-EL) to map the electrochemical reactivity of a microelectrode array at the nanoscale. With ultra low leakage currents, we observe currents on the order of tens of pA over electronically active electrodes.

Introduction

Chemical and biological processes that occur at solid-liquid and liquid-liquid interfaces typically involve charge transport or storage. The nanoscale electrochemical reactivities at these surfaces govern the macroscale performance, function, lifetime, and failure of a system. Understanding the electrochemical dynamics of these systems is crucial for a variety of applications ranging from classic electrochemical problems in corrosion and catalysis to energy storage, sensing, and biology.¹

SPT-EL Features for AFM-SECM

To explore these phenomena, combining atomic force microscopy with scanning electrochemical microscopy (AFM-SECM) provides a powerful tool that enables correlative structural and electrochemical



Figure 1 | A,B. The SPT-EL features a flexible easy to use handle with reliable electrical contacts to the chip. C. Scanning electron microscopy shows the insulation and the sharp, exposed Pt electrode at the tip apex.

characterization at nanometer length scales. To date, one of the shortcomings of the technique is the laborious preparation of the nanoelectrode. Researchers struggle to make reproducible and clean electrical connections, particularly when working in liquids.² The SPT-EL is a unique and easy-to-use solution with a fully insulated electrical connection and a flexible handle that connects directly to the chip (Fig. 1A-1B). For reliable low-noise electrochemical measurements that are localized at the region of interest, only the tip apex is electroactive and the remainder of the probe is insulated to prevent delocalization of the electric field in polar solvents (Fig. 1C).²

The handle is easily inserted into a universal zero insertion force (ZIF) connector to accommodate a variety of commercial AFM instruments. Examples include the Asylum Research MFP-3D (Fig. 2A), JPK Nanowizard (Fig. 2B), and Bruker Nanoscope (Fig. 2C).

SECM Mode: Tip Collection/Sample Generation

In SECM, the current from the electrode is measured as it is scanned over a surface and perturbations in this current are collected to learn about electrochemistry occurring at the sample surface. Typically SECM is performed using ultramicroelectrodes (with a characteristic dimension smaller than 25 μ m), which limits spatial resolution of the measurement and topography information is convoluted with electrochemical information.⁴

There are several modes of operation in SECM experiments. Current can be generated or collected at either the tip or sample surfaces and can also be monitored while in competition with an external reaction. One method is tip collection-substrate generation (TC/SG) mode, where the redox mediator is converted at the substrate surface and collected at the tip. Here we perform SECM in TC/SG mode on a microelectrode array using the SPT-EL to demonstrate the probe capabilities for electrochemical applications.

AFM-SECM of a microelectrode array



Figure 2 | The SPT-EL is compatible with commercially available atomic force microscopes as shown here in the **A**. Asylum Research MFP-3D, **B**. JPK Nanowizard and **C**. Bruker Multimode. In all of the images a zero insertion force connector is mounted to electrically connect the tip for current measurements.

To evaluate the electrical performance of the SPT-EL cantilevers, we performed cyclic voltammetry (CV) on each cantilever. Representative data can be visualized in Fig. 3A where a clear oxidation and reduction reaction are observed. Over time, the current is stable while imaging the surface. Fig. 3B shows representative CV curves of a SPT-EL cantilever that is mounted in the AFM and used in an AFM-SECM experiment for 6 hours.







Figure 4 | **A.** Sample generation-tip collection mode schematic over conductive and insulating surfaces. **B.** A schematic showing the operation of AFM-SECM where a topography scan is performed (Height trace) and the tip is lifted away from the surface with a defined height (lift height) and a second trace (Current trace) is performed to measure current. **C.** An optical image of the microelectrode array with 5 µm diameter electrodes that are connected along three sides (blue). AFM-SECM images of **D.** topography and **E.** current of the microelectrode array. Scan size: 35 x 35 µm. Reference electode: Ag/AgCl. Counter electrode: Pt.

To perform TC/SG mode AFM-SECM, we used ruthenium hexaammine ($Ru(NH_3)_6Cl_3$) as a redox mediator with a KNO₃ supporting electrolyte using an Asylum Research MFP-3D AFM. In solution, the electroactive species are predominantly in an oxidized state. When the substrate is held at the switching potential, the substrate reduces the oxidized species in solution and are subsequently collected at the tip as shown in Fig. 4A and in the equations below (assuming that only O species are initially in the solution as for $Ru(NH_3)_6Cl_3$):



When the tip is positioned over a conducting surface with a sample bias, enhanced currents are expected. When imaging over an insulated region, depletion of the sample-generated species will result in a lower current (Fig. 4A). To probe the spatial distribution of the electroactive species, a topography image was obtained using tapping mode and a correlative electrochemical map of tip current was acquired at a lift height of 200 nm from the sample surface (Fig. 4B). To perform TC/SG SECM mode, the sample bias was set to -0.35 V vs. AgCl to reduce $[Ru(NH_3)_6]^{3+}$ and the tip voltage was set to +0.1 V vs. AgCl to oxidize $[Ru(NH_3)_6]^{2+}$.

The microelectrode array used in this study consists of a 5 x 5 array of circular platinum electrodes each 5 μ m in diameter with insulated tracks that run below an insulating film. These tracks are exposed and connected at the outside edge of the chip (Fig. 4C). The electrodes on one side of the sample were intentionally left as inactive (floating) while all other electrodes were connected to the sample working electrode using a bipotentiostat.

The sample topography shows clear 5 μ m diameter holes in the insulating layer that connect to the platinum electrodes beneath, as expected. The electrical leads that are positioned under the insulation show an increased height and the morphology matches the optical microscopy images (Fig. 4C). The insulating layer measures approximately 1 μ m in height from the electrode surface (Fig. 4D). The SECM current image was performed with a sample bias of -0.35V vs. AgCl to reduce the oxidized species in solution and the tip was biased at 0.1V vs. AgCl to oxidize the species generated by the sample. Over the biased electrodes, we observe

currents of ~60 pA from the redox reaction that occurs with ruthenium hexaammine. Electrodes that were left at a floating bias exhibit slightly negative currents (Fig. 4E, arrows) that likely correlate to a reduced rate of conversion compared to bulk concentrations of the redox mediator.

Overall, the deconvoluted topography and current maps provided by AFM-SECM combined with SPT-EL nanoelectrodes offer advantages over classic SECM and have begun to push the limits of nanoscale electrochemistry.

A microelectrode array with biased and unbiased platinum electrodes was characterized using AFM-SECM using SPT-EL probes operating in tapping mode. Electrochemical current maps and correlative topography revealed ~60 pA currents above connected electrodes. AFM-SECM is a powerful tool that not only measures the electrochemical activity at the electroactive surfaces as demonstrated here, but can also be applied to explore reaction rates at the nanoscale.





SPT-EL Properties*

Resonance Frequency: air	70 kHz
Resonance Frequency: water	26 kHz
Spring Constant	0.8 N/m
Cantilever Length (Triangular)	100 µm
Total Cantilever Thickness	1.7 µm
Exposed Tip Height	<0.7 µm
Lead Resistance	<20 Ω
Parasitic Capacitance	<40 pF
Typical Current @ -0.35V**	<600 pA
*Typical values **Current values are taken in 5 mM ruthenium chloride + 100 mM potassium ni	hexaammine trate

References

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