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Design of a Scanning Tunneling Microscope for Electrochemical Applications

by

Moris M. Dovek, Michael J. Heben, Christoph A. Lang, Nathan S. Lewis, and Calvin F. Quate

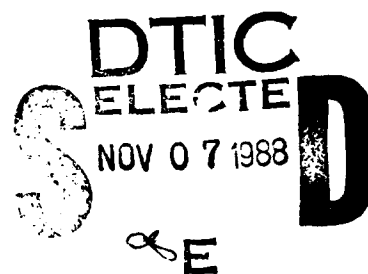
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Lewis^{2*}, and Calvin F. Quate^{1*}.

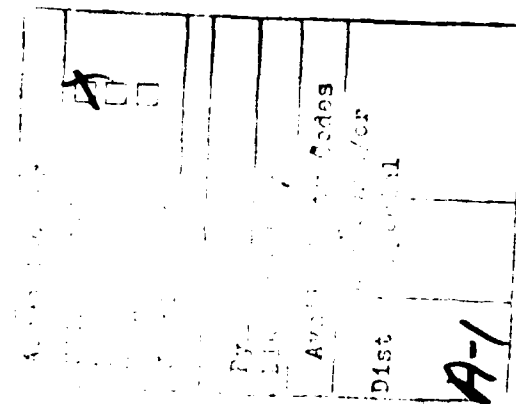
¹Department of Applied Physics, Stanford University, Stanford, CA 94305.

²Department of Chemistry, Stanford University, Stanford, CA 94305.

* Address correspondence to these authors.

ABSTRACT

We present a design for a scanning tunneling microscope that is well suited for electrochemical investigations. The construction of the microscope insures that only the tunneling tip and the sample participate in electrochemical reactions. The design also allows rapid replacement of the tip or sample, and enables facile introduction of auxiliary electrodes for use in electrochemical experiments. The microscope utilizes stepper motor driven approach mechanics in order to achieve fully remote operation and to allow reproducible coarse control of tip/sample spacings for electrochemical experiments. This microscope has enabled us to image highly ordered pyrolytic graphite at atomic resolution in air and aqueous solutions.



I. INTRODUCTION

Unlike most other electron and ion based surface characterization techniques, Scanning Tunneling Microscopy (STM) has the potential to yield *in situ* information regarding surface structure at liquid interfaces¹. For non-reactive surfaces, it has been shown that images obtained with the tunneling microscope are virtually identical for surfaces in contact with air^{2,3}, UHV⁴, or liquids⁵⁻⁷. Thus the STM is an interesting tool for a number of potential electrochemical applications, including topographic and spectroscopic studies of solid/liquid interfaces, and extremely high resolution lithography^{6,8}. Additionally, the STM's capability to control tip/sample spacings should allow space- and time-resolved studies of diffusion layer profiles. However, the use of STM in most electrochemical experiments will require modification of conventional gas phase/vacuum microscopes. Important instrumental capabilities include accurate coarse and fine distance control, remote microscope operation, compatibility with most electrochemical solvents, and the ability to perform conventional potentiostatic and galvanostatic experiments using either the sample or the tip as the working electrode. In this report, we describe a microscope design that has been constructed specifically to achieve these goals and to provide versatile use in electrochemical studies.

There have been a few previous reports of STM's for certain electrochemical experiments. *Ex situ* topographical information about surfaces subjected to prior electrochemical cycling^{9,10} or passivation¹¹ and *in situ* images of solution covered samples have been obtained^{5,7,12,13}. Also, STM tips have been used as electrodes to electroplate and then image metal deposits on a 220 nm scale¹⁴. The STM's used in these experiments were of varied experimental capability.

For example, the design of Sonnenfeld *et al*¹⁵ uses only a drop of liquid, and is therefore difficult to operate with high vapor pressure solvents (e.g. CH_3CN or alcohols) or with auxiliary electrodes, as would be required for most electrochemical investigations. Another microscope designed by Sonnenfeld *et al*⁵ is better suited for electrochemical work, but exposes potentially active materials (e.g. steel) to the electrochemical environment. Itaya *et al*⁷ have also constructed a tunneling microscope that has produced atomic resolution images in liquids, but their microscope does not allow for reproducible or automated control over large distance excursions in the z-direction.

We present a scanning tunneling microscope (STM) that overcomes many of these problems, and also yields atomic resolution images while in an operating electrochemical cell. Noteworthy features of the instrument include a modular design to accomodate rapid tip and/or sample exchange, inert components (e.g. Pyrex, Teflon, etc.) contacting the electrolyte, a large fluid capacity, a novel vibration isolation system, and stepper motor driven approach mechanics. Details of the microscope, as well as examples of its imaging capabilities, are given below.

II. DESIGN of the MICROSCOPE

The structure of the microscope is shown in Figure 1. The microscope body consists of two major parts; the microscope base and the approach mechanics. These are discussed separately below.

A. The Base of the Microscope

In order to insure compatibility with most common electrochemical solvents, the base of the tunneling microscope was made of Pyrex. This base contained mating points for mounting of sample holders, and also

provided attachment joints and support for the approach mechanics.

Positioning points for the approach mechanics were obtained by grinding three equally spaced dimples into the top surface of the base.

In order to immerse the tip/sample assembly, the microscope required approximately 200 ml of solution; however, straightforward modifications to the microscope could enable use of smaller liquid volumes. A viewing hole was provided in the microscope base in order to facilitate coarse tip/sample positioning in the absence of solution and to allow the inside of the structure to be readily filled with liquid.

The base was mated with a cylindrical Teflon support that was machined to fit snugly into, and lie at the bottom of, the solution containment vessel. This Teflon support served to occupy some of the volume within the beaker and thereby reduce the amount of liquid needed to completely cover the tip and sample. More importantly, the weight of the Teflon greatly enhanced the stability of the microscope by lowering its center of mass. This resulted in substantial reductions in the effectiveness of vibrational coupling to the STM.

The vibration isolation system employed in the microscope was similar to an arrangement described by Binnig *et al*¹⁶. It consisted of brass plates separated by silicone rubber feet (see Fig. 1). This arrangement has been shown to yield excellent isolation with minimum space and machining requirements.

B. The Approach Mechanics

The second major part of the STM is the approach mechanics for the tip. In our design, the mechanics were held in position on the Pyrex base by use of springs. As indicated in Figure 1, the spring tension was applied between attachment hooks that were part of the base and

small bolts that protruded from the uppermost stainless steel plate of the approach mechanics.

Guidance rails for the piezoelectric scanner and the tip were fabricated from three stainless steel rods. The rods were press-fit in a steel plate, and also were mated with the dimples in the Pyrex base. This arrangement provided a method to align the upper and lower portions of the microscope. The scanner and tip were mounted on a second, lower stainless steel plate. This plate was spring loaded to the upper plate by two springs. This arrangement was used to achieve an asymmetric loading for improved stability in the plane of the sample. To obtain a controlled approach between the sample and the tip, the second plate was pushed toward the sample by a stepper motor¹⁷ that was anchored to the upper plate.

C. Sample Holders

Sample holders were made of Pyrex, and the shape of the holders was a disk with a pedestal. The disk had a capillary opening along the z-axis of the pedestal, and the pedestal was centered and projected from the plane of the disk. The sample holders were affixed to the base of the microscope using Teflon screws, which were directed through two slots that were machined in the sample holder disk.

Samples were cemented to the top of the pedestal with silver paint, and electrical connections were made via the capillary opening. After mounting, the edges of the sample and the Ag paint were insulated from solution with epoxy. The sample wire was fully insulated from the solution by Teflon tubing, and the wire traveled to a current preamplifier that was positioned just outside of the solution.

D. The Piezoelectric Scanner and Tip Mounting

The single tube piezo was constructed from PZT-5H material¹⁸, and was of the design described by Binnig and Smith¹⁹. The piezo tube was protected from solution by a sheath that was made from heatshrink-type Teflon tubing.

To facilitate mounting of tip holders, a piece of brass was cemented into the piezo tube (Figure 1 inset). Threaded tip holders were screwed onto the brass to form an O-ring compression seal with the piezo. Additionally, a drop of silicone rubber sealant was used to insulate the exposed metal of the uncoated tip shaft and mounting chuck. This procedure enabled rapid interchange of tips, and also allowed mounting of several alternate tips without disturbing the operation of the microscope.

E. Stepper Motor Drive Electronics

Circuitry was constructed in order to drive the stepper motor with either pulsed or DC voltages. Under DC operation, the tip could be translated at rates up to 0.2 mm/s either towards or away from the sample. This capability was found to be extremely useful in coarse tip/sample positioning. In the pulse mode, the stepper mode could be driven either with a train of pulses or with a single pulse. The pulses were of 10 ms duration and consisted of arbitrarily programmable voltages between the limits of 3.5 V to 6 V.

The amount of tip travel in response to a single voltage pulse was found to be a function of the stiffness of the springs employed to load the stepper motor. By appropriate adjustment of loading and pulse voltage, it was found that the steel plate that carries the piezo and

tip could be reproducibly moved as little as 100Å in response to a single, manual voltage pulse to the stepper motor.

In automatic mode, the circuitry sent 10 ms pulses to the stepper motor every 100 ms. This mode was extremely useful for the final approach of the tip into tunneling range. To prevent shorting between the tip and the sample, the pulse train was terminated if a current in excess of a given setpoint value (typically 1 nA) was sensed. Exceeding the setpoint also caused the circuitry to fully retract the piezo tube by applying the full voltage (approximately 150 V) to the piezo. Tunneling was then re-established by allowing the piezo voltage to capacitively discharge, which enabled a smooth approach of the tip toward the sample until feedback control was established.

III. DISCUSSION

As described above, the overall construction and choice of materials make this microscope modular and chemically inert. In particular, the threaded tip holders and slotted sample holders enable rapid tip/sample exchange, while all metallic or potentially reactive surfaces are insulated from solution by either Teflon, chemically inert epoxy or neoprene. Furthermore, the large fluid capacity of the STM avoids solution compositional changes and greatly facilitates inclusion of auxiliary electrodes for electrochemical investigations. This combination of properties makes the instrument quite attractive for use in electrochemical applications.

The use of a stepper motor to move the scanner and tip made this STM somewhat top-heavy, and therefore led to increased susceptibility to vibrations. To counteract this, the Teflon support (which serves to lower the center of mass of the microscope itself) and the brass vibration isolation plates were designed to work in concert to

effectively isolate the STM from low frequency mechanical vibrations. Furthermore, when loaded with the microscope and solution, the system of plates served to lower the center of gravity of the whole system, because the microscope's bottom was supported by the uppermost plate at a level equal in height to the lowest plate. Additionally, the lossy silicone rubber feet proved to provide effective damping between adjacent plates. The entire system was found to provide sufficient stability that atomic resolution images of graphite and MoS_2 could be obtained under a variety of different conditions.

An advantageous feature of this microscope design is that the stepper motor driven approach mechanics and supporting electronics provide capabilities for fully remote operation. This automatic approach facility, in conjunction with the modularity of microscope design, make this instrument ideal for use in inert atmosphere gloveboxes where manual dexterity is compromised. Because tip speeds in the automatic approach mode range from $0.1 \mu\text{m}/\text{sec}$ to $5 \mu\text{m}/\text{sec}$ (depending on spring tension and voltage pulse height), macroscopically large distances (c.a. $100 \mu\text{m}$) can be traversed in less than 1 minute. Thus, the conditions on coarse tip-sample positioning are less stringent than with manual controls, where the tunneling tip must be visually placed within a few microns of the sample for the rapid final approach into tunneling range. This arrangement also minimized inadvertent "crashing" of the tip (direct physical contact between the tip and the sample) during coarse positioning. In fact, it was found that the ability to detect tunneling current, deactivate the pulse train, and retract and relax the piezo tube were so effective at preventing tip/sample shorting that most W and Pt/Ir tips yielded atomic resolution images without further procedures.

Figure 2 is an image of highly ordered pyrolytic graphite obtained under an aqueous 1 M NaCl solution with our microscope operating in fast scan mode²⁰. It is virtually identical to images we have obtained of these surfaces in contact with air. These images compare quite favorably with those of pyrolytic graphite obtained by Schneir and Hansma⁶ (in non-polar liquids), Itaya and Sugawara⁷ (in DI water), and Sonnenfeld and Schardt¹² (in .050 M AgClO₄). Of note is that all of these cases, including our own, required use of glass coated Pt-Ir tips²¹ that expose only about 20 μm^2 of metal in order to minimize residual faradaic currents.

A final noteworthy feature of the microscope is the ability to accurately achieve large variations in the distance between the tip and sample. To achieve such control, single voltage pulses are employed to adjust the Z-piezo voltage at which tunneling occurs. Complete retraction of the piezo then yields the desired tip/sample spacing. This technique can be used to accurately control tip/sample distances for values as large as the full travel of the piezo tube (0.75 μm). Calibration of the piezo travel in response to a pulse (for a given pulse height and set of springs) allows coarser distance variation over the travel of the stepper motor. This procedure has applications in potentiometric, galvanostatic or cyclic voltammetry experiments where the STM tip is used as a microelectrode at well defined small tip/sample spacings. We are currently exploiting these instrumental capabilities in several electroanalytical applications, and will describe the results of these experiments in subsequent publications.

IV. CONCLUSION

We have constructed a scanning tunneling microscope that is well suited for electrochemical investigations. This STM incorporates

several novel features that have not been employed elsewhere, including remote operation, compatibility with electrochemical solvents, variable distance control, facile tip/sample interchange, modular design, and adaptability to most electroanalytical applications. With this microscope, highly ordered pyrolytic graphite has been imaged at atomic resolution in air and aqueous solutions.

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FIGURE CAPTIONS

- Figure 1: Idealized depiction of scanning tunneling microscope designed for electrochemical applications. The inset shows a detailed view of the scanner construction.
- Figure 2: Image of highly ordered pyrolytic graphite taken under 1 M NaCl with our STM. The tip bias was +550 mV and the tunneling current was 1 nA. Commercially available glass coated Pt-Ir²¹ tips were used. In this representation dark spots correspond to carbon atoms at a separation of 2.5Å.

Figure 1

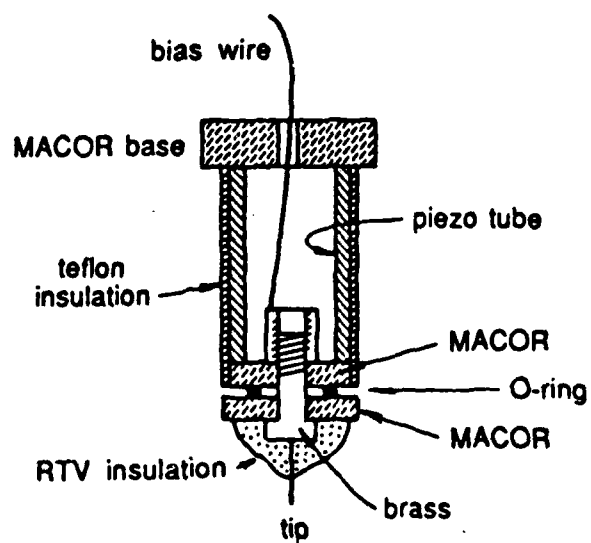
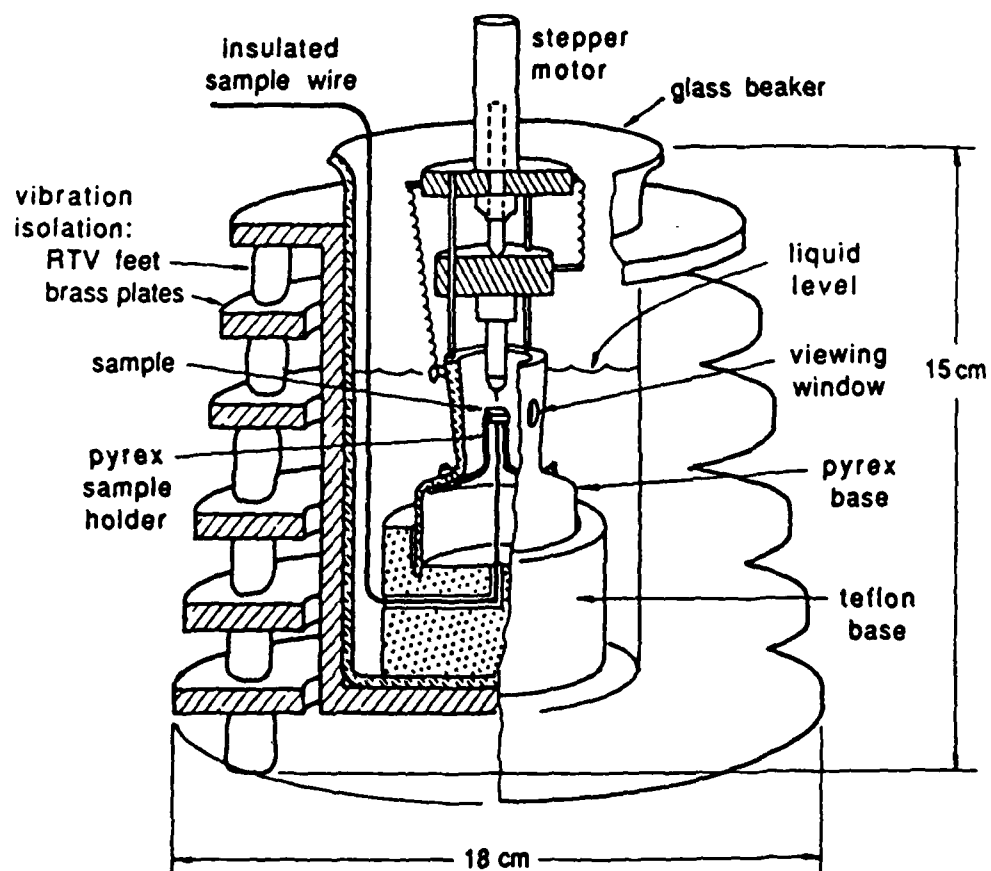
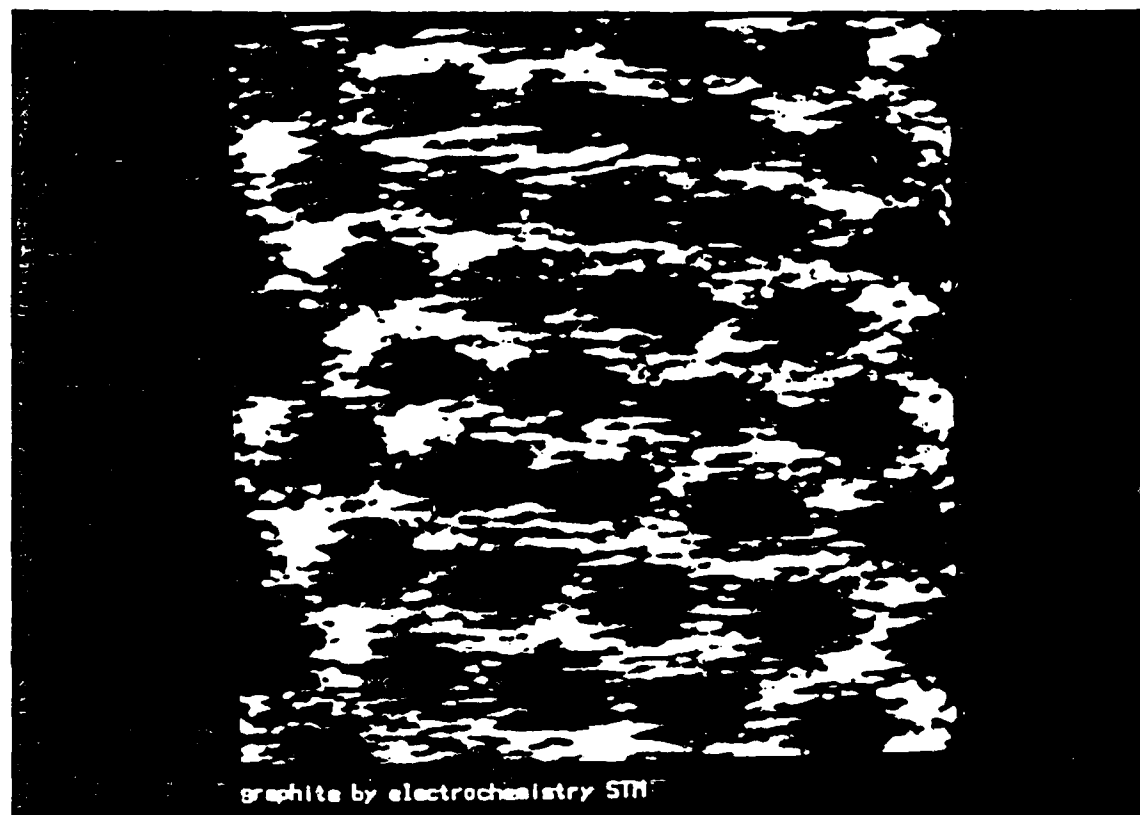


Figure 2



graphite by electrochemistry STN

—▶| |◀—
2.5 Å