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Preparation of STM Tips for *In-Situ* Characterization of Electrode Surfaces

by

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PREPARATION OF STM TIPS FOR *IN-SITU* CHARACTERIZATION OF ELECTRODE SURFACES

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Summary

The total current between the tip and the sample in a scanning tunneling microscopy study of a solid/liquid interface can be dominated by faradaic charge transfer currents. In such a situation feedback control of the tunneling gap, and imaging, is precluded. In this contribution we describe the preparation of glass or polymer coated STM tips that possess $< 100 \text{ \AA}^2$ of exposed metal. These tips effectively discriminate against faradaic current and enable STM imaging in the presence of reversible electroactive solution species at appreciable tip/sample biases.

Introduction

The invention of Scanning Tunneling Microscopy (STM) by Binnig *et al.* (1982) has allowed investigators to study the surfaces of electrically conductive materials in a variety of environments at atomic resolution (c.f. Binnig & Rohrer, 1984; Dovek *et al.*, in press (a); Hansma & Tersoff, 1987). Geometric information about atomic surface structure, or larger scale morphological information, can be obtained by rastering across contours of constant electron density with the tunneling tip (Hansma & Tersoff, 1987; Lang, 1986; Tersoff & Hamann, 1985). The spatial distribution of electronic surface structure (c.f. Demuth *et al.*, 1986; Kaiser & Jaklevic, 1986; Stroscio *et al.*, 1987) or adsorbate vibrational modes (Binnig *et al.*, 1982; Persson & Demuth, 1986; Smith *et al.*, 1987) may also be determined on an atomic scale by employing dI/dV spectroscopy techniques. Additionally, the STM possesses the ability to yield information about the spatial variation of local barrier heights (c.f. Binnig & Rohrer, 1983; Khaikin & Troyanovskii, 1985; Wiesendanger *et al.*, 1987).

Recent demonstrations of atomic resolution imaging in the presence of ionically conductive electrolyte solutions (c.f. Dovek *et al.*, in press (a); Gewirth & Bard, in press; Itaya & Sugawara, 1987; Sonnenfeld & Hansma, 1986; Sonnenfeld & Schardt, 1986; Weichers *et al.*, 1988) signal that STM might be a powerful tool for the characterization of electrode surfaces. In the past, electrochemists have needed to resort to *ex situ* or indirect methods to study the solid/liquid interface (Arvia, 1987; Dovek *et al.*, in press (a)) because vacuum techniques (e.g. SEM, LEED, ion diffraction and AES) are either not available for, or are extremely difficult to apply to, *in situ* studies of solid/solution interfaces. The

possibility of using STM's capabilities for *in situ* electrode characterization processes thus presents an exciting challenge to the electrochemist and surface scientist.

However, the electrochemical environment poses new problems to the tunneling microscopist. The total current between tip and sample may contain a substantial component attributable to faradaic charge transfer reactions. This current interferes with conventional STM imaging, because it thwarts feedback control of the tunneling current. Previous investigators have had to carefully choose the electrode/electrolyte system to insure that electrochemically active redox reagents were not present, and/or have had to constrain their ability to image by working at electrode and tip biases where faradaic tip/sample currents were minimal (see for example Gewirth & Bard, *in press*; Itaya & Sugawara, 1987; Lustenberger *et al.*, 1988; Sonnenfeld & Hansma, 1986; Sonnenfeld & Schardt, 1986; Weichers *et al.*, 1988). Since most electrode/electrolyte combinations of interest typically contain high concentrations of redox active reagents, these constraints will not provide a general method for successful imaging using conventional STM techniques. In this contribution, we describe the preparation of coated STM tips that relax this restriction. Such tips have less than $100 \text{ \AA}^2$ of exposed metal area at the apex, and apparently completely discriminate between the faradaic charge transfer currents and the tunneling current. To our knowledge, these tips exhibit the smallest amount of exposed metal area of any tips employed in STM studies to date. Below, we describe our procedures for tip etching and tip coating, and then describe the imaging capabilities that these tunneling tips have demonstrated.

Tip Etching

In order to obtain an electrochemically compatible tip material, we have chosen to use Pt-Ir tips for imaging in electrolyte solutions. The coating of these metal tips by glass and polymer layers (*vide infra*) was found to be a function of the sharpness, surface roughness, and cone angle of the etched tips. Consequently, as a crucial starting point to tip preparation, the etching characteristics of 0.020" Pt-Ir (30%) (Engelhard Industries, Carteret, New Jersey, U.S.A.) wire were investigated.

The electrochemical etching bath consisted of an unstirred solution of 6 M NaCN and 2 M KOH. Similar baths have been used elsewhere for Pt-Ir etching (Guld, 1964; Wolbarsht *et al.*, 1960). The

cyanide salt was employed to provide complexation of Pt and Ir ions in order to hasten electrochemical dissolution of the tip. The presence of OH^- served to inhibit the formation of HCN. All etching was performed in a fume hood.

To control the depth of immersion, the tips were mounted in a chuck which had an adjustable distance travel. A 3" inner diameter wax-impregnated graphite ring was used as the counter electrode, and this ring was centered around the Pt-Ir tip. Using this arrangement, the tip and counter electrode were lowered simultaneously into the etching bath. During etching, an AC potential was applied between the tip and counter electrode, and the current was monitored as a function of time in the etching solution.

Figure 1a shows a representative I vs. t curve for a tip etched at 25 RMS volts (60 Hz). Two distinct regions may be discerned in the figure. The transition from region I to region II was abrupt if the initial current, which was related to the initial depth of immersion, was at least 1.25 to 1.5 amps.

In stage I, visual inspection of the tip indicated that the diameter of the immersed portion of the tip was uniformly reduced with etching time, while the length remained essentially unchanged. The transition to stage II corresponded to a dramatic change in the etching mechanism of the tip. During this second stage a long and narrow metal filament, a result of stage I etching, was reduced in length without further reduction in diameter. The shapes of tips emerged at points labeled "A" or "B" in Figure 1a are schematically represented in the corresponding portions of Figure 1b. A tip removed 5 seconds after the abrupt transition from stage I to stage II etching, symbolized in the portion of figure 1b labelled "stop", was repeatably found to be morphologically smooth and sharp, with an aspect ratio of approximately 2 (height/radius). An electron micrograph of such a tip is shown in Figure 2. These tips were well suited for subsequent coating by either polymer or glass.

Over a variety of runs, we observed that etched tips varied widely in geometry and morphology as a result of changes in etching voltage, etching time or the age of the etching solution. Fortunately, the current vs. time relationships of the tips provided a bath-independent means by which the etching process could be monitored. Such curves reliably described the evolution of the tip structure for most

experiments, and the above etching procedure was found to be quite satisfactory for producing the desired tip features.

Tip Coating

In order to limit the amount of electrochemically active area (and thereby suppress faradaic currents in STM imaging mode), the etched tips were coated with either a glass or a polymer layer. Two similar methodologies were employed.

Glass Coating A coating apparatus was constructed in order to apply controllable, uniform coatings of non-porous glass insulation to the etched Pt-Ir tips. The apparatus is depicted in Figure 3, and consisted of a tip positioner that facilitated variable speed translation and a filament that produced molten glass beads to coat the tip.

The glass was maintained at the desired temperature by a resistively-heated ($T \leq 1700\text{ }^{\circ}\text{C}$) 0.020" Pt filament. In order to localize molten glass beads by surface tension, part of the filament was bent into a tear-drop shape that measured approximately 1.5 mm in inner diameter. To provide for measurement of the filament's temperature, 0.005" Pt and Pt-Rh(10%) thermocouple wires were welded to the Pt filament. Support for the filament consisted of two brass posts that were fed through a plexiglass base. The brass posts were cooled by water that flowed through the posts and through a rubber tubing bridge that connected them while the filament was heated. The posts also provided electrical contact to the filament. Prior to melting the glass, the entire filament-post system was covered with a bell jar and was evacuated through a port in the plexiglass base.

A soda-lime glass (Corning Glass # 0080) was chosen for tip coating because its thermal expansion coefficient (α), $3.5 \times 10^{-6}\text{ }^{\circ}\text{C}^{-1}$ (Bansal & Doremus, 1986), closely matched that of Pt-Ir(30%) (estimated to be $\sim 8.3 \times 10^{-6}$ by assuming α varies linearly from α_{Ir} to α_{Pt} with Ir content (CRC, 1975)). Additionally, the working point of the soda-lime glass (990 $^{\circ}\text{C}$) was readily accessible with a Pt filament (Bansal & Doremus, 1986). Prior to use, the glass was cleaned with $i\text{-C}_3\text{H}_7\text{OH}$ and deionized water.

To prepare the glass for coating the metal tip, glass from a 2 mm diameter rod was fed into the tear-drop of the electrically heated filament (c.a. 1400 °C). The filament was then cooled to room temperature and the system was enclosed with the bell jar and evacuated. When the interior pressure reached 40 mtorr, the filament was electrically heated to 1450 ± 20 °C for 5 minutes. During this time period, trapped gases were evolved from the molten glass bead. While maintaining a constant filament temperature, the bell jar was then vented to atmospheric pressure. This step served to insure that unescaped gas bubbles collapsed to a size that did not introduce pinholes in the STM tip's coating. The temperature of the glass was then reduced to a value used for the actual coating process, typically 1350 ± 20 °C.

The freshly etched tip was then mounted in a collet (Fig. 3), and positioners were used to center the tip relative to the molten glass bead. A manual micrometer drive then advanced the tip in the Z direction into the glass (Fig 3.). Tip speeds between 0.05 and 5 mm/min were maintained as the tip was introduced into, and translated through, the tear-drop of molten glass. During this process, glass was transferred from the tear-drop to the tip. The electric heating current was frequently adjusted to maintain a constant filament temperature despite the changing thermal mass of the filament. The progress of the coating was monitored by observing the filament from above during the coating process. In all cases, virtually all the glass was removed from the filament with 5 to 7 mm of tip translation. Further translation exposed a portion of the bare shaft, which was subsequently gripped with tweezers in order to remove the tip from the collet.

At tip speeds greater than ≈ 1 mm/min, the tip was not coated, but rather the glass bead was pushed out of the tear drop by the advancing tip. Speeds less than ≈ 0.5 mm/min allowed the tip to punch through the molten glass bead, and resulted in relatively large amounts of exposed metal area at the apex. Although these tips were not optimal for STM work, we have used tips made with these slow translation speeds to produce ultramicroelectrodes with sizes in the range of 0.01 to $25 \mu\text{m}^2$ (Penner *et al.*, in press). Intermediate tip speeds were the most desirable for STM tip fabrication. The correct tip speed was achieved when the shape of the apex of the tip could be seen emerging from the glass bead. It is important to note that, at present, this tip-coating process can only be qualitatively controlled.

Approximately 1 in 5 tips are suitable for STM imaging under solution in the most demanding electrochemical conditions (*vide infra*).

Polymer Coating. The procedure used for polymer coating was qualitatively similar to that for glass coating. Poly(α -methylstyrene) (P α MS) (Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A.), with a molecular weight of $\approx 60,000$, was found to have mechanical properties well suited for tip coating. The P α MS consisted of small polymer beads (weight ≈ 20 mg) that proved to be approximately the correct size for coating a single Pt-Ir(30%) wire. During coating, the polymer melt was adjusted to a temperature of approximately 210 ± 10 °C, which is ≈ 100 degrees higher than T_m for this polymer as determined by an iron-constantan thermocouple immersed in the polymer melt. Although the color of as-received P α MS was milky white, films cast from a polymer melt using this procedure were optically transparent.

Because of the lower temperatures involved in the polymer coating process, and the lack of the need to remove bubbles in the P α MS, a simpler polymer coating apparatus was sometimes substituted for that shown in Figure 3. This simpler apparatus consisted of a soldering iron onto which an "omega" shaped wire (dia. = 2-3 mm) was attached. The polymer bead was then supported by this wire and heated by the soldering iron. An AC RMS voltage of 110V-120V was applied to the soldering iron, and this yielded a polymer melt of the desired viscosity.

The coating of etched Pt-Ir(30%) wires was then accomplished by translating (by hand) the etched tip through the polymer melt. In the case of polymer coated Pt-Ir(30%) wires, the rate of tip translation during the coating process did not appear to be as important a variable as was found for the glass coating procedure. A typical tip translation speed was approximately 0.5 mm/sec, although qualitatively similar STM tip behavior was observed for tip speeds between 0.25 and 1.0 mm/sec. As in the case of the glass-coated tips, only about 20% of the polymer coated tips were found to be suitable for imaging in the most demanding electrochemical environments (*vide infra*).

Characterization

One of the key properties of electrochemical STM tips is the area of metal that is exposed to the electrolyte. The primary goal of our tip-coating processes is to reduce and control this exposed area, in order to minimize the faradaic current that is produced from a given tip/sample bias voltage. No information is currently available in the electrochemical STM literature concerning the active area of STM tips; consequently, there is a need to develop procedures that allow quantitative measurement of the exposed metal area of various tips. In this work, cyclic voltammetry was found to offer a convenient technique to determine the exposed electrochemically active area of the various STM tips. The microelectrode-type behavior of small metal hemispheres and disks has been recently described in the electrochemical literature (c.f. Aoki *et al.*, 1984; Dayton *et al.*, 1980), with the limiting current and the scan rate dependence of the I-V behavior providing information on the apparent radius and area of the active metal.

The tips of interest were used as the working electrode in a conventional potentiostatically-controlled 3-electrode cell. The reference electrode was a saturated calomel electrode, and the counter electrode was a Pt flag. The tips were held in such a way that only the coated ends of the tip were exposed to solution. In all measurements, the electrolyte was an unstirred aqueous solution containing 4.0 mM $K_4Fe(CN)_6$ and 1.0 M KCl.

Cyclic voltammetry data for an uncoated Pt-Ir tip wire clearly displayed diffusional waves associated with macroelectrode behavior, and, as expected, yielded large ($\approx mm^2$) exposed areas of metal. Figure 4 displays cyclic voltammograms and scanning electron micrographs for several types of tips. Figure 4a depicts the cyclic voltammetry of a typical commercially available (Longreach Scientific Resources, Orr's Island, Maine, U.S.A.) glass coated Pt-Ir(30%) tip. The voltammetry for this tip at a 50 mV/sec sweep rate displayed the steady state behavior indicative of a microelectrode. Using the well known expression for the limiting current at a hemispherical microelectrode (Dayton *et al.*, 1980), the area of exposed metal was determined to be $330 \mu m^2$. The size of the area seen at the tip's apex in the SEM photograph qualitatively agrees with the electrochemically determined area. This conclusion was

substantiated by energy dispersive X-ray analysis (EDAX), which indicated that the exposed metal consisted of Pt-Ir.

The tips shown in Figure 4b and 4c were fully insulated with polymer and glass, respectively. In contrast to the large faradaic current seen for the specimens used in Figures 4a, the cyclic voltammograms for these tips are featureless (except for spurious electrical noise) to less than 0.5 pA of faradaic current, even in the presence of 4 mM Fe(CN)_6^{4-} . A steady state current of 1 pA would correspond to an active area of $100 \text{ \AA}^2$, indicating that an upper limit of $100 \text{ \AA}^2$ can be established for the exposed metal area of these tips. Consistently, at the limiting resolution of the SEM ($\approx 1 \text{ }\mu\text{m}$), the underlying metal in the tips of Figures 4b and 4c was completely obscured by the coatings. In addition, the characteristic X-ray lines of Pt and Ir were not observed in EDAX analysis. We thus concluded that the tips were completely coated with insulation, and we had achieved our initial goal of eliminating the faradaic currents at the metal tip. Approximately one in four tips that were coated at optimal conditions were found to exhibit this behavior. The ultimate success of this procedure relies on the fact that the tip is essentially completely insulated by the coating, but the insulating layer is thin enough that, with one further preparative step, tunneling processes can still occur in a conventional STM arrangement. Examples of this process are described in the next section.

Imaging

Tips that were fully coated with insulation, as evidenced by the presence of the voltammetric behavior depicted in Figures 4b or 4c, were prepared for imaging in solution by mounting them in a scanning tunneling microscope (Figure 5) that was constructed specifically for electrochemical investigations (Dovek *et al.*, in press (b)). A typical electrode sample was highly ordered pyrolytic graphite (HOPG). The coated tips were moved towards the sample surface in $\approx 500 \text{ \AA}$ steps by voltage pulses sent to the stepper motor that drives our STM's approach mechanics. During this process the STM was operated in air. Tip potentials during approach were typically +10 V and +0.2 - +0.3 V (vs. the sample) for the glass and polymer coated tips, respectively.

Despite the fact that these tips were totally electrically insulated to faradaic current flow in the aqueous $\text{Fe}(\text{CN})_6^{4-}$ electrolyte, a tunneling current of 1 nA was sensed by the instrument upon approach to the graphite surface. Upon sensing this tunneling current, the pulse train to the stepper motor was electronically deactivated and the piezoelectric tube scanner was fully retracted. The voltage that controlled the retraction of the tube was then capacitively discharged, and the tip subsequently relaxed back into tunneling range. During this relaxation, for the case of the glass coated tips, the potential on the tip was manually reduced to values typically used for imaging in air (c.a. ± 20 to ± 400 mV). At this point, the tip was suitable for use both in conventional STM imaging experiments and for use in electrochemical STM experiments.

The physics associated with the approach/retraction process described above are uncertain. The process is definitely useful to prohibit prolonged intimate physical contact between the tip and the sample. Additionally, we speculate that dielectric breakdown of the coated tips may expose enough metal area so that tunneling then occurs. We call this step in the preparation of tips "field emission". We note that a similar procedure has been utilized to clean the apex of commercially available glass coated tips that had been insulated further by a SiO layer. The tips prepared in this manner were used to perform localized electrodeposition (Schneir *et al.*, in press).

In experiments in which HOPG was imaged in air, we observed that the large tip potential used for the field-emission procedure with the glass coated tips (+10 V) resulted in a reduced noise level of the tunneling currents. However, approximately 20-30% of the tips prepared in this manner did not allow the Z-piezo voltage to vary smoothly with the tunneling current. In these cases, feedback control could not be established, presumably due to an excessively thick residual coating at the apex of the tip. It is interesting to note that virtually all tips that enabled feedback control and that successfully completed the "field emission" process yielded atomic resolution images of HOPG in air. In contrast, in our trials, only 60-70% of uncoated Pt-Ir(30%) tips yielded atomic resolution images of HOPG in air. This observation suggests that a sharpening effect is also occurring as a result of the field emission process. One possible explanation of this phenomena might involve the transport of metal atoms along a crack in the coating.

The success of the tip insulation process was evidenced by the low faradaic current level from these tips during STM tunneling and imaging experiments. If the tip was retracted from the surface while imaging under solution (*vide infra*), no faradaic current was detectable above the noise level of the current preamplifier, implying that the level of faradaic current was less than 10-20 pA. However, the fragile nature of these tips, and the experimentally demanding constraints on tip insulation quality, were repeatedly evidenced by the fact that if the tip physically contacted the sample, then faradaic currents would completely overwhelm the tunneling current (i.e. $i_{\text{faradaic}} \gg 1 \text{ nA}$), and would disable feedback control at tip-sample biases as small as 10 mV.

Tips that successfully completed the insulation and field-emission procedure yielded atomic resolution STM images in a variety of electrolyte solutions. To date, we have succeeded in obtaining images of HOPG in DI water and aqueous 1.0 M NaCl at tip biases of $\pm 1.5 \text{ V}$, and in aqueous solutions simultaneously containing 0.1 M $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M $\text{Fe}(\text{CN})_6^{4-}$ and 1.0 M NaCl at biases of $\pm 0.8 \text{ V}$. This latter experiment represents the most dramatic suppression of faradaic current to date, and to our knowledge, is the only example of STM imaging in electrolytes containing such high concentrations of reversibly electroactive redox species. Notably, we have succeeded on rare occasions in achieving similar imaging capabilities using glass insulated tips that were made to our specifications by a commercial manufacturer (Longreach Scientific Resources, Orr's Island, Maine, U.S.A.). Such tips were constructed according to the restriction that they be as insulated as possible. Unfortunately, less than 4% of the tips we received were as insulated as the tips presented in figures 4b and 4c. Furthermore, only a small fraction of these well insulated tips were able to image, after field emission, in aqueous solutions at appreciable biases. Figure 6 shows an image obtained of HOPG with such a tip under 1M NaCl (bias of +0.550 V, tip positive) that is representative of images we have obtained with tips prepared in our laboratories. The need to reproducibly fabricate insulated STM tips that enable the imaging capabilities described above prompted us to develop the in-house tip preparation schemes that we have described. This procedure should open the door to the use of STM in a variety of unprecedented, real-time, *in situ* electrochemical investigations. Additional efforts to stabilize the desirable tip properties, and to take advantage of this tip production procedure, are underway at present.

Summary and Conclusions

We have described a procedure that yields insulated Pt-Ir tips for electrochemical STM experiments. These tips can be obtained by utilizing either glass or polymer layers as the insulating material. In both cases, tips can be prepared that totally suppress faradaic current at most tip/sample biases, even in concentrated aqueous solutions containing high concentrations of redox-active species. To obtain successful STM images, a tunneling current must be obtained, and we have described a field-emission approach and retraction procedure using the STM to reach this goal. Field-emitted tips have been prepared that allow tunneling currents to flow and enable atomic resolution STM imaging in numerous electrolyte solutions. Applications of this methodology to other electrode/electrolyte combinations is currently underway.

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Figure Captions

Figure 1. a) Current vs. time curve for a 0.020" Pt-Ir(30%) wire etched in an unstirred aqueous solution that contained 6M NaCN and 2M KOH. The etching voltage was a 25 V RMS potential. A description of stage I and stage II etching is found in the text. b) Diagrammatic representation of tip shapes found after emersion at points labelled "A", "B" and "STOP" in part a) of this figure.

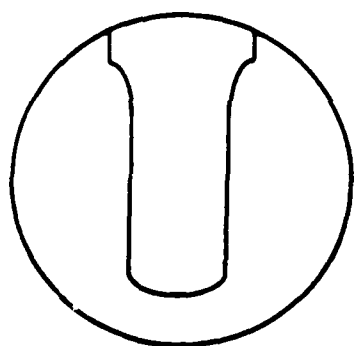
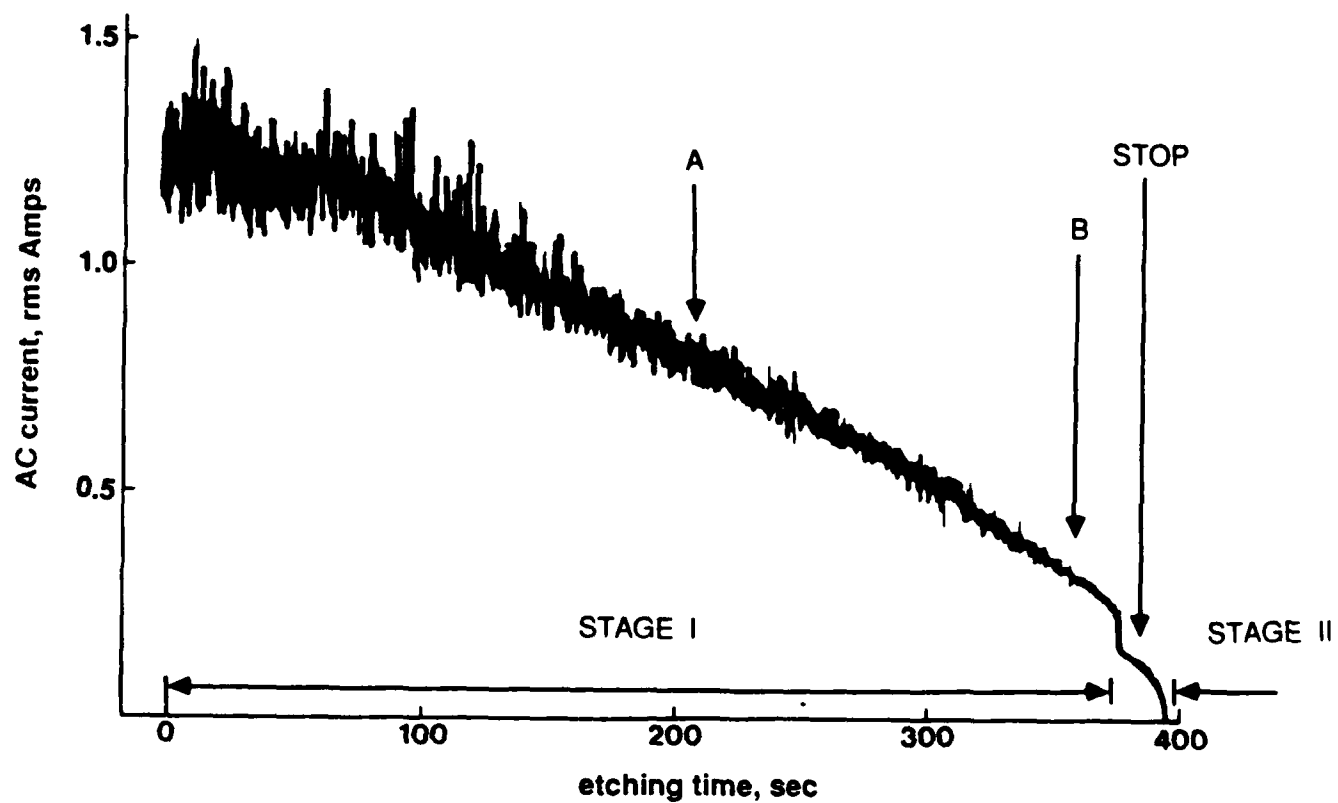
Figure 2. Scanning electron micrograph of a freshly etched Pt-Ir(30%) wire that was well suited for coating by either polymer or glass.

Figure 3. Schematic diagram of apparatus used to apply glass or polymer layers to etched Pt-Ir(30%) wires. A complete description may be found in the text.

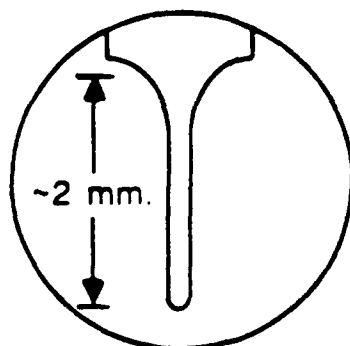
Figure 4. Comparison of cyclic voltammetry, electrochemically determined area and scanning electron micrographs for several coated STM tips. a) Commercially available glass coated tip. b) Fully insulated glass coated tip. c) Fully insulated polymer coated tip. Cyclic voltammetry was performed at 50 mV/sec in an unstirred aqueous solution containing 4 mM $K_4Fe(CN)_6$ and 1 M KCl.

Figure 5. Schematic diagram of the electrochemical STM.

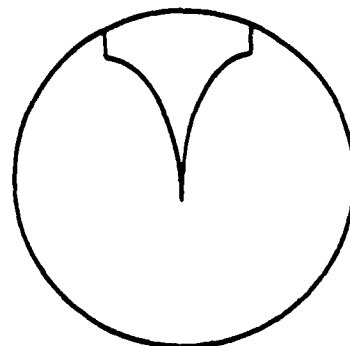
Figure 6. Scanning tunneling microscope image of HOPG obtained under an aqueous 1 M NaCl solution with a fully insulated glass coated tip. The tip potential was +0.550 V with respect to the sample. The tunneling current was 1 nA. The microscope was operated in fast scan mode and dark spots, separated by $\sim 2.5 \text{ \AA}$, correspond to large tunneling currents.



A



B



STOP

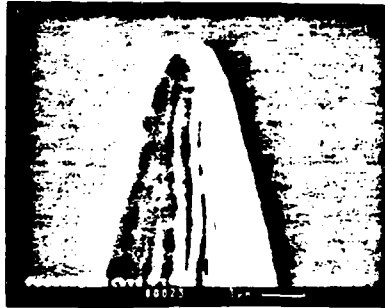


Fig 2

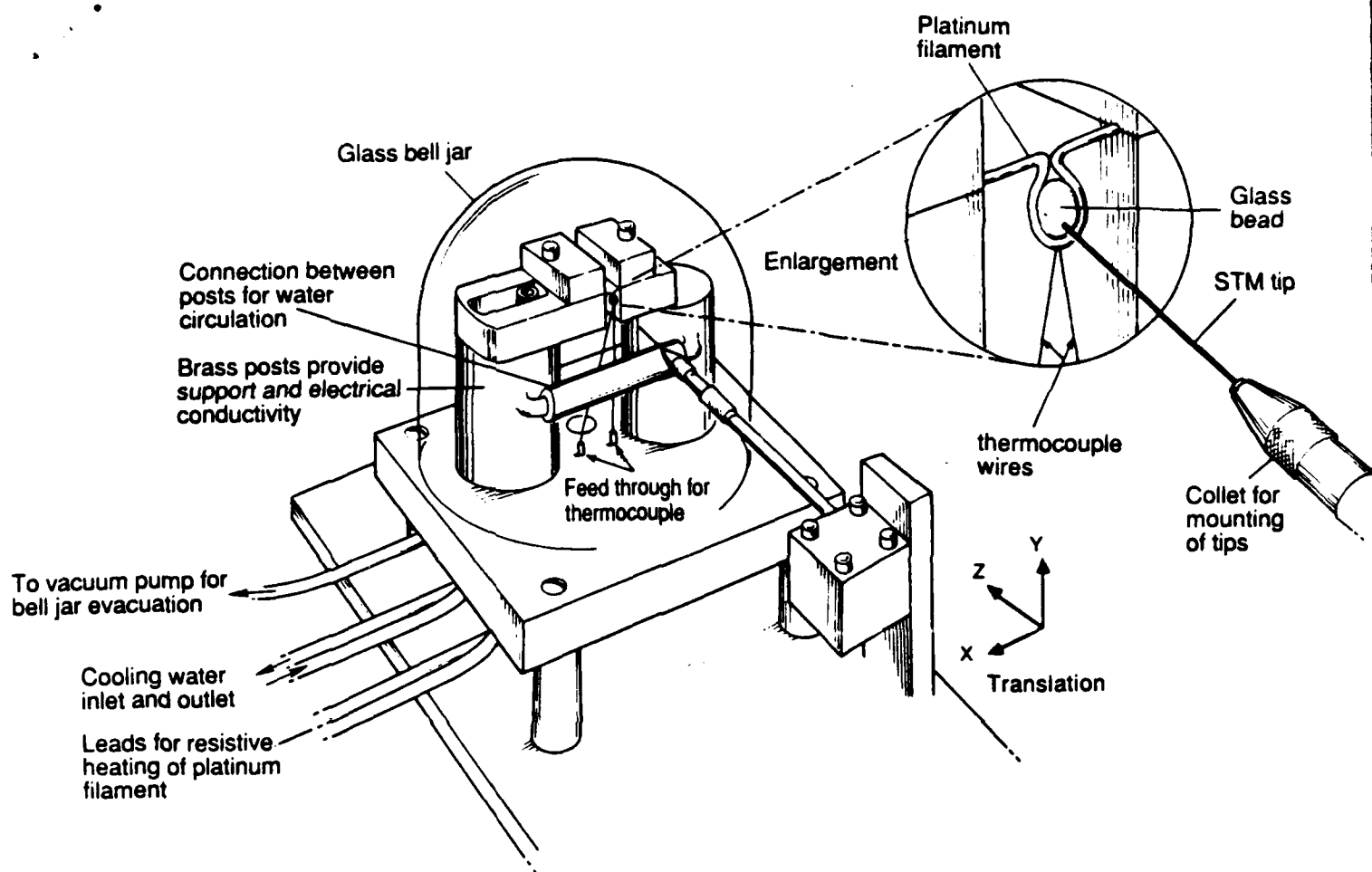


Fig 3

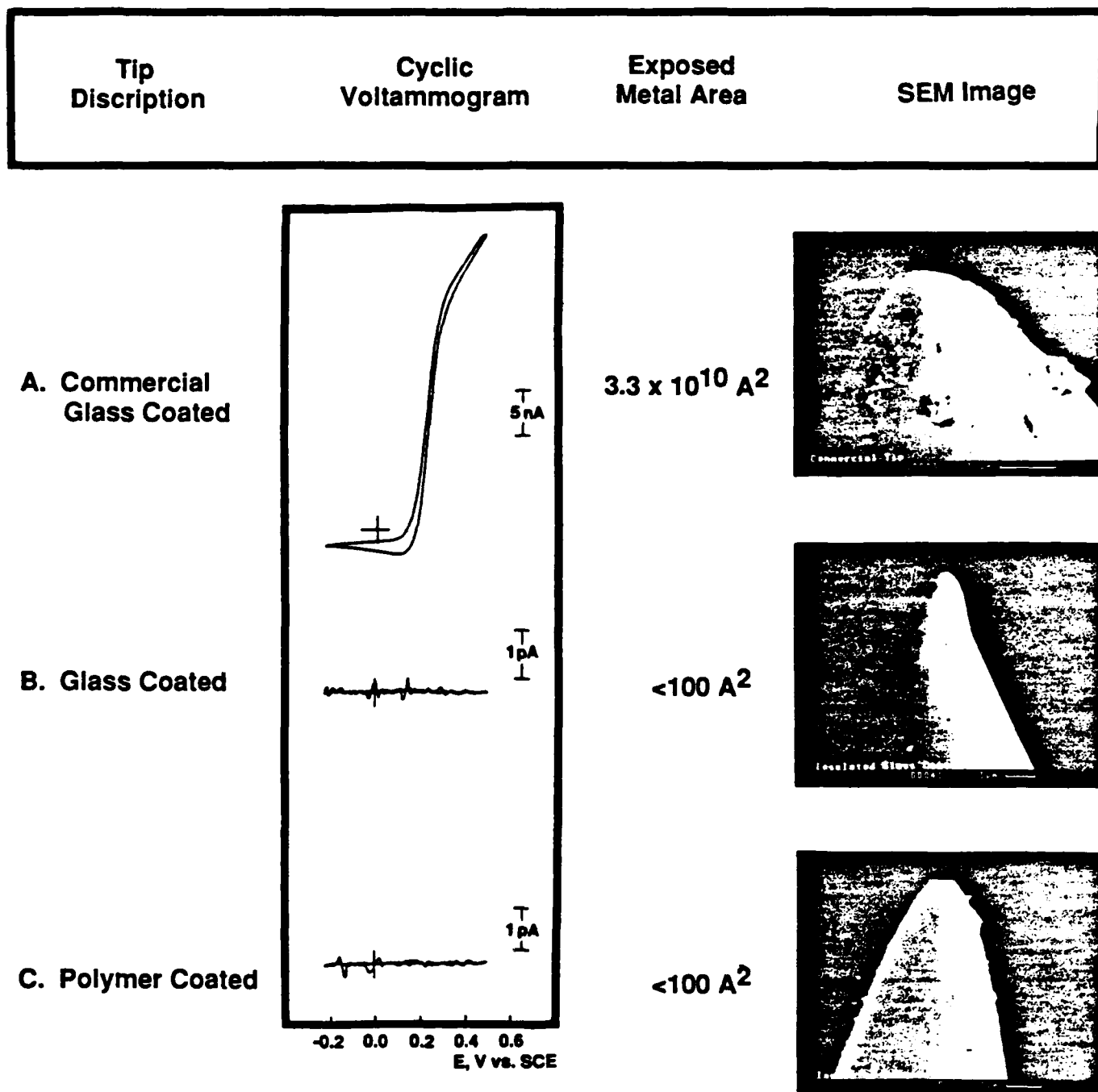


Fig 4

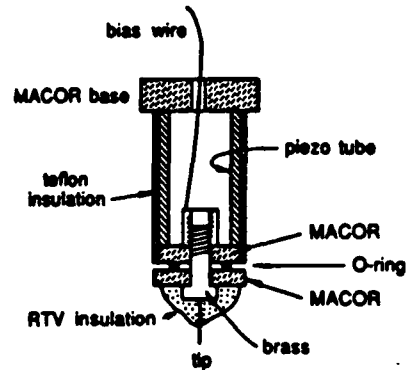
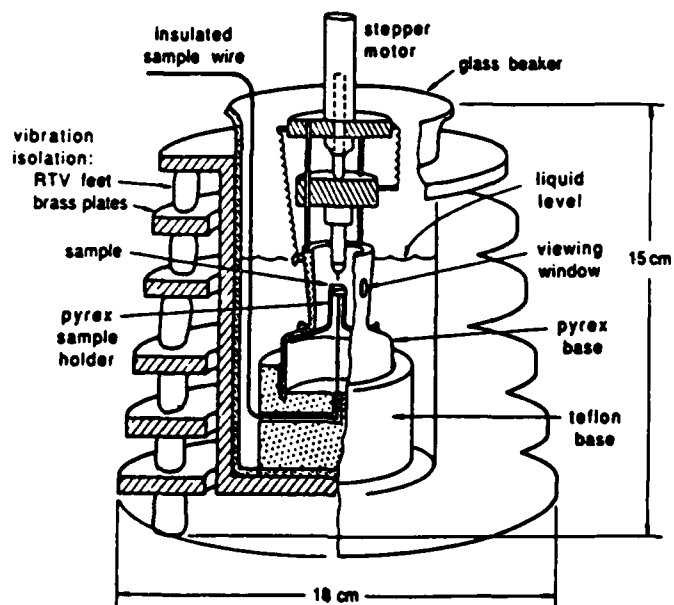


Fig. 5.

