

A new method of STM tip fabrication for in-situ electrochemical studies

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A new method of STM tip fabrication utilizing the electrophoresis technique and the ability of mercury to expand and shrink upon changing the temperature is introduced, and experimental details for tip etching and tip plating are described. Tips electrophoretically plated in 601 water-soluble electrophoretic varnish at 40 V for more than 30 min show good insulation behavior with exposed tip electrode disk radii around 0.8 μm . The apices of the plated tips remain undestroyed and clean after undergoing the mercury-touching procedure and the electrophoretic process. The characterization of ultramicroelectrode behaviors and the STM imaging capability of the plated tips are demonstrated.

I. Introduction

Apart from commercially available glass-coated tips, there have been contributions from several research groups to the construction of insulated STM tips for use with samples in the presence of a liquid (see, e.g., refs. [1–6]). These tips show qualities either in their simplicity of fabrication [6] or their small exposed area [3–5] or their capability of suppressing the Faradaic current [1,2]. In general, preparations of these tips are based on either a mechanical process or a physical process or a combination of both, except for W and Mo [1,2] on which oxide layers are spontaneously formed chemically.

In this note, we report a new method of protected tip preparation utilizing the electrophoretic technique. Procedures for tip etching and tip plating are described, and characterization and imaging capability of the insulated tips are demonstrated.

2. Experiment

2.1. Tip etching

Tips were prepared from a 0.3 mm \varnothing Pt–Ir(20%) wire by electrochemical etching in a mixture of 4M CaCl_2 , H_2O and HCl (60%, 36% and 4% by volume, respectively). A piece of the Pt–Ir wire (1.5 cm in length) was inserted into a small disk of silicon rubber. The purpose of using such an insertion method is to more easily indicate the etching terminal point by the drop-off of the silicon rubber as well as to form better-shaped tips within a short time period without complicating the experimental set-up. The other end of the Pt–Ir wire was inserted into a stainless steel tube which was mounted on the head of an adjustable microscope. The Pt–Ir wire was then immersed in the solution with the silicon rubber disk about 1–2 mm below the solution surface. An AC voltage of 20–30 V rms was applied to the Pt–Ir

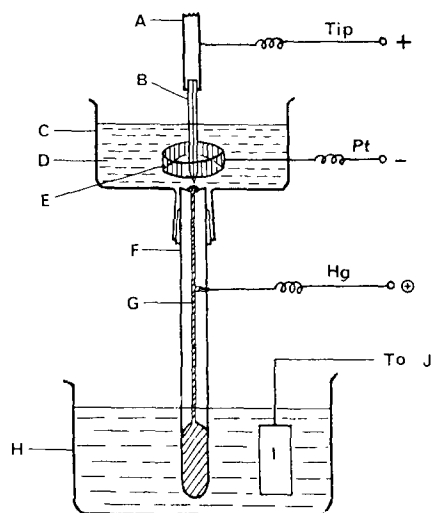


Fig. 1. Schematic diagram of experimental set-up for electroplating of etched tips. A - stainless steel tube adjustable in x , y , z directions, B - etched tip, C - cell, D - 601 electroplating varnish, E - Pt cylindrical foil as counter-electrode, F - glass capillary tube, G - mercury, H - temperature-controlled water bath, I - heater, J - bath temperature-control system.

against a tungsten ring until the silicon rubber disk dropped off, which took around 7–9 min in a completely new solution. The length of the cone part of the tip can be varied by varying the depth of the solution covering the silicon rubber disk, for uses with different purposes.

2.2. Tip plating

The side body of the etched tip was protected by electroplating in 601 water-soluble electroplating varnish [7]. A schematic diagram of the experimental set-up for electroplating of etched tips is shown in fig. 1.

The main part of the set-up is a glass capillary with a hollow at the bottom. The hollow and the capillary were gradually filled up with mercury until the mercury surface reached 2–3 mm below the top end of the capillary. The opening of the top was made cone-shaped to prevent the tensioned mercury hemisphere from drifting away from the capillary when heating (*vide infra*). The

etched tip, after being immersed in aqua regia for 10 s and then cleaned with distilled water, was inserted into a stainless steel tube which was mounted in an X - Y - Z -direction-adjustable stage. The tip was allowed to be positioned at a certain distance from the mercury. While the water bath was heated, the mercury gradually expanded until it reached the tip apex. The temperature of the bath was allowed to rise for another 2–3°C and remained constant through a temperature regulator to make sure that good contact between the tip and mercury had been achieved. The 601 electroplating solution was now filled into the cell and the electroplating started. During the plating, a DC voltage of 40 V was applied between the tip and the Pt counter-electrode and more than 30 min was usually needed to form an evenly insulated plating layer. To ensure that only the very end of the tip apex was free from plating, the DC voltage was applied between the mercury and the Pt counter-electrode in the last 10 min or so of plating when mercury was made to shrink by gradually cooling down the water bath with an approximate cooling rate of 0.3°C/min. At the time when the mercury eventually left the tip apex, the electroplating was automatically terminated.

The plated tip was washed with distilled water and dried at 100°C for a few hours.

2.3. Tip characterization

Ultramicroelectrode characterization of the plated tip was performed using a home-made potentiostat with an internal sweeping programmer. Solutions were prepared from chemicals of AR grade with triply distilled water. Three-compartment cell arrangement was used and potentials were quoted with respect to SCE.

2.4. STM measurement

STM measurements were performed in air using an instrument described in another paper in this volume contributed by the authors' group.

3. Results and discussions

The insulation capability of the plated 601 varnish layer is strongly dependent on the electrophoretic voltage as well as the time spent in the process. It can be shown that electrophoresis at 40 V for 30 min forms an almost completely insulating layer on a piece of Pt–Ir wire with a residual current of less than 0.05 nA in a solution of 5mM $\text{K}_3\text{Fe}(\text{CN})_6 + \text{K}_4\text{Fe}(\text{CN})_6 + 0.1\text{M KCl}$. Taking into consideration that a prolonged plating time might lead to the formation of a thicker plating layer around the cone part of the tip, which tends to geometrically block the apex of the cone in STM measurements, approximately 12 min of plating time was tentatively chosen in the present work for gradually plating the cone towards the apex of it.

Fig. 2 gives the cyclic voltammogram of the plated tip microelectrode. The appearances of the cyclic voltammograms of different plated tips prepared under the same conditions are reproducible in shape and value of the steady-state currents. The approximate areas of the tip electrodes were estimated using the equation for the steady-state current obtained at an ultramicrodisk electrode given by [8]

$$i_{s,s} = 4\pi FrcD,$$

where c and D are the concentration and diffusion coefficient, respectively, of the electroactive species, F is Faraday's constant and r is the

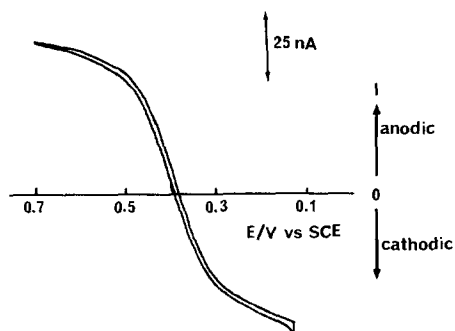


Fig. 2. Cyclic voltammogram of a plated tip electrode in a solution of 50mM $\text{K}_3\text{Fe}(\text{CN})_6 + \text{K}_4\text{Fe}(\text{CN})_6 + 0.1\text{M KCl}$. Sweeping rate: 2 mV/s.

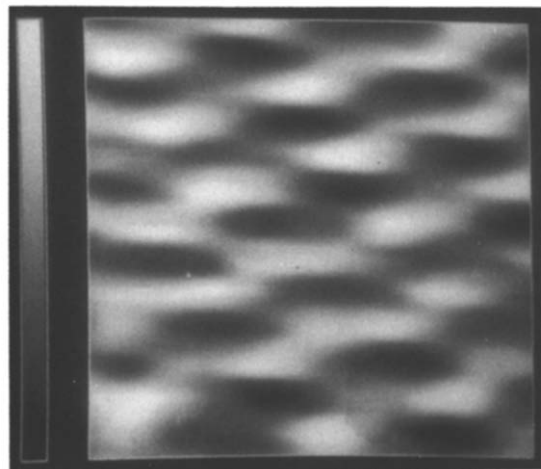


Fig. 3. STM image of HOPG surface in air using a plated tip.

radius of the disk electrode. The typical radius of the tip microelectrode with the steady-state current of 50 nA in 50mM $\text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$ solution was estimated at 0.8 μm . Measurements for the stability of the insulated tips in acidic solution were made. It has been found that the tips experiencing 14 h dipping in 0.5M HClO_4 solution do not degrade significantly with only a slight increase of the steady-state current of the ferri–ferrocyanide system.

The apices of the plated tips remain intact and clean after undergoing the mercury-touching procedure and the electrophoretic process. These were verified both with SEM and STM. Fig. 3 shows a STM image with atomic resolution of a highly oriented pyrolytic graphite [9] surface in air using a plated tip.

It should be noted that although a prolonged plating time of the cone part of the tip (i.e. the mercury shrinking rate was made low) might lead to bad performance of the tip in STM measurements, the time of plating in this period can be increased really without too many worries. While not having optimized the mercury shrinking rate, it is likely that the exposed areas of the plated tips can be further reduced.

An in-situ STM image of Cu/HOPG in air-saturated aqueous solution of $10^{-3}\text{M H}_2\text{SO}_4$ was obtained with the insulated tips [10], and further in-situ studies are currently in progress.

4. Conclusion

The results show that electrophoretically plated tips have good insulation behavior with exposed tip electrode disk radii around $0.8 \mu\text{m}$. The apices of the plated tips remain intact and clean after undergoing the mercury-touching procedure and the electrophoretic process. It is likely that the exposed areas of plated tips can be further reduced by decreasing the water bath cooling rate.

Acknowledgments

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