

# Atomic resolution imaging of electrode surfaces in solutions containing reversible redox species

Michael J. Heben, Reginald M. Penner, and Nathan S. Lewis<sup>a)</sup>

*Division of Chemistry and Chemical Engineering, Contribution No. 7891,  
California Institute of Technology, Pasadena, California 91125*

Moris M. Dovek and Calvin F. Quate<sup>a)</sup>

*Department of Applied Physics, Stanford University, Stanford, California 94305*

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Procedures are described for insulating metal scanning tunneling microscope (STM) tips with either glass or polymer coatings. In solutions containing 0.10 M of a reversible redox couple,  $\text{Fe}(\text{CN})_6^{3-/4-}$ , the faradaic limiting current to polymer coated tips was 200–500 pA and that for glass coated tips was < 10 pA. For polymer insulated tips, steady-state currents of 10–100 pA were observed at tip-sample displacements less than 0.3  $\mu\text{m}$ . The suppression of faradaic current achieved by these coating procedures enabled the collection of the first atomic resolution STM images of highly ordered pyrolytic graphite electrodes in contact with redox-active electrolytes. Preliminary data for the *in situ* electrochemical characterization of these tips are also discussed.

Although scanning tunneling microscopy (STM) has demonstrated considerable promise for the *in situ* characterization of electrode surfaces, a serious problem is control of the tip/sample tunneling current in the presence of substantial faradaic currents. To date, all STM images of the electrode/electrolyte interface have been obtained either in electrolytes which did not contain redox active reagents<sup>1</sup> or at tip/sample biases that precluded faradaic tip/sample currents in the particular solution of interest.<sup>2</sup> Even in these solutions, the presence of residual faradaic impurities severely limited the available tip/sample bias voltage.<sup>1,2</sup> Alternative schemes based on three or four electrode systems have been proposed to overcome this problem<sup>3</sup>; however, in all such schemes, the tip/sample bias necessary for producing a tunneling current will inevitably result in a faradaic tip/sample current when electrochemically active species are present. A more general method of avoiding this problem is to attempt to insulate the body of the tip from faradaic current flow, while maintaining facile tunneling probability at the end of the tip.<sup>4</sup> In this letter, we present two insulated tip fabrication procedures that have yielded STM tips which suppress faradaic current even in the presence of high concentrations ( $\approx 0.1$  M) of redox-active reagents. We also demonstrate that it is possible to use these tips to obtain atomic resolution STM images of electrode surfaces over a wide range of tip/sample biases in these highly conducting electrolytes.

To obtain suitable tips, etched Pt-Ir wires<sup>5</sup> were coated with a thin layer of glass by translation through a molten glass bead.<sup>6</sup> Manipulation of the tip translation speed (0.5–1 mm/min) and the glass temperature ( $\approx 1400$  °C) provided control over the thickness and quality of the insulating glass coating. Similarly, etched tungsten wires were coated by translation (2–5 mm/s) through a film of a 35 wt/vol % solution of poly( $\alpha$ -methylstyrene)<sup>7</sup> dissolved in  $\text{CH}_2\text{Cl}_2$ .

The polymer coated the surface of the wire as the solution evaporated in air. In a subsequent step, a field-emission process (*vide infra*) was employed to expose an extremely small amount of metal at the apex of the tip.

For tips coated by either method, the exposed metal area, estimated by measuring the steady-state diffusion-limited faradaic current<sup>8</sup> to the tip in aqueous 4 mM  $\text{Fe}(\text{CN})_6^{4-}$ , 1 M KCl solutions, was less than 100  $\text{\AA}^2$  (limiting current < 1 pA). In contrast, the exposed metal areas of partially glass-coated Pt-Ir STM tips obtained from a commercial manufacturer<sup>9</sup> were typically  $10^9$ – $10^{11}$   $\text{\AA}^2$ , and the resulting large faradaic currents precluded STM imaging in the redox-active electrolytes of interest.

The tip insulation process described above thus successfully suppressed faradaic current processes. However, as fabricated, these tips were unsuitable for use in STM imaging. Typically, a controllable tunneling gap could not be formed when conducting substrates were approached in air with normal biases of 200–500 mV. Occasionally, feedback control of the tunneling current setpoint could be maintained after approaching. In these instances, tip/sample contact was evident in the distorted current traces that were obtained when the *x-y* scans were activated. Tips processed in this manner apparently maintained enough insulating material at the apex to interfere with feedback control of the tunneling gap. In order to circumvent this problem, the insulated tips were placed in a STM that was specifically constructed for electrochemical studies<sup>10</sup> and a field-emission process was performed in an air ambient. The insulated tip was maintained at a large positive bias (+ 15 V) as it was moved with a stepper motor towards a highly ordered pyrolytic graphite (HOPG) sample. An electronically sensed tunneling current (1 nA) automatically terminated the pulse train to the stepper motor and fully retracted ( $\approx 0.75$   $\mu\text{m}$ ) the piezo tube scanner along its *z* axis. The potential on the tip was then reduced to a value typically used for imaging ( $\approx 300$  mV), the electrolytic solution of choice was intro-

<sup>a)</sup> Authors to whom correspondence should be addressed.

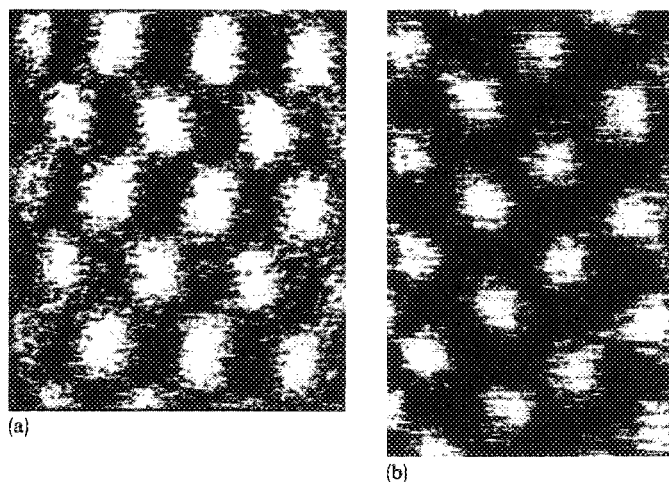


FIG. 1. STM images of highly ordered pyrolytic graphite. (a) Image obtained in air with a bare tungsten tip: bias = +200 mV, tunneling current = 0.5 nA. (b) Image obtained in a solution containing 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 0.1 M  $\text{Fe}(\text{CN})_6^{4-}$ , 1.0 M KCl using a polymer coated tungsten tip: bias = +200 mV, tunneling current = 1.0 nA.

duced into the STM, and the tunneling tip was brought smoothly into tunneling range as the voltage on the piezo was reduced. Tips prepared with this process exhibited an exponential dependence of tunneling current on tip/sample displacement. Moreover, the field-emission operation allowed tunneling to be established without damaging the tip coating. These tips suppressed faradaic currents, even in highly conductive electrolytes, to values of less than 0.5 nA.

Using this procedure, STM images (employing conventional fast scan feedback methods) were readily obtained in a variety of electrolyte solutions. Figure 1 displays images of HOPG in air and in an aqueous solution containing 0.1 M  $\text{Fe}(\text{CN})_6^{3-}$ , 0.1 M  $\text{Fe}(\text{CN})_6^{4-}$ , 1.0 M KCl. Carbon atoms, separated by  $\sim 2.5 \text{ \AA}$ , are clearly evident in both of these images. It is interesting to note that, except for the difference in scale, the two images are virtually identical despite the fact that the image in Fig. 1(a) was obtained in air and the image in Fig. 1(b) was obtained at a surface in contact with a redox-active electrolyte. Furthermore, the HOPG surface of Fig. 1(b) is evidently free of adsorbates that can be detected by the STM imaging procedure. This observation is in accord with the expected chemical inertness of the basal plane surfaces of graphite.

STM images similar to those shown in Fig. 1(b) were obtained over a range of tip/sample biases in a variety of electrolytes. To date, we have successfully imaged HOPG at tip/sample biases of  $\pm 1.5 \text{ V}$  in pure  $\text{H}_2\text{O}$  and in aqueous 1 M NaCl, and at biases of  $\pm 0.8 \text{ V}$  in aqueous solutions of 0.1 M  $\text{Fe}(\text{CN})_6^{3-}$ , 0.1 M  $\text{Fe}(\text{CN})_6^{4-}$ , 1.0 M KCl. These data represent the first atomic resolution images of an electrode surface in contact with liquids containing both forms of a reversible redox couple.

It is of interest to determine the relationship between the observed current and the tip/sample separation for glass and polymer insulated tips. Current versus tip/sample separation ( $s - s_0$ ) data were obtained by translating the tip toward the sample at a rate of  $10 \text{ \AA/s}$  (Fig. 2). The approach was automatically halted by the feedback circuit as the tip

was brought into tunneling range. Currents for polymer/W tips and a HOPG sample in aqueous 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 50 mM KCl were less than the noise in the current measurement (i.e.,  $< 10 \text{ pA}$ ) for tip/sample separations larger than  $\approx 50 \text{ \AA}$  (curve A). In solutions containing larger concentrations of the redox active ions [0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 1 M KCl] the maximum faradaic currents at polymer/W tips were 200–500 pA (curve B). Qualitatively similar behavior was observed for polymer/W tips with a Pt sample<sup>11</sup> (curve C). The limiting currents of 200–500 pA observed for tips of this type correspond to exposed metal areas of  $\approx 10^3\text{--}10^5 \text{ \AA}^2$ .<sup>12</sup> In contrast, currents for glass/Pt-Ir tips in 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 1 M KCl were  $< 10 \text{ pA}$  at all tip-sample displacements greater than  $\approx 50 \text{ \AA}$  (curve D). This limiting current corresponds to  $< 30 \text{ \AA}^2$  of exposed metal area.<sup>12</sup> The observed suppression of faradaic current at small tip/sample separations for polymer/W tips is not in accord with qualitative models based on macroscopic diffusion theory,<sup>13</sup> but these models may not be applicable when extremely small numbers of electroactive molecules are present in the tip/sample gap region. A quantitative investigation of this faradaic current process will be presented in a separate study; however, the data suggest that the insulated tips described here may allow electron tunneling currents to be significantly decoupled from the electrochemical environment, even in solutions where unacceptably high faradaic currents are present at large tip/sample separations.

In principle, the tip insulating procedures described here should provide a general means of applying *in situ* atomic resolution STM imaging and spectroscopy methods to many electrochemically important systems. The accessi-

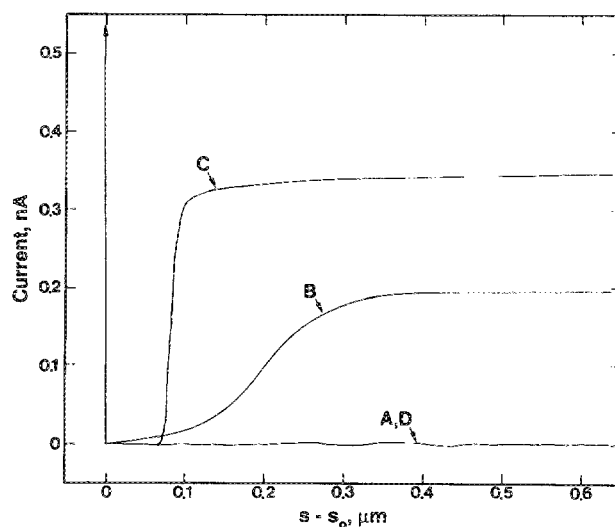


FIG. 2. Dependence of total current on tip-sample displacement,  $s - s_0$ , for polymer coated tungsten tips and glass coated Pt-Ir tips. Tip translation velocity =  $10 \text{ \AA/s}$ , bias = +250 mV, tunneling current setpoint = 1.0 nA. Current noise of  $\approx 20 \text{ pA}$  peak to peak amplitude has been removed for clarity. (A) Polymer/W tip and HOPG sample in contact with 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 50 mM KCl, (B) polymer/W tip and HOPG sample in contact with 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 1.0 M KCl, (C) polymer/W tip and Pt(111) sample in contact with 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 1.0 M KCl, (D) glass/Pt-Ir tip and HOPG sample in contact with 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$ , 1.0 M KCl.

ble bias range achieved in this work is also significant in that it should enable inelastic electron tunneling methods to be performed on surfaces while in contact with these redox-active electrolyte solutions.<sup>14</sup> Additionally, STM imaging with potential control of electrode surfaces can be performed without concurrent adjustment of the tip/sample bias potential to suppress faradaic current processes. Finally, the small exposed tip radius of the coated wires should enable local electrodeposition processes and spatially resolved electroanalytical detection methods to be performed on conventional metal electrode surfaces. Experiments exploiting these new capabilities will be described in separate publications.

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<sup>5</sup>Pt(70%)-Ir(30%) wire (diam. = 0.5 mm, Engelhard Ind.) was electrochemically etched in aqueous 6 M NaCN, 2 M KOH to yield sharp conical tips.

<sup>6</sup>Corning glass No. 0800, melt temperature = 1350 ± 50 °C. The molten glass (1400 °C) was outgassed at 40 mTorr for 5 min immediately prior to use. A description of the glass coating apparatus can be found in M. J. Heben, M. M. Dovek, N. S. Lewis, R. M. Penner, and C. F. Quate, *J. Microsc.* (in press).

<sup>7</sup>Poly( $\alpha$ -methylstyrene) MW = 60 000 g/mol, from Aldrich Chemical Co. was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was supported by a wire loop at room temperature.

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<sup>11</sup>Pt(111) single crystals were polished with 1.0, 0.3, and 0.05  $\mu$ m alumina powders prior to use.

<sup>12</sup>The exposed metal area was calculated from the hemispherical diffusion equation:  $i_s = nFDC(2\pi A)^{1/2}$ , where  $F = 96487$  C/eq.,  $D = 8 \times 10^{-6}$  cm<sup>2</sup>/s,  $C$  is the concentration, and  $n = 1$  eq<sup>-1</sup>; M. A. Dayton, J. C. Brown, K. J. Stutts, and R. M. Wightman, *Anal. Chem.* **52**, 946 (1980).

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