

A new electrochemical scanning tunneling microscope

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A new in-situ electrochemical scanning tunneling microscope (ECSTM) has been designed in our laboratory with the following main features: (1) The normal electrochemical current at the tip during scanning can be automatically corrected by a newly designed special feedback loop and computer program. (2) The tip-sample bias potential and the individual electrode potential of tip or sample can be adjusted, scanned or cycled by computer according to the requirement. (3) Driving and adjusting the tip to a nanometer distance from the sample surface can be carried out by a computer-controlled motor. A preliminary example of application to electrochemical systems is presented.

1. Introduction

Scanning tunneling microscopy and related methods are attractive and powerful tools for in-situ studies of electrochemical phenomena and processes at electrode/electrolyte interfaces on an atomic or near-atomic scale. Achievements have been obtained by many research groups [1-5]. Here we report a scheme for correction of the electrochemical current of the tip.

The tip current consists of two parts: the tunneling current and the electrochemical current (mainly Faradaic current). The electrochemical current depends on the electrode potential and the compositions of electrolytic solution and tip. It can be comparable to or even much greater than the tunneling current and cannot be distinguished from the latter. Even the direction of the electrochemical current may be different from that of the tunneling current.

The interference of the electrochemical current should be reduced in order to improve the in-situ performance. A simple way is to restrict

the applied electrode potential to a narrow range or to confine the composition of the electrolytic solution. But the field of application is also restricted to a very small area in this case. There are two better ways: (1) to make the exposed tip area as small as possible by suitable techniques of tip fabrication [5-9]; (2) to distinguish the tunneling current at the tip from the electrochemical current at the tip by an appropriate design of the electronic circuit and computer program of the STM instrument which can be called electrochemical scanning tunneling microscope (abbreviated to ECSTM).

In addition, the barrier height is an important structural parameter and can be calculated via the Fowler-Nordheim relationship:

$$\text{barrier height/eV} = [d(\log i)/d(s/\text{\AA})/1.025]^2,$$

where i is the tunneling current and s is the tip-sample distance [10]. If the electrochemical current, which is essentially independent of the tip-sample distance, is not separated from the

tunneling current, this relationship cannot be used or the obtained barrier height would be too small.

Robinson suggested a circuit using an isolated battery supply to permit separate control of the electrochemical current at the sample, independently from the tip current [11], but this circuit cannot yet separate the total tip current into the electrochemical component and the tunneling current.

A new in-situ electrochemical scanning tunneling microscope (ECSTM) has been designed in our laboratory, and will be described in this paper, which has the following main features:

- (1) The normal electrochemical current of the tip during scanning can be automatically corrected using a special feedback loop as well as computer program described in this paper.
- (2) The tip-sample bias potential and the individual electrode potential of tip or sample can be adjusted or cycled by computer according to the requirements.
- (3) Automatic positioning and adjusting the tip to a nanometer distance from the sample surface can be carried out by a computer controlled motor.

2. Principle and experimental design for the correction of the electrochemical current

2.1. Operation principle of the instrument

The operation principle of our ECSTM is illustrated in the schematic of fig. 1 and is based on the fact that the electrochemical component of the tip current depends much less on the tip-sample preparation than the tunneling current. The instrumental operation is designed for STM measurements in the constant-current mode. In addition to the normal electrolytic STM technique, it involves after each scan cycle in X direction the following special tip withdrawal/approach sequence to determine the electrochemical current component:

- (1) After termination of a scan cycle in X direction, the scan in Y direction proceeds by one step, and the Z signal for the piezoelectric tube scanner control is sampled and held by the first sample-and-hold circuit SHZ (fig. 1).
- (2) The feedback loop is then interrupted, and an extra value V_{extra} is added to the Z signal in order to withdraw the tip from the sample to a

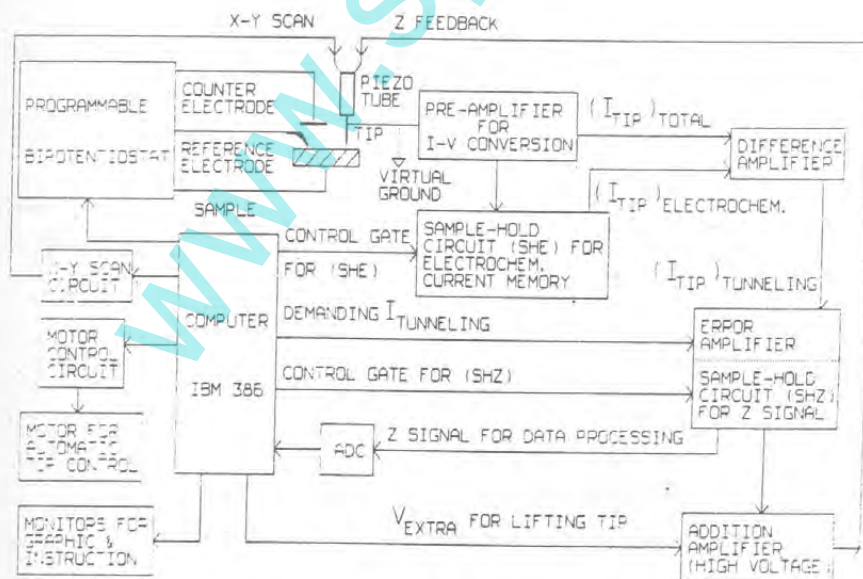


Fig. 1. Schematic diagram of the electrochemical STM enabling correction of the electrochemical current at the tip.

distance where the tunneling current can be neglected and the remaining tip current equals the normal electrochemical current at the tip.

(3) This electrochemical current at the tip is then sampled and held by the second sample-and-hold circuit SHE (fig. 1).

(4) the above-mentioned value V_{extra} applied to the Z signal is removed, and the feedback loop is closed again. This causes the tip to reapproach the sample and the tunneling regime to be re-established.

(5) then the next scan cycle in X direction is continued in the following manner: The difference between the value of the tip current (consisting of the sum of tunneling and electrochemical current) and the value sampled at SHE (electrochemical current) is measured and compared with the value of the preset tunneling current to obtain the error signal. The error signal is amplified and fed back into the control circuit for the Z distance, to adjust the tip to a Z position, where the error signal is minimized. The corrected Z signal is then recorded by the computer for data processing.

2.2. Programmable potentiostat

A specially designed programmable bipotentiostat, presented schematically in fig. 2, facili-

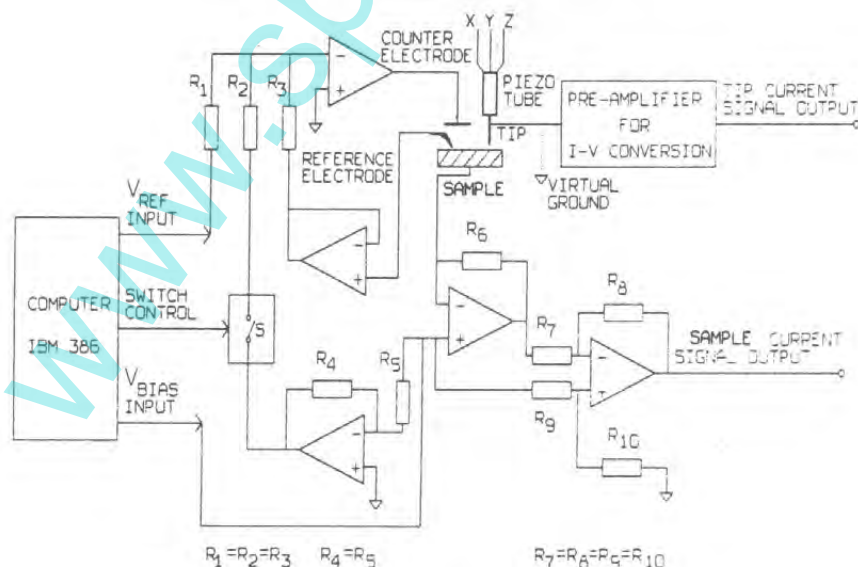


Fig. 2. Schematic diagram of the programmable bipotentiostat.

Table 1

Control of the potential differences between tip, sample and reference electrode by input signals for different control modes (cf. fig. 2)

Mode	T	S
Switch S	Off	On
$E_{tip\ vs\ ref} =$	V_{ref}	$V_{ref} - V_{bias}$
$E_{sample\ vs\ ref} =$	$V_{ref} + V_{bias}$	V_{ref}
$E_{sample\ vs\ tip} =$	V_{bias}	V_{bias}

tates different control modes of the potential differences between tip, sample and reference electrode, summarized in table 1: By applying either mode T or mode S, the input voltage V_{ref} will control either the tip potential $E_{tip\ vs\ ref}$ or the sample potential $E_{sample\ vs\ ref}$. In both modes the bias voltage $E_{sample\ vs\ tip}$ between sample and tip is controlled by the input bias voltage V_{bias} .

3. Preliminary results

Fig. 3 shows as a preliminary result an in-situ STM image of electrochemical Cu deposition on HOPG using the ECSTM instrument described above. Cu was first electrodeposited onto HOPG from an aqueous solution of $2 \times 10^{-4} M$ $CuSO_4 + 10^{-3} M$ H_2SO_4 . The in-situ STM image was then

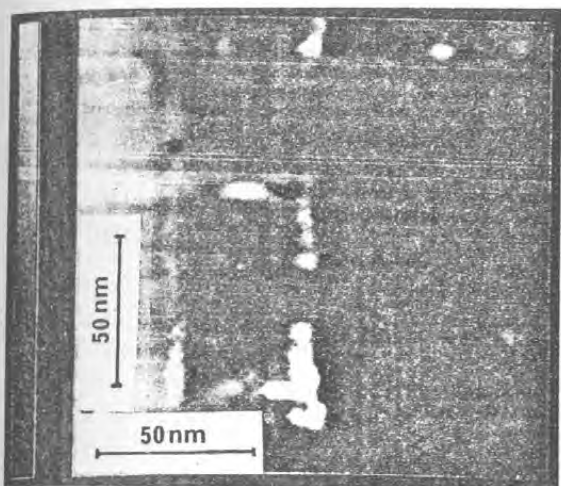


Fig. 3. In-situ STM image of Cu/HOPG (electrodeposited from an aqueous solution of $2 \times 10^{-4} \text{M}$ $\text{CuSO}_4 + 10^{-3} \text{M}$ H_2SO_4) in an air-saturated aqueous solution of 10^{-3}M H_2SO_4 (see text). The full graytone scale of Z comprises 2 nm. Sample at open-circuit potential; $E_{\text{sample vs tip}} = -400 \text{ mV}$; tunneling current = 4 nA.

obtained in an air-saturated aqueous solution of 10^{-3}M H_2SO_4 under open-circuit potential of the sample. The tip was fabricated in our laboratory using an electrophoresis technique described elsewhere [12]. The electrochemical reduction current of the dissolved oxygen was about 40 nA and was corrected automatically. As a preliminary result, it can be seen that Cu cluster formation took place presumably along a surface defect of the HOPG. More detailed experiments are in progress in our laboratory.

4. Conclusion

We have shown that the electrochemical current at the tip, which would perturb the STM

measurement in electrochemical systems, can be corrected under computer control and by using a special design of the feedback loop of the electronic circuit.

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