

Spring 2008 MSAE E4990y
Introduction to STM and AFM

Lecture 4
Electrochemistry STM
 February 4, 2008

Outline

- Basics of electrochemistry
- The three-electrode electrochemical cell
- The four-electrode electrochemical STM
- Electrochemical tip generation
- Tip preparation for EC-STM
- Substrate preparation for EC-STM
- Real-time atomic-scale observation of the reduction-oxidation (redox) process
- Molecules at the liquid-solid interface

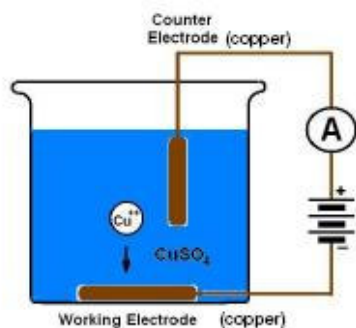
References: Sections 1.5.2, 13.2, 13.6.

Basics of Electrochemistry

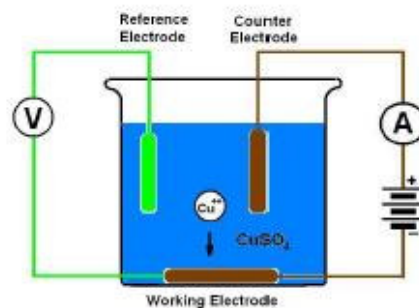
Faradaic current
 electrical current
 carried by ions.

Typical magnitude of
 the Faradaic current:
 $-1 \mu\text{A}/\text{cm}^2$.

Study of chemical reactions at the interface of an ionic conductor (electrolyte) and an electron conductor (typically metal).



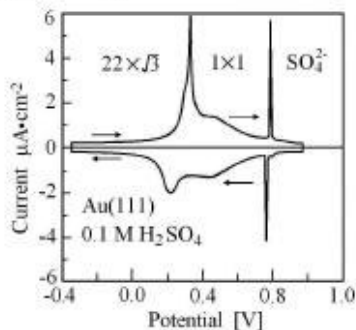
The three-electrode electrochemical cell



By adding a reference electrode to the electrochemical cell, the absolute value of the potential at the working electrode versus the standard can be determined.

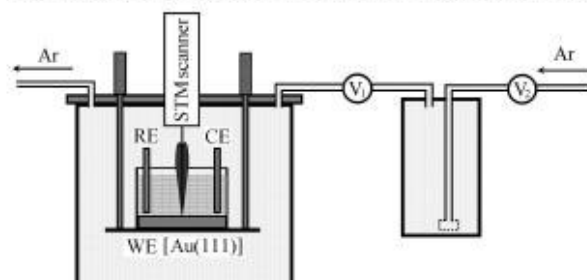
Using an electronically controlled variable power supply to ramp the potential up and down, a voltammogram is generated as a record of the redox process.

A typical cyclic voltammogram



Starting with fresh-made Au(111) surface at -0.35V. At +0.35V, a reconstruction takes place. At +0.8V, a layer of SO_4^{2-} is formed. The process is reversible.

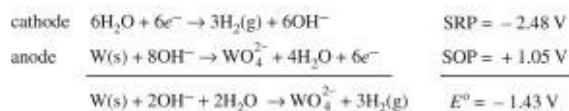
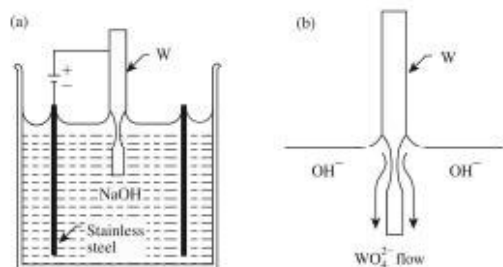
The four-electrode electrochemical STM



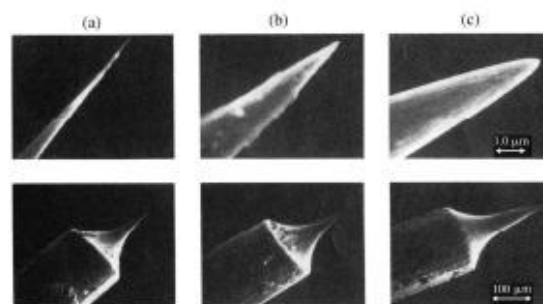
In addition to the working electrode (WE, the sample), the counter electrode and the reference electrode, the STM tip is introduced as the fourth electrode.

To eliminate oxygen, the STM chamber is flushed with argon gas.

Tip preparation using electrochemistry

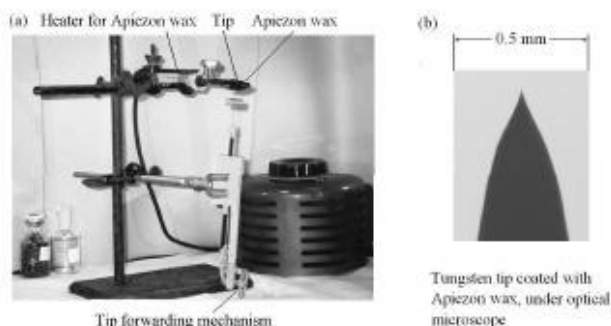


Dependence of tip shape on cutoff time



The radius of curvature of the tip is related to the cutoff time after the lower part of the W wire drops off. (a) $t = 600 \text{ ns}$, $r = 32 \text{ nm}$. (b) $t = 140 \text{ ms}$, $r = 58 \text{ nm}$. (c) $t = 640 \text{ ms}$, $r = 100 \text{ nm}$. Therefore, a short cutoff time is preferred.

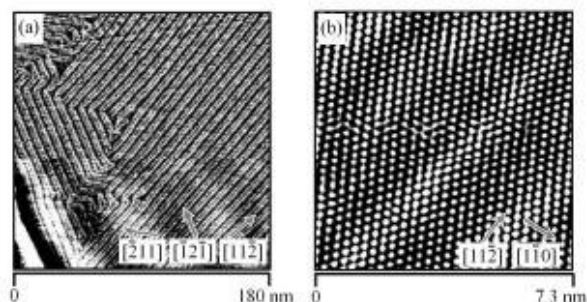
A simple apparatus to coat the tip for EC-STM



The typical Faradaic current is $-1 \mu\text{A}/\text{cm}^2$, or $-0.01 \text{ pA}/\mu\text{m}^2$.

To make the Faradaic current $< 1 \text{ pA}$, the exposed area should be $< 100 \mu\text{m}^2$.

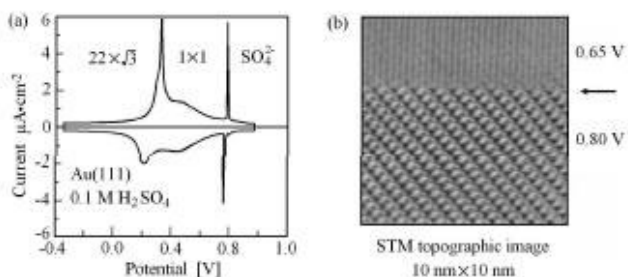
Au(111) surface imaged by STM in a liquid



(a) At relatively large scale, the Au(111) $22 \times \sqrt{3}$ reconstruction is observed.

(b) At smaller scale, under good conditions, individual atoms are observed.

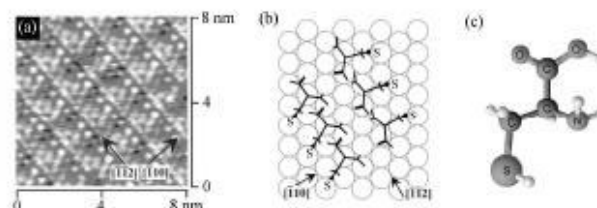
Voltammogram and STM images of Au(111)



The structure of a crystal surface in an electrolyte can be controlled by potential.

(a) The voltammogram. At about 0.78 V, the Au(111)- 1×1 surface is covered by an ordered layer of sulfate ion. (b) By changing the potential during a single scan, the STM image changes from Au(111)- 1×1 to a sulfate-ion layer.

Self-assembled monolayer of cysteine on Au(111)



In order to observe large biomolecules using STM, the molecules must be immobilized on a conducting surface.

A proven method is to start with a single-crystal metal surface, such as Au(111), form a self-assembled monolayer of molecules which could form a strong bond on that metal surface, for example, a thiol (organic molecule containing a $-\text{SH}$ group).