Electrochemical Scanning Tunneling Microscopy

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From pretty pictures ….

… to useful data.
Topics

Basics
- introduction into STM
- in-situ STM in electrochemical environment
- sample preparation

Applications
- electrode surface structure
- structure of adsorbate layers
- adsorbate dynamics
- growth processes
- surface phase transitions
Scanning Tunneling Microscopy – Experimental Issues

Mechanical stability

Problems and artifacts
- piezo nonlinearity
- creep
- noise
- drift
Scanning Tunneling Microscopy - Principle of Operation

\[ I_t \propto U_t \cdot \exp(-\text{const.} \cdot \sqrt{\phi} \cdot \Delta z) \]
Scanning Tunneling Microscopy - Modes of Operation

**Constant Current Mode**
- Constant Current (0.1 - 10 nA)
- Feedback-controlled tip motion
- Measured signal: z-control
- Absolute height information
- Relatively slow scan speed

\[ I_t \propto U_t \cdot \exp(-\text{const.} \cdot \sqrt{\phi} \cdot \Delta z) \]

**Constant Height Mode**
- Constant Height (z = 3 - 10 Å)
- No feedback-control
- Measured signal: \( I_t \)
- No absolute height information
- Relatively fast scan speed
- Not applicable for rough surfaces
Scanning Tunneling Microscopy – Image generation

Topview image

3D image
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In-situ electrochemical STM

Diagram showing the setup for in-situ electrochemical scanning tunneling microscopy (STM). The diagram includes labels for CE, RE, tip, WE, $I_{f,\text{sample}}$, $I_{SECM}$, $I_{f,\text{tip}}$, $U_t$, $U_{bias}$, and $U_s$. The diagram illustrates the flow of currents and the setup of the electrodes.
In-situ electrochemical STM

tip potential controlled versus electrolyte ('Bipotentiostatic setup')

Electrochemical Cell

Potentiostat

\[ U_{\text{sample}} \]
\[ U_{\text{tunnel}} \]
\[ U_{\text{tip}} \]

Counter electrode
Reference electrode
Tip
Sample

\[ I_{\text{tunnel}} + I_{\text{ion}} \]

Feedback

\[ V_{\text{tip}} \]
STM tips

Problems:
- Faradaic processes (currents, tip changes)
- Double layer capacity (noise)

Solved by:
- controlled tip potential
- tip coating
  - apiezon wax
  - polyethylene
  - electrophoretic paints
  - glas
  - nail polish

→ faradaic currents <10 pA
   tip capacitance < 10 pF
In-situ STM - Setup

coarse approach
single tube scanner
electrochemical cell

sample
Reference electrodes:

- wire (Pt, Pd/H, Cu)
- conventional RE + liquid bridge
Spatial resolution

High-resolution images of:
- close-packed metal lattices
- ordered adsorbate layers

→ similar as under UHV conditions

Au(100)  Au(111)  Au(110)

8 x 8 nm²
Tunneling barrier in electrolytes:
- On clean electrode surfaces $\phi \approx 1$ eV
- Oscillations in $\phi$ due to liquid structure

STS in electrochemical environment

- **I/V measurements**: limited bias range, limited tip stability
- **Local barrier height**: only qualitative information
- **Redox-reaction studies**: fast transfer rates

Au(111) in 0.1 M HCl after sequential deposition of 0.5 ML Pd and 0.25 ML Au

![STM images showing Au(111) substrate, Pd deposit, and Au deposit]
Tunneling Spectroscopy of Redox Centers

Resonant tunneling through redox states

Example: Graphite / Fe-Porphyrin / STM-tip

Problem: modification of structure / dynamic behavior due to presence of STM tip

- direct effects:
  - mechanical interactions (for $d_{\text{tunnel}} \ll$)
  - $e_{\text{tunnel}}$ induced effects
  - exchange processes between tip and sample

- electrostatic effects
  (for $d_{\text{tunnel}} < d_{\text{DL, tip}} + d_{\text{DL, sample}}$)

- geometric effects (shielding, accumulation) for processes involving exchange with solution
Tests for tip effects

- variation of scanned surface area
- variation of tip-sample distance $d_{\text{tunnel}}$ ($\rightarrow i_t, U_t$)
- variation of interaction time
- comparison with macroscopic measurements ($\rightarrow$ electrochemical data)

Ni deposition on Au(111)

4 nA
100 nm

1.6 nA
210 nm

F. Möller, PhD thesis (1996)
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Sample preparation

Sample requirements for high-resolution STM:
• Atomically smooth samples
• surface contamination < 0.1 ML for several hours → High purity of electrolyte and cell

Sample preparation methods:

• flame annealing
  Gold(hkl), Au films
  Pt(hkl)

• electropolishing / chemical polishing
  Cu(hkl)
  Ag(hkl)
  Si(111)-H

• electrochemical reduction
  Ni(hkl)

• in-situ deposition
  Pd$_x$Au$_{1-x}$
Au(hkl), Au films:
- Bunsen burner
- Cooling in air

Pt(hkl):
- H$_2$ flame
- Cooling in Ar

Au(111) herringbone reconstruction (sample immersed under potential control)
Electropolishing / chemical polishing

Cu(hkl):
- 66% H₃PO₄
- 1.8 V vs. Pt, 10s

Ag(hkl):
- Chromate etch

Ag(111)

10⁻³ M NiSO₄
10⁻² M H₃BO₃
10⁻¹ M HCl

-0.4 V Ag/AgCl
Electrochemical reduction

Oxidized Ni(111)  Reduced Ni(111)

Annealed in H₂
Exposed to air at 300K

0.05 M H₂SO₄
-0.31 V SCE
In-situ deposition

Diffusion-controlled alloy deposition:

- $D_{Au} \approx D_{Pd} \rightarrow$ stoichiometry $\approx c_{Au}/c_{Pd}$
- Surface diffusion increased by Cl$^-$
  $\rightarrow$ atomically smooth films

$\leq 12 \times 10^{-3}$ ML/min
$Pd_{0.1}Au_{0.9}$
Applications of EC STM

• structure and reactivity of alloy electrodes

• adsorbate layers

• adsorbate dynamics

• metal electrodeposition

• phase transitions at metal electrode surfaces
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**AuPd / Au(111): Composition and Atomic Structure**

**Pd$_x$Au$_{1-x}$ supported catalysts:**

Catalysts for anode reaction in low-temperature fuel cells (PEM - FC)

Model system: electrodeposited Pd$_x$Au$_{1-x}$(111) films

**In-situ STM Analysis:**

<table>
<thead>
<tr>
<th>Chemical contrast:</th>
<th>Selective Pd dissolution:</th>
</tr>
</thead>
<tbody>
<tr>
<td>→ $\approx 7%$ Pd</td>
<td>$\theta_{\text{holes}} \approx 0.07 \text{ ML}$</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow \approx 7%$ Pd</td>
</tr>
</tbody>
</table>
AuPd / Au(111): distribution of Pd surface atoms

Statistical analysis of STM images:
→ surface density of Pd atom ensembles (monomers, dimers, trimers)
→ tendency towards 2D mixing

F. Maroun et al., Science 293, 1811 (2001)
AuPd / Au(111): H Adsorption

H adsorption peaks:
With increasing Pd content gradual increase of $q_{H-Ad}$ ($\theta_H << \theta_{Pd}$)

Critical ensemble for H adsorption:
Pd dimers

F. Maroun et al., *Science* 293, 1811 (2001)
Oxidation of preadsorbed CO monolayers:

\[ \theta_{\text{CO}} \approx \theta_{\text{Pd}} \]

Critical ensemble for CO adsorption:
Pd monomers

In situ FTIR Spectroscopy (SNIFTIRS):
- On-top adsorption of CO on Pd monomers
- Bridge/three-fold bound CO on larger Pd ensembles

F. Maroun et al., Science 293, 1811 (2001)
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Sulfate / Au(111): adlayer phase transition

Surface reconstruction: (22x√3) ↔ (1x1)

Sulfate adlayer ordering disordered ↔ (√7x√3)

Au(111)
0.1 M H₂SO₄
10mV/s

E [V SCE]

j [μA cm⁻²]
Sulfate / Au(111): adlayer phase transition

1.0 M H$_2$SO$_4$

Sulfate / Au(111): adlayer structure

0.1 M H$_2$SO$_4$
0.85 V$_{SCE}$

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Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

- 0.01 M HCl + 50 $\mu$M Na$_2$S
- $-0.36 \ V_{Cu/Cu^+}$
- 20 images/s
- real time

$S_{ad}$ hopping between neighbouring $c(2\times2)$ lattice sites

[Diagram showing $Cu$, $Cl_{ad}$, and $S_{ad}$]
Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

0.01 M HCl + 50 µM Na$_2$S

-0.36 $V_{Cu/Cu^+}$

20 images/s

automatic image recognition

$S_{ad}$ hopping between neighbouring $c(2x2)$ lattice sites
Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

Determination of jump distribution functions

0 ms

67 ms

4c(2x2) $\leq d_{NN}$

Model

Experiment

$f_{fit} = 4.1 \text{ s}^{-1}$

$470 \text{ mV}_{SCE}$

$\Delta t = 100 \text{ ms}$

$\theta_{S-ad} = 0.008 \text{ ML}$

probability

0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

displacement / $a_0$

0

1

$\sqrt{2}$

2

$\sqrt{5}$

$2\sqrt{2}$

3

0 1 2 1 2 2

$\sqrt{5}$

$\sqrt{5}$

$2\sqrt{2}$

$\sqrt{2}$
Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

Influence of STM-tip on $S_{ad}$ diffusion → negligible for $i_t \leq 9$ nA

$S / Cu(100)$ in 0.01 M HCl

$-0.3 \, V_{Cu/Cu^+}$

![Graph showing hopping rate vs. tunnel-current]
Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

Results of quantitative measurements:
- Arrhenius behavior
- Potential-independent preexponential factors $v_0 = 2 \cdot 10^{12} \text{ s}^{-1}$
- Potential-dependent diffusion barrier $E_a$

Diffusion of atomic adsorbates: $S_{ad}/Cu(100)$

$$E_{\text{diff}} = 0.94 \text{ eV} + 0.50 \text{ eV} \cdot \phi / \phi_{\text{SCE}}$$


**Graph:**
- $E_d (\text{eV})$ vs. $\phi (V_{\text{SCE}})$
- $\nu_s (\text{s}^{-1})$ vs. $E_d (\text{eV})$

S / Cu(100) in 0.01 M HCl

296 K
Potential-dependence of $S_{ad}$ diffusion

$E_{\text{diff}} = 0.94 \, eV + 0.50 \, eV \cdot \phi/V_{\text{SCE}}$

Electrostatic contribution to free energy of adsorption:

$$\Delta G_{ad} = \Delta G_{ad}^0 + \frac{p_{ad}}{\varepsilon_0} \cdot \sigma$$

→ potential-dependence:

$$\frac{d (\Delta G_{ad})}{d \phi} = \frac{p_{ad}}{\varepsilon_0} \cdot C_d$$

Difference in adsorbate charge state / dipole moment between adsorption site and activated state

→ electrostatic contribution to diffusion barrier:

$$E_{\text{diff}} = \left( \Delta G_{ad,\text{act}} - \Delta G_{ad,c(2 \times 2)} \right) = E_{\text{diff}}^0 + \frac{C_d}{\varepsilon_0} \cdot \left( p_{ad,\text{act}} - p_{ad,c(2 \times 2)} \right) \cdot \phi$$

Similar field-effects for all adsorbates / surface defects

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Growth on the atomic scale

Issues in growth and dissolution processes

- Nucleation:
  - homogeneous/heterogeneous
  - sites

- Growth morphology:
  - 2D/3D
  - island shape

Influence of interface structure

- Attachment / Detachment
- Intralayer-diffusion
- Interlayer-diffusion
- Nucleation
**Cu(100) in HCl: Adsorbate effects in kink dynamics**

**Cu(100) growth/dissolution in HCl solution**
- at individual, well separated kink sites
- kink structure determined by Cl adlayer
  → growth/dissolution in form of $(\sqrt{2} \times \sqrt{2})$R45° rows
- high local growth/dissolution rates

0.01 M HCl
-0.23 V_{SCE}
10 images/s
slow motion: × 2


Cu(100) in HCl: Kinks in monolayer steps

Phase relation of c(2x2) at monolayer steps
→ structural anisotropy
→ anisotropic deposition/etching

0.01 M HCl, -0.23 V_{SCE}
10 images/s

Heteroepitaxy: metal nucleation

Ru / Au(111)  Ni / Ag(111)

Ru / Au(111)  Pt / HOPG
**Au/Pt(111): heteroepitaxial growth**

Effect of coadsorbates on surface transport

-0.20 $V_{SCE}$

0.00 $V_{SCE}$

0.26 $V_{SCE}$

0.50 $V_{SCE}$

Nucleation density $\Gamma$

$\rightarrow$ Au surface mobility:

- increased at intermediate Cl coverage
- decreased at saturation Cl coverage

Au/Pt(111): heteroepitaxial growth

Stranski-Krastanov growth

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Au / Pt(111): Potential-induced Dislocation Networks


- reversible, potential-induced phase transitions from (1x1) to uniaxial and hexagonal dislocation networks in Au mono- and double layer
- potential-dependent spacing of dislocations
Potential-induced reconstruction of Au(100)

0.01 M Na$_2$SO$_4$ + 1mM HCl
10 mV/s
Potential-induced reconstruction of Au(100)

- Solution: 0.01 M Na$_2$SO$_4$ + 1mM HCl
- Scan rate: 10 mV/s
- Display rate: x10

20 images/s
(1 min. video)

0.01 M Na$_2$SO$_4$
+ 1mM HCl
10 mV/s
Mobility of metal nanostructures

0.01 M Na₂SO₄ + 1mM HCl
-0.21 Vₑ
160 Å × 210 Å
20 images/s

Transversal mobility of "hex" strings

Model of "hex" string mobility: nucleation and 1d motion of highly mobile dislocations

Mobility of double strings

Static string distortions: $l_{\text{dist}} \geq 15$ Å
Mobility of reconstruction strings

Quasi-collective motion of “hex” strings:
- perpendicular to string direction
- along string direction
Mobility of Au Adatoms on ,,hex“ strings

Interaction Au adatom / “hex” string
→ 1d transport along string
→ channeling of Au\textsubscript{ad} to string end

$\Delta E_{1\times1} = 0.79 \text{ eV}$
$\Delta E_{\text{hex}} = 0.11 \text{ eV}$
$\Delta E_{1\times1 \rightarrow \text{hex}} = 0.66 \text{ eV}$
$\Delta E_{\text{hex} \rightarrow 1\times1} = 0.10 \text{ eV}$

DFT calculations: C. Ramirez, W. Schattke
Summary

How EC STM can help you to understand electrocatalysis/electrochemistry:

• clarify electrode structure:
  defects (steps, kinks), reconstructions, composition (→alloys)
• detect ordered adlayers
• get local spectroscopic information (difficult!)
• obtain insight into mechanisms of surface processes
• perform quantitative measurements on surface processes,
  e.g.: energy of surface defects, surface transport rates,
  phase transition kinetics

What can STM do for you?
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Postdoc position available