Introduction and Principles of Scanning Electrochemical Microscopy

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Figure 2
Schematic representation of the SECM experiment. (a) Steady-state diffusion to the tip far from substrate. (b) Tip is near a conductive substrate. Positive feedback. (c) Tip is near an insulating substrate. Negative feedback.
Electrochemical Cell Configuration

Tip (Working Electrode): Pt - a typically 0.5 to 12.5 μm

Reference & Counter Electrodes: Pt wire

Substrate: 3 mm diameter Pt disk
Experimental Set Up

- Biopotentiostat
- Inchworms
- Micro-position Controller
- Electrochemical Cell

SECM
E applied (V)

0.5

0

-0.2

Quiet time

1 segment

1 voltammogram

time
Voltammogram at 25 μm diameter tip

1 mM FcMeOH
Voltammogram at 3 mm diameter Pt substrate

1 mM FcMeOH
Feedback Mode

Approach Curves
Feedback mode

Measure $i_T/i_{T,\infty}$ (or $I_T$) vs. $d/a$ or $(L)$
CONCENTRATION PROFILES IN FEEDBACK MODE

Digital simulations by Explicit FD Method

Conditions:

\[ a = 12.5 \, \mu m \]
\[ RG = 2 \]
\[ d = 10 \, \mu m \]
\[ i_T = -9.82 \, nA \]
\[ k(E) = 1 \]
Feedback Mode

Measure $i_T/i_{T,\infty}$ (or $I_T$) vs. $d/a$ or $(L)$

Tip Approach -
Ideal
$I_T = \frac{i_T}{i_{T,\infty}}$

**FIG. 4** Diffusion-controlled steady-state tip current as a function of tip-substrate separation. (A) Substrate is a conductor; (B) substrate is an insulator. (From Ref. 2.)
Approach curve for insulator (glass or Teflon)

\[ I(L) = \frac{1}{\left(0.292 + \frac{1.5151}{L} + 0.6553 \exp\left(-\frac{2.4035}{L}\right)\right)} \]

\[ \text{RG} = 10 \]
\[ i_T = nFDC_O^* \pi a^2 / d \]

Thin layer feedback

\[ D = 5 \times 10^{-6} \text{ cm}^2/\text{s} \quad C_O^* = 10^{-5} \text{ mol/cm}^2 \]

\[ a = 12.5 \mu\text{m} \]
\[ i_T = \left( nFDC_O^* \pi a^2 / d \right) + 4nFDC_O^* a \]

Total current

\[ D = 5 \times 10^{-6} \text{ cm}^2/\text{s} \quad C_O^* = 10^{-5} \text{ mol/cm}^2 \]

\[ a = 12.5 \mu\text{m} \]
Approach curve for conductor (Pt)

\[
I(L) = 0.68 + \frac{0.78377}{L} + 0.3315 \exp \left( -\frac{1.0672}{L} \right)
\]

RG = 10
Tip Approach - Bad alignment
RG \sim 3
Tip Approach -
Bad alignment
RG ~8
Experiment

Theory - conductor
Other Modes

Tip Generation - Substrate Collection

Substrate Generation - Tip Collection
SECM Modes

Feedback

- Measure $i_T$, Steady state
- Area interrogated controlled by tip size

SG/TC

- Measure $i_T$ and $i_s$
- Low collection efficiency
- No steady state $i_s$

Large substrate

Small substrate

SG/TC

- Measure $i_T$ and $i_s$
- Low to medium collection efficiency
- Steady state $i_s$

TG/SC

- Measure $i_T$ and $i_s$
- High collection efficiency
- Steady state $i_s$
Tip Generation - Substrate Collection (TG-SC)

Measure $i_T$ and $i_S$ as function of $d$ and $E$

$$C_O = \bar{C}_O$$

$$C_R = 0$$

UME Tip

Electroactive Substrate
Substrate Generation - Tip Collection (SG-TC)

Measure $i_T$ and $i_S$ as function of $d$ and $E$

\[ C_O = C_O^* \]
\[ C_R = 0 \]
Imaging
Imaging with the SECM

Constant height: $i_T$ vs. $x,y$ position at constant $z$

Constant current: $z$ vs. $x,y$ position at constant $i_T$
Figure 4. Scans of a 50-μm platinum wire on a glass slide at different tip locations from sample: tip electrode, 5.5 μm radius carbon disk tip electrode at 0.80 V vs AgQRE; solution, 10 mM TBAP, 5 mM ferrocene in acetonitrile; scanning speed, 19.7 μm/s; (A) far from sample, (B) close (about 17.8 μm, see text) to sample, (C) 2.18 μm closer than B, (D) 4.36 μm closer than B.
CYCLOPORE POLYCARBONATE MEMBRANE FILTER

0.2 μm pore size

Z axis: 0.15 - 0.45 nA

0.2 M K₄Fe(CN)₆

0.2 M Na₂SO₄
SECM image of a polycarbonate filter membrane

Pt,
\[ a = 5 \mu m \]
\[ d \leq 1 \mu m \]

C,
\[ a = 3.5 \mu m \]
\[ d \leq 1 \mu m \]
How does one distinguish conductive and insulating regions from the tip current?

From magnitude of tip current

From phase angle of tip current
Heterogeneous Kinetics and Reaction Rate Imaging
\[ k_f \rightarrow 0 \quad \text{Insulator (negative feedback)} \]

\[ k_f \rightarrow \infty \quad \text{Conductor (positive feedback)} \]
Effect of heterogeneous kinetics on SECM approach curves

<table>
<thead>
<tr>
<th>d/a</th>
<th>Rate constants (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. 1</td>
<td>f. 0.01</td>
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<tr>
<td>b. 0.5</td>
<td>g. 0.005</td>
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<tr>
<td>c. 0.1</td>
<td>h. 0.002</td>
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<tr>
<td>d. 0.025</td>
<td>i. 0.0001</td>
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<tr>
<td>e. 0.015</td>
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</table>
Effect of heterogeneous kinetics on SECM approach curves

Rate constants (cm/s)

- a. 1
- b. 0.5
- c. 0.1
- d. 0.025
- e. 0.015
- f. 0.01
- g. 0.005
- h. 0.002
- i. 0.0001
Fabrication and Micropatterning
SECM Fabrication - Direct method

Fig. 2. SEM picture of a pattern of silver lines deposited in a Naflon film. Tip material = tungsten, bias = 5 V, tip current $\approx 0.5$ nA, and scan rate $\approx 900$ Å/s. Tip reaction, $\text{Ag}^+ + e^- \rightarrow \text{Ag}$; substrate reaction, $\text{Ag} \rightarrow \text{Ag}^+ + e^-$. 

Scheme 1: Schematic Representation of the Approach for Attaching Organic and Biological Molecules onto Surfaces Using the SECM

- Optical reflected micrograph
- SECM image 2.8 µm Pt disk
- Optical fluorescence micrograph
25-µm Au disk

air-saturated 50 mM glucose/0.1 M phosphate buffer (pH 7.4)

$E_T = 0.4 \text{ V vs. Ag/AgCl}$

Si: open-circuit

B: addition of catalase ("chemical lens" effect)

C: blank
Probing Surfaces with SECM

Catalytic Surfaces

Membranes

Active site

Inactive site