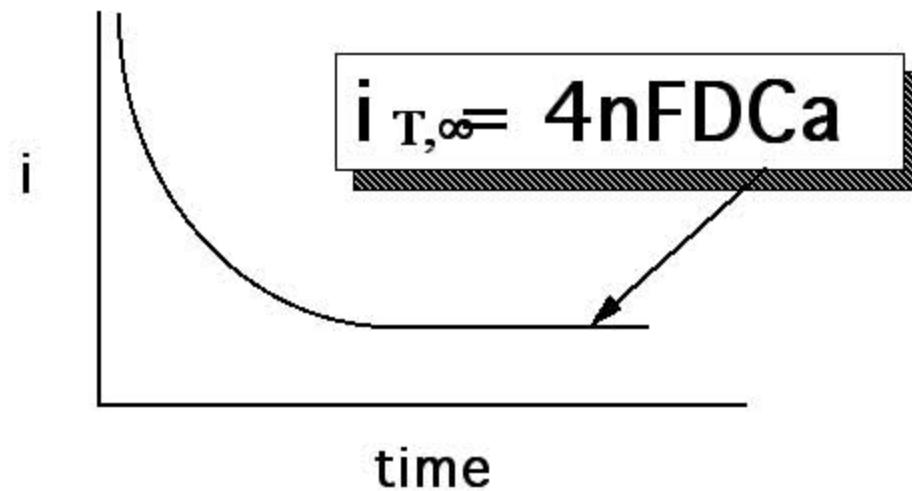
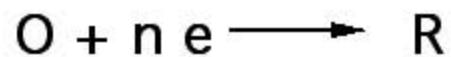
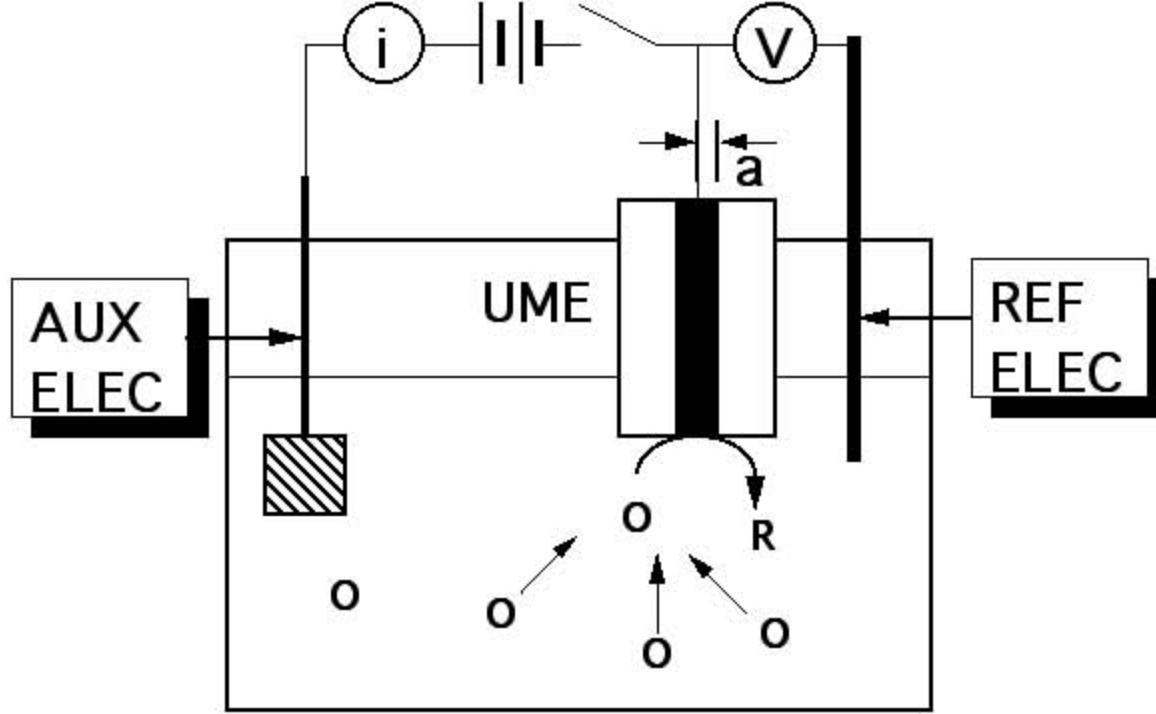


Introduction and Principles of Scanning Electrochemical Microscopy

Allen J. Bard



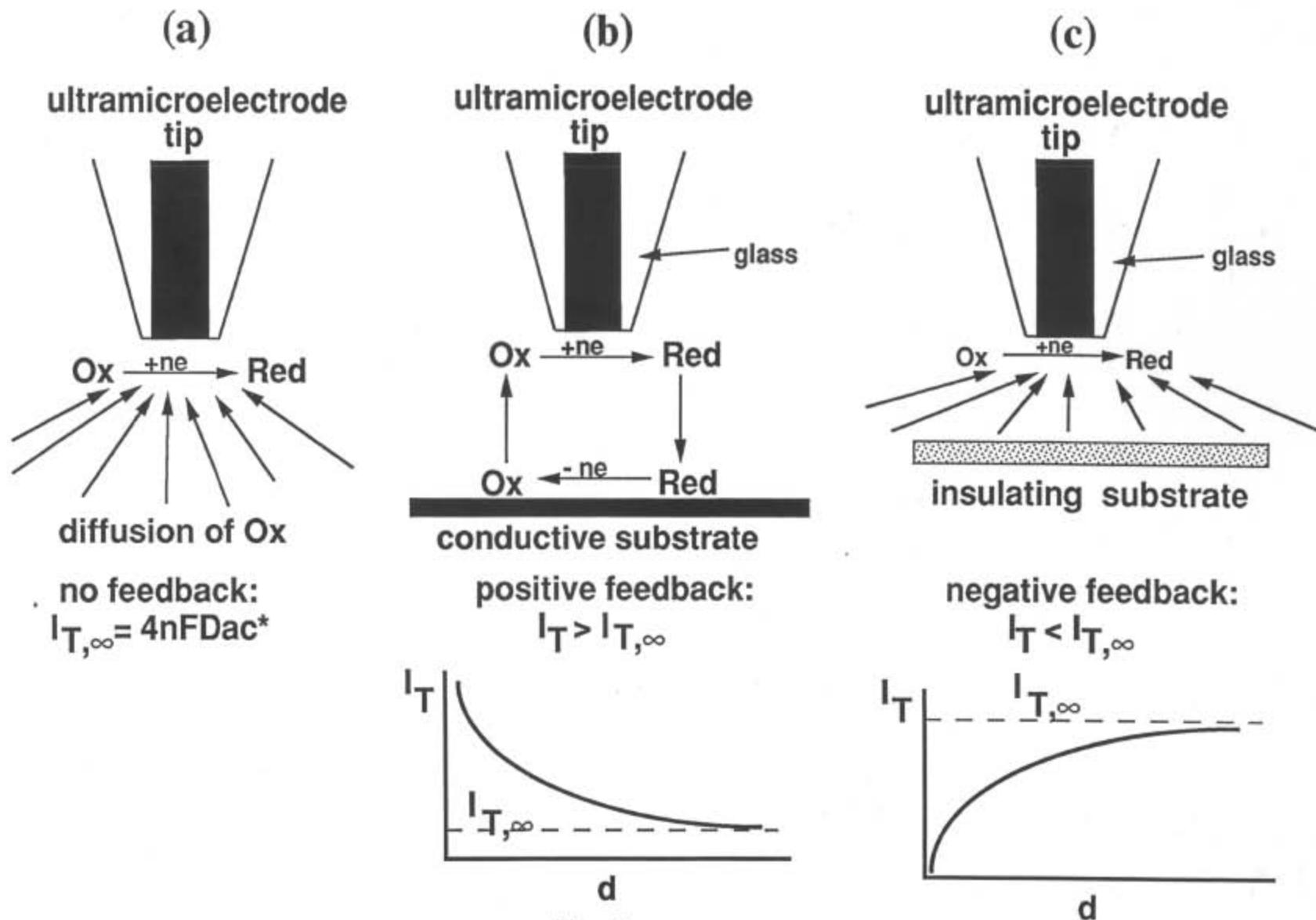
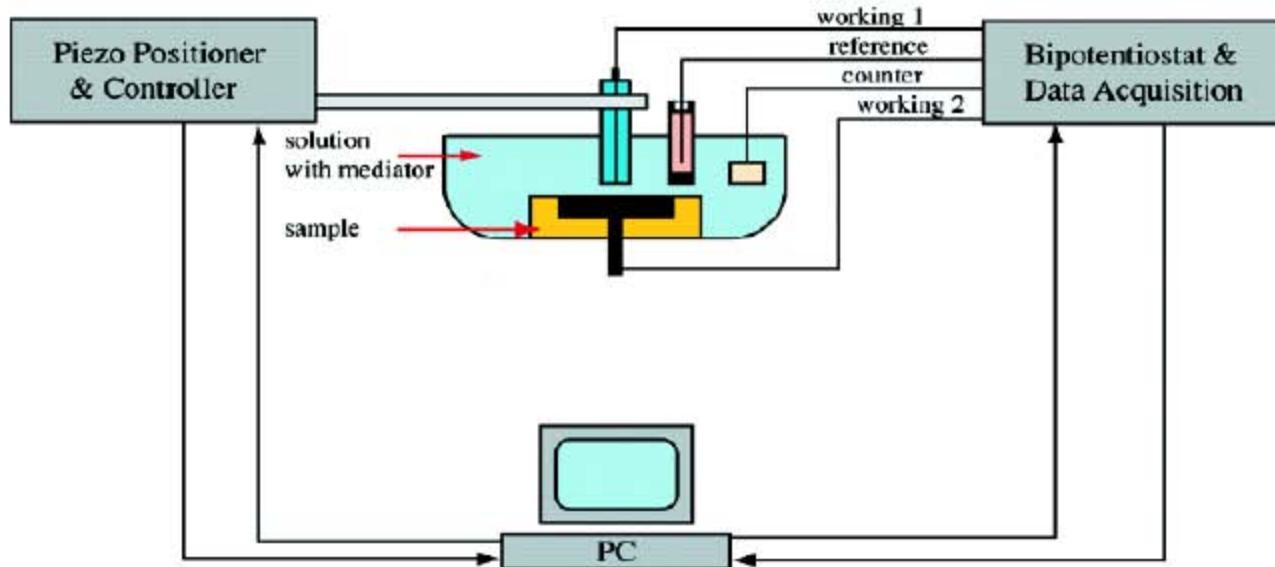


Figure 2
 Schematic representation of the SECM experiment. (a) Steady-state diffusion to the tip far from substrate. (b) Tip is near a conductive substrate. Positive feedback. (c) Tip is near an insulating substrate. Negative feedback.

Electrochemical Cell Configuration

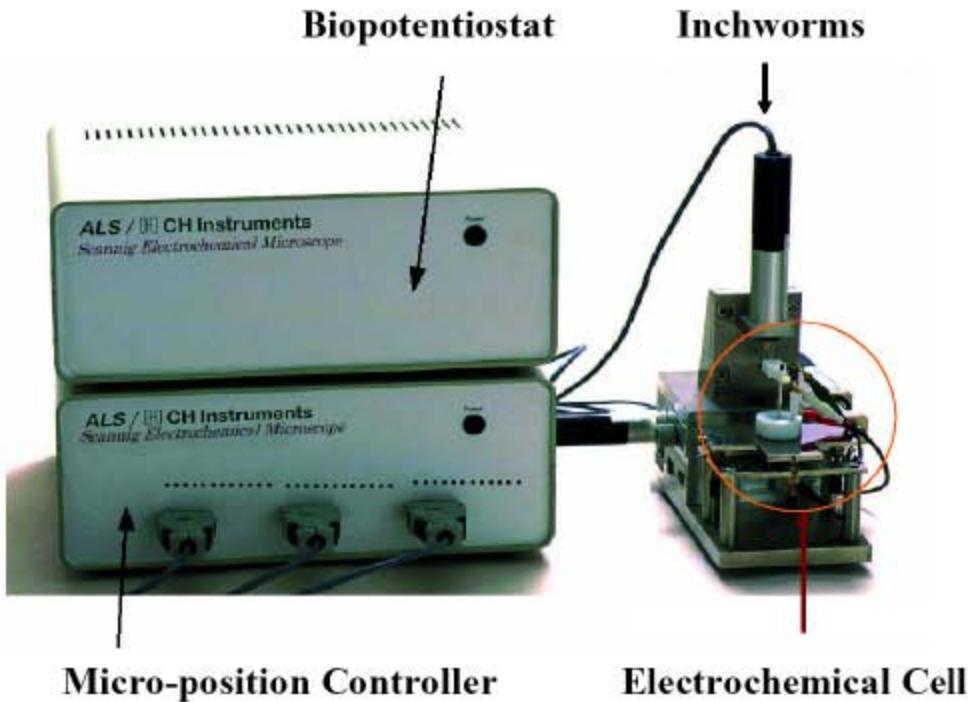


Tip (Working Electrode): Pt - a typically 0.5 to 12.5 μm

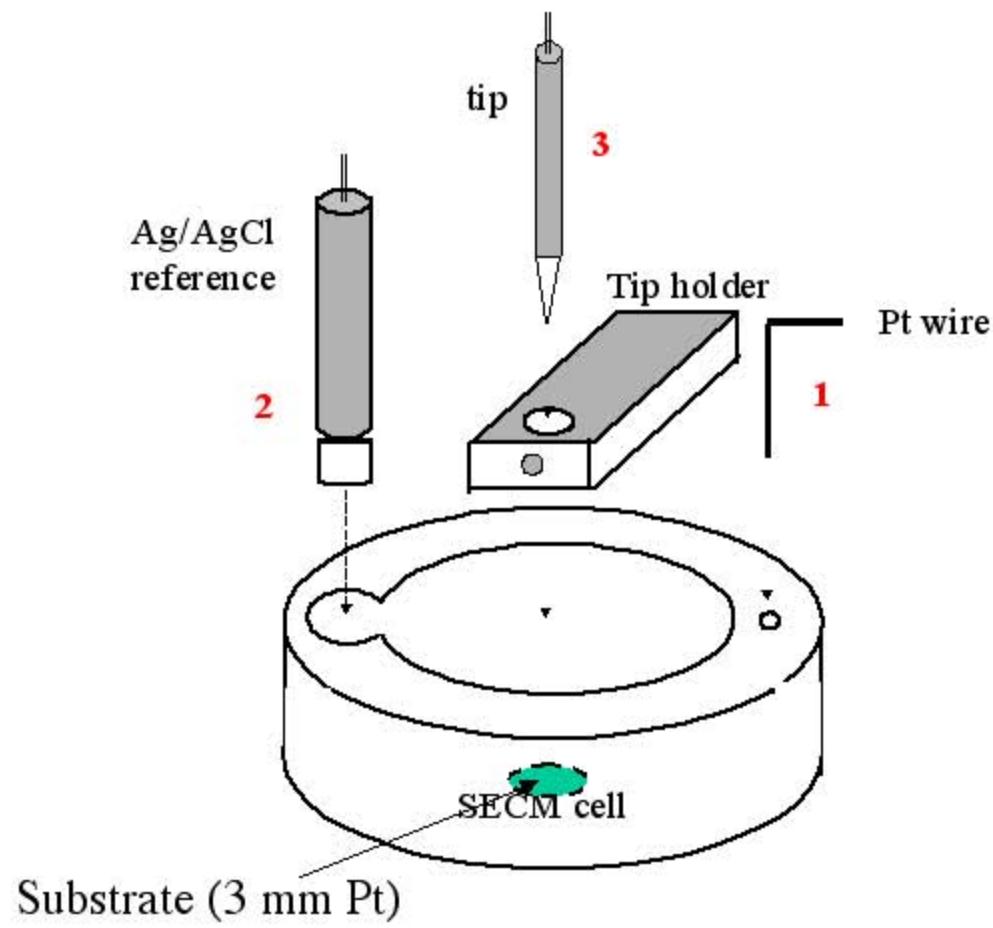
Reference & Counter Electrodes: Pt wire

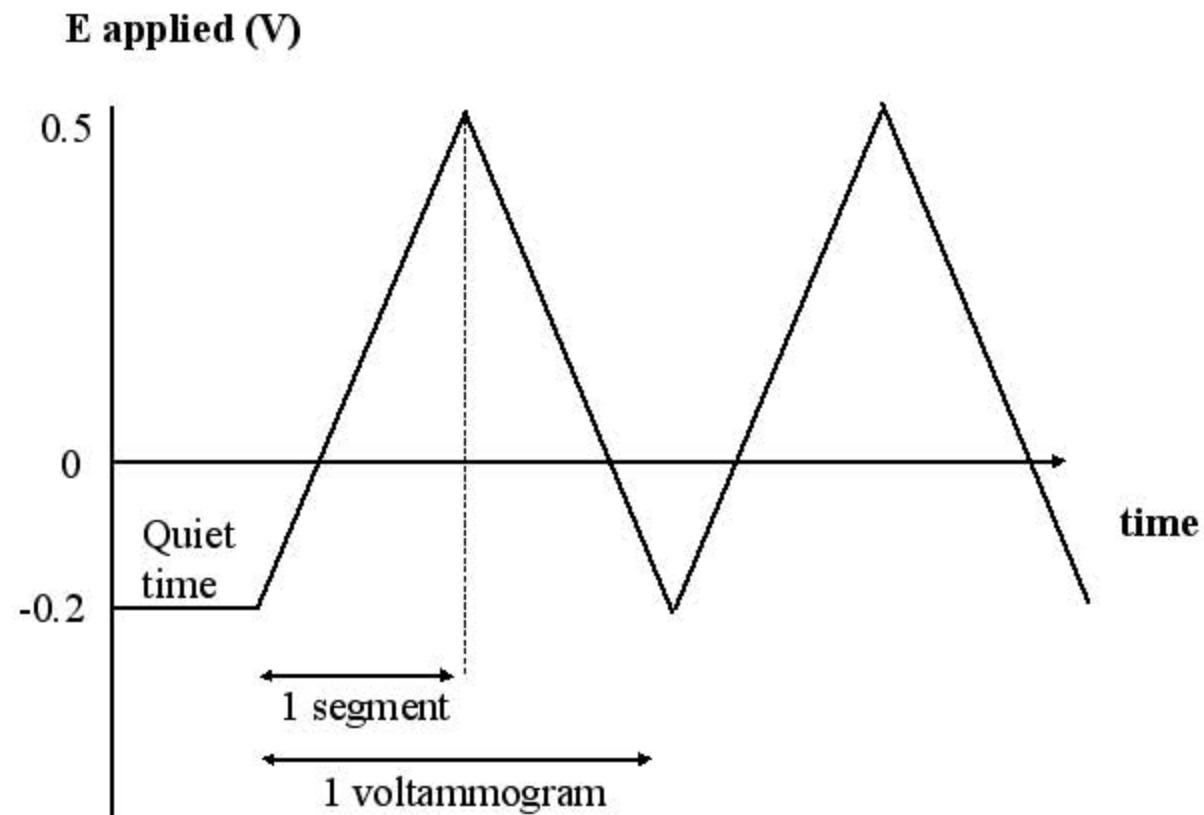
Substrate: 3 mm diameter Pt disk

Experimental Set Up

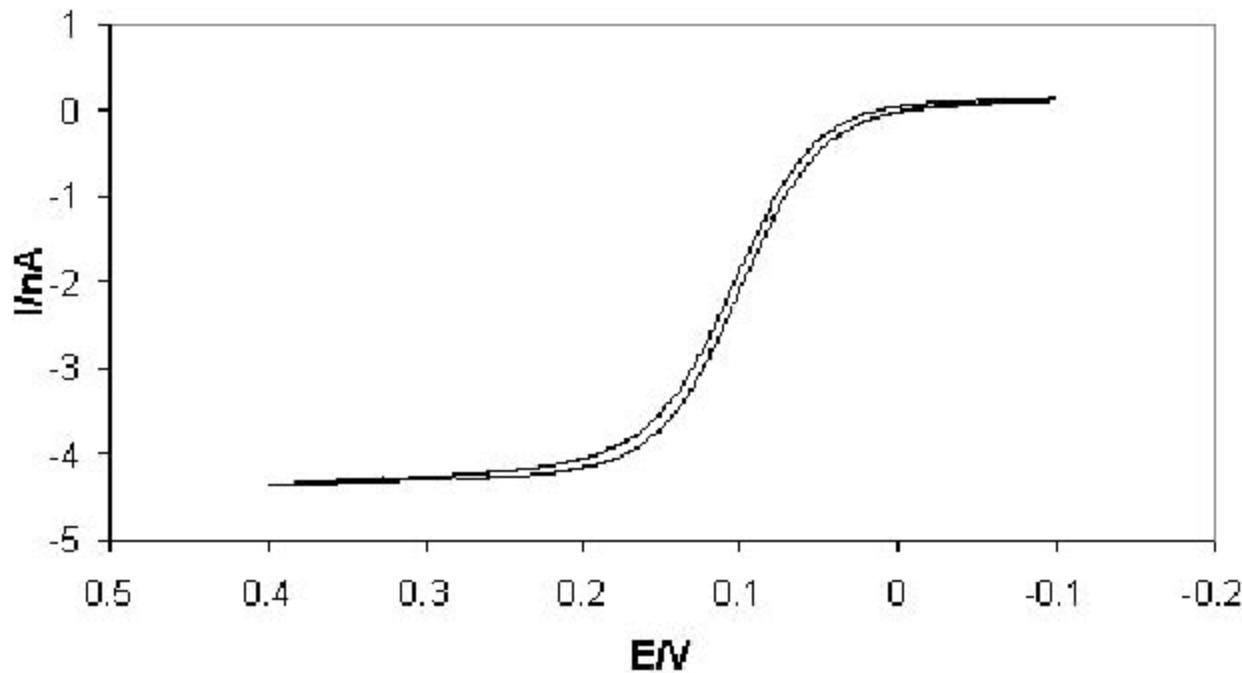


SECM



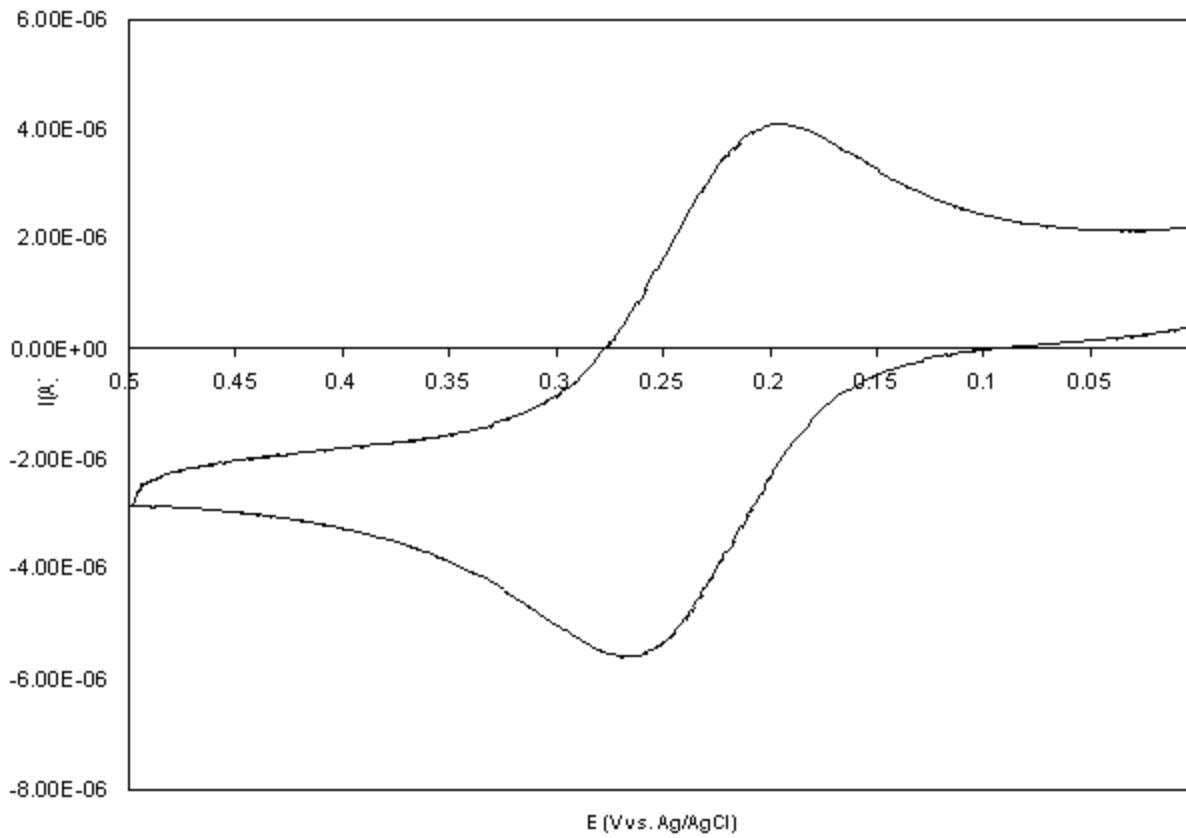


Voltammogram at 25 μm diameter tip



1 mM FcMeOH

Voltammogram at 3 mm diameter Pt substrate



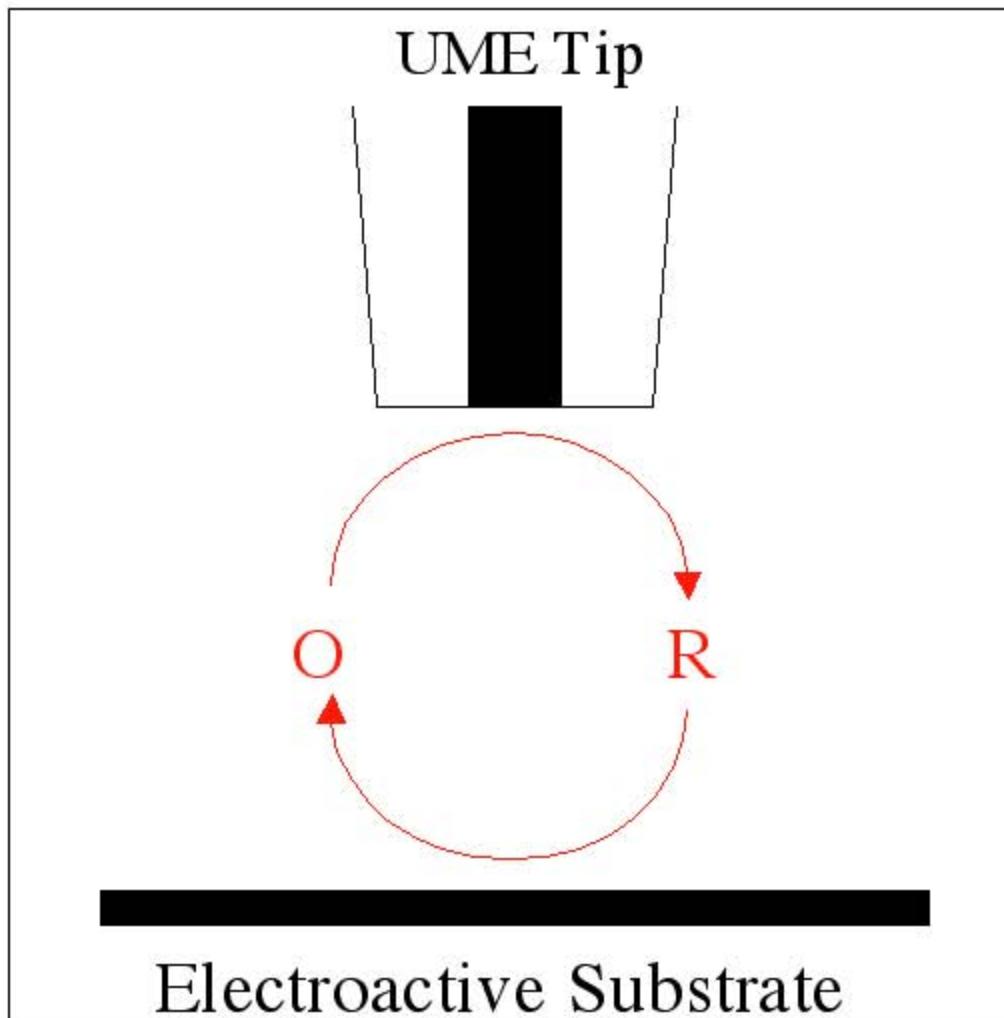
1 mM FcMeOH

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:

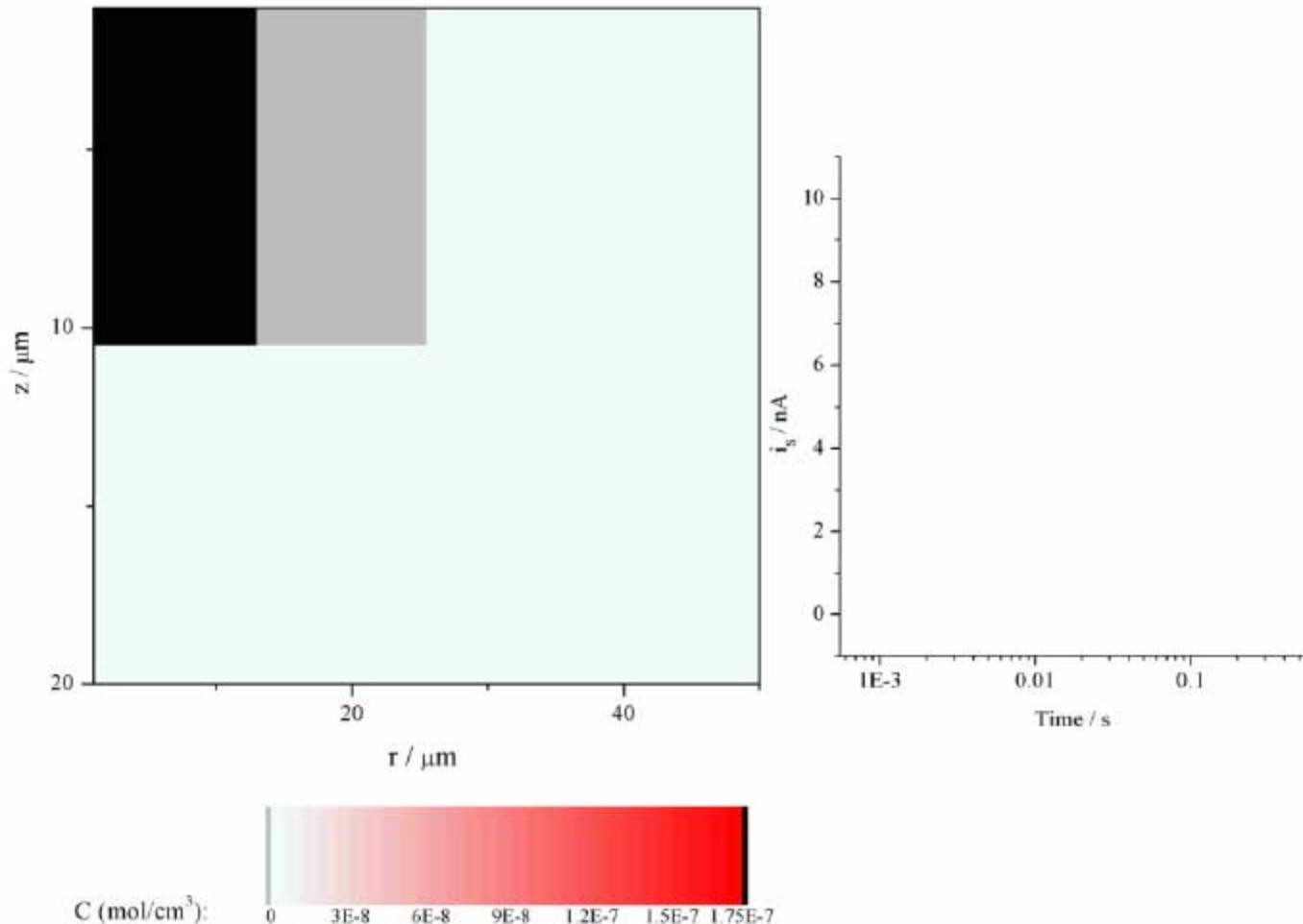
$$a = 12.5 \text{ } \mu\text{m}$$

$$\text{RG} = 2$$

$$d = 10 \text{ } \mu\text{m}$$

$$i_T = -9.82 \text{ nA}$$

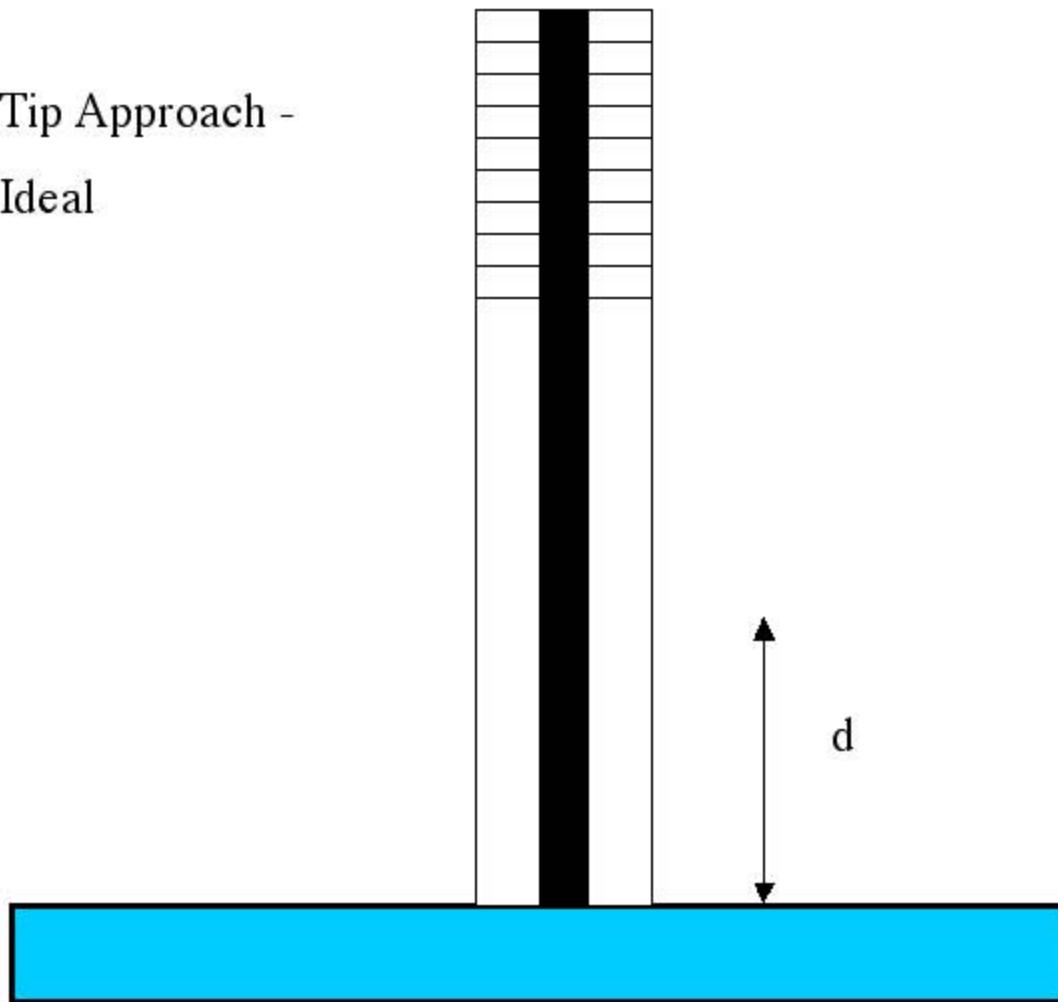
$$k(E) = 1$$



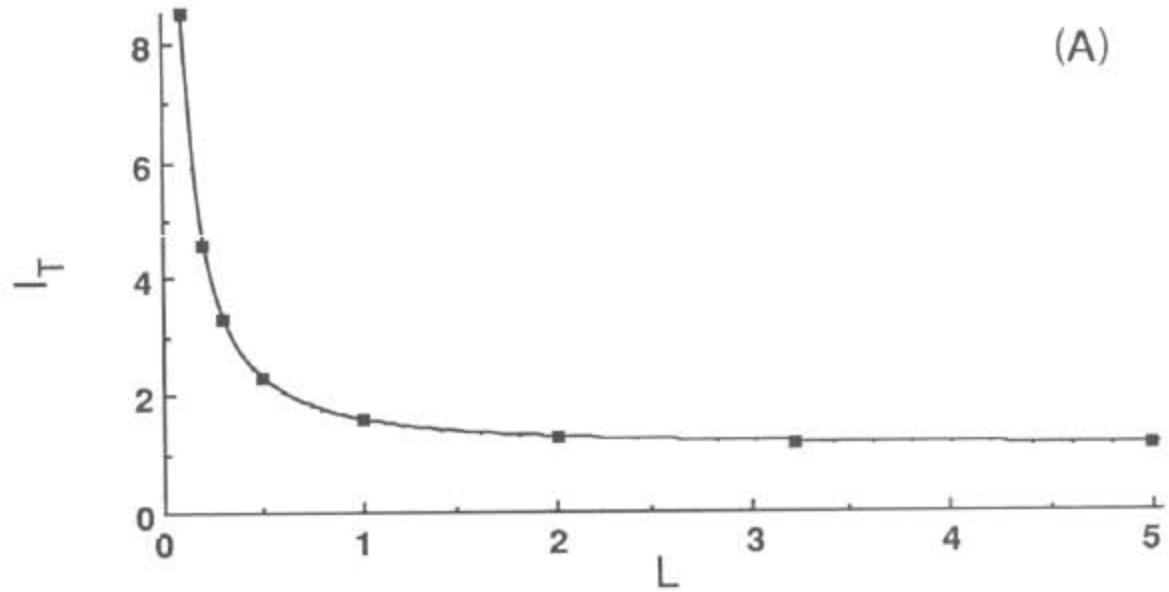
Feedback Mode

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

Tip Approach -
Ideal



$I_T = i_T / i_{T,\infty}$



$L = d/a$

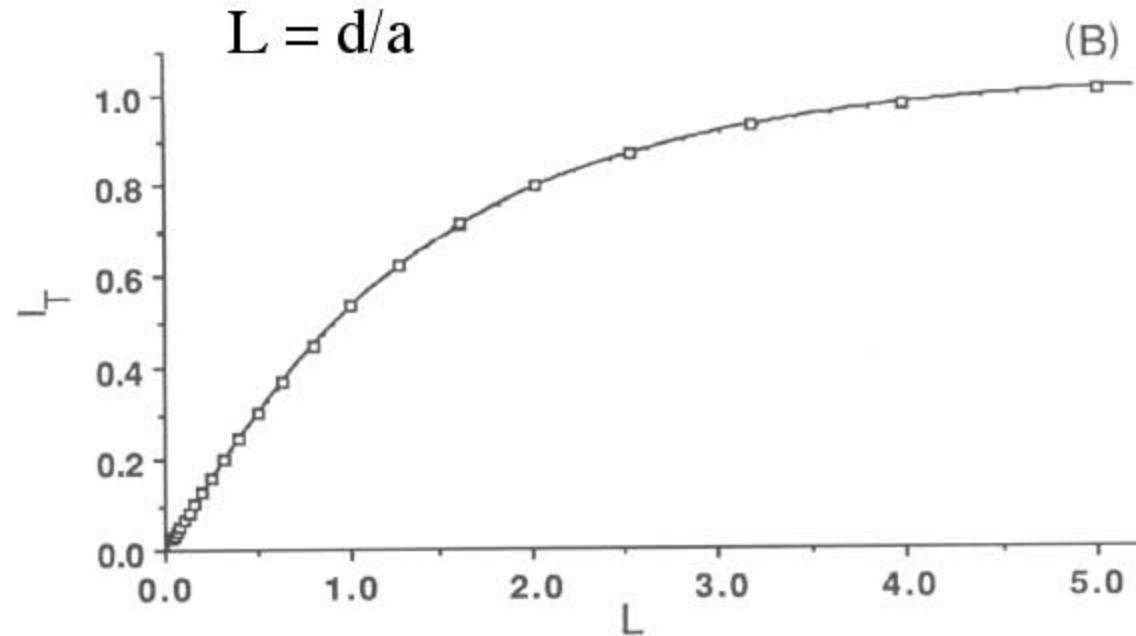
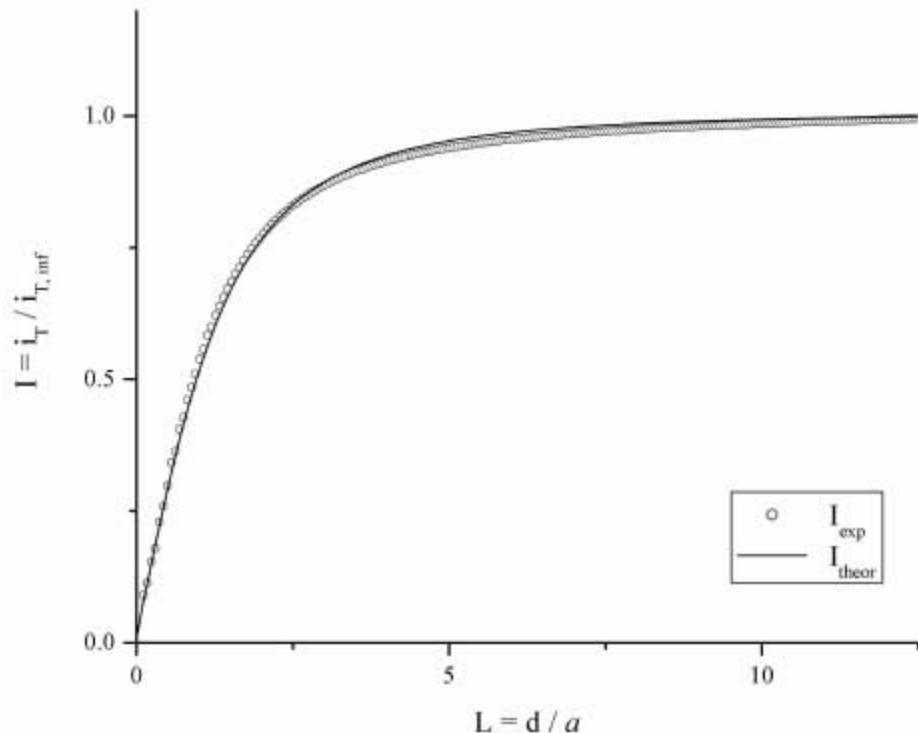


FIG. 4 Diffusion-controlled steady-state tip current as a function of tip-substrate separation. (A) Substrate is a conductor; (B) substrate is an insulator. (From Ref. 2.)

Approach curve for insulator (glass or Teflon)

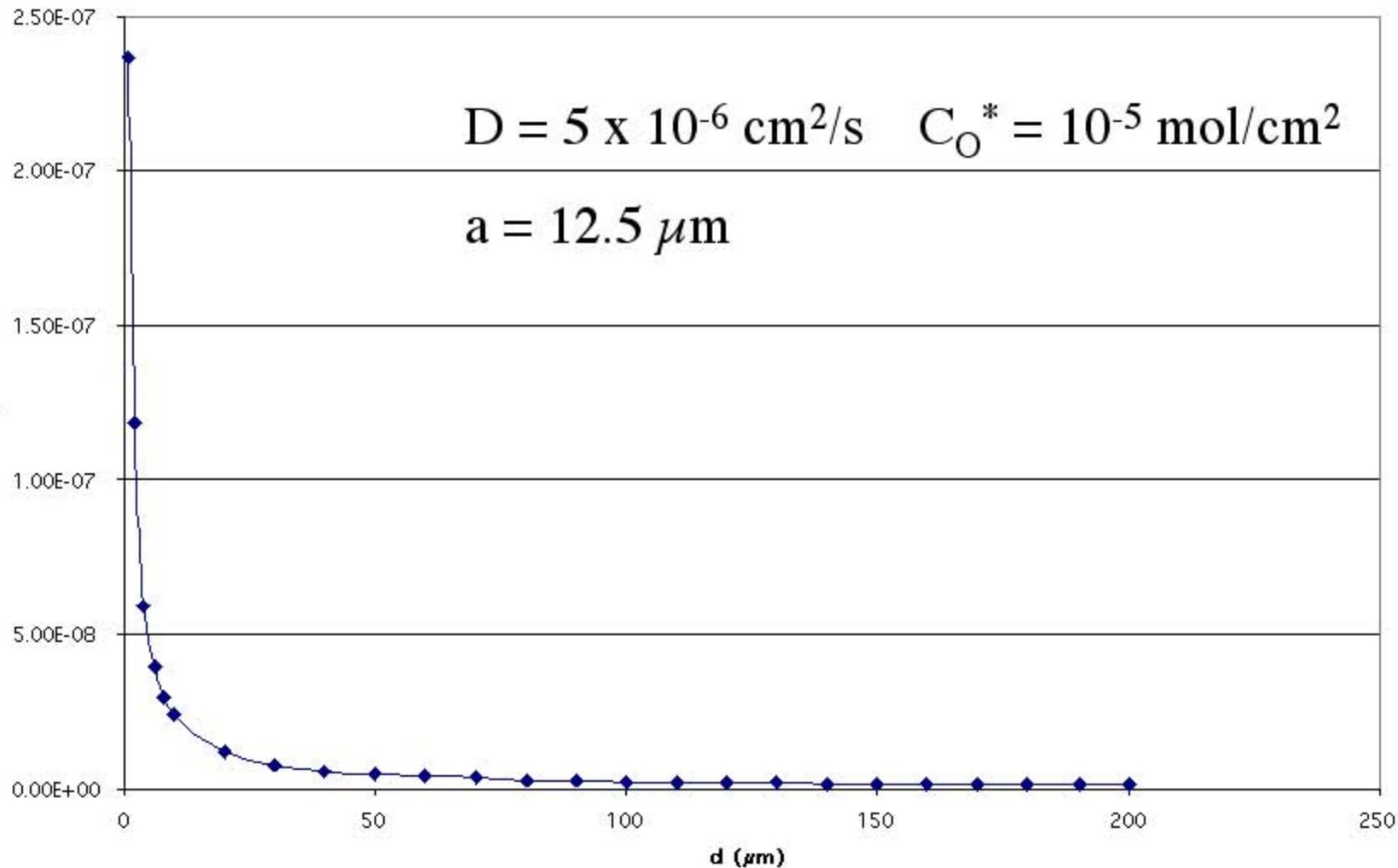


$$I(L) = \frac{1}{0.292 + \frac{1.5151}{L} + 0.6553 \cdot \exp\left(-\frac{2.4035}{L}\right)}$$

RG = 10

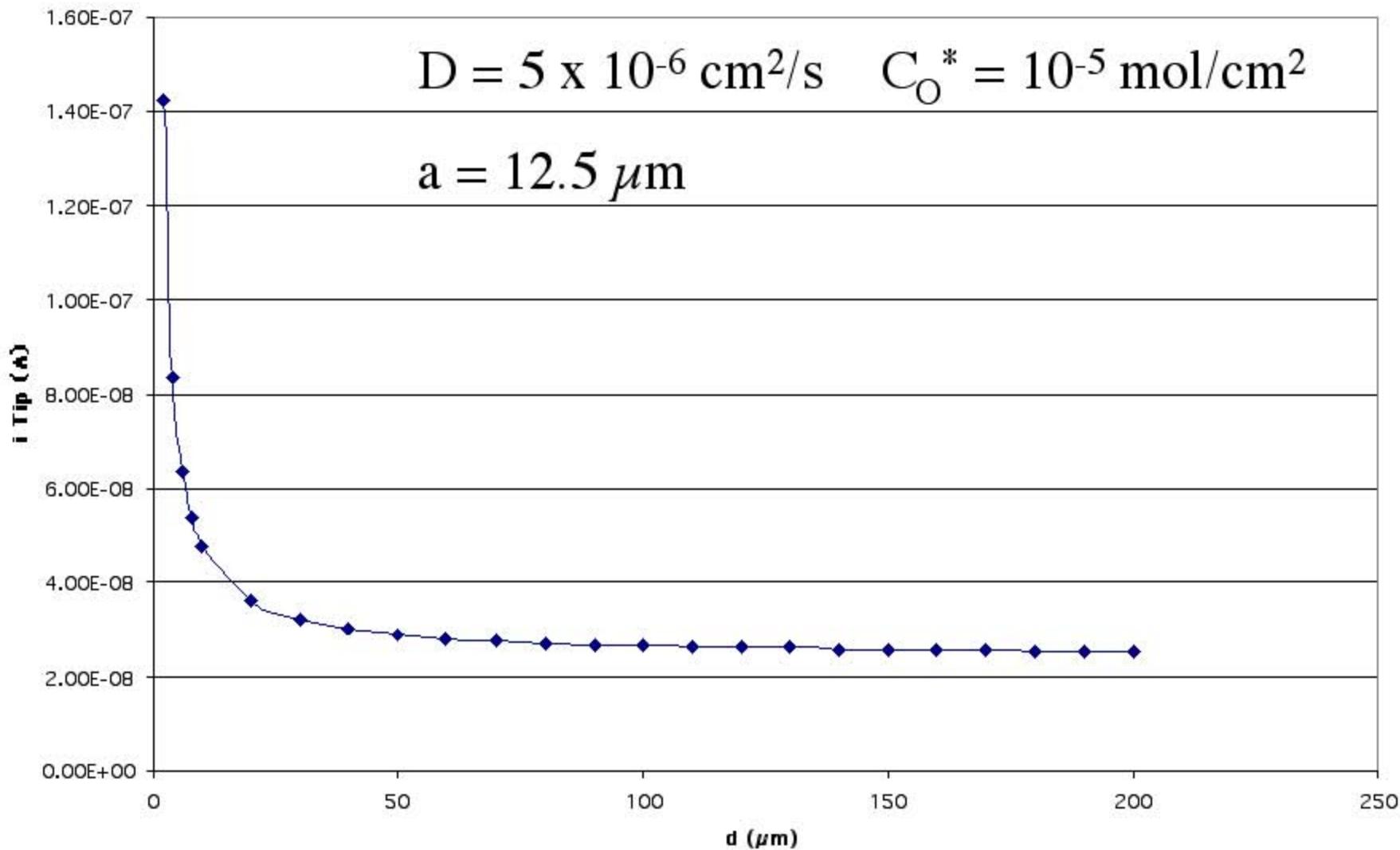
$$i_T = nFDC_O^* \pi a^2 / d$$

Thin layer feedback

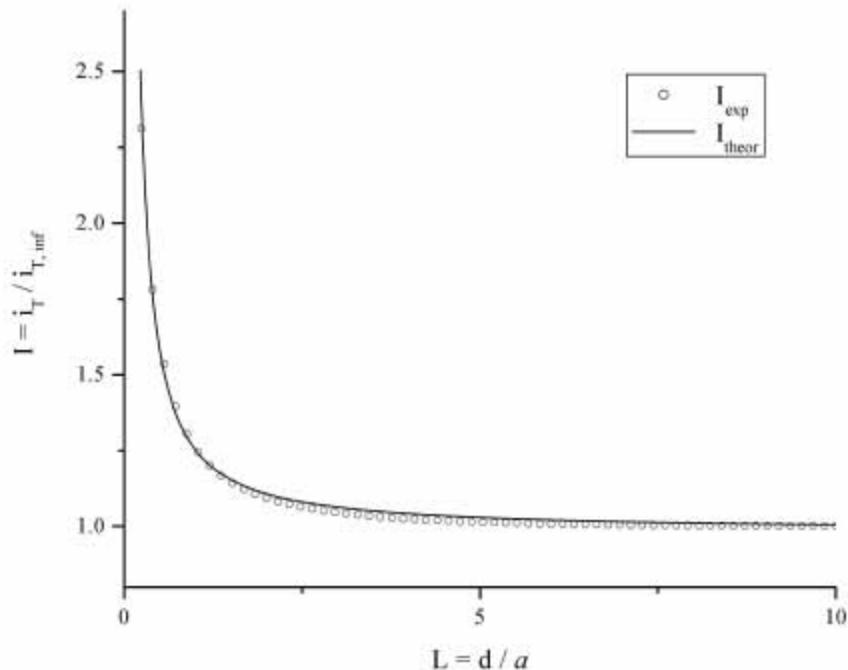


$$i_T = (nFDC_O^* \pi a^2 / d) + 4nFDC_O^* a$$

Total current



Approach curve for conductor (Pt)



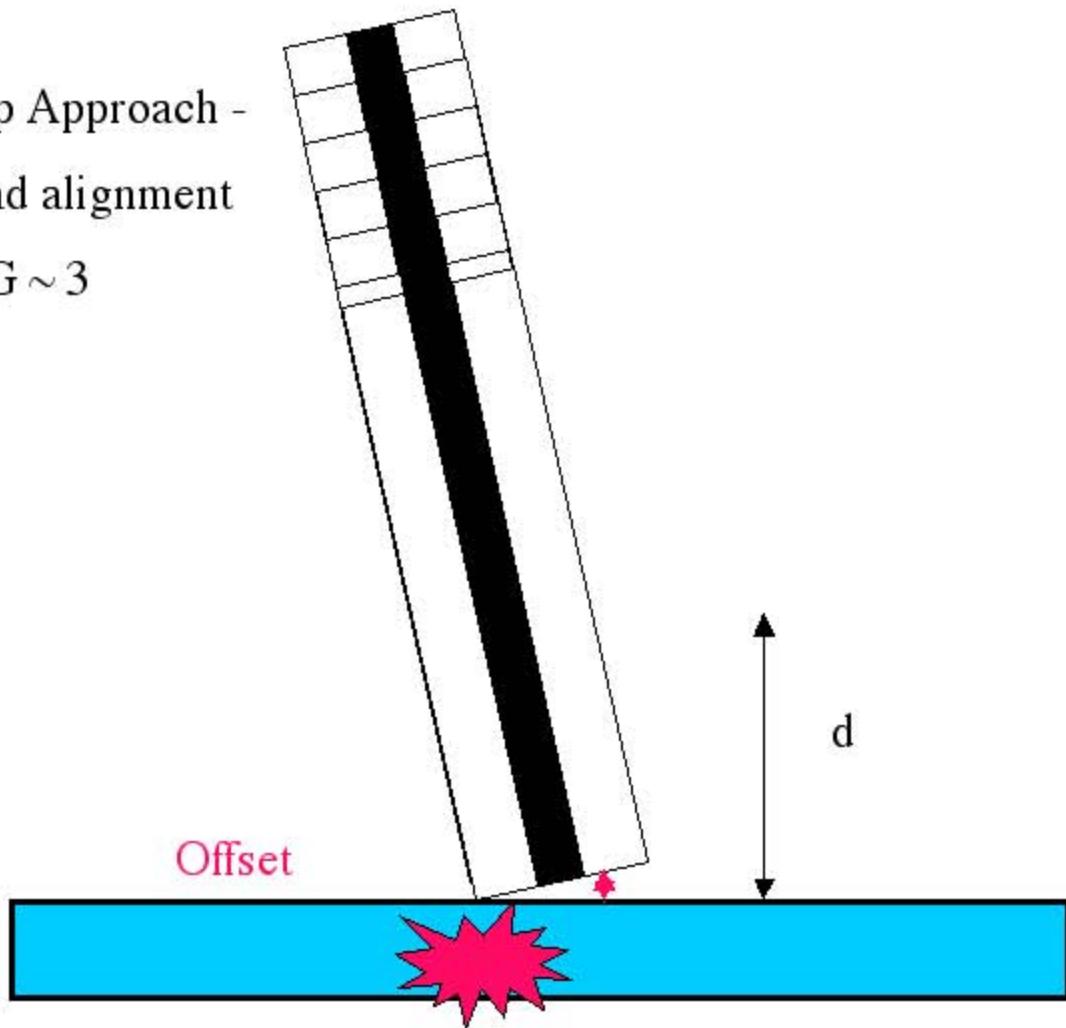
$$I(L) = 0.68 + \frac{0.78377}{L} + 0.3315 \cdot \exp\left(-\frac{1.0672}{L}\right)$$

RG = 10

Tip Approach -

Bad alignment

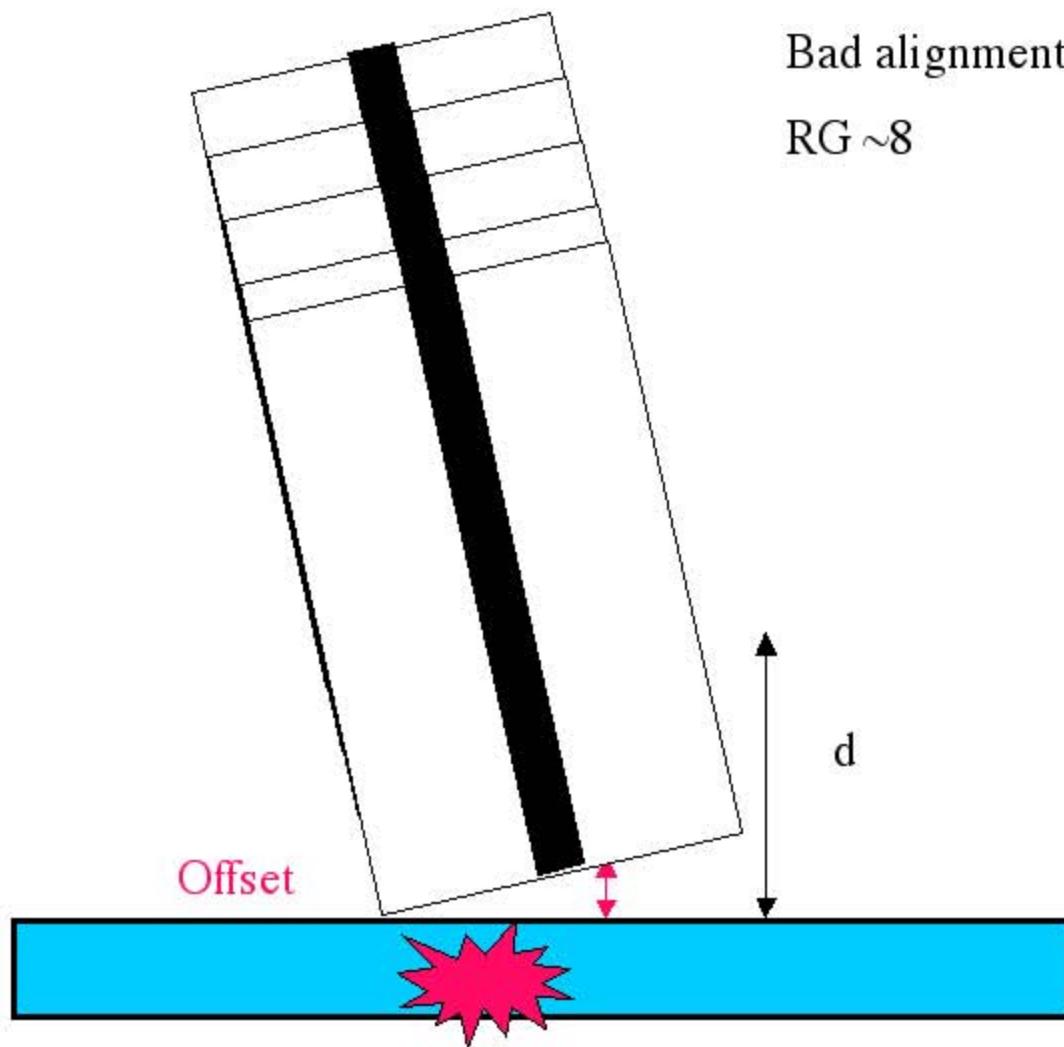
$RG \sim 3$

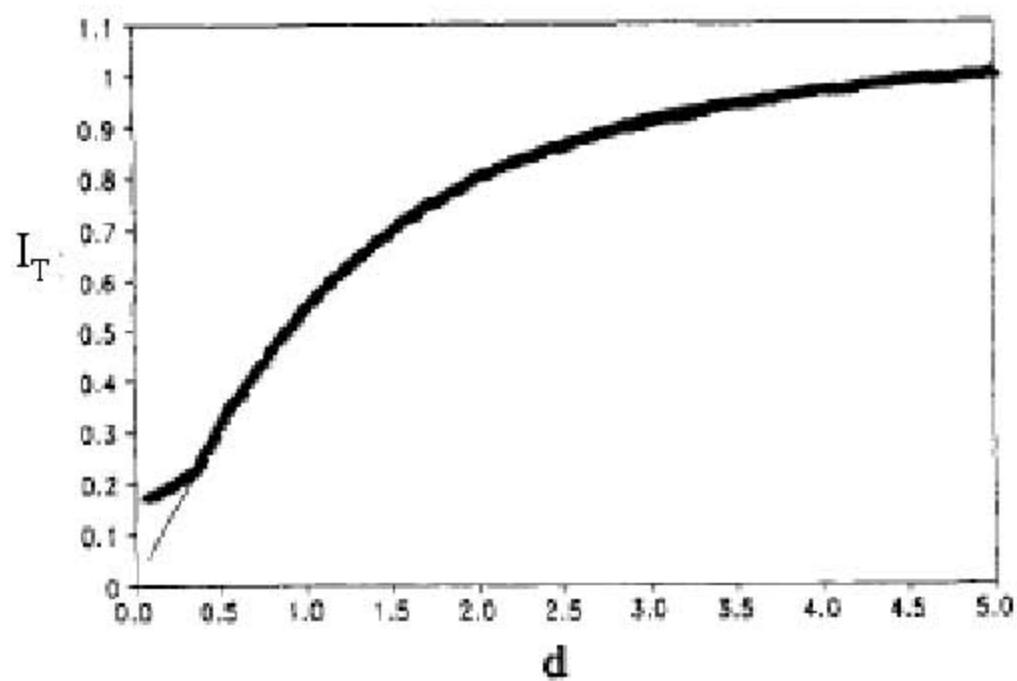


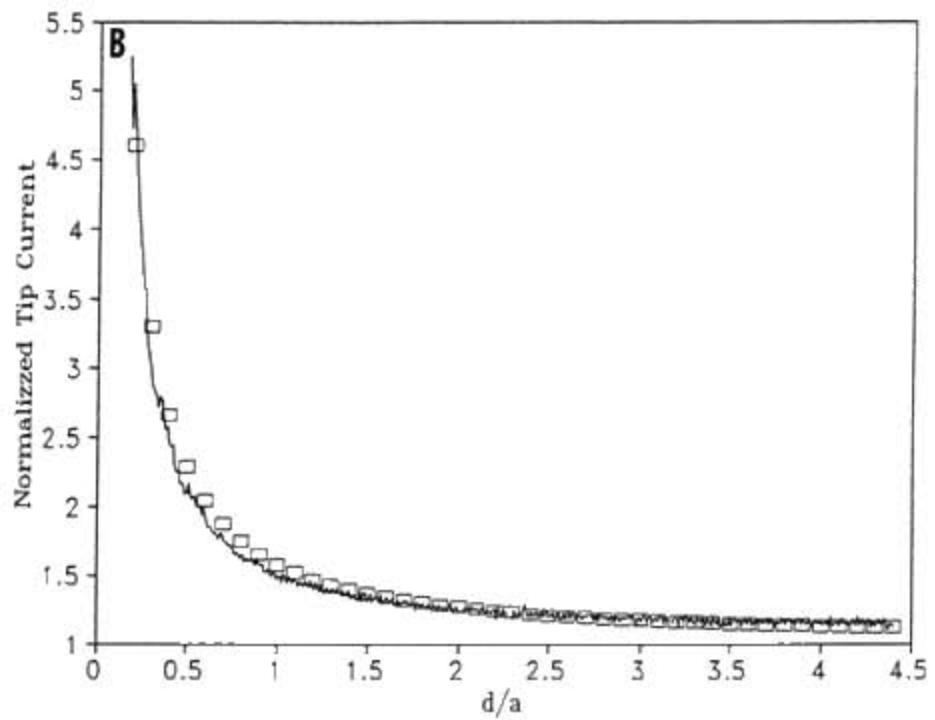
Tip Approach -

Bad alignment

$RG \sim 8$







Experiment

□ Theory -conductor

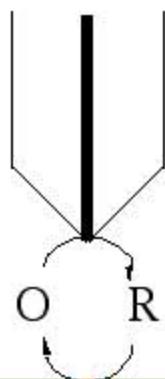
Other Modes

Tip Generation - Substrate Collection

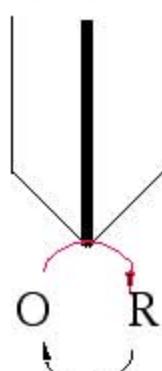
Substrate Generation - Tip Collection

SECM Modes

Feedback

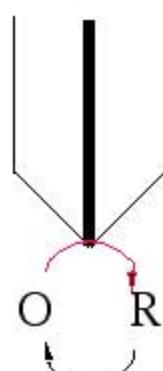


SG/TC



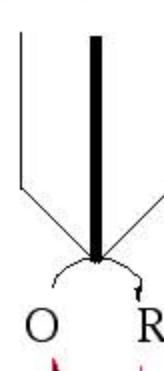
Large substrate

SG/TC



Small substrate

TG/SC



Measure i_T Steady state

Area interrogated
controlled by tip size

Measure i_T and i_s

Low collection
efficiency

No steady state i_s

Measure i_T and i_s

Low to medium
collection efficiency

Steady state i_s

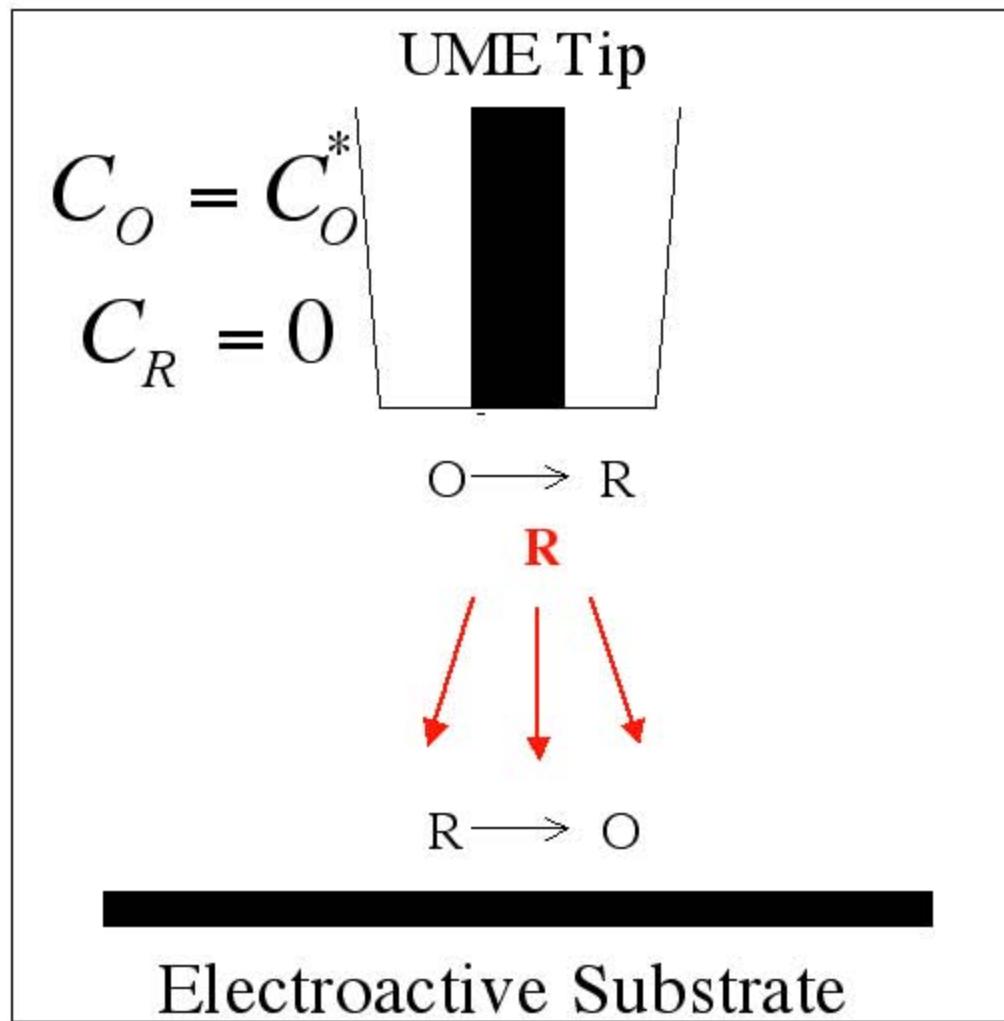
Measure i_T and i_s

High collection
efficiency

Steady state i_s

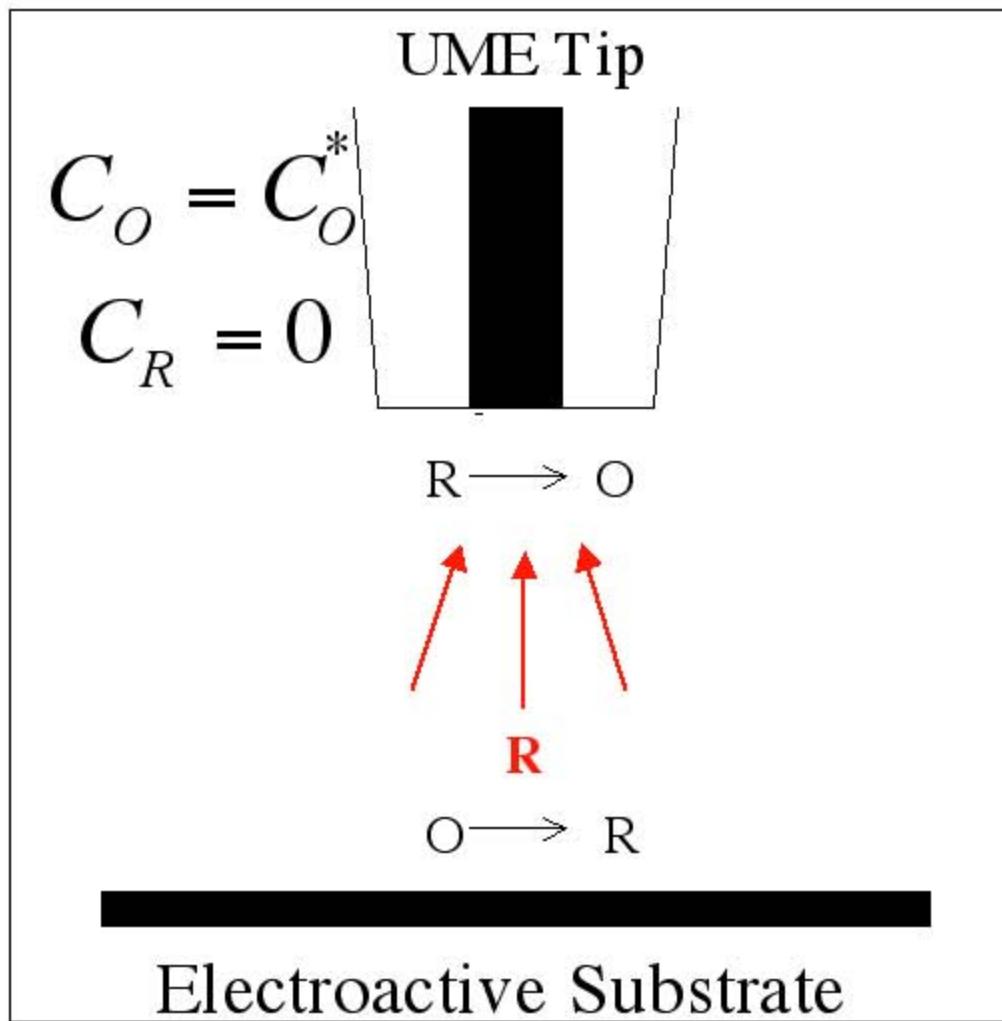
Tip Generation - Substrate Collection (TG-SC)

Measure i_T and i_S as function of d and E



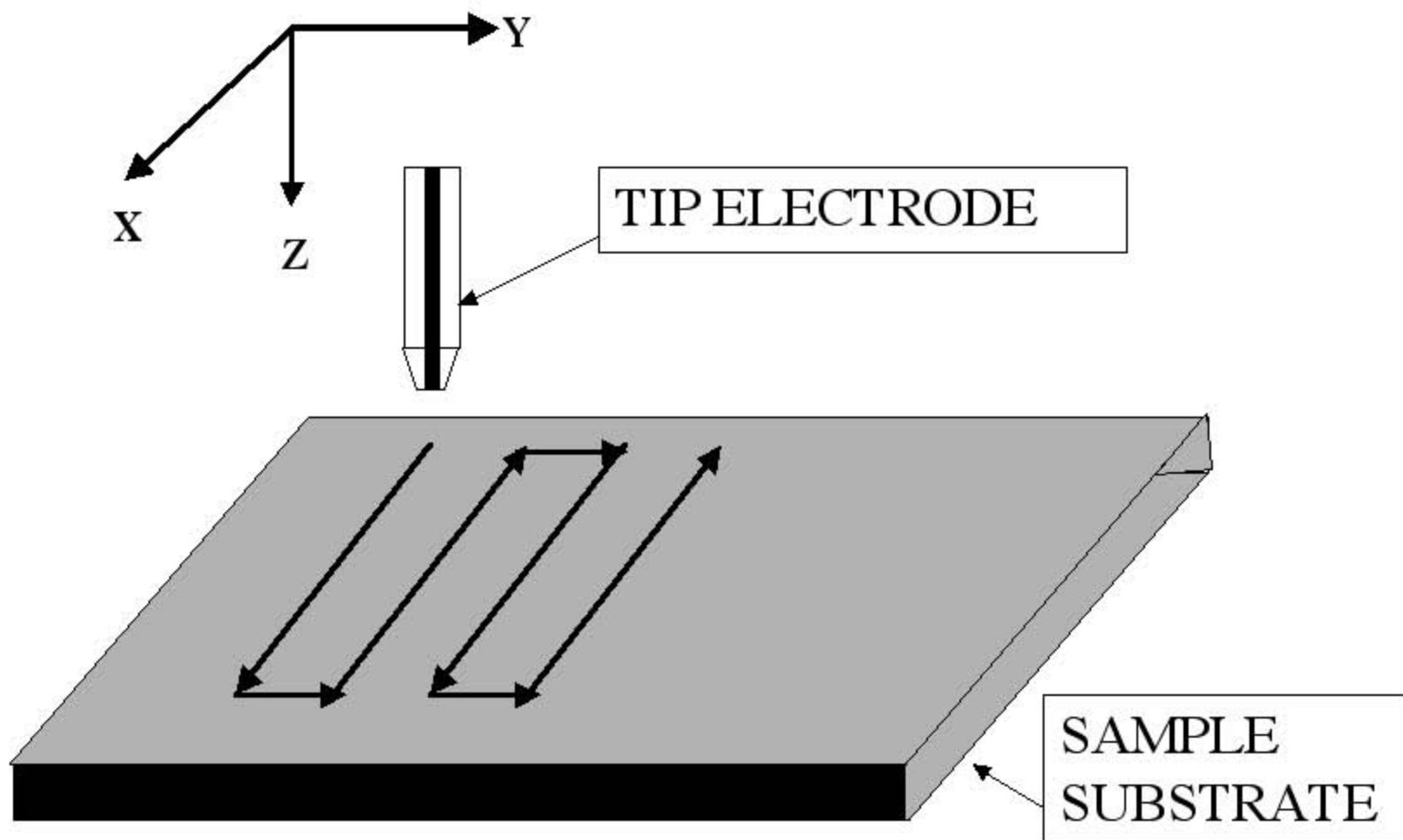
Substrate Generation - Tip Collection (SG-TC)

Measure i_T and i_S as function of d and E



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

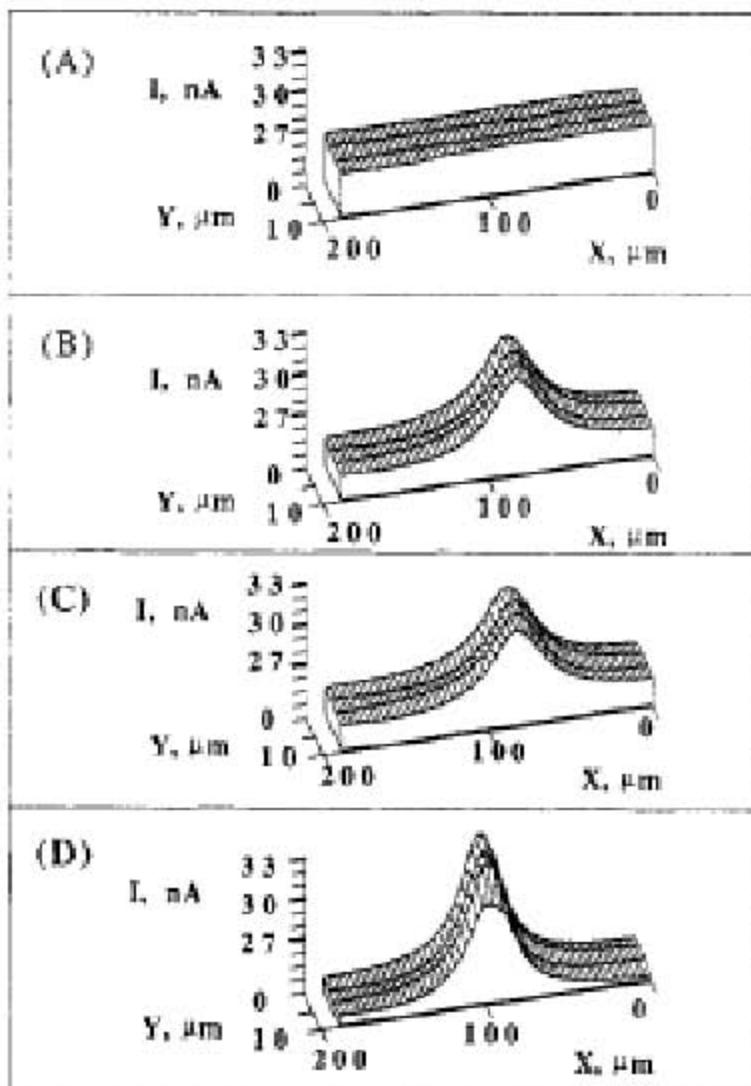
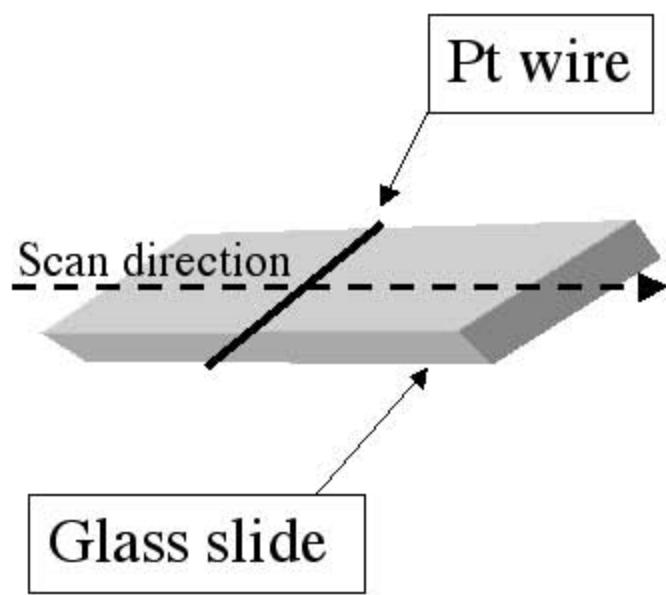


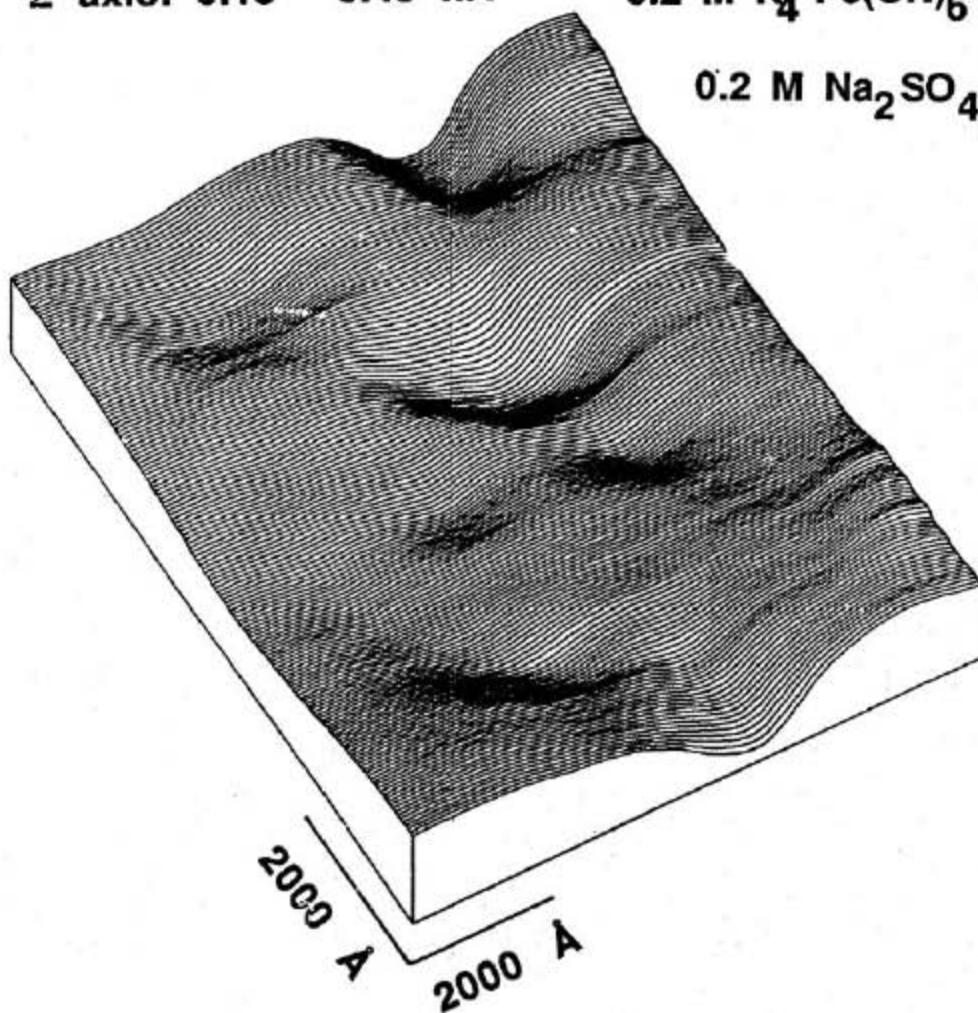
Figure 4. Scans of a 50- μm platinum wire on a glass slide at different tip locations from sample: tip electrode, 5.5 μm radius carbon disk tip electrode at 0.80 V vs AgQRE; solution, 10 mM TBAP, 5 mM ferrocene in acetonitrile; scanning speed, 19.7 $\mu\text{m}/\text{s}$; (A) far from sample, (B) close (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

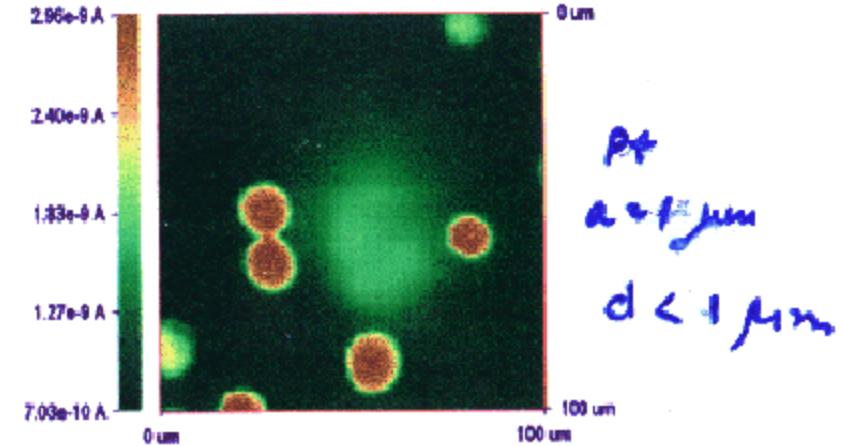
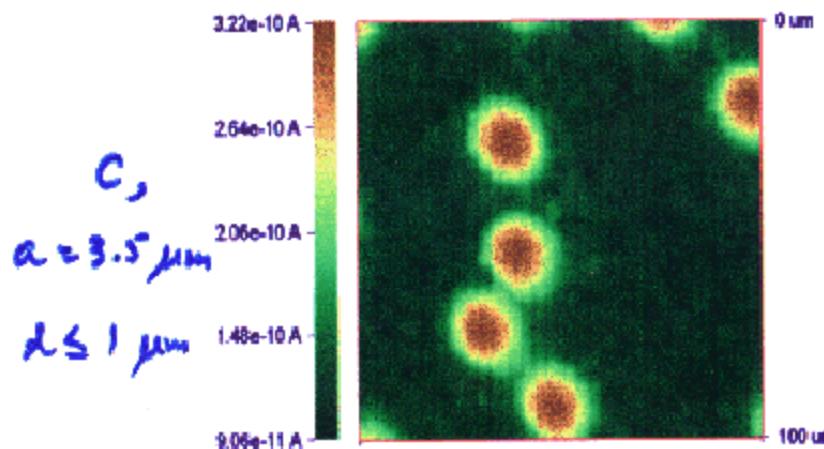
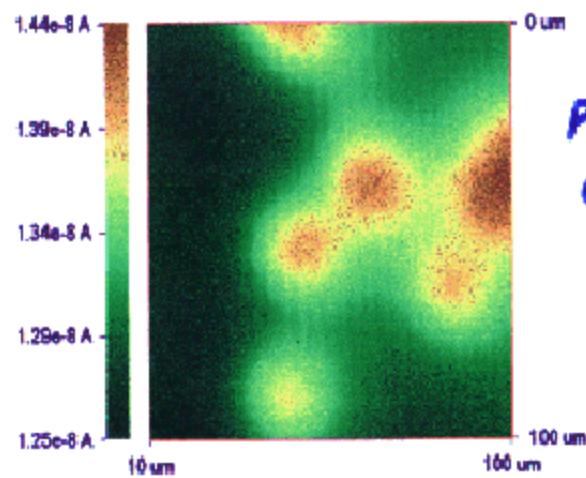
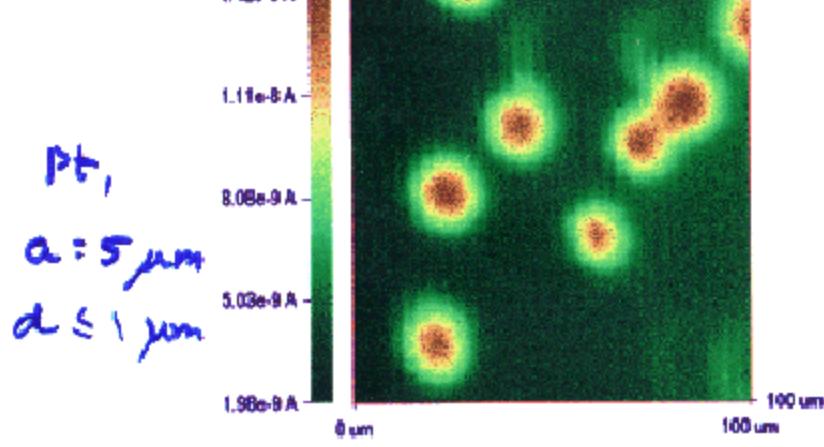
Z axis: 0.15 - 0.45 nA 0.2 M $\text{K}_4\text{Fe}(\text{CN})_6$,

0.2 M Na_2SO_4

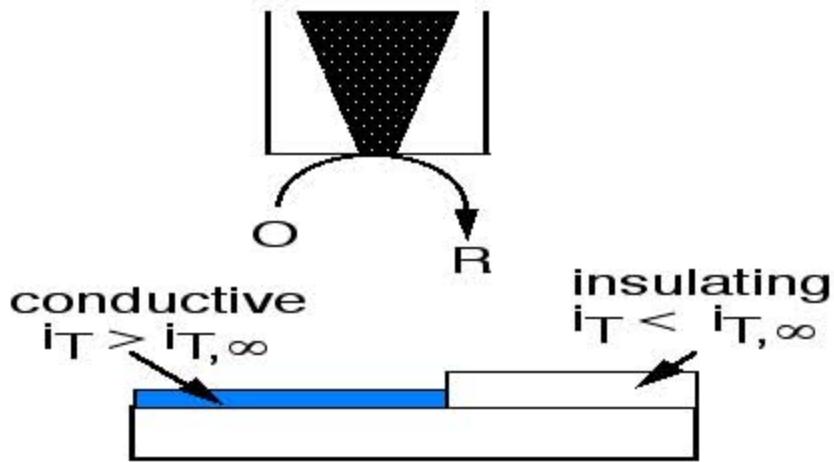


$1 \text{ mM Ru(NH}_3\text{)}_6^{3+}$
 0.1 M KCl

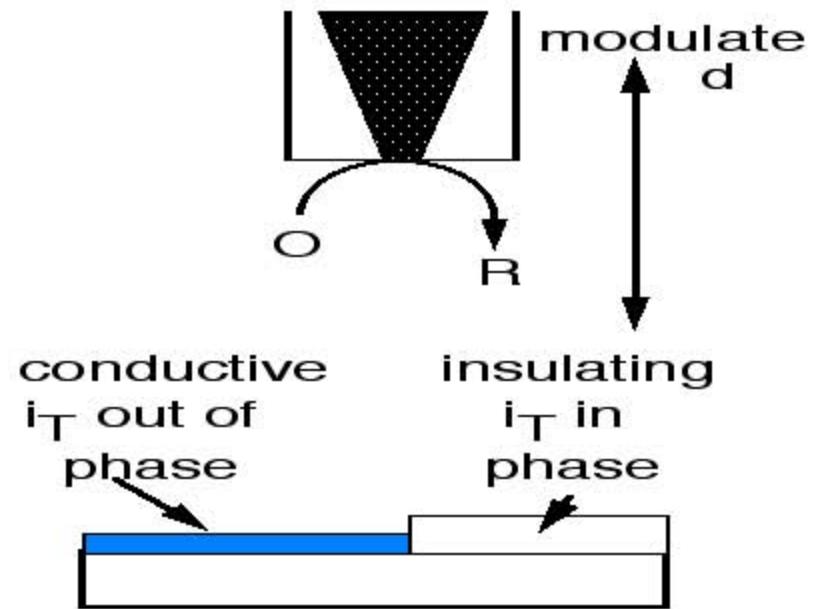
SECM image of a polycarbonate filter membrane



How does one distinguish conductive and insulating regions from the tip current?

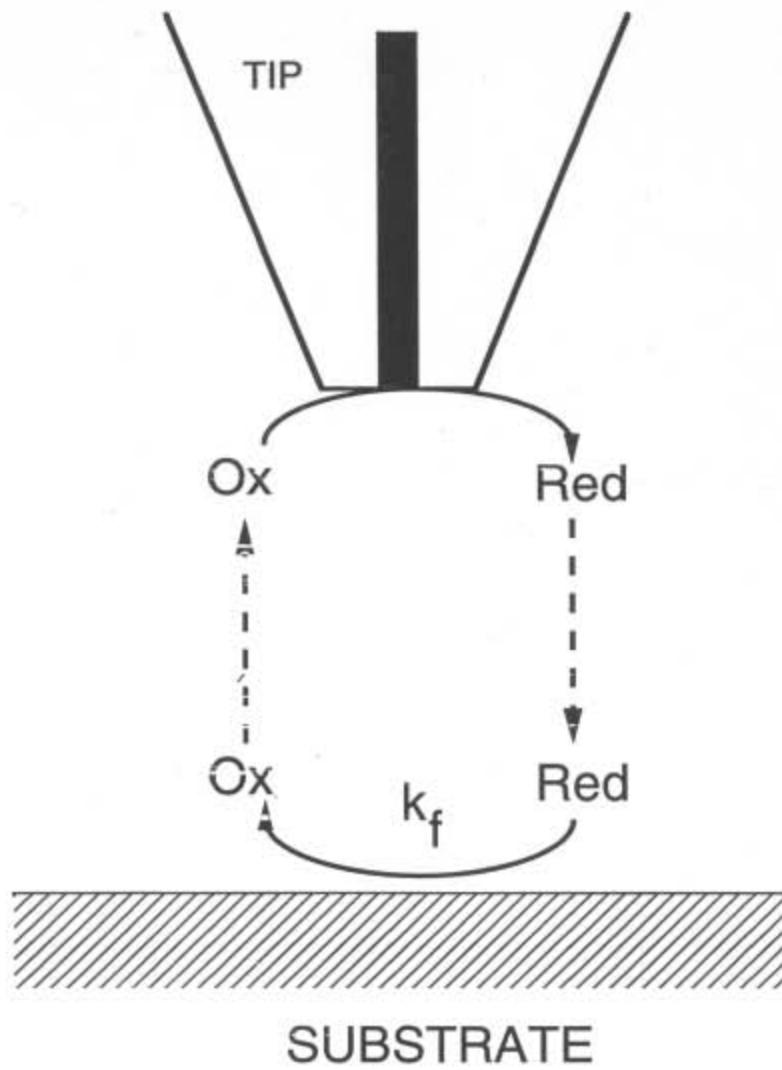


From magnitude of tip current



From phase angle of tip current

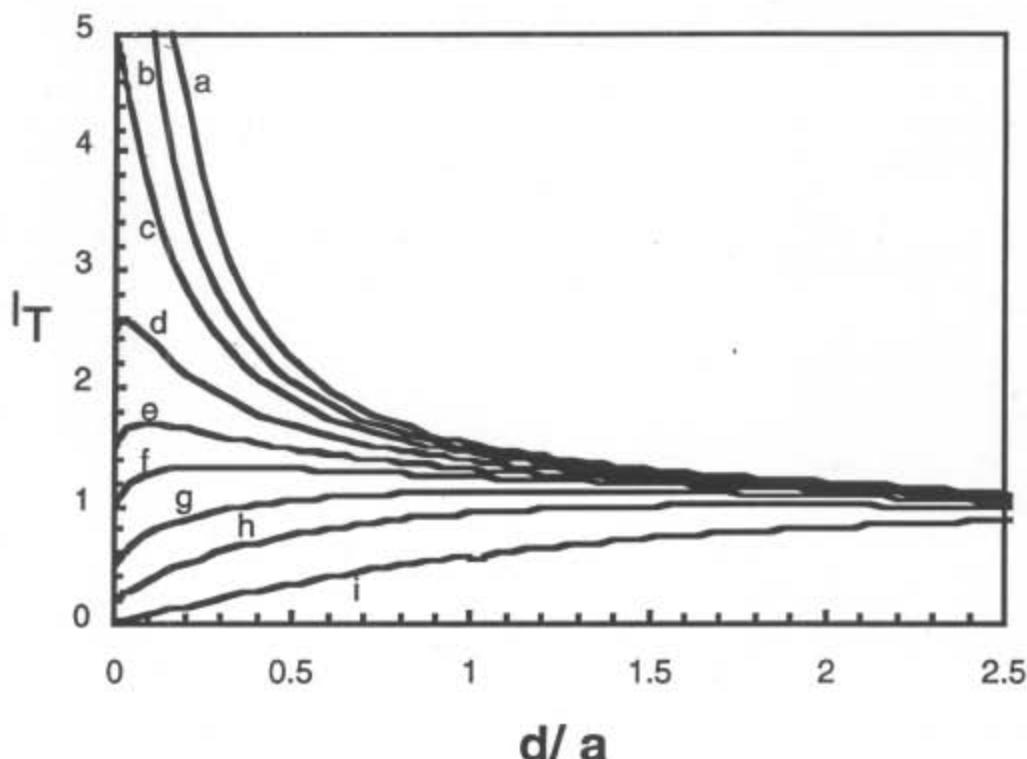
Heterogeneous Kinetics and Reaction Rate Imaging



$k_f \rightarrow 0$ Insulator (negative feedback)

$k_f \rightarrow \infty$ Conductor (positive feedback)

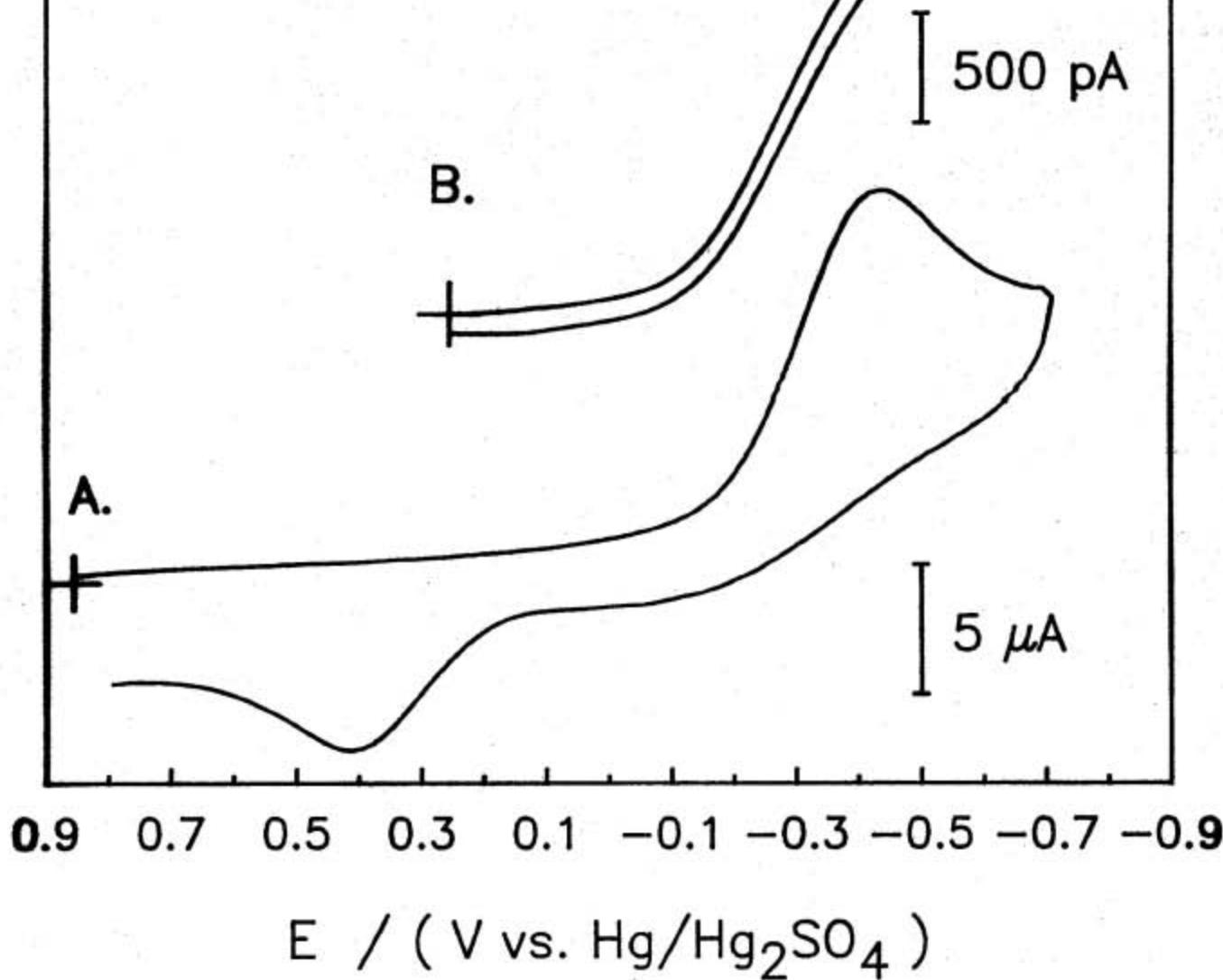
Effect of heterogeneous kinetics on SECM approach curves



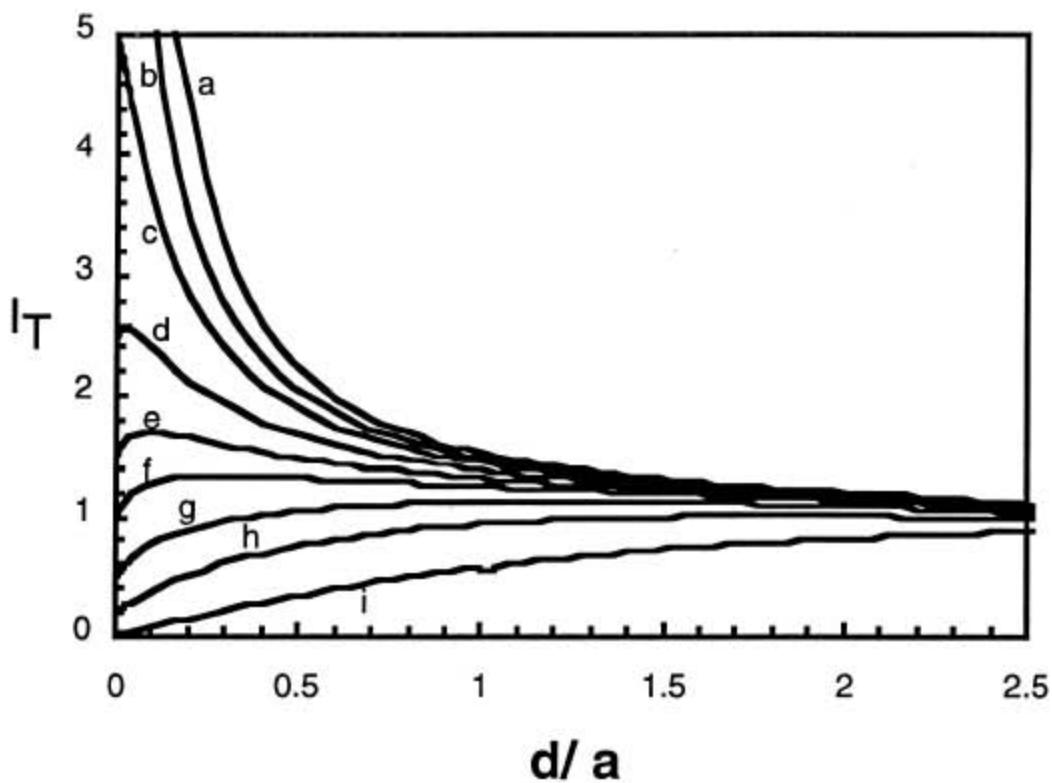
Rate constants (cm/s)	
a. 1	f. 0.01
b. 0.5	g. 0.005
c. 0.1	h. 0.002
d. 0.025	i. 0.0001
e. 0.015	

2.1 mM Fe(III)

1.0 M H₂SO₄

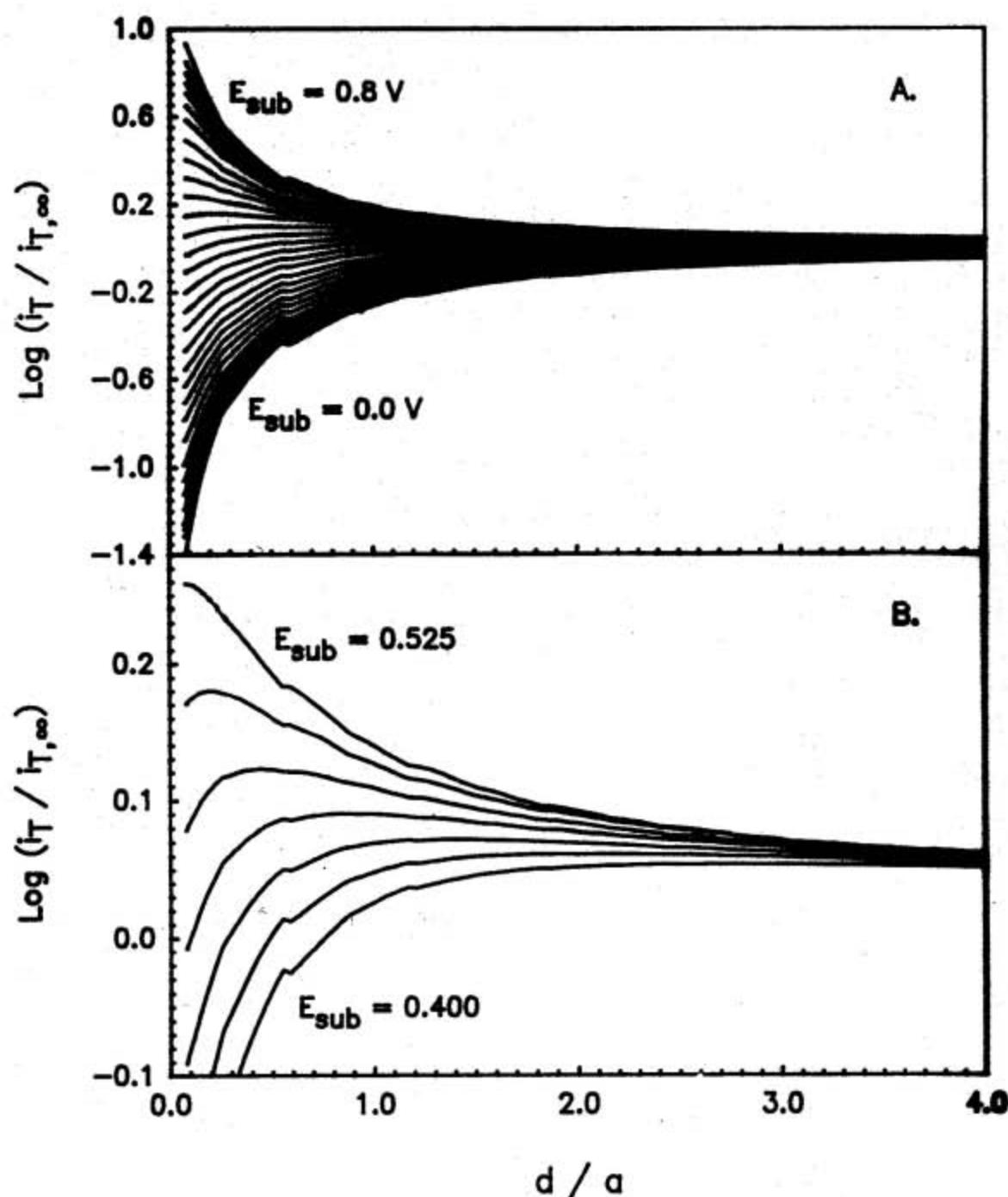


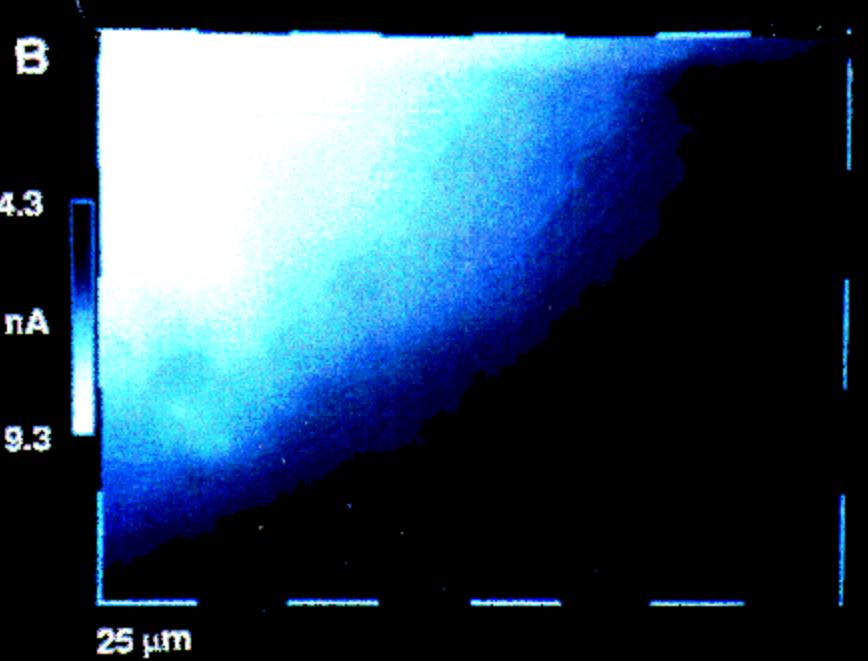
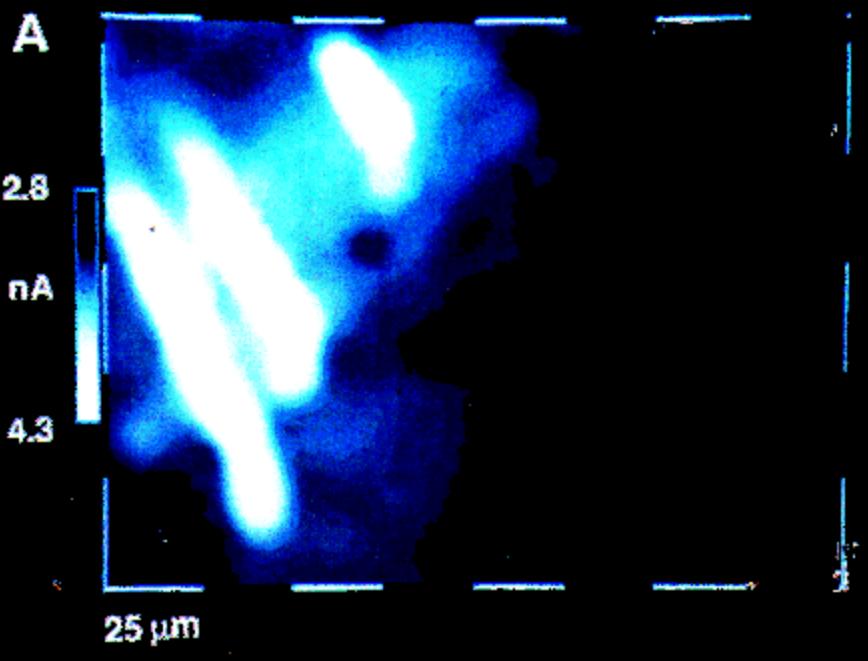
Effect of heterogeneous kinetics on SECM approach curves



Rate constants (cm/s)

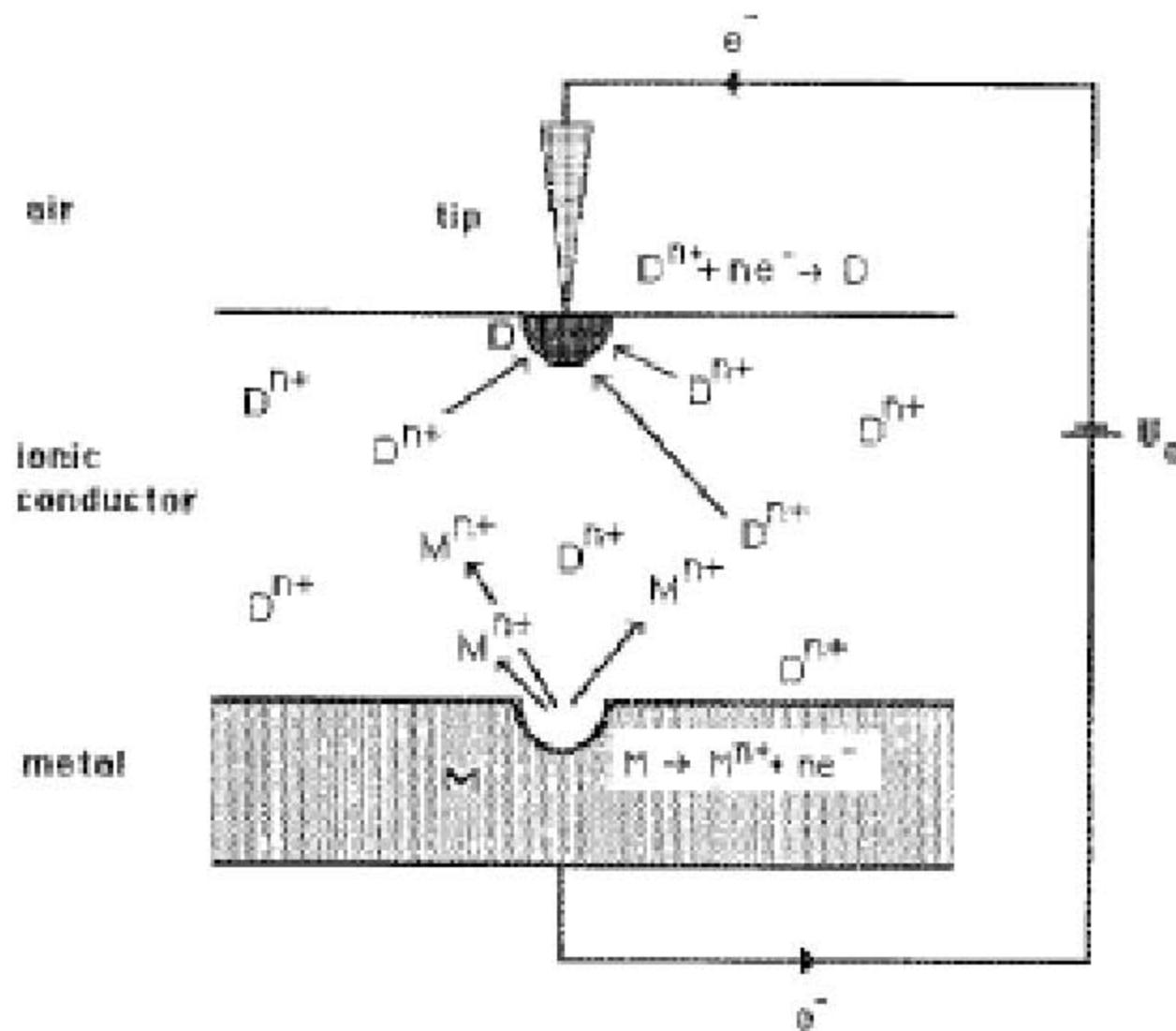
a. 1	f. 0.01
b. 0.5	g. 0.005
c. 0.1	h. 0.002
d. 0.025	i. 0.0001
e. 0.015	





Fabrication and Micropatterning

SECM Fabrication - Direct method



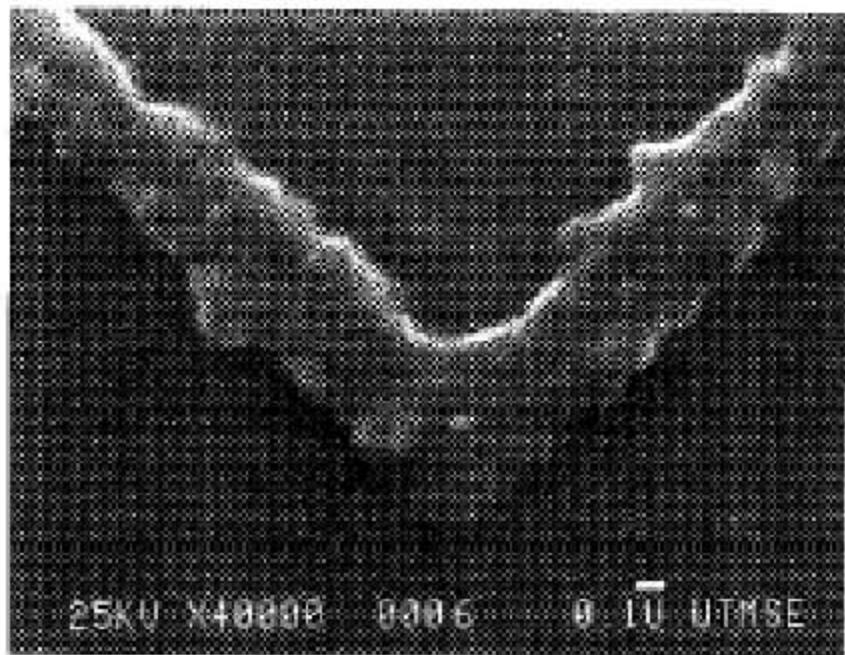
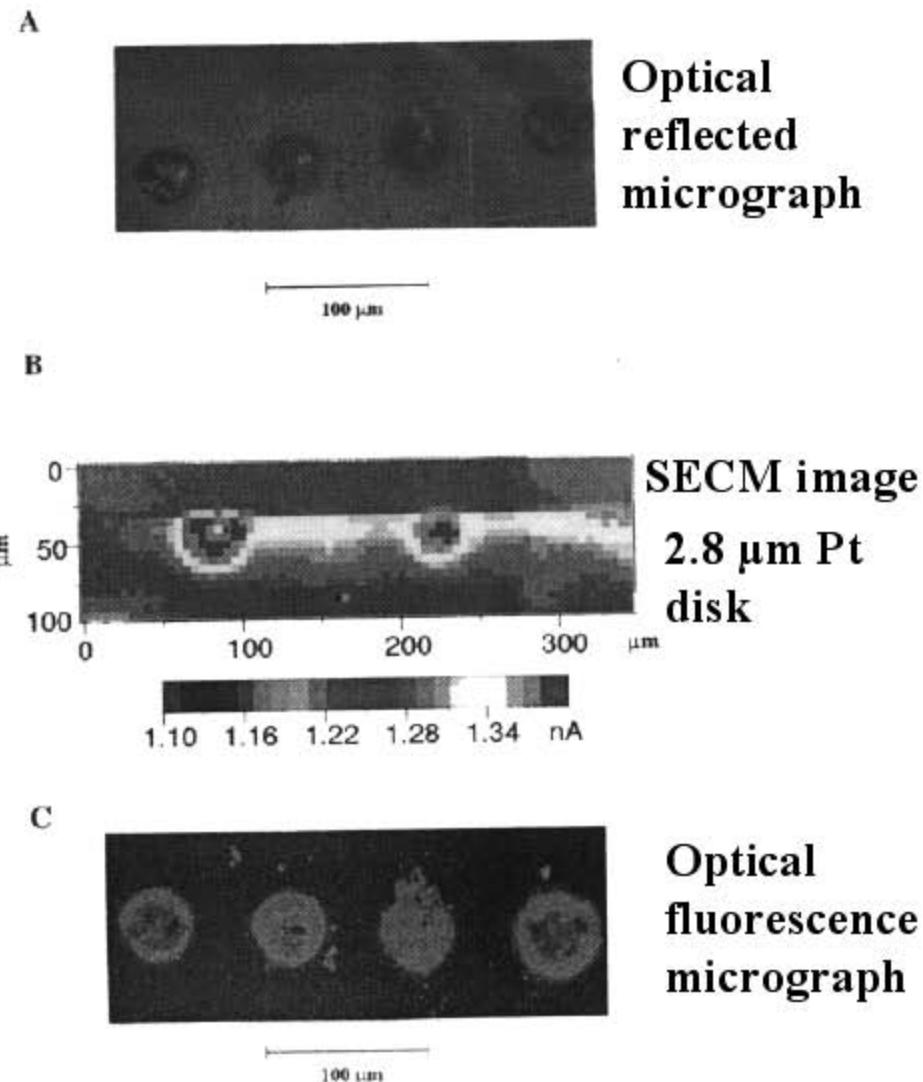
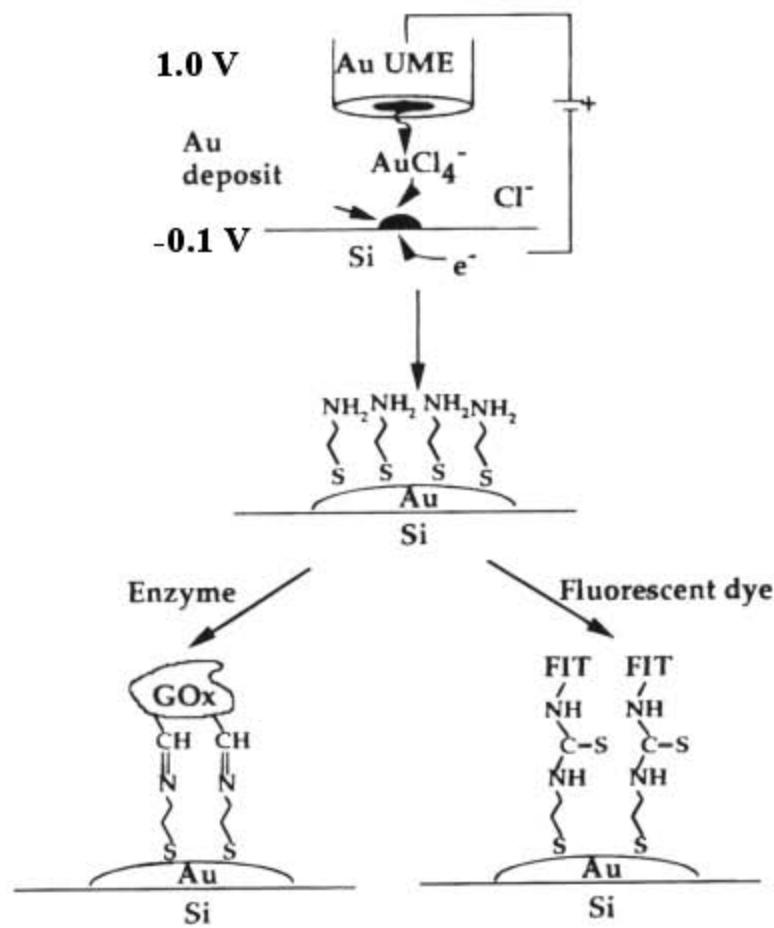
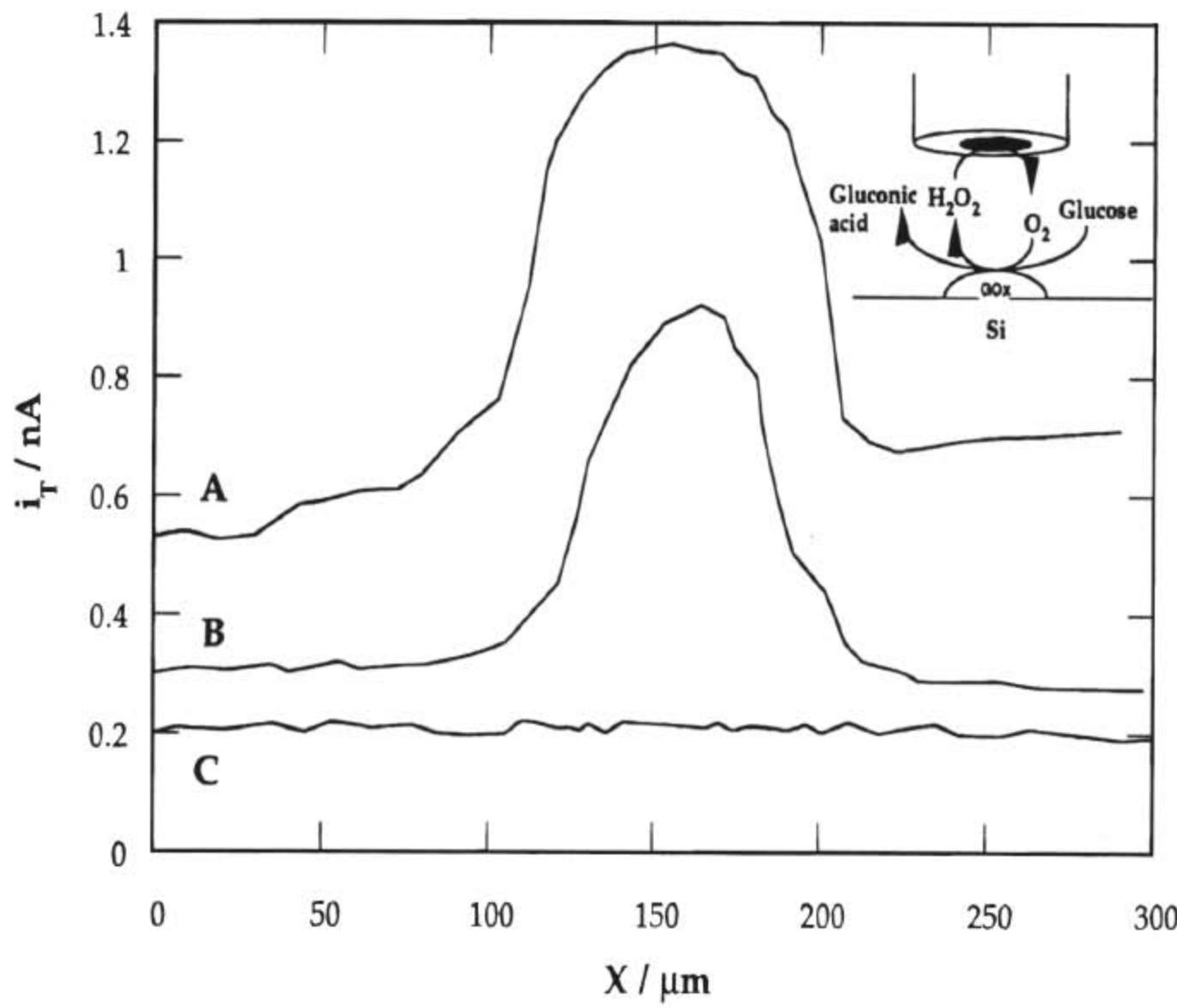


FIG. 2. SEM picture of a pattern of silver lines deposited in a Naflon film. Tip material = tungsten, bias = 5 V, tip current ≈ -0.5 nA, and scan rate ≈ 900 Å/s. Tip reaction, $\text{Ag}^+ + e^- \rightarrow \text{Ag}$; substrate reaction, $\text{Ag} \rightarrow \text{Ag}^+ + e^-$.

Turyan et al., "Patterning and characterization of surfaces with organic and biological molecules by the SECM," Anal. Chem. (2000), 72, 3431.

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



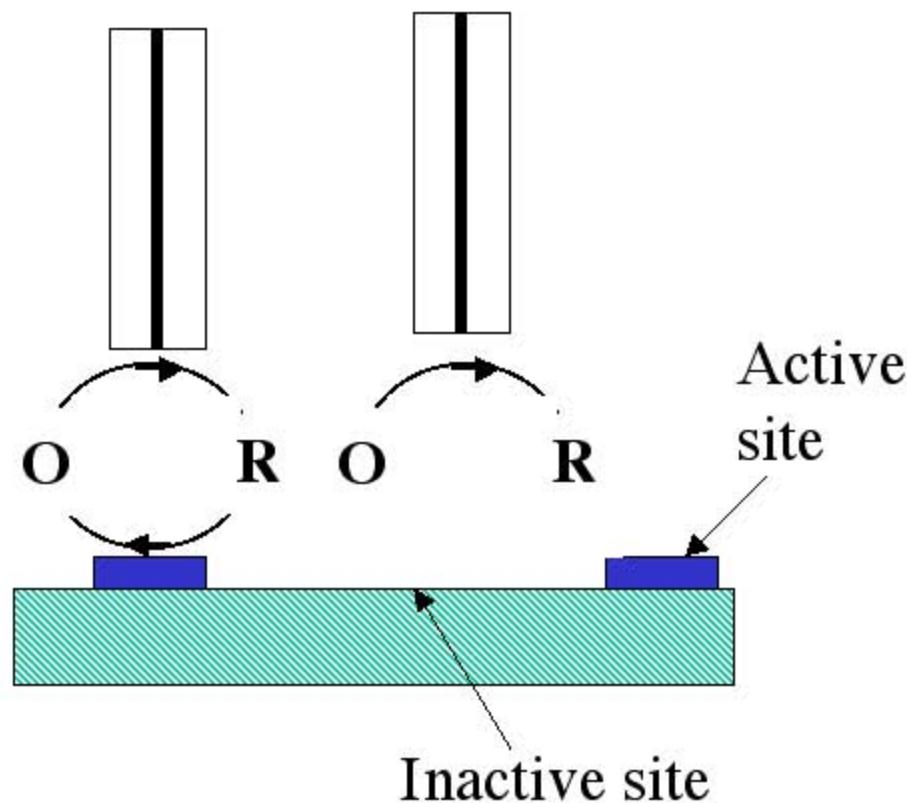


25- μm Au disk
air-saturated 50 mM glucose/0.1 M phosphate buffer (pH 7.4)
 $E_T = 0.4 \text{ V vs. Ag/AgCl}$
Si: open-circuit

B: addition of catalase ("chemical lens")
C: blank

Probing Surfaces with SECM

Catalytic Surfaces



Membranes

