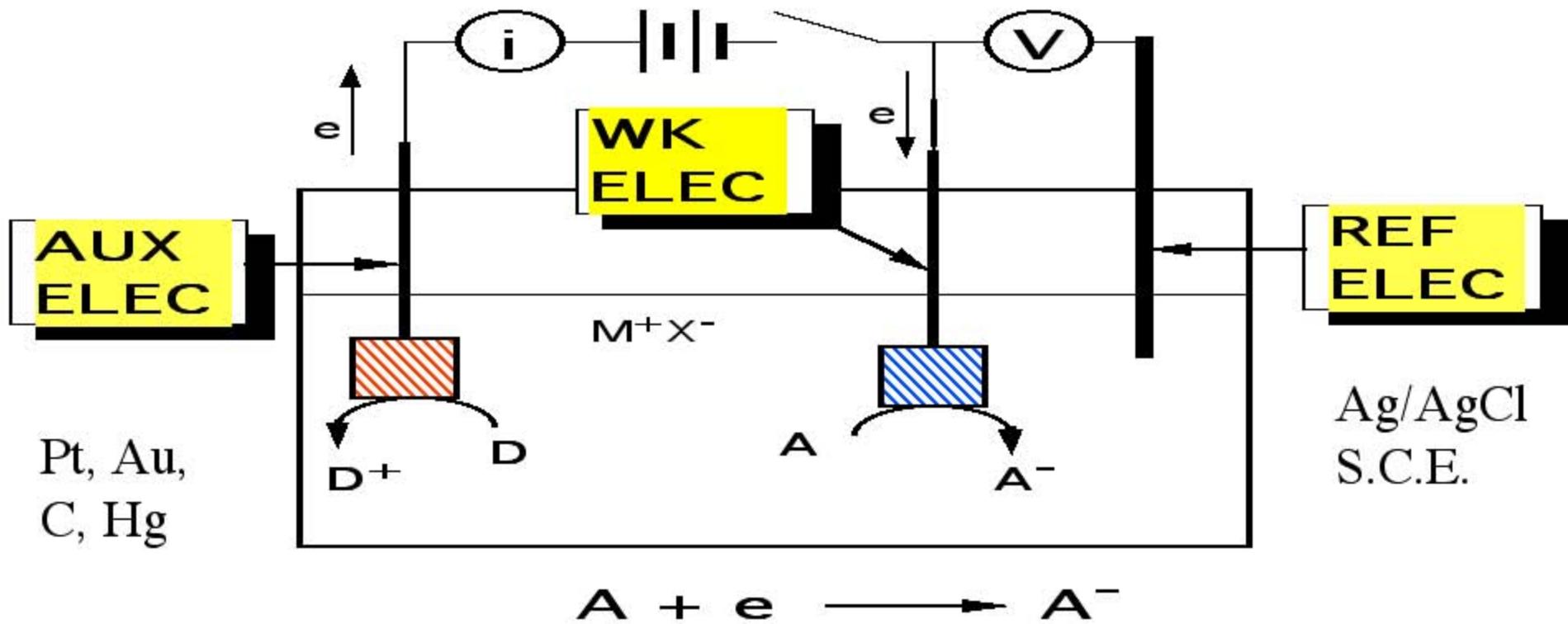


Introduction and principles of electrochemistry and microelectrodes

ELECTROCHEMICAL CELL



Pt, Au,
C, Hg

Ag/AgCl
S.C.E.



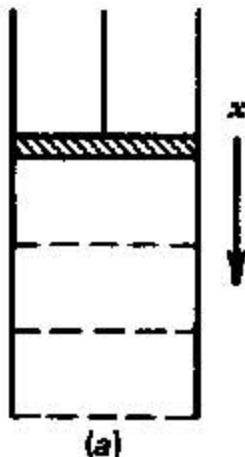
$$N \text{ (mol/s)} = i \text{ (A)} / nF$$

$$F = 96,485 \text{ C/mol}$$

1 pA equivalent to 10^{-17} mol/s

Potential Step Semi-infinite Linear Diffusion

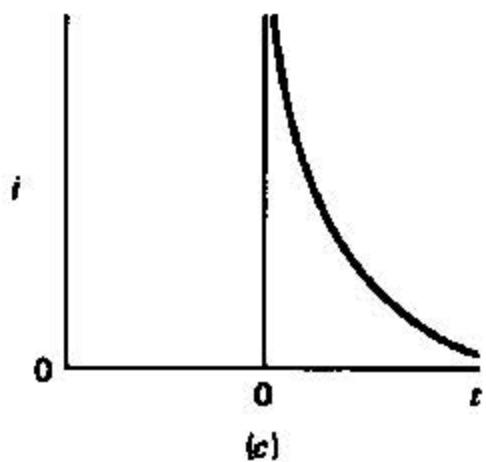
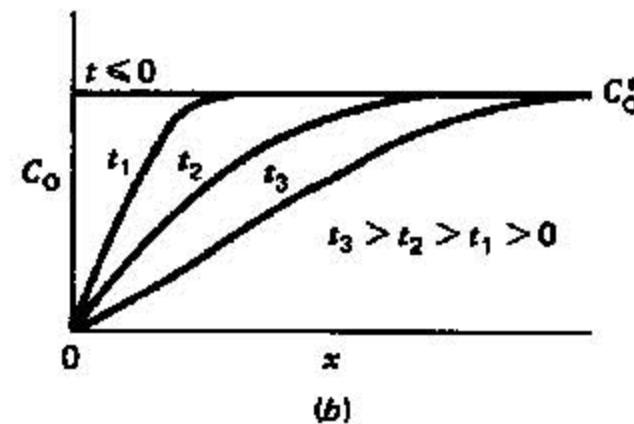
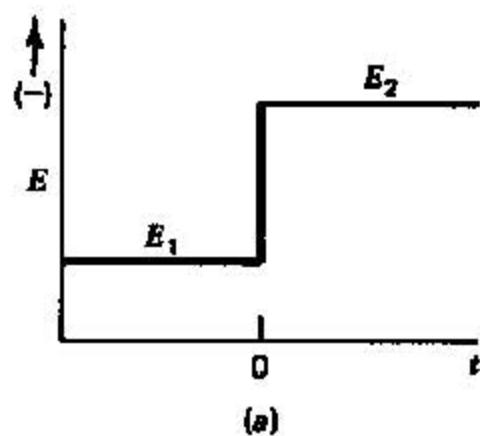
Linear Diffusion to a Planar Electrode



Electrode reaction: $A + e \rightleftharpoons A^-$ at $x=0$, rate constant
 k^0 (cm/s)

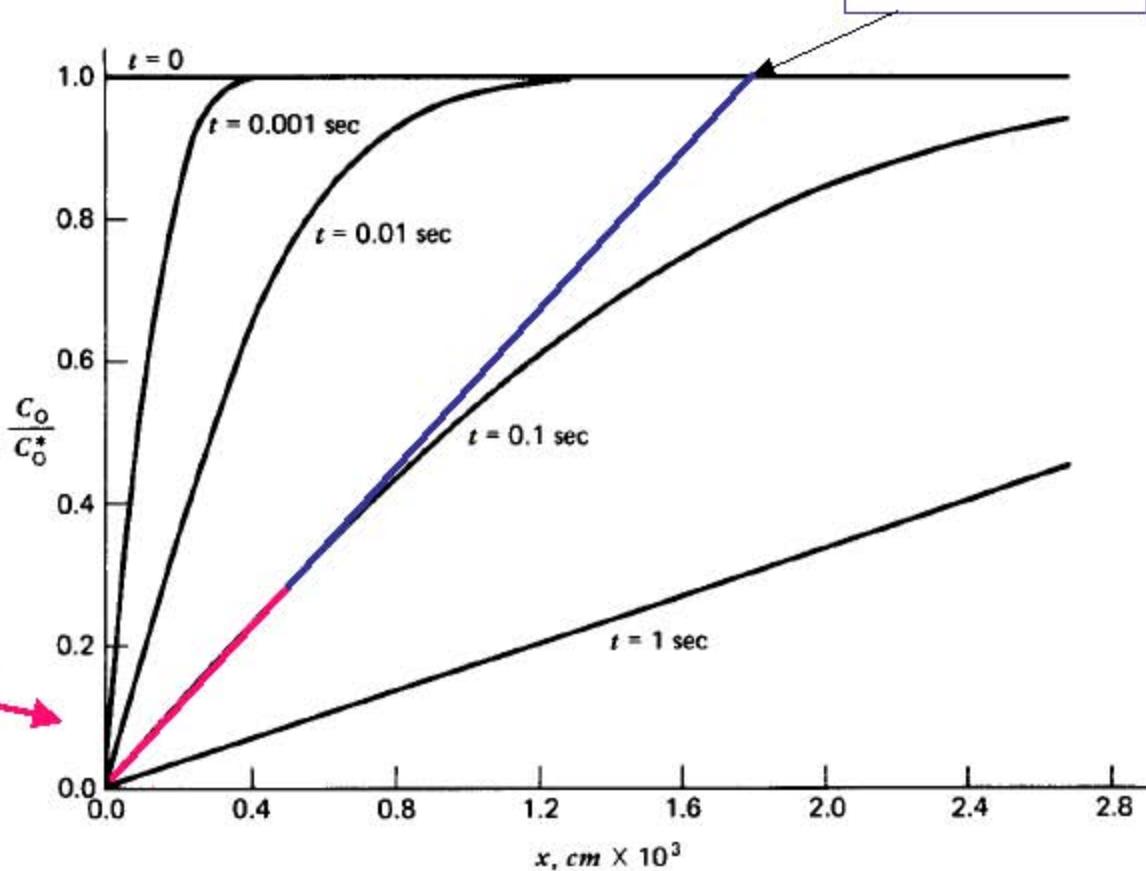
In solution: $A_{\text{bulk}} \rightarrow A_{x=0}$ by diffusion

Potential Step at a Planar Electrode



Concentration Profiles in Potential Step at Planar Electrode

$$\delta = 2(Dt)^{1/2}$$



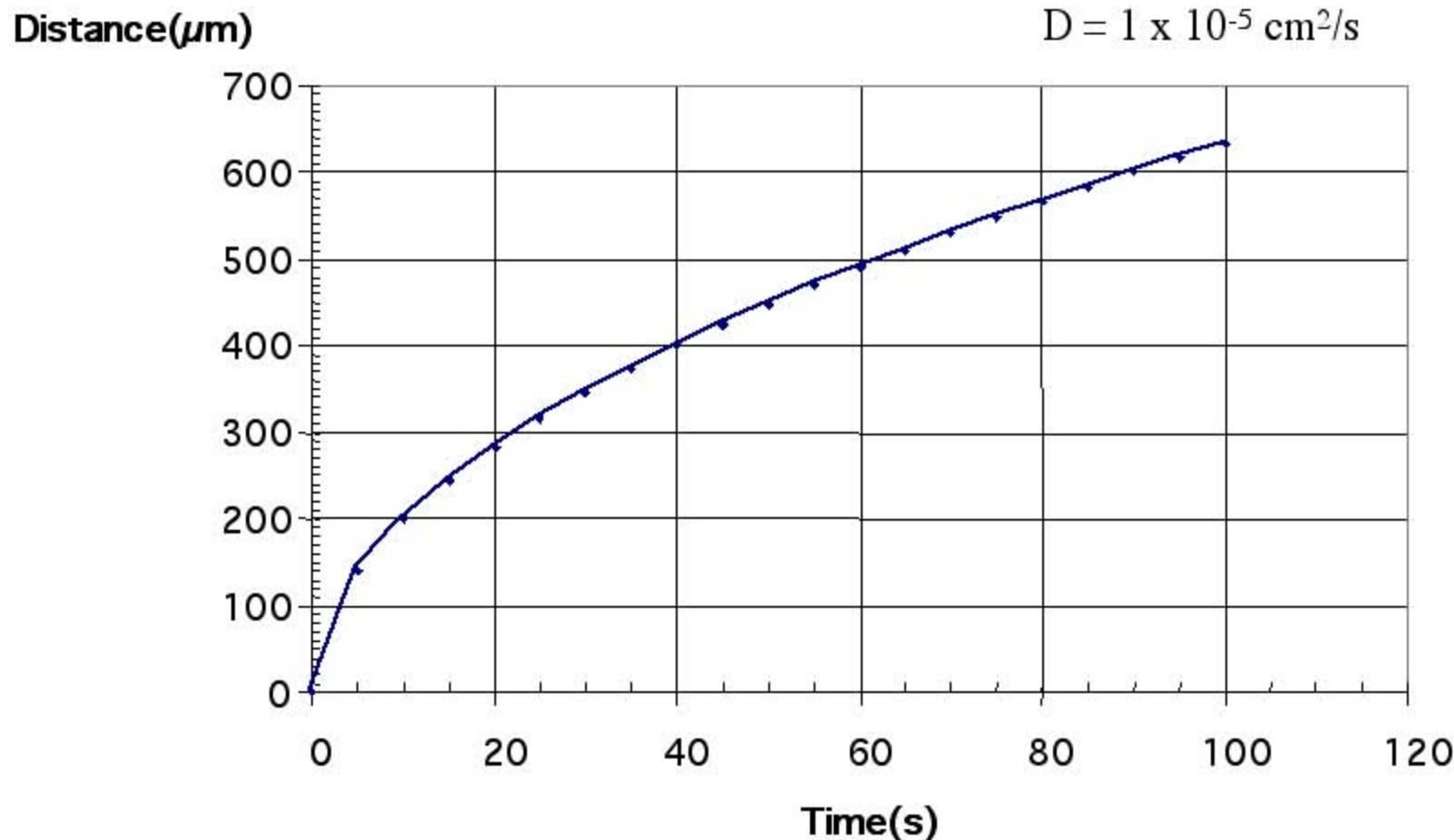
$$\frac{i}{nFA} = D_O \left[\frac{\partial C_O}{\partial x} \right]_{x=0}$$

Cottrell Equation

$$i = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

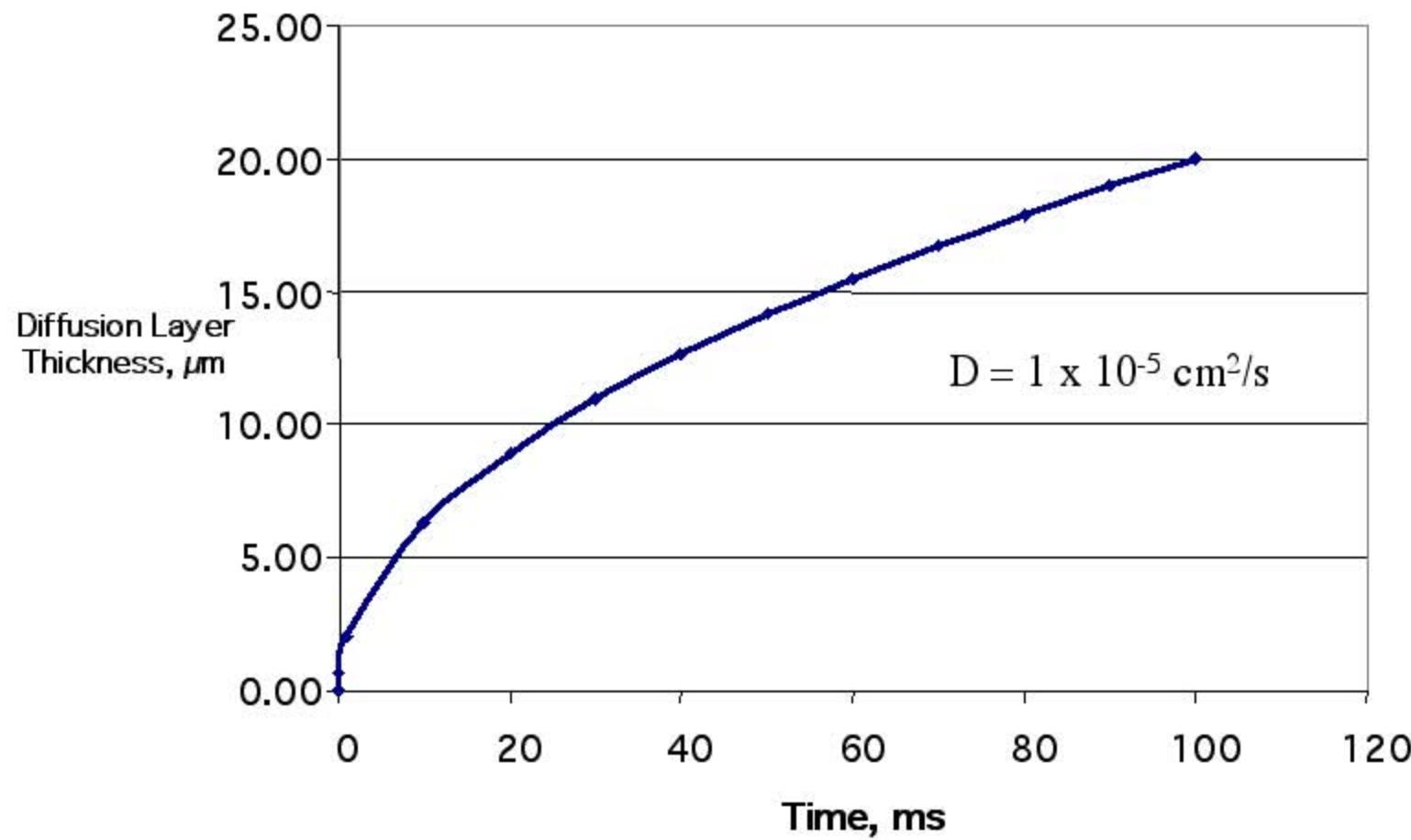
Diffusion Layer Thickness

$$\delta = 2(Dt)^{1/2}$$



Diffusion Layer Thickness

$$\delta = 2(Dt)^{1/2}$$



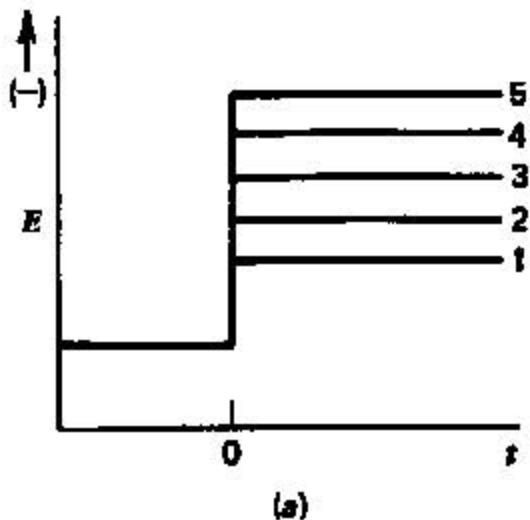
Velocity of Diffusion

$$velocity = \frac{\Delta x}{\Delta t} = \frac{2D}{\Delta x} = \left(\frac{2D}{\Delta t} \right)^{1/2}$$

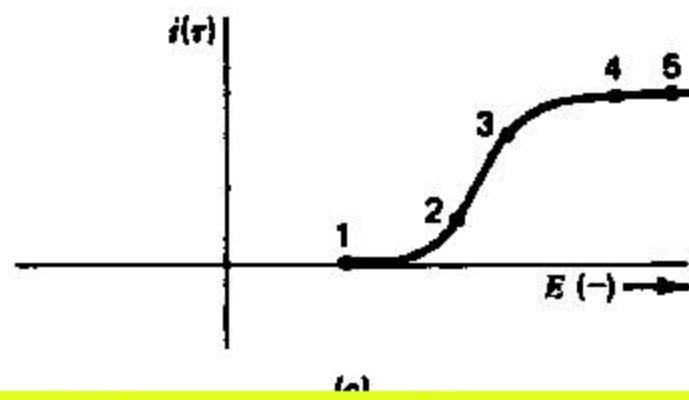
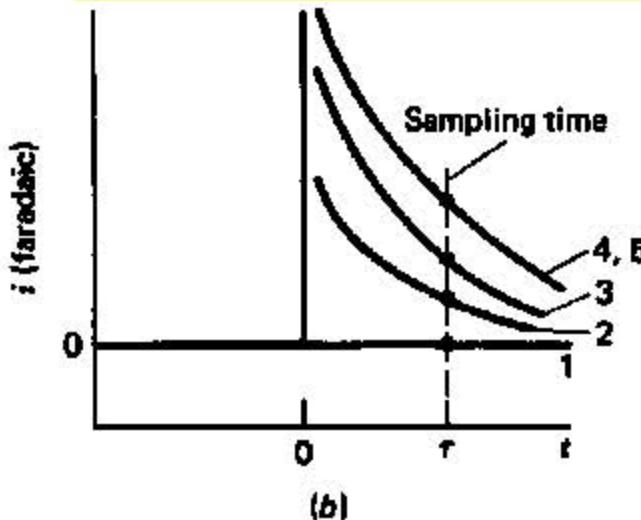
time, t (s)	$\Delta x, \mu m$	velocity ($\mu m/s$)
0.0001	0.32	3.16E+03
0.001	1.00	1.00E+03
0.005	2.24	4.47E+02
0.01	3.16	3.16E+02
0.05	7.07	1.41E+02
0.1	10.00	1.00E+02
0.5	22.36	4.47E+01
1	31.62	3.16E+01
5	70.71	1.41E+01
10	100.00	1.00E+01
50	223.61	4.47E+00
100	316.23	3.16E+00

Sampled Current Voltammetry

Steps to different potentials

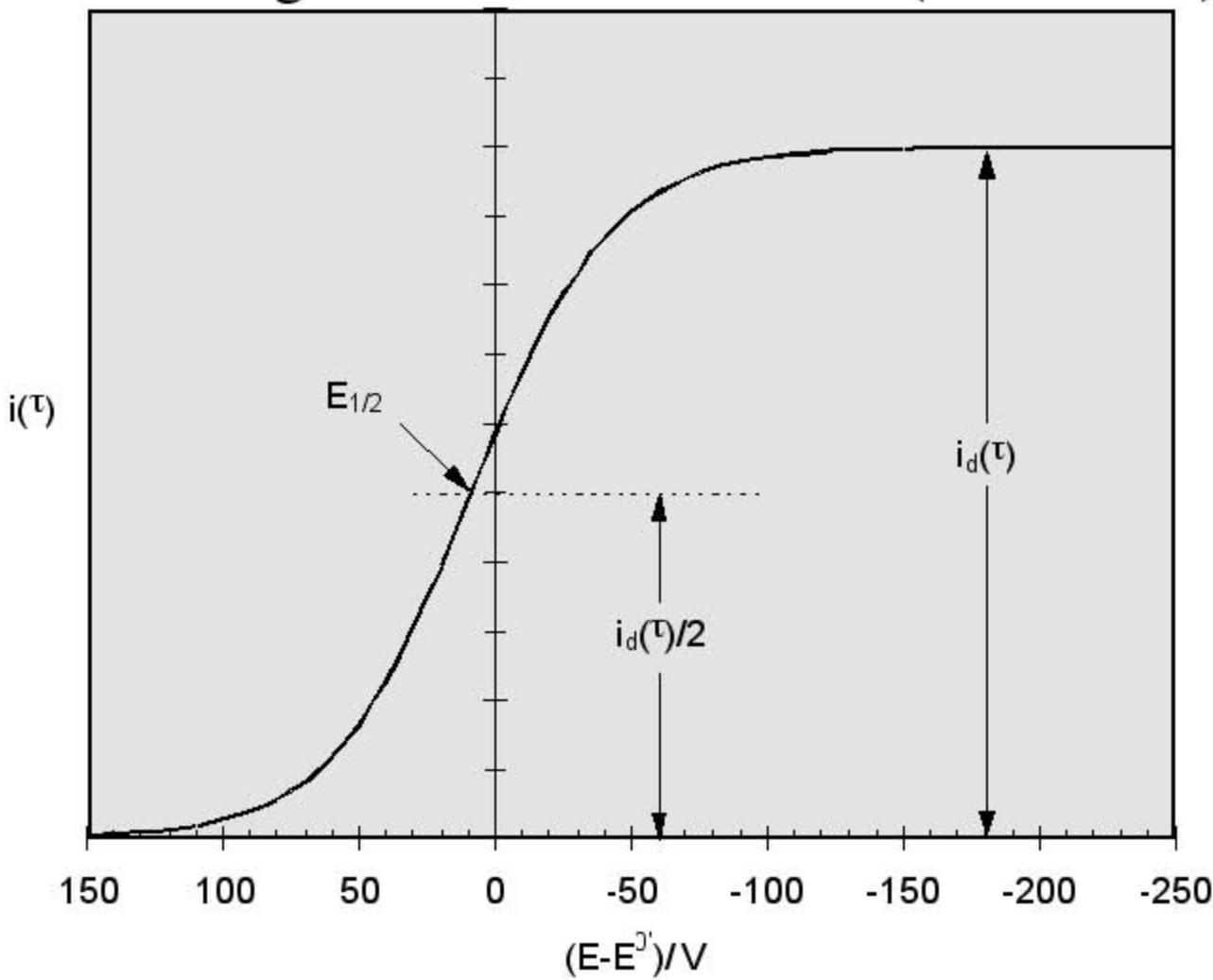


Current-time curves



Sampled current voltammogram

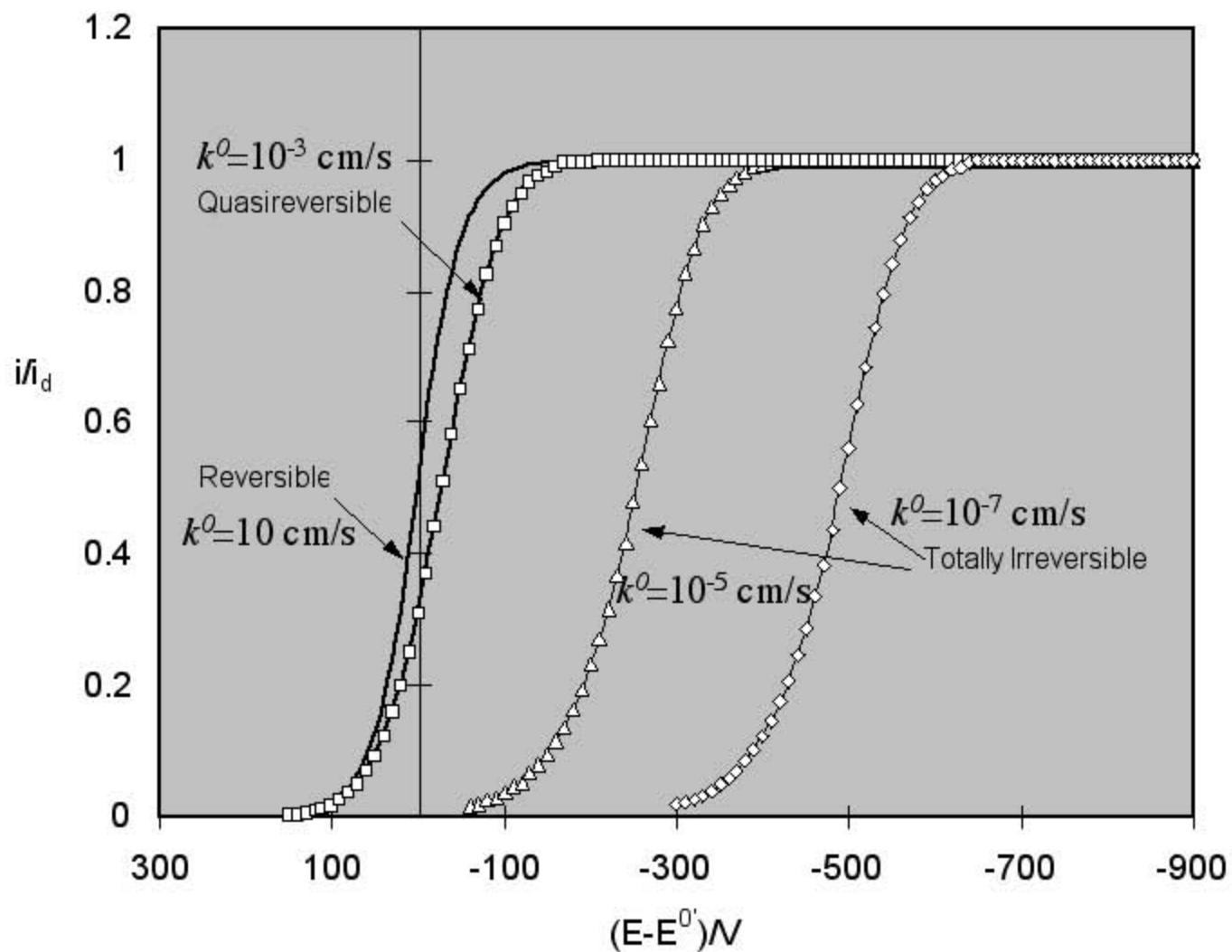
Voltammogram for a Reversible (Nernstian) Reaction



$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d(\tau) - i(\tau)}{i(\tau)}$$

$$E_{1/2} = E^{\circ'} + \frac{RT}{nF} \ln \frac{D_R^{1/2}}{D_O^{1/2}}$$

Voltammograms for Various Kinetic Regimes



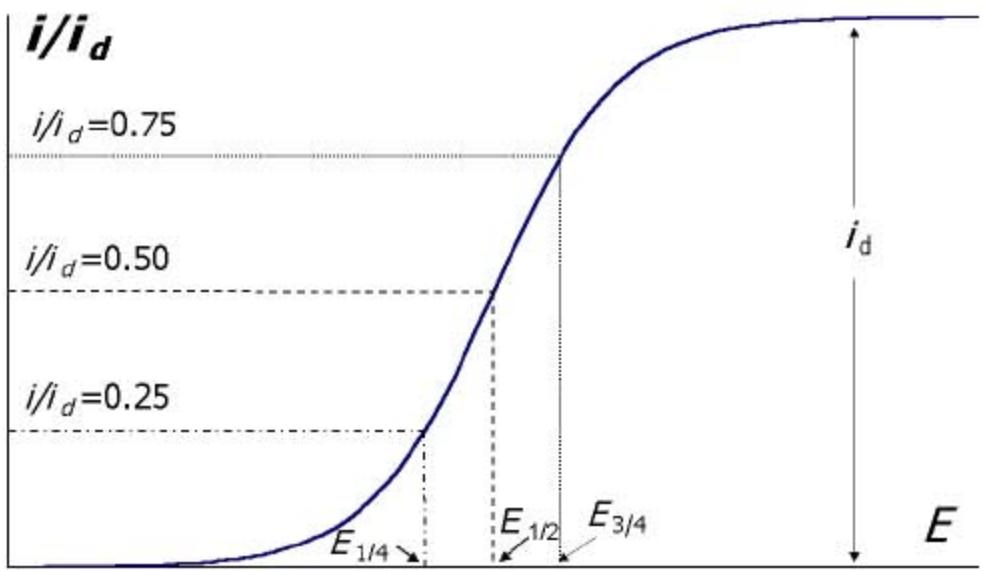
$$D_O = D_R = 10^{-5} \text{ cm}^2/\text{s}, \alpha = 0.5, \tau = 1 \text{ s}$$

Evaluation of Steady State Voltammogram

Nernstian reaction:

Tomes criterion:

$$|E_{3/4} - E_{1/4}| = 56.4/n \text{ mV}$$



$$E \text{ vs. } \log [(i_d - i)/i]$$

$$\text{Slope} = 59.1/n \text{ mV}$$

Kinetic limitations

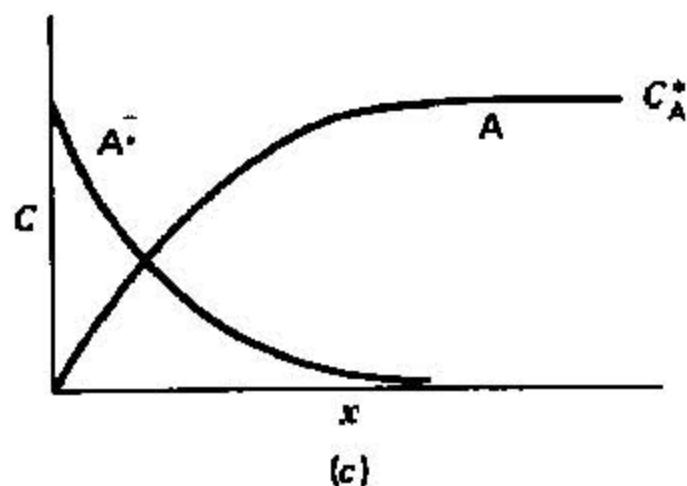
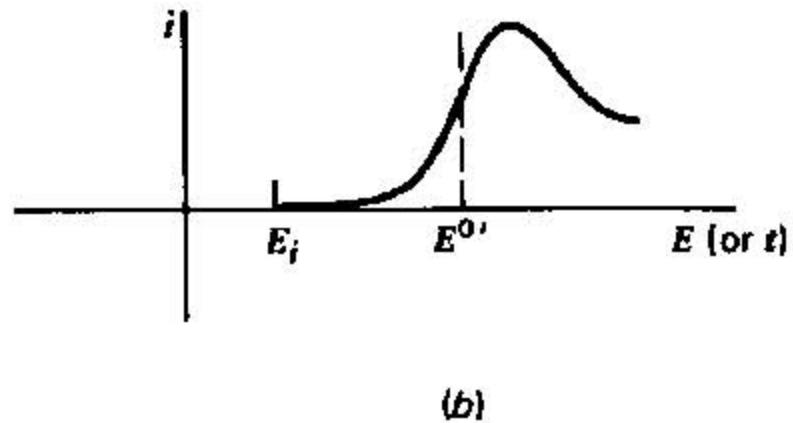
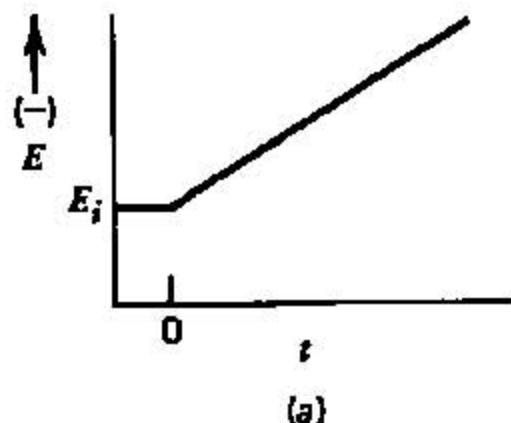
$$|E_{3/4} - E_{1/4}| > 56.4 \text{ mV}$$

Rate constants can be

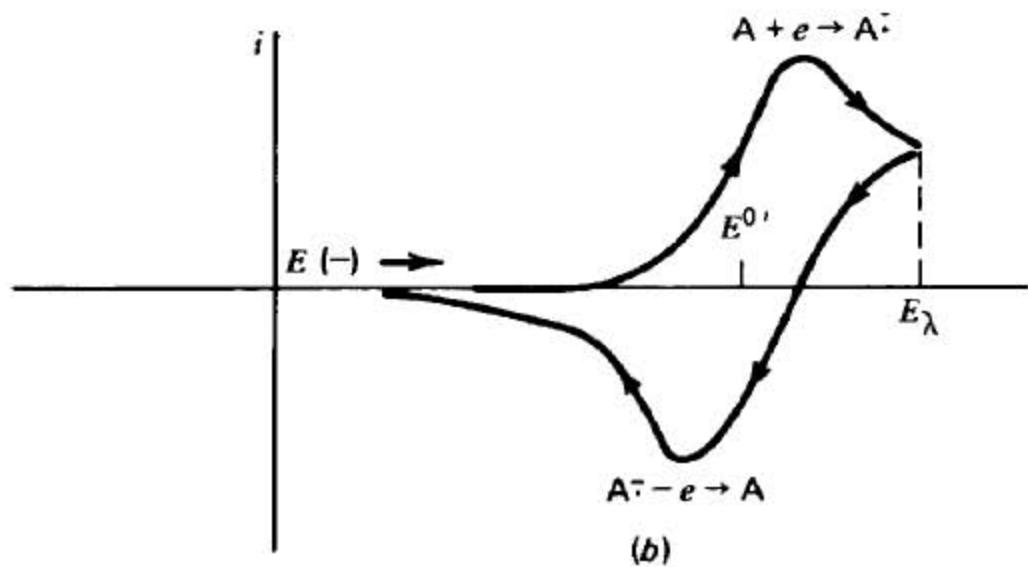
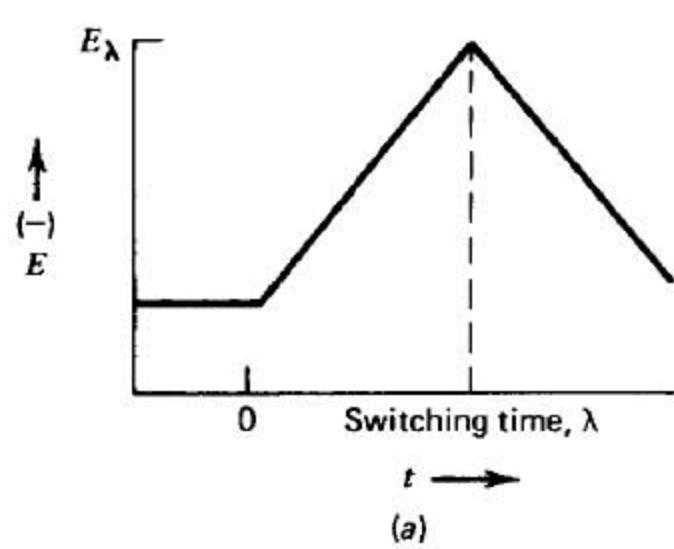
evaluated from $|E_{3/4} - E_{1/2}|$
and $|E_{1/2} - E_{1/4}|^*$

*For data treatment, see M. V. Mirkin and A. J. Bard, Anal. Chem. **97**, 7672 (1993).

Potential Sweep Voltammograms



Cyclic Voltammograms



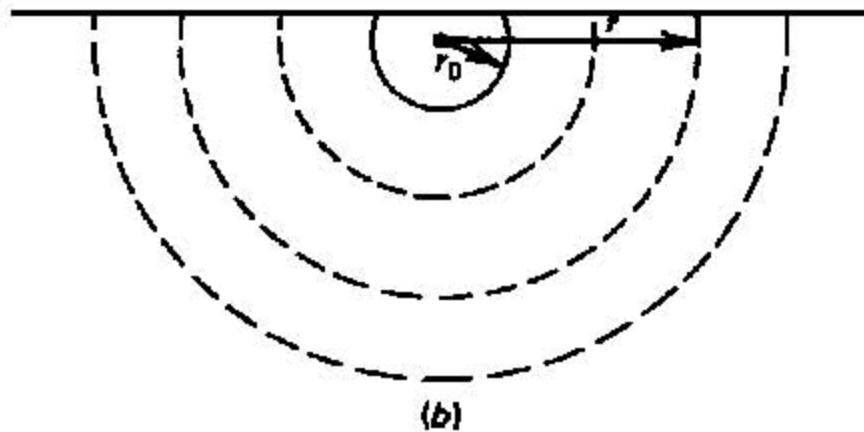
Potential Step Hemispherical Diffusion

Hemispherical Diffusion

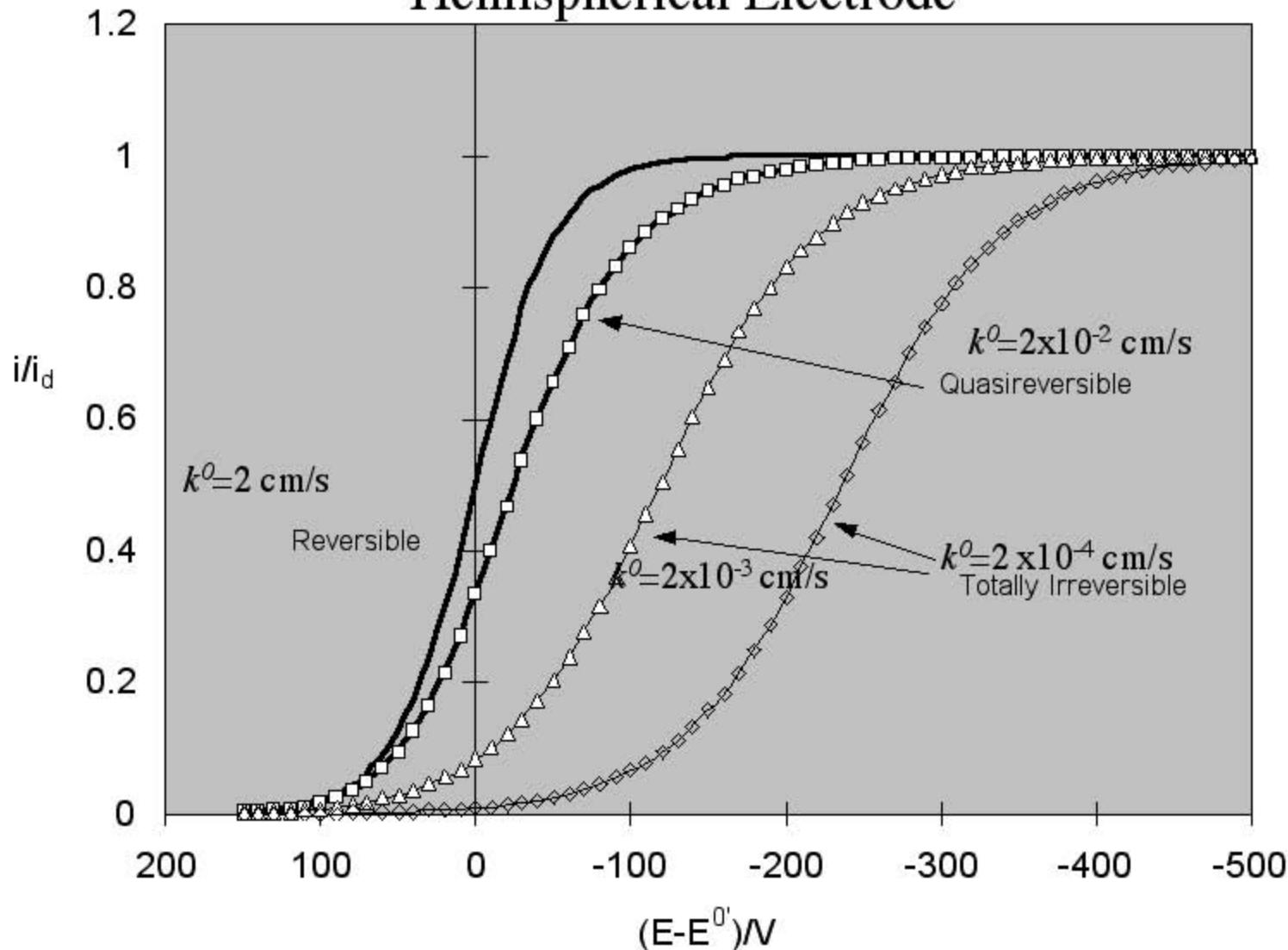
$$i_d(t) = nFAD_0C_0^* \left[\frac{1}{(\pi D_0 t)^{1/2}} + \frac{1}{r_0} \right]$$

$$\lim_{t \rightarrow 0} i_d = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2} t^{1/2}}$$

$$\lim_{t \rightarrow \infty} i_d = \frac{nFAD_0C_0^*}{r_0}$$



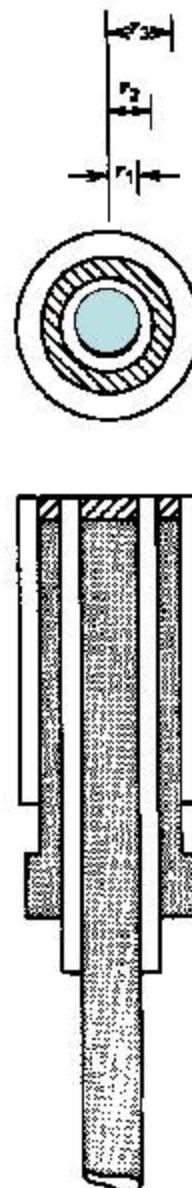
Steady-state Voltammograms for Various Kinetic Regimes at a Hemispherical Electrode



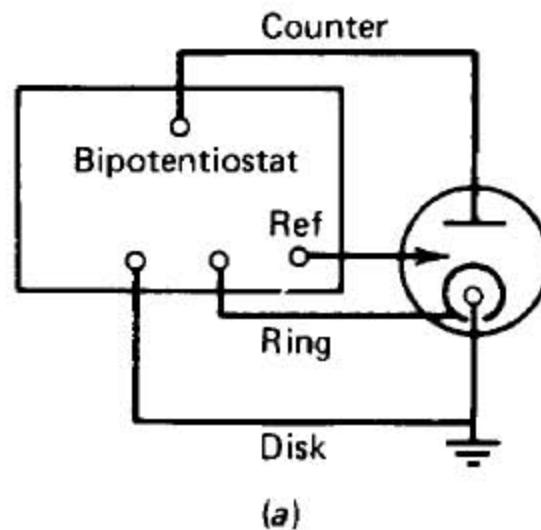
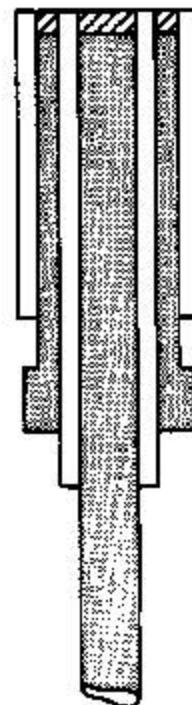
$$D_O = D_R = 10^{-5} \text{ cm}^2/\text{s}, \alpha = 0.5, r_0 = 5 \mu\text{m}$$

Rotating Ring-Disk Electrode

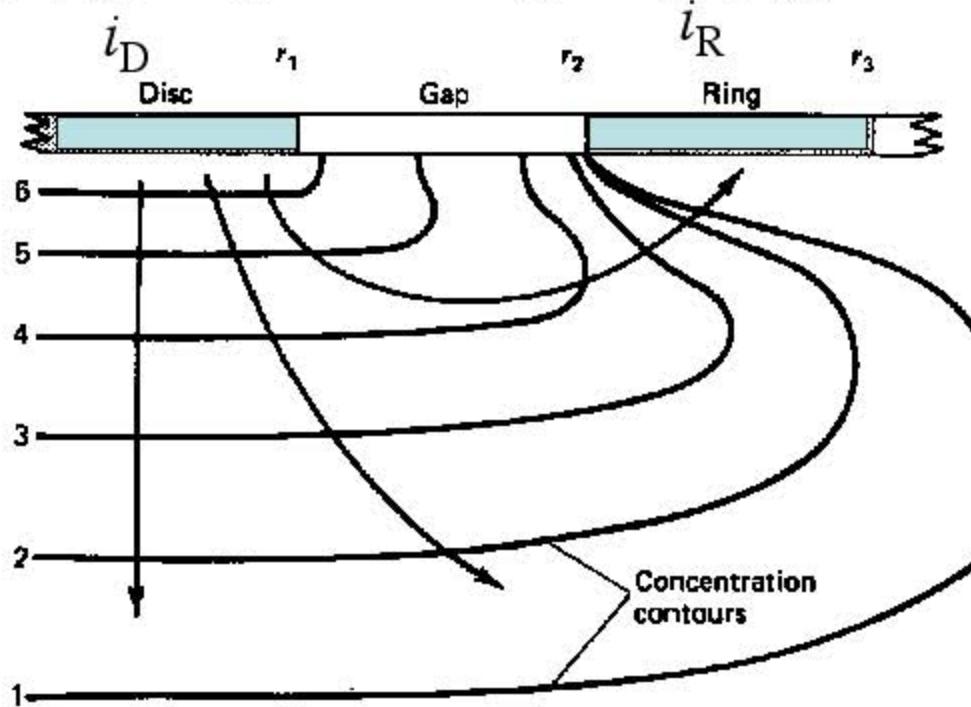
Rotating Ring-Disk Electrode



- Electrode material (e.g., platinum)
- Insulator (e.g., Teflon)
- Shaft and ring material (e.g., brass)



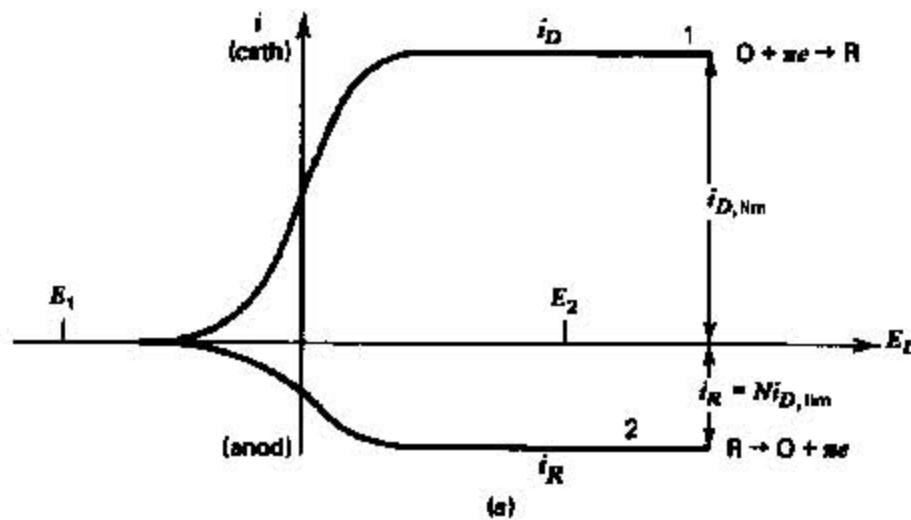
Concentration Profiles at the RRDE



$$N = \frac{-i_R}{i_D}$$

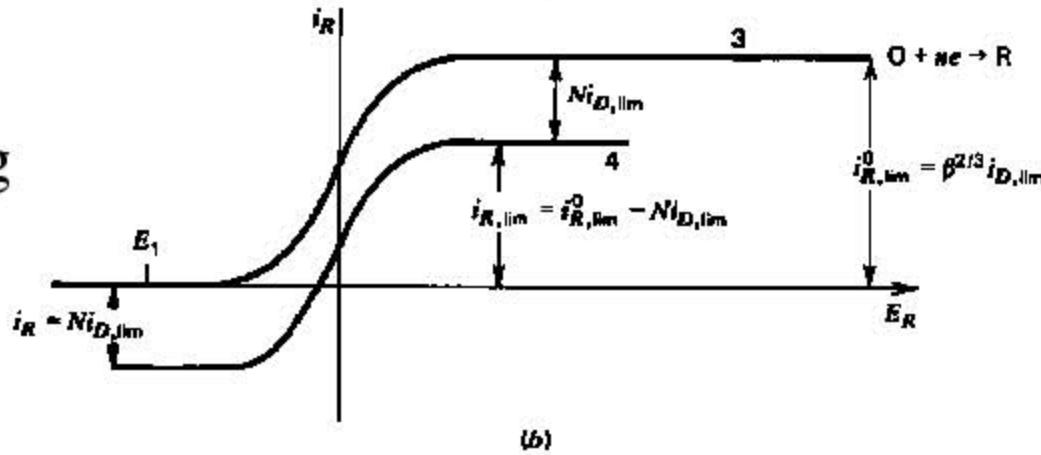
Disk and Ring Voltammograms at the RRDE

Collection



(a)

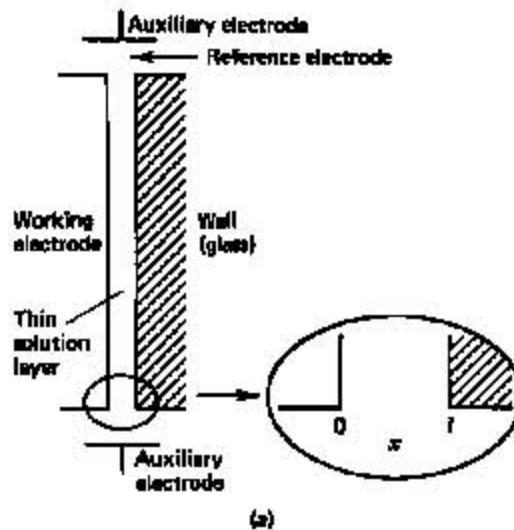
Shielding



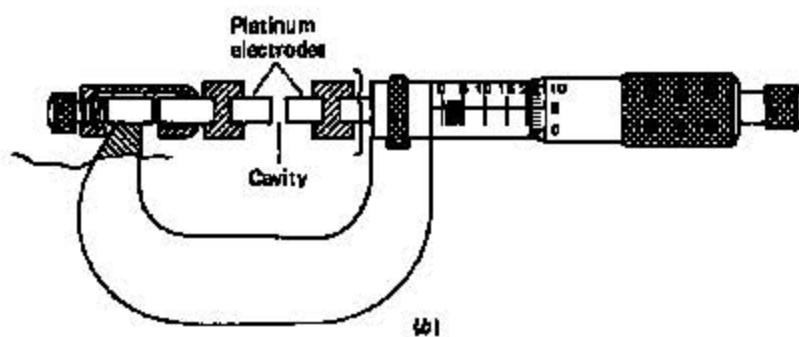
(b)

Thin Layer Cell

Thin Layer Cells

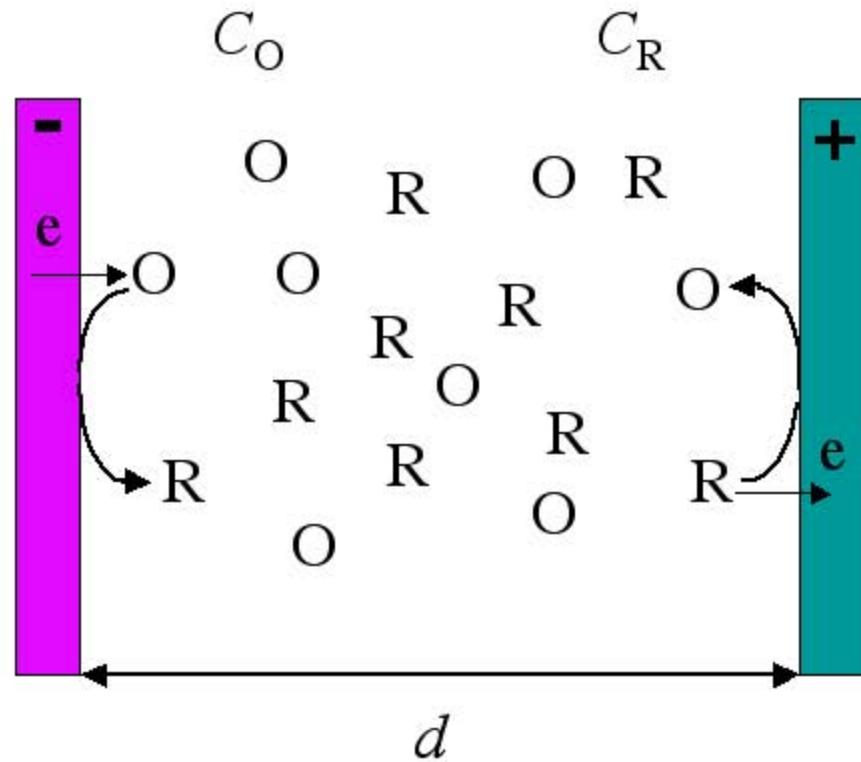


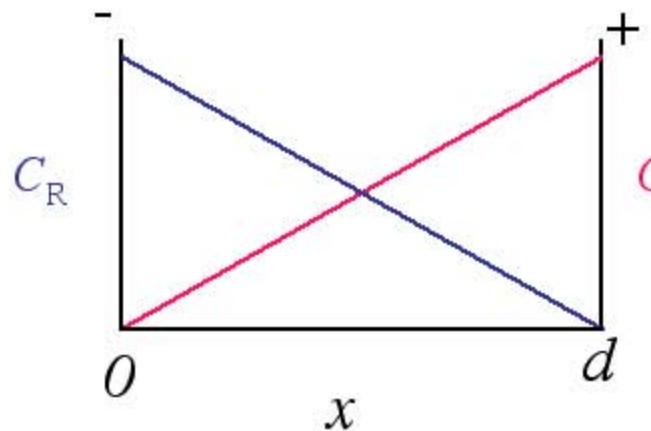
(a)



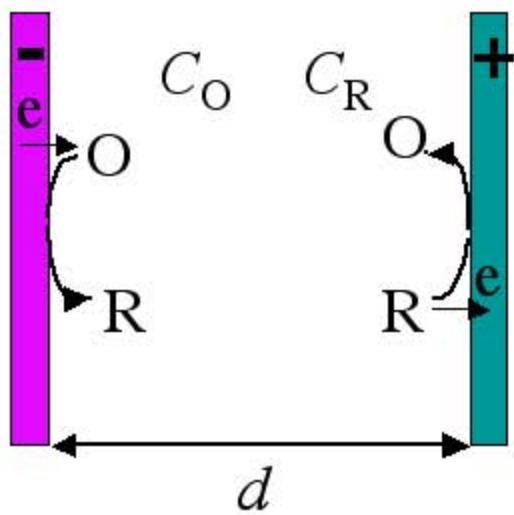
(b)

Twin Electrode Thin Layer Cell



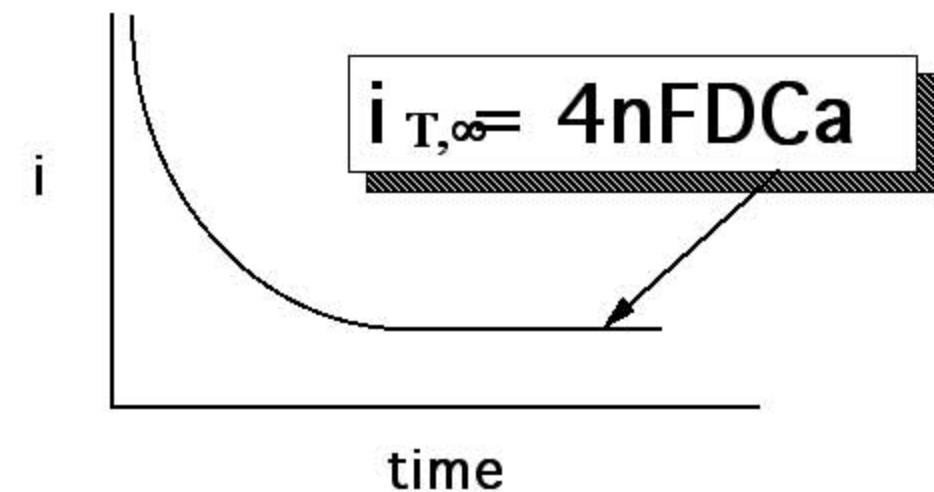
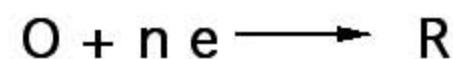
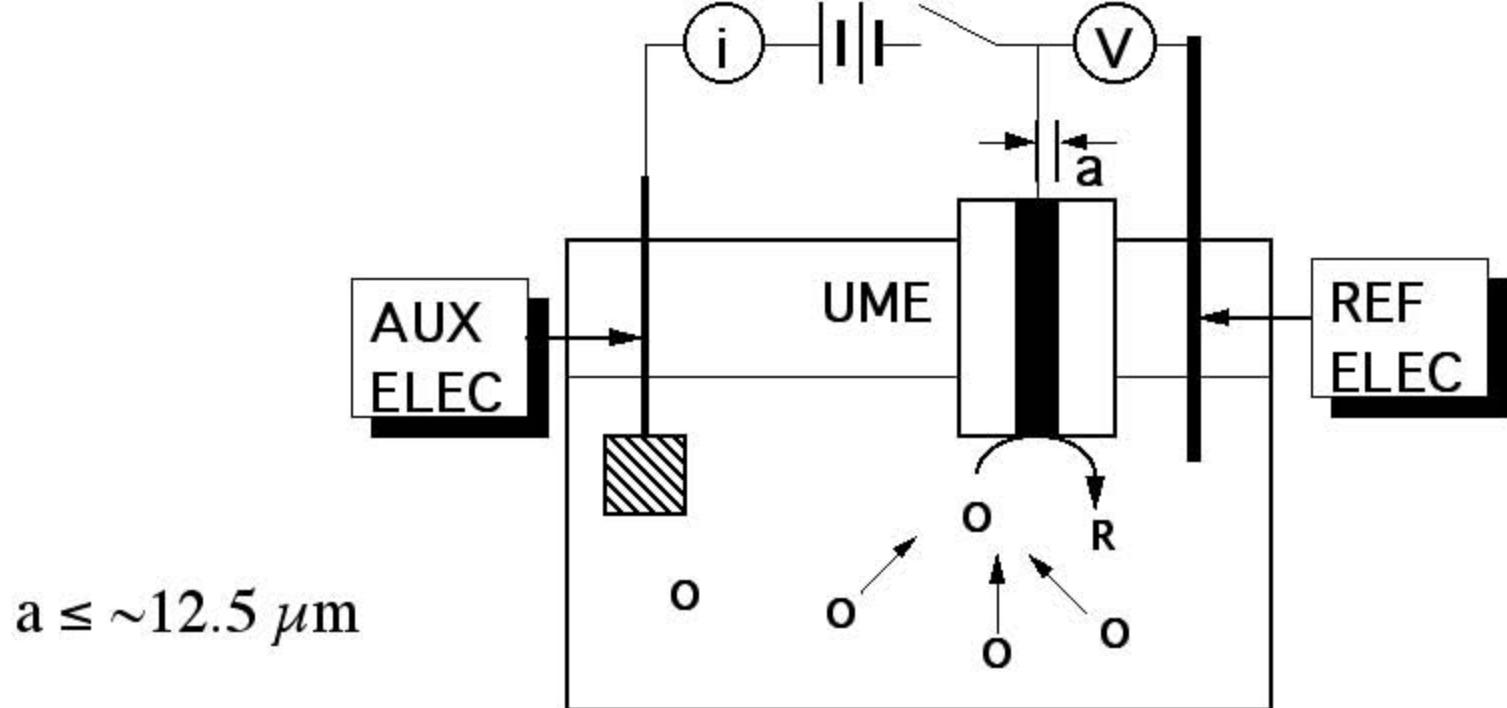


$$\frac{i_{ss}}{nFA} = D_O \frac{\partial C_O}{\partial x} = D_O \frac{C_O^*}{d}$$

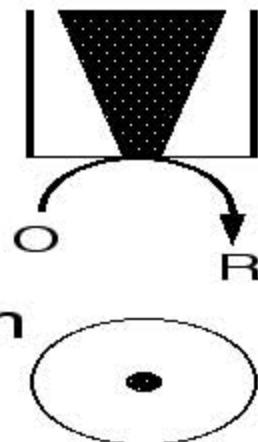


$$i_{ss} = \frac{nFAD_O C_O^*}{d}$$

Ultramicroelectrodes



Ultramicroelectrode



Radius, a , \sim nm - μ m

$$i_{lim} = 4nFDC^*a \quad (\text{typically pA - nA})$$

$$R_u = 1/(4\pi\kappa a) \quad (R_u = \text{uncomp. resistance})$$

$$C = \pi a^2 C_d \quad (C_d \sim 10 - 20 \mu F/cm^2)$$

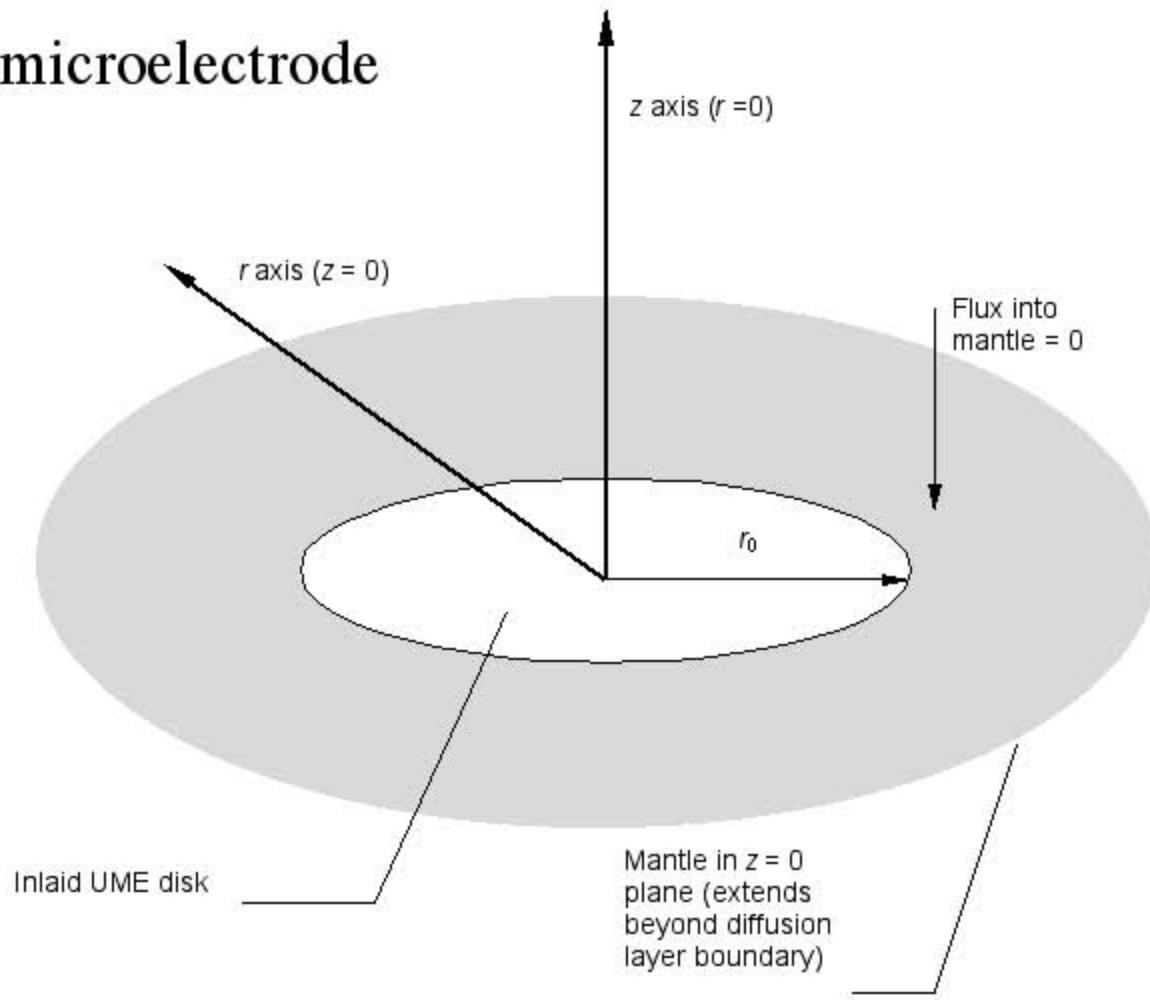
$$\text{Time const.} = R_u C = C_d a / 4\kappa$$

$$\kappa = 0.01 \text{ ohm}^{-1}\text{cm}^{-1} \quad a = 1 \mu\text{m}$$

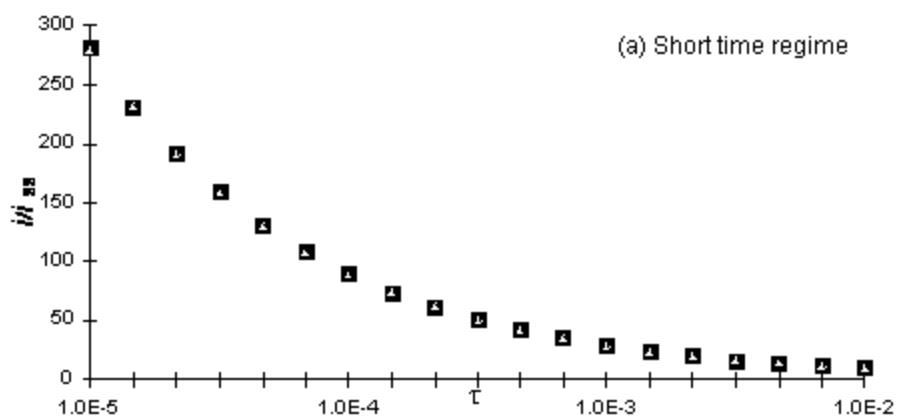
$$R_u = 250 \text{ k}\Omega \quad RC = 80 \text{ ns}$$

$$a = 1 \text{ nm} \quad R_u = 250 \text{ M}\Omega \quad RC = 80 \text{ ps}$$

Ultramicroelectrode

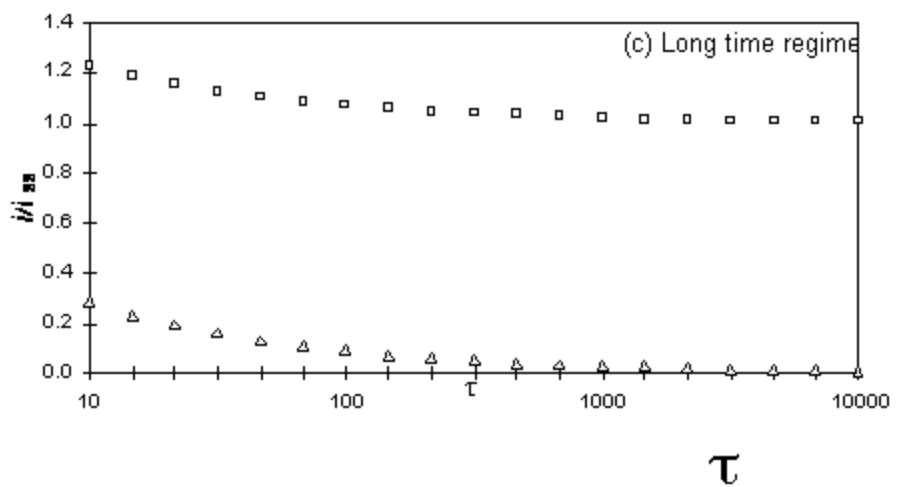
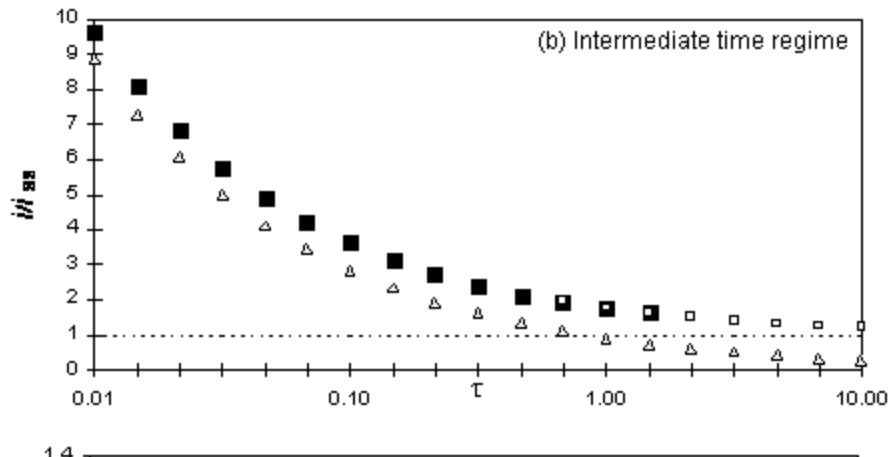


UME: $r_0 \leq \sim 12.5 \mu\text{m}$

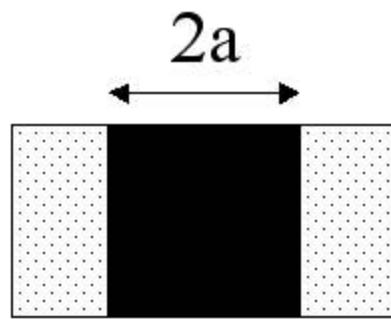


Δ Cottrell behavior

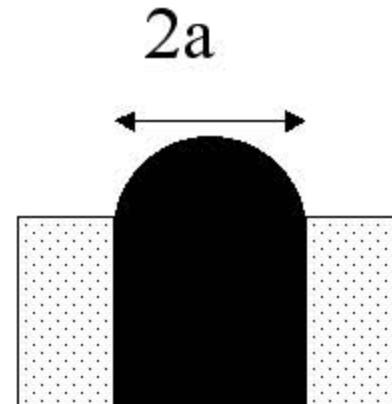
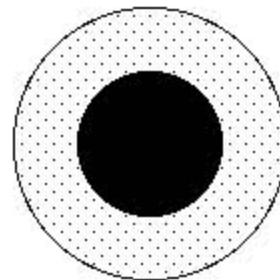
$$\tau = 4D_o t / r_0^2$$



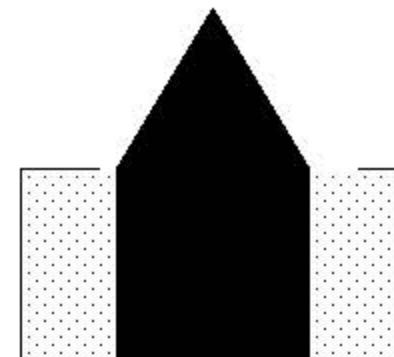
UMEs: Usual Geometries



Inlaid Disc

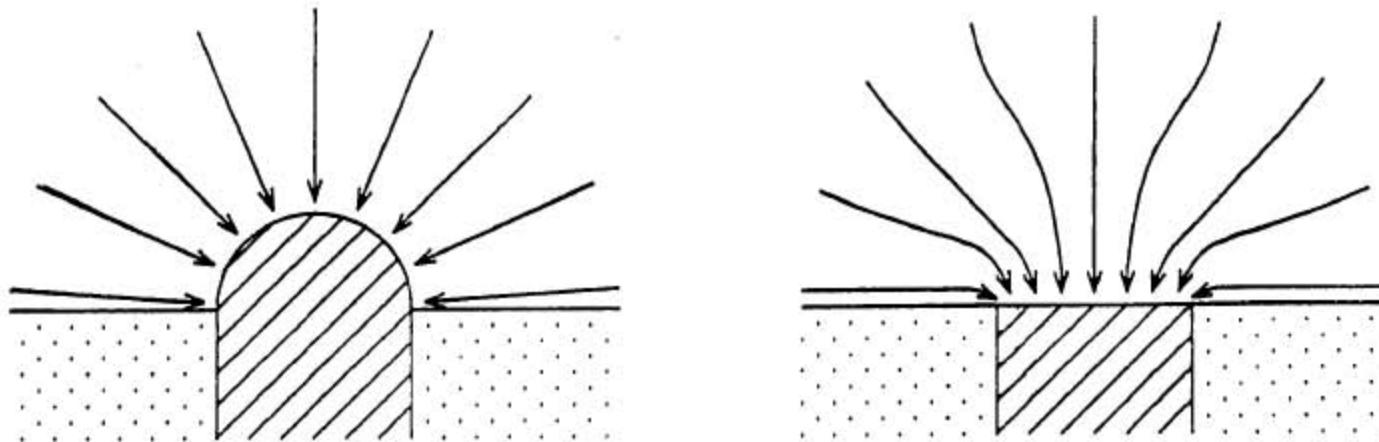


Hemisphere



Cone

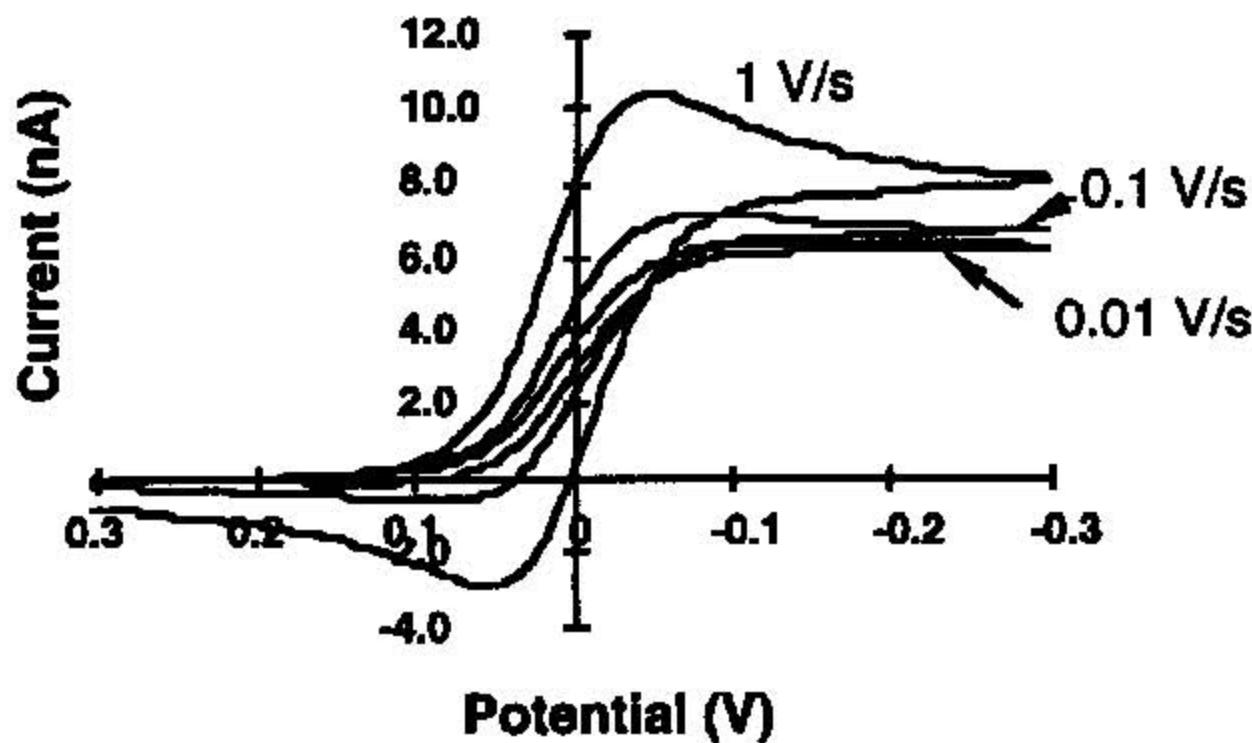
UMEs: Convergent Diffusion



$$t_{ss} \propto \frac{r_o^2}{D} \approx 25 \text{ ms}$$

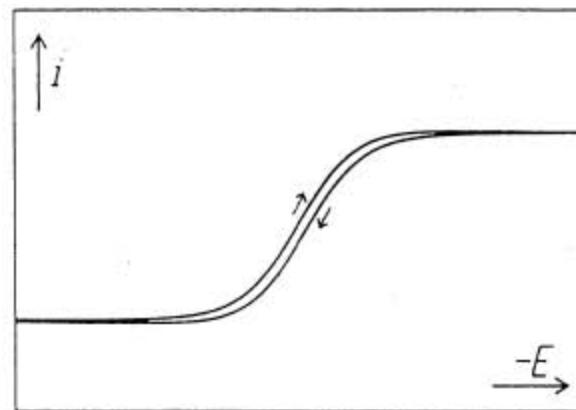
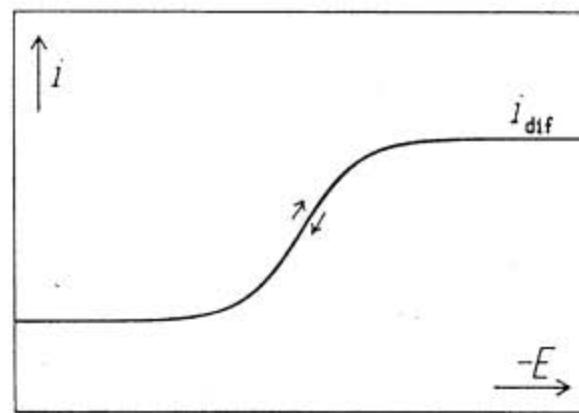
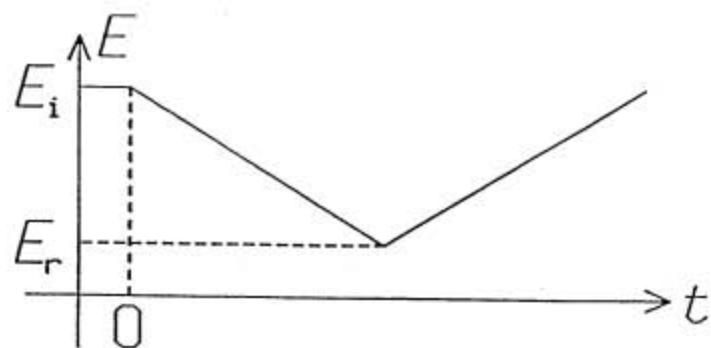
$$r_o = 5 \mu\text{m}, D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$$

Effect of Sweep Rate on Voltammogram at UME



$$D_O = D_R = 10^{-5} \text{ cm}^2/\text{s}, C_O^* = 1 \text{ mM}, a = 10 \mu\text{m}, n=1$$

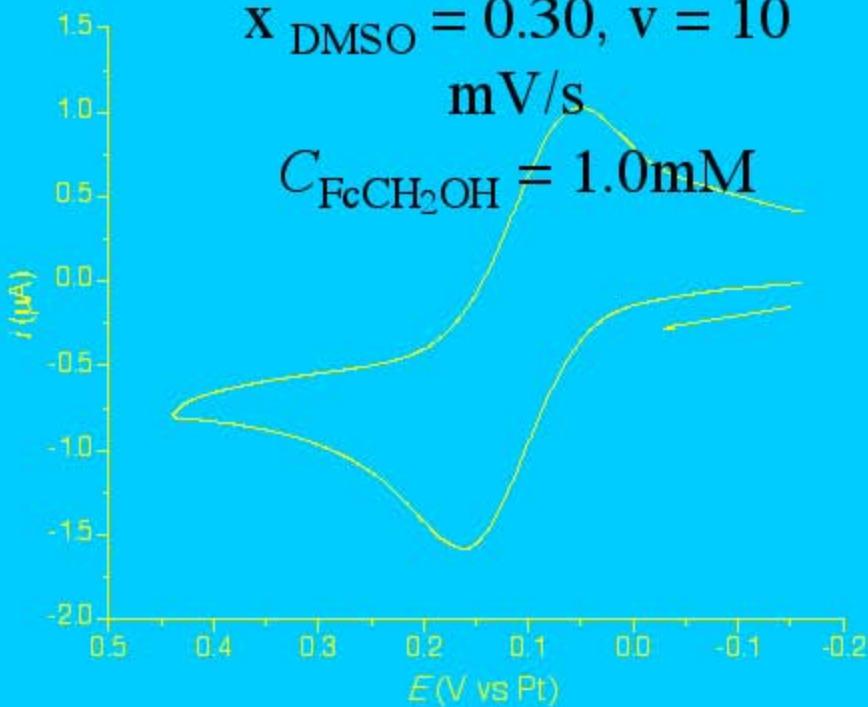
Steady-State Voltammetry



CVs of FcCH_2OH in DMSO- H_2O

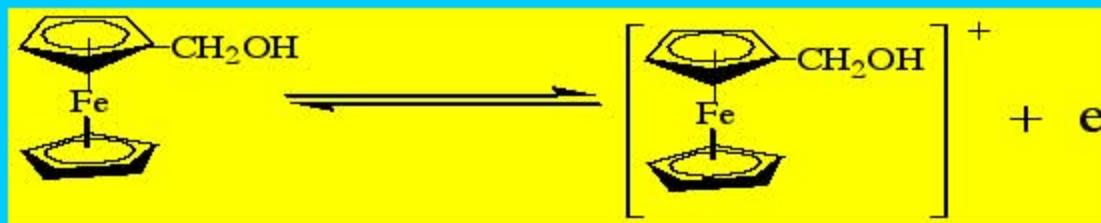
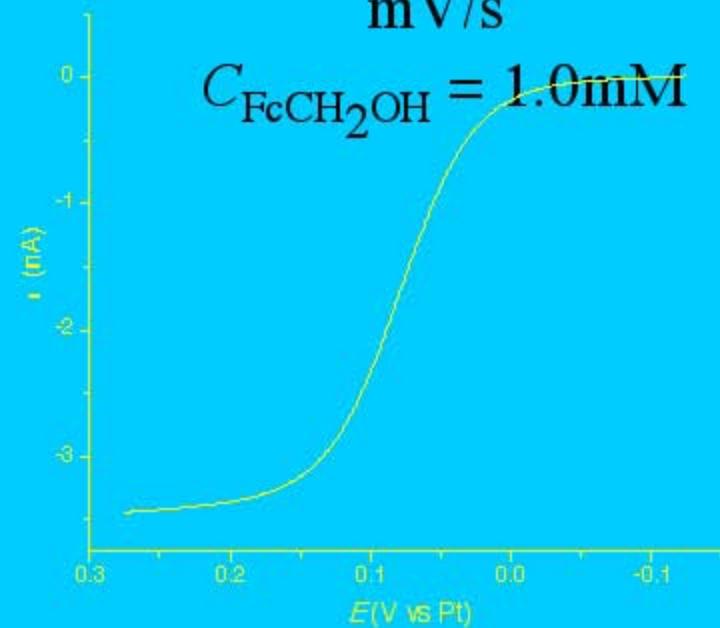
At $a = 1.5 \text{ mm}$ Pt

$x_{\text{DMSO}} = 0.30$, $v = 10$



At $a = 2.56 \text{ mm}$ Pt

$x_{\text{DMSO}} = 0.50$, $v = 20$



$$i_{T, \infty} = 4nFDc^0 a$$

Steady-state limiting current

Number of electrons transferred per molecule

Faraday's constant

Bulk concentration

Radius of the tip

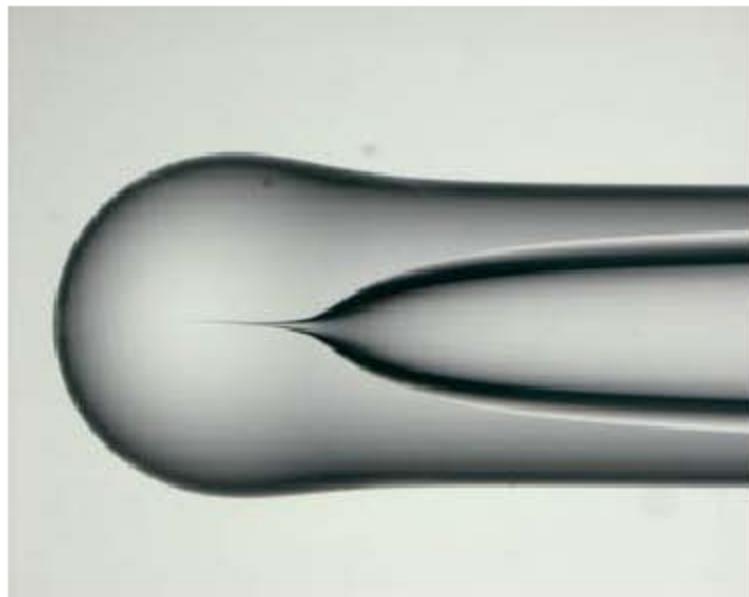
Diffusion coefficient

UMEs: Fabrication

- **Disk-in-glass UME**
- 2 cm Pt, Au, or C fiber
 - 2-mm OD Pyrex tube (10-cm long) sealed at one end
 - Vacuum pump, rheostat, nichrome wire
 - Optical microscope, polishing wheel
 - Sandpaper: 180, 400, 600, 1200 grit
 - Alumina: 1, 0.3, 0.05 μm
 - Micropolishing cloths
 - Ag epoxy, epoxy, 0.5 mm Cu wire

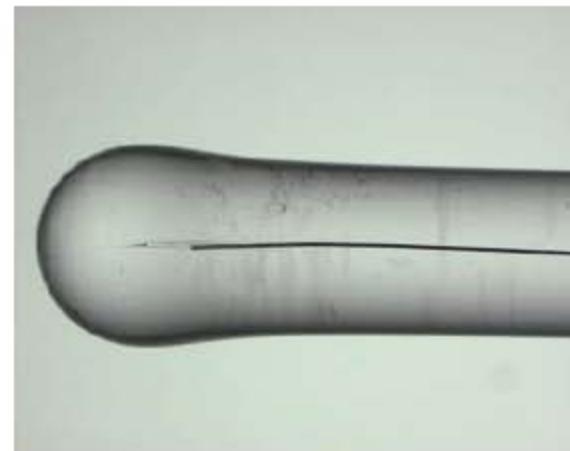
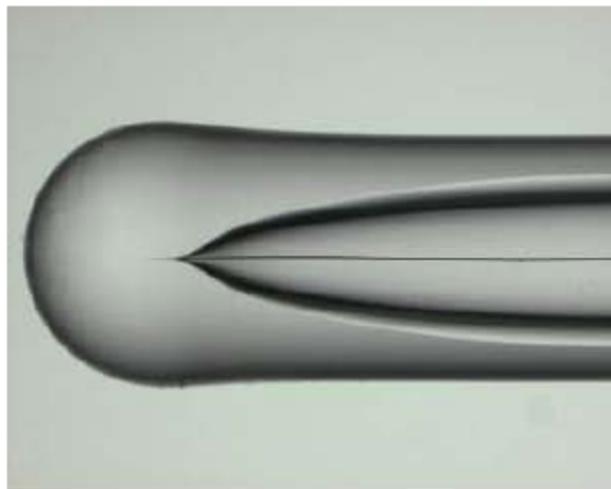
UMEs: Fabrication - Step 1

- Flame seal capillary tube



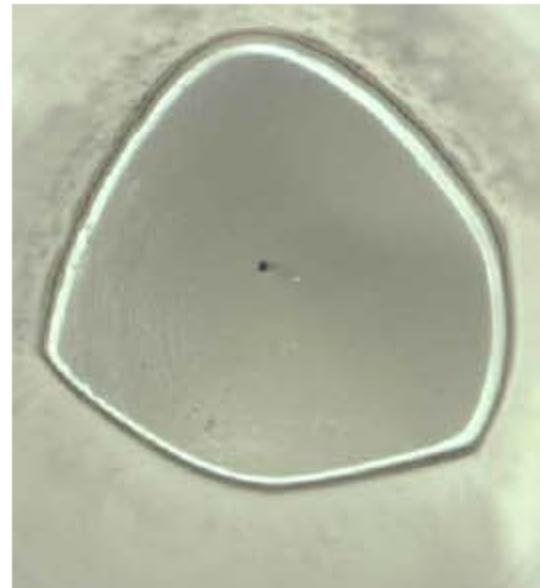
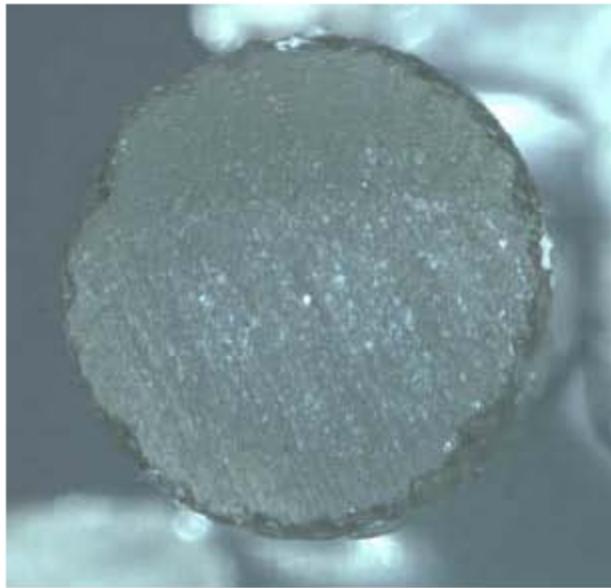
UMEs: Fabrication - Step 1

- Place fine wire in tube
- Desorb impurities from wire: connect open end to vacuum line, position in nichrome wire coil, heat about 1 hour
- Seal wire in glass: increase T of nichrome wire



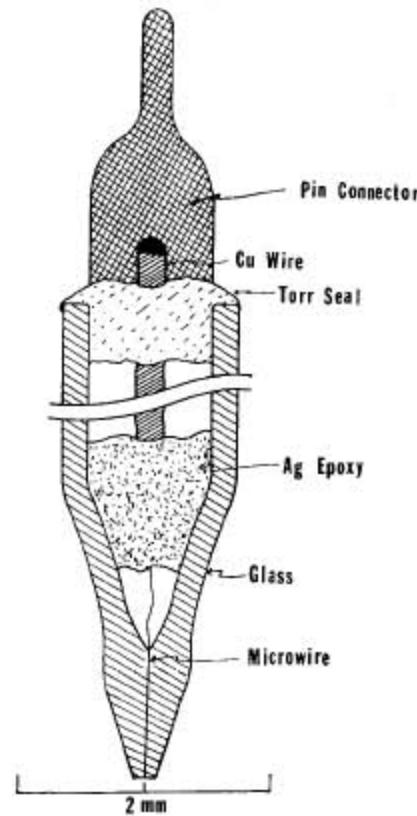
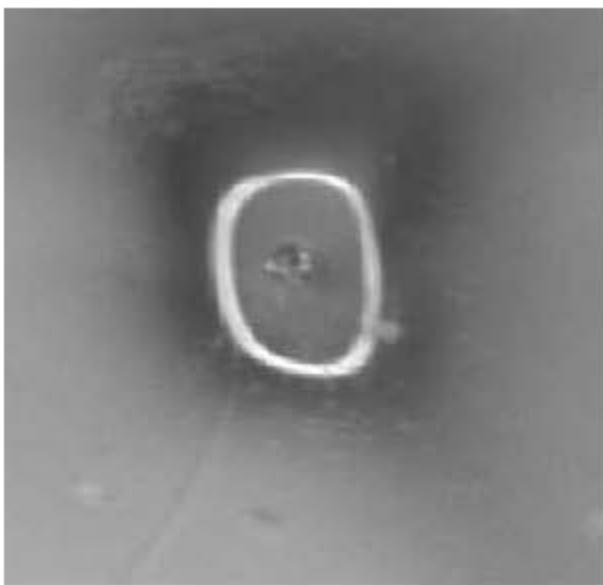
UMEs: Fabrication - Step 1

- Form tip: expose wire with sandpaper, polish to shiny surface with alumina
- Electrical connection: Ag epoxy, Cu wire, epoxy,cure



UMEs: Fabrication - Step 2 (Sharpen)

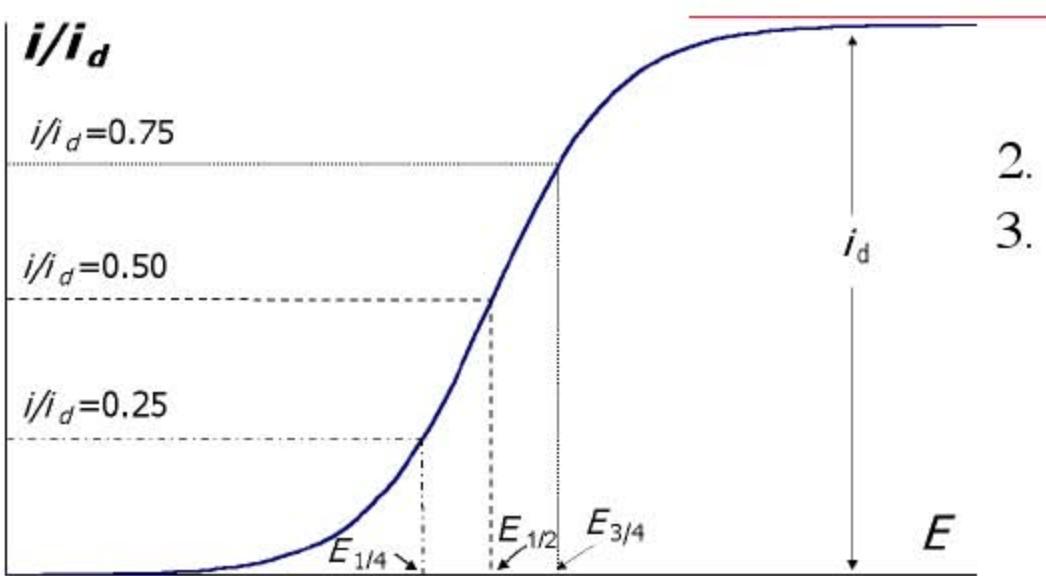
- Test electrode from step 1 by doing voltammetry
- Grind down glass to decrease RG
- Inspect in microscope
- Iterate
- Test voltammetry and SECM approach curves



UMEs: Testing

- Electrochemical Systems: Reversible
- ***Oxidations*** : (1mM, 0.10 M KCl)
 - Ferrocene methanol
 - $(C_5H_5)_2CH_2OHFe \rightarrow (C_5H_5)_2CH_2OHFe^+ + e$
 - Ferrocyanide: $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e$
- ***Reductions***: (1mM, 0.10 M KCl)
 - Ruthenium Hexamine
 - $Ru(NH_3)_6^{3+} + e \rightarrow Ru(NH_3)_6^{2+}$
 - Ferricyanide: $Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$

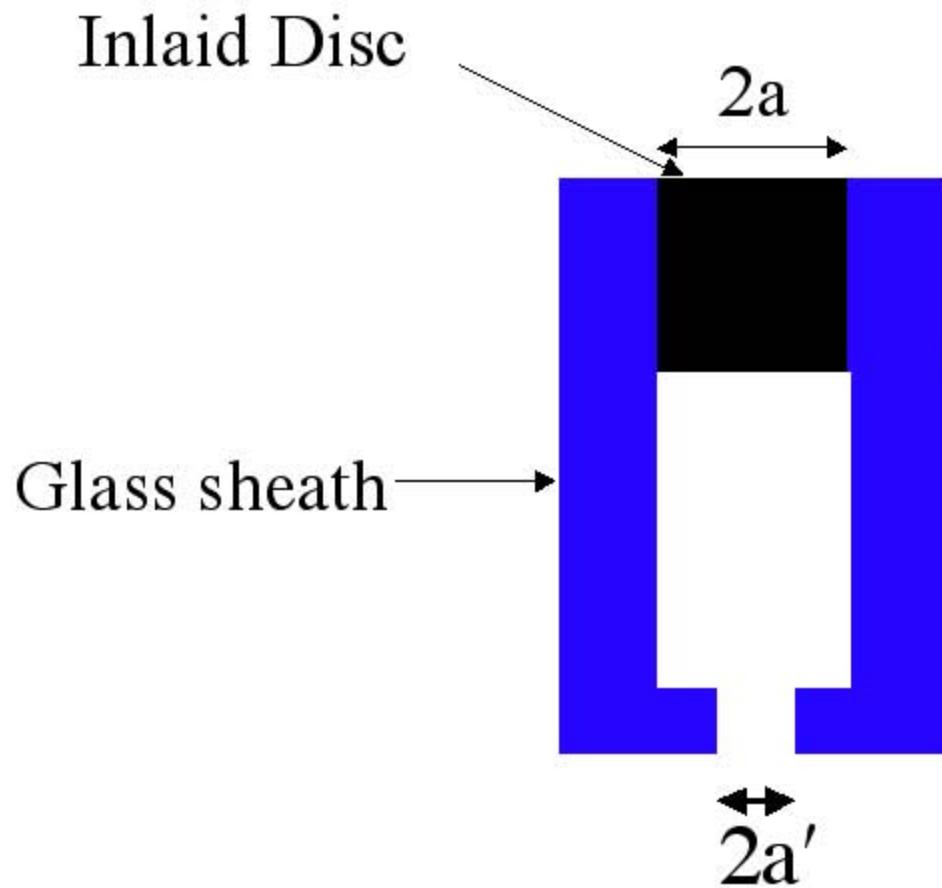
Criteria for good tip from steady state voltammogram



1. Flat (not sloping) diffusion plateau
 - Hemisphere:
 - $i_d = 2\pi nFC * Da$
 - Inlaid Disk:
 - $i_d = 4nFC * Da$
2. No hysteresis
3. For nernstian wave
 - Tomes criterion:
 - $|E_{3/4} - E_{1/4}| = 56.4/n \text{ mV}$
 - E vs. $\log [(i_d - i)/i]$
 - Slope = $59.1/n \text{ mV}$

Note. The steady-state voltammogram is not a good indicator of tip geometry

Recessed Tip



(a) Baranski, A. S. J. Electroanal. Chem. 1991, 307, 287.(b)
Oldham, K. B. Anal. Chem. 1992, 64, 646