525

Lecture #14 of 18(?)

526

Time-Dependence in Electrochemistry

Chapters 4 and 5

527

Q: What's in this set of lectures?
A: B&F Chapters 4 & 5 main concepts:

- Section 4.4.2: Fick's Second Law of Diffusion
- Section 5.1: Overview of step experiments
- Section 5.2: Potential step under diffusion controlled
- Sections 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry

528

Looking forward… Section 4.4.2 and Chapter 5

- Fick's Second Law of Diffusion
- Linear Diffusion = time-dependent current (Cottrell Equation)
- Anson Plots for surface adsorbed species
- Radial Diffusion = time-independent current (at steady-state)
- **Ultramicroelectrodes (UMEs)**
- **Scanning Electrochemical Microscopy (SECM)**
- **Single molecule electrochemistry**

528

529

RECALL:

… so in a potential step experiment…

1. current changes continuously with time.
2. radial diffusion (AKA "edge effects") limits the data acquisition time window to ~1 – 10 s.
3. charging imposes a lower limit of 0.1 – 0.5 µs on this data acquisition time window.
4. theoretically, maximum current densities are > 60 mA cm^{-2} initially, but just 100 µA cm^{-2} at S/N ≈ 10.

… but, why do we care?

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Why do we care? One reason…

RECALL:

we need to push this up in order to perform meaningful measurements of the kinetics of rapid redox reactions

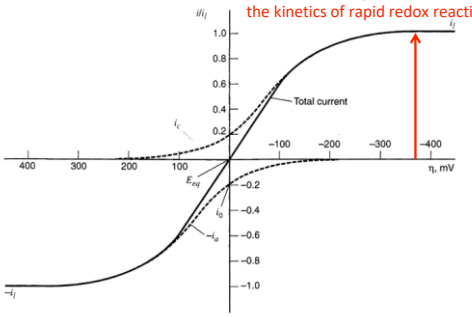


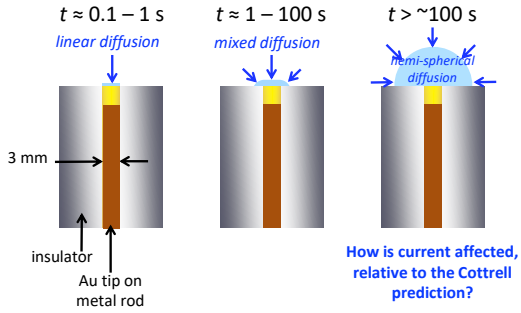
Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

530

… but deleterious edge effects also suggest an opportunity: 531

RECALL:

What if instead of avoiding radial diffusion, we exploit it?… Wait, what?



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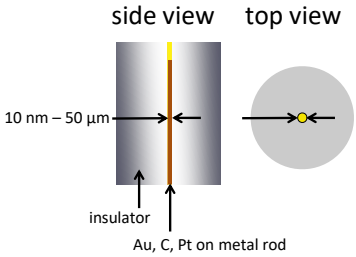
Let's design an experiment in which we intentionally operate in this radial diffusion limit the "entire" time! 532

RECALL:

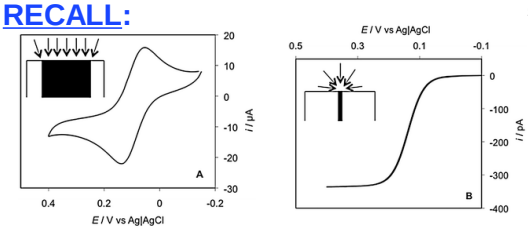
… well we actually start in the linear regime, and then switch over quickly…



… called "ultramicroelectrodes" or "UMEs"

532

RECALL: 533



… steady-state is "often" reached at each applied potential at a UME during a sweep

… Let's quantify it… steady-state occurs when $v << RTD/(nFr_0^2)$

… v (mV s^{-1}) << 26 mV x (D/r_0^2)… for a *BASi* UME with r_0 = 5 µm…

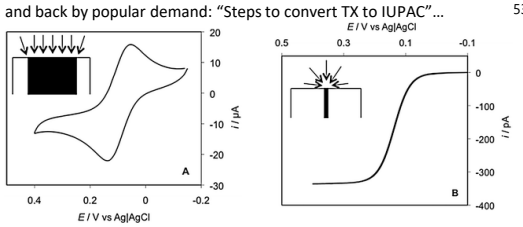
… 26 mV x $((0.5 \times 10^{-5}\ cm^2\ s^{-1}) / (0.5 \times 10^{-3}\ cm)^2)$ = 26 mV x (20 s^{-1})

… v << 0.5 V s^{-1}… Wow, you can still scan quite fast!

Walsh, Lovelock, & Licence, *Chem. Soc. Rev.*, 2010, *39*, 4185

533

… and back by popular demand: "Steps to convert TX to IUPAC"… 534



(1) Change sign of currents, because B&F indicates that positive current is cathodic
… this is likely because electrons are the charge carrier of current
… but physicists disagree; also, ions can be + or – so no need to focus on e^-

(2) Mirror image the plot through the origin so that the axes look like math axes

Walsh, Lovelock, & Licence, *Chem. Soc. Rev.*, 2010, *39*, 4185

534

… and back by popular demand: "Steps to convert TX to IUPAC"… 535

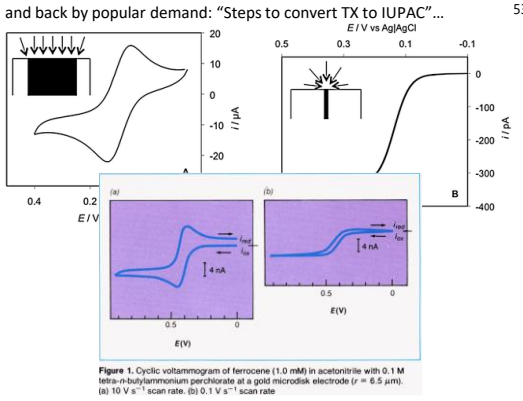
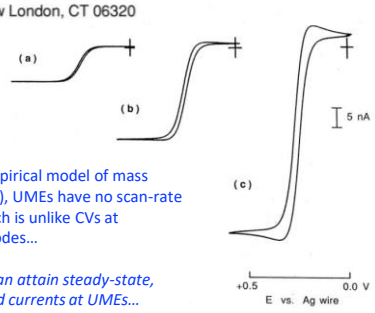


Figure 1. Cyclic voltammogram of ferrocene (1.0 mM) in acetonitrile with 0.1 M tetra-*n*-butylammonium perchlorate at a gold microdisk electrode (r = 6.5 μm). (a) 10 V s^{-1} scan rate. (b) 0.1 V s^{-1} scan rate

Wightman, *Anal. Chem.*, 1981, *53*, 1125A

535

Stanton Ching, Ray Dudek, and Elie Tabet
Connecticut College, New London, CT 06320



… akin to the semi-empirical model of mass transfer (Section 1.4.2), UMEs have no scan-rate dependence to I_l, which is unlike CVs at traditional disk electrodes…

… this is because we can attain steady-state, mass-transport-limited currents at UMEs…

… without stirring at all!

Figure 3. Cyclic voltammograms of 1 mM ferrocene in 0.1 M $TBAPF_6/CH_3CN$ solutions obtained with (a) 10; (b) 25; (c) 50 μm-diameter Pt disks. The scan rate in 50 mV/s.

Ching, Dudek, & Tabet, *J. Chem. Educ.*, 1994, *71*, 602

536

and the diffusion-limited current pre-factor depends on ***electrode geometry***… 537

RECALL: $i_l = "x"nFDC^*r_0$ … but not scan rate!

electrode geometry	"x"	
sphere	4π	
hemisphere	2π	
disk	**4**	
ring	$\frac{\pi^2(b+a)}{r_0 \ln\left[16\,{}^{(b+a)}/_{(b-a)}\right]}$	

… disk and ring–disk electrodes are real things that we will cover later

537

… how tiny (or large) is this diffusion-limited current (density)? 538
Let's assume D = 0.5 x 10^{-5} cm^2 s^{-1} and C^* = 10^{-6} moles cm^{-3} (1 mM)

r_0	$i_l = 4nFDC^*r_0$	$i_l/A = i_l/(\pi {r_0}^2)$
100 µm	20 nA	60 µA/cm^2
10 µm	2 nA	0.6 mA/cm^2
1 µm	0.2 nA	6 mA/cm^2
100 nm	20 pA	60 mA/cm^2
10 nm	2 pA	0.6 A/cm^2
1 nm	0.2 pA	6 A/cm^2

… super tiny currents… *… but huge current densities… = AWESOME!… … for studies of electrocatalysis!*

538

Again, Why do we care? One reason… 539

we need to push this up in order to perform meaningful measurements of the kinetics of rapid redox reactions

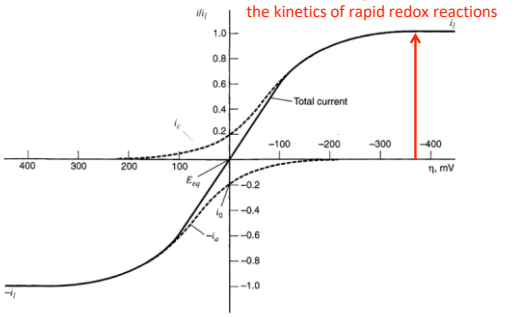


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a.

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r_0	$i_l = 4nFDC^*r_0$	$i_l/A = i_l/(\pi r_0^2)$
100 µm	20 nA	60 µA/cm^2
10 µm	2 nA	0.6 mA/cm^2
1 µm	0.2 nA	6 mA/cm^2
100 nm	20 pA	60 mA/cm^2
10 nm	2 pA	0.6 A/cm^2
1 nm	0.2 pA	6 A/cm^2

… so what is iR_u for these electrodes?

… well R_u is fairly large, but iR_u is nearly constant…

$$R_u = \frac{1}{4\pi\kappa r_0}\left(\frac{x}{x + r_0}\right) \xrightarrow{x \gg r_0} \frac{1}{4\pi\kappa r_0}$$

540

Recall this? This was measured using a UME! Reaction is $Tl^+ + e^- \rightleftharpoons Tl^0$ 541

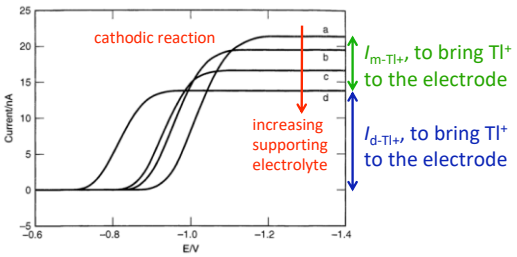


Figure 4.3.5 Voltammograms for reduction of 0.65 m*M* Tl_2SO_4 at a mercury film on a silver ultramicroelectrode (radius, 15 µm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 m*M* $LiClO_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

541

… and here is another example of this… 542

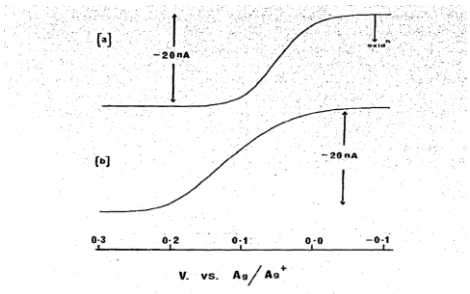


Fig. 2. Voltammogram for oxidation of 10^{-3} M ferrocene in acetonitrile at 18 °C using a 25-µm radius Pt microelectrode in (a) presence and (b) absence of 0.1 M Et_4NClO_4. Scan rate = 5 mV s^{-1}.

Bond, Fleischmann & Robinson, *J. Electroanal. Chem. Interfac. Electrochem.*, 1984, *168*, 299

542

… additional/final points to address about UMEs: 543

1) You can buy them; how do you make them?
2) UME arrays and ensembles
3) Potential step experiments with UMEs…
4) How rapidly is steady-state attained?

543

… arrays of UMEs (from B&F)… 544

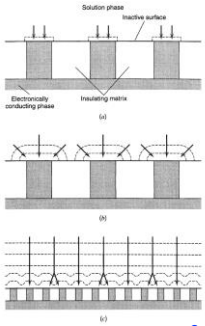


Figure 5.2.4 Evolution of the diffusion field during chronoamperometry at an electrode with active and inactive areas on its surface. In this case the electrode is a regular array such that the active areas are of equal size and spacing, but the same principles apply for irregular arrays. (*a*) Short electrolysis times, (*b*) intermediate times, (*c*) long times. Arrows indicate flux lines to the electrode.

Semi-infinite linear diffusion

Semi-infinite mixed diffusion

Semi-infinite linear diffusion, *again*

… no matter what some papers suggest… you can ***never*** beat overall linear diffusive flux over the total projected area of the diffusive solution region!

544

… this is because a UME must behave like a macroscopic electrode at sufficiently small times (and if neighboring electrodes are too close), right?... *Right!* 545

macroscopic planar electrode: $i(t) = \frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}}$

disk UME: $i(t) = \frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}} + 4nFDC^*r_0$

hemispherical UME: $i(t) = \frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}} + 2\pi nFDC^*r_0$

Cottrell eq.

steady-state current eq.

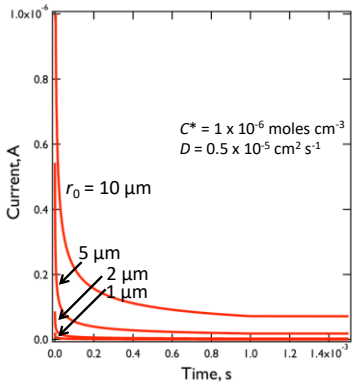
545

… additional/final points to address about UMEs: 546

1) You can buy them; how do you make them?
2) UME arrays and ensembles… **GOT IT!**
3) Potential step experiments with UMEs…
4) How rapidly is steady-state attained?

546

… at longer times, the current asymptotically approaches i_l… 547



547

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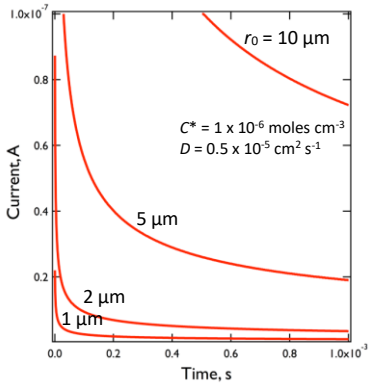

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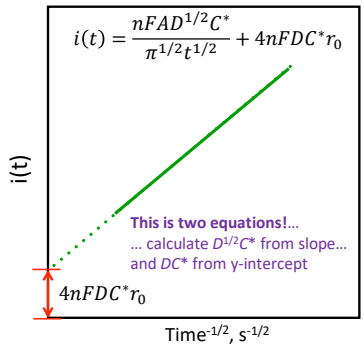
note that the $i(t)$ versus $(1/t^{1/2})$ plot no longer intersects "0"…
… and *D can be calculated without knowing C**… How?

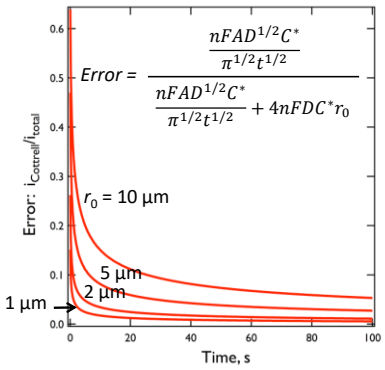
549



549

… how long does it take for UME's to attain steady-state?

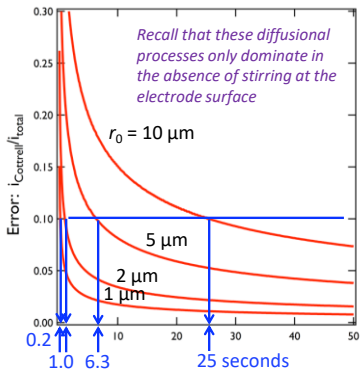
550



550

… how long does it take for UME's to attain steady-state?

551



551

the short time limit imposed by R_uC_d for a macroscopic electrode is ~100 μs…

552

… but UMEs charge *much* faster!

r_0	r_0	$t_{steady\text{-}state}$	R_uC_d*
10^{-3} cm	10 μm	25 s	1.7 μs
10^{-4} cm	1 μm	0.25 s	170 ns
10^{-5} cm	100 nm	2.5 ms	17 ns
10^{-6} cm	10 nm	25 μs	1.7 ns
	$\alpha\ r_0^2$	$\alpha\ r_0$	

… recall that R_u is nearly independent of the WE–RE separation:

$$R_u = \frac{1}{4\pi\kappa r_0}\left(\frac{x}{x + r_0}\right)$$

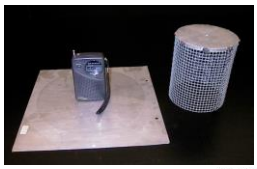
($\alpha\ r_0^{-1}$; α 1)

552

… and lastly, two things you'll really want for these experiments…

553

needed for $i_i < 10$ *nA*: a Faraday cage…



… and a Keithley 428 programmable current amplifier grounded to the cage

Key Features and Benefits:

- 2μs rise time
- 1.2fA rms noise
- Up to 10^{11} V/A gain
- IEEE-488 interface

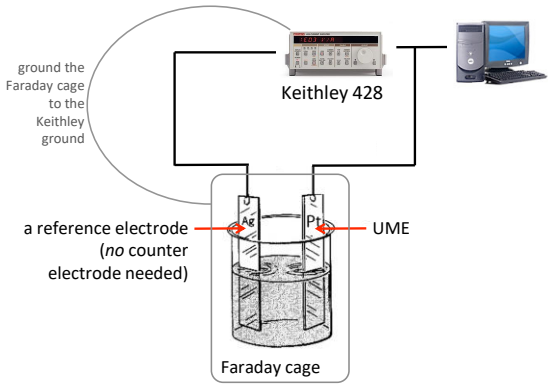
The Model 428-PROG Programmable Current Amplifier converts fast, small currents to a voltage, which can be easily digitized or displayed by an oscilloscope, waveform analyzer, or data acquisitionsystem. It uses a sophisticated "feedback current" circuit to achieve both fast rise times and sub-picoamp noise. The gain of the Model 428-PROG is adjustable in decade increments from 102V/A to 1011V/A, with selectable rise times from 2μs to 300ms.

http://www.columbia.edu/cu/physics/demo-images/ http://www.keithley.com/products/

553

… there are also a few things you will *not* be needing…

554



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UME take-home messages:

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After rapid double-layer charging…

… operate UMEs at either short times
= linear diffusion…
Can determine effects of rapid catalysis without complications from double-layer charging

… or long times
= steady-state radial diffusion…
Can determine *D* without knowing *C

555

We only have time to look at techniques/publications by one of these four UME pioneers… **Guess who?**

556

- Ralph “Buzz” Adams (d. Univ. Kansas)
- Mark Wightman (UNC Chapel Hill)
- Allen Bard (UT Austin)
- Henry White (Univ. Utah)

556

Bard and scanning electrochemical microscopy (SECM)…

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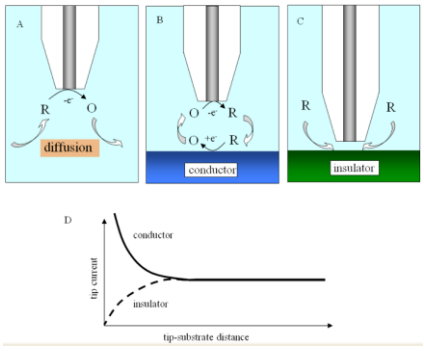

http://electrochem.cwru.edu/ed/encycl/art-m04-microscopy.htm

557

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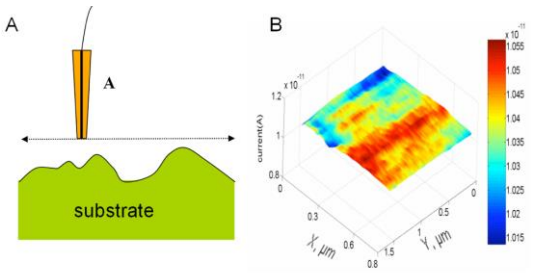

Fig. 5. Substrate imaging. (A) Tip is maintained at constant height while scanning horizontally. (B) SECM image of a portion (1 μm × 1 μm) of a human breast cell membrane acquired with a 47 nm radius ultramicroelectrode.

http://electrochem.cwru.edu/ed/encycl/art-m04-microscopy.htm

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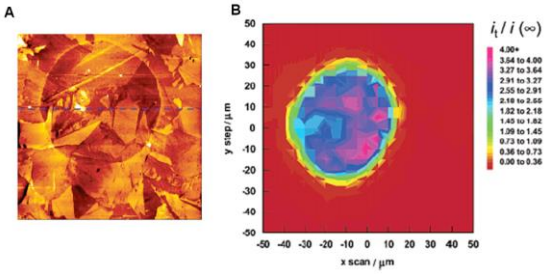


Fig. 7. (A) 80 μm × 80 μm atomic force microscopy image of a disk-like region of boron-doped diamond. (B) SECM image over such a region.

http://electrochem.cwru.edu/ed/encycl/art-m04-microscopy.htm

559

560

Electrochemical Detection of Single Molecules

Fu-Ren F. Fan and Allen J. Bard*

The electrochemical behavior of a single molecule can be observed by trapping a small volume of a dilute solution of the electroactive species between an ultramicroelectrode tip with a diameter of ~15 nanometers and a conductive substrate. A scanning electrochemical microscope was used to adjust the tip-substrate distance (~10 nanometers), and the oxidation of [(trimethylammonio)methyl] ferrocene (Cp_2FeTMA^+) to Cp_2FeTMA^{2+} was carried out. The response was stochastic, and anodic current peaks were observed as the molecule moved into and out of the electrode-substrate gap. Similar experiments were performed with a solution containing two redox species, ferrocene carboxylate (Cp_2FeCOO^-) and $Os(bpy)_3^{2+}$ (bpy is 2,2'-bipyridyl).

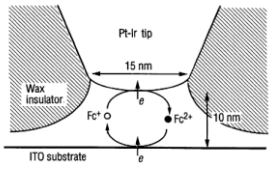


Fig. 1. Idealized schematic illustration of the tip geometry and the tip-substrate configuration used.

Fan & Bard, *Science*, 1995, *267*, 871

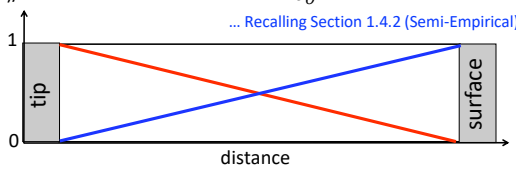
560

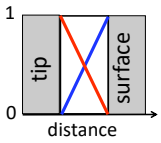
the magic of "thin layer electrochemistry"... 561

$$J_i(x) = -D_i \frac{C_O^* - C_O(x=0)}{\partial_O}$$

C(x)/C*

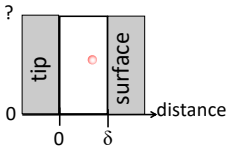
... Recalling Section 1.4.2 (Semi-Empirical)





561

A feasibility assessment... 1 molecule is trapped within a 1 µm x 1 µm x 10 nm volume between an SECM tip and a surface. *What's the value of the limiting current?* 562



$$i = -nFAD\frac{\Delta C}{\delta}$$ *m*

$$C_{1\ \text{molecule}} = (1\ \text{molecule})\left(\frac{1\ \text{mol}}{6.022\ \text{x}\ 10^{23}\ \text{molecules}}\right)\left(\frac{1}{(10\ \text{x}\ 10^{-7}\ \text{cm})(1\ \text{x}\ 10^{-4}\ \text{cm})^2}\right)$$

$$C_{1\ \text{molecule}} = 1.66\ \text{x}\ 10^{-10}\ \text{mol/cm}^3$$

562

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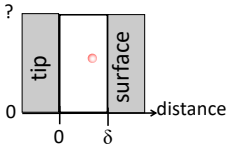

$$i = -nFAD\frac{\Delta C}{\delta}$$ *m*

$$i = (1\ \text{eq/mol})(96485\ \text{C/eq})\left(1\ \text{x}\ 10^{-4}\ \text{cm}\right)^2\left(1\ \text{x}\ 10^{-5}\ \text{cm}^2/\text{s}\right)\left(\frac{1.66\ \text{x}\ 10^{-10}\ \text{mol/cm}^3}{10\ \text{x}\ 10^{-7}\ \text{cm}}\right)$$

$$= 1.6\ \text{x}\ 10^{-12}\ \text{A} = 1.6\ \text{pA}$$

... so we're talking about pA's. We can measure that!

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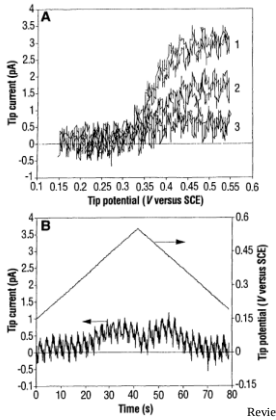

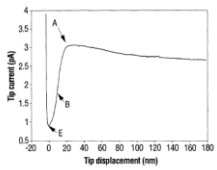

Fig. 2. Dependence of tip current on relative tip displacement over a conductive ITO substrate in a solution containing 2 mM Cp_2FeTMA^+ and 2.0 M $NaNO_3$. The ITO substrate was biased at −0.3 V versus SCE and the tip was biased at 0.55 V, where the redox reactions on both electrodes were diffusion-controlled. The tip moved to the substrate surface at a rate of 30 Å/s. The data were 800 points averaged at each location. The significance of points A, B, and E is discussed in the text. See also Fig. 4.

Fan & Bard, *Science*, 1995, *267*, 871
Reviewed in Bard & Fan, *Acc. Chem. Res.*, 1996, *29*, 572

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Q: What ***was*** in this set of lectures?
A: B&F Chapters 4 & 5 main concepts:

- Section 4.4.2: Fick's Second Law of Diffusion
- Section 5.1: Overview of step experiments
- Section 5.2: Potential step under diffusion controlled
- Sections 5.3 & 5.9: Ultramicroelectrodes
- Sections 5.7 – 5.8: Chronoamperometry/Chronocoulometry

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A detailed review of Section 4.4.2 and Chapter 5

- Fick's Second Law of Diffusion
- Linear Diffusion = time-dependent current (Cottrell Equation)
- Anson Plots for surface adsorbed species
- Radial Diffusion = time-independent current (at steady-state)
- Ultramicroelectrodes (UMEs)
- Scanning Electrochemical Microscopy (SECM)
- Single molecule electrochemistry

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