Lecture #9 of 17
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
RECALL FROM LAST TIME… Step #3 using Step #2…

\[-J_o(0, t) = C^* \sqrt{\frac{D_o}{\pi t}}\]

…and with \( i = nFAJ(0, t) \)…

\[i(t) = i_d(t) = \frac{nFAD_o^{1/2}C_o^*}{\pi^{1/2}t^{1/2}}\]

the Cottrell Equation

Frederick Gardner Cottrell, in 1920
b. January 10, 1877, Oakland, California, U.S.A.
d. November 16, 1948, Berkeley, California, U.S.A.

… established Research Corp. in 1912

… initial funding from profits on patents for the electrostatic precipitator, used to clear smokestacks of charged soot particles
Cottrell, then at UC Berkeley, invented the electrostatic precipitator used to clear smokestacks of charged soot particles...

http://en.wikipedia.org/wiki/Electrostatic_precipitator
http://en.wikipedia.org/wiki/Corona_discharge
Air Pollution Control Innovations

Wet electrostatic precipitator technology

Posted by Ron Patterson on Fri, Jul 10, 2009 @ 03:10 PM

In 1824, the German mathematician M. Hohifeld described the removal of particles from gas streams by electrical forces. However, it was almost a century later when Dr. Frederick G. Cottrell at the University of California, Berkeley commercialized the technology by building the first wet electrostatic precipitator.

A wet electrostatic precipitator uses electrical forces to move particles entrained in a gas stream onto collection surfaces. Electrodes in the wet electrostatic precipitator are held at high voltage which creates a corona discharge. Particles receive an electrical charge as they pass through the corona. The charged particles then follow electric field lines from the charging electrodes to collection surfaces, where they are removed from the gas stream.

Dr. Cottrell applied wet electrostatic precipitator technology to the removal of sulfuric acid mist and lead oxide dust emitted from various acid-making and smelting activities. At the time, vineyards in Northern California were being adversely affected by the lead emissions. Dr. Cottrell's innovative wet electrostatic precipitator solved their problem.

Fast forward to the 2000's. Envitech brought the control of lead and sulfur dioxide to a new level by installing our most advanced wet electrostatic precipitator technology on a secondary lead smelting facility in Southern California. The resulting wet electrostatic precipitator system which removes both sulfur dioxide and lead particles is said to set a new standard in air emission control at lead smelting facilities worldwide.

With over thirty years in the industry, we wanted to start sharing the knowledge and expertise that we have gained from cleaning gas streams of unwanted contaminants. Look for future postings that examine various aspects of state-of-the-art air pollution control technologies.

Tags: wet electrostatic precipitators
... OK, so what does it predict?

\[ i(t) = i_d(t) = \frac{nFAD_{O}^{1/2}C_{O}^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\( D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \)
\( D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \)
... OK, so what does it predict?

\[ i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\[ D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

\[ D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \]

* Plot data like this only for visualization purposes, and not for fitting the data as your statistics and thus best-fit values will be affected and incorrect.
... OK, so what does it predict?

\[ i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_*^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\[
\text{slope} = nFA\pi^{-1/2}D^{1/2}C_*^* \\
(\text{long time}) \hspace{1cm} (\text{short time})
\]
\[ i(t) = i_d(t) = \frac{nFAD_0^{1/2}C^*_O}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\[ \text{slope} = nFA\pi^{-1/2}D^{1/2}C^*_c \]

… OK, so what does it predict?

Brett Kralj and Robert A. W. Dryfe

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Fax: + 44 (0)161 200 4559
... use the Cottrell Equation to measure $D$!

... but what are the problems with this approach?

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

the Cottrell Equation

1) Huge initial currents… compliance current!
2) Noise.
3) $RC$ time limitations decrease current at really short times.
4) Roughness factor increases current at short times.
5) Adsorbed (electrolyzable) gunk increases current at short times.
6) Convection, and “edge effects,” impose a “long” time limit on these types of experiments.
... use the Cottrell Equation to measure $D$!
... but what are the problems with this approach?

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_*}{\pi^{1/2}t^{1/2}}$$  
the Cottrell Equation

1) Huge initial currents… compliance current!
2) Noise.
3) $RC$ time limitations decrease current at really short times.
4) Roughness factor increases current at short times.
5) Adsorbed (electrolyzable) gunk increases current at short times.
6) Convection, and “edge effects,” impose a “long” time limit on these types of experiments.

... Solution: Integrate it, with respect to time...

$$Q_d = \frac{2nFAD_O^{1/2}C_*t^{1/2}}{\pi^{1/2}}$$  
the integrated Cottrell Equation
the integrated Cottrell Equation

$$Q_d = \frac{2nFAD_O^{1/2}C^*_O t^{1/2}}{\pi^{1/2}}$$

Figure 5.8.2
Chronocoulometric response for a double-step experiment performed on the system of Figure 5.8.1. The reversal step was made to 0.0 V vs. QRE. [Data courtesy of R. S. Glass.]
... this is called an Anson plot.

What is this positive intercept?

Figure 5.8.1  Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-n-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: −1.892 V vs. Pt QRE. \( T = 25^\circ\text{C}, \) \( A = 0.018 \text{ cm}^2. \) \( E_0' \) for DCB + e \( \rightleftharpoons \) DCB\(^-\) is −1.63 V vs. QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to \( t < 250 \text{ ms}. \) [Data courtesy of R. S. Glass.]
... this is called an Anson plot.

\[ Q = \frac{2nFAD^{1/2}C^* t^{1/2}}{\pi^{1/2}} + Q_{dl} + nF\Phi \Gamma_O \]  

(5.8.2)

with \( \Gamma_O \), the surface excess of O (mol cm\(^{-2}\))

What is this positive intercept?

**Figure 5.8.1** Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 mM 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 M tetra-\( n \)-butylammonium fluoborate. Initial potential: 0.0 V vs. Pt QRE. Step potential: \(-1.892 \) V vs. Pt QRE. \( T = 25^\circ\)C, \( A = 0.018 \) cm\(^2\). \( E^{0'} \) for DCB + e \( \rightleftharpoons \) DCB\(^-\) is \(-1.63 \) V vs. QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to \( t < 250 \) ms. [Data courtesy of R. S. Glass.]
Preface

Tribute to Fred Anson and list of publications

Fred Anson

Fred’s scientific accomplishments in over 300 publications cover the gamut of inorganic, analytical, and physical electrochemistry. He started out in his Ph.D. work with J.J. Lingane and in his early work at Caltech looking at various reactions at Pt electrodes and in coulometry and coulometric titrations. In his early days at Caltech, he had a number of papers dealing with the ‘rediscovered’ technique of chronopotentiometry. This led, in a classical example of serendipity, to the discovery of what is now termed thin-layer electrochemistry. His interest in surface processes at electrodes led, somewhat later, to the discovery of chronocoulometry. His pioneering contributions to this area eventually led to the naming of the ‘Anson plot’ of $Q$ vs. $t^{1/2}$ after him. While primarily an experimentalist, he has contributed to a theoretical understanding of inner and outer sphere reactions and double layer effects at electrodes. A major theme to be found in Fred’s publications is an interest in the electron transfer kinetics and mechanisms of
reversal methods allow you to get data on both O and R, even if you start with just one in solution.

Figure 5.7.1 General waveform for a double potential step experiment.

\[ Q = \frac{2nFAD_O^{1/2}C_O^* t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA \Gamma_O \]

\[ Q(t > \tau) = \frac{2nFAD_R^{1/2}C_R^* \left[ \tau^{1/2} + (t - \tau)^{1/2} - t^{1/2} \right]}{\pi^{1/2}} + Q_{dl} + nFA \Gamma_R \]

**FOR YOUR REFERENCE**

**Figure 5.8.3** Linear chronocoulometric plots for data from the trace shown in Figure 5.8.2. For \( Q(t < \tau) \) vs. \( t^{1/2} \), the slope is 9.89 \( \mu \text{C/s}^{1/2} \) and the intercept is 0.79 \( \mu \text{C} \). For \( Q_r(t > \tau) \) vs. \( \theta \), the slope is 9.45 \( \mu \text{C/s}^{1/2} \) and the intercept is 0.66 \( \mu \text{C} \). [Data courtesy of R. S. Glass.]
... back to one potential step = one data set, from “one” experiment... where either plot allows you to calculate $D$!

<table>
<thead>
<tr>
<th>experiment</th>
<th>observable</th>
<th>governing equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>chronoamperometry</strong></td>
<td>meas $I(t)$ (or use $dQ(t)/dt$)</td>
<td>$i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$</td>
</tr>
<tr>
<td>(or differentiate CC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>chronocoulometry</strong></td>
<td>meas $Q(t)$ (or use $I(t)$ area)</td>
<td>$Q = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}}$</td>
</tr>
<tr>
<td>(or integrate CA)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
... how else can one calculate $D$? ...
... how about not using electrochemistry, **but NMR**... What?
... Yes! **Pulsed-Field Gradient (PFG) NMR**!

http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/
... how else can one calculate $D$? ...
... how about not using electrochemistry, but NMR... What? ...
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http://chem.ch.huji.ac.il/nmr/techniques/other/diff/diff.html
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3003887/
So, where is the non-ideal data in a Cottrell and Anson plot?

Short times... check!

Long times... what is this due to again?
we have equations for the “signal” and the “noise,” so… we can calculate the signal-to-noise ratio for a potential step experiment

**signal**

\[ i_d(t) = \frac{nFAD_O^{1/2}C^*_O}{\pi^{1/2}t^{1/2}} \]

**noise**

\[ i = \frac{E}{R} \exp\left(\frac{-t}{RC}\right) \]

... here we assume \( E = 0.6 \) V, \( R = 100 \) Ω
we have equations for the “signal” and the “noise,” so...

we can calculate the signal-to-noise ratio for a potential step experiment

**signal**

\[ i_d(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \]

**noise**

\[ i = \frac{E}{R} \exp\left(\frac{-t}{RC}\right) \]

... here we assume \( E = 0.6 \text{ V}, \ R = 100 \ \Omega \)
... the RC time constant of the cell imposes a lower limit on the accessible time window (~100 µs) for a potential step experiment...

... but what is the origin of the long time limit?

![Graph showing the current density over time with a green shaded area indicating the 'take data here' time window.](image)

\[
i_d(t) = \frac{nFAD_O^{1/2}C_0^*}{\pi^{1/2}t^{1/2}}
\]

\[
i = \frac{E}{R} \exp \left( \frac{-t}{RC} \right)
\]

... here we assume \( E = 0.6 \text{ V}, \ R = 100 \ \Omega \)
A typical electrode used in a laboratory electrochemistry experiment has an area of 0.05 cm² to 1 cm².

\[ A = \pi (0.15)^2 = 0.0706 \text{ cm}^2 \approx 7 \text{ mm}^2 \]
The Cottrell Equation can be used to describe the behavior during a potential step experiment as long as the thickness of the diffusion layer is small relative to the electrode dimension (and, of course, the boundary layer / stagnant layer / Nernst diffusion layer ($\delta$))…

… So, how long is that?

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$\sqrt{2Dt}$</th>
<th>$\frac{\sqrt{2Dt}}{r_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0014</td>
<td>0.009</td>
</tr>
<tr>
<td>1</td>
<td>0.0045</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>0.014</td>
<td>0.09</td>
</tr>
<tr>
<td>100</td>
<td>0.045</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$D = 10^{-5}$ cm$^2$/s

$r_0 = 0.15$ cm

(value from previous slide)

Answer: $< 1$ s
When the diffusion layer approaches the dimensions of the electrode diameter, radial diffusion to the edges of the electrode cause the flux to be larger than predicted by the Cottrell Equation, and non-uniform.

How is current affected, relative to the Cottrell prediction?
... so in a potential step experiment...

1. current changes continuously with time.

2. radial diffusion (AKA “edge effects”) limit the data acquisition time window to ~1 s.

3. charging imposes a lower limit of 100 – 500 µs on this data acquisition time window.

4. maximum current densities are > 60 mA cm$^{-2}$ initially, but just 100 µA cm$^{-2}$ at S/N ≈ 10.

... but, why do we care?
Why do we care? One reason…

we need to push this up to perform meaningful measurements of the kinetics of fast reactions

Figure 3.4.1  Current-overpotential curves for the system $O + e \rightleftharpoons R$ 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 $i_a$. 
... but deleterious edge effects also suggest an opportunity:

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

How is current affected, relative to the Cottrell prediction?
Let’s design an experiment in which we intentionally operate in this radial diffusion limit the “entire” time!

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

… called “ultramicroelectrodes” or “UMEs”
Recall that for linear diffusion from a plane, *current changes continuously with time*...

... this means:

\[
\frac{\partial C(x, t)}{\partial t} = 0 = D \left( \frac{\partial^2 C(x, t)}{\partial x^2} \right) \text{ has no solution}
\]

... but recall from Section 1.4.2 that the boundary layer / stagnant layer / Nernst diffusion layer (\(\delta\)) ends up reaching a steady-state distance due to natural convection...

... anyway, this doesn’t help us simplify our experiment...
... the linear diffusion layer grows with time (indefinately)...

\[ C^* = 1 \times 10^{-6} \text{ M} \]
\[ D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

\[ C_O(x, t) = C^*_O \text{ erf} \left[ \frac{x}{2(D_O t)^{1/2}} \right] \]

\[ \sqrt{2Dt} = 4 \mu \text{m} \]
\[ \text{14 \mu m} \]
\[ \text{40 \mu m} \]

... use the geometric area for calculations
... and thus linear-diffusion-controlled currents decay with time (indefinitely)...

\[ i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \]

the Cottrell Equation

\[ D = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \]

\[ D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
... but the same is **not true** for purely spherical diffusion:

\[
\frac{\partial C(r, t)}{\partial t} = 0 = D \left( \frac{\partial^2 C(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r, t)}{\partial r} \right)
\]

... which has solutions:

\[
C(r, t) = B + \frac{A}{r}
\]

... for a spherical diffusion field:

\[
\frac{\partial^2 C(r, t)}{\partial r^2} = \frac{2A}{r^3}
\]

\[
\frac{\partial C(r, t)}{\partial t} = \frac{-A}{r^2}
\]

and so...

\[
\frac{\partial C(r, t)}{\partial t} = 0 = D \left( \frac{2A}{r^3} + \frac{2}{r} \left( \frac{-A}{r^2} \right) \right)
\]
1. semi-infinite boundary condition...

\[
\lim_{r \to \infty} C(r, t) = C^* = B + 0
\]

\[
B = C^*
\]

2. electrode surface (edge/circumference) boundary condition...

\[
C(r_0, t) = 0 \quad 0 = C^* + \frac{A}{r_0}
\]

\[
A = -C^*r_0
\]

... so Fick's 2\textsuperscript{nd} Law predicts that the steady-state concentration gradient is:

\[
C(r, t) = C^* - \frac{C^*r_0}{r} = C^* \left[ 1 - \frac{r_0}{r} \right]
\]

... notice that here we can reach a \textit{time-independent} condition!

... What?
... the diffusion layer “thickness” is $10r_0$, no matter how small $r_0$ is!

$$r_0 = 10 \mu m$$

$C(r, t) = C^* \left[1 - \frac{r_0}{r}\right]$ *This spatial behavior is independent of time...
... the diffusion layer “thickness” is $10r_0$, no matter how small $r_0$ is!

$C(r, t) = C^* \left[1 - \frac{r_0}{r}\right]$  

... recall, that for transient linear diffusion...

$r_0 = 10 \, \mu m$

$C_O(x, t) = C^*_O \text{ erf} \left[\frac{x}{2(D_O t)^{1/2}}\right]$  

$\Delta = \sqrt{(2d)Dt} = \sqrt{\left(\frac{\text{cm}^2}{s}\right) s} = \text{cm}$  

$10 \times 10^{-3}$  

$1 \, \mu m$

$10 \, \text{nm}$

$100 \, \text{nm}$
the diffusion-limited current pre-factor depends on electrode geometry…

\[ i = "x" nFDC^*r_0 \quad \ldots \text{but not scan rate!} \]

<table>
<thead>
<tr>
<th>geometry</th>
<th>&quot;x&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>(4\pi)</td>
</tr>
<tr>
<td>hemisphere</td>
<td>(2\pi)</td>
</tr>
<tr>
<td>disk</td>
<td>4</td>
</tr>
<tr>
<td>ring</td>
<td>(\frac{\pi^2(b + a)}{r_0 \ln \left[16\frac{(b + a)}{(b - a)}\right]})</td>
</tr>
</tbody>
</table>
the UME: You can buy one from BASi

### Ordering Information

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF-2005</td>
<td>10 μm diameter Platinum Microelectrode</td>
</tr>
<tr>
<td>MF-2006</td>
<td>10 μm diameter Gold Microelectrode</td>
</tr>
<tr>
<td>MF-2007</td>
<td>11 μm (±2 μm) diameter Carbon Fiber Microelectrode</td>
</tr>
<tr>
<td>MF-2150</td>
<td>100 μm diameter Platinum Microelectrode</td>
</tr>
</tbody>
</table>

Custom fabrication is available, e.g., 33 μm carbon, 25 μm silver, 25 μm gold, etc. Please Contact us for your requirements.
... each potential during a sweep using a UME “often” reaches steady-state.

... steady-state occurs when $v \ll \frac{RTD}{(nF r_0^2)}$.
... each potential during a sweep using a UME “often” reaches steady-state.

... steady-state occurs when \( v << \frac{RTD}{(nFr_0^2)} \)

... \( v \text{ (mV s}^{-1} \text{)} << 26 \text{ mV} \times (D/r_0^2) \text{... for a BASi UME with } r_0 = 5 \text{ \(\mu \text{m} \text{...}}

... \( \frac{(1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}{(0.5 \times 10^{-3} \text{ cm})^2} = 26 \times 40 \text{ mV s}^{-1} \text{s} \)

... each potential during a sweep using a UME “often” reaches steady-state

... steady-state occurs when $v << \frac{RTD}{(nF r_0^2)}$

... $v \text{ (mV s}^{-1}) << 26 \text{ mV} \times (D/r_0^2)$... for a BASi UME with $r_0 = 5 \mu m$...

... $(1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) / (0.5 \times 10^{-3} \text{ cm})^2 = 26 \times 40 \text{ mV s}^{-1}$

... $v << 1 \text{ V s}^{-1}$... Wow!

Walsh, Lovelock, & Licence, Chem. Soc. Rev., 2010, 39, 4185
(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 plot through the origin so that the axes look standard as +, +, –, –
... scanning is “often” steady-state at a UME

... steady-state occurs when $\nu << RTD/(nF r_0^2)$

... $\nu$ (mV s$^{-1}$) $<< 26$ mV x $(D/r_0^2)$... for a BASi UME with $r_0 = 5 \mu$m...

... $(1 \times 10^{-5}$ cm$^2$ s$^{-1}) / (0.5 \times 10^{-3}$ cm$)^2 = 26 \times 40$ mV s$^{-1}$s

... $\nu << 1$ V s$^{-1}$... Wow!
Figure 3. Cyclic voltammograms of 1 mM ferrocene in 0.1 M TBAPF$_6$/CH$_3$CN solutions obtained with (a) 10; (b) 25; (c) 50 µm-diameter Pt disks. The scan rate in 50 mV/s.
... akin to the semi-empirical model of mass transport (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!

Figure 3. Cyclic voltammograms of 1 mM ferrocene in 0.1 M TBAPF$_6$/CH$_3$CN solutions obtained with (a) 10; (b) 25; (c) 50 μm-diameter Pt disks. The scan rate in 50 mV/s.
... how tiny (large) is this diffusion-limited current (density)? Let’s assume $D = 10^{-5}$ cm$^2$ s$^{-1}$ and $C^* = 10^{-6}$ moles cm$^{-3}$ (1 mM)

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$i = 4\pi nFD C^* r_0$</th>
<th>$i/A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µm</td>
<td>120 nA</td>
<td>386 µA/cm$^2$</td>
</tr>
<tr>
<td>10 µm</td>
<td>12 nA</td>
<td>3.86 mA/cm$^2$</td>
</tr>
<tr>
<td>1 µm</td>
<td>1.2 nA</td>
<td>38.6 mA/cm$^2$</td>
</tr>
<tr>
<td>100 nm</td>
<td>120 pA</td>
<td>386 mA/cm$^2$</td>
</tr>
<tr>
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</tr>
<tr>
<td>1 nm</td>
<td>1.2 pA</td>
<td>38.6 A/cm$^2$</td>
</tr>
</tbody>
</table>

... super tiny currents...  ... but huge current densities... = AWESOME...  ... for studies of electrocatalysis!
Again, Why do we care? One reason... we need to push this up to perform meaningful measurements of the kinetics of fast reactions.

Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ 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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<th>$i = 4\pi n F D C^* r_0$</th>
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<td>10 µm</td>
<td>12 nA</td>
<td>3.86 mA/cm$^2$</td>
</tr>
<tr>
<td>1 µm</td>
<td>1.2 nA</td>
<td>38.6 mA/cm$^2$</td>
</tr>
<tr>
<td>100 nm</td>
<td>120 pA</td>
<td>386 mA/cm$^2$</td>
</tr>
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<td>10 nm</td>
<td>12 pA</td>
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</tr>
<tr>
<td>1 nm</td>
<td>1.2 pA</td>
<td>38.6 A/cm$^2$</td>
</tr>
</tbody>
</table>

... so what is $iR_u$ for these electrodes?
... how tiny (large) is this diffusion-limited current (density)? Let's assume $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $C^* = 10^{-6}$ moles cm$^{-3}$ (1 mM)

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$i = 4\pi nFD C^* r_0$</th>
<th>$i/\text{A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 $\mu$m</td>
<td>120 nA</td>
<td>386 $\mu$A/cm$^2$</td>
</tr>
<tr>
<td>10 $\mu$m</td>
<td>12 nA</td>
<td>3.86 mA/cm$^2$</td>
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</tr>
</tbody>
</table>

... so what is $iR_u$ for these electrodes? ... well $R_u$ is fairly large, but $iR_u$ is nearly constant...

$$R_u = \frac{1}{4\pikr_0} \left( \frac{x}{x + r_0} \right)$$
Recall... Does the following make sense? Reaction is: $\text{Tl}^+ + e^- \rightleftharpoons \text{Tl}^0$

$\text{I}_m$-$\text{Tl}^+$, to bring $\text{Tl}^+$ to the electrode

Increasing supporting electrolyte

$\text{I}_d$-$\text{Tl}^+$, to bring $\text{Tl}^+$ to the electrode

Figure 4.3.5 Voltammograms for reduction of 0.65 mM $\text{Tl}_2\text{SO}_4$ at a mercury film on a silver ultramicroelectrode (radius, 15 $\mu$m) in the presence of (a) 0, (b) 0.1, (c) 1, and (d) 100 mM 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.]
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 Et₄NClO₄. Scan rate = 5 mV s⁻¹.
... additional/final points to address about UMEs:

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?