Lecture #27 of 26
(actually out of 27... obviously)

Time-Dependent Electrochemical Techniques
Chapters 6, 9 & 10

Q: What’s in this final set of lectures?
A: B&F Chapters 9, 10, and 6 main concepts:

- Sections 9.1 – 9.4: Rotating (Ring-)Disk Electrochemistry (R(R)DE)
- Sections 10.1 – 10.4: Electrochemical Impedance Spectroscopy (EIS)
- Sections 6.1 – 6.6, 11.7, 14.3: Linear Sweep Voltammetry (LSV), Thin-Layer Electrochemistry, Molecular Electrocatalysis, Cyclic Voltammetry (CV)

... to learn even more about your experimental systems...
... go beyond steady-state conditions and modulate things!
... recall that in standard cyclic voltammetry you scan back and forth...

... and this is what happens in solution over time (slow interfacial charge transfer)... Wow!

... for a Nernstian, reversible reaction, $\Delta E_p = 57 \pm 60$ mV... for $n = 1$

### Table 6.5.1 Variation of $\Delta E_p$ with $E_\lambda$

<table>
<thead>
<tr>
<th>$n(E_{pc} - E_\lambda)$ (mV)</th>
<th>$n(E_{pa} - E_{pc})$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.5</td>
<td>60.5</td>
</tr>
<tr>
<td>121.5</td>
<td>59.2</td>
</tr>
<tr>
<td>171.5</td>
<td>58.3</td>
</tr>
<tr>
<td>271.5</td>
<td>57.8</td>
</tr>
<tr>
<td>$\infty$</td>
<td>57.0</td>
</tr>
</tbody>
</table>
How do you measure $i_p$?

... well, for the first forward scan, you just measure it...

![Graph showing cyclic voltammetry](image)

Figure 6.5.2 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an i$/$d format, $E_2$ of $E_1$; $E_2 = 900 \text{ mV}$; $E_2 = 1500 \text{ mV}$; $E_2 = 2000 \text{ mV}$; $E_2$ for potential held at $E_x$ until the cathodic current decays to zero (Curve 4 results from reflection of the cathodic $i$-$E$ curve through the $E$-axis and then through the vertical line at $E - E_x = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i$-$E$ curve (1', 2', or 3')).

... and now, what is happening here?

![Graph showing Cottrellian current transient](image)

$F(t)$, Cottrellian current transient

... so $i_p$ for the reverse scan must be measured from the decaying, Cottrellian current of the forward scan!

![Graph showing Cottrellian current phenomenon](image)

Figure 6.5.1 Cyclic voltammograms for reversal at different $E_1$ values, with presentation on time base.
... a similar problem exists if you have two processes in close proximity, in terms of potential... here is a solution...

![Diagram of potential vs time with two processes]

Figure 6.6.2 Method for obtaining baseline for measurement of $E_2$ of second wave. Upper curves: potential programs. Lower curves: resulting volumograms with (curve 1) potential stopped at $E_1$, and (curve 2) potential scan continued. System as in Figure 6.6.1.

... and how is this "reversible CV" affected by slow electron transfer kinetics? (small $k^o, \alpha$?)

![Diagram showing cyclic voltammetry curves]

Figure 6.5.3 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an i-dE format. $E_1$ of (1) $E_1 = -900$, (2) $E_1 = -1300$, (3) $E_1 = -2000$ mV. All for potential held at $E_{1/2}$ until the cathodic current decays to zero. Curve 4 results from reflection of the cathodic i-dE curve through the $E$ axis and then through the vertical line at $E = E_{2/2} = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic i-dE curve (1, 2', or 3').

Answer: $\Delta E_p$ increases from ~60 mV to larger values...

![Graph showing peak potentials vs scan rate]

Peaks can be:
(a) Electrochemically reversible,

$E_{1/2} = E^o + \frac{RT}{nF} \ln \left( \frac{D_+}{D_-} \gamma_+ \gamma_- \right)^{1/2}$


... recall... $E^{o'} = E^o - \frac{RT}{nF} \ln \frac{Y_a}{Y_b}$

![Graph showing variation of peak-to-peak current function $\Psi(\Delta)$ for different values of $\Delta$ (as indicated in each graph)]

$\Psi(\Delta)$ for quasireversible current function, $\Psi(\Delta)$ for different values of $\Delta$ (as indicated in each graph) and the following values of $A$ (-1): (1) $A = 10^{-1}$, (2) $A = 10^{-2}$, (3) $A = 10^{-3}$. Dashed curve to indicate a quasireversible reaction. $\Psi(\Delta) = \frac{\Delta + \gamma_+ \gamma_-}{\Delta + \gamma_+ \gamma_-}$ and $\Delta = E^o(2nFRT)^{1/2}$. For $A = 10^{-1}$, $\gamma_+ = 0.25$, Frumkin II, Mzurna and A. A. Scat, J. Electroanal. Chem. 1966, 40, 399, with permission. Abcissa label adapted for this text.
Peaks can be:
(a) Electrochemically reversible,
(b) Quasi-reversible (|E_{pa} – E_{pc}| > ~60/nmV at room temperature, after iR_u and/or other potential corrections),
(c) Irreversible (i_{pc} ≠ i_{pa}, and they are not even close)

... Slow kinetics and iR_u are indistinguishable by CV (thus, keep iR_u small and/or correct for it).

Figure 4.6.1: Variation of quasi-reversible current function, i_c, for different values of E_{applied} (indicated in each graph) and the following values of A: (II) A = (III) A = 10.00 M, (IV) A = 10.0 M. Dashed curve is for a reversible reaction, i_c = (nFAD)_{(E)} (E_{applied} – E)^{1/2} and A = (nFAD)_{(E)} (E_{applied} – E)^{1/2} (for E = E_0). (From S. Marsden and Y. Aoyama, J. Electrochem. Soc. 99, 404 (1952), with permission. Abelson label adapted for this text.)

... but beware...
... the presence of iR_u means that the scan rate is not constant, since i changes as a function of E; the potential that influences the CV and not iR_u changes too...

peak current increases with v^{1/2}... but, is larger scan rate better?

... what about signal-to-noise ratio?

Randles–Ševčík Equation (T = 298 K)

signal: \[ i_0 = (2.69 \times 10^5)n^{3/2}AD^{1/2}C_d\nu^{1/2} \]

noise: \[ i_c = C_d\nu \quad \text{Double-layer charging} \]

ratio: \[ S:N = \frac{(2.69 \times 10^5)n^{3/2}AD^{1/2}C^*\nu^{1/2}}{C_d\nu^{1/2}} \]

... Therefore, for better S:N, slow scan rates are best!
... but UMEs can help measure things... *like fast kinetics!*

- measuring processes that occur in small spaces
e.g. single cells, SECM, etc. \((i \text{ is small; } j \text{ is large})\)
- measuring in highly resistive media \((R_u \text{ is "small"-ish})\)
e.g. solvent glasses, no supporting electrolyte, nonpolar solvents, gas phase reactions
- observing and measuring the kinetics of fast reactions
  \((C_d \text{ is small; } R_u \text{ is "small"-ish})\)

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

... but wait... Recall that for better S:N slow scan rates are best... *Uh oh!*

Experimentally, we also observe an overpotential that is intrinsic to the electron transfer process...

\[\text{anthracene} \rightarrow \text{anthracene}^- + \text{e}^-\]

\[\text{[Ru}^2(2,2'-\text{bipyridine})]^{3+} + \text{e}^- \rightarrow \text{[Ru}^3(2,2'-\text{bipyridine})]^{2+}\]

\[\text{[Ru}^3(2,2'-\text{bipyridine})]^{2+} + \text{e}^- \rightarrow \text{[Ru}^2(2,2'-\text{bipyridine})]^{3+}\]

... e.g., these are two of the fastest known heterogeneous electron-transfer reactions

Hey look who led this study!
... steady-state is "often" reached at each applied potential at a UME during a sweep

... Let's quantify it... steady-state occurs when $v \ll \frac{RT}{D/nF}$

... $v \text{[mV s}^{-1}] \ll 26 \text{ mV x (D/r_0^2)}$ for a BASi UME with $r_0 = 5 \text{ μm}$...

... 26 mV x [(0.5 x 10^{-5} cm² s⁻¹) / (0.5 x 10^{-3} cm)²] = 26 mV x [20 s⁻¹]

... $v \ll 0.5 \text{ V s}^{-1}$... Wow!

Walsh, Lovelock, & Licorne, Chem. Soc. Rev., 2010, 39, 4185

Ultrafast cyclic voltammetry: performing in the few megavolts per second range without ohmic drop

Christian Anagnostou, Emmanuel Maisonneuve, Giorgi Simonous

Department of Chemistry, Swiss Federal Institute of Technology, ETH Zürich, Switzerland

November 19th, 2019

Abstract

A new approach to fast cyclic voltammetry by applying high electric-field voltages to a small-area microelectrode is described. The technique is based on the use of a microelectrode with a diameter of 1 μm or less, which is inserted into a microfluidic channel. The microelectrode is connected to an external high-voltage power supply, which is used to generate an electric field of up to 1 MV cm⁻¹. This allows for the measurement of fast transient currents that are not possible with conventional cyclic voltammetry.

Keywords: Ultrafast cyclic voltammetry, microelectrode, fast voltammetry, microfluidics, microelectrode, microelectrode-based voltammetry.
scan rate is in megavolts s\(^{-1}\) 
That is MV s\(^{-1}\)...
... Wow!

\[ \text{anthracene} \rightarrow ^{+1e^-} \rightarrow \text{anthracene}^- \]

\[ \text{[Ru(2,2'-bipyridine)]}^{2+} \text{ and anthracene are not that similar, chemically...} \]

\[ \text{so what do these two ultrafast electron-transfer reactions have in common?} \]

\[ \text{[Ru(2,2'-bipyridine)]}^{2+} \leftrightarrow [Ru(2,2'-bipyridine)]^{3+} + 1e^- \]

Crystal and Molecular Structures of [Ru(bpy)\(_3\)](PF\(_4\))\(_2\) and [Ru(bpy)\(_3\)](PF\(_4\))\(_2\) at 105 K

M. Rinner, H. B. Bregli, A. Lüth, and C. Riedi

PLACES
Crystal and Molecular Structures of \([\text{Ru(bpy)}_2]\)(PF_6)_3 and \([\text{Ru(bpy)}_2]\)(PF_6)_2 at 105 K.

M. Bode, H.-B. Burgi, A. Laul, and C. Rüde

Contribution from the Institute für Anorganische Chemie, Universität Bern, CH-3012 Bern 9, Switzerland, and Lehrstuhl für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. Received November 21, 1980.

Table III. Selected Intersatomic Distances (Å) and Angles (deg) for III and II

<table>
<thead>
<tr>
<th>compound</th>
<th>([\text{Ru(bpy)}_2])(PF_6)_3</th>
<th>([\text{Ru(bpy)}_2])(PF_6)_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp. (K)</td>
<td>310</td>
<td>310</td>
</tr>
<tr>
<td>a (Å)</td>
<td>17.846</td>
<td>18.328</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.923</td>
<td>16.216</td>
</tr>
<tr>
<td>space group</td>
<td>(\text{R}3)</td>
<td>(\text{R}3)</td>
</tr>
<tr>
<td>symmetry of Ru</td>
<td>3+</td>
<td>3+</td>
</tr>
<tr>
<td>lattice const (Å)</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Ru-N</td>
<td>2.057 (2)</td>
<td>2.053 (2)</td>
</tr>
<tr>
<td>Cl-N</td>
<td>3.060 (5)</td>
<td>3.053 (2)</td>
</tr>
<tr>
<td>Cl-C2</td>
<td>3.05 (4)</td>
<td>3.05 (2)</td>
</tr>
<tr>
<td>(\mu)</td>
<td>5.084 (10)</td>
<td>5.08 (2)</td>
</tr>
</tbody>
</table>

[\text{Ru}(2,2\text{-bipyridine})_2]^{2+} and anthracene are not that similar, chemically...

So what do these two ultrafast electron-transfer reactions have in common?

1) reactant and product are almost structurally identical

2) electron transfer involves no bond-making or bond-breaking

3) in polar solvents, bigger is faster...

... thus, exchange current (density) is large...

... due to "small" reorganization energy (i)!

RECALL: — Marcus Theory... the idea...

- Minor assumptions to go from internal (potential) energy to free energy
  \(\Delta G = \Delta H - T \Delta S\)
- Three regions of electron transfer: (I) Normal, (II) Barrierless, (III) Inverted
- Marcus reorganization energy, \(\Lambda\), is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to the product potential-energy surface, while at the nuclear arrangement of the reactant (and \(\Delta G^0 = 0\)
**RECALL:** ... without stirring, the diffusion layer grows over time... and with a "big" potential step (... and then even bigger, then a little smaller again...), the Cottrell equation results...

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**FLASHBACK**

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Why are hysteretic CVs used, when steady-state Tafel Plots seem ideal?...

- CVs are not pure Butler–Volmer behavior "ever," unless you do what?
- Why are Tafel Plots (and/or with RDE) better than CVs? ... **Stir**
  - Not limited by mass transfer and so one can measure interfacial faradaic charge-transfer kinetic parameters with ease ($\alpha$, $j_0$, $k_0$)

---

**Why are hysteretic CVs used, when steady-state Tafel Plots seem ideal?**

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- Why are Tafel Plots (and/or with RDE) better than CVs? ... **Stir**
  - Not limited by mass transfer and so one can measure interfacial faradaic charge-transfer kinetic parameters with ease ($\alpha$, $j_0$, $k_0$)

- Why are CVs better than Tafel Plots?
  - One can tell if species are adsorbed to the electrode surface by performing a facile scan-rate dependence (linear $i_p$ vs. $v^{1/2}$ = homogeneous reaction... ... linear $i_p$ vs. $v^1$ = heterogeneous reaction)

  Easier to decipher between 1- and 2-electron transfer steps, as $i_p$ contains $n$

  Randles–Ševčík Equation ($T = 298$ K)

  $$i_p = (2.69 \times 10^5 \frac{n^2}{A D G^2} C^{3/2})$$
Why are hysteretic CVs used, when steady-state Tafel Plots seem ideal?...

- CVs are not pure Butler–Volmer behavior “ever,” unless you do what?
- Why are Tafel Plots (and/or with RDE) better than CVs? ... Stir!
  Not limited by mass transfer and so one can measure interfacial faradaic charge-transfer kinetic parameters with ease ($a_i, j_0, k_0$)
- Why are CVs better than Tafel Plots?
  One can tell if species are adsorbed to the electrode surface by performing a facile scan-rate dependence (linear $i$ vs. $v^{1/2}$ = homogeneous reaction... linear $i$ vs $v^1$ = heterogeneous reaction)
  Easier to decipher between 1- and 2-electron-transfer steps, as $i$ contains $n$
  ... determine kinetics based on the shape... if you are a computer
- And lastly... what is the midpoint potential for Tafel plots versus CVs?
  $$\frac{E_{eq}}{2} = E^{o}$$
  ... if $D_O = D_K$

RECALL: Course goal, i.e. the best 2-hour-long final-exam question ever!

Q: Explain cyclic voltammetry.

From syllabus

WE DID IT!

Course philosophy

Theory/Experiments versus Technologies (me vs you)
I will teach the theory, history, and experimental specifics, and you will teach the technologies, and real-world and academic state-of-the-art


Q: What was in this final set of lectures?
A: B&F Chapters 9, 10, and 6 main concepts:

- Sections 9.1 – 9.4: Rotating (Ring-)Disk Electrochemistry (R(R)DE)
- Sections 10.1 – 10.4: Electrochemical Impedance Spectroscopy (EIS)
- Sections 6.1 – 6.6, 11.7, 14.3: Linear Sweep Voltammetry (LSV), Thin-Layer Electrochemistry, Molecular Electrocatalysis, Cyclic Voltammetry (CV)
While this is all great, and really sums it up nicely, if you’ve paid very close attention to everything in the entire course (not a simple task), then you may have noticed that we never derived the most fundamental equation in all of electrochemistry...

THE NERNST EQUATION!

... you didn’t think I’d let us get through this entire course without doing that, did you?...

Let’s do it now!... since only now are we fully prepared to grasp the enormity of the thermodynamic equation for $E_{cell}$...

Let’s do it for a simple cell...

$\text{Ag (s)} | \text{AgCl (s)} | \text{HCl } (100 \text{ mM, aq}) || \text{HCl } (1 \text{ mM, aq}) | \text{AgCl (s)} | \text{Ag (s)}$

with some additional simplifying assumptions so that we don’t get bogged down in the math... see B&F Section 2.2 for more detailed explanations.

RECALL: Half reactions, at non-unity activity, obey the Nernst equation...

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

$-nFE = -nFE^0 + RT \ln Q$

$\frac{E}{E^0} = \frac{-RT}{nF \log e}$

$E = E^0 - \frac{RT}{0.4343 F \log Q}$

$E = E^0 - 2.3026 \frac{RT}{nF} \log Q$

... and at 298.15 K, $E = E^0 - 0.05915 \text{V} - \frac{0.5915 \text{V}}{n} \log Q$.

Memorize $\sim 60 \text{ mV per order in log}_{10}$, but do not forget $n$ and that this is at 25°C!

EXAMPLE: $\text{Ag (s)} | \text{AgCl (s)} | \text{HCl } (100 \text{ mM, aq}) || \text{HCl } (1 \text{ mM, aq}) | \text{AgCl (s)} | \text{Ag (s)}$

Based on first-principles thermodynamics, the following holds at equilibrium, shown for the left redox reaction only... $\text{AgCl + e}^{-} \leftrightarrow \text{Cl}^{-} + \text{Ag}$

$\dot{\mu}_{\text{AgCl}} + \dot{\mu}_{e} = \dot{\mu}_{\text{Cl}^{-}} + \dot{\mu}_{\text{Ag}}$

... now most people assume $\alpha_{\text{AgCl}} = 1$ and $\alpha_{\text{e}} = 1$, because they are solids...

... and one can define, but not overdefine, some $\dot{\mu}_{i}^{0}$... and choosing 0 is helpful... but none of this is necessary and I only do it here to simplify things...

Anyway, doing this for $\text{AgCl}$ and $\text{Ag}$ ($z = 0$) means $\dot{\mu}_{\text{AgCl}} = 0$ and $\dot{\mu}_{\text{Ag}} = 0$, so...

$\dot{\mu}_{e} = k_{B} T \ln a_{e} - z_{e} q \Phi_{e} = k_{B} T \ln a_{e} - z_{e} q \Phi_{e}$

... each $\dot{\mu}_{i}^{0}$ can be at any location $x$ in phase $\omega$ and is versus any reference state (usually far away in a vacuum), such that a single $\phi_{i}^{0}$ just like a single half-reaction, is really a $\Delta \theta_{i}^{0}$ versus a reference state... further supporting the fact that we use two electrodes and report a difference...

$\Delta \theta_{\text{AgCl}} - \Delta \theta_{\text{Ag}} = \Delta G = -nFE_{\text{cell}}$
Example: Ag(s) | AgCl(s) | HCl (100 mM, aq) || HCl (1 mM, aq) | AgCl(s) | Ag(s) 

… now, to be totally rigorous—which most textbooks are not—we should not assume $E_{\text{cell}}$ equals a difference in $\phi$, which it only does for two metallic electrodes and no intervening potential drops from the interface to the potentiostat (i.e. $j = 0$ and/or $R_{\text{wires}} = 0$ and/or no semiconductor–based leads)

… either way, potentiostats sense—and influence—the difference in $\bar{\phi} - \beta$, between the right versus the left electrode, and thus...

$$-nF E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{c_{\text{right}}}{c_{\text{left}}} \right) + \frac{RT}{nF} \ln \left( \frac{\phi_{\text{right}} - \beta}{\phi_{\text{left}} - \beta} \right) + \frac{RT}{nF} \ln \left( \frac{\phi_{\text{left}} + \beta}{\phi_{\text{right}} + \beta} \right)$$

… and $\mu_i^0$ and $y_i^o$ (activity coefficient) are (typically) the same for electrolytes in the same phase conditions, and thus...

$$E_{\text{cell}} = -\frac{RT}{nF} \ln \left( \frac{c_{\text{right}}}{c_{\text{left}}} \right) + \frac{RT}{nF} \ln \left( \frac{\phi_{\text{right}} - \beta}{\phi_{\text{left}} - \beta} \right) = -\frac{RT}{nF} \ln Q + \Delta \phi$$

… which is a simplified Nernst equation, plus contributions due to electric potential differences between the sites of electron transfer at each electrode... $\Delta \phi$ can be further deconvoluted into membrane, LI, $iR_u$ potentials...

… with an intervening anion-exchange membrane...

$$\Delta \phi = \left( \phi_{\text{Donnan}} - \phi_{\text{Donnan}} \right) = \frac{RT}{zF} \ln \left( \frac{c_{\text{right}}}{c_{\text{left}}} \right)$$

… so $E_{\text{cell}} = 0$

… or with an intervening frit instead...

$$\Delta \phi = \phi_{\text{LJ Type 1}} = \left( f_a - f_d \right) \frac{RT}{zF} \ln \left( \frac{c_{\text{right}}}{c_{\text{left}}} \right)$$

… so $E_{\text{cell}} > E_{\text{Nernst}}$

… or even several things...

$$\Delta \phi = \left( \phi_{\text{Donnan}} - \phi_{\text{Donnan}} \right) + \phi_{\text{LJ Type 1}} + iR_u$$

… so $E_{\text{cell}} > E_{\text{oc}}$ means $i > 0$

WOW!... ELECTROCHEMISTRY IS GREAT!... ALL DONE!