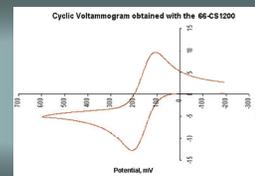


Experiments in Analytical Electrochemistry



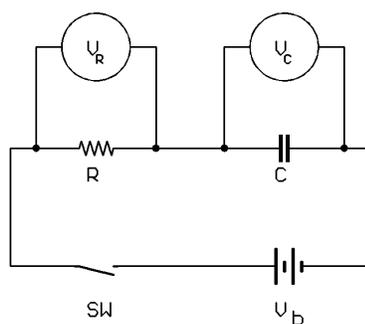
3. Chronoamperometry With a Planar Solid Electrode

PURPOSE: To determine the double layer capacitance of an electrode and the diffusion coefficient of an electroactive species.

BACKGROUND: Chronoamperometry (CA) is an electrochemical method in which a step potential is applied and the current, i , is measured as a function of time, t . This $i-t$ response is comprised of two components: the current due to charging the double-layer and the other due to the electron transfer reaction with the electroactive species. Of course, the extent to which both occur simultaneously depends on the initial, E_i , and the final value, E_f , of the potential. The results are most easily interpreted when a planar (flat) electrode is used in a quiet, unstirred solution, and the applied potential is sufficient to reduce or oxidize the electroactive species as fast as it gets to the electrode surface, i.e., at a diffusion-controlled rate. A hardcopy general reference is listed at the end of the experiment.

THEORY: Let us examine the nature of the double-layer capacitance first before discussing the electron transfer reaction. The current (i.e., electrons) flows to the working electrode (WE) in order to bring its potential to some desired value. A potentiostat with a 3-electrode cell provides the current via the auxiliary electrode (AE) to the WE while the potential is measured with respect to a reference electrode (RE). Thus, the current can be ascribed wholly to that which flows to change the potential of the WE from E_i to E_f with respect to RE. It is instructive to model this situation as being analogous to charging a capacitor, as illustrated in Figure 1. In this circuit, a resistor, R , represents the cell resistance. It is placed in series with a capacitor (C) that represents the electrode double-layer capacitance. A switch, SW , when closed, imposes the voltage of a battery, V_b , to the circuit. Two voltage-measuring devices monitor the voltages, V_R and V_C , across the resistor and the capacitor, respectively.

Figure 1.



At open circuit (i.e., time $t = 0$), prior to the closure of SW , V_R and $V_C = 0.0$ volt. When SW is closed, the instantaneous value of $V_R \Rightarrow V_b$ and the instantaneous (i.e., initial current) current, i_0 , is given by: $i_0 = V_b/R$. That is, the entire V_b is imposed across R since there is no charge yet residing on the capacitor. The current, after its initial rise, decays exponentially as a function of time: $i_t = i_0 \exp(-t/RC)$. This $i_t - t$ profile is shown in Figure 2. The voltage of the capacitor rises exponentially with time -

$V_C = V_b [1 - \exp(-t/RC)]$. At $t \Rightarrow \infty$, $V_R = 0$ and $V_C = V_b$. Thus, V_C vs. t is a mirror image of i_t vs. t .

In a real electrochemical cell, the value of R is usually much smaller and the value of C depends on the type and area of the electrode (Pt, Au, GC or other material) and the solution condition. That is, the type of solvent, and the type and concentration of electrolyte. Nominal values of C are in the range of $10 - 20 \mu\text{F}/\text{cm}^2$ for most electrodes.

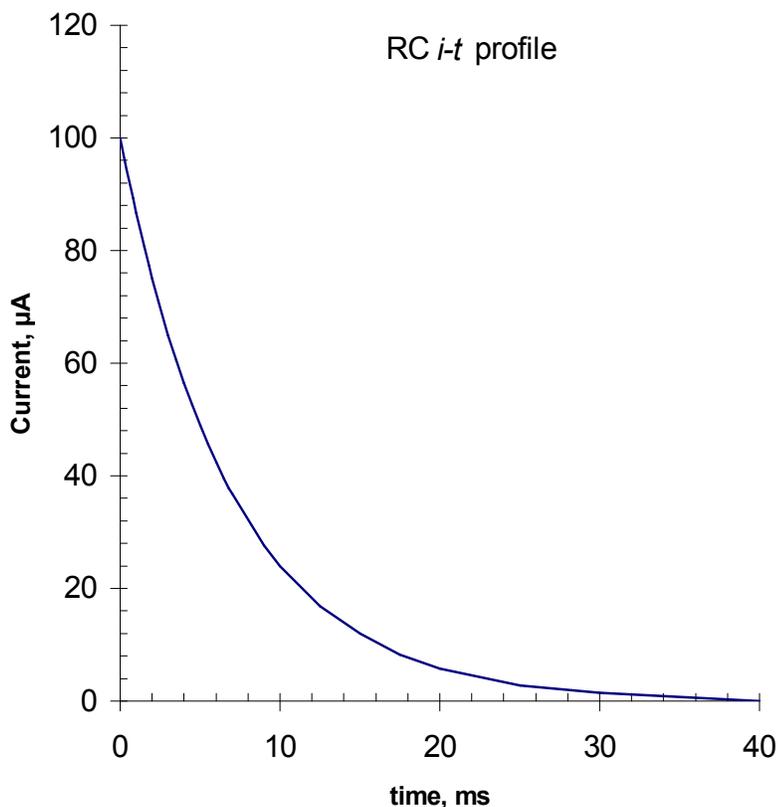


Figure 2. Calculated chronoamperometry i vs. t profile for $V_b = 1.0$ volt, $R = 10,000 \Omega$ and $C = 2 \mu\text{F}$ with a 3 mm diameter disk electrode.

Often, the i - E wave obtained with cyclic voltammetry is used to calculate C . That is, the charge, q , is given by: $q = it = CAE$ where E is the potential of the electrode (vs. reference electrode), A is the area, and the other terms have their usual meaning. Differentiating the equation with respect to time, t , and rearranging terms, one obtains: $i = CA(dE/dt)$ where dE/dt is the scan rate. The relationship assumes that the capacitance remains constant independent of the applied potential; i.e., $(dC/dE) = 0$. Such is seldom the case since nearly all electrodes undergo some finite surface reaction that consumes charge. However, a good estimate of C can be obtained by scanning the electrode over a relatively narrow potential window. The C value can be calculated from the i - E envelope.

an electron transfer reaction at a diffusion-controlled rate. Under these conditions, the current is given by the Cottrell relationship:

$$i = \frac{n F A D^{1/2} C^b}{(\pi t)^{1/2}} \quad (1)$$

where n is the number of electron(s) transferred per electroactive molecule or ion; F is Faraday's constant; A is the area of the electrode surface in cm^2 ; D is the diffusion coefficient in cm^2/s ; C^b is the concentration of the electroactive species in mol/cm^3 ; and t is time in second. The current rises rapidly to a maximum value when the potential goes from its initial value, E_i , where reaction occurs, to its final value, E_f , and then decays as a function of $t^{1/2}$, as seen in Figure 3.

The value of $it^{1/2}$ as a function of t should be constant. The value of $nD^{1/2}$ can be determined from this value, assuming that A (the area) and C^b (bulk concentration) are known.

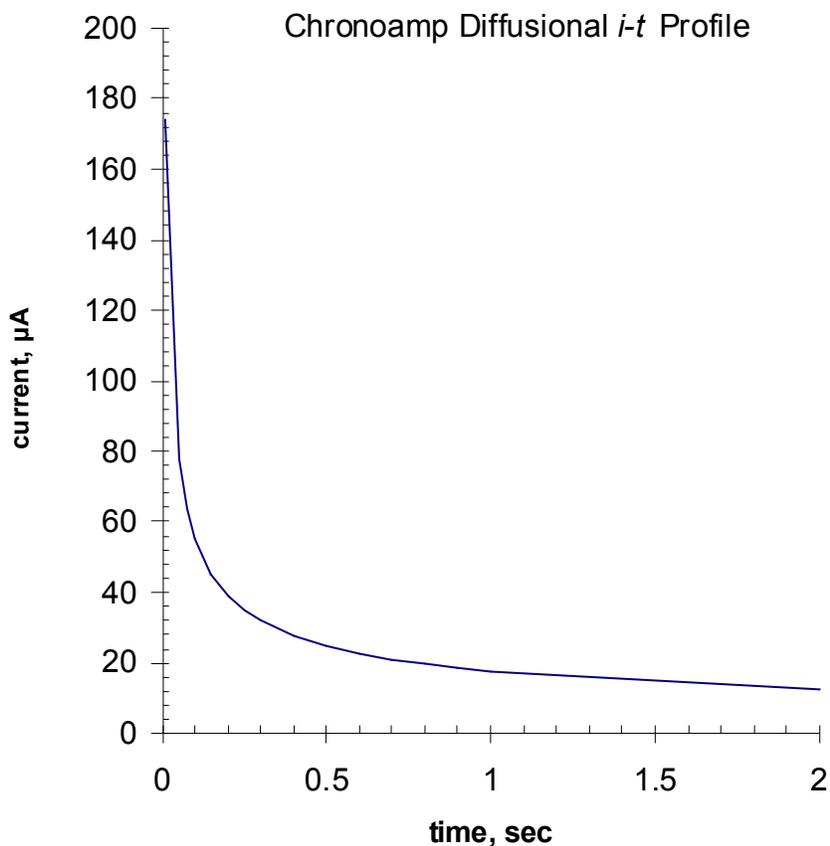


Figure 3. Cottrell Diffusion i - t profile for 3 mM disk electrode in 1 mM ferricyanide.

What should be the values of the initial, E_i , and final potential, E_f ? E_i should be at a value where no electrode reaction occurs. You can decide what this value should be by looking at a cyclic voltammogram (see Experiment titled: *Cyclic Voltammetry at Solid Electrodes* for directions). E_f is set at a value that is 0.120 to 0.180 V greater than the reversible potential, E^0 . For example, in the case of ferri/ferricyanide:



Values of E_f can be calculated

$$E_f = E^0 - 0.120 \text{ V} = 0.24 \text{ V for reduction of Fe(CN)}_6^{-3} \text{ to ferrocyanide.} \quad (3)$$

$$\text{or } E_f = E^0 + 0.120 \text{ V} = 0.48 \text{ V for oxidation of Fe(CN)}_6^{-4} \text{ to ferricyanide.} \quad (4)$$

Please remember to correct these potentials for the type of reference electrode you are using!

Think about why the potential is moved to more positive values when you want to remove electrons and to more negative values when you want to add electrodes to a species.

The current is a composite of the double-layer charging and the faradaic current - the latter due to the electron transfer reaction with an electroactive species. The former current decays much more rapidly as an exponential function compared to the square root of time for a diffusion-controlled reaction.

It is instructive to have a mental picture of the diffusional profile of the oxidized and reduced forms of the electroactive species for a CA experiment. If the concentration of the reduced species is 1 mM $\{C_R(t=0) = 1 \text{ mM}\}$ before the potential is applied and the concentration of the oxidized species is zero $\{C_{OX}(t=0) = 0\}$, these concentrations are reversed in the solution phase adjacent to the electrode when E_f is applied. That is, R is oxidized to OX, the ratio of $C_{OX}/C_R \Rightarrow 100/1$, assuming E_f changes by +120 mV from E_i at $t > 0$. The depletion of C_R at the electrode causes R species to be transported from the bulk solution to the electrode and OX to be transported out as the electrolysis proceeds. A concentration gradient of these respective species is created, extending further into the bulk solution with time. Graphic illustrations of gradient profiles are illustrated in the website:

<http://www.epsilon-web.net/EC/manual/Techniques/Chronol/ca.html>.

Scroll down to "Analysis of Current Response" to see these profiles.

How far into the solution does this concentration gradient, δ , or diffusion layer extend? It depends on the time and the value of the diffusion coefficient, D , or the designated D_R and D_{OX} , the reduced and oxidized species, respectively. The computed values of δ vs. t are for ferri-/ferrocyanide (D value of $0.65 \times 10^{-5} \text{ cm}^2/\text{s}$ at $T = 25^\circ\text{C}$) as plotted in Figure 4. The thickness changes very rapidly initially and then decreases more slowly with time, but overall, δ is small¹ (e.g., 0.0052 cm at 10 second).

Sample Calculation: Figure 3 gave an illustrative Cottrell current as a function of time. Calculate and plot values of this current for the following experimental conditions and include them in your laboratory report.

$$\begin{aligned}n &= 1 \\A &= 0.0706 \text{ cm}^2 \text{ (for a 3 mM diameter planar electrode)} \\D &= 0.65 \times 10^{-5} \text{ cm}^2/\text{s} \\C_R &= 1.0 \text{ mM } (t = 0, x = 0 \text{ to } \infty) \\C_{OX} &= 0.0 \text{ mM } (t = 0, x = 0 \text{ to } \infty) \\F &= 96,486 \text{ coulomb/mole}\end{aligned}$$

¹ An approximate value of δ is given by: $\delta = (2/\pi) (Dt)^{1/2} = 0.69 (Dt)^{1/2}$

A famous chemist once said: *things move approximately 1 cm/day in aqueous solution*. Why only 1 cm/day? Remember that the solution is quiet, not stirred, without any convection. Most D values lie in the range of 1.0×10^{-5} to $0.2 \times 10^{-5} \text{ cm}^2/\text{sec}$ (the cm^2 comes from the area of a planar electrode).

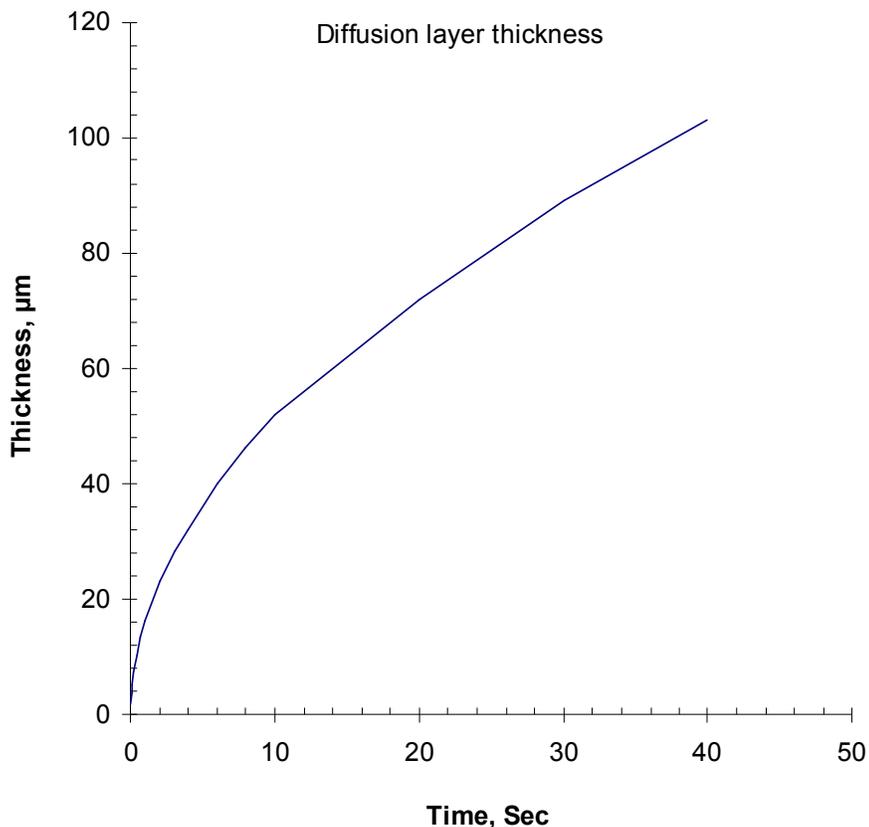


Figure 4. Diffusion layer thickness as a function of time for ferricyanide reduction.

EXPERIMENT

Equipment

For a real cell where the time constant of the cell is fairly long (i.e., several milliseconds) an analog potentiostat with an inexpensive digital oscilloscope for data acquisition with a printer readout is recommended. With a computer-controlled potentiostat, fast data acquisition with readout is part of the instrument.

- An analog or computerized potentiostat with appropriate data acquisition capability is needed. Please see your laboratory instructor about the potentiostat and accompanying manual.
- Test circuit
 - 100 Ω and 10,000 Ω resistors
 - 2 μF capacitors (not electrolytes)
- Small volume (< 5 ml) cell and electrodes
 - 3 – 4 mm diameter glassy carbon or Pt planar tip working electrode
 - Ag/AgCl reference electrode
 - Pt auxiliary electrode
 - Small volume cell
 - Electrode polishing kit
- Pipettes and other laboratory glassware and supplies

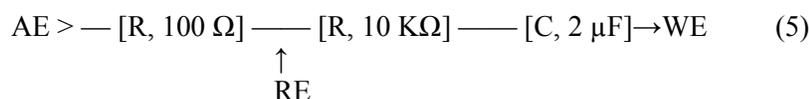
Chemical Solutions:

- 100 ml of 5 mM potassium ferricyanide in 0.1 M KNO₃
 - 100 ml of 0.1 M KNO₃ solution
 - 10 ml of 5 mM ferrocene carboxylic acid (FCA) in pH 7 buffer (provided by instructor)
 - Pure water for dilutions
- Note:** The concentrations of ferricyanide and FCA should be known to 3 significant figures.

Procedure

I. Test of RC circuit –

1. Connect in series a 100 Ω resistor, a 10,000 Ω resistor and a 2 μF capacitor. Use a solid-state capacitor, not an electrolytic one.
2. The AE connector from the potentiostat is attached to the 100 Ω resistor, the RE between the two resistors, and WE to the end of the capacitor:



The 100 Ω resistor helps to stabilize the potentiostat at short rise times (< 20 μS).

3. Please obtain directions for the operation of the potentiostat from the instructor.
4. Set the potential and current measurement parameters on the potentiostat to the following values:

$E_i = 0.00 \text{ V}$ Current scale: 50 μA
 $E_1 = 0.500 \text{ V}$ Filter: < 100 μS
 $E_2 = 0.00 \text{ V}$
Operate the potentiostat in the chronoamperometry mode

If the time duration of E1 can be set on the potentiostat, a 100 – 1,000 mS time duration is sufficient, depending on the RC time constant. Exact timing is not critical so that you can start/stop the experiment within 1 or 2 seconds.

The instantaneous current is given by $E_1/R = 50 \mu\text{A}$. The current decreases exponentially.

II. Determine the value of the diffusion coefficient, D

1. With a 3 mm diameter disk electrode (either GC or Pt), fill the cell with a 0.1 M KNO₃ solution.
2. Step the potential from 0.0 V to +0.500 V for 200 mS and then step back to 0.0 V. Repeat the experiment and record the *i-t* profiles.
3. Repeat with a 5 mM ferricyanide in 0.1 M KNO₃ solution. Step the potential from an initial 600 mV to 0.0 V for 300 mS and then return the potential to 600 mV. Wait 5 minutes and then repeat the experiment. Save and record the *i-t* profiles.

Repeat the procedure with a 5 mM ferrocene carboxylic acid solution in a pH 7 buffer solution, stepping the potential from 0.0 V to 600 mV for 300 mS and then back to 0.0 V. Wait 5 minutes and then repeat the experiment. Save and record the *i-t* profiles.

Please note that the potential is stepped from 600 mV to 0 V for ferricyanide, a reduction, whereas the potential is stepped from 0 V to 600 mV for ferrocene carboxylic acid, an oxidation.

REPORT (Data analysis and discussion):

Consult with the laboratory instructor about the contents and format of your report for this experiment. Suggestions and questions to help write your report are –

1. Write a short summary of what you did in this experiment, noting any deviations or substitutions in the procedure.
2. Show i - t profile with the test circuit ($R = 10,000 \Omega$ and $C = 2 \mu\text{F}$) and any others you may have obtained.
3. Calculate the current for times of 0.1, 1.0, 2.0, 5 and 10 mS and compare the calculated vs. experimental currents. How well do they agree? Any discrepancies? If so, why?
4. Calculate the capacitance of the 3 mm diameter electrode from i - t profile of the electrode in 0.1 M KNO_3
5. Figure 3 shows i vs. t for the calculated Cottrell relationship. The parameters for the calculations are listed in the text of this experiment. Show example calculations using these parameters for times of 10 mS, 100 mS and 1 second. Do they agree with the data in Figure 3?
6. Calculate the D value for ferrocene carboxylic acid from the experimental i - t profile. [Suggestion: Since $it^{1/2}$ is a constant, pick 3 or 4 values of i at different times, t , and take an average of the $it^{1/2}$ values to calculate D]. Is this D value less or larger than the value for ferricyanide? Offer an explanation for this difference (hint: size and ionic charge considerations).

OPTIONAL EXPERIMENT

Chronocoulometry (CC) is a technique in which the CA i - t is integrated to give charge, Q , vs. time, t , where $Q = \int i dt$. The current, i , is the rate of electrolysis at any given time, t , and Q is the amount of charge transferred to time, t . In the case of an electron-transfer reaction, we can integrate the Cottrell relationship, denoting the Q due to a diffusing species as Q_{diff} .

$$Q_{\text{diff}} = \frac{2nFAC^b D^{1/2} t^{1/2}}{\pi^{1/2}} \quad (6)$$

The total charge, Q_T , is comprised of two other components: the Q_{dl} due to charging the double layer, as already discussed, and Q_{ads} , due to electrolysis of any electroactive species adsorbed on the electrode surface [i.e., $Q_T = Q_{\text{diff}} + Q_{\text{dl}} + Q_{\text{ads}}$]. Since the latter two terms are time independent (involves charge only of the surface), a plot of Q vs. $t^{1/2}$ should be linear with the extrapolated intercept at $t = 0$ due to $Q_{\text{dl}} + Q_{\text{ads}}$.

With the i - t data from the chronoamperometry of ferricyanide reduction or FCA oxidation, obtain Q values at times of 50 mS, 100 mS, 200 mS and 300 mS. Plot Q vs. $t^{1/2}$ and obtain the intercept value, which is due to Q_{dl} . Is this value reasonable for the charging of the double-layer?

GENERAL REFERENCE

1. A. J. Bard & L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed (2001), Published by J. Wiley & Sons, NY, pgs. 156-164.