You have been asked to measure the kinetics of nickel deposition from a Watts nickel plating bath. The conductivity of the plating solution is 3.5 S/m. The reference electrode is located 2 cm from the working electrode. The electrode area is 5 cm 2 (with only one side of the electrode active). You may neglect the impact of the concentration overpotential. You may also assume that the current density is nearly uniform.

a. Recommend a reference electrode for use in this system (hint- what is in the Watts bath?).

b. You apply a potential of 1.25 V and measure an average current density of 5 mA/cm 2

What is the surface overpotential? Is the IR drop in solution important? (assume a 1D

uniform current density for this part).

c. How good is the assumption of uniform current density? What type of cell geometry would satisfy this assumption? How would your results be impacted if the current density were not uniform?

a. Watts Bath

Principal Components

- 1) Nickel Sulfate
- 2) Nickel Chloride
- 3) Boric Acid

Easiest to use a common reference electrode reversible to Cl^-

Use Ag/AgCl or SCE

b. Assume uniform current density between two electrodes that are $5cm^2$ in area.

$$A = 5cm^2$$

L = 2cm = distance between ref. electrode and working electrode.

$$\kappa = 3.5 S/m$$

$$R = \frac{L}{\kappa A} = \frac{2cm}{(3.4\frac{S}{m})(\frac{m}{100cm})5cm^2}$$

$$= 11.4 \Omega$$

Voltage loss between ref. and working.

$$\Delta V = IR = (0.025)(11.4) = 0.285V$$

Surface Overpotential =

$$\Delta V_{working-ref} - \Delta V_{\Omega} = 1.25 - 0.285$$
$$= 0.965V$$

c. 1-D assumption is not often accurate for experimental cells, due to geometry.

In other words, the primary current distribution is typically not uniform.

The current distribution can still be uniform if Wa >> 1 (see chap. 4)

A rectangular cell where the electrodes (working and counter) occupied the complete surfaces of two opposite faces would have a uniform current distribution.

For a non-uniform current distribution, the surface overpotential would vary across the electrode and the ohmic drop between the working and reference electrodes would depend on the exact position and not just the separation distance. Chapter 6

One of your lab colleagues is attempting to measure the kinetics of the following reaction

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$
,

which is used in the cathode of vanadium-based redox flow batteries. To simplify things, he is making the measurement at constant current. He finds that the potential decreases slightly with time, followed by an abrupt decrease and substantial bubbling.

- a. Qualitatively explain the observed behavior.
- b. Given the following parameters, how long will the experiment proceed until the abrupt change in potential is observed? Assume that there is excess H^+ in solution, and that the electrode area is 2 cm².

 $D_{VO_2^+} = 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ $c_{VO_2^+} = 25 \text{ mM}$ I = 1 mA

Part (a) The observation is likely due to a drop in the surface concentration due to mass transfer limitations.

Part (b) Use the Sand Equation to determine the time required to reach the mass transfer limit

Ι	1 mA	
Area	2 cm^2	
n	1	
F	96485	
Di	4.00E-06 cm^2/s	4.00E-10 m^2/s
ci∞	0.025 M	25 mol/m^3
i	0.0005 A/cm^2	5 A/m^2

$$\frac{i\tau^{0.5}}{c_i^{\infty}} = \frac{nFD_i^{0.5}\sqrt{\pi}}{2}$$
$$t = 73.1 \text{ s}$$

t (s)	I (mA)
0.5	6.2
1.0	4.1
5.0	1.7
10.0	1.28
25.0	0.86
60.0	0.58
600	0.17
6000	0.052

0.043

10,000

An estimate of the diffusivity can be obtained by stepping the potential so that the reaction is mass transfer limited as described in the chapter. From the following data for V^{2+} in acidic solution, please estimate the diffusivity. The reaction is as follows

$$V^{2+} \rightarrow V^{3+} + e^{-}$$
.

The bulk concentration of $V^{2+} \mbox{is } 0.01$ M, and the area of the electrode is 1 $\mbox{cm}^2.$

1 cm^2	1.00E-04 m^2
1 eq/mol	
96485 C/eq	
0.05 M	50 mol/m^3
	1 cm^2 1 eq/mol 96485 C/eq 0.05 M

Based on the Cotrell Equation

$$i = \frac{nF\sqrt{D_i}c_i^{\infty}}{\sqrt{\pi t}}$$

we can plot the current density as a function of 1/sqrt(t), and then solve for D from the slope

t (s)	1/sqrt t	I (mA)	i (A/m^2)
0.5	1.4142	6.2	62.0
1	1.0000	4.1	41.0
5	0.4472	1.7	17.0
10	0.3162	1.28	12.8
25	0.2000	0.86	8.6
60	0.1291	0.58	5.8
600	0.0408	0.17	1.7
6000	0.0129	0.052	0.5
10,000	0.0100	0.043	0.4





In section 6-4 we examined the time constant associated with charging of the double layer. In doing so, we assumed that the physical situation could be represented by a resistor (ohmic resistance of the solution) and a capacitor (the double layer) in series. However, the actual situation is a bit more complex since there is a faradaic resistance in parallel with the double layer capacitance as shown in Figures 6-6 and 6-24. This problem explores the impact of the faradaic resistance on double layer charging. Our objectives are two-fold: 1) determine the time constant for double layer charging in the presence of the faradaic resistance, and 2) determine an expression for the charge across the capacitor as a function of time.

- a. Initially, there is no applied voltage, no current, and the capacitor is not charged
- b. At time zero, a voltage V is applied
- c. Your task is to derive an expression for the charge across the double layer as a function
- of time, and report the appropriate time constant. Use the symbols shown in Figure 6-17
- for the circuit components.

Approach: The general approach is identical to that used in the chapter with the simpler model. In this case, you will need to write a voltage balance for each of the two legs, noting that the voltage drop must be the same. Remember that where "1" is the capacitor leg and "2" is the faradaic leg. Once you have written the required balances, you can combine them into a single ODE and solve that equation for the desired relationship and time constant. Finally, please explain physically how the characteristic time that you derived can be smaller than that determined for the simpler situation explored in the chapter.



I is a function of t, as are i_1 and i_2 Express i_1 and i_2 in terms of Q_1 and Q_2

Problem 6.4

$$\frac{dQ}{dt}R_{\Omega} + \frac{Q_1}{c} = V \tag{1}$$

$$\frac{dQ}{dt}R_{\Omega} + \frac{dQ_2}{dt}R_f = V \tag{2}$$

$$\frac{dQ}{dt} = \frac{dQ_1}{dt} + \frac{dQ_2}{dt}$$
(3)

$$\begin{split} \left(\frac{dQ_1}{dt} + \frac{dQ_2}{dt}\right) R_\Omega + \frac{dQ_2}{dt} R_f &= V \\ \frac{dQ_1}{dt} R_\Omega + \left(R_\Omega + R_f\right) \frac{dQ_2}{dt} &= V t \\ \frac{dQ_2}{dt} = \frac{V - \frac{dQ_1}{dt} R_\Omega}{(R_\Omega + R_f)} \\ \frac{dQ_2}{dt} &= \frac{V}{R_\Omega + R_f} - \frac{R_\Omega}{R_f + R_\Omega} \frac{dQ_1}{dt} \\ &+ \frac{Q_1}{C} = V \\ \frac{dQ_1}{dt} \left(R_\Omega - \frac{R_\Omega^2}{R_f + R_\Omega}\right) + \frac{Q_1}{C} &= V \left(1 - \frac{1}{R_\Omega + R_f}\right) \\ \frac{dQ_1}{dt} \left(\frac{R_\Omega (R_\Omega + R_f) - R_\Omega^2}{R_\Omega + R_f}\right) + \frac{Q_1}{C} &= V \left(1 - \frac{1}{R_\Omega + R_f}\right) \end{split}$$

$$\frac{dQ_1}{dt} \left(\frac{R_\Omega R_f}{R_\Omega + R_f} \right) + \frac{Q1}{C} = V \left(1 - \frac{1}{R_f + R_\Omega} \right)$$
$$a \frac{dQ_1}{dt} + \frac{Q_1}{i} = b$$
$$a \frac{dQ_1}{dt} = b - \frac{Q_1}{C}$$
$$-C \left(\frac{-\frac{1}{C} dQ_1}{b - \frac{Q_1}{C}} \right) = \frac{1}{a} dt$$

$$\int_{0}^{Q_{1}} \frac{-\frac{1}{C} dQ_{1}}{b - \frac{Q_{1}}{C}} = -\frac{1}{aC} \int_{0}^{t} dt$$

 $\ln\left(b - \frac{Q_1}{C}\right)\Big|_{0}^{Q_1} = -\frac{1}{aC}t$

$$\ln\left(b - \frac{Q_1}{C}\right) - \ln b = \frac{-1}{aC}t$$

Check limiting case

$$\begin{array}{c} b \to V \\ a \to R_{\Omega} \end{array} \} as R_f = \infty$$

$$\ln\left(1 - \frac{Q_1}{CV}\right) = \frac{-1}{RC}t$$

$$\frac{Q}{Q_{final}} = 1 - exp^{-\frac{t}{RC}} \quad \text{(checks)}$$

$$\ln\left(1 - \frac{Q_1}{bc}\right) = \frac{-1}{aC}t$$

$$b = V\left(1 - \frac{1}{R_{\Omega} + R_f}\right)$$

$$a = \frac{R_{\Omega}R_f}{R_{\Omega} + R_f}$$

$$\left(1 - \frac{Q_1}{bC}\right) = \exp\left(\frac{-t}{aC}\right)$$

This equation provides the charge in the capacitor "leg" as a function of a time starting from a zero charge condition. The time constant is $aC = \frac{R_{\Omega}R_fC}{R_{\Omega}+R_f}$

Time constant is smaller because full voltage does not have to be across the capacitor. In other words, the final current $\neq 0$ and the capacitor does not need to be charged to the same level.

GITT (Galvanostatic Intermittent Titration Technique) uses short current pulses to determine the diffusivity of solid phase species in, for example, battery electrodes where the rate of reaction is limited by diffusion in the solid phase. This situation occurs for several electrodes of commercial importance. The concept behind the method is to insert a known amount of material into the surface of the electrode (hence the short time), and then monitor the potential as it relaxes with time due to diffusion of the inserted species into the electrode. In order for the

method to be accurate, the amount of material inserted into the solid must be known. For this reason, the method uses a galvanostatic pulse for a specified time, which permits determination of the amount of material with use of Faraday's Law assuming that all of the current is faradaic (due to the reaction).

- a. While it is sometimes desirable to use very short current pulses, what factor limits accuracy for short pulses?
- b. Assuming that you have a battery cathode, how does the voltage change during a current pulse?
- c. For a current of 1mA and a 5cm^2 WE, what is the shortest pulse width (s) that you would recommend? Assume that you have a small battery cathode at open circuit, and that the drop in voltage associated with the pulse is 0.15 V. The voltage during the pulse can be assumed to be constant. The error associated with the pulse width should be no greater than 1%.

a) A key limiting factor is the time required for charging the double layer.b)



- c) $Q = I \cdot t = (0.001A)t$ $\Delta V = 0.15$ V as per problem statement
 - Q = CV assume $C_{DL} = 0.2 F/m^2$ $Area = 5cm^2 = 0.0005 m^2$ $C = C_{DL} \cdot A = 1x10^{-4}F$ $Q_{DL} = (1 \times 10^{-4}F)(0.15V)$

=
$$1.5 \times 10^{-5}$$
C (charge for DL)
Maximum Error = $1\% = 0.01$

$$\frac{Q_{DL}}{Q_{total}} = 0.01 \qquad Q_{total} = 0.0015 \text{ C}$$

To get time,

$$Q_{total} = I \cdot t \qquad t = \frac{Q_{total}}{I}$$
$$t = \frac{0.0015C}{0.001} = 1.5 s$$

Assumes:

- Flat surface

Constant capacitance
 Constant V in pulse
 Note that C changes with electrode size.

Assume that you have 50 mM of A^{2+} in solution, which can be reduced to form the soluble species A^+ . Assume that the reaction is reversible with a standard potential of 0.2V. There is essentially no A^+ in the starting solution. Please qualitatively sketch the following:

- a. The IV curve that results from scanning the potential from a high value (0.5V above the standard potential of the reaction) to a low value (0.5V below the standard potential of the reaction).
- b. The IV curve that results from scanning the potential from a low value (0.5V below the standard potential of the reaction) to a high value (0.5V above the standard potential of the reaction).
- c. Why are the curves in (a) and (b) different?
- d. Assuming that you started from the open circuit potential, in which direction would you recommend scanning first? Why?
- a) (requests qualitative sketch) The actual curve for a sweep from 0.7 to -0.3V at 0.005 V/s as per simulation is



b) (requests qualitative sketch) The actual curve for a sweep from -0.3 to 0.7 V at 0.005 V/s as per simulation is

Problem 6.6



c) In (a), the scan starts in the oxidizing range at 0.7 V, and no current is observed initially since the reactant is already oxidized. Once the potential is sufficiently low, a cathodic current is observed, which peaks and then drops as typical for CV experiments.

In (b), the scan starts at -0.3V and a current is immediately observed due to reduction of the existing reactant. No peak is observed since both diffusion and the increasing potential lead to a reduction in the rate of the cathodic reaction. At positive potentials, a peak is observed as the reduced species near the electrode is oxidized.

d) Starting at the OCV, it makes sense to scan in the negative direction, since there are no reduced species in solution to react.

0.672

0.815

0.650

0.700

2.20

11.49

-20.00

Problem 6.7

The following CV data were taken relative to a Ag/AgCl reference electrode located 1 cm from the working electrode. You suspect that the results may be impacted by IR losses in solution. The conductivity of the solution is 10 S/m.

- a. Determine whether or not IR losses are important and, if needed, correct the data to account for IR losses.
- b. Is it possible to determine n for the reaction from the data? If so, please report the value. If not, please explain why not.

	DV _{ir} iL/k	
Data	L 1 c	
	k	0.1 S/cm

Do IR correction and compare plots. Start with 100 mV/s data



IR Correction makes a big difference. Need to compare corrected results to data at different scan rate to determine if reversible
Chapter 6Problem 6.76.7/2

Scan Rate of 10 mV/s

		Current
Potential (V V-il	Density	
		(mA/cm^2)
0.755	0.700	5.48
0.813	0.740	7.28
0.841	0.780	6.07
0.868	0.820	4.83
0.900	0.860	4.04
0.972	0.940	3.17
1.047	1.020	2.70
1.124	1.100	2.39
1.201	1.180	2.17
1.201	1.180	2.08
1.120	1.100	1.94
1.039	1.020	1.82
0.958	0.940	1.72
0.876	0.860	1.60
0.790	0.780	0.91
0.730	0.740	-1.02
0.652	0.700	-4.82
0.597	0.661	-6.32
0.569	0.621	-5.11
0.542	0.581	-3.87
0.510	0.541	-3.08
0.438	0.461	-2.22
0.363	0.381	-1.75
0.286	0.301	-1.46
0.208	0.221	-1.25
0.208	0.219	-1.16
0.289	0.299	-1.02
0.370	0.379	-0.92
0.451	0.459	-0.82
0.532	0.539	-0.72
0.619	0.619	-0.05
0.677	0.659	1.85
0.755	0.700	5.48





IR correction is important at both scan rates

The corrected data indicate that the peak positions are in the same place. Likely that the reaction is reversible.

(b) Since the system appears to be reversible, should be able to determine n Data are limited, but we will see how it goes.

Peak to peak from 100) mV/s data	
V positive peak	0.740	
V negative peak	0.665	
Difference	0.075	
	This is larger than the 60	M mV arrested for $n-1$ under to the limitations of the d

This is larger than the 60 mV expected for n=1, undoubtedly due to the limitations of the data.

For hydrogen adsorption on polycrystalline platinum, the accepted loading is 2.1 C/m^2 . Using the (100) face shown in the diagram, calculate the amount of H adsorbed on this FCC surface assuming one H per Pt atom. Then, convert this number to the corresponding amount of charge per area. Assume a pure platinum surface with an FCC lattice parameter of 0.202 nm and compare your moults to the polycopytalline number.



of 0.392 nm, and compare your results to the polycrystalline number. Provide a possible explanation for any differences between the calculated and accepted values.

First, we need to find the atoms per area. Based on the diagram above, the area is equal to 4a x 5a, where a is the diameter of a Pt atom. We can find the diameter of a Pt atom from the lattice parameter

$$a = \frac{0.392}{\sqrt{2}} = 0.277 \ nm$$

Therefore, the area is $4a \ge 5a = 20a^2 = 1.537 \text{ nm}^2 = 1.537 \ge 10^{-18} \text{ m}^2$

In this area, there are 20 Pt atoms.

$$\frac{20 \text{ atoms}}{1.537 \cdot 10^{-18} \text{ m}^2} \frac{\text{mol Pt}}{6.023 \times 10^{23} \text{ atoms}} \frac{\text{mol CO}}{\text{mol Pt}} \frac{2 \text{ equiv.}}{\text{mol CO}} \frac{96485 \text{ C}}{\text{equiv.}} = 4.17 \text{ C m}^{-2}$$

This is the same number calculated in Section 6-6, and assumes that all the Pt sites are occupied. The accepted value is about half of this value, which implies that not all of the sites are occupied in practice, and/or that the single crystal density overestimates the number of sites where H can be absorbed.

Chapter 6

$$V = L \frac{dI}{dt}$$

where L is the inductance. Use this equation and the procedure illustrated in section 6-7 to derive an expression for the complex impedance, Z. Compare your answer to that found in Table 6-4.

The behavior of an inductor is described by the following differential equation

$$V = L \frac{dI}{dt}$$

where L is the inductance. Use this equation and the procedure illustrated in section 6-7 to derive an expression for the complex impedance, Z. Compare your answer to that found in Table 6-4.

$$V = L \frac{dI}{dt}$$

$$\mathcal{I} = \Delta I e^{j(\omega t - \emptyset)} \qquad \text{(Complex Current)}$$

$$\frac{dJ}{dt} = j\omega \Delta I e^{j(\omega t - \emptyset)}$$

$$\mathcal{V} = L \frac{dJ}{dt} = Lj\omega \Delta I e^{j(\omega t - \emptyset)}$$

$$Z(\omega) = \frac{\mathcal{V}(\omega)}{\mathcal{I}(\omega)} = \frac{Lj\omega \Delta I e^{j(\omega t - \emptyset)}}{\Delta I e^{j(\omega t - \emptyset)}}$$

$$Z(\omega) = Lj\omega \qquad \text{same as Table 6-3}$$

```
In [14]: from numpy
                                 import *
         from scipy.optimize
                                 import *
         from matplotlib.pyplot import *
         %matplotlib inline
         #input data
         ro = 0.001
                                               #electrode radius m (1 mm)
         R = 8.314;
                                               #Gas constant J/mol-K
         T = 298;
                                               #Temperature K
         F = 96485;
                                               #Faraday's Constant C/mol
         kappa=10;
                                               #conductivity S/m
         cdl = 0.1;
                                               #specific capacitance F/m<sup>2</sup>
         inot = 10;
                                               #exchange current density A/m^2
                                               #electrode area m^2
         Area = pi*ro**2.
         C = cdl*Area
                                               #capacitance, F
         Rohm = 1/(4.*kappa*ro)
                                               #resistance to 1mm electrode (assumes
          other electrodes at infinity)
         Rf = R^{T}/(F^{inot^{Area}})
                                              #kinetic resistance (linear kinetics,
          alphas add to 1)
         def zcircuit(w):
                                              #w = frequency rad/s
             zc = 1./(w*C*1j)
                                              #impedance for capacitor
             zcir = Rohm+1./(1./(Rf)+1./zc); #calculate impedance for circuit ohms
             return zcir;
                                              # return circuit impedance
         w=logspace(-2,6,100);
                                              #define frequency vector using log spa
         cing because of large range of w
         z=zcircuit(w);
         x=z.real;
         y=-z.imaq;
         plot(x,y,'k-o');
         rc("font",size=12);
         ax = gca()
         xlabel(r'Real(Z)', size=16);
         ylabel(r'-Im(Z)',size=16);
         gcf().subplots_adjust(bottom=0.20);
         savefig('ch6_6_3.jpg')
```



Chapter 6

Please examine your response to previous problem and address the following

- a. How does the magnitude of the kinetic and ohmic resistances compare to those calculated in Illustration 6-5? Please rationalize the differences and/or similarities.
- b. How is it possible to use just the formula for the disk electrode to estimate the ohmic resistance? Do you expect this to be accurate? Why or why not?
- c. In what ways does a large counter electrode influence the impedance results?
- a. The property values in Illustration 6-5 and the previous problem are the same. The electrode sizes and geometry are different. From Illustration 6-5,

To determine the resistance of the electrolyte, we use equation 4-8c

$$R_{\Omega} = \frac{L}{\kappa A} = \frac{0.01}{(10)(0.0025)} = 0.4 \,\Omega$$

For the kinetic resistance, we assume open circuit as the steady-state condition, with small oscillations around that point. Because the magnitude of the potential change is small, linear kinetics can be used to determine the resistance according to equation 4-62

$$R_f = \frac{1}{A} \frac{d\eta}{di} = \frac{RT}{Fi_o A} = \frac{(8.314)(298)}{(96,485)(10)(0.0025)} = 1.03 \ \Omega$$

The analogous values from Problem 6-8 are

$$R_{\Omega} = \frac{1}{4\kappa r_o} = \frac{1}{4(10)(0.001)} = 25 \,\Omega$$
$$R_f = \frac{1}{A} \frac{d\eta}{di} = \frac{RT}{Fi_o A} = \frac{(8.314)(298)}{(96,485)(10)\pi(0.001)^2} = 817 \,\Omega$$

In both cases, the kinetic resistances are higher. However, the resistances for the microelectrode are much larger. Resistance relates the current (I) and the voltage (V), not the current density to the voltage. The resistances are much higher for the microelectrode because it is so much smaller and thus takes a much higher voltage to provide the same current (I).

- b. Essentially all of the ohmic loss occurs at the microelectrode (within 10-20 radii of the electrode). Therefore, the ohmic losses associated with that electrode essentially represent the total ohmic loss.
- c. Use of a large counter electrode reduces its influence on the experiment by reducing kinetic losses ohmic losses and double layer capacitance effects. It is frequently a good idea to use a large counter electrode.

```
In [76]: from numpy
                                 import *
         from scipy.optimize
                                 import *
         from matplotlib.pyplot import *
         %matplotlib inline
         #input data
         np = 100
                                               #number of frequency points used (log
          spaced)
         ro = 0.001
                                               #electrode radius m (1 mm)
         R = 8.314;
                                               #Gas constant J/mol-K
         T = 298;
                                               #Temperature K
         F = 96485;
                                               #Faraday's Constant C/mol
                                               #conductivity S/m
         kappa=10;
         cdl = 0.1;
                                               #specific capacitance F/m^2
         inot = 10;
                                               #exchange current density A/m^2
         D = 1.e-9;
                                               #diffusivity m^2/s
         co = 10;
                                               #mol/m^3
         Area = pi*ro**2.
                                               #electrode area m^2
         C = cdl*Area
                                               #capacitance, F
         Rohm = 1/(4.*kappa*ro)
                                               #resistance to 1mm electrode (assumes
          other electrodes at infinity)
         Rf = R*T/(F*inot*Area)
                                               #kinetic resistance (linear kinetics,
          alphas add to 1)
         def zcircuit(w):
                                              #w = frequency rad/s
             zc = 1./(w*C*1j)
                                              #impedance for capacitor
             zw = R*T/(F**2*Area*D*co)*sqrt(D/(1j*w))
                                                        #warburg
             zcir = Rohm+1./(1./(Rf+zw)+1./zc); #calculate impedance for circuit o
         hms
             return zcir;
                                              # return circuit impedance
         w=logspace(-2,8,np);
                                             #define frequency vector using log spac
         ing because of large range of w
         z=zcircuit(w);
         x=z.real;
         y=-z.imag;
         a=abs(z);
         ar=-y/x
         p=[None]*np
         for i in range(0,np):
             p[i]=degrees(arctan(ar[i]));
         #set up two plots
         figure(figsize=(5,4))
         plot(x,y,'k-');
         rc("font",size=10);
         ax = gca()
         xlabel(r'Real(Z)', size=16);
         ylabel(r'-Im(Z)',size=16);
         gcf().subplots_adjust(bottom=0.20);
         savefig('ch6_6_10_nyquist.jpg')
         fig=figure(figsize=(5,4))
         ax = fig.add_subplot(111)
         lns1=ax.plot(w,a,'k-',label='Magnitude');
         rc("font",size=10);
         ax = gca()
         ax.set_xscale('log')
         xlabel(r'Frequency (rad/s)', size=16);
         ylabel(r'Amplitude',size=16);
         ax2 = ax.twinx()
         lns2=ax2.plot(w,p,'k--',label='Phase');
         ax2.set_ylabel(r'Phase',size=16)
         ax2.set_ylim(-90, 40)
         lns = lns1 + lns2
         labs = [l.get_label() for l in lns]
         ax.legend(lns, labs, loc=9)
         gcf().subplots_adjust(bottom=0.20);
```

savefig('ch6_6_10_bode.jpg')





EIS data were taken for a system at the open circuit potential. Given the Nyquist diagram below,

- a. Estimate the ohmic resistance
- b. Estimate the kinetic resistance
- c. Is it likely that the experimental system included convection? Why or why not?



- a) Ohmic resistance can be estimated by "completing" the semicircle at the left side of the diagram. The value is approximately 1 ohm.
- b) By continuing the semicircle on the right side, the sum of the kinetic and ohmic resistances is approximately 7.5 Ohm. Therefore, the kinetic resistance is 6.5 Ohm.
- c) The diagram on the low frequency side does not continue linearly, but tapers off. This is reflective of a mass transfer layer with a finite thickness, and is likely the result of convection.

When measured about the open-circuit potential, the kinetic resistance is frequently larger than the ohmic resistance. However, for systems where mass transfer is not limiting, the ohmic drop inevitably controls at high current densities.

- a. Given that the relative magnitude of the ohmic and kinetic resistance at high current densities has changed, is this because the ohmic resistance has increased or because the kinetic resistance has decreased? Please justify your response.
- b. For the resistance that changed (kinetic or ohmic), please derive a relationship that describes how that resistance depends on the value of the current density.
- a) The ohmic resistance stays constant. In other words, the ratio between the voltage drop in solution and the current density is a constant.

In contrast, the rate of the kinetic reaction is an exponential function of potential. Therefore, the apparent resistance decreases with increasing potential.

b) Assume Tafel Kinetics

$$i = i_o \exp\left(\frac{\propto_a F}{RT}(V - U)\right)$$
$$\frac{di}{dV} = \frac{i_o \propto_a F}{RT} \exp\left(\frac{\propto_a F}{RT}(V - U)\right)$$
$$\frac{di}{dV} = \frac{1}{A_{elec}R_\Omega} = \frac{\alpha_a F}{RT}i$$
$$\therefore R_\Omega \propto \frac{1}{i}$$

The kinetic resistance is inversely proportional to the current, and therefore decreases with increasing current density.

Problem 6.15

The following data were taken with a RDE operating at the limiting current for a range of rotation speeds. The radius of the disk is 1 mm, and the reaction is a two-electron reaction. Assume a kinematic viscosity of 1.0×10^{-6} m² s⁻¹. The concentration of the limiting reactant is 25 mol m⁻³. Please use a Levich plot to determine the diffusivity from the data given. Make sure that all quantities are in consistent units.

n	2 eq/	/mol			
F	96485 C/	eq		Area	3.14159E-06 m2
r	1 mr	n	0.001 m		
v	1.00E-02 cm	n2/s	1.00E-06 m2/s		
с	25 mc	ol/m3			
Speed (rpm) s	sqrt omega I (u	uA)]	I (A/m2)		
100	3.24	104	33.10		
500	7.24	230	73.21		
1000	10.23	325	103.45		
1500	12.53	404	128.60		
2000	14.47	470	149.61		
2500	16.18	520	165.52		
3000	17.72	565	179.85		
3500	19.14	607	193.21		
4000	20.47	660	210.08		
Slope	10.207				
D^(2/3)	3.4125E-07				
D	1.9935E-10 m2	2/s			



Illustration 6-6 is a Koutecký-Levich for oxygen reduction in water, where the bulk concentration is the solubility of oxygen in water as given in the problem. These data represent oxygen reduction in acid media, and the potential values given are relative to SHE. The equilibrium potential of oxygen is 1.23 V vs. SHE under the conditions of interest.

- a. Using the data from the illustration, calculate the rate of reaction for oxygen at the bulk concentration at each value of the overpotential given in the illustration.
- b. Determine the exchange-current density and Tafel slope assuming Tafel kinetics.
- c. What assumption was made regarding the concentration dependence of i_o in the analysis above? Is the assumption accurate for oxygen reduction?

Rotation	rate	$1/W^{0.5}$	i, A/m ²	1/i	i, A/m ²	1/i	i, A/m ²	1/i	i, A/m ²	1/i
rate, rpm	rad/s		0.7V		0.65V		0.6V		0.4V	
2500	262	0.06178021	13.33	0.0750188	20.41	0.048996	26.67	0.03749531	45.45	0.022
1600	167	0.07738232	12.66	0.0789889	19.23	0.052002	24.69	0.04050223	38.46	0.026
900	94.2	0.10303257	11.9	0.0840336	17.39	0.057504	22.22	0.0450045	31.75	0.0315
400	41.9	0.15448737	10.53	0.0949668	14.71	0.067981	18.18	0.0550055	23.81	0.042
0	Intercept			0.0621703		0.036225		0.02581899		0.00921



U 1.23 Intercept data i vs. V 7.17E-01 Tafel Slope 0.377 io f h i_intercept i fit error (normalized) 0.4 -0.83 108.530241 114.06 -5.09E-02 0.6 -0.63 38.7311838 33.62 1.32E-01 0.65 -0.58 24.77 27.6055235 1.03E-01 0.7 -0.53 16.0848593 18.25 -1.35E-01 4.87E-02 sumsqerror

Analysis assumes that the concentration dependence is first order. This is not necessarily correct.

Problem 6.17

Suppose that you have a disk-shaped microelectrode that is 100 μ m in diameter. At what value of time would the electrode be within 1 % of its steady-state current density? At what value of time would the electrode be within 10 % of its steady-state current density? What is the value of the limiting current at steady state in amperes? Assume a two-electron reaction with a diffusivity of 1×10^{-9} m² s⁻¹ and a bulk concentration of 25 mM.

d n F D Cb a	100 um 2 eq/mol 96485 C/eq 1.00E-09 m2/s 25 mM 0.00005 m	$i(t) = \frac{4nFD_i c_i^{\infty}}{\pi a} + \frac{\frac{8}{\pi^2} nFD_i^{0.5} c_i^{\infty}}{\sqrt{\pi t}}$ mol/m3
Steady-	state current	
i	122.8 A/m2	Equation 6-68 (steady portion only)

Desire time (t) where the transient term in the equation is 1% of the steady-state value

$$\frac{\frac{8}{\pi^2} nFD_i^{0.5} c_i^{\infty}}{\sqrt{\pi t}} = 0.01 \text{(steady-state current)}$$

Ι	9.65E-07 A	(just under a microamp)
I Area	= i*Area 7.85398E-09 m^2	
t t	0.54 minutes	Time to 10% of steady state
t	27 c	
t t	53.8 minutes	Time to 1% of steady state
t	3225 s	

You have been asked to design a disk-shaped microelectrode for use in kinetic measurements. You need to make measurements up to a maximum current density of 15 mA cm⁻². The concentration of the limiting reactant in the bulk is 50 mol m⁻³, and its diffusivity is 1.2×10^{-9} m² s⁻¹. The conductivity of the solution is 10 S m⁻¹. Assume a single-electron reaction.

- a. What size of microelectrode would you recommend? Please consider the impact of the limiting current and the uniformity of the current distribution.
- b. What would the measured current be at the maximum current density for the recommended electrode?

Hint: Can you do kinetic measurements at the mass transfer limit? How does this affect your response to this problem?

a. The size of the electrode depends on how you decide to constrain the problem. For example, if you want to perform kinetic measurements up to a current density of 15 mA/cm2 at a surface concentration that does not change more than 10%, then you would need to operate at no more than 10% of the limiting current as per equation 6-70. Therefore,

a.
$$\frac{i}{i_{lim}} = 0.1 \qquad i_{ln} = \frac{15\frac{\text{mA}}{\text{cm}^2}}{.1} = 150\frac{\text{mA}}{\text{cm}^2}$$
$$a = \frac{4nFD_ic_i^{\infty}}{\pi i_{lim}} = 4.91 \times 10^{-6} \text{ m}$$
$$\text{radius} \approx 5 \,\mu\text{m}, \text{ diameter} \approx 10 \,\mu\text{m}$$

If, on the other hand, you are willing to account for the surface concentration and take measurements at different concentrations, you can take measurements up to the limiting current, although concentrations near the limiting current will be low and the tertiary current distribution will not be uniform for a disk electrode. At 90% of the limiting current

$$a = \frac{4nFD_i c_i^{\infty}}{\pi i_{lim}} = 4.42 \times 10^{-5} \text{m}$$

Radius $\approx 44 \text{ }\mu\text{m}$
Diameter $\approx 88 \text{ }\mu\text{m}$

Wa evaluates the uniformity of the secondary current distribution. To be conservative, we evaluate Wa for the largest electrode using the diameter as the characteristic length. For a current density of 15 mA/cm², assuming Tafel kinetics and an alpha value of 0.5 (see Chapter 4), the 88 micron electrode yields

$$Wa = \frac{RT\kappa}{diam F} \frac{1}{i_{avg}\alpha_c} \approx 400$$

Chapter 6

This indicates that the secondary current distribution is nearly uniform.

b. The magnitude of the current is typically an issue of concern for microelectrodes. For the smaller electrode in (a) above,

$$I = i_{max} \pi r^2 = 1.14 \times 10^{-8} \text{A or about 10 nA}$$

This represents the maximum current, and is very small indicating one of the difficulties with use of an electrode close to 10 microns in diameter.

Derive an expression for the ratio of the iR drop associated with a microelectrode to that associated with a large electrode. Each of these two working electrodes (the microelectrode and the large electrode) is tested in a cell with the same current density at the electrode surface, and with the same reference electrode and counter electrode. Assume that any concentration effects can be neglected and that the current distribution is one-dimensional for the large electrode. Also assume that the distance L from the working electrode to the reference electrode is the same in both cases, and that L is large enough to be considered at infinity relative to the microelectrode.

Resistance for microelectrode disk

$$R_{\Omega} = \frac{1}{4\kappa a}$$

Where a is the disk radius. Assuming that the disk is sufficiently small so that the reference and counter electrodes are at infinity.

$$\Delta V_{microelectrode} = IR_{\Omega}$$
$$= iA_d R_{\Omega}$$
$$= \frac{iA_d}{4\kappa a}$$

For a large electrode located a distance L from the reference electrode.

$$R_{\Omega} = \frac{L}{\kappa A_{L}}$$
$$\Delta V_{large} = IR_{\Omega}$$
$$= \frac{iA_{L}L}{\kappa A_{L}} = \frac{iL}{\kappa}$$
$$\frac{\Delta V_{disk}}{\Delta V_{large}} = \frac{\frac{iA_{d}}{4\kappa a}}{\frac{iL}{\kappa}} = \frac{A_{d}}{4aL}$$
Given $A_{d} = \pi a^{2}$
$$\frac{\Delta V_{disk}}{\Delta V_{large}} = \frac{\pi a^{2}}{4aL} = \frac{\pi a}{4L}$$

The ΔV_{disk} at the same current density is much smaller. The ratio scales approximately as $\frac{a}{r}$

Qualitatively sketch the current response of a microelectrode to a slow voltage scan in the positive direction from the open-circuit potential. Assume that the solution contains an equal concentration of the reduced and oxidized species in solution. How does this response differ from that of a typically sized electrode? Please explain. Hint—What is the steady-state behavior of a microelectrode and how might this impact the shape of the CV curve?

There are two or three things about a microelectrode that make it different in a scan. The first is that the current will be much lower due to the small size of the electrode. Second, the current reaches a steady-state even under diffusion conditions (see Sec. 6-10). The third is that the time constant to reach steady-state is relatively fast. Because of these characteristics, the CV curve will reach a flat value, and show much less hysteresis on the return scan as the curve will tend to approach the steady-state value.



(Note- a fast scan may show a slight peak prior to flattening out. However, it will still flatten out, while a large electrode continues to decline). You need to measure the reduction kinetics of a reaction where the reactant is a soluble species. The reaction is a single electron reaction. The diffusivity is not known. As you answer the following, please include the equations that you would use and consider the implications of both mass transfer and the current distribution.

- a. Can a rotating disk electrode be effectively used to make the desired measurements? If so, how would you proceed? If not, why not?
- b. Is it possible to use a microelectrode to measure the quantities needed to determine the reduction kinetics? If so, how would you proceed? If not, why not?
- c. What are the advantages and disadvantages of the two methods? Which would you recommend? Please justify your response.
- d. What role, if any, does a supporting electrolyte play in the above experiments?
- a. A rotating disk electrode can be used for the desired kinetic measurements provided that the range of current densities of interest is below the limiting current. The limiting current can be increased by changing the rotation rate. The procedure might be:
 - 1) Determine the diffusivity with use of experiments at the limiting current and different rotation rates. The current is related to the diffusivity by

$$i = 0.62 n F D^{2/3} \Omega^{1/2} v^{-1/6} c^{\infty}$$

and a Levich plot can be used to find D_i.

2) Perform the kinetic measurements below the limiting current density. If the maximum current density at which a measurement is made is less than about 10% of the limiting current, then the bulk concentration can be used without introducing much error. Otherwise, the surface concentration needs to be determined as used as part of the analysis of the kinetics. The surface concentration can be estimated from

$$i = 0.62nFD^{2/3}\Omega^{1/2}\nu^{-1/6}(c^{\infty} - c_i)$$

where c_i is the concentration at the surface.

- 3) Note that although the mass transfer limited current is uniform with a rotating disk electrode, the secondary distribution is not necessarily uniform and may have an adverse impact on the accuracy of the results obtained. The uniformity of the secondary current distribution should be checked with use of Wa. Reduction of the disk size can improve uniformity.
- 4) Depending on the length of the experiments and the container size, etc., one should make sure that the bulk concentration does not change appreciably during the experiment.

- b. The same principles mentioned for the RDE also apply to a microelectrode.
 - 1) Measurements should be performed below the limiting current density, which can be estimated by

$$i_{lim} = \frac{4nFD_ic_i^{\infty}}{\pi a}$$

for a disk electrode, assuming that the transient time constant is fast for the small electrode.

- Perform the kinetic experiments below the limiting current density. In most cases, the limiting current density should be sufficiently high that the desired measurements can be made without the need to make a concentration correction. In needed, a correction for concentration can be made, although the concentration distribution at a disk electrode is not uniform.
- 3) The secondary current distribution should be checked, but will likely be close to uniform for a very small electrode. Ideally, you should size your electrode so that this is so. Use the Wa number to guide you.
- c. The microelectrode will generally permit measurements at higher current densities. The disadvantage of the microelectrode is the small magnitude of currents that must be measured accurately. The RDE system is also a bit more complex to operate.
- d. The above measurements and analyses do not account for the impact of migration, which will influence transport in the absence of a supporting electrolyte. This may impact your experiments under certain conditions, but is not likely to be a significant factor in situations where kinetic limitations dominate. Still, you should check its impact in situations where a supporting electrolyte is not used.

Problem 6.22

A CV experiment is performed using a microelectrode with a diameter of 100 µm at room temperature. The potential is swept anodically at ν =10 mV/s. The double layer capacitance is 0.2 F/m². Recall that the charging current is $i_c = \nu C_{DL}$. The diffusivity of the electro-active species is 3×10^{-9} m²/s. Assume that the fluid is stagnant. The concentration of the redox species is 100 mol/m³ and the solution conductivity is 10 S/m. From the data for a sweep in the positive direction, determine the exchange-current density and the anodic transfer coefficient. The potentials are measured relative to a SCE reference electrode located far away from the microelectrode. The equilibrium potential of the reaction relative to SHE is 0.75V.

n	1		
D	3.00E-09 m2/s		
v	10 mV/s		
a	5.00E-05 m	50) mm
cbulk	100 mol/m3		
Cdl	0.2 F/m2		
Κ	10 S/m		
U	0.75 V	Hydrogen	
U	0.506 V	SCE	(assumes SCE at 0.244 V)

Data

V (SCE)	I (nA)
0.600	0.50
0.650	1.35
0.700	3.30
0.750	9.10
0.800	25.00
0.850	62.50
0.900	168.00
0.950	425.00
1.001	1200.00
1.052	3150.00
1.104	8000.00

Since we want kinetic data, want to be no more than about 10% of the mass transfer limit. This will give us kinetic values at the bulk concentration.

Calculate the mass transfer limit i 737 A/m2 (current at mt limit- SS)

Use data in Tafel region to fit parameters Equilibrium voltage is ~0.5, values should be > 0.6

			= IR $=$ I/4K	la			
V (SCE)	I (nA)	i (A/m2)	i (cap) A/m2	i (kinetic)	ln i	V(ohmic)	Eta
0.600	0.50	0.06	0.002	0.06	-2.7861	2.50E-07	0.094
0.650	1.35	0.17	0.002	0.17	-1.7726	6.75E-07	0.144
0.700	3.30	0.42	0.002	0.42	-0.8719	1.65E-06	0.194
0.750	9.10	1.16	0.002	1.16	0.14553	4.55E-06	0.244
0.800	25.00	3.18	0.002	3.18	1.15723	1.25E-05	0.294
0.850	62.50	7.96	0.002	7.96	2.07389	3.13E-05	0.344
0.900	168.00	21.39	0.002	21.39	3.06285	8.40E-05	0.394
0.950	425.00	54.11	0.002	54.11	3.99103	2.13E-04	0.444
1.001	1200.00	152.79	0.002	152.79	5.02904	6.00E-04	0.495
1.052	3150.00	401.07	0.002	401.07	5.99413	1.58E-03	0.546
1.104	8000.00	1018.59	0.002	1018.59	6.92617	4.00E-03	0.598
		_			Ν	Not significa	nt



 Slope
 19.38711

 Intercept
 -4.591

a_a 0.498 i_o 0.010 A/m2 Chapter 6

Given an elementary single-electron reaction described by the following kinetic expression

$$i\left[\frac{A}{\mathrm{m}^{2}}\right] = 10.0 \left(\frac{c_{ox,\mathrm{surf}}}{c_{ox,\mathrm{bulk}}}\right)^{0.5} \left(\frac{c_{red,\mathrm{surf}}}{c_{red,\mathrm{bulk}}}\right)^{0.5} \left[\exp\left(\frac{0.5F\eta_{s}}{RT}\right) - \exp\left(-\frac{0.5F\eta_{s}}{RT}\right)\right],$$

where the bulk concentration of each of the two reactants is 50 mM. You are to use a rotating disk electrode to measure the current density as a function of V for two different disk sizes, one with a 10 mm diameter, and a second with a diameter of 1 mm. V is measured against a SCE reference electrode located more than 5 cm from the disk, and the standard potential of the reaction is 0.1V SCE. Plot the *i* vs. *V* curve for each of the two electrodes for a range of current densities from -150 to 150 A/m^2 at a rotation speed of 500 rpm. Comment on any similarities and differences between the two curves. How does the size of the disk impact the mass transfer and the ohmic losses? You should account for the difference between the surface and bulk concentrations, including its impact on the equilibrium potential. Hint- it is easier to start with the current than it is with the voltage.

io	10	A/m2		W	500	rpm	52.3599	rad/s			
credb	50	mol/m3		D	1.00E-09	m2/s					Yellow items need to be added to problem statemen
coxb	50	mol/m3		n	1.00E-06	m2/s					
U	0.1	V									
k	10	S/m			Add stoichiomet	ry to probl	em statem	ent			
i = 0.62	$2nFD_i^{2/3}\Omega$	$2^{\frac{1}{2}}v^{-\frac{1}{6}}(c^{\circ})$	$(\sim -c_i)$								
$R_{\Omega,disk}$	$=\frac{V}{I}=\frac{1}{4\kappa a}$		$V = p i r_{o'}$	4k	formula to calcu	late ohmic	drop in so	lution			
						10 mm dis	1 mm disk	ζ	10 mm	1 mm	
i	coxsurf	credsurf	U	Vsurf	solver	V (ohmic)	V (ohmic)	Usurf - Ubul	V	V	
150) 84.65	15.35	0.14387	0.29987	-3.5929E-05	0.0589	0.00589	0.0438713	0.40265	0.34964	
100) 73.10	26.90	0.12569	0.2505	-2.72343E-05	0.03927	0.00393	0.0256862	0.31546	0.28012	
20) 54.62	45.38	0.10476	0.15018	4.87319E-06	0.00785	0.00079	0.0047617	0.1628	0.15573	
5	5 51.16	48.84	0.10119	0.1139	-6.71241E-07	0.00196	0.0002	0.0011872	0.11705	0.11528	
1	1 50.23	49.77	0.10024	0.1028	1.64577E-09	0.00039	3.9E-05	0.0002374	0.10343	0.10308	
0.1	1 50.02	49.98	0.10002	0.10028	-2.09037E-09	3.9E-05	3.9E-06	2.374E-05	0.10034	0.10031	
C) 50.00	50.00	0.1	0.1	0	0	0	0	0.1	0.1	
-0.1	49.98	50.02	0.09998	0.09972	-8.32158E-05	-4E-05	-4E-06	-2.374E-05	0.09966	0.09969	
-1	1 49.77	50.23	0.09976	0.0972	2.01217E-12	-0.0004	-4E-05	-0.0002374	0.09657	0.09692	
-5	5 48.84	51.16	0.09881	0.0861	3.58913E-12	-0.002	-0.0002	-0.0011872	0.08295	0.08472	
-20) 45.38	54.62	0.09524	0.04982	-1.04359E-05	-0.0079	-0.0008	-0.0047617	0.0372	0.04427	
-100) 26.90	73.10	0.07431	-0.0505	-1.48546E-05	-0.0393	-0.0039	-0.0256862	-0.1155	-0.0801	
-150) 15.35	84.65	0.05613	-0.0999	-2.05151E-05	-0.0589	-0.0059	-0.0438713	-0.2027	-0.1496	
	200							_			
	150		- 10 mm dis	k							
								1			



Notes

- 1) Start by specifying the current density, which simplifies the solution of the problem.
- Once the current density is known, the surface concentration can be calculated with the RDE equation 2)
- 3) With the current density and the surface concentration, the equilibrium potential at the surface and the applied voltage can be determined. I used the solver (line-by-line) to do this.
- 4) With the current density, the equation for the disk can be used to estimate the ohmic drop (do for both sized disks)
- Calculate the difference in the equilibrium potential between the surface and the bulk 5)
- 6) Can finally calculate the value of the "measured" potential and plot the requested i vs. V curves

```
In [8]: from numpy
                               import *
        from matplotlib.pyplot import *
        from math
                               import *
        %matplotlib inline
        #constants
        R = 8.314;
                                              #Gas constant J/mol-K
        T = 298.15;
                                              #Temperature K
        F = 96485;
                                              #Faraday's Constant C/eq
        #input data
        Dox = 1.e-5
                                              #Diffusivity cm^2/s
        Dred = 1.e-5
                                              #Diffusivity cm^2/s
        L = 1.0;
                                              #Domain Length cm
        Nx = 200
                                              # x grid points
        cfl = 0.5
                                              # maximum value for stability
        cox = 0.0
                                              #Initial concentrations (M)
        cred = 0.100
        neq = 1
                                              #eq./mol for species of interest
        Unot = 0.7
        Estart = 0.3
        Eend = 1.1
        vscan = 0.005
                                              # V/s (use negative for negative scan
        tend = (Eend-Estart)/vscan
                                              # end time(s)
        # define spatialgrid
        x = linspace(0, L, Nx+1)
                                              # mesh points in space
        dx = x[1] - x[0]
                                              # calculate dx (evenly spaced)
        # time step definition
        D = min(Dox, Dred)
                                              #use minimum D for timestep calcs
                                              \# stable time step (half of maximum \boldsymbol{v}
        dt = dx^{*2/D/2.*cfl}
        alue)
                                              # number of time steps
        Nt = int(ceil(tend/dt));
        t = linspace(0, tend, Nt+1)
                                             # mesh points in time
        FFox = dt*Dox/dx**2
                                            #ratio of parameters for oxidation equ
        ation
        FFred = dt*Dred/dx**2
                                             #ratio of parameters for reduction equ
        ation
        #define and initialize (zero) arrays
        u = zeros(Nx+1)
                                               # unknown cox at new time level
        u_1 = zeros(Nx+1)
                                              # cox at the previous time level
        uu = zeros(Nx+1)
                                              # unknown cred at new time level
        uu_1 = zeros(Nx+1)
                                               # cred at the previous time level
                                               # current density calculated from fl
        cur = zeros(Nt+1)
        uх
        # Set initial condition u(x,0) = cox, uu(x,0) = cred
        for i in range(0, Nx+1):
            u_1[i] = cox
            uu_1[i] = cred
        # Time loop (explicit integration of equations- no iteration required)
        for n in range(0, Nt+1):
            # Compute u at inner mesh points
            for i in range(1, Nx):
                # Calculate new concentrations based on values from previous time
        step
                u[i] = u_1[i] + FFox*(u_1[i-1] - 2*u_1[i] + u_1[i+1])
                uu[i] = uu_1[i] + FFred*(uu_1[i-1] - 2*uu_1[i] + uu_1[i+1])
            # Insert boundary conditions far away from surface
            u[Nx] = cox
            uu[Nx] = cred
            # Boundary condition at surface- calculate concentrations from applied
         potential and flux B.C.
            E = Estart + vscan*t[n]
            ratio = exp(neq*F/R/T*(E-Unot))
            uu[0] = (uu[1]+Dox/Dred*u[1])/(Dox/Dred*ratio+1)
            u[0]=uu[0]*ratio
```

Out[8]: <matplotlib.text.Text at 0x8d9f9f0>

