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Exercise Series 6

Due date: Dec. 1, 2006

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1) Clear concepts and terminology:
Sort out the following terms and briefly explain the underlying concepts (a question like this should be an easy bringer of points in any exam and, anyway, in your future life as an electrochemist!!) – try to be clear and concise in your answers (use equations in answers if appropriate)!

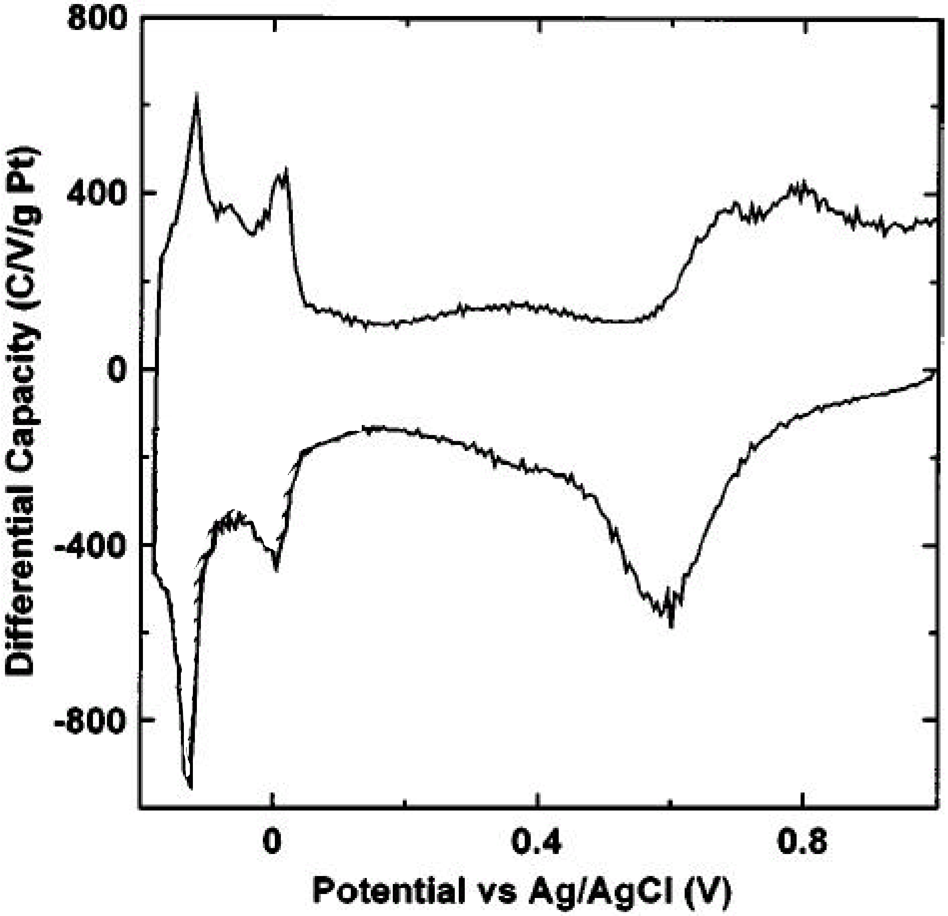
a) Ideally polarizable electrode – ideally nonpolarizable electrode
b) Working electrode – reference electrode
c) Faradaic current – capacitive current
d) Reversible reaction – irreversible reaction
e) Compact layer – diffuse layer
f) Activation control – diffusion control
g) Equilibrium – non-equilibrium
h) Steady state performance – transient performance

If you search the lecture notes, you could probably find many more terms that could be listed here. Let's leave it at that for now!

2) Cyclic voltammetry is used for the electrochemical characterization of carbon-supported platinum electrocatalysts for PEM Fuel Cells. Since platinum is an expensive material (limited resources) the search for advanced catalysts with high active area is a foremost objective in fuel cell research. In this problem we will explore how CV could be used for the determination of the catalyst surface area by adsorption and desorption of protons. The following figure, taken from *D. A. Stevens and J. R. Dahn, J. Electrochem. Soc., Volume 150, Issue 6, pp. A770-A775 (June 2003)*, shows the CV of a Pt electrode (Pt nanoparticles supported on a carbon substrate) in 0.1 M $HClO_4$.

(a) Indicate in this figure the scan direction. Label the regions that correspond to different interfacial processes (adsorption/desorption, double layer charging, charge transfer).

Note that in this plot currents are normalized to the scan rate and to the mass of Pt, m_{Pt}. The current axis displays the property $I/(v\ m_{Pt})$ instead of just I. Due to this normalization we will not need to know the value of the sweep rate for the following calculations. Can you explain why?

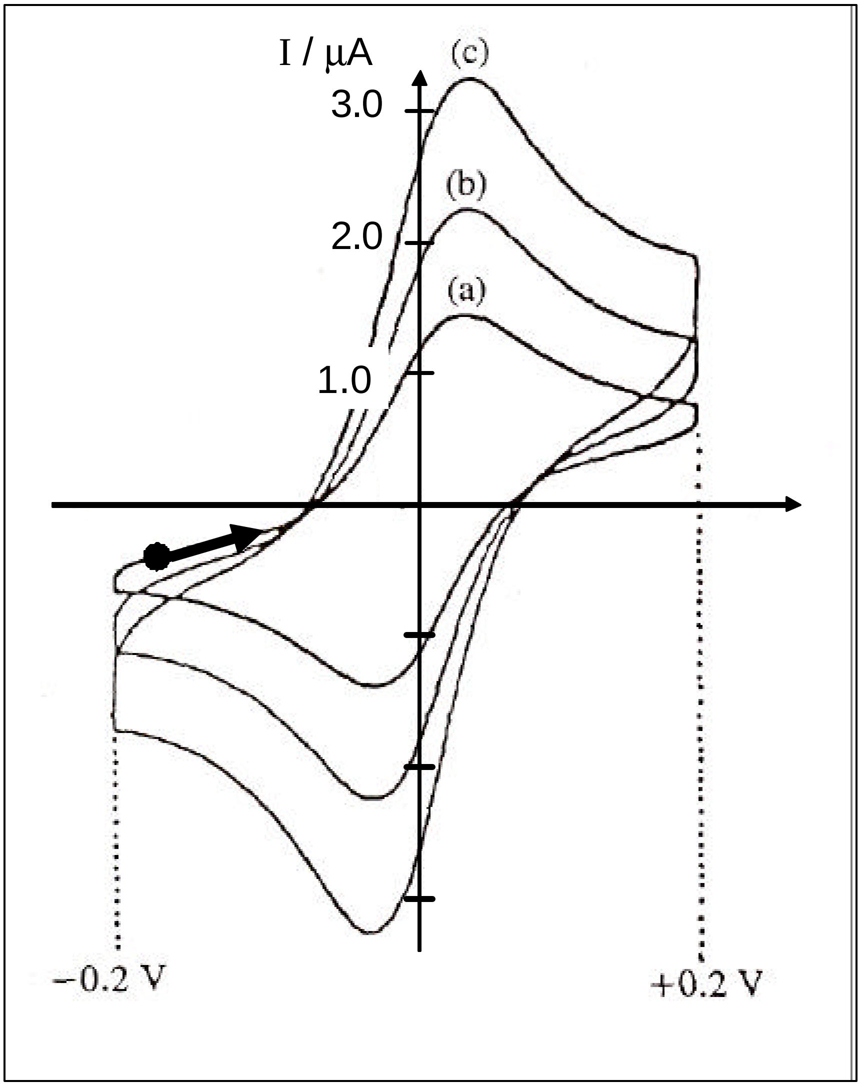


(b) Use the capacitive region to determine the total double layer capacitance of the electrode, normalized to m_{Pt}, i.e. determine $C_{\text{dl}}^{\text{el}}/m_{\text{Pt}}$. Assume a specific capacity of $C_{\text{dl}} = 20\ \mu\text{F cm}^{-2}$ in order to estimate the total surface area $A^{\text{total}}/m_{\text{Pt}}$ (normalized to m_{Pt}) that contributes to double layer charging.

(c) Indicate the hydrogen adsorption region in the plot. Take into account that you have to correct for capacitive currents. This region encompasses several peaks. Explain why! From the total area of the H_{ad} adsorption region (including all relevant peaks) estimate the total surface area of the catalyst (normalized to m_{Pt}) that contributes to hydrogen adsorption. Use the proportionality constant $210\ \mu\text{C cm}^{-2}$ that corresponds to the amount of charge transferred upon adsorption of one monolayer of hydrogen at a platinum surface.

(d) Compare the surface areas determined in (b) and (c) and discuss the difference (if any).

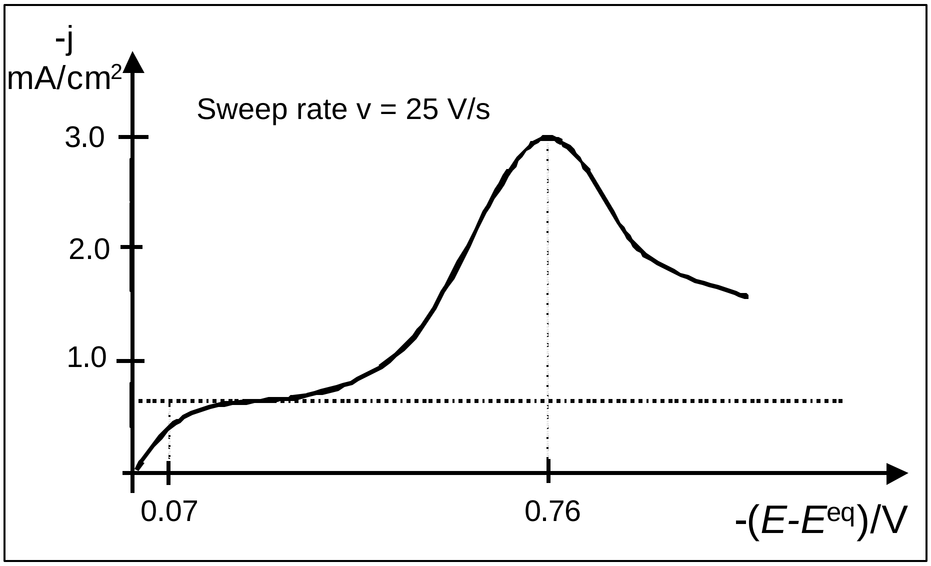
3) The following picture shows **cyclic voltammograms** of horse heart ferricytochrome c (5 mg cm^{-3}, molar mass 11702 g) in NaClO4 (0.1 M), phosphate buffer (0.02 M) at pH 7 in the presence of 4,4'-bipyridyl (10^{-2} M). The working electrode was a (flat) gold disk of 1.7 mm radius. The 4,4'-bipyridyl forms an adsorbed conducting monolayer on the gold surface and, thereby, enables direct electron transfer to take place between the electrode and the ferricytochrome c. The reference electrode was a saturated calomel electrode. The sweep rates were (a) 20 mV s^{-1}, (b) 50 mV s^{-1}, (c) 100 mV s^{-1} [from *M.J. Eddowes et al., JACS 101, 4462, 1979*].



a) What type of cyclic voltammogram is this? Write down the criteria on which your answer is based. What type of current is observed (capacitive, faradaic or adsorptive)?
b) Label in the plot the position of the half-wave potential, the peak potentials and the peak currents. Indicate the anodic and cathodic regions.
c) Start at the position indicated by the dot and follow the CV in the direction of the arrow. Explain why the current passes through zero at a potential negative of the origin. As the current density increases further, explain the occurrence of the peak.
d) What type of electron transfer process is the oxidation/reduction of the ferricytochrome c, i.e. how many electrons are being transferred? What can you say about the rate constant of this reaction (is it a fast or a slow reaction)?
e) Determine the diffusion coefficient of ferricytochrome c in the solution.
f) Is that it? What would you suggest to do to find $\boldsymbol{k}^{0}$ and a from cyclic voltammetry?

Additional practice problem (as discussed in tutorial):

1) The following CV has been measured for an irreversible (!) reaction (cathodic sweep direction). The sweep rate is 25 V/s, as indicated in the figure. The concentration of electroactive species in the bulk is 0.76 mM. Assume a diffusion coefficient $\boldsymbol{D} = \mathbf{1.0 \times 10^{-5}\,cm^2 s^{-1}}$. The number of electrons transferred in the reaction is $\boldsymbol{n} = \mathbf{1}$.



This plot contains, as you know, a vast amount of information, which is good in general, since we can learn a lot about the electrode/solution system and reactions therein. Extracting this information is, however, cumbersome. But as you will hopefully see: it is worth the effort! We will go through the calculations systematically.

a) Identify the capacitive current density (j_C) and the faradaic peak current density ($j_{p,c}$) in this plot. Determine these values as accurately as possible.
b) Calculate the double layer capacitance from j_C.
c) The potential that corresponds to the double layer charging time is indicated in the plot (0.07 V). Use the known sweep rate to calculate the double layer charging time. Now you can use this time and the value of the double layer capacitance to calculate the uncompensated solution resistance (in [? ?m^2]).
d) The reference electrode is placed at a separation of 5 mm in front of the working electrode. What is the conductivity of the electrolyte solution (in [S cm^{-1}])?
e) Now, let's focus on the faradaic processes. Use the relation for $j_{p,c}$, as given in the lecture, to calculate the cathodic transfer coefficient a.

f) The peak potential E_p is indicated in the plot. Use this value of E_p and the previously determined value of a to calculate the rate constant k^0 of this reaction. Considering this value of k^0, would it be possible to perform a reversible CV scan with this system? What would be the required scan rate?

g) Now, give your recommendations: what would you suggest to do in order to reduce the capacitive current? What would you do to reduce the effect of the uncompensated solution resistance? Compared to a reversible CV, what are the advantages of performing the CV in the irreversible region?