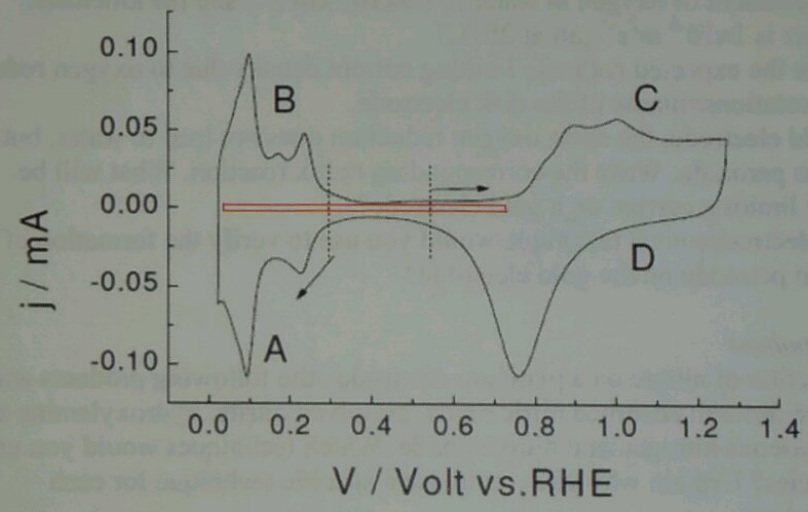
Electrochemistry Exam 13 March 2018, 9:00 – 11:00, room DM1.19

Question 1 (10 points)

(a) Given that the standard equilibrium potentials for the Cu^{2+}/Cu and the Cu^{+}/Cu redox couples are 0.38 and 0.52 V vs. NHE, calculate the standard equilibrium for the Cu^{2+}/Cu^{+} redox couple.

(b) The solubility product of $Cu(OH)_2$ is 2.2×10^{-20}. Draw a potential-pH diagram showing the stability regions of Cu, Cu^{2+} and $Cu(OH)_2$, at standard conditions.

Question 2 (10 points)



The figure shows the "blank voltammetry" of a platinum electrode in sulfuric acid. Describe what happens in regions A, B, C and D, and in which potential window you would determine the double-layer capacity of platinum.

If we adsorb a monolayer of carbon monoxide onto the platinum electrode, we observe that the voltammogram changes to the red curve in the figure. Explain why the CV looks like this in the presence of adsorbed CO.

Question 3 (10 points)

The oxidation of chloride ions to chlorine gas $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ has a standard equilibrium potential of 1.358 V vs. NHE.

(a) On certain catalysts we find a Tafel slope ($\ln j$ vs. E) of 30 mV/dec ; on other catalysts the Tafel slope is closer to 120 mV/dec. Give mechanisms that explain these Tafel slopes. What can you say about the strength with which the chloride intermediate binds to the electrode surface for these two mechanisms ?

(b) Is the equilibrium potential of the chloride to chlorine reaction pH dependent when referred to the RHE (Reversible Hydrogen Electrode) potential scale ?

Question 4 (10 points)

The reduction of oxygen ($O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$) is studied at a platinum rotating disk electrode in a perchloric acid solution. The solubility of oxygen in water is 1.3 mM, the diffusion coefficient of oxygen in water is $1.9 \times 10^{-5}\ cm^2 s^{-1}$, and the kinematic viscosity of water is $1 \times 10^{-6}\ m^2 s^{-1}$ (all at 25 ^{0}C).

(a) Calculate the expected cathodic limiting current density due to oxygen reduction at 1600 rotations/minute of the disk electrode.

(b) On a gold electrode, the same oxygen reduction does not lead to water, but to hydrogen peroxide. Write the corresponding redox reaction. What will be cathodic limiting current on a gold electrode?

(c) Which electrochemical technique would you use to verify the formation of hydrogen peroxide on the gold electrode?

Question 5 (10 points)

During the reduction of nitrate on a platinum electrode , the following products and intermediates are formed: adsorbed nitric oxide, dissolved nitrite, hydroxylamine and ammonia, and gaseous nitrogen and nitrous oxide. Which techniques would you use to detect these species? Explain why you would use a specific technique for each intermediate/product.