Birla Institute of Technology and Science, Pilani, Rajasthan 333031
Comprehensive Examination 1st Semester, 2015-2016

CHEM F327: ELECTROCHEM FUNDA & APPL **(Open Book)** **Max. Marks: 70**
Time: 3 h. **Date: 07.12.2015**

Instructions to the students:

1. There are **six questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. Write brief answers to the point with proper justifications.
4. Do not exchange your book and calculator.

Q.1.a. Figure 1 shows a cyclic voltammograms (CV) for the following electrochemical reaction, taken at v = 10 V/s.

$$R \rightleftharpoons A \text{ and } A + e \rightleftharpoons O$$

(i) What is the approximate concentration of O at the start of the scan (assume, both A and O are soluble and O is initially present at a concentration C_O^* and $C_A^* = 0$)? (ii) Calculate i_p by assuming that the preceding reaction does not affect the behavior, and (iii) compare the result to the observed value of i_p (from Figure 1). The relevant parameters for this problem are as follows: C_R^* = 1mM, $D_R = D_A = D_O = 10^{-5}$ cm^2/s, K = 10^{-3}, A = 1 cm^2, i = 2 μA, m_O = 0.5 cm/s and T = 25 ^{0}C. **[6]**

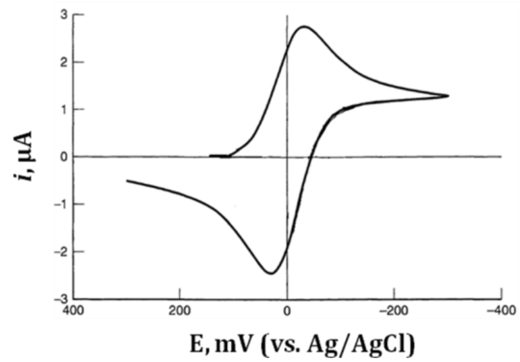

Figure 1

1.b. Consider the following systems:

$$A + e \rightleftharpoons B \quad (E = -0.5 \text{ V } vs. \text{ SCE})$$
$$B \longrightarrow C$$
$$C + e \rightleftharpoons D \quad (E = -1.0 \text{ V } vs. \text{ SCE})$$

Both charge-transfer reactions have large values of $k°$. Draw the expected cyclic voltammograms with proper labeling for scans beginning at 0.0 V *vs.* SCE and reversing at -1.2 V. Show curves for scan rates of 50 mV/s and 20 V/s. **[2+2]**

Q.2.a. 50 mL of a $ZnSO_4$ solution are transferred to an electrolytic cell with a mercury cathode, and enough solid KNO_3 is added to make the solution 0.1 *M* in KNO_3. The electrolysis of Zn^{2+} is carried to completion at a potential of -1.3 V *vs.* SCE with the charge of 241 *C*. Write the electrolysis reaction and calculate the initial concentration of Zn^{2+} ion. **[1+3]**

2.b. Consider the electrolysis of a 0.10 *M* NaOH solution at platinum electrodes, where the reactions are:

$$\text{(Anode) } 2OH^- \longrightarrow 1/2O_2 + H_2O + 2e$$
$$\text{(Cathode) } 2H_2O + 2e \longrightarrow H_2 + 2OH^-$$

Calculate transference number of sodium and hydroxyl ions in the electrochemical solution? [Ionic conductivity, λ_0 (cm^2 Ω^{-1} equiv^{-1}) of Na^+ and OH^- ions are 50.11 and 198, respectively] **[3]**

2.c. A spherical ultramicroelectrode (UME) of radius 13.1 μm is used to measure D_0 for $Ru(bpy)_3^{2+}$ inside a polymer film. The value of D_0 for the one-electron oxidation of $Ru(bpy)_3^{2+}$ is found to be 2×10^{-10} m^2/s. The steady-state current, i_{ss}, for the same UME is 12.0 nA. If critical dimension of the UME is equal to its radius then calculate the concentration of $Ru(bpy)^{2+}$ in the film? **[3]**

Q.3.a. An alternative potentiostatic circuit is shown in Figure 2. What simple amplifier circuit is it based on? Identify the voltage input point and its relationship with voltage output. **[1+1+2]**

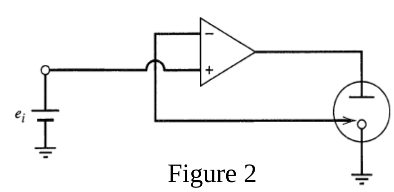

Figure 2

3.b. SECM approach curves (X and Y) for steady-state currents at two different substrate are shown in Figure 3. (i) identify both the substrate (ii) In which of the substrate, oxidation of $Os(bpy)_3^{2+}$ will occur and why? (iii) What are the advantages of SECM in studying this kind of reaction compared to CV. **[1+3+2]**

3.c. To identify the electrode surfaces in an electrochemical environment Scanning Tunneling Microscope (STM) is very useful. Justify your answer in no more than 3 sentences. **[2]**

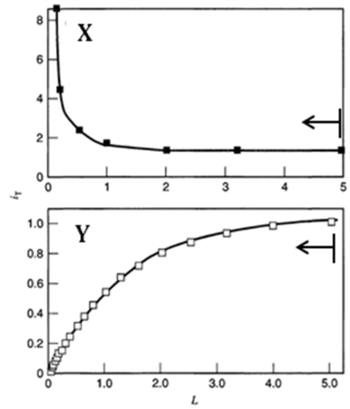

Figure 3

Q.4.a. Consider a semiconductor electrode, ZnO/Pt (ZnO: photo-anode and Pt: cathode), which operates under illumination of UV light. Aqueous acidic solution was used as an electrolyte. Answer the following questions: (i) show the energy level situation of semiconductor electrode and flow of electron between the electrodes (ii) write the probable electrode reactions (cathode and anode). **[3+2]**

4.b. The standard reduction potential ($E°$) value for the following electrode reactions are given below:

$$TMPD^{\bullet +} + e \rightleftharpoons TMPD,\ E^{o} = +0.32\ V$$
$$Py + e \rightleftharpoons Py^{\bullet -},\ E^{o} = -2.00\ V$$

(i) Calculate the free energy released in the reaction, $TMPD^{\bullet +} + Py^{\bullet -} \longrightarrow TMPD + Py$.

(ii) Electrochemiluminescence is observed for first excited singlet, $^{1}Py_{*}$ at 400 nm, comment on the probability of forming $^{1}Py_{*}$ in the reaction between $TMPD^{\bullet +}$ and $Py^{\bullet -}$.
[2+3]

4.c. The most-frequently used ECL-active label is $Ru(bpy)_3^{2+}$**.** Justify your answer with an example. **[2]**

Q.5.a. Calculate the standard potential arising from the reaction in which NADH is oxidized to NAD^+ and the corresponding standard reaction Gibbs energy. Given, the biological standard half-cell potentials $E^0(O_2, H^+, H_2O) = 0.82$ V and $E^0(NAD^+, H^+, NADH) = -0.32$ V. **[2+2]**

5.b. Devise electrochemical cells in which the flowing reactions could be made to occur. **[2+2]**

$$\text{(i) } H_2\,(g) + O_2\,(g) \longrightarrow H_2O_2\,(aq)$$
$$\text{(ii) } 2CuCl\,(aq) \longrightarrow Cu\,(s) + CuCl_2\,(aq)$$

5.c. State what you would expect to happen to the cell potential for the following cell reaction when (i) HCl and (ii) $FeCl_2$ are added to both compartments. Confirm your prediction by using the Nernst equation.

$$3FeCl_2\,(aq) \longrightarrow Fe\,(s) + 2FeCl_3\,(aq)$$ **[2+2]**

Q.6.a. Can chlorine gas oxidize water to oxygen gas under standard conditions in basic solution? **[3]**

6.b. Using standard potential data calculate the equilibrium constants (K) of the following reactions at 25 ^{0}C.

$$3Au^+\,(aq) \rightleftharpoons 2Au\,(s) + Au^{3+}\,(aq)$$ **[3]**

6.c. A fuel cell is constructed in which both electrodes make use of the oxidation of methane. The left-side electrode makes use of the complete oxidation of methane to carbon dioxide and water; the right-side electrode makes use of the partial oxidation of methane to carbon monoxide and water. Identify which electrode is cathode and which one anode. Justify your answer.**[2+2]**

6.d. Figure 4 shows a CV taken for a solution containing benzophenone (BP) and tri-*p*-tolylamine (TPTA), both at 1 *mM* in acetonitrile. Benzophenone can be reduced inside the working range of acetonitrile and TPTA can be oxidized. However, BP can't be oxidized, and TPTA can't be reduced. The scan shown here begins at 0.0 V *vs.* SHE and first moves toward positive potentials. (i) Assign the voltammetric features between +0.5 and 1.0 V and between -1.5 and -2.0 V to appropriate electrode reactions and identify the onset potential for BP reduction and TPTA oxidation. **[3+1]**

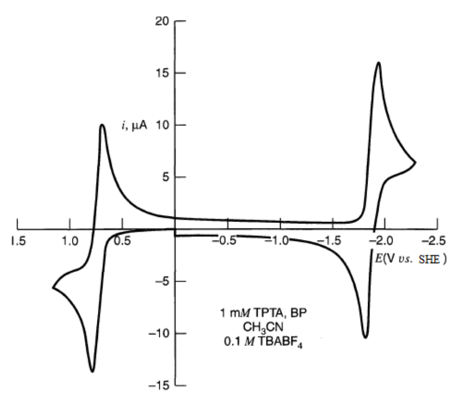

Figure 4

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