

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. Write all the associated steps for a derivation.
4. Do not exchange your calculator.

Q. 1. Schematic representation for the fabrication of monolayer metallic Pt decorated metallic Au nanofilm on p-silicon is given in Figure 1, which consists of three steps. All the different color spherical balls are represented for different meaning. Product a, b, and c are metallic Au nanofilm on p-silicon, metallic Cu decorated Au nanofilm on p-silicon, and metallic Pt decorated Au nanofilm on p-silicon, respectively.

Answer the following questions:

(a) What is/are the involved chemical reaction in step I to get product a? **(b)** What is the best suited method in step II to synthesize product b and why? **(c)** What is the advantage of step III and mention the reducing agent used in this step? **(d)** If you compare this fabrication method over co-electrodeposition of Au^{3+} and Pt^{2+} ions on p-silicon, which method would be more useful to form metallic AuPt nanofilm and why? **(e)** Show schematically how the monolayer metallic Pt or metallic Au nanofilm is constituted on the electrode surface using the concept of electrode-electrolyte double layer formation. In the scheme show how the diffusion of solvated M^{n+} ions occur on the electrode surface. **(f)** The as-synthesized final catalyst, product c, exhibit enhanced photoactive sensor property as glucose sensor. Show all the photoactive steps for the catalyst to be a glucose sensor. Consider, gluconic acid as an oxidized product in glucose sensor.

[2+2+2+2+3+3]

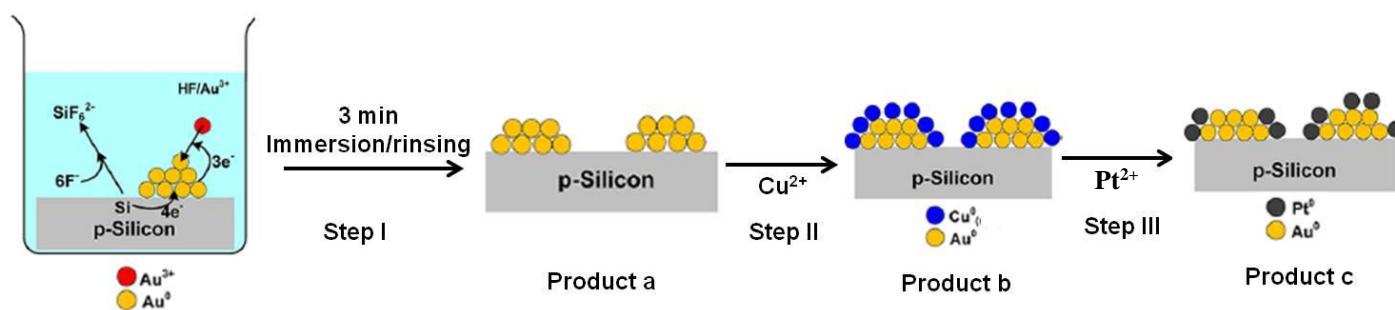


Figure 1

Q. 2. (a) J. Y. Kim and co-workers reported (*Sci. Rep.*, 3, 2013, 2681) “Single-crystalline, wormlike hematite photoanodes for efficient solar water splitting”. Show overall schematic representation with electrochemical setup and all the reaction steps for photoelectrochemical water oxidation on hematite photoanode surface. [3]

(b) (I) Define primary cell. **(II)** An example of primary cell is Leclanché or Dry cell, which is given below. Write both cathodic and anodic cell reactions for the following primary cell. [3]



(c) Two half wave electrochemical reactions are given below. [2]



Estimate the free energy released in the reaction $\text{TMPD}^{\cdot+} + \text{Py}^{\cdot-} \longrightarrow \text{TMPD} + \text{Py}$

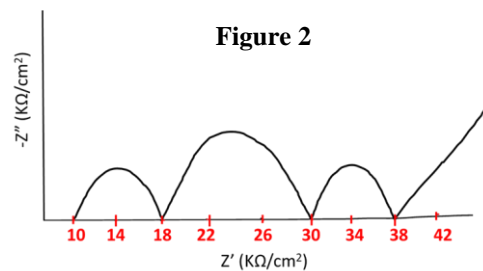
(d) Electrochemiluminescence (ECL) from $\text{Ru}(\text{bpy})_3^{2+}$ was first reported in 1972 in acetonitrile (MeCN) using tetrabutylammonium tetrafluoroborate (TBABF_4) as the electrolyte. ECL was generated by alternate pulsing of an electrode potential. Show the mechanism of ECL generation in an electrode surface using $\text{Ru}(\text{bpy})_3^{2+}$ complex and oxalate ion ($\text{C}_2\text{O}_4^{2-}$) by representing all the associated reactions. Draw a probable cyclic voltammogram (CV) curve for the oxidation and reduction reaction. Given, $E^0_{\text{Ru}^{2+}/\text{Ru}^{3+}} = +1.2 \text{ V vs. SCE}$ and $E^0_{\text{oxalate}/} = -1.1 \text{ V vs. SCE}$. [4]

(e) In electrocatalytic water splitting reaction H_2 gas evolution occur based on few important steps, known as Volmer step and Heyrovsky Step or Tafel step. Discuss how H_2 evolution occur following Volmer-Tafel steps. [2]

Q. 3. (a) The Nyquist plot for a simple charge transfer reaction is made of a semi-circle arc lying on the x-axis. Draw the equivalent circuit for the given Nyquist plot (Figure 2). Identify the value of solution resistance (R_s) from Figure 2.

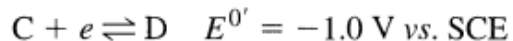
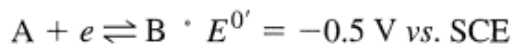
(b) Impedance spectroscopy is made up ideal circuit elements such as resistors and capacitors. In electrochemical impedance spectroscopy, discuss resistor, capacitor, and constant phase element.

(c) Assume that one molecule of a species A, reversibly oxidizable to A^+ , is trapped between an SECM tip and a substrate located 10 nm from the tip. Assume also that $D_A = D_{\text{A}^+} = 5 \times 10^{-6} \text{ cm}^2/\text{s}$. **(I)** Use the diffusion layer approximation to find about how long it takes for A to diffuse between the tip and the substrate. **(II)** About how many round-trip excursions of A would occur in 1 s? **(III)** If A is oxidized to A^+ at the tip and A^+ is reduced to A at the substrate, what current will result? Given, charge of a single electron is 1.6×10^{-19} coulombs.



(d) How many electrons flow when a current of 1 pA passes for 1 μs ? Do you think this current could be measured? [3+3+4+3]

Q. 4. (a) Consider the following system:



The half-life of B is 100 ms. Both charge-transfer reactions have large values of k° . Draw the expected cyclic voltammograms (CV) for scans beginning at 0.0 V vs. SCE and reversing at -1.2 V. Show CV curves for rates of 1 V/s and 20 V/s. [3]

(b) A disk ultramicroelectrode gives a plateau current of 2.32 nA in the steady-state voltammogram for a species known to react with $n = 1$ and to have a concentration of 1 mM and a diffusion coefficient of $1.2 \times 10^{-5} \text{ cm}^2/\text{s}$. What is the radius of the electrode? [2]

(c) Fick's first law of diffusion states that the flux $\{J_o(x,t)\}$ is proportional to the concentration gradient. Derive a relation between the flux of a substance and its concentration as a function of time and position. [3]

(d) Draw a cyclic voltammogram of a quasi-reversible process for the following redox reaction. How do you differentiate the CV of a quasi-reversible process with a reversible process? $O + ne \rightleftharpoons R$ [2]

(e) Reductions of many organic substances involve the hydrogen ion. Derive the steady-state voltammogram for the reversible reaction $O + pH^+ + ne \rightleftharpoons R$, where, both O and R are soluble substances, and only O is initially present in solution at a concentration C_O^* . [4]

Q. 5. (a) For one step one electron process; $O + e \rightleftharpoons R$, the Butler-Volmer formulation of electrode kinetics equation is given in (X). The expression for exchange current is also given in equation (Y).

(I) Derive the current-overpotential ($i-\eta$) relationship. **(II)** Using the $i-\eta$ equation identify the cathodic and anodic contribution. **(III)** Draw a curve based on the behavior predicted by $i-\eta$ equation. Briefly discuss the curve at large positive η , large negative η , and extreme η . [6]

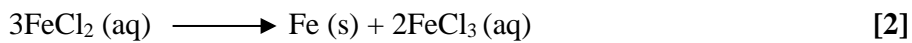
$$i = F A k^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha)f(E - E^{0'})} \right] \quad \text{---- (X)}$$

$$i_0 = F A k^0 C_O^{*(1-\alpha)} C_R^{*\alpha} \quad \text{---- (Y)}$$

(b) According to G. Scherer and F. Willig (*J. Electroanal. Chem.*, 85, 1977, 77) the exchange current density, j_0 , for Pt/ $\text{Fe}(\text{CN})_6^{3-}$ (2.0 mM), $\text{Fe}(\text{CN})_6^{4-}$ (2.0 mM), NaCl (1.0 M) at 25°C is 2.0 mA/cm². The transfer coefficient, α , for this system is about 0.50. Calculate **(I)** the value of k° and **(II)** the charge-transfer resistance of a 0.1 cm² electrode in a solution 10⁻⁴ M each in ferricyanide and ferrocyanide. [4]

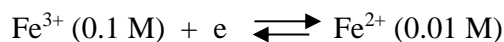
(c) Consider the electrode reaction $O + ne \rightleftharpoons R$. Under the conditions that $C_R^* = C_O^* = 1 \text{ mM}$, $k^\circ = 10^{-7} \text{ cm/s}$, $\alpha = 0.3$, and $n = 1$, assume, $m_O = m_R = 10^{-3} \text{ cm/s}$. Calculate the exchange current density, $j_0 = I_0/A$, in A/cm² unit. [3]

Q. 6. (a) State what you would expect to happen to the cell potential for the following cell reaction when (i) HCl and (ii) FeCl₂ are added to both compartments. Confirm your prediction by using the Nernst equation.

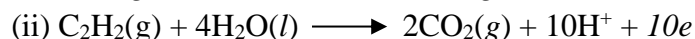
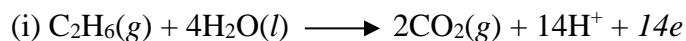


(b) Can chlorine gas oxidize water to oxygen gas under standard conditions in basic solution? Justify your answer with cathode and anode reactions. Given, $E^\circ_{\text{Cl}_2/2\text{Cl}^-} = 1.36 \text{ V vs. NHE}$ and $E^\circ_{\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V vs. NHE}$. [3]

(c) Define formal potential. Calculate formal potential for the following half reaction at 298 K. (Given, $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.76 \text{ V}$) [3]



(d) Several hydrocarbons and carbon monoxide have been studied as possible fuels for use in fuel cells. Using given thermodynamic data derive E° for the following reactions both (i) and (ii) at 25°C. Given, $\Delta G^\circ_{\text{CO}_2} = -394.6 \text{ kJ/mol}$, $\Delta G^\circ_{\text{C}_2\text{H}_2} = 209.3 \text{ kJ/mol}$, $\Delta G^\circ_{\text{H}_2\text{O}} = -237.3 \text{ kJ/mol}$, $\Delta G^\circ_{\text{C}_2\text{H}_6} = -32.9 \text{ kJ/mol}$, and $\Delta G^\circ_{\text{H}_2} = 0.0 \text{ kJ/mol}$. [4]



*****END*****