CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN INDUSTRIAL CHEMISTRY

CHIN 428: INDUSTRIAL ELECTROCHEMISTRY AND CORROSION

STREAMS: BSC **TIME: 2 HOURS**

DAY/DATE: THURSDAY 23/09/2021 **8.30 A.M – 10.30 A.M.**

INSTRUCTIONS:

- **Answer question ONE and any other TWO questions.**

QUESTION ONE

1. (a) (i) Outline four major advantages of electro analytical methods over other analytical techniques. (2 marks)

(ii) Discuss Faradaic and Nonfaradaic processes. (5 marks)

(iii) Explain using suitable examples what you understand by ideal polarized electrode. (2 marks)

(iv) Describe the stern model on the existence of an electric double layer (use a suitable diagram) (6 marks)

(v) Explain what you understand by electrocapillary effect. (5 marks)

(b) (i) Write short notes on ion-selective electrodes (ISEs). (4 marks)

(ii) State and explain two important experimental problems in controlled-current coulometry which must be solved if accurate results are to be obtained.

($2\frac{1}{2}$ marks)

(iii) When analysis a voltammogram it is important to consider whether the electron transfer rate is reversible or irreversible in nature. Discuss the main features of a voltammogram that can readily be used to qualitatively decide whether a voltammogram indicates reversible or irreversible electron transfer. ($3\frac{1}{2}$ marks)

QUESTION TWO (20 MARKS)

2. (a) (i) Discuss the principles and applications of spectroelectrochemistry. (4 marks)

(ii) The statistical (Einstein) view of diffusion is a random walk process which suggests that the root mean-square distance diffused by a species in time t is

$$d = \sqrt{2\Delta t}$$

Where a small molecule in aqueous solution has a diffusion coefficient $\Delta \simeq 10^{-5} CM^2 S^{-1}$. Approximately how far would such a molecule diffuse in one second and one day. Comment on any implications for electrochemical experiment.

(b) Account for the following features of cyclic voltammograms.

(i) Peak current is proportional to the square root of scan rate. ($2\frac{1}{2}$ marks)

(ii) Peak current less in the limit of slow electrode kinetics. ($2\ \frac{1}{2}$ marks)

(iii) Altering the diffusion coefficient of the product ¿) for a given diffusion coefficient of the reactant (D_A) affect the forward peak potential but not the forward peak current. ($2\frac{1}{2}$ marks)

(iv) A plot of Ipf vs C often not go through the origin. (2 marks)

(c) (i) For an electrochemically reversible wave measured at a microdisc electrode for the process.

$$¿ - ne^{-¿ \rightleftharpoons ox ¿}$$

The half-wave potential, $E_{\frac{1}{2}}$, is related to the formal potential E_f^{θ} by the expression

$$E_{\frac{1}{2}} = E_f^{\theta} + \frac{RT}{nF} \in \frac{Dred}{Dox}$$

Where Dred and Dox are the diffusion coefficients of Red and Ox respectively for the ferocene/Ferocenium couple in the room temperature ionic liquid

$(C_{Ampyrr} ¿(NTf_2)$

$Dred = 2.31 \times 10^{-7} CM^2 S^{-1}$ and
$Dox = 1.55 \times 10^{-7} CM^2 S^{-1}$

Calculate ¿) and comment on the significance of the result.(2 marks)

(ii) For an electrochemically irreversible reduction at a micro disc or microsphere electrode of radius re, the variation of the voltammetric half-wave potential, $E_{\frac{1}{2}}$, under steady state conditions can be shown to vary as

$$\frac{d E_{\frac{1}{2}}}{d \ln re} = \frac{RT}{\alpha F}$$

Where α is the transfer coefficient =0.25. The following data were obtained for the reduction of hydrogen. Peroxide at isolated silver nanoparticles supported on an inert but conducting substrate electrode.

rNP/nm 15 30 50
$E_{pf/v}$ −1.575 −1.503 −1.453

Explain why the peak shifts with the particle radius. If the substrate were covered with a monolayer of the silver nanoparticles, explain qualitatively what would be seen. (2 marks)

QUESTION THREE (20 MARKS)

3. (a) Linear sweep voltammetric methods often result in poor limits of detection. Pulse voltammetry is frequently used to improve these.

(i) Sketch the potential wave form which is applied to the working electrode during a differential pulse voltammetry (DPV) experiment and give typical values for the pulse amplitudes and times ($2\frac{1}{2}$ marks)

(ii) At what points on the potential waveform is the current sampled and how is the current plotted. ($\frac{1}{2}$ mark)

(iii) Explain how DPV allows lower limits of detection to be attained your answer should include information on the time scale for the decay of both the faradaic and capacitive currents. (2 marks)

(b) (i) Describe how a stripping voltammetry experiment works and also explain why is it possible to achieve low detection limits $\left(\simeq 10^{-10} M\right)$ (4 marks)

(ii) How is it possible to differentiate between different metals contained within one solution using a stripping voltammetry? (2 marks)

(iii) What are the advantages and disadvantages of using a mercury based electrode in voltammetry? (3 marks)

(c) (i) A steel tank is hot dipped in a deaerated acid solution of $5 \times 10^{-4} mol/cm^3$ molality zinc chloride ($zncl_2$) so that a 0.15 mm zinc coating is deposited on the steel surface. This process produces a galvanized steel tank. Calculate the time it takes for the zinc coating to corrode completely at a $pH=4$. Data; $E_{zn}=-0.8V$ $iozn=10\,\mu A/cm^2$, $io,H=10^{-3}\mu A/cm^2$ $\beta a=0.08V, \beta_C=0.12V, T=25^0C. e_{zn}=7.14\,g/cm^3$. (6 marks)

QUESTION FOUR (20 MARKS)

4. (a) (i) Distinguish between (dry) chemical and (wet) electrochemical corrosion. (5 marks)

(ii) Explain into detail how the environment can be modified in order to prevent corrosion. (10 marks)

(b) Write short notes on pourbaix diagram in connection with electrochemical systems. (5 marks)
