Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031

I Semester 2017-2018

CHEM F327	Electrochemistry: Fundamentals and Applications	
Comprehensive Examination		Part A (Closed Book)
Max. Marks: 50 2017	Duration: 60 minutes	Date: 8 th December

NOTE: There are two parts in the question paper: Part A (Closed Book) and Part B (Open Book). Take separate answersheets for each part.

There are FIVE questions in all in part A. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.

Please collect part B (Open Book) after submitting the Part A answer sheet.

Q.1 (i) What are the different types of batteries? Explain by citing one example of each type. (Example should include anode, cathode, reactions occurring at the electrodes and electrolytes) (ii) What are fuel cells? Describe one type of fuel cell with proper schematic diagram. [8+8]

Q.2 For the reduction of anthracene to anion radical in DMF, explain the *i* verses *t* plot in a basic potential step experiment in which the potential is made more negative from E_1 (potential region where Faradaic processes do not occur) to E_2 (mass transfer limited region). [Draw the concentration profiles for various times into the experiment and current flow vs. time with proper labeling] [8]

Q.3 Draw a well labeled schematic diagram of a diaphragm cell used in chlor alkali industry.Why it is advantageous to use membrane cell instead of diaphragm cell?[4+4]

Q.4 (i) Explain electrogenerated chemiluminescence with the example of Rubrene (R) and tetramethylene-p-phenylenediamine (TMPD). (ii) Draw the concentration profiles during an ECL step experiment involving R and TMPD. [4+4]

Q.5 Draw a well labeled current-potential curves for a solution containg O/R couple with n-type semiconductor as an electrode (i) in dark and (ii) under irradiation and explain photo assisted electrode reactions. [5+5]

END

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I Semester 2017-2018

CHEM F327	Electrochemistry: Funda	amentals and Applications
Comprehensive Examination		Part B (Open Book)
Max. Marks: 70	Duration: 2 hrs.	Date: 8 th December 2017
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NOTE: There are EIGHT questions in all in part B. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.

Q.1 The oxidation of *o*-dianisidine occurs in a nerstian 2e reaction. For a 2.27mM solution of odianisidine in 2M H₂SO₄ at a carbon paste electrode of area 2.73 mm² with a scan rate of 0.5 V/min, $i_p = 8.19\mu$ A. Calculate the D value for o-dianisidine. What i_p is expected for v = 100 mV/s? What i_p will be obtained for v = 50 mV/s and 8.2mM o-dianisidine? [4+4+4]

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

(anode) $2OH^{-} \rightarrow 1/2 O_2 + H_2O + 2e$

(cathode) $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Show the balance sheet for the system operating at steady state Assume 20e are passed in the external circuit per unit time. ($\lambda_{0,Na^+} = 50.11$ and $\lambda_{0,OH^-} = 198$) [10]

Q.3 For a given electrochemical system to be described by equations involving semi infinite boundary conditions, the cell wall must be at least five "diffusion layer thickness" away from the electrode. For a substance with $D = 10^{-5}$ cm²/s, what distance between the working electrode and the cell wall is required for a 100-s experiment? [5]

Q.4 A 0.1 cm² electrode with $C_d = 20 \ \mu F/cm^2$ is subjected to a potential step under conditions where R_s is 100 Ω . What is the time constant, and what is the time required for the double-layer charging to be 95% complete? [5]

Q.5 Consider the nernstian half-reaction:

$$A^{3+} + 2e \rightleftharpoons A^+ \quad E^0_{A^{3+}/_{A^+}} = -0.500 V vs. NHE$$

The *i*-*E* curve for a solution at 25°C containing 2.00 mM A³⁺ and 1.00 mM A⁺ in excess electrolyte shows $i_{l,c} = 4.00 \ \mu A$ and $i_{l,a} = -2.40 \ \mu A$. (i) What is $E_{l/2}$ (V vs. NHE)? (ii) Sketch the expected *i*-*E* curve for this system. [4+4]

Q.6 Explain with proper schematic diagram the electrochemistry behind the response of nerve cell membrane towards nerve impulse. [10]

Q.7 Derive Fick's second law of diffusion for spherical diffusion. [10]

Q.8 Consider one-electron electrode reactions for which $\alpha = 0.50$ and $\alpha = 0.10$. Calculate the relative error in current resulting from the use in each case of:

(i) The linear $i-\eta$ characteristic for overpotentials of 20 and 50 mV.

(ii) The Tafel (totally irreversible) relationship for overpotentials of 100 and 200 mV. [5+5]

END