Second Semester Examination
Academic Session 2020/2021

July 2021

KAT346 – Electroanalytical Method
[Kaedah Elektroanalisis]

Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of **SIX (6)** pages of printed material before you begin the examination.

Answer **FOUR (4)** questions only.

SECTION A : Answer all the questions.

SECTION B : Select and answer only **ONE (1)** question.

Answer each question on a new page. You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answered more than four questions, only the first four questions in order of the arrangement in the received answer script will be marked.

PART A

1. (a) The glass membrane electrode is one of the types of ion-selective electrodes (ISEs), and it is a commonly used method to measure the pH of a solution.

   (i) Sketch a schematic diagram for the cell scheme of a conventional pH glass membrane electrode.

   (ii) Commonly, any pH $\geq$ 10 measured by a pH glass electrode is always erratic. Explain this problem.

   (7 marks)

   (b) Discuss the mechanism of the glass membrane electrode responses for pH measurement.

   (5 marks)

   (c) Describe the formation of flux that occurs at the electrode/electrolyte interface during voltammetric measurements by using a sketched diagram.

   (5 marks)

   (d) By using a suitable schematic diagram, discuss the fundamental concepts of an electrical double-layer at the electrode/electrolyte interface for voltammetric measurement.

   (8 marks)

2. (a) The potential of a cell for a saturated calomel electrode (SCE) reference electrode is -0.845 V. Calculate the potential if the standard hydrogen electrode (SHE) is used. (The cell potential using the SHE is 0.242 V less negative than SCE).

   (7 marks)

(b) Calculate the electrode potential of a half-cell consisting of a platinum electrode immersed in a 0.1 M HCl solution through which chlorine gas is being passed at a partial pressure of 1.15 atm.

Given balance half-reaction: $Cl_2^-(g) + 2e^- \rightleftharpoons 2\,Cl^-(aq.)$ $E° = 1.36$ V

(8 marks)

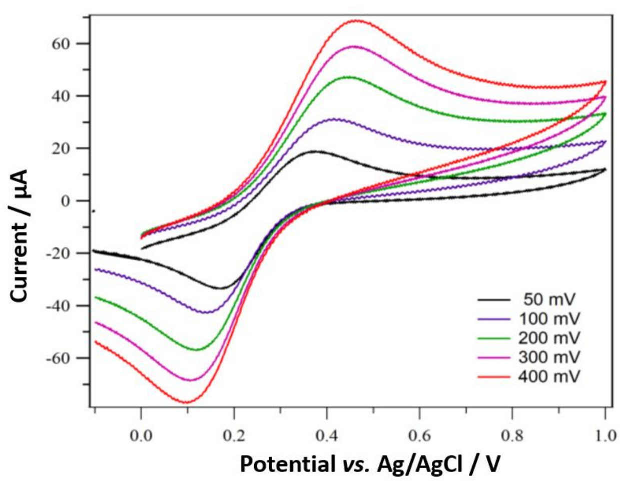
(c) A beaker containing 50 mL of 0.15 M H_3AsO_3 and 0.610 M H_3AsO_4 in acidic solution has an electrode potential of 0.494 V. Determine pH of the solution.

Given balance half-reaction:
$H_3AsO_4\,(aq.) + 2H^+\,(aq.) + 2e^- \rightleftharpoons H_3AsO_3\,(aq.) + H_2O\,(l)$ $E° = 0.559$ V

(10 marks)

3. (a) In the hydrodynamic experiment, the diffusion-controlled limiting current of Cu^{2+} from an unknown solution of 20 mL was determined to be 10 µA. Another 2 mL of 1.0×10^{-4} M Cu^{2+} was then added to the unknown solution. The current increased to 38.2 µA. Calculate the concentration of copper ions in the unknown solution before the addition of Cu^{2+}.

(5 marks)



(b) The figure above shows cyclic voltammograms (CVs) for 0.05 M ferrocyanide at different scan rates. Essentially, the Randel-Sevcik equation is connected to the CV scan rate. Outline your approach in determining the diffusion coefficient of ferrocyanide.

(8 marks)

(c) The data below were obtained for the diffusion-limited current and it can be described by a Cottrell equation, where the concentration of the reduced species was 5 mM and the diffusion coefficient (D_o) was found to be 1.2×10^{-5} cm^2 s^{-1}. Calculate the number of electron(s) transferred in the redox reaction using the Cottrell plot.

***t* (s)**	***j* (mA cm^{-2})**
1	0.94
4	0.47
9	0.31
16	0.24
25	0.19
36	0.16

(12 marks)

PART B

4. (a) Discuss the significance of the selectivity coefficient and methods to determine its value.

(7 marks)

(b) A nitrate ISE and a reference electrode were dipped into a nitrate solution with a concentration of 1.00×10^{-3} M. The potential of the nitrate ISE was found to be -122.4 mV. Both electrodes were then dipped into a solution, both containing nitrate and chloride, each of which had a concentration of 1.00×10^{-3} M. The potential of the nitrate ISE in this solution was -124.8 mV. The temperatures of both solutions were 25 °C. Calculate the selectivity coefficient of the nitrate ISE over chloride.

(6 marks)

(c) The diffusion-limited current at a stationary electrode following a large potential step that drives the oxidation of a reduced species is given by the Cottrell equation below:

$$\boldsymbol{j} = \frac{n\,FD^{\frac{1}{2}}C_R}{\pi^{\frac{1}{2}}\,t^{\frac{1}{2}}}$$

(i) Define each of the symbol in the equation.

(ii) Sketch a series of curves that illustrate the development of the concentration profile of the reduced species (C_R) with time, following the potential step.

(7marks)

(d) A 25 mL sample of Ni^{2+}, gave a differential pulse polarogram (DPP) peak of 2.36 µA (corrected from the residual current in a polarographic analysis). When 0.5 mL of a solution containing 28.7 mM of Ni^{2+} was added, the peak height increased to 3.79 µA. Calculate the concentration of Ni^{2+} in the unknown sample.

(5 marks)

5. (a) (i) Describe one way to prepare a membrane for the potentiometric measurement of either Ag^{+} or Pb^{2+}.

(ii) Specify its primary interfering ion and a way to minimize it.

(6 marks)

(b) Discuss any three major sources of error in potentiometric measurements.

(6 marks)

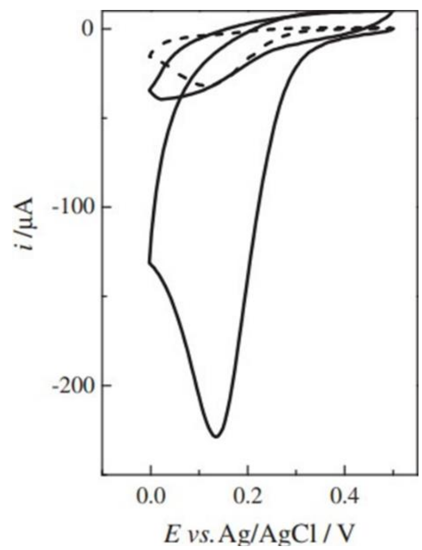
(c) Differential pulse voltammetry (DPV) is one of the pulse techniques that can offer a very sensitive electroanalytical measurement.

(i) Give the differences between modern DPV and DPP techniques.

(ii) DPV technique is more sensitive than the CV technique. Discuss the statement.

(8 marks)

(d) The surface of a gold electrode was modified by cycling the potential from 0.4 to 0 *versus* Ag/AgCl in a solution with the presence of a Boc compound. The Boc group is commonly used as a protecting group for a diazonium salt linker. Meanwhile, the corresponding cyclic voltammograms (CVs), recorded during the first 3 cycles are shown in the figure below. Based on the shape of the voltammograms and the data over the first 3 cycles, explain the electrochemical behaviour of the reaction based on the CVs shown.



(5 marks)

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