UNIVERSITI SAINS MALAYSIA

Second Semester Examination

2011/2012 Academic Session

June 2012

KAA 504 – Electrochemical Methods

[Kaedah Elektrokimia]

Duration : 3 hours

[Masa : 3 jam]

Please check that this examination paper consists of NINETEEN pages of printed material before you begin the examination.

Instructions:

Answer **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answer each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

In the event on any discrepancies, the English version shall be used.

1. (a) The current-overpotential equation for the electrode reaction involving one step, one electron process, O + e ⟶ R is:

$$i = i_o\left[\frac{C_o(o,t)}{C_o^*}e^{-\alpha f\eta} - \frac{C_R(o,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]$$

where

i = the anodic or cathodic current
i_o = exchange current
C_O^*, C_R^* = bulk concentration of species O or R
$C_O(0,t)$, $C_R(0,t)$ = concentration of species O or R at the electrode surface at time, t,
α = transfer coefficient
η = overpotential, $E - E_{eq}$
$f = F/RT$

Derive an equation of the Nernst form relating the electrode potential and the surface concentrations of O and R, regardless of the current flow.

(6 marks)

(b) The Butler – Volmer equation is:

$$i = i_o[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}]$$

Show the Tafel behavior at large η and the linear characteristic at small η.

(6 marks)

(c) The data below refer to the anodic current through a platinum electrode of area 2.0 cm^2 in contact with an Fe^{3+}, Fe^{2+} aqueous solution at 298.15 K. Calculate the exchange current density and the transfer coefficient for the electrode process.

Overpotential, η/mV	50	100	150	200	250
Anodic current, i/mA	8.8	25.0	58.0	131	298

$F = 96485\ C\ mol^{-1}$ $R = 8.3145\ J\ K^{-1}\ mol^{-1}$

(8 marks)

2. (a) Discuss and draw clearly the main structural features of the electrical double layer.

(10 marks)

(b) Describe the three modes of mass transport-controlled reactions. Write down the equation that describes all the three modes and indicate in the equation for each mode.

(6 marks)

(c) Which experiment conditions assure that the movement of the electroactive species is limited by diffusion? How do these conditions suppress the migration and convection effects?

(4 marks)

3. (a) What is meant by anodic corrosion protection? Briefly explain with the aid of a schematic diagram, how the anodic protection can be achieved.

(8 marks)

(b) Nickel experiences corrosion in an acid solution according to the reaction

$$Ni + 2H^{+} \longrightarrow Ni^{2+} + H_2$$

The rate of both oxidation and reduction half – reactions are controlled by activation polarization. Based on the following polarization data, calculate:

(i) Corrosion current density.

(ii) The value of the corrosion potential.

(iii) The rate of corrosion (in mpy) if the molar mass and density of Ni are 58.69 g mol^{-1} and 8.90 g cm^{-3}, respectively.

Nickel	Hydrogen
E^{0}_{rev} = -0.25 V	E^{0}_{rev} = 0.00 V
$i_a = 1 \times 10^{-8}$ A cm^{-2}	$i_c = 6 \times 10^{-7}$ A cm^{-2}
β_a = 0.12 V $decade^{-1}$	β_c = -0.10 V $decade^{-1}$

(12 marks)

4. (a) Briefly describe the advantages and disadvantages of electrochemical impedance spectroscopy (EIS) as compared to potentiodynamic polarization in corrosion study.

The performance of protective coating on steel can be studied by means of EIS.

(i) Draw the equivalent circuits which reflect the intact coating and a coating that has suffered major damages. Briefly discuss the role of each circuit elements.

(ii) Show the Nyquist and Bode plots for coatings that has developed low pore resistance and a coating with freely corroding metal substrate.

(iii) What is meant by Warburg impedance? In what conditions might Warburg impedance be included in the circuit diagram?

(12 marks)

(b) In a polarization experiment of steel in 0.5 M HCl the value of Tafel constants, β_c, are 0.040 V decade^{-1} and -0.010 V decade^{-1}, respectively. If the measured polarization resistance (R_p) is 12.18 Ohm, calculate the corrosion current and the corrosion rate (in mil per year) of steel. The molar mass and the density of steel are 55.86 g mol^{-1} and 7.80 g cm^{-3}, respectively.

(8 marks)

5. (a) A cyclic voltammogram (CV) may have as much information on the analysis done as a spectrum has in any spectroscopic analysis. Discuss.

(7 marks)

(b) Why is reversibility important in most electrochemical analysis? How do you work this out in case your experiment is not reversible?

(6 marks)

(c) The following CVs in Figs. 1 and 2 have been obtained from modified electrodes in the analysis of heparin from a plant *A.sessiliflorus* in 20% 0.1M citric-NaOH (pH = 3.7)and in methanol with scan rate 100 mVs^{-1}. Briefly discuss what transpires from these Figures. (Please see Appendix 1 for information).

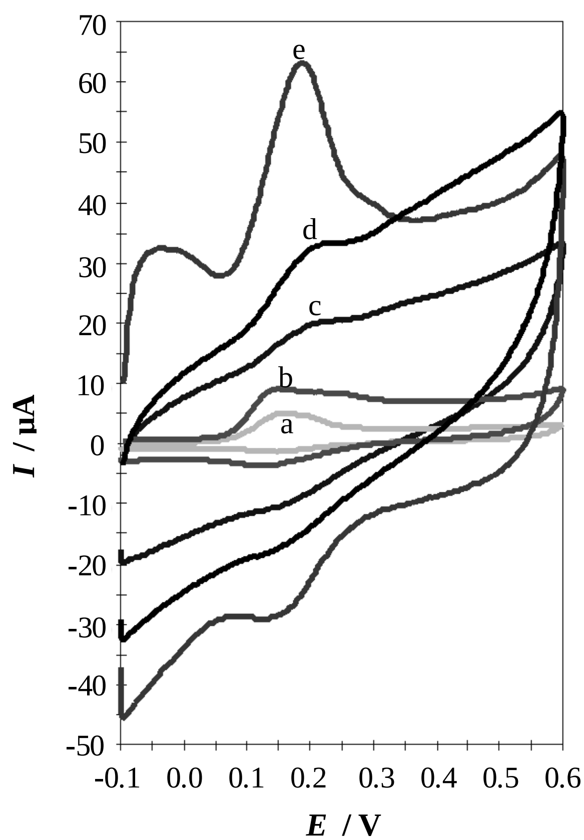


Fig. 1

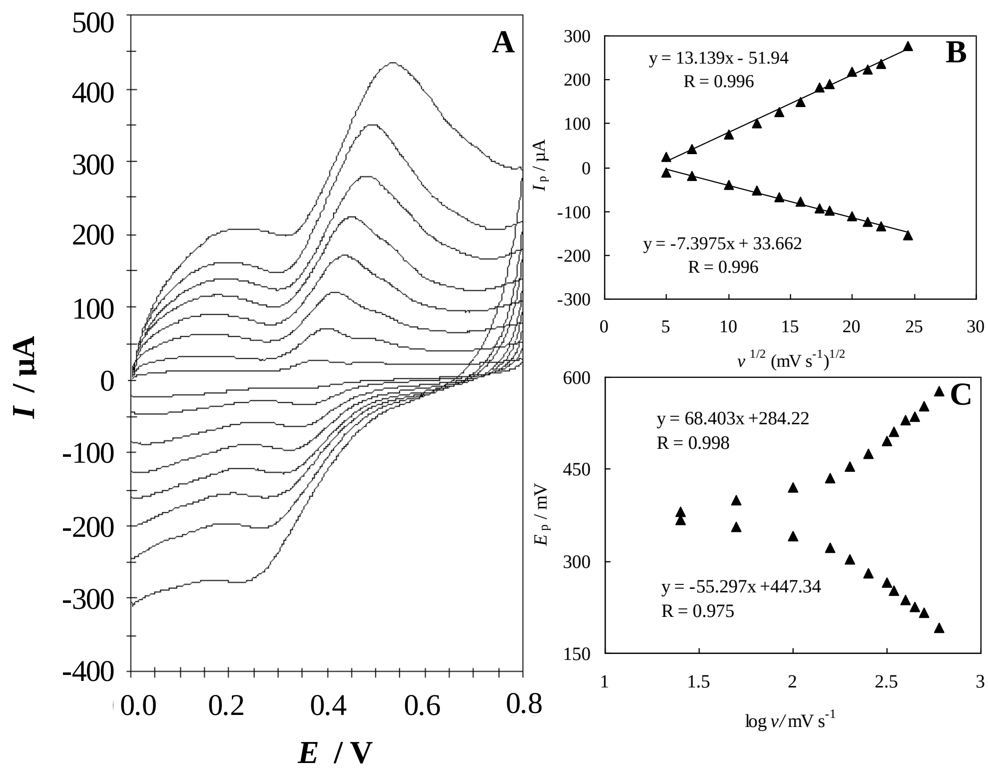


Fig. 2

(7 marks)

6. (a) What are chemically modified electrodes (CME)? Describe how CME improves the overall performance of a solid electrode.

(6 marks)

(b) Why is it important to measure the interfacial conductivity of a CME? Describe a technique frequently used for this purpose.

(7 marks)

(c) Briefly discuss the Nyquist plot (Fig. 3), Bode plot (Fig. 4) and the Randles' circuit (Fig. 5) obtained from the analysis of heparin from a plant *A.sessiliflorus* in 20% 0.1M citric-NaOH (pH = 3.7) and in methanol with scan rate is 100 mVs^{-1}. (Please see Appendix 1 for information).

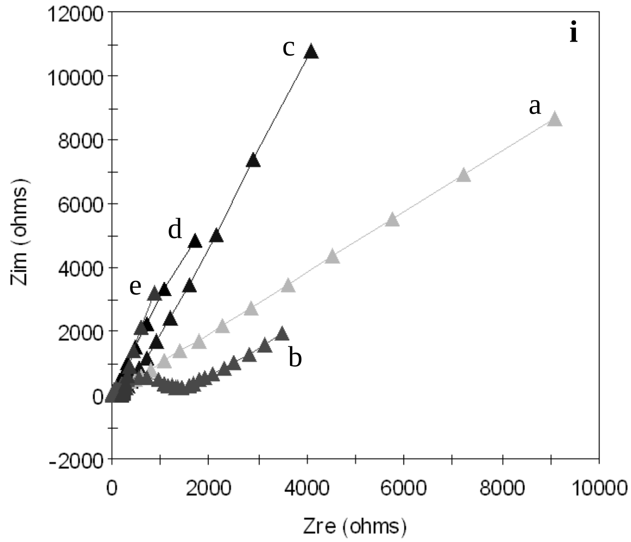


Fig. 3

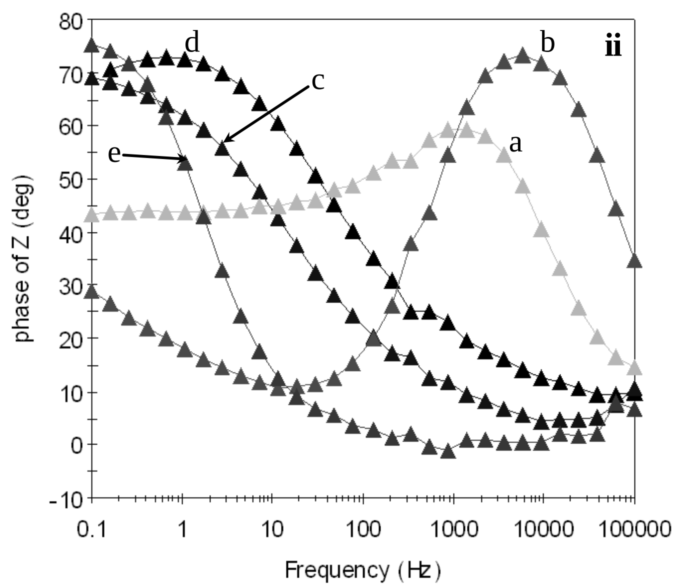


Fig. 4

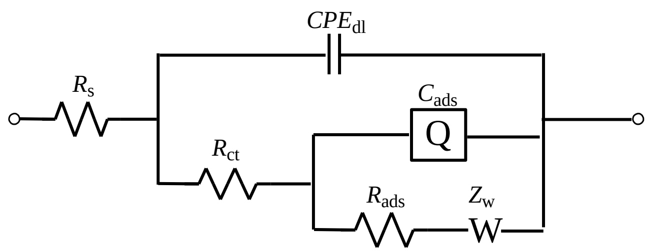


Fig. 5

(7 marks)

Appendix 1

Electrodes	$R_{ct}/\Omega cm^2$	K_{app}/cm s^{-1}
a. GCE	986.0	1.1×10^{-6}
b. GPE	1146.0	9.4×10^{-7}
c. Nafion/GPE	820.0	1.3×10^{-6}
d. MWCNT/GPE	68.3	1.6×10^{-5}
e. Nafion/MWCNT-GPE	8.3	1.3×10^{-4}

R_{ct} is charge transfer resistance, K_{app} is apparent standard rate constant, GCE is glassy carbon electrode, GPE is graphite paste electrode and MWCNT is multiwalled carbon nanotube.

1. (a) Persamaan arus-keupayaan lampau bagi tindak balas elektrod melibatkan proses satu langkah dan satu elektron, O + e $\rightarrow$ R ialah:

$$i = i_o\left[\frac{C_o(o,t)}{C_o^*} e^{-\alpha f\eta} - \frac{C_R(o,t)}{C_R^*} e^{(1-\alpha) f\eta}\right]$$

dengan

i = arus anodic atau katodik

i_o = arus pertukaran

C_O*, C_R* = kepekatan pukai bagi spesies O atau R

$C_O(0,t)$, $C_R(0,t)$ =kepekatan spesies O atau R pada permukaan elektrod pada masa, *t*

α = pekali pemidahan

η = keupayaan lampaul, E – E_{eq}

f = F/RT

Terbitkan satu persamaan berbentuk Nernst yang berhubung keupayaan elektrod dan kepekatan permukaan bagi O dan R, dengan tidak berkira aliran arus.

(6 markah)

(b) Persamaan Butler – Volmer ialah:

$$i = i_o[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}]$$

Tunjukkan kelakuan Tafel pada nilai η yang besar dan ciri linear pada nilai η yang kecil.

(6 markah)

(c) Data yang berikut merujuk kepada arus anodik melalui satu elektrod platinum yang luasnya 2.0 cm^2 bersentuh dengan larutan akueus Fe^{3+}, Fe^{2+} pada 298.15 K. Kiralah arus pertukaran dan pekali pemindahan bagi proses elektrod.

Keupayaan lampau, η/mV	50	100	150	200	250
Arus anodik, i/mA	8.8	25.0	58.0	131	298

F = 96485 C mol^{-1} R = 8.3145 J K^{-1} mol^{-1}

(8 markah)

2. (a) Bincang dan lukiskan dengan jelas ciri struktur yang utama bagi lapisan ganda dua elektrik.

(10 markah)

(b) Huraikan tiga cara bagi tindak balas kawalan pemindahan jisim. Tulislah persamaan yang menghuraikan kesemua tiga cara ini dan tunjukkan dalam persamaan bagi setiap cara.

(6 markah)

(c) Apakah keadaan eksperimen yang memastikan bahawa pergerakan spesies elektroaktif dihadkan oleh cara pembauran? Bagaimanakah keadaan itu mencegah kesan penghijrahan dan kesan perolakan?

(4 markah)

3. (a) Apakah yang dimaksudkan dengan pencegahan kakisan secara anodik? Terangkan dengan ringkas dengan bantuan lakaran rajah, bagaimana pencegahan anodik dapat dilakukan.

(8 markah)

(b) Nikel mengalami kakisan dalam larutan asid menurut persamaan

$$Ni + 2H^+ \longrightarrow Ni^{2+} + H_2$$

Kadar bagi kedua-dua tindak balas setengah pengoksidaan dan penurunan adalah dikawal oleh pengkutuban pengaktifan. Berdasarkan data pengkutuban berikut, hitunglah:

(i) Ketumpatan arus kakisan.

(ii) Nilai keupayaan kakisan.

(iii) Kadar kakisan nikel (dalam mpy) jjika jisim molar dan ketumpatan nikel ialah masing-masing 58.69 g mol^{-1} and 8.90 g cm^{-3}.

Nikel	Hidrogen
E^0_{rev} = -0.25 V	E^0_{rev} = 0.00 V
$i_a = 1 \times 10^{-8}$ A cm^{-2}	$I_c = 6 \times 10^{-7}$ A cm^{-2}
β_a = 0.12 V $decade^{-1}$	β_c = -0.10 V $decade^{-1}$

(12 markah)

4. (a) Jelaskan dengan ringkas kelebihan dan kekurangan spektroskopi elektrokimia impedan (EIS) berbanding dengan pengutubatan potensiodinamik dalam kajian kakisan.

Prestasi litupan pelindung pada keluli boleh dikaji dengan menggunakan EIS

(i) Lakarkan litar setara yang mengambarkan litupan yang tidak mengalami perubahan dan litupan yang mengalami kerosakan yang teruk. Bincangkan dengan ringkas peranan setiap elemen pada litar tersebut.

(ii) Tunjukkan plot Nyquist dan Bode plots bagi litupan yang mempunyai kerintangan liang yang rendah dan litupan dengan sustrat keluli yang terkakis.

(iii) Apakah yang dimaksudkan dengan impedan Warburg? Pada keadaan apakah impedan Warburg perlu disertakan pada gambarajah litar?

(12 markah)

(b) Dalam eksperimen pengutuban keluli di dalam 0.5 M HCl didapati bahawa nilai pemalar Tafel, β_a dan β_c ialah masing-masing 0.040 V decade^{-1} dan -0.010 V decade^{-1}. Jika kerintangan pengutuban (R_p) ialah 12.18 Ohm, hitunglah arus kakisan dan kadar kakisan (dalam mil per tahun) keluli tersebut. Jisim molar dan ketumpatan keluli ialah masing-masing 55.86 g mol^{-1} dan 7.80 g cm^{-3}.

(8 markah)

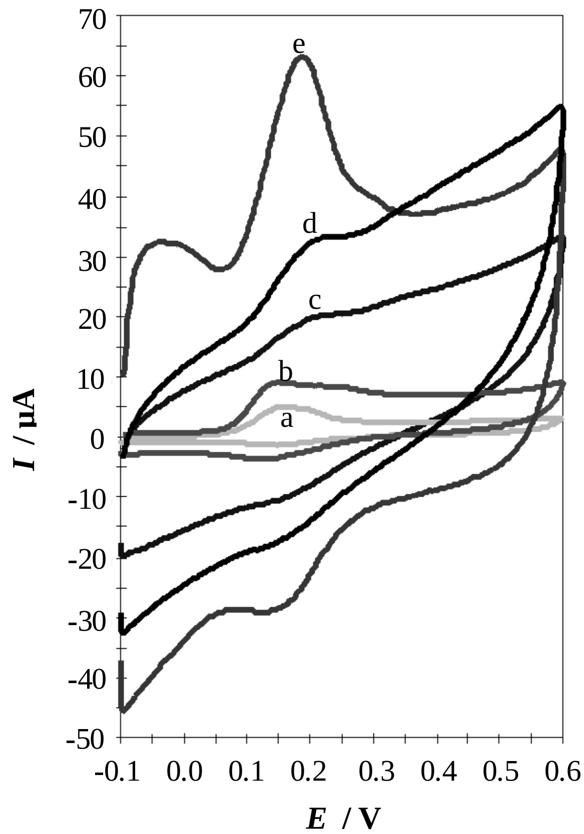
5. (a) Suatu voltammogram berkitar (CV) berupaya memberikan sekian banyak maklumat terhadap analisis yang dilakukan sepertimana spektrum dalam suatu analisis spektroskopi. Bincangkan.

(7 markah)

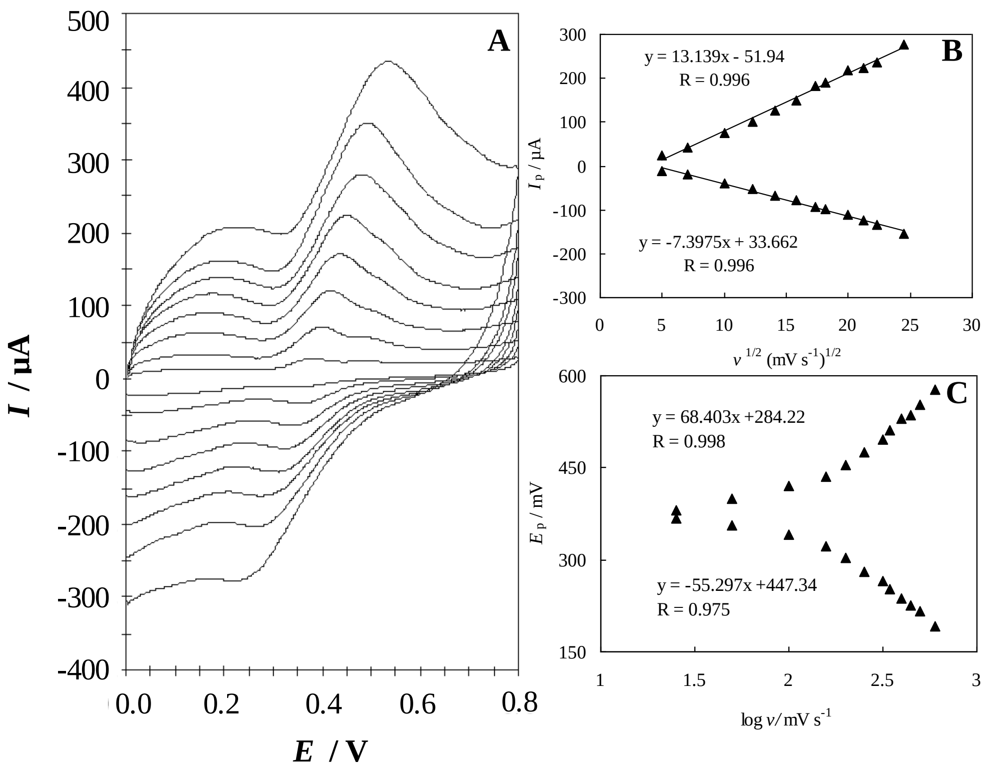
(b) Mengapakah keberbalikan itu penting bagi kebanyakan analisis elektrokimia? Bagaimanakah anda mengusahakan ini sekiranya eksperimen anda tidak berballik?

(6 markah)

(c) CVs dalam Rajah 1 dan 2 telah diperolehi daripada beberapa elektrod terubahsuai dalam analisis heparin daripada tumbuhan *A.sessiliflorus* dalam 20% 0.1M sitrik-NaOH (pH = 3.7) dan dalam metanol dengan kadar imbasan 100 mVs^{-1}. Daripada rajah-rajah ini bincangkan dengan ringkas apa yang berlaku. (Sila lihat Lampiran 1 untuk maklumat)


70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
I / μA
-0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6
E / V
a
b
c
d
e

Rajah 1



Rajah 2

(7 markah)

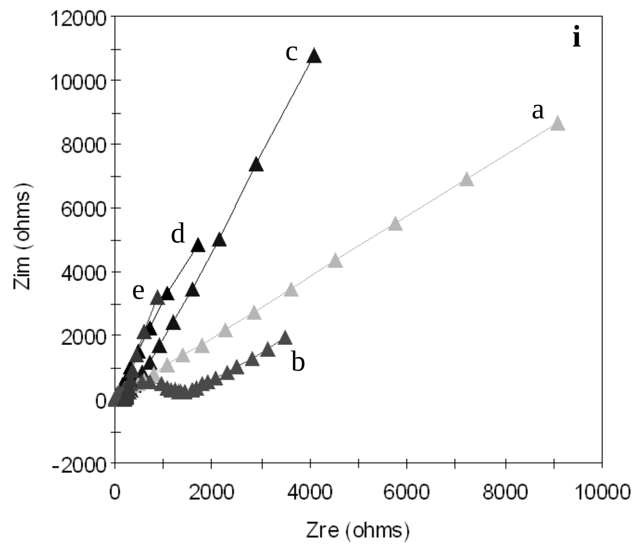
6. (a) Apakah elektrod terubahsuai secara kimia (CME)? Nyatakan bagaimana CME memperbaiki prestasi keseluruhan suatu elektrod pepejal.

(6 markah)

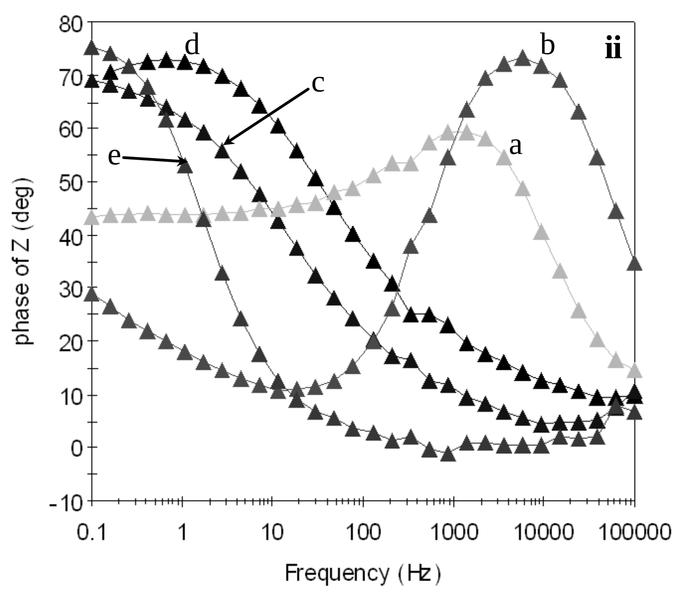
(b) Mengapakah penting menyukat kekonduksian antara muka suatu CME? Nyatakan satu teknik yang kerap digunakan bagi tujuan ini.

(7 markah)

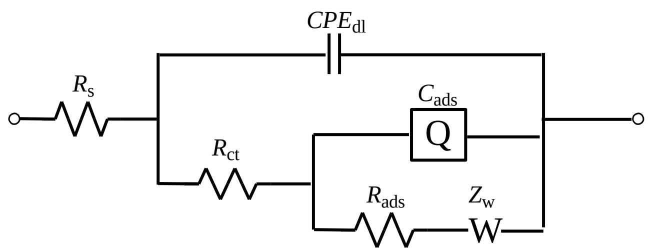
(c) Dengan ringkas bincangkan plot Nyquist (Rajah 3), plot Bode (Rajah 4) dan litar Randles (Rajah 5) yang diperoleh daripada analisis heparin daripada tumbuhan *A.sessiliflorus* dalam 20% 0.1M sitrik-NaOH (pH = 3.7) dan dalam metanol dengan kadar imbasan 100 mVs^{-1}. (Sila lihat Lampiran 1 untuk maklumat).



Rajah 3



Rajah 4



Rajah 5

(7 markah)

Lampiran 1

Elektrod	$R_{ct}/\Omega cm^2$	K_{app}/cms^{-1}
a. GCE	986.0	1.1×10^{-6}
b. GPE	1146.0	9.4×10^{-7}
c. Nafion/GPE	820.0	1.3×10^{-6}
d. MWCNT/GPE	68.3	1.6×10^{-5}
e. Nafion/MWCNT-GPE	8.3	1.3×10^{-4}

R_{ct} ialah rintangan pemindahan cas, K_{app} ialah pemalar kadar piawai nyata, GCE ialah elektrod karbon bak kaca, GPE ialah elektrod pes grafit dan MWCNT ialah karbon nanotiub berbilang dinding.

-oooOooo-