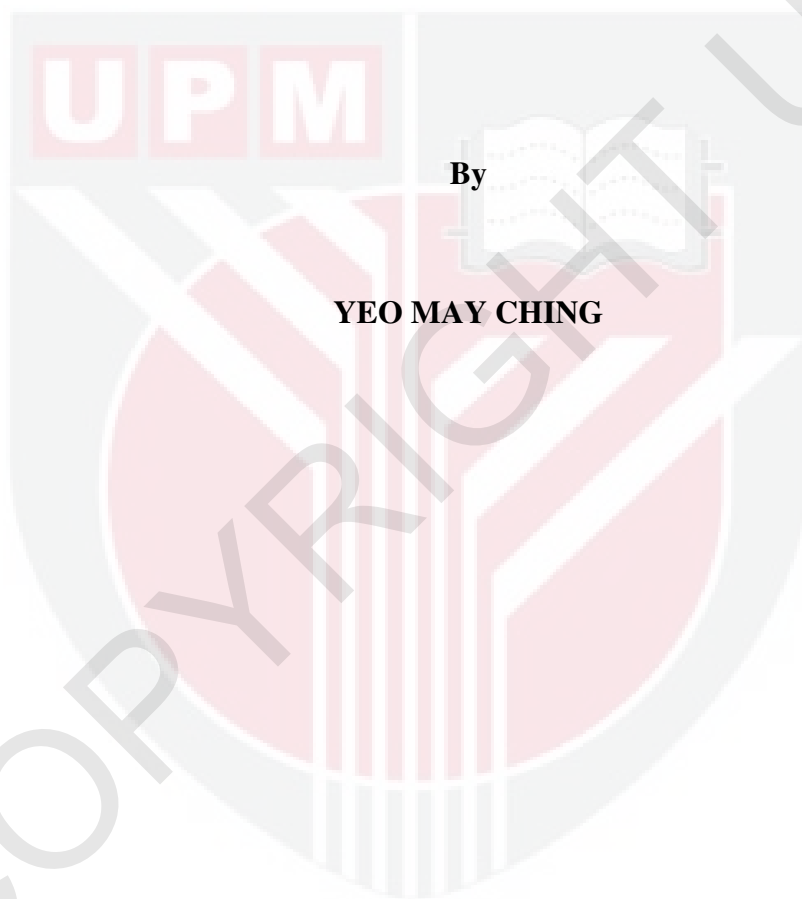**ELECTROCHEMICAL OXIDATION/REDUCTION OF SELECTED COMPOUNDS MEDIATED BY INDIUM TIN OXIDE DOPED WITH LITHIUM AND GLASSY CARBON ELECTRODE MODIFIED WITH TIN DIOXIDE**

YEO MAY CHING

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ELECTROCHEMICAL OXIDATION/REDUCTION OF SELECTED COMPOUNDS MEDIATED BY INDIUM TIN OXIDE DOPED WITH LITHIUM AND GLASSY CARBON ELECTRODE MODIFIED WITH TIN DIOXIDE

By

YEO MAY CHING

Thesis Submitted to the School of Graduate Studues, Universiti Putra Malaysia in Fulfillment of the Requirements for the Degree of Master of Science

November 2012

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

ELECTROCHEMICAL OXIDATION/REDUCTION OF SELECTED COMPOUNDS MEDIATED BY INDIUM TIN OXIDE DOPED WITH LITHIUM AND GLASSY CARBON ELECTRODE MODIFIED WITH TIN DIOXIDE

By

YEO MAY CHING

November 2012

Chairman   : Associate Professor Tan Wee Tee, PhD

Faculty   : Science

The new chemically modified electrodes based on indium tin oxide (ITO) doped with lithium (Li^+/ITO) and tin oxide modified glassy carbon electrode (SnO_2/GCE) were fabricated by potential cycling and mechanical attachment methods, respectively. The Li^+/ITO electrode and SnO_2/GCE has been characterized using voltammetric techniques of cyclic voltammetry, chronoamperometry and chronocoulometry in this work.

The Li^+/ITO electrode was applied in the electrochemical determination of 50 µM Mn(II) in 0.1 M KCl (pH 6.9) and 50 µM Hg(II) in 0.1 M KCl (pH 6.4). The current enhancements of 2.9 times for the reduction of Mn(II) and 2.7 times for the reduction of Hg(II) were obtained by using the Li^+/ITO electrode compared to unmodified ITO

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electrode. Under the optimized parameters, the linear calibration graph showed correlation coefficient of 0.992 for the reduction of 10 µM to 1.0 mM Hg(II) and 0.995 for the concentration isotherm of Mn(II) in the range of 10 µM to 1.0 mM, with a linearity up to 0.2 mM. From this calibration plot, high sensitivity response of 2298.1 µA/mM with detection limit of 78.3 nM for the reduction of Hg(II) and 1777.3 µA/mM with detection limit of 100 nM for the reduction of Mn(II) at the Li^+/ITO electrode were obtained Effect of scan rate of Hg(II) and Mn(II) was studied in the range of 5 mV/s to 200 mV/s, and linear relation was observed. Based on the plot of log reductive current vs. log scan rate, experimental slopes of 0.38 and 0.84 were obtained for Hg(II) and Mn(II) respectively, indicating that the reaction under diffusion controlled and surface complex reaction respectively. Diffusion coefficient was calculated as 5.75×10^{-6} cm^2/s and 2.54×10^{-7} cm^2/s from the chronocoulometry study, and the activation energy obtained was 20.79 kJ/mol and 12.42 kJ/mol for Mn(II) and Hg(II) respectively in aqueous media at the Li^+/ITO electrode. Excellent analytical and recovery rates have been obtained using either lake or sea water samples spike with the analyte.

Besides, the bulk SnO_2/GCE was used for the electrochemical determination of 1.0 mM of ascorbic acid in 0.1 M KCl (pH 5), whereas spherical SnO_2/GCE was applied in the electrochemical determination of 1.0 mM of Hg(II) in 0.1 M KCl (pH 7.4). The current enhancements of 1.4 times for the oxidation of ascorbic acid and 1.5 times for the reduction of Hg(II) were also obtained by using bulk SnO_2/GCE and spherical SnO_2/GCE respectively compared to bare GCE. Calibration plot reveals linearity from

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the range of 20 µM to 2.0 mM with a correlation coefficient of 0.993 for the detection of ascorbic acid and concentration isotherm of Hg(II) in the range 0.5 µM to 1.0 mM, with linearity of up to 10 µM with a correlation coefficient of 0.999. The sensitivity and detection limit was estimated to be 23.47 µA/mM and 2.5 µM respectively for ascorbic acid and 61.79 µA/mM and 75 nM respectively for Hg(II). Furthermore, the diffusion coefficient and activation energy of ascorbic acid using bulk SnO_2/GCE were estimated to be 8.09 x 10^{-9} cm^2/s and 14.26 kJ/mol respectively while the values of the diffusion coefficient and activation energy of Hg(II) using spherical SnO_2/GCE were 2.84×10^{-6} cm^2/s and 21.66 kJ/mol respectively. Practically, SnO_2 modified GC electrode could be used for the determination of ascorbic acid in rose syrup sample and Hg(II) in sea water sample. Therefore, the use of Li^+/ITO electrode and SnO_2/GCE are highly sensitive, selective and stable in electrochemical measurement.

In addition, the surface morphology of the Li^+/ITO electrode and SnO_2 film before and after electrolysis was studied by scanning electron microscopy (SEM) and the percentage of the elements in components was examined by energy dispersive X-ray (EDX). Both of the SEM and EDX evidences that the Li^+/ITO electrode and SnO_2 film before and after electrolysis are solid to solid conversion.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

**PENGOKSIDAAN / PENURUNAN ELEKTROKIMIA SEBATIAN TERPILIH
YANG BERPERANTARAAN OLEH INDIUM TIN OKSIDA DIDOPKAN
DENGAN LITHIUM DAN ELEKTROD KARBON BERKACA MODIFIKASI
DENGAN TIMAH OKSIDA**

Oleh

YEO MAY CHING

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Pengerusi   : Profesor Madya Tan Wee Tee, PhD

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Elektrod terubahsuai secara kimia yang baru berdasarkan indium timah oksida (ITO) didopkan dengan lithium (Li^+/ITO) dan elektrod karbon berkaca terubaisuai timah oksida (SnO_2/GCE) telah dibuat dengan kaedah kitaran potensi dan kaedah lekatan mekanikal masing-masing. Elektrod Li^+/ITO dan SnO_2/GCE yang telah dianalisis menggunakan teknik voltammetri iaitu voltammetri berkitar, kronoamperometri, kronokulometri.

Elektrod Li^+/ITO telah digunakan dalam penentuan elektrokimia 50 μM Mn (II) di 0.1M KCl (pH 6.9) dan 50 μM Hg (II) dalam 0.1 M KCl (pH 6.4). Pertambahan arus

sebanyak 2.9 kali ganda untuk penurunan Mn (II) dan 2.7 kali ganda untuk penurunan Hg (II) telah diperolehi dengan menggunakan elektrod Li$^+$/ITO apabila dibandingkan dengan elektrod ITO tanpa diubah suai. Di bawah parameter optimum, graf kalibrasi linear menunjukkan pekali korelasi 0.992 untuk penurunan 10 μM - 1.0 mM Hg (II) dan 0.995 untuk isoterm kepekatan Mn (II) dalam julat 10 μM - 1.0 mM, dengan julat linear hingga 0.2 mM. Dari plot kalibrasi ini, sensitiviti yang dibaikan adalah tinggi sebanyak 2298,1 μA/mM dengan had pengesanan 78.3 nM untuk penurunan Hg (II) dan 1777.3 μA/mM dengan had pengesanan 100 nM untuk penurunan Mn (II) di Li$^+$/ITO elektrod telah diperolehi. Pengaruh kadar imbasan Hg (II) dan Mn (II) telah dikaji dalam julat 5 mV/s – 200 mV/s, dan hubungan linear telah diperolehi. Berdasarkan plot log arus penurunan vs. log kadar imbasan, kecerunan eksperimen 0.38 dan 0.84 telah diperolehi bagi Hg (II) dan Mn (II) masing-masing, menunjukkan bahawa tindak balas adalah jenis difusi terkawal dan tindakbalas kompleks permukaan masing-masing. Pekali difusi yang dikira adalah 5.75×10^{-6} cm^2/s dan 2.54×10^{-7} cm^2/s daripada kajian kronokulometri dan tenaga pengaktifan yang diperolehi adalah 20.79 kJ/mol dan 12.42 kJ/mol bagi Mn (II) dan Hg (II) masing-masing dalam media akueus pada elektrod Li$^+$/ITO. Analisis dan kadar dapatsemula yang baik telah diperolehi dengan menggunakan sama ada sampel air tasik atau air laut melalui kaedah penambahan piawai.

Selain daripada itu, SnO$_2$/GCE pukal telah digunakan dalam penentuan elektrokimia 1.0 mM asid askorbik dalam 0.1 M KCl (pH 5) manakala SnO$_2$/GCE sfera telah digunakan dalam penentuan elektrokimia 1.0 mM Hg (II) dalam 0.1 MKCl (pH 7.4). Pertambahan arus sebanyak 1.4 kali bagi pengoksidaan asid askorbik dan 1.5 kali untuk penurunan Hg

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(II) juga diperoleh dengan menggunakan SnO_2/GCE pukal dan SnO_2/GCE sfera masing-masing apabila dibandingkan dengan GCE tanpa diubahsuai. Plot tentukuran adalah linear dari julat 20 μM-2.0 mM dengan pekali korelasi sebanyak 0.993 untuk mengesan asid askorbik dan isoterm kepekatan Hg (II) dalam julat 0.5 μM -1.0 mM, dengan kelinearan sehingga 10μM dengan pekali korelasi sebanyak 0.999. Sensitiviti dan had pengesanan dianggarkan sebanyak 23.47 μA/mM dan 2.5 μM masing-masing untuk asid askorbik dan 61.79 μA/mM dan 75 nM masing-masing untuk Hg (II). Tambahan pula, pekali pembauran dan tenaga pengaktifan asid askorbik menggunakan SnO_2/GCE pukal telah dianggarkan menjadi 8.09 x 10^{-9} cm^2/s dan 14.26 kJ/mol masing-masing manakala nilai pekali pembauran dan tenaga pengaktifan Hg (II) menggunakan sfera SnO_2/GCE ialah 2.84x10^{-6} cm^2/s dan 21.66 kJ/mol masing-masing. Secara praktikalnya, elektrod GC terubaisuai SnO_2 boleh digunakan untuk penentuan asid askorbik dalam sampel sirap ros dan Hg (II) dalam sampel air laut. Oleh itu, penggunaan elektrod Li$^+$/ITO dan SnO_2/GCE adalah sangat sensitif, terpilih dan stabil dalam pengukuran elektrokimia.

Di samping itu, morfologi permukaan filem elektrod Li$^+$/ITO dan SnO_2 sebelum dan selepas elektrolisis telah dianalisis dengan mikroskopi pemimbaran elektron (SEM) dan peratusan elemen dalam komponen dianalisis oleh sinar-X penyebaran tenaga (EDX). Kedua-dua SEM dan EDX menunjukkan bahawa elektrod Li$^+$/ITO dan filem SnO_2 filem sebelum dan selepas elektrolisis adalah penukaran pepejal kepada pepejal.

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I certify that a Thesis Examination Committee has met on 7 November 2012 to conduct the final examination of YEO MAY CHING on her thesis entitled " **ELECTROCHEMICAL OXIDATION/REDUCTION OF SELECTED COMPOUNDS MEDIATED BY INDIUM TIN OXIDE DOPED WITH LITHIUM AND GLASSY CARBON ELECTRODE MODIFIED WITH TIN DIOXIDE**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

YEO MAY CHING

Date:

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LIST OF ABBREVIATIONS

A	Area
BAS	Bioanalytical Systems
BPPGE	Basal plane pyrolytic graphite electrode
C	Concentration
CA	Chronoamperometry
CC	Chronocoulometry
CE	Counter electrode
CME	Chemically modified electrode
CV	Cyclic voltammetry
D	Diffusion coefficient
E	Potential
E_a	Activation energy
EDX	Energy dispersive of X-ray
F	Faraday
GCE	Glassy carbon electrode
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
ITO	Indium Tin Oxide
Li^+/ITO	Lithium doped/indium tin oxide
LSV	Linear sweep voltammogram
MAM	Mechanical attachment method
n	Number of electron
Ox	Oxidation

Pt	Platinum
RE	Reference electrode
R	Reduce
Red	Reduction
SEM	Scanning electron microscopy
SnO_2/GCE	Tin oxide/glassy carbon electrode
t	Time
WE	Working electrode
υ	Scan rate

CHAPTER 1

INTRODUCTION

1.1   Chemical Modified Electrode

The definition of a chemically modified electrode (CME) is: a conducting or semiconducting material that has been coated with a monomolecular, multi-molecular, ionic, or polymeric film which alters the electrochemical, optical, and other properties of the interface (Edwards et al., 2007).

In recent years there has been a great deal of interest in the development of various type of electrochemical sensors that target to increase selectivity, sensitivity, chemical and electrochemical stability, as well as a larger usable potential window and improved resistance to fouling (Christian, 2004). Such deliberate alteration of electrode surfaces, through the incorporation of an appropriate surface modifier, can meet the needs of many electroanalytical problems, and may form the basis for new analytical applications and different sensing device (Uslu et al., 2007). Therefore, the need for improved electrode performance and logically designed interfaces is rapidly developing in many areas of science.

There are also various ways in which CMEs can benefit analytical applications. These include acceleration of electron transfer reactions, preferential accumulation, or selective membrane permeation. These steps can impact higher selectivity,

sensitivity or stability to electrochemical devices. There are many types of chemically modified electrode such as self-assembled monolayers, sol-gel encapsulation of reactive species, electrocatalytic modified electrode and many more. Electrocatalytic modified electrode will be of prime interest of these studies.

Electrocatalysis at a modified electrode is usually an electron transfer reaction between the electrode and some solution substrate which, when mediated by an immobilized redox couple (i-e., the mediator), proceeds at a lower over potential than would otherwise occur at the bare electrode (Durst et al., 1997).

1.2   Elecytroanalysis

Electroanalytical technique are concerned with the interplay between electricity and chemistry, namely measurements of electrical quantities, such as current, potential, or charge, and their relationship to chemical parameters. The use of electrical measurements for analytical purpose has found a vast range of applications, such as environmental monitoring, industrial quality control, and biomedical analysis (Wang et al., 2000) .

Electrochemical proposes take place at the electrode- solution interface which is in contrast to many chemical measurements that involve homogeneous bulk solution. The two principal types of electroanalytical measurements are potentiometric and potentiostatic. Potentiostatic technique can measure any chemical species that is electro

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active, in other words, that can be made to reduce or oxidize from the resulting current that reflects the rate at which electrons move across the electron-solution interface. Non-electro active compounds may also be detected in connection with indirect or derivatization procedures.

Controlled-potential (potentiometric) techniques deal with the study of charge-transfer processes at the electrode-solution interface. Here, the electrode potential is being used to derive the electron-transfer reaction and the resultant current is measured. The role of the potential is analogous to that of the wavelength in optical measurements. Such a controllable parameter can be viewed as "electron pressure", which forces the chemical species to gain or lose an electron (reduction or oxidation, respectively).

The advantages of electroanalytical techniques include high sensitivity, selectivity towards electro active species, a wide linear range, portable and low cost instrumentation, speciation capability, and a wide range of electrons that allow assays of unusual environments. These advantages could be useful in constructing chemical sensors, and environmental studies (Wang et al., 1990).

1.3   Fundamental of Voltammetric Techniques

Voltammetry is the electrochemical technique in which the current at an electrode is measured as a function of the potential, or voltage, applied to the electrode. The potential is varied in some systematic manner and the resulting current- potential plot is called a voltammogram. The most common application of voltammetry is for analytical purposes.

Voltammetry can be used to analyze any chemical species that is electroactive that is it can be oxidize or reduce. The potential of the electrode is the controlled parameter that causes the chemical species to be oxidized or reduced.

1.3.1   Linear Sweep Voltammetry

Linear sweep voltammetry is the simplest voltammetric technique, which uses waveform. The current response is measured when the potential is applied to the working electrode as a function of time as shown in Figure 1.1 (Bontempelli et al., 2009).

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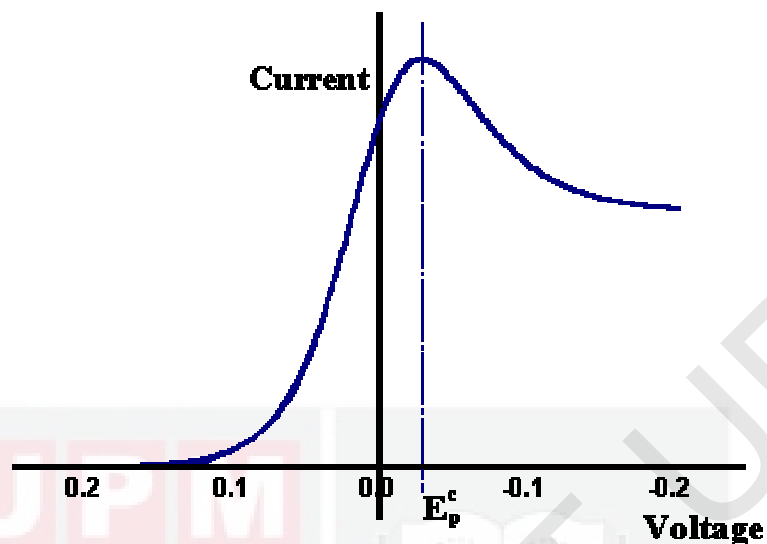
Figure 2.1 Linear Sweep Voltammetry

The slope of this ramp has units of volts per unit time, and is generally called the scan rate of the experiment. Interestingly, with a linear potential ramp, the faradaic current is found to increase at higher scan rates. This is due to the increased flux of electroactive material to the electrode at the higher scan rates. The value of $E_{1/2}$ can be used to identify unknown species, and the height of the limiting current can be used to determine concentration.

1.3.2 Cyclic voltammetry (CV)

Cyclic Voltammetry (CV) is one of the effective and common electroanalytical techniques that widely used by electrochemists for the study of redox processes. Cyclic voltammetry is characterized by smooth increase of a working electrode potential from one potential limit to the other and back. A potential is applied to the system, and the faradaic current response is measured (a faradaic current is the current due to a redox reaction). The current response over a range of potentials is measured, starting at an initial value and varying the potential in a linear manner up to a pre-defined limiting value. At this potential, the direction of the potential scan is reversed, and the same potential window is scanned in the opposite direction. This means that, for example, species formed by oxidation on the first (forward) scan can be reduced on the second (reverse) scan. This technique is commonly used, since it provides a fast and simple method for initial characterization of a redox-active system. In addition to providing an estimate of the redox potential, it can also provide information about the rate of electron transfer between the electrode and the analyte, and the stability of the analyte in the electrolyzed oxidation states.

Cyclic voltammetry (CV) is based on the same principles as linear sweep voltammtery. In this case the voltage is swept between two values at a fixed rate, however now when the voltage reaches V2 the scan is reversed and the voltage is swept back to V1 and shows at figure 1.2 (Parker, 1986).
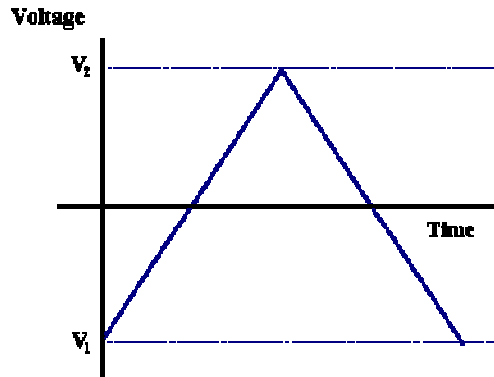
Figure 2.2 Cyclic potential sweep

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in figure 1.3 (Parker, 1986). At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidised form (point A). As the redox potential is approached, there is a net anodic current which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidised to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence is qt resulting in an asymmetric peak shape.

Upon reversal of the scan (point C), the current continues to decay with a qt until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current which eventually produces a peak shaped response (point D).

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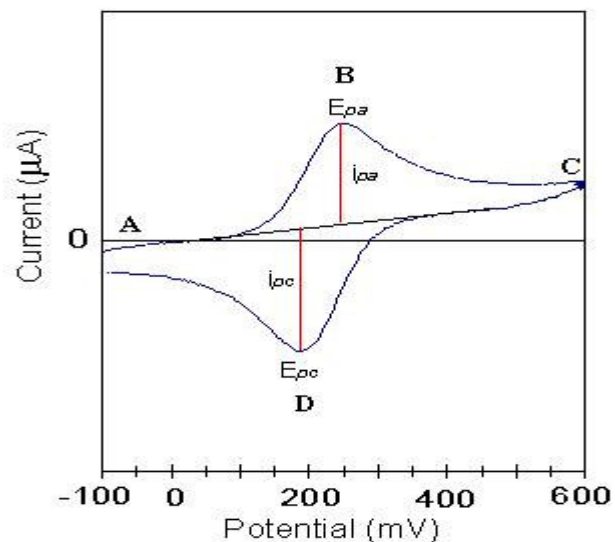
Figure 2.3 Typical current response for cyclic voltammetry

A redox system which remains in equilibrium throughout the potential scan possesses an electrochemical reaction said to be reversible. When electron-transfer kinetics is slow relative to mass transport, the process is no longer in equilibrium and therefore does not obey the Nernst equation. The electrochemical reaction is an irreversible one. Intermediate cases in which the kinetics of both the forward and reverse electron-transfer processes is taken account of are described as being quasi-reversible. For this type of system, the scan rate has a considerable effect on the nature of the cyclic voltammetry.

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For a reversible electron transfer process (Eklund et al., 1999),

- The separation of the forward and reverse peak (ΔE_p) is given by 56/n mV (where n is the number of electron equivalents transferred during the redox process) at $25^\circ C$ for all scan and the current is independent on scan rate.

- The peak width is equal to 28.5/n mV for all scan rates.

- The peak current ratio (i_{pa}/i_{pc}) is equal to 1 for all scan rates.

- The half wave potential, E ½ is related to the peak potentials by the expression

$$E\, ½ \;=\; (E_p^{ox} \,+\, E_p^{red})/2$$

- The peak current is given by the Randles-Sevcik equation (Equation 1) which is

$$I_p^{ox} \;=\; -I_p^{red} \;=\; +\, (2.69 \times 10^5)\, n^{3/2} ACD^{½} v^{½} \qquad \text{(Equation 1)}\; .$$

where   n = the number of moles of electrons transferred in the reaction

        A = the area of the electrode (cm^2)

        C = the analyte concentration (mol/cm^3)

        D = the diffusion coefficient (cm^2/s)

        v = the scan rate of the approved potential (mV/s)

For an irreversible process,

- There is no reverse peak because the reverse electron-transfer process does not occur.

- The peak current is given by the expression

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$$I^{ox} = (2.99 \times 10^5)n\,(\alpha na)^{1/2}\,ADA^{1/2}\,.v^{1/2}\,[A]_o$$

- The peak potential is a function of scan rate, as scan rate increase, the peak becomes wider thus the peak of oxidation potential shift to more positive potentials.

For a quasi-reversible process,

- The peak separation is larger than 56/n mV
- The peaks becomes broader as the scan rate increase and the peak current is below the value expected for a reversible electron-transfer process
- The ratio of the peak currents is equal to 1.

1.3.3 Chronoamperometry (CA)

Chronoamperometry (CA) is an electrochemical method in which a step potential is applied and the current, i, is measured as a function of time, t. This i-t response is comprised of two components: the current due to charging the double-layer and the other due to the electron transfer reaction with the electroactive species. Of course, the extent to which both occur simultaneously depends on the initial, E_i, and the final value, E_f, of the potential. The results are most easily interpreted when a planar (flat) electrode is used in a quiet, unstirred solution, and the applied potential is sufficient to reduce or oxidize the electroactive species as fast as it gets to the electrode surface, i.e., at a diffusion-controlled rate (Bard et al, 2001).

As shown at figure 1.4, the potential is changed instantaneously from the initial potential to the first step potential, and it is held at this value for the first step time (Wilson, 1994). This is a single potential step experiment. In a double potential step experiment, the potential is changed to the second step potential after the first step time, and it is then held at this value for the second step time.
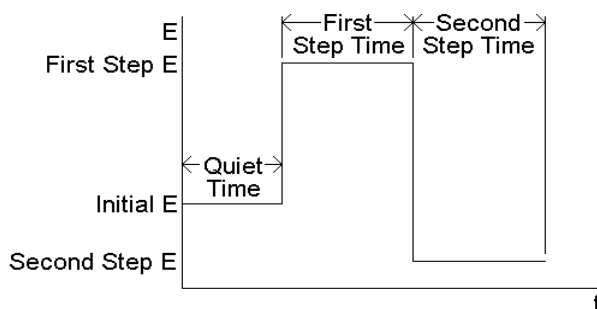
Figure 2.4 Potential wave form for chronoamperometry

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The current response depends on the values of the initial and final potential. If not faradaic reaction occurs at either potential, then the response is due to charging of the electrode. The response is a current "spike", which decays exponentially.

The initial potential is a potential at which no faradaic reaction occurs and the final potential is a potential at which the faradaic reaction occurs very rapidly. As they arrive at the surface of the working electrode, the electroactive molecules are electrolyzed. The current is determined by the rate of mass transport from the bulk solution to the surface of the working electrode.

The typical current response is shown as figure 1.5 (Wilson, 1994). In a typical experiment, the potential is stepped from a value at which no redox process occurs at the electrode (i=0) to a value at which diffusion – controlled reduction or oxidation occurs.
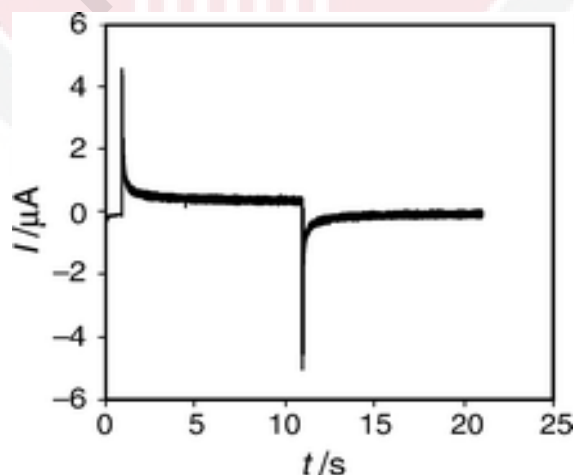
Figure 2.5 Chronoamperogram (current-time response) for double potential step

CA

The diffusion-controlled current is given by the Cottrell equation (Equation 2) (Wilson, 1994):

$$I = nFAC(D/\pi)^{1/2}t^{1/2} \qquad \text{(Equation 2)}$$

Where I = current (A)

N = number of electron transferred /molecule (eq/mol)

F = Faraday's constant (96500C/eq)

A = electrode area (cm²)

D = diffusion coefficient (cm²/s)

C = concentration (mol/cm³)

t = time (s)

Current versus time plot is displayed during the experimental run. For diffusion-controlled systems, these are straight-line plots and are referred as the Cottrell plot as shown in figure 1.6 (Nishiumi et al., 2005).
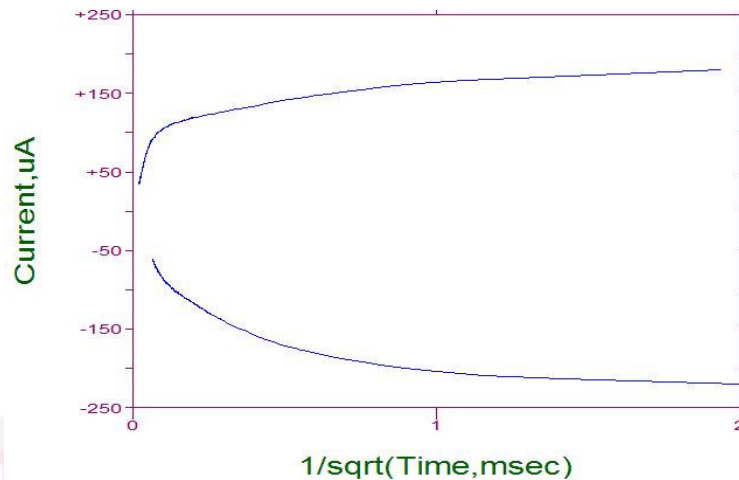
Figure 2.6 Cottrell plot

1.3.4   Chronocoulometry

Chronocoulometry (CC) is one of the classical electrochemical techniques frequently used in electroanalytical chemistry. As its name implies, CC is the measurement of charge (coulombs) as a function of time (chrono). The shape of the resulting chronocoulogram can be understood by considering the concentration gradients in the solution adjacent to the electrode surface. Chronocoulometry is useful for measuring electrode surface areas, diffusion coefficients, the time window of an electrochemical cell, adsorption of electroactive species, and the mechanisms and rate constants for chemical reactions coupled to electron transfer reactions.

The potential excitation function of chronocoulometry is same as chronoamperometry. This also can explain that the CC is CA in which the cell current is integrated to

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calculate charge. The potential is stepped from an initial potential where no redox

reaction occurs to a final potential.
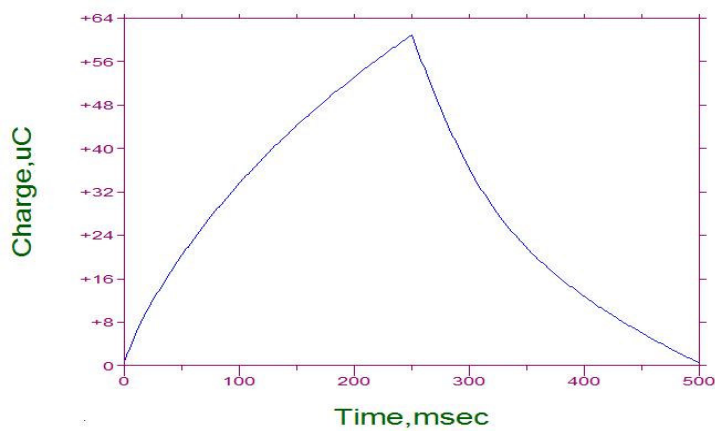
Figure 2.7 Chronocoulogram (charge-time)

Chronocoulometry offers several advantages over chroamperometry. Firstly, the latter

parts of the response are least distorted by no ideal potential rise and offer better signal-

to-noise rations while retaining the information from the early response. Secondly, is the

integration eliminates random noise and the last one is contributions from diffusion and

interfacial components are easily separated.

The diffusion-controlled charge is given by Anson equation (Equation 3) (Bott et al.,

2004):

$$Q = 2nFAC \ (Dt/\pi)^{1/2} \qquad \text{(Equation 3)}$$

Where Q = charge response (C)

n = number of electrons transferred/molecule (eq/mol)

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F = Faraday's constant (96500 C/eq)

A = electrode area (cm²)

D = Diffusion coefficient (cm²/s)

C = bulk concentration (mol/cm³)

t = time (s)

Q versus time plot is displayed during the experimental run and a plot of Q versus $t^{1/2}$ is often referred as Anson plot and it is shown at figure 1.8 (Bott et al, 2004). There is a linear relationship between the charge and the square root time.
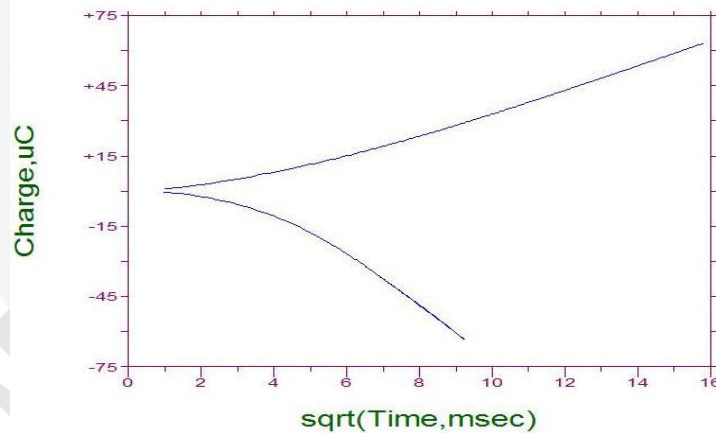
Figure 2.8 Anson plot

The electrolysis of solution species is diffusion-controlled and depends on $t^{1/2}$. In contrast, the electrolysis of adsorbed species is essentially instantaneously as the double layer charging. The equation for the total charge Q is:

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$$Q = Q_{diff} + Q_{ads} + Q_{dl}$$

Or

$$Q = 2nFAC \ (DT/\pi)^{1/2} + nFA\Gamma o + Q_{dl} \qquad \text{(Equation 4)}$$

Where Q_{diff} = charge due to electrolysis of solution species

Q_{ads} = charge due to electrolysis of adsorbed species

Q_{dl} = double-layer charging

Γo = surface concentration of adsorbed species (mol/cm²)

Thus, the intercept of the Anson plot is the sum of Q_{dl} and Q_{ads}. Q_{dl} can be eliminated from the equation by running the identical experiment on the electrolyte alone. However, this approach assumes that Q_{dl} is the same both in the presence and in the absence of the adsorbed analyte, which is generally not a valid assumption.

Therefore, both CA and CC can be used to measure one of the numbers of electrons transferred per molecule, the concentration of the bulk solution, electrode area and diffusion coefficient by measure the gradients of these straight line plots, provided the other three constants are known.

1.4 Indium Tin Oxide (ITO)

Indium tin oxide (ITO) is an oxide film composed of mainly indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2). ITO also known as the degenerate n-type semiconductor (Meng et al., 1997). ITO which has its high optical transmittance (more than 80- 90% at 550 nm wavelength) and low sheet resistivity (lower than 2×10^{-4} V cm), is an important optoelectronic material (Huang et al., 2003).

Indium tin oxide (ITO) is a transparent conducting and photoelectric material that have attracted the interest of many researchers in the field of electrochemistry due to their good electrical conductivity and photo-penetrability (Gardonio et al., 2008). Liquid crystal display (LCD) and light emitted diode (LED) are some of the examples for the application of ITO in electronic and photoelectric devices (Joshi et al., 1995). Besides that, the high electrical conductivity of ITO films results in a high reflectivity in the infrared region, which gives applications to thermal insulation of windows, prevention of radiative cooling (Lampert, 1981). Thus, we suspected that lithium doped modified ITO electrode was used to enhance the electrode conductivity, facilitating the electron transfer and improving the analytical sensitivity and selectivity.

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1.5   Tin Oxide (SnO$_2$)

The wide variety of electronic and chemical properties of metal oxides makes them exciting materials for basic research and for technological applications alike. Oxides span a wide range of electrical properties from wide band-gap insulators to metallic and superconducting. Tin dioxide belongs to a class of materials that combines high electrical conductivity with optical transparency and thus constitutes an important component for optoelectronic applications.

Tin oxide is a compound of tin and oxygen where tin has the oxidation state of +2. Tin oxide (SnO$_2$) is a very important electronic material. Tin oxide is an n-type semiconductor with a large band gap of 3.6 eV (Li et al., 2008). SnO$_2$ is very stable, has got high carrier density and supports enormous concentration of intrinsic and stoichiometry-violating vacancies, which is correlated to its electrical conductivity (Das et al., 2008).

The surface and materials properties of SnO$_2$ are attributed to three major applications. These applications are (i) as a transparent conducting oxide (TCO), (ii) as an oxidation catalyst, and (iii) as a solid state gas sensing material. For example, SnO$_2$ applied as optoelectronic devices, dye-based solar cells, catalysts, gas sensors, electrochromic devices and electrode materials (H. Wang et al., 2010). Though SnO$_2$ particles are widely applied for gas sensing application due to their high mobility of conduction electrons, good chemical and thermal stability under the operating conditions of sensors

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(Xing et al., 2011), this material has rarely been envisaged as a chemical sensor for heavy metal ions in an aqueous condition.

1.6 Manganese

Manganese is a very common compound that can be found everywhere on earth. Manganese has an atomic mass of 54.94 and a density of 7.21–7.44 g cm^{-3} depending on the allotropic form. It melts at 1244 °C, boils at 1962 °C (Gerber et al., 2002). Manganese (abbreviated Mn) can exist in various oxidation states. The most common oxidation states of manganese are +2, +3, +4, +6 and +7. The most stable oxidation state for manganese is +2, which has a pale pink color (Brown et al., 2008; Cotton et al., 1999). Manganese (IV) compound, potassium permanganate is a common oxidizing agent and widely used for volumetric analysis. (Skoog et al., 2004).

Manganese is one of the toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. However, health problems will also occur when the uptake is too high. The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis (Normandin et al., 2004).

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Naturally occurring Mn is commonly found in drinking water supplies and is essential for human health at low concentrations (Heal, 2001). Thus, the World Health Organization (WHO) has set a guideline value of 0.4 mg l^{-1} (WHO, 2008) for drinking water. Besides that, the manganese limits for air concentration recommended by the WHO (World Health Organization) is 0.3 mg/m^3, whereas the limits for OSHA (Occupational Safety and Health Organization) is still set at 5 mg/m^3. (Gerber, et al., 2002).

Manganese is one of the most used metals in the industry. Manganese is mainly used in iron and steel production and in ferro- and silicomanganese alloys. Other uses are in alloys with Cu or Al to reduce corrosion, in batteries as MnO_2, for colouring glasses and ceramics and, as permanganate, for oxidation reactions in chemical industries. Permanganate is employed to treat skin diseases (Frumkin et al., 1997).

1.7 Mercury

Mercury is a chemical element with the symbol Hg. Mercury is one of the most toxic heavy metals known to organisms and the environment because of its high reactivity, its extreme volatility and its relative solubility in water and living tissues (Panta et al., 2009). Contamination with toxic heavy metal ions may have severe effects on human health and environment. Mercury and its related compounds are widely related to

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global pollutant due to its highly toxic characteristic. Mercury contamination is widespread in different ecological compartments such as atmosphere, soil and water.

Mercury exists in two main oxidation states that are I and II. However, Mercury (II) is the most common oxidation state in nature. Mercury mainly used for the manufacture of industrial chemicals or for electrical and electronic applications. It is most commonly used as thermometers, especially to measure high temperatures and gaseous mercury in fluorescent lamps. Mercury has limited application compared to other metal due to health and safety regulations.

The United Nations Environmental Programme (UNEP) estimated that an annual release of mercury was 4400 and 7500 metric tonnes as a result of natural sources and human activities respectively (Hylander et al., 2006) which contaminates the food chain and the environment. The mercury limits for wastewater discharge and drinking water established by the World Health Organization (WHO), Environmental Protection Agency (EPA) and Ministry of the Environment of Japan are $5 - 10$ μgL^{-1} (ca. 25 - 50 nM) and $0.5 - 2$ μgL^{-1} (ca. 2.5 – 10 nM), respectively (Zhu et al., 2009).

1.8 Ascorbic Acid

L-ascorbic acid is a naturally occurring organic compound with antioxidant properties. L-ascorbic acid also well known as Vitamin C. It is usually prepared by synthesis from glucose, or extracted from plant sources like rose hips, blackcurrants or citrus fruits. Ascorbic acid is a white solid, but impure samples can appear yellowish. It is an antiscorbutic product. On exposure to light, it gradually darkens. In the dry state, it is reasonably stable in air, but in solution it rapidly oxidizes. Ascorbic acid (vitamin C) is freely soluble in water; sparingly soluble in alcohol; insoluble in chloroform, in ether, and in benzene. The empirical formula of ascorbic acid is $C_6H_8O_6$, and the molecular weight is 176.13 (Monograph). The molecular structure is shown in figure 1.9.
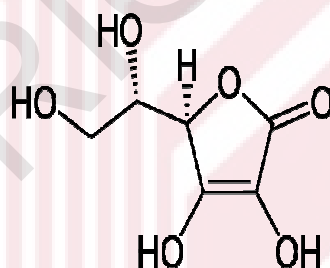
Figure 2.9 Structure of Ascorbic Acid

Ascorbic acid (Vitamin C) is a water-soluble vitamin, which is needed by the body to form collagen in bones, cartilage, muscle, and blood vessels, and which aids in the absorption of iron (Goh et al., 2008). Therefore, the supply must be taken daily either from food containing high vitamin C or supplements. Good sources of vitamin C include fresh fruits and vegetables, particularly citrus fruits such as oranges.

Vitamin C is used most often for the prevention or treatment of the common cold (Douglas et al., 2007).

1.9 Problem Statement

In recent years, electroanalysts focus on development of new chemically modified electrodes, because currently available working electrodes such as glassy carbon, gold and platinum are lack of sensitivity and selectivity (Gooding, 2005). The new electrode should be able to possess following advantages: highly sensitive, good detection limit, stability, selectivity, reproducibility, low cost and simplicity. Recent published works used indium tin oxide (ITO) electrode and GCE modified with a thin layer or nanoparticles (Goyal et al., 2010; Goyal et al., 2009). Typically using modified ITO electrode and GCE for electroanalysis the claimed benefits include good detection limits, increased sensitivity, resistance to surface fouling and decreased overpotentials (J. Wang, 1990).

Combining the unique properties of lithium and SnO_2, such as high electrical conductivity, is expected to enhance the electrocatalytic activity of SnO_2/GC and Li^+/ITO electrodes. To date, there are no published reports on the usage of SnO_2 modified GC and Li doped ITO electrode. Therefore the main objectives of the present study were to develop new chemically modified electrode based on the Li^+/ITO and SnO_2/GC electrode. The outcomes of this research will have substantial contribution to the field of electroanalytical chemistry.

1.10 Objectives

The objectives of this study are as follows:

1. To fabricate a solid electrode based on modified lithium ion doped/ indium tin oxide electrode (Li^+/ITO) and tin oxide/glassy carbon electrode (SnO_2/GCE).

2. To investigate the usefulness of the fabricated electrodes as electrochemical sensors for the detection of Mn(II), Hg(II) and ascorbic acid.

3. To compare the electro catalytic behaviors between ITO with and without Li^+ dopant and GCE modified with and without SnO_2, on the Mn(II), Hg(II) and ascorbic acid.

4. To determine the optimum physical and chemical conditions for maximum current enhancement for the selected analyte ions.

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APPENDIX

LIST OF PUBLICATION AND CONFERENCES/SEMINARS ATTENDED

1. Yeo May Ching, Tan Wee Tee, Zulkarnain Zainal (2011). Electrochemical Studies of Mn(II) mediated by Li^+ doped Indium Tin Oxide(ITO) electrode. *International Journal of Electrochemical Science*, 6, 5305-5313.

2. H.N.Lim, R.Nurzulaikha, I. Harrison, SS Lim, W.T.Tan, and M.C. Yeo (2011). Spherical Tin Oxide,SnO_2 Particles Fabricatedvia Facile Hydrothermal Method for The Detection of Mercury (II) ions. *International Journal of Electrochemical Science,* 6, 4329 – 4340

3. H.N. Lim, R. Nurzulaikha, I. Harrison, S.S. Lim, W.T. Tan, M.C. Yeo, M.A. Yarmo, N.M. Huang (2012). Preparation and characterization of tin oxide, SnO_2 nanoparticles decorated graphene. *Ceramics International, 38, 5, 4209-4216*

4. Yeo May Ching, Tan Wee Tee, Yaw Ching Wey, 2010 Electrochemical Reduction of Arsenic (V) ion Mediated by Carbon NanoTube. Seminar Kimia Industri, , Universiti Putra Malaysia (Poster Presentation)

5. Shazwani Samson, Wee Tee Tan, Nurul Hudah Rahman, May Ching Yeo, 2011, Voltammetric Oxidation of Ascorbic Acid mediated by Nanoparticles of Fe0 modified glassy carbon electrode. Seminar Kimia Industri, , Universiti Putra Malaysia (Poster Presentation)

6.   Yeo May Ching, Tan Wee Tee, Zulkarnain Zainal, 2011, Electrochemical Studies of Mn(II) mediated by Li^+ doped Indium Tin Oxide(ITO) electrode. Fundamental Science Congress, Universiti Putra Malaysia (Poster Presentation).

7.   M.C. Yeo, W.T. Tan, H. N. Lim, Zulkarnain Zainal, 2012, Electrochemical Analysis of Mercury (II) Ions Mediated by Tin Oxide (SnO_2) modified glassy carbon electrode (GCE). Fundamental Science Congress, Universiti Putra Malaysia (Poster Presentation)

8.   M.C. Yeo, W.T. Tan, H. N. Lim, Zulkarnain Zainal, 2012, Electrochemical Analysis of Mercury (II) Ions Mediated by Tin Oxide (SnO_2) modified glassy carbon electrode (GCE). (submitted soon)

9.   M.C. Yeo, W.T. Tan, Zulkarnain Zainal, Electrochemical Studies of Hg(II) mediated by Li^+ doped Indium Tin Oxide(ITO) electrode.(drafted to be submit)

BIODATA OF STUDENT

Yeo May Ching was born in Melaka. She received her primary education in Sekolah Rendah Kebangsaan Cina Notre Dame and secondary education in Sekolah Menengah Kebangsaan Notre Dame, Melaka. She pursued her secondary education in Sekolah Menengah Gajah Berang, Melaka in 2005. She completed her Bachelor of Science (Honours) majoring in Chemistry degree with Second Class Upper Honours from Chemistry department, Faculty of Science, Universiti Putra Malaysia in 2010. In the same year she enrolled for full time Master of Science degree course majoring in Electrochemistry at Chemistry Department, Faculty of Science, Universiti Putra Malaysia. During her studies, she was offered as a laboratory demonstrator to assist undergraduates in practical classes since semester July 2011/2012 to semester July 2012/2013.