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DEVELOPMENT OF HYDROQUINONE AMPEROMETRIC SENSOR USING A MODIFIED PASTE ELECTRODE BASED ON IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM BROMIDE

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ABSTRACT

This study aims to develop a graphene composite modified paste electrode (GrPE) based on ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIMBr) to detect hydroquinone. The electrochemical properties of the modified electrode were determined using square wave voltammetry and electrochemical impedance spectroscopy. The results showed that under optimal conditions, the modified electrode showed a linear concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a detection limit of hydroquinone, 2.77×10^{-7} M. The interferences from Ba^{2+}, Cu^{2+}, Na^{+}, K^{+}, NO^{3-}, Cl^{-}, SO_4^{2-}, glycine, glucose, fructose and sucrose were negligible. Electrochemical impedance spectroscopy indicated that the charge transfer at the electrode-solution interface was excellent. The proposed electrode was successfully applied to determine hydroquinone in wastewater samples and cosmetic creams with range of recovery 97 – 104%. In conclusion, the modified electrode that has been developed is able to detect hydroquinone. Therefore, the modified electrode is a suitable alternative for the determination of hydroquinone due to its sensitivity, selectivity and high reproducibility.

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PEMBANGUNAN PENGESAN AMPEROMETRIK HIDROKUINON MENGGUNAKAN ELEKTROD PES GRAPHENE TERUBAH SUAI BERASASKAN CECAIR IONIK 1-ETIL-3-METILIMIDAZOLIUM BROMIDA

ABSTRAK

Kajian ini bertujuan membangunkan elektrod pes terubah suai komposit graphene (GrPE) berasaskan cecair ionik 1-etil-3-metilimidazolium bromida (EMIMBr) bagi mengesan hidrokuinon. Sifat-sifat elektrokimia elektrod terubah suai telah ditentukan menggunakan kaedah voltammetri gelombang segiempat sama dan spektroskopi impedans elektrokimia. Dapatan kajian menunjukkan julat kepekatan linear 1.0×10^{-6} sehingga 1.0×10^{-2} M dengan had pengesanan 2.77×10^{-7} M. Gangguan-gangguan oleh Ba^{2+}, Cu^{2+}, Na^{+}, K^{+}, NO^{3-}, Cl^{-}, SO_4^{2-}, glisina, glukosa, fruktosa dan sukrosa adalah terabaikan. Spektroskopi impedan elektrokimia menunjukkan bahawa pemindahan caj pada antara muka elektrod-larutan adalah sangat baik. Elektrod yang dicadangkan telah berjaya digunakan untuk menentukan hidrokuinon dalam sampel air buangan dan krim kosmetik dengan julat pengembalian semula 97-104%. Kesimpulannya, elektrod terubah suai yang telah dibangunkan ini mampu mengesan hidrokuinon. Implikasinya, elektrod terubah suai adalah alternatif yang sesuai untuk pengesanan hidrokuinon disebabkan oleh kepekaan, kepilihan dan kebolehulangan yang tinggi.

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TABLE OF CONTENTS

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 1 INTRODUCTION

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 2 LITERATURE REVIEW

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 3 METHODOLOGY

3.2 Apparatus

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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LIST OF FIGURES

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF TABLES

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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LIST OF SCHEMATIC DIAGRAM

LIST OF ABBREVIATIONS

Ag/AgCl	Argentum/Argentum chloride
CMCPE	Chemically modified carbon paste electrode
CPE	Carbon paste electrode
CV	Cyclic voltammetry
CNT	Carbon nantube
DPASV	Different pulse anodic stripping voltammetry
DPCSV	Different pulse cathodic stripping voltammetry
DPV	Different pulse voltammetry
EMIMBr	1-ethyl-3-methylimidazolium bromide
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
Gr	Graphene
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
MWCNT	Multiwall carbon nanotube
SCE	Saturated calomel electrode
SWASV	Square wave anodic stripping voltammetry
SWV	Square-wave voltammetry

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CHAPTER 1

INTRODUCTION

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1.1 Introduction of Hydroquinone

Hydroquinone is the polyphenolic organic compound which also known as quinol, arctuvin, benzoquinol, hydroquinol or 1,4-benzenediol. It has a chemical formula, $C_6H_6O_2$ as shown in Figure 1.1 and molecular weight of 110.1 g/mol. Hydroquinone has its own physical appearance such as colourless, hexagonal prisms or crystals with a melting point and boiling point of 170-171 ˚C and 285-287 ˚C, respectively. Hydroquinone is soluble in water, ether, alcohol, acetone and benzene (slightly soluble) (Food and Drug Administration). Hydroquinone can be produced by aniline

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or phenol oxidation, by the reduction of quinine or by the reaction of carbon monoxide and acetylene (Merck, 2006).

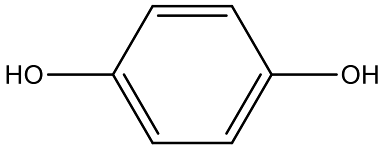

Figure 1.1. Chemical structure of hydroquinone.

Hydroquinone has been used in numerous field because of its advantage as a reducing agent (water-soluble). It is used in cosmetics (up to 2%) as a depigmenting agent also called as a bleaching creams and in medicine (up to 5%) to cure dyschromias (Blakley, Henry, & Smith, 2001; Hu et al., 2012). Hydroquinone make the skin more lighten through melanocyte toxicity and melanogenesis inhibition. Most of women who applying creams containing hydroquinone have permanent dark stain on their skin (Melisa & Jay, 2009). It also used as a reducing agent in developing solution of photographic, rubber antioxidants manufactured, dyes and almost all the antioxidants. Hydroquinone acts as inhibitor in polymerization process for certain chemicals and used as stabilizer in paints. Besides use in bleaching agent, it also use up in other type of cosmetics such as nails color coating and hair dyes (Lewis, 1993).

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Hydroquinone can occurs naturally in certain plants as free hydroquinone or as arbutin (hydroquinone β-ᴅ-glucopyranoside) and others customer products such as vegetables, fruits, coffee, beer and wine (DeCaprio, 1999). The process of production, formulation and chemical intermediate may release the hydroquinone into the

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environment. The hydroquinone substance may cause severe damages to human health that can cause chronic damages such as defects and cancer. If the hydroquinone is taken orally at high doses, its can affects the central nervous system. Hydroquinone is also the high toxic compound with low degradability in the environmental ecology. Hence, hydroquinone is banned by the European Union (EU) and Environmental Protection Agency (EPA) from the European cosmetic market (Deconinck, Bothy, Desmedt, Courselle, & De Beer, 2014). Many laboratory device can be used to detect the hydroquinone and its isomer such as high performance liquid chromatography (Marrubini, Calleri, Coccini, Castoldi, & Manzo, 2005), spectroscopy (Afkhami & Khatami, 2001), chemiluminescence (Zhao, Lv, Yuan, Zhou, & Xiao, 2007), pH based-flow injection analysis (Garcia-Mesa & Mateos, 2007) and electrochemical methods (Yang, Zhu, Chen, & Wang, 2009; Yin, Zhang, Zhou, Ma, Liu, Zhu, & Ai, 2011) have been used for the hydroquinone determination. Electrochemical methods have attracted enormous attentions because of their advantages such as high accuracy, rapid responses

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1.2 Introduction of Ionic Liquids

An ionic liquid is the liquid that containing only ions. Recently, ionic liquid is commonly is the term used for salts which melting point is relatively low (below 100 ˚C). in 1982, Wilkes et al. has reported the first room-temperature ionic liquids (RTILs) named 1-alkyl-3-methylimidazolium salts as tetrachloroaluminates (Wilkes,

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Levisky, Wilson, & Hussey, 1982). Generally, ILs was synthesized by using standard methods developed and stated in the literature. ILs is completely composed from the organic cation and anion that having unique properties such as great solubility and viscosity, broad electrochemical window that are resistant to oxidation and reduction, good ionic conductivity and high chemical stability (Hasanzadeh, Shadjou, Eskandani, & Guardia, 2012; Liu, He, Li, Sun, Shi, Liu, & Li, 2005; Opallo & Lesniewski, 2011; Shiddiky & Torriero, 2011; Sun & Armstrong, 2010; Zhou & Antonietti, 2003). These properties make them fascinating media in electrochemical biosensors and devices.

ILs has two groups according to their solubility in water. The water-immiscible (hydrophobic) IL is the first type such as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]). The imidazolium salts are increasingly used as hydrophobic ILs due to the hydrolysis of PF_6^- ion. In the other hand, the second type of ILs, is called water-miscible (hydrophilic) IL such as 1-butyl-3-methylimidazolium tetrafluoroborate. Contrast with the water-immiscible ILs, this type of ILs unstable in aqueous solutions but it still can form films with active electrochemical properties on glassy carbon electrode and can be used in aqueous media (Yu et al., 2005). The miscibility of ILs in water is very dependent on the anions (Liu et al., 2005). Cl^-, Br^-, NO_3^- and CH_3COO^- are anions that make the ILs miscible in water.

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In last decade, ionic liquids (ILs) have been used to be efficient binders/modifiers in the electrode fabrication. In order to enhance the sensitivity of electrochemical sensors, the applications of ionic liquids for electrode modification

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has become a trend. ILs has widely been used to detect ions via electroanalytical methods, such as potentiometric and voltammetric measurement. Trace amount of ion has been determined electrochemically by using linear sweep, square wave and cathodic stripping voltammetry. Liu and the groups has been proposed the IL-type carbon paste electrode (CPE) (Liu et al., 2005). While Maleki and co-workers developed a carbon ionic liquid electrode (CILE) with electrochemical properties that will well-suited for use in biosensor and sensor applications (Maleki, Safavi, & Tajabadi, 2006).

Safavi et al. described a non-enzymatic composite electrode by mixing the nanoscale $Ni(OH)_2$ with graphite powder and ionic liquid, $[Opyr][PF_6]$. The proposed electrode showed excellent electrocatalytic activity towards oxidation of glucose in an alkaline solution (Safavi, Maleki, Farjami, & Mahyari, 2009).

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Various electrode materials, such as glassy carbon (GC), gold (Au), CPE and screen-printed electrodes have widely been used. The task of paraffin was replaced with ILs that act as a conductor and binder because CPEs exhibit defects because of their poor fabrication reproducibility and fragile mechanical compared to other metal electrodes. Hence, ILs become the great and efficient alternative to construct the sensor. Maleki and co-workers shows that the electrodes that they fabricated by the applications of ILs as a binder agent produce more uniform electrodes than traditional CPEs which used paraffin as a binder. The presence of specific functionalities in ILs plays important role in their applications for modified electrode. For example, the

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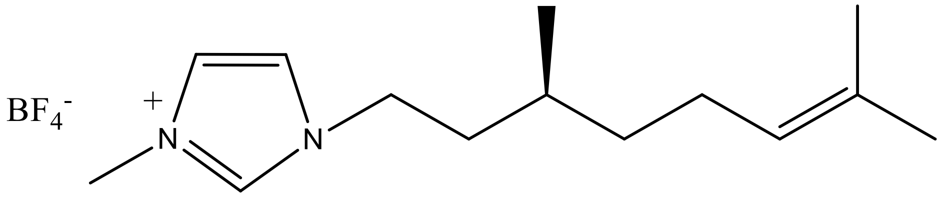
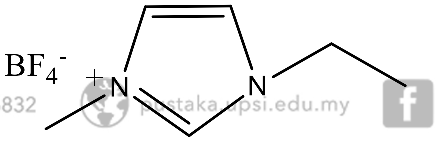
introduction of complexed metal ions as IL cations, give the electroactive IL-modified electrode (Wang, Jian, & Zhuang, 2009) and the use of aminoacid-functionalized IL that provides stable enzyme immobilization (Wang, Deng, Nie, Xu, & Yao, 2009). Figure 1.2 below shows the example of ionic liquid which the most often used for electrode modification.



1-methyl-3-(2,6-(S)-dimethylocten-2-yl) tetrafluoroborate (EMIMBF$_6$)



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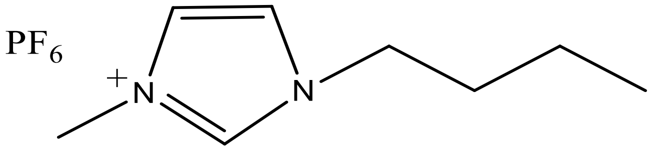
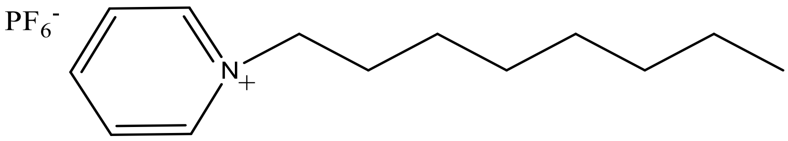
1-ethyl-3-methylimidazolium tetrafluoroborate



N-Butylpyridinium hexafluorophosphate (BPyPF$_6$)



Octylpyridinum hexafluorophosphate (OPyPF$_6$)

Figure 1.2. Examples of ionic liquid most often used for electrode modification.

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1.3 Electrochemistry

1.3.1 Amperometry Method

Amperometric is an electroanalytical technique which involves the subsequent measurement of the resulting steady-state current and the application of a constant reducing or oxidizing potential to an indicator (working electrode). The term ‘amperometry’ is comes from the word ‘ampere’ which is the current measurement and the measurement device ‘meter’ used in this method. The important of the amperometry’s application is in the construction of chemical sensor. The first amperometric sensor was developed by L. C. Clark in year 1956. He was developed this sensor to measure dissolved O_2 in blood. (Harvey, 2002)

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The design of the sensor is showed in Figure 1.3. This type of method offers the potentiality to distinguish selectivity between a number of electroactive species in solutions. Numerous analytical methods nowadays choose amperometric measurements in their work. For instance, amperometric titrations have been widely used for various substances in sample from water sample to radioactive materials. The amperometric sensors, for example a biosensors are extensively used for industrial, clinical and environmental monitoring (Harvey, 2002).

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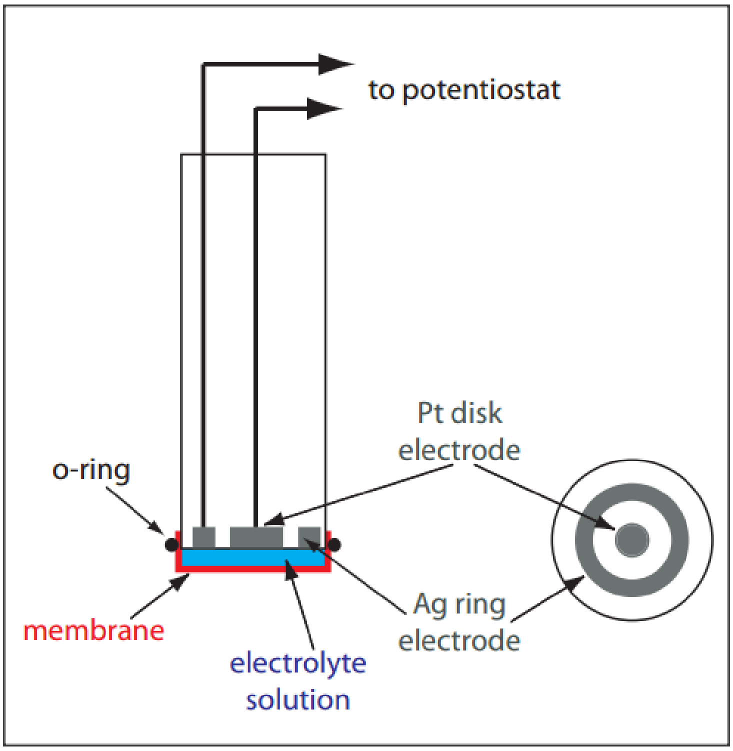

Figure 1.3. Clark amperometric sensor for determining dissolved O2. The diagram on the right is a cross-section through the electrode, showing the Ag ring electrode and the Pt disk electrode.

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Recently, many compounds has been successfully accomplish in detection by constant potential amperometric detection of many compounds has been successfully accomplish using Ni, Cu, others non-noble metal electrodes and glassy carbon electrodes (Hidayat, Hibbert, & Alexander, 1997; LaCourse, 1997; Luo, Zhang, & Baldwin, 1991).

Besides, another option is carbon paste with an embedded (Cui, Liu, & Lin, 2005). By applying potential, the resulting current is measured when conversion of electroactive species generated in the enzyme layer occurs at the electrode (Mehrvar & Abdi, 2004). Almost all of aromatic compounds such as phenols, aminophenols and

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catecholamines are simply detected by using this type of method. Amperometric sensors can perform in two- or three-electrode configurations. The two-electrode configuration, however, have the disadvantage which is limited control of the potential on the working electrode surface when the currents is high, so as a consequences the linear range will become shortened. Hence, to solve the issue, a third auxiliary electrode is employed (Thomas & Henze, 2001).

1.4 Introduction to Working Electrode

In voltammetric field, the electrodes play crucial role in contact with analyte solution. At electrode surface, the analytes change their charge by exchanging one or more electron through redox reaction. The working electrode is the area where the redox reaction of interest takes place. Electrical current at the working electrode due to transfer of electrons is termed as *faradic current*. The window of the electrode is the potential range within which the electrode can be polarized, because only this range can be used for measurements. The working electrode can be used for measurements only if has potential range required for measurement (Scholz, 2002).

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The performance of voltammetric measurement is depends on the working electrode material which have strong influence on it. This including many factor such as the surface reproducibility, electrical conductivity, potential window, availability, cost, mechanical properties, toxicity, and the geometry of the electrode. Noble metals,

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mercury and carbon are the most well-liked electrode materials for the voltammetric measurement (Wang, 2000). Several working electrodes (Figure 1.4) have different potential range depend on electrode material and composition of electrolyte that used (Skoog, Holler, & Crouch, 2007).

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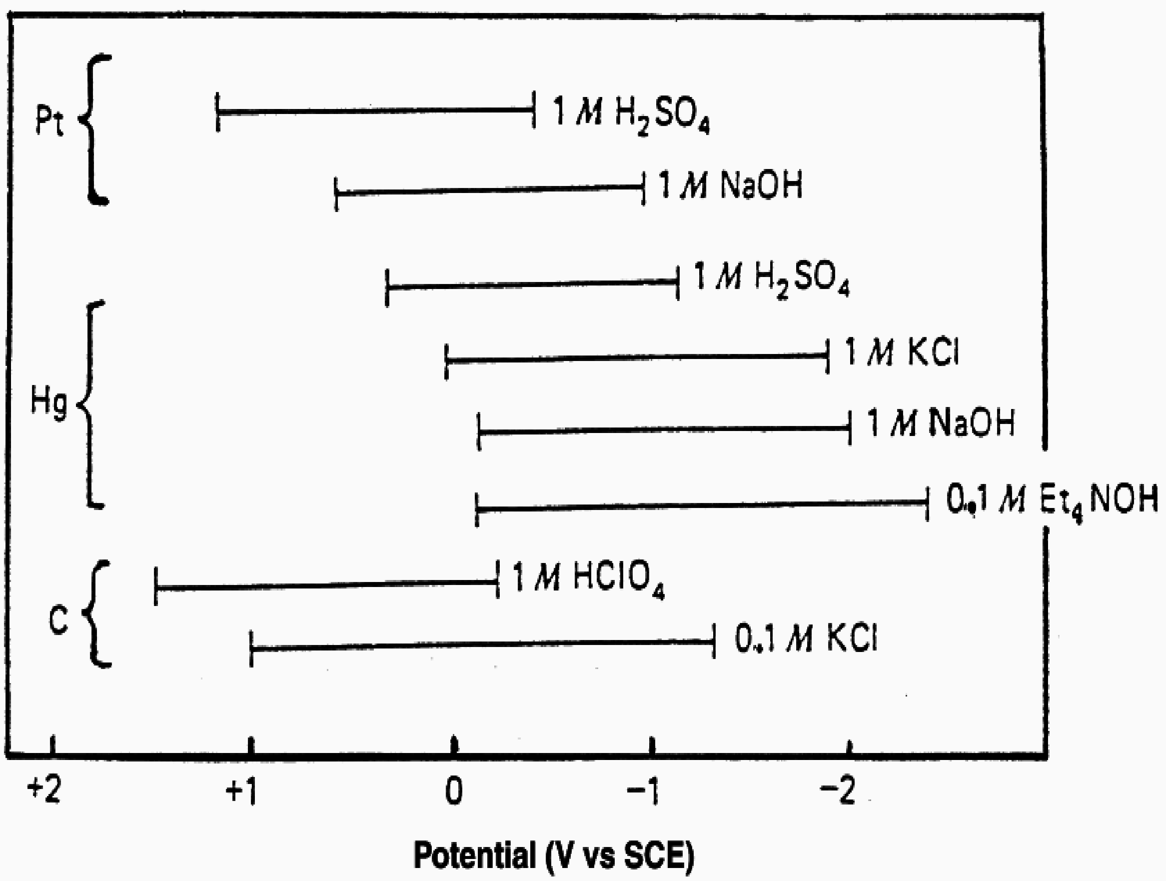

Figure 1.4. Potential range for of carbon, mercury, and platinum electrodes in various supporting electrolyte (Wang, 2000).

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1.4.1 Solid Electrodes

Solid electrodes have broad anodic potential windows compared to mercury electrodes which can only measure oxidizable compounds due to its limited potential range. Thus, solid electrodes have attracted interest being electrochemical electrode. No surprise when this type of electrodes has been used in electroanalytical chemistry for nearly five decades until now.

This type of electrodes have unique characteristics such as great electrical conductivity, stable chemically and electrochemically over a wide range conditions, fast electron transfer and reproducible electrical, microstructural and chemical properties to be function as working electrode (Zoski, 2007).

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There are many types of solid electrode that consist from variety of solid materials such as carbon, platinum, and gold. These three examples of solid materials are the most frequently used as working electrode. For specific applications, silver, nickel, and copper can also be used as working electrode (Wang, 2000). The solid electrode requires pretreatment and polishing to obtain reproducible results. Hence, the response of electrode surface is important factor in application of solid electrode. The pretreatment for solid electrodes is depends on the materials of the electrode. The metal electrodes used mechanical polishing and potential cycling for reproduce the electrode surface. In the other hand, pretreatment electrode can use various electrochemical, chemical, and thermal surface procedures. Solid electrodes have

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heterogeneous surface with respect to the electrochemical activity. Moreover, solid electrodes usually in planar disk configuration consist of short cylindrical rod of electrode material such as gold, platinum, or carbon, and tube of insulating material (Wang, 2000).

1.4.2 Carbon Electrodes

In electroanalytical measurement, carbon has been used widely as electrode materials due to many advantages such as have broad potential window, low background current, chemical inertness, high suitability for various sensing, and good detection application.

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However, carbon surface possess slower electron transfer rate than those observed at metal electrode. Carbon materials are built from the basic structure of six-membered aromatic ring and sp^2 bonding.

Glassy carbon, carbon paste, and carbon fiber are the example of the most popular carbon electrode materials. Each types of carbon have different properties in terms of interfacial capacitance, adsorption, and electron transfer rate. Interestingly, carbon electrodes are capable to form strong covalent bonds with a wide variety of surface modifier, therefore providing an attractive substrate for fabricating chemically modified electrodes. Recently, carbon electrode is the trendy electrode applied as

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detector for inorganic and organic compound determination (McCreery, 1991; Wang, 2000).

1.4.2.1 Glassy Carbon Electrodes

The first application of glassy carbon as an electrode was introduced in 1965 and referred to as vitreous carbon or the most commonly used carbon electrode for electroanalysis. It is a versatile electrode materials since it is chemically inert with a wide potential range and also because it is non-porous and can be polished (Pocard, Alsmeyer, McCreery, Neenan, & Callstrom, 1992). Glassy carbon is prepared by controlling heating on carbonization of premodeled polymeric, such as polyacrylonitrile or phenol formaldehyde in the 300-1200ºC temperature range. The carbonization should be performs under high temperature and in very slowly temperature to ensure the elimination of nitrogen, oxygen, and hydrogen. It has thin structure with tangled ribbons of cross-linked graphite-like sheets. Figure 1.5 shows the schematic structure of glassy carbon. Glassy carbon has small pore size so it does not require impregnating procedure, high density, polishable, mechanically strong. Therefore, this material is one of the most frequently carbon electrode materials (McCreery, 1991; Wang, 2000).

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Glassy carbon has become an interesting and a widely applied electrode material because of their physical and chemical properties. It exhibits a low oxidation rate and high chemical inertness, a small gas and liquid permeability, make glassy

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