

**Fabrication and Characterisation of the Electrical and
Physical Properties of the Graphite Paste Electrodes for
Application in Biochemistry Sensing**

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EXECUTIVE SUMMARY

Biochemistry and heavy metal contamination in waste water are problems of paramount concern. Instant measurement of the degree of contamination is the long term aim of this work. This project proposed the fabrication of mask printed graphite electrodes based on natural graphite, micronized graphite powder and carbon composite (HSF54) that have potential for sensing heavy metal in water. The graphite paste were prepared by mixing silicone oil and graphite powder at certain ratios and they were coated via a mask on a paper substrate using squeegee method. A two-probe station, a field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) and contact angle measurement system were applied to investigate the electrical and physical properties of the electrodes. Contact angle measurement device was developed and used in determining the wettability of the electrodes. The results show that natural and micronized graphite paste electrode has a mean resistivity of $1.69 \times 10^{-3} \Omega\text{m}$ and $1.25 \times 10^{-3} \Omega\text{m}$, respectively for a thickness of approximately 100 μm . Comparatively, HSF54 has a lower resistivity in the range of $\times 10^{-5} \Omega\text{m}$. The huge difference found in the conductivity of both type of electrodes was associated with the particle gap size (percolation), density, dimension of graphite electrodes and the presence of a binder. Based on the contact angle obtained, the critical surface tensions of the natural graphite planar electrode, micronized graphite planar electrode and HSF 54 electrodes are 38, 34 and 37 mN/m, respectively. The three types of graphite planar electrodes were found to be moderately hydrophobic relatively. The ability of the electrodes to be wetted by water shows that it is a good candidate to interact with the biochemistry or heavy metal contaminants in waste water.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Heavy metals have been extensively studied due to their effects to human health and also reviewed by international bodies such as WHO [1]. The contamination of heavy metal in waste water is a problem of utmost concern, for example the waste copper as a byproduct the fabrication of PCB etching. Heavy metals are usually monitored with use of toxic mercury drop electrodes [2]. One of the possibilities for ecological measurement of heavy metals is the use of solid electrodes.

The use of graphite in fabrication of thick film electrodes is promising because of several properties such as economically available, easily reproducible and they are comparable with classical electrochemical cells [3]. Graphite is a form of elemental carbon. It is one of the allotropes of carbon other than diamond and fullerenes. Graphite is used in making a pencil which is a mixture of powdered graphite and clay. Graphite conducts electricity by delocalization of vast number of electrons within the carbon layers. These valence electrons are free to move within the plane of layers leading to electrical conductivity. The conductive properties of powdered graphite allowed its use as semiconductor substitute in early carbon microphones [4].

In this work, the graphite paste electrodes were prepared using paraffin oil as a binder and coated on paper substrates which is a good absorbent for water compared to plastic transparent and cotton fabric [5]. This work also investigated the surface property of the graphite loaded paper in correlation with the electrical conductivity of the graphite. The surface morphologies and thickness of the graphite loaded paper will

be characterised using FE-SEM. In relation to these physical properties, the I-V characteristic curve of the GPEs and conductivity will be presented using a two probe station. The purity of the GPEs in terms of the carbon content will be investigated using energy dispersive X-ray spectroscopy (EDS) analyzer. Carbon based sensor for used in ecological measurement requires the interaction of analyte solution and electrodes. The surface tension of the carbon electrode characterizes the wettability of the electrodes. The aim of this work was to analyze the surface tension of the graphite planar electrodes by means of contact angle measurements. The outcome of the research is expected to suggest the suitability of graphite electrode for use as a heavy metal sensor.

1.2 Background Study of Graphite

Graphite is one of the allotropes of carbon other than diamond and fullerenes. It is used in making a pencil which is a mixture of powdered graphite and clay. Graphite is a well known non-metallic conductor with a high electrical conductivity (1.276×10^6 S/m). The in-plane resistivity of single crystal graphite is approximately 2.5×10^{-6} to $5 \times 10^{-6} \Omega\text{m}$ at room temperature [6]. Other than the industrial application, graphite is a non-metallic conductor which is commonly used as electrodes, brushes for electric motors, batteries and fuel cells conductor because of its excellent electrical conductive properties.

The fundamental units of Graphite are carbon atoms. That are arranged in hexagonal lattice with a separation of 0.142nm [7]. Graphene sheet are the layers that form the planar structure of graphite. The distance between the planes is 0.335 nm (

Figure 1-1). The two known forms of graphite, hexagonal (alpha) and rhombohedral (beta) have very similar physical properties. The hexagonal graphite may either be flat or buckled [8]. The alpha form can be converted to the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated

above 1300 °C [9]. There are three physical existence of natural graphite: Crystalline flake graphite, amorphous graphite and lump graphite. Commercially, the fine flake graphite is called amorphous graphite.

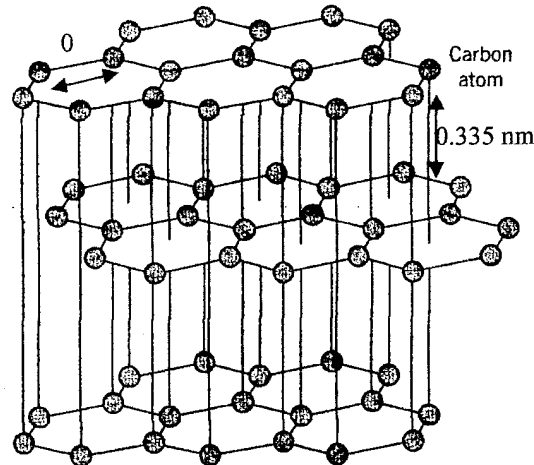


Figure 1-1: Graphite atoms arrangements in hexagonal shape

Graphite conducts electricity by delocalization of vast number of electrons within the carbon layers. These valence electrons are free to move within the plane of layers, therefore, they conduct electricity. The electron mobility within the planes is high due to the overlapping between the π orbitals on adjacent atoms [10]. However, the mobility of electrons perpendicular to the planes is relatively low [10]. The conductive properties of powdered graphite allowed its use as a semiconductor [11] substitute in early carbon microphones.

Following the announcement of the 2010 Nobel prize awarded to the researchers from the University of Manchester for studying the physical properties of Graphene, this material related to graphite has received vast attentions due to its strong physical properties. Graphene is an extract monolayer of carbon lattice from the graphite. Currently, the research on carbon, graphite, and graphene is a very active research area.

1.3 Literature review

Carbon is widely used in the fabrication of both electrochemical and biochemical sensors. Carbon materials have been used as components in electrochemical biosensors for over a decade. Currently, huge attention is focused on applying carbon nanotubes (CNTs) in biosensing since it was discovered by Ijima in 1991 [12] because of their unique electronic, chemical and mechanical properties [13]. In addition, recent developments in the fields of CNT-based chemiresistors and chemically sensitive field-effect transistors are presented [14]. Moreover electrochemical biosensors are currently among the most popular of the various types of biosensors. Carbon nanotubes (CNTs) are promising materials for sensing applications due to several intriguing properties [14]. Nano-materials are explored due to the advantage of a larger surface area for the biomolecules to be immobilized.

Carbon nanotubes are rolled up cylinders of graphene sheets. However, CNTs sensor having a large surface is a trade-off of long response time to sense a gas which could be due to the diffusion speed of gas into the crowded nano-network structure [15]. As an alternative to the carbon nanotubes, graphite is one of the variants of carbon which is chemically inert, highly conductive and strength and presents low background noise and economically producible electrodes [16].

Graphite nano-platelet has been shown to be highly sensitive and fast response in glucose sensing [17]. The use of graphite in fabrication of thick film electrodes is promising because of these properties. Graphite also been used in thick film sensor area due to cheap, easily producible and they are comparable with classical electrochemical cells [18]. Nevertheless, the thick film of graphite sensors design is not efficient for electrochemical measurement and it is insufficient in sensitivity. One of the reasons is that the binding material to form graphite paste is not water permeable [18].

Graphite is commonly used as a measurement electrode along with a counter or a reference electrode made of silver ink in screen printed biosensors. In this type of biosensor, the graphite ink are patterned by screen printing on a strip coated with a solution for example is enzyme which will be in contact with an analyte such as, glucose, in which the electron flow of the redox activities will be monitored via an amperometry, voltametry or galvanostate measurement techniques. These measurement

techniques are dependent on stationary measurement equipment stationed in the laboratory. Besides that, the coating thickness, grain size, anisotropy and the volume fractions of the graphite have affect the conductivity of the graphite based planar electrode [11].

Screen printing technology is a highly demanding area because of the possibility for mass production and economic fabrication. The attractiveness of screen printed carbon electrodes including low-cost, chemical inertness and suitability for mass production are the reasons of their wide acceptance as a biosensor in biomedical diagnosis and electrochemical analysis. Screen printed carbon electrodes are found in the application of serum and glucose monitoring [19]. These electrodes are produced by a screen printer or mask technique and lying in a plane on an insulating film or PVC substrate. The conducting material can be in the form of ink or paste [20].

On the other hand, graphite is generally very stable in corrosive environments and also exhibits a good oxidation resistance. At high temperature and in oxidizing atmosphere, graphite “burns” primarily at the edges of the layers, where the most reactive sites are located [21]. Graphite also can be electrospun to produce carbon polymer nanofibers which is a type of carbon composite. As a result, it was found that when frequency of electric field is high, the AC conductivity also increases. Electrospinning is one of the simplest techniques which are a process by which fiber with sub-micron diameters can be obtained from an electrostatically driven jet polymer solution [21].

Polyaniline-Graphite/epoxycomposite (GEC-PANI) is another form of carbon composite that is highly conductive material [22]. It can be seen that the conductivity of composites increased with increasing graphite content. The conductivity found for polyaniline (PANI) was 0.00249 Scm^{-1} . However it increased significantly to the maximum rate conductivity of $28\mu \text{ Scm}^{-1}$ with addition of 1, 2 and 3 w/w % of graphite [22].

From the previously literature [11], equation that described the conductivity of graphite pellet as a function of volume fraction was proposed by McLachlan (1986, 1987) [11]. The general equation proposed is:

$$\frac{f(\Sigma_1 - \Sigma_m)}{\Sigma_1 + [f_c/(1-f_c)]\Sigma_m} + \frac{(1-f)(\Sigma_h - \Sigma_m)}{\Sigma_h + [f_c/(1-f_c)]\Sigma_m} = 0 \quad (1-1)$$

Where f is the volume of the low-conductivity component $f_c = 1 - f'_c$ is the critical low conductivity volume fraction at which the high conductivity component first forms a continuous percolation path across the medium. $\Sigma_1 = \sigma_1^{1/t}$, $\Sigma_h = \sigma_h^{1/t}$ and $\Sigma_m = \sigma_m^{1/t}$ where σ_1 is the conductivity of the low-conductivity component, σ_h is the conductivity high-conductivity component and σ_m (f) the conductivity of the medium itself. t is an exponent related to the critical volume fraction f_c and the shapes of the grains making up medium. This equation also can be applied to the dielectric constant, thermal conductivity and magnetic susceptibility of binary mixtures [11]. In this study [11], the conductivity of the graphite pellets of four graphite powders (Natural Flaky Graphite (NFG), Technical Graphite Powder (TGP), Synthetic Graphite Powder (SGP) and Electro Graphite Dust (EGD)) was reported. The results of this study show that NGF which has the flakiest structure of the powders is more oriented (96%) and this powder has the largest ratio of axial and transverse conductivities. Conversely, the smallest ratio is for the least oriented, most 'spherical' EGD while TGP and SGP ratios are very similar, as are the percentage orientations near full compaction. Unfortunately no real conclusions can be made about what actually determines the critical volume fraction as stated in [11]. Since the layers are stacked parallel to each other with the atoms within ring bonded covalently, whereas the layers are loosely bonded together by Van der Waal's forces [23].

1.4 Problem Statement

Heavy metals have been used in many different areas for thousands of years and these metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO [1]. Heavy metal pollution also can arise from many sources but most commonly arises from the purification of metals such as the melting of copper and the preparation of nuclear fuels. The contamination of heavy metal in waste water is a problem of utmost concern, for example the waste

copper after the fabrication of PCB etching that are discarded into drains. Therefore this project proposed the fabrication of mask printed graphite paste electrodes which have potential for sensing different level of heavy metal contamination in water.

The reproducibility of graphite based electrodes is very much depends on the formulation of the printing inks. The physical formation of the carbon electrode requires a mixture of graphite, organic oil and binders such as polyester resin, ethyl cellulose, epoxy or even polymeric binder [22]. The use of polymer binder requires additional process which is plasma etching to remove the resin polymer from the carbon electrode [22] and it may reduce the sensitivity of the carbon electrode. Moreover, the residue binder doped in the inner body of the electrode remained attached to the graphite flakes resided at the inner layer and the intrinsic problem has not been solved.

In this context, both the surface and inner layers of the carbon electrodes are part of the conduction network when the electrode is used in contact with an analyte in heavy metal analysis. Several methods were previously used to improve the sensitivity of the carbon-based electrodes [11, 14, 21, 22]. Pre-anodization, electrochemical cycling, metal-dispersion, soaking and electrochemical metallization are among the techniques believed can enhance the response of the carbon-based electrodes.

This research suggests applying the percolated graphite paste electrode to trap the heavy metal particles leading to the conductivity change in the electrodes. Therefore, different concentration of the graphite powders in water can be detected. Therefore, we proposed to fabricate mask printed graphite paste electrodes using silicon oil as a binder. This electrode will be fabricated on paper substrate which would absorb and remove the binder from the overall body of the electrode.

Different forms of graphite powder including natural graphite powder, micronized graphite powder and HSF 54 composite will be used to produce the mask printed graphite paste electrodes. The graphite paste will be squeegee coated via a mask to form patterns on the paper substrate and planar layer of electrodes will be formed. The compaction of the electrode paste packs the graphite flakes together but porosity remains in between the flakes. The porous area will be the trapping region for the the heavy metals particles deposited. The proposed fabrication method is forseen as a restoration of a graphite network of sp^2 bonds. Therefore, the physical re-arrangement

of the graphite powder could affect the conductivity of the graphite layer. However, the interaction between the planes of graphite is weak, due only to Van der Waals forces. The weak Van der Waal's forces govern the bonding between the individual layers and also there are no bonds between the layers and it can easily slip off one to another. These circumstances make it an ideal lubricant and resulting in a reduced coefficient of friction [22].

This work will also investigate the surface science of the graphite loaded paper in correlation with the electrical conductivity of the graphite. The contact angle, surface morphologies, and thickness of the graphite loaded paper will be studied and characterised. In relation to these physical properties, the I-V curve and conductivity of the graphite loaded paper will be investigated. The outcome of the research is expected to suggest the suitable fabrication method to develop paper based graphite electrode for use as a heavy metal sensor.

1.5 Objective

The objective of the research is to achieve the long term aim. The five objectives for this master project are to:

- a) Fabricate mask printed graphite electrode on plain white papers with micronized graphite powder, natural graphite powder and HSF 54 composite using mask printing technique.
- b) Characterise the resistivity and conductivity distribution with reference to the coating thickness.
- c) Study the topography of these coatings in relation to the conductivity measured.
- d) Study the wettability of the different graphite coatings and determine the density of the mask printed graphite electrodes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the literature review focused on the atomic structure, the substrate material, the explanation about the resistivity and conductivity, percolation theory and some previous research will be described.

2.2 Atomic Structure of Carbon

2.2.1 Graphite

Graphite is a dark gray, soft and porous material with adsorption ability and it is naturally abundant and often used as highly conductive fillers (with an electrical conductivity of 1.276×10^6 S/cm) for conducting polymer composites [4]. It also has an electrical resistivity approximately 2.5×10^{-6} to 5×10^{-6} Ω m at room temperature. It consists of many flat layers of hexagons (like a wire fence). The layers are called graphene sheets. Each carbon atom is joined to three other carbon atoms. Each layer by itself is a network of giant molecules with very strong covalent bonds is held together attraction to form many layers. Two sheets are separated by a distance of 3.4 \AA is because of this property of graphite, the graphite sheet graphite can slide over each other upon an application of force lead to a smooth material.

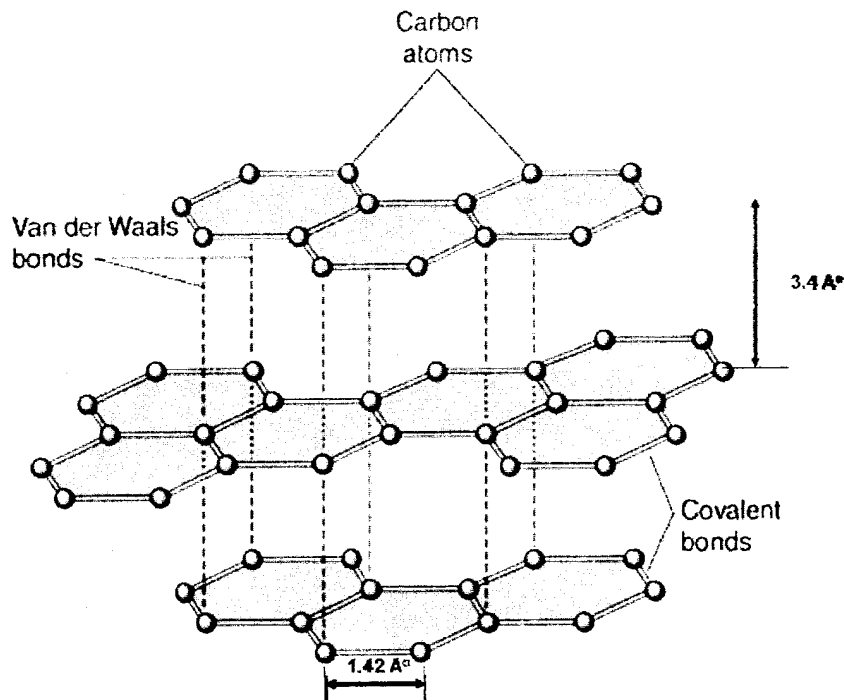


Figure 2-1. Graphite atom arrangement in hexagonal sheet

2.2.1 Graphene

Graphene is a two-dimensional single atomic planar sheet of sp^2 atoms that are densely packaged into a very large polyaromatic hydrocarbon. Graphene is an sp^2 hybridized carbon lattice with a hexagonal lattice structure. Graphene is a two-dimensional material, thus in addition to existing in its planar state, graphene can be ‘wrapped’ into zero-dimensional spherical buckyballs, ‘rolled’ into one carbon nanotubes (CNTs) or stacked into three together by weak Van der Waals forces of the slippage of the material and graphite is shape into bonded carbon honeycomb lattice structure. This is the essential building block for all fullerene allotropic three-dimensional graphite where stacks generally consist of more than ten graphene sheets [6]. Figure 2-2 shows the atomic structure of a graphene. Graphene was discovered in 2004 and has since sparked much interest in the field of condensed matter physics [7]. Graphene is an atomically thin sheet of carbon arranged in a two dimensional honeycomb crystal. The Mermin-Wagner Theorem predicts that a perfect crystal cannot

exist in two dimensional spaces, so it was surprising when graphene was first observed [7].

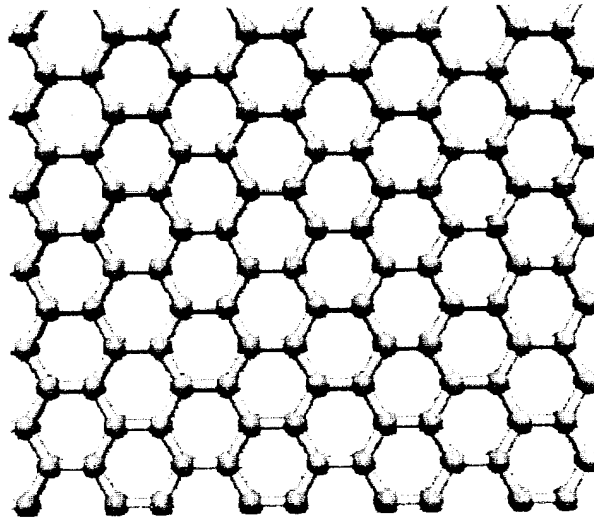


Figure 2-2. Atomic structure of graphene

2.2.2 Fullerene

The 1996 Nobel Prize for chemistry has been won by Harold W. Kroto, F. Curl and Richard E. Smalley for their discovery in 1985 of a new allotrope of carbon, in which the atoms are arranged in closed shells. It was discovered during the experiment of laser vaporization of graphite rod, under high vacuum chamber. This is because the graphite sheets break down to form spherical fullerenes. Fullerene is a cage like structure (Figure 2-3) having C atoms in C_{60} are on the surface hence they C_{60} resembles a soccer ball of the type made of 20 hexagons and 12 pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

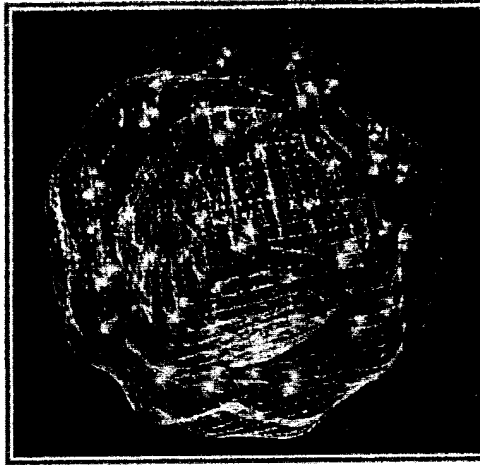


Figure 2-3. Atomic structure of fullerene [5]

2.3 Paper as a Substrate

Paper is a thin material mainly used for writing upon, printing upon, drawing or for packaging. It is produced by pressing together moist fibers, typically cellulose pulp derived from wood, rags or grasses, and drying them into flexible sheet. Compared with plastics, paper substrates can dramatically improve film adhesion, greatly simplify the coating process, and significantly lower the cost [21].

2.4 Resistivity and Conductivity

Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) quantifies how strongly a given material opposes the flow of electric current [8]. A low resistivity indicates a material that readily allows the movement of electric charge. Resistivity is commonly represented by the Greek letter ρ (rho). The SI unit of electrical resistivity is the ohm-metre ($\Omega\cdot\text{m}$). Resistivity is the opposite of conductivity, so it follows that good conductors have low resistivity per circular mil foot. Based on Figure 2-4, the resistivity chart shows that carbon is in the range of a conductive material which is $3.5 \times 10^{-5} \Omega\cdot\text{m}$. The inverse of resistivity is called conductivity. There are contexts where the use of conductivity is more convenient. The unit for conductivity is Siemens per meter (S/m).

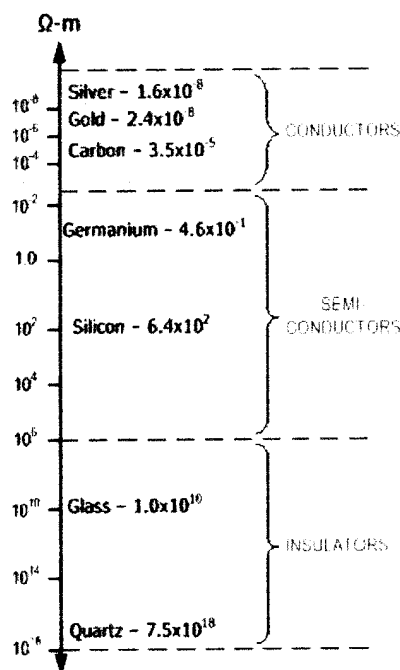


Figure 2-4. Resistivity Chart

2.5 Previous Graphite Paste Electrode Fabrication Technique

Carbon paste is used for construction of carbon paste electrode (CPE) for voltametric determination, which are made usually of high purity graphite powder or another type of carbon such as carbon nanotubes, dispersed in a non-conductive mineral oil such as paraffin or silicone oil to form a paste [10]. Table 2.1 shows some of the graphite paste electrode technique according to some researches that had been made before.

2.6 Sensor Application

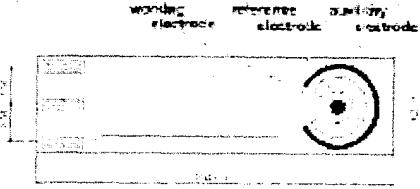
Graphite paste electrodes are attractive component for sensor applications. Table 2-2 is the summary of the review presented the use of carbon for sensor. It covers numerous applications demonstrate the widespread applicability of carbon paste in the field of electrochemical analysis, such as voltammetry, amperometry, potentiometry, and also as an electrode for electrochemical detectors in flow systems. Table 2.2 below shows the example method for every detection technique that uses graphite paste electrode.

Table 2-1. Fabrication technique of previous researchers

| Electrode types | Materials | Techniques | Reference |
|--------------------------------------------|---------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 1. Carbon Nanotube Paste Electrode (CNTPE) | <ul style="list-style-type: none"> • Carbon nanotube powder • Mineral oil | <ul style="list-style-type: none"> • Fabricated by mixing 5.0% (w/w) multi-walled carbon nanotube powder, 75.0% (w/w) high purity graphite powder and 20.0% (w/w) mineral oil. | [11] |
| 2. Carbon Paste Electrode (CPE) | <ul style="list-style-type: none"> • Graphite powder • Mineral Oil | <ul style="list-style-type: none"> • Fabricated by mixing graphite powder and mineral oil in a ratio 80.0% (w/w) total powder and 20.0% (w/w) mineral oil. • The resulting paste was filled firmly into the cavity of a glass tube (4 mm inner diameter). | [11] |
| | <ul style="list-style-type: none"> • Graphite Powder • Paraffin Wax | <ul style="list-style-type: none"> • The graphite powder with grain size of 1 to 2 μm mixed with paraffin wax with melting temperature from 52° to 58°. | [12] |
| | <ul style="list-style-type: none"> • Graphite Powder • Mineral Oil | <ul style="list-style-type: none"> • Prepared by mixing the graphite powder mineral oil with the ratio of 90:10 wt%. • These components were mixed in a gate mortar and packed in a teflon tube with an aperture at the end of the tube of 3mm in diameter. | [16] |

| | | | |
|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| | <ul style="list-style-type: none"> • Graphite powder • Organic substance contained titanium with water free binder | <ul style="list-style-type: none"> • The graphite pastes were fabricated by mixing graphite powder (Timrex SFG-44) and organic substance contained titanium called Tyzor & GBA with water free binder. | [17] |
| <p>3. Nanoporous Pseudo-Carbon Paste Electrode (Nano-PPCPE)</p> | <ul style="list-style-type: none"> • Pseudo microsphere • High pure graphite powder • Pyrrole | <ul style="list-style-type: none"> • Fabricated by mixing Pseudo microspheres, high pure graphite powder and pyrrole. • Pseudo microspheres were centrifuged and dried from emulsion. Pseudo microspheres and high pure graphite powder were mixed by ultrasonic, and then pyrrole was added to the mixture, the paste was gained by adjusting the content of pyrrole. • The PPCPE was constructed by packing the paste into a glass tube (4 mm inner diameter) and providing it with a copper wire, and then the electrode was immersed in 2 M FeCl₃ solution until the paste blend was polymerized completely. | [11] |

Table 2-2. Example of application of graphite for sensor

| Detection Technique | Method | Reference |
|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Amperometric | <ul style="list-style-type: none"> A standard Thick Film Technology (TFT) amperometric sensors (Figure 2.3) deposited on Al₂O₃ substrate using the standard commercial graphite paste or special prepared TFT graphite paste were used for measurements. The sensor type AC1.W2.RS had the Pt (100%) working, AgPd (98.2%) reference and Pt (100%) auxiliary electrode This sensor type is usually used as the sensor for basic electrochemical and bio-electrochemical measurement, e.g. for H₂O₂, glucose, ferricyanide, pesticide determine and for enzymes deposition. This type of sensor is used as the substrate for graphite pastes that were deposited on its working electrode surface <div style="text-align: center;">  <p>The diagram shows a rectangular substrate with three distinct electrode regions. The leftmost region is labeled 'working electrode', the middle region is 'reference electrode', and the rightmost region is 'auxiliary electrode'. A circular inset on the right side of the substrate shows a magnified view of the electrode surface, which appears to have a porous or textured structure.</p> </div> <p style="text-align: center;">Figure 2.5. Standard TFT Amperometric Sensor</p> | [12] |
| Voltametric | <ul style="list-style-type: none"> All the voltammetric measurements are carried out in a 100 mL thermostated glass cell at 25 °C, in a three-electrode configuration. Carbon paste electrode is used as a working electrode. The reference electrode was an Ag/AgCl/KCl sat and the counter electrode is a platinum plate Cyclic voltammetric measurements are performed in an EG&G PARC Model 263 potentiostat galvanostat (Princeton Applied Research Corp., NJ, USA) connected to a desktop computer and controlled by a software (Echem). Cyclic voltammograms were registered from -0.5 to +1.3 V at a sweep rate of 0.1 V·s⁻¹ (except otherwise indicated). | [14] |

2.7 Percolation Theory

Percolation theory is the simplest but not exactly solved model displaying phase transition [18]. The original problem was introduced by Broadbent and Hammersley (1957), and has been studied intensively by mathematicians and physicists thereafter. The problem is to solve the question

where; suppose a large porous rock is submerged under water for a long time, will the water reach the center of the stone? The network is said to percolate if there is an infinite open cluster containing the origin. Figure 2-5 shows the illustration of bond percolation.

The percolation theory is a branch of probability theory dealing with the properties of randomly distributed media in general [19]. The main idea of the percolation theory is to predict the macroscopic behavior of a randomly distributed composite material in dependence on its microscopic properties which are expressed purely by statistical data.

In the study of infinite conductivity of graphite particles in the filler [19], the macroscopic behavior of the joint is described by the probability for a connection path between the two mating pads through the filler particles. The percolation theory shows that there exists a distinct threshold particle content in excess to which the probability for the formation of an infinite cluster of particles, the conductance is larger than zero and in which, it rapidly increases with rising particle content. This threshold is known as the percolation threshold [19].

As the case of graphite, there are some open clusters between every graphite flakes in the graphite paste. There may be no connection between the graphite flakes and therefore, no conductivity or current flow at some localized area which is closely associated with the percolation theory. In percolation theory, the concern is whether a fluid can reach to the center of the porous material. The permeation of fluid can be influenced by the surface tension of the material under study. It is worth to investigate the surface tension of the graphite electrode surface.

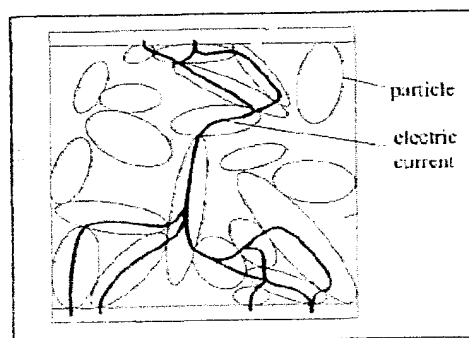


Figure 2-5. Bond of percolation [19]

2.8 Contact Angle and Surface Tension

The study of surface tension has wide application in applied surface science. Surface tension is related to the surface energy of a surface and it is determined by determining the contact angle of a sessile drop of liquid on a solid surface. Contact angle is measured by fitting a mathematical expression to the shape of the drop and then calculating the slope of tangent to the drop at the liquid-solid-vapor (LSV) interface line [24]. The interfacial tension of liquid-solid is related to the surface tension of the liquid and vapors at the interface by Young's relation. According to the Young's equation (Equation 2-1 and 2-2), the contact angle, θ measurement is governed by interfacial tension at the solid/vapour (γ_{sv}), solid/liquid (γ_{sl}) and liquid/vapor (γ_{lv}). This equation states that there are three tangential forces that arise from the interfacial tensions of the three interfaces and the balance between these three forces determines the contact angle.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (2-1)$$

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2-2)$$

A contact angle (θ) is the interior angle formed by the substrate being used and the tangent to the drop interface at the apparent intersection of the three phase boundary (solid, liquid and vapour). The equation (Eq. 2-1) and the measured value of the contact angle are used as basis for calculating the surface energy [25]. This intersection is called the contact line. A static contact angle on a flat surface is defined by the Young's Equation which relates interfacial surface tensions between solid and liquid, γ_{sl} , solid and vapor, γ_{sv} and liquid and vapor, γ_{lv} . Young's equation is essentially a force balance in the horizontal direction of a surface. Fox-Zisman method is used to determine the critical surface free energy (γ_c). According to Zisman [26], the value of γ_c of a solid is equal the value of γ_1 of a liquid being in contact with this solid and for which the contact angle is zero [25]. Based on the theory, γ_c value consists of the contact angle measurements for the studied solid and liquids of a homologous series of compounds. Then the plot is constructed in a coordination system with the y-axis corresponding to the cosine values of the

contact angle and the x-axis relating to the surface tension of different probe liquids.

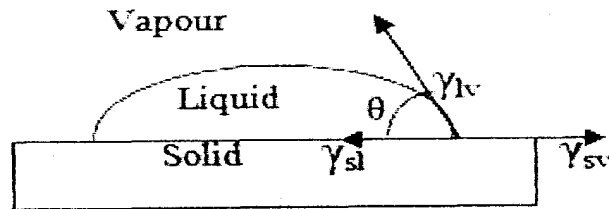


Figure 2-6. Equilibrium of a liquid with a solid surface

Contact angle measurements of a solid surface can be materialized using a simple approach as presented in [24]. However, in the previous system, the simplified apparatus requires the use of a separate lens and the back light system consists of a light bulb. The lens was used to magnify the captured image to an ordinary digital camera. The contact angle measurement was analyzed off-line. The presented system is cumbersome and this paper aims to develop an improved system with more functionalities.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This project is implemented to identify the conductivity characteristic of two types of graphite electrodes which is natural graphite paste electrode (NGPE) and micronized graphite paste electrode (MGPE). The development of the experimental process can be summarized in term of flow chart diagram as shown in Figure 3-1.

Morphology and interconnection of the graphite grains affect the conductivity of the graphite electrodes. For this reason, Field-Emission Scanning Electron Microscope (FE-SEM) will be used to investigate the cross section arrangement of the three types of graphite electrodes.

The long term aim of the research is to apply the fabricated electrode as a heavy metal and therefore, the contact with a fluidic solution cannot be avoided. The study on the water contact angle of the three electrodes produced will be included in this work. It involves the use of a digital USB microscope with a magnification of $\times 500$ and ImageJ software. The flow chart for the work plan is as shown in Figure 3-1.

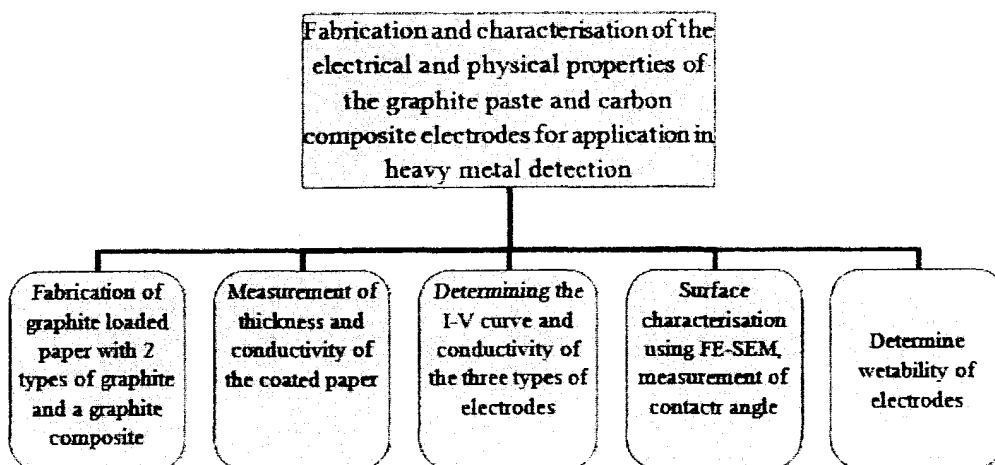


Figure 3-1. Flow chart for the work plan

3.2 Preparation of Electrodes

Graphite paste electrodes were fabricated using graphite paste which was synthesized by mixing graphite powder and paraffin oil as binder. The natural graphite powder and micronized graphite powder (UK Graphite Trading, UK) were mixed with paraffin oil at different ratios. The natural graphite paste (NGP) was prepared by mixing 6 g of natural graphite powder and 6 ml of paraffin oil. The micronized graphite paste was produced by mixing 6 g of micronized graphite powder and 12 ml of paraffin oil. These two types of pastes were coated via a mask with square patterns of dimension using squeegee method to form natural graphite paste electrode, NGPE and micronized graphite paste electrode, MGPE on chlorine free A4 sized paper.

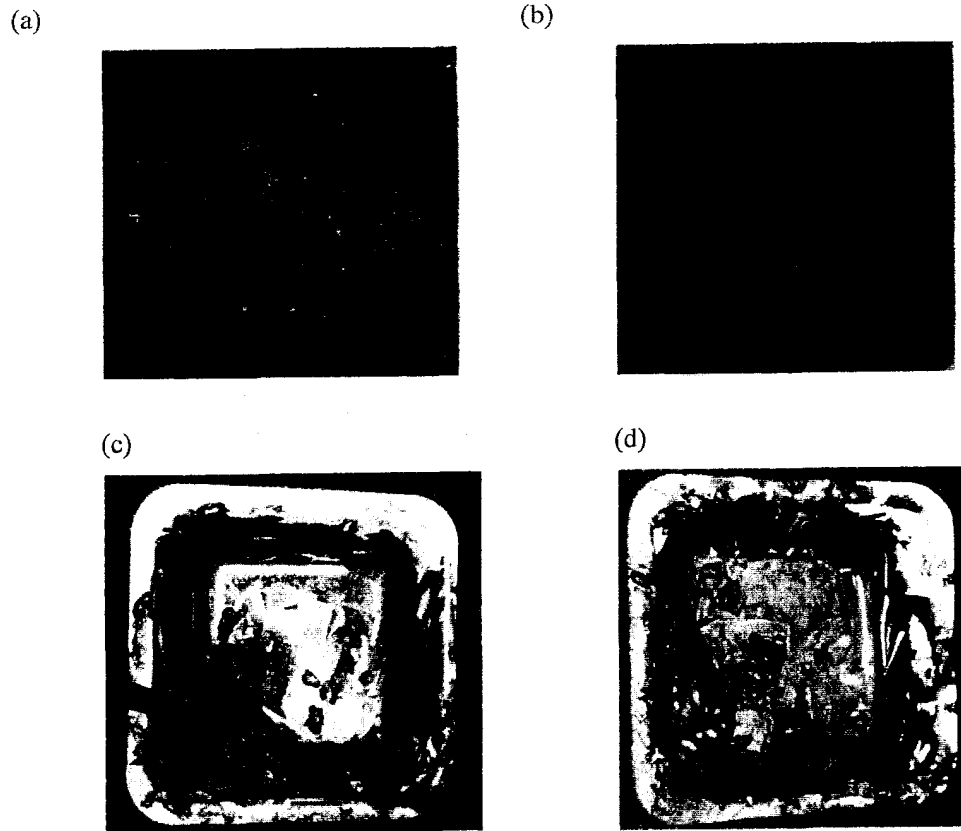


Figure 3-2. (a) Natural and (b) micronized graphite powder, (c) natural graphite paste and (d) micronized graphite paste

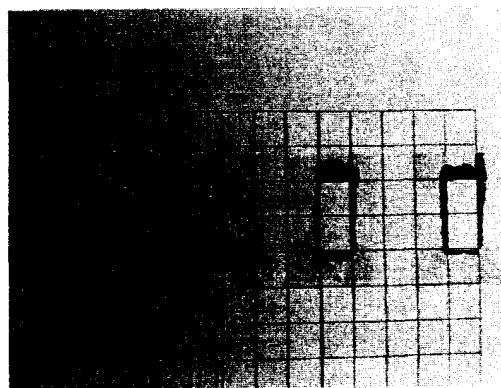


Figure 3-3. Scotch tape mask used for the squeegee coating on the paper substrate

These two types of resulting pastes were smear-coated on an A4 size white paper (Double-A, anti-chlorine paper) to form circular graphite paste

electrodes using a mask punched with circular holes as in Figure 3.3. The holes have diameter of 10 mm. Double A paper (anti-chlorine) was used as a substrate due to its good coupling with the slippage graphite paste.

3.2 Preparation of HSF 54 Carbon Composite Electrodes

HSF 54 carbon composite paste electrodes were coated using a sticky tape mask in rectangular pattern using squeegee method on chlorine free A4 sized paper as shown in Figure 1. The thirty samples were prepared with size of length were 1 cm, 2cm, 3cm and 4 cm.

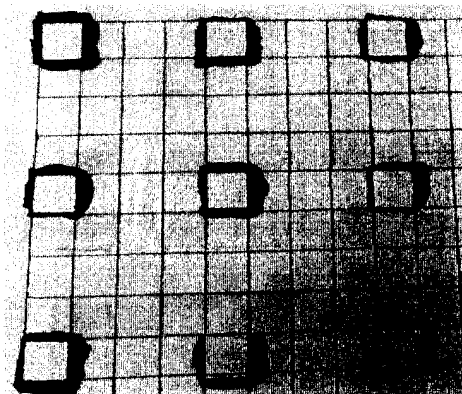


Figure 3-4. 1 cm masking of HSF 54 Carbon Composite Paste Electrodes using scotch tape

3.3 Analysis of Structural Characteristics of HSF 54 carbon composite electrodes

The structure of the HSF 54 carbon composite electrodes was determined using a field emission scanning electron microscopy, FE-SEM (JEOL JSM-7500F).

3.3 Sputter Coating for contact points

Circular platinum contact points for conductivity test were sputtered on the surface of the electrodes using a JEOL JFC-1600 Autofine coater machine. The contact point will be used for the I-V measurement of the samples. First of all, the sample was put onto the sample stage, then being closed securely so that the air from outside will not come in. The process started by selecting the

current setting which was 30 mA followed by pressing the “Display” button to select “Sec” mode. The up and down button was pressed to select the desired timing which in this process, it will need 50 seconds.

The “display” button was pressed once again to select “Pa” mode. Wait for about 2 minutes until the display showing the countdown. When the countdown had reached 17 Pa, the “Start” button was pressed. When the “Start” indicator stops blinking, that’s mean, the countdown had completed. A pinkish/purplish colour of gas argon was sprayed towards the sample to form a platinum contact point.

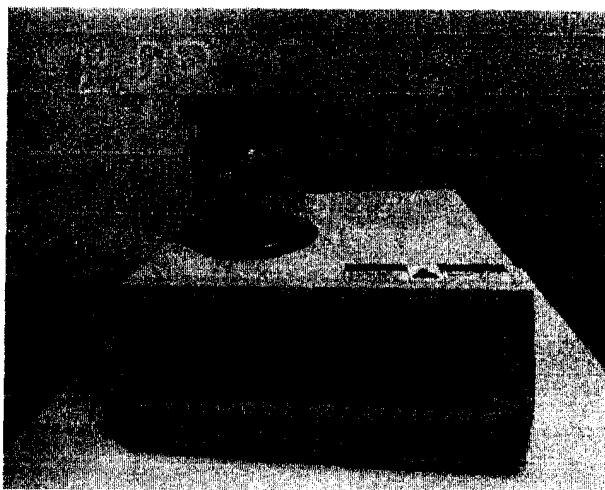


Figure 3-5. Sputtering process using JEOL JFC-1600 Autofine Coater machine

These contact points were sputter-coated using PVC mask punched drilled with 1.5 mm diameter holes (Figure 3.4). The distance between each hole is 2 mm. The result of this process is supposed to be as in the Figure 3.5.

3.4 Thickness Profiling of Graphite Paste Electrode

The thickness of the graphite paste electrode samples were measured using Alpha-Step IQ Surface Profiler (KLA Tencor Corporation) with scan length of 5000 μm and scan speed of 200 $\mu\text{m}/\text{s}$. Thirty two samples of NGPE and MGPE were prepared and the thickness measurements were repeated three times for each electrode samples. The mean \pm standard deviations of the sample thickness were calculated.

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