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Fabrication and characterisation of the electrical and physical properties of the mask printed graphite paste electrodes on paper substrates

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Abstract

Heavy metal contamination in waste water is a problem 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 paste electrodes based on natural graphite and micronized graphite powder which has potential for sensing heavy metal in water. The graphite paste were prepared by mixing paraffin 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 was used to characterize the I-V curve of the mask printed electrodes, in which the result was used for determining the resistivity of the graphite paste electrodes. A field emission scanning electron microscopy (FE-SEM) was used to investigate the structure of the graphite powder and surface structure of the graphite paste electrode. The purity of the carbon in the electrode was investigated using energy dispersive X-ray spectroscopy (EDS). The result shows that natural and micronized graphite paste electrode has a mean resistivity of 1.69 x 10^{-3} Ωm and 1.25 x 10^{-3} Ωm, respectively. The slight difference found in the conductivity of both electrodes is associated with the particle gap size, density and dimension of graphite electrodes which are associated with the percolation theory.

Keywords: Graphite paste electrode; Conductivity; Percolation; Paper based sensor.

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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 conductive. The conductive properties of powdered graphite allowed its use as semiconductor substitute in early carbon microphones [4].

In this work, the mask printed graphite paste electrodes were prepared using paraffin oil as a binder and coated on paper substrates which is a good absorbent 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. 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.

2. Materials and Methods

2.1 Preparation of Natural Graphite Paste Electrode and Micronized Graphite Paste Electrode

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.

2.2 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 µm/s. Thirty two samples of NGPE and MGPE were prepared and the thickness measurements were repeated three times for each electrode samples. The mean ± standard deviations of the sample thickness were calculated.

2.3 I-V Curve Characterization Measurement

The electrical conductivity, I-V characterization were measured for each planar electrode sample using a two point probe stations as shown in Fig. 1. For electrical measurement, circular contact points of silver paint were deposited on each electrode using silver conductive paint (RS Components, Malaysia). Two sharp probes were placed in contact with the two silver contact points during the electrical conductivity characterization. The measurement of the resistance and I-V curve were obtained using ORIEL Instrument software bundled to the Keithley voltmeter (Keithley Instrument, Inc).

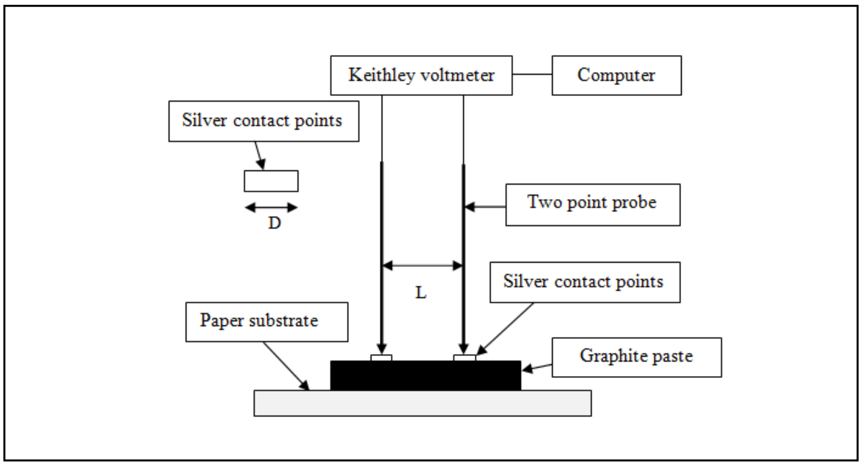

Fig. 1: Computerized two point probe diagram to characterize I-V curve of graphite paste electrodes with silver conductive paint.

The resistance (V/I) determined by the measurement system was used to calculate the resistivity, Rs using equation (1):

$$Rs = V/I \times A/L \ (\Omega m) \qquad (1)$$

where Rs is the resistivity, V is the voltage (v), I is the current (A), A is the area which is diameter of the silver paint point, D (mm) times with thickness of the sample, t (µm), and L is the distance between two metal contact (mm). The resistance of thirty two samples of NGPE and MGPE were measured and the resistivity for these two groups of GPEs was calculated individually.

2.4 NGP and MGP Morphology

The structure of the graphite powder and surface structure of the graphite paste electrode were determined using a field emission scanning electron microscopy, FE-SEM (JEOL JSM-7500F).

2.5 EDS Analysis

The purity of carbon used without elemental metal was determined using a Hitachi Tabletop Microscope, SEM (TM-3000). During the EDS analysis, the samples were exposed to a high energy electron beam inside the SEM machine.

3. Results and Discussion

3.1 Structural Characteristics of Graphite Particles and Electrodes

The morphology obtained in FE-SEM microscopy shows the particles of natural graphite powder (mean ± SD = 19.48 ± 5.67 μm) are larger than micronized graphite powder (mean ± SD = 5.18 ± 1.64 μm) as shown in Fig. 2a and 2b, respectively. NGPE consists of flakes graphite that is intercalated loosely in the paste as shown in Fig. 2c. In comparison, micronized graphite paste electrode consists of particle flakes of smaller size that were packed in smaller gaps (Fig. 2d). Besides, it was observed that the color of natural graphite paste is a bit silvery in colour while the color of micronized graphite paste is pure black.

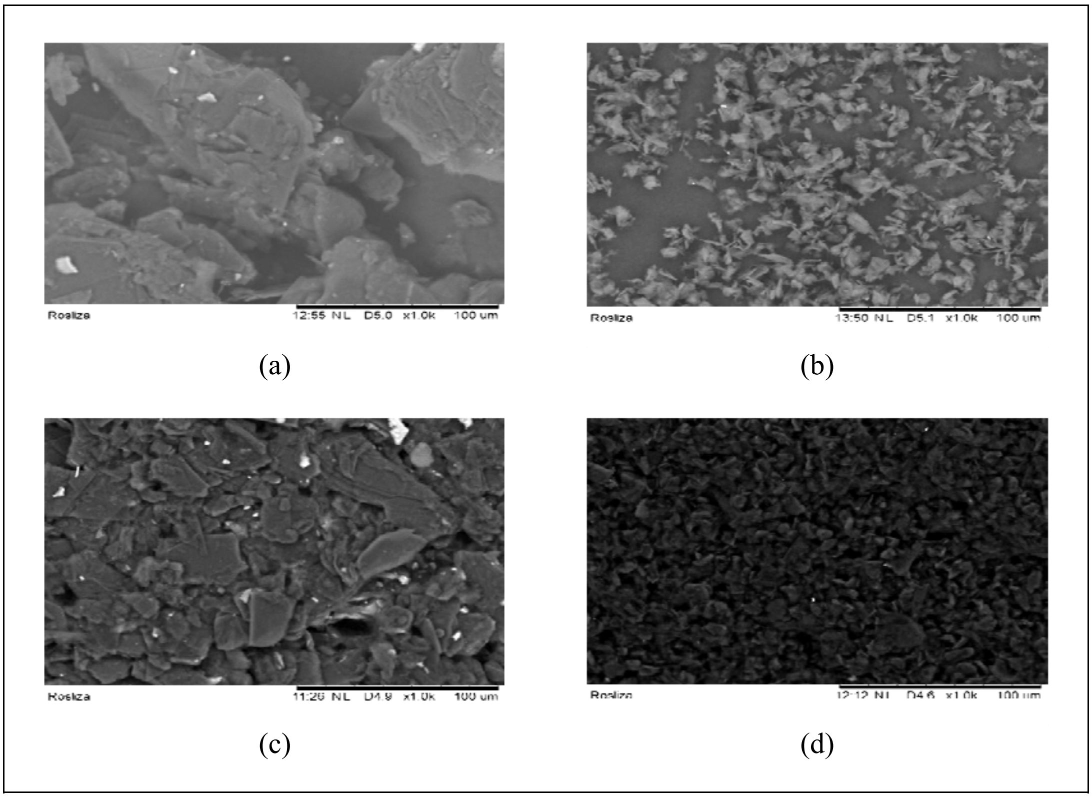

Fig. 2: FE-SEM micrographs of (a) natural graphite powder, (b) micronized graphite powder, (c) natural graphite paste electrode, and (d) micronized graphite paste electrode.

These are the fracture surfaces of graphite flakes perpendicular and parallel to the electric field. The particle size of natural graphite paste was ranging from 6 to 18μm while for micronized graphite paste was ranging from 5 to 10 μm. If particle size is smaller, the inter particle spacing can be reduced under the compression effect during the squeegee process, this provide better physical stability and shorter path length for the electrons to flow.

3.2 Thickness of the Graphite Paste Electrodes

The thickness for both types of GPEs corresponding to the resistivity is as shown in Table 1. The thickness of both GPEs was found similar due to the sample template of mask used. The difference in the thickness of the two types of electrodes is about 17.03%. The resistivity, Rs of each GPEs was found to increase as the thickness increases.

Table 1: The overall result of the thickness, I-V, diameter of the contact point, distance between contact point and the resistivity of each GPE

Type	Resistance (Ω)	Thickness (μm)	Diameter of the contact point, D (mm)	Distance between contact point, L (mm)	Resistivity, Rs (Ωm)
NGPE	20.87	108.00 ± 4.47	1. 5	2	1.69×10^{-3}
MGPE	16.25	102.5 ± 5.74	1. 5	2	1.25×10^{-3}

3.3 Resistivity of the GPEs

The resistivity NGPE and MGPE are 1.69×10^{-3} and 1.25×10^{-3} Ωm, respectively. The Rs was calculated using equation (1) and average overall result is recorded in Table 1. Based on Figure 3, the current is directly proportional to voltage measured. MGPE has lower resistivity or higher conductivity than NGPE. Previous study [5], reported the conductivity ratio measured for the graphite coated on paper, transparency and cotton fabric as substrates. The study showed that combination of graphite and paper presented a higher conductivity.

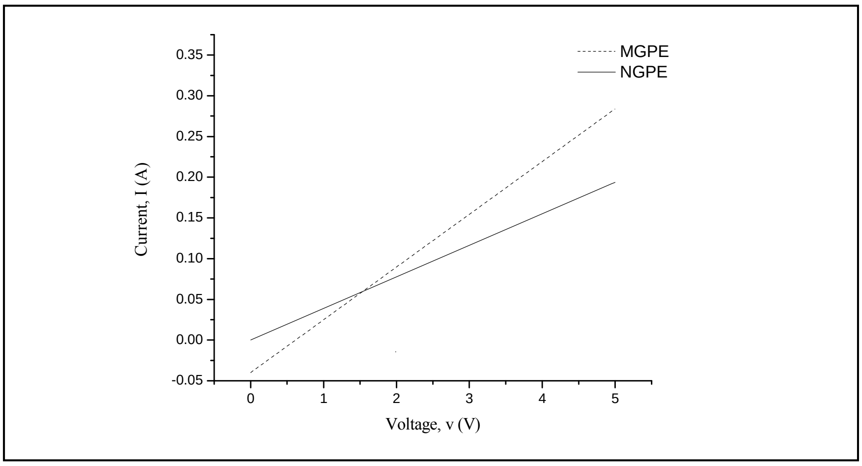

Fig. 3: I-V curve of NGPE and MGPE.

According to Table 1, NGPE is more resistive than MGPE. This result is associated with the particles arrangement of the electrodes. Such an organization could influence electrons hopping or tunnelling across the gaps or creating energy barriers between conducting particles [6]. In the present result, the resistivity of MGPE is lower than NGPE. As shown in Table 1, MGPE is more conductive than NGPE due to the tight packing of the particles size.

Percolation theory gives a phenomenological equation for computing the conductivity of a system near to insulator-conductor transition [6]. According to the theory, the percolation threshold corresponds to the onset of the transition from an insulator to the semiconductor [7]. For a GPE, to increase the electrical conductivity, a lower percolation threshold is required. This can be achieved by increasing the packing density, reducing the carbon particle size or lowering the energy barrier.

3.4 Purity of Natural Graphite Paste Electrode and Micronized Graphite Paste Electrode

EDS is a powerful tool for microanalysis of elemental constituents. Via the entering of x-ray and elements in the EDS spectrometry, the elemental composition of the sample can be determined. NGPE and MGPE contain 94.72 and 100 atomic percent of carbon, respectively. This shows that the GPE produced using the technique yielded high purity of carbon content in the electrodes.

4. Conclusion

The fabrication of natural graphite paste electrode and micronized graphite paste electrode has been described. They were fabricated by mixing the graphite powder with an oil binder and the oil can be effectively removed by using paper as a substrate. This work found that MGPE with tight particles packing in the paste form showed higher conductivity characteristic. From the characterization results, the percolated electrode produced could be used to trap heavy metal particle leading to the detection of heavy metal.

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