Development and Analysis of Graphene-polymer Composite Flexible Electrode

Ibrahim Abdulrahman, Aini Zuhra Abdul Kadir*, Muhamad Azizi Mat Yajid, Nor Hasrul Akhmal Ngadiman, Mohd Zamri Mohd Yusop

School of Mechanical Engineering, Faculty of Engineering
Universiti Teknologi Malaysia
81310 UTM Johor Bahru
Johor, Malaysia

ABSTRACT

Composite flexible electrode made up of a carbon nanotubes (CNTs) added with graphene has a remarkable potential in overcoming the limitations of a metal-based electrode of higher surface contact between the skin which creates lower resistance and consistent current flow. In medical application, the function is as a conductor to convert ionic potential into electronic potentials through the skin suitable to sense signals for EEG or ECG. However, this electrode still requires further exploration in terms of design and composition for it to become affordable. Therefore, this study aims to develop a flexible electrode made of graphene-CNT composite based on selected design and to analyse the conductivity levels of the electrode with and without cable connections. Two-probe measurement system was used to measure the conductivity levels of the developed electrodes containing various composite compositions as well as various cable connection types. The results showed that 20% CNTs mixture with 2% Graphene was the best conductor with approximately ±20µA recorded. When SOMK cables with and without copper ring were used, 9.091A current was recorded.

Keywords: *Flexible electrode, graphene, conductivity, carbon nanotubes, silicone rubber*

1.0 INTRODUCTION

Electrode is a device that converts ionic potentials into electronic potentials. In medical application, electrodes are categorized into three main classes which include microelectrodes, body surface electrodes and needle electrodes [1]. It comes in variety of shapes, materials, functions and capabilities targeting at different applications and usage. For example, it is suitable to sense signals or currents for EEG, ECG, etc. The body surface electrodes are those which are placed in contact with the skin of the subject in order to obtain bioelectric potentials from the surface. Some examples include immersion electrode, plate electrode, floating electrode, disposable electrode and suction electrode. These electrodes are commonly made of metals which consists of a metallic conductor such as stainless steel, silver, platinum and gold in contact with the skin with a thin layer of an electrolyte gel between the metal and the skin to establish its contact [2].

*Corresponding email: aini@mail.fkm.utm.my

Major disadvantages of these conventional electrodes are the inconsistency of current flow due to low surface contact to the skin, the need to use saline water/electrolyte gel to reduce resistance, potential to skin irritation, rigid shape with difficulty of mounting on skin and the need of clean and care after use.

Apart from that, the design can be flimsy which makes it easy to dislocate the wire [2]. To overcome these limitations, flexible and conductive polymer can be a solution. However, the conducting polymer alone still faces several challenges such as low manufacturability, poor mechanical properties and biocompatibility which leads to various studies to investigate the chemical modification techniques in producing good combination composites [3]. Conductive flexible electrodes are commonly made of metal-filled polymer such as carbon nanofibers, carbon nanotubes (CNTs) and graphene [4-6]. CNTs are allotropes of carbon with a cylindrical shaped nanostructure. They are no less than 100 times stronger than steel. In developing the electrodes, CNT will be embedded in the rubber-based polymer to enhance the electrical conductivity and maintain a higher surface contact between the electrode and surface to stabilize the current flow [7].

Previous work performed on CNTs with rubber-based polymer have shown positive results with low current density being recorded. Previous study tested three types of electrodes; the silicon rubber, embedded polymer and coated polymer. The results showed that the embedded electrodes led to unsatisfying result. Generally, silicone polymer is an insulator material which resist electrons to flow. However, in this work, we are challenging to embed CNTs and graphene as nanofiller in the polymer matrix to enhance its conductivity [8]. This becomes the main motivation of the current study.

Furthermore, in recent years, graphene has shown potential application in electrode development [9-11]. Graphene has an overall excellent material property and has been regarded as an ideal material to fabricate electrodes [12]. In terms of conductivity, it consists of conductive electrons where the particles can make up electricity [13]. With the capability of graphene to act as conductor and the flexibility of CNTs polymer characteristics, flexible electrode can then be developed [14]. Therefore, the aims of this study are twofold; to develop mixture of graphene-CNTs composites of a flexible electrode based on selected design and to analyse the conductivity levels of the developed electrode with and without cable connections.

2.0 METHODOLOGY

The methodology is divided into two phases; (i) material preparation and (ii) electrode design development. Phase 1 involves the preparation of electrode material samples made of a mixture of CNTs and graphene. The variation of CNTs and graphene ratio were set in preparation for mixing and sonification. Once ready, the samples were all labelled for future analysis. Phase 2 involves the electrode design development which include electrode cable fabrication and two-probe system setup. Details of the methodology is given in the following sub-sections.

2.1 Material Preparation

Preliminary work based on previous study [15] was first performed in order to obtain a feasible range of mixture composition for material preparation. The details steps involve in preparation of silicon rubber and dispersion of nanotubes are given in the following sub-sections.

2.1.1 Preparation of the silicon rubber

During the polymer preparation, 6 g of silicon rubber elastomer was mixed with 0.6 curing agent solvent with as ratio of 10:1 in a petri dish and carefully stirred to ensure a homogeneous reaction. The mixture is then left in the oven and let to cure for 24 hours at a temperature of 60ºC. Once set, it was then removed and cut to dimensions of 1 × 1 cm. Following that, the coating solution for the substrate was produced by mixing Graphene powder with Dichloromethane (DCM) with a ratio of 1:99 by weight % 6.633 g. Next, 5 ml of DCM was added to 0.0066 g graphene powder and the mixture was sonicated using *3510 Branson Ultrasonicator* at different time durations; 1 hour and 2.5 hours to increase the graphene dispersion.

2.1.2 Dispersion of nanotubes

The dissolution or dispersion of CNT's in the solvent is necessary in preventing the CNTs from clinging together and forming lumps. CNTs was added and the solution was sonicated for 10 minutes to get the desired vibration to achieve the wanted dispersion of CNTs. Four different graphene-polymer composite configurations, labelled as Composite A, Composite B, Composite C and Composite D, were prepared containing CNTs and graphene mixture in various weight ratios percentage as shown in Table 1.

Table 1: Graphene-polymer composite configuration weightage (%)

Composite	CNTs (%)	Graphene (%)	Silicone rubber polymer (%)
A	20	0.0	80.0
B	20	1.0	79.0
C	20	1.5	78.5
D	20	2.0	78.0

2.2 Electrode Design Development

The electrode design as shown in Figure 1 was developed with the intention to analyse the effect of conductivity with and without cable attachment to the silicon rubber. The electrode was designed in order to achieve a maximal surface contact and attachment at all times. The flexible electrode consists of a square-shaped 20 mm × 20 mm × 2 mm grapheme-polymer composite pad with chamfered edge at the corner, a button tab and various types of 75 cm length cables of different specifications. The types of cables include (i) SOMK cable with copper ring, (ii) SOMK cable without copper ring, (iii) SOMK cable with copper ring (smaller diameter), (iv) iPhone cable with copper ring, (v) Auxiliary (AUX) cable with copper ring and (vi) AUX copper without copper ring.

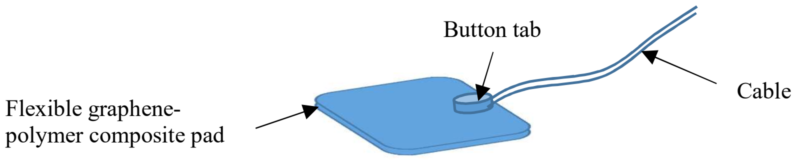

Figure 1: Electrode design schematic

2.3 Two Point Probe System Method

Conductivity measurements were performed on the developed electrodes samples using the 'Two Point Probe (TPP) system method' or simply, a two-probe system. It works by connecting two pins to the sample at opposite sides, one of them discharges a voltage into the sample and the other collects the resulting output voltage as shown in Figure 2.

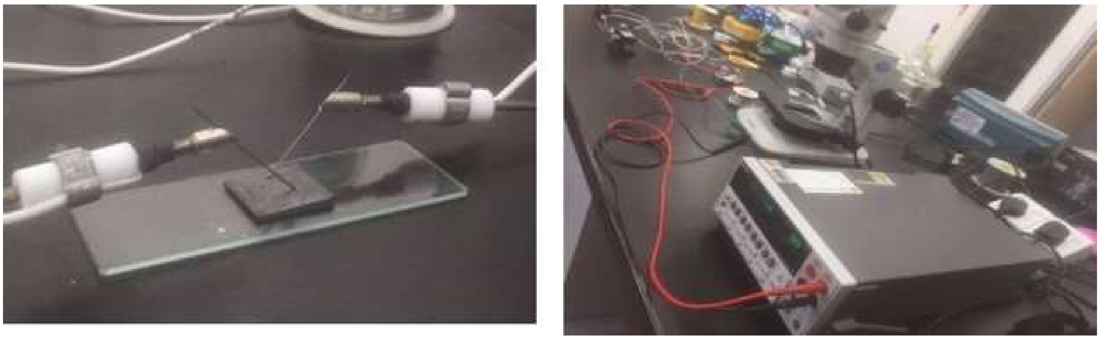

Figure 2: A two-probe system

Insulated copper micro-wires were used to connect the paste onto the sample and the tin islands on the board, since they are very thin and can be easily attached with the conductive paste. Their ends were previously exposed by means of a scalpel under an optical microscope. Insulated copper micro-wires were utilized to connect to the paste onto the sample and the tin islands on the board.

3.0 RESULTS, ANALYSIS AND DISCUSSION

In order to ensure the practicability of the developed electrode design, the current was measured and analysed. The results were presented and discussed in the following sub-sections.

3.1 Electrode Conductivity Analysis without Cable

Conductivity analysis of the electrode containing 20% CNTs with 1%, 1.5% and 2% of graphene without cable connection has shown significant current detected as depicted in Figure 3. The relationship obeys the *Ohm's* law where there are barely any fluctuations seen when a high voltage was applied to it. The maximum and minimum currents achieved are at the same rate between both negative and positive values. From Figure 3, it can be observed that by adding 1% graphene with CNTs 20%, it can be observed that there are discrepancies between the maximum current achieved and the minimum current achieved. The minimum current achieved is up to 500 µA while the maximum current achieved is 420 µA. There is less of a mirror effect due to the gaps between the minimum and maximum values. When more graphene is added at 1.5%, a smooth linear effect was again observed. The maximum current achieved is ±150 µA. Similarly, at 2% graphene, approximately ±20 µA was recorded. The results proved that by increasing the percentage of graphene, the conductivity will exponentially increase by 10 times as compared to a conductor without graphene.

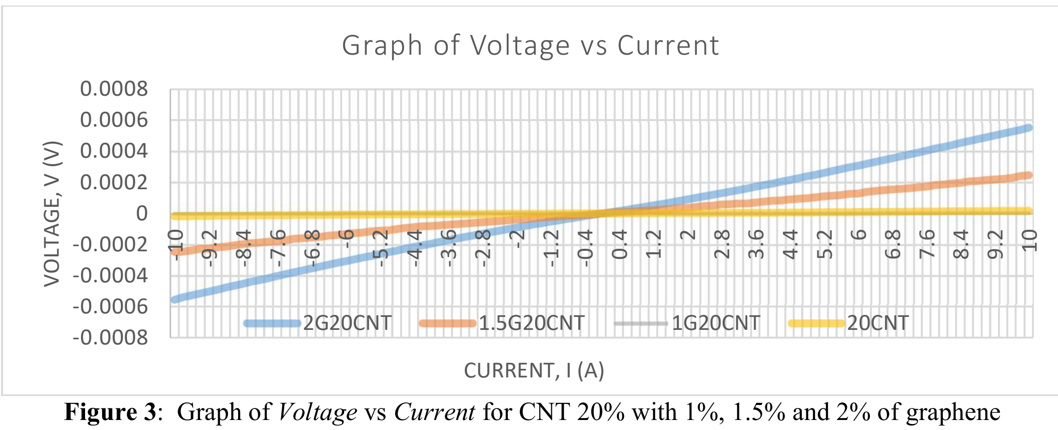

Figure 3: Graph of *Voltage* vs *Current* for CNT 20% with 1%, 1.5% and 2% of graphene

3.2 Electrode Conductivity Analysis with Cable

Conductivity analysis was also performed on the electrodes using 2% graphene + 20% CNTs after assembled with various types of cables. Fig. 4 and Table 2 show the electrode conductivity analysis tested using different types of cables. The electrode and voltage range used are made constant at 20% and 10.0 V, respectively. Overall, lowest resistance indicates a better electrode design with the amount of current detected. From Table 2, the results showed that SOMK cables with and without copper ring recorded similar and the lowest resistance value of 1.1 Ω with 9.091 A curent. For this type of cable, the use of copper ring has showed no significant effect towards the electrode performance. On the other hand, the AUX cables recorded the highest resistance and lowest current. The AUX cables has shown some variation in the values when copper ring is used where with copper detected 3.3 Ω resistance with 3.03 A current while without copper recorded 2.8 Ω resistance with 3.571 A current. iPhone cable with copper ring has also showed acceptable value of resistance and current of 1.4 Ω and 7.143 A, respectively.

Table 2: Conductivity analysis of the flexible electrode with various cable types

No	Cable type	Resistance, R (Ω)	Current, I at 10 V (A)
C1	SOMK cable with copper ring	1.1	9.091
C2	SOMK cable without copper ring	1.1	9.091
C3	SOMK cable with copper ring (smaller diameter)	2.6	3.846
C4	iPhone cable with copper ring	1.4	7.143
C5	AUX cable with copper ring	3.3	3.030
C6	AUX cable without copper ring	2.8	3.571

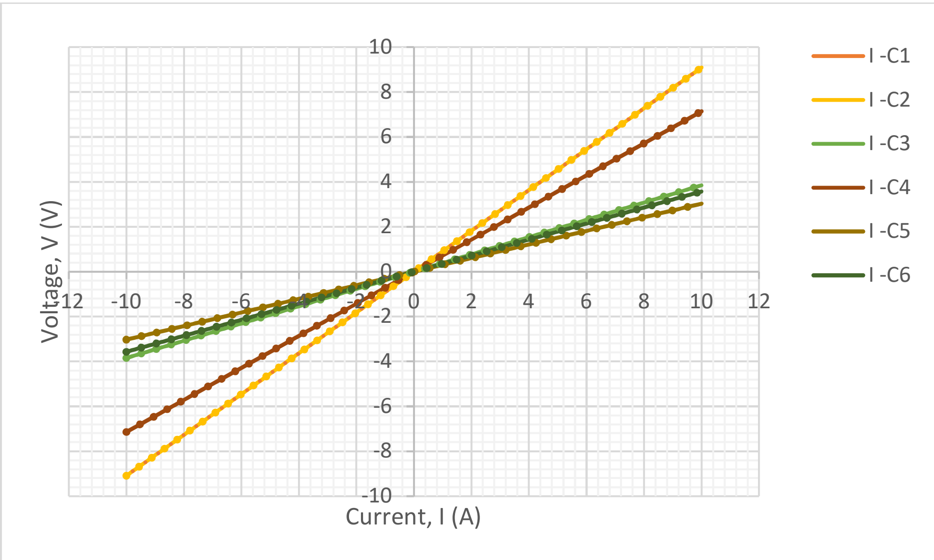

Figure 4: Comparison of current generated using different types of cables

4.0 CONCLUSION

The results obtained have proven that combination of graphene and CNTs can be used in developing a flexible graphene-polymer composite electrode. From the graphs illustrated, it was found that increasing the amount of graphene, will gradually increase the amount of current at the same voltage value. Two conductivity tests using the two-probe system were performed on the flexible electrode; with and without cable connections. Test without cable showed that 2% graphene and 20% CNTs was found to be the best composite mixture where no fluctuations of the current recorded during the when voltage was applied. In general, the current increased exponentially by ten times. Test using different cables has recorded various current and voltage values, where SOMK cables with and without copper ring recorded similar and the lowest resistance value of 1.1 Ω with 9.091 A current. AUX cable type was found to be the worst electrode combination. Therefore, future analysis is looking at designing variation of electrode with other composite mixture, shape and connection.

ACKNOWLEDGMENTS

The authors appreciate the funding from the Tier 1 Grant Vote No. 16H12 within the Frontier Material Research Alliance, Universiti Teknologi Malaysia (UTM).

REFERENCES

1. Rylie G., Sungchul B., Laura P.W. and Penny M., 2010. Conducting Polymer-hydrogels for Medical Electrode Applications, *Sci Technol Adv Mater*., 11(1): 1-13, 014107.
2. Neuman M.R., 2000. Biopotential Electrodes, in *The Biomedical Engineering Handbook*, Second Edition, Joseph D. (Ed.), Bronzino Boca Raton: CRC Press LLC.
3. Kaur G., Adhikari R., Cass P., Bown M. and Gunatillake P., 2015. Electrically Conductive Polymers and Composites for Biomedical Applications, *RSC Advances*, 5(47): 37553-37567
4. Debasish G., Pradip G., Masaki T., Akari H., Yasuhiko H., Kawasaki S., Noboru M., Mohd Z.Y. and Toru A., 2011. Highly Transparent and Flexible Field Emission Devices Based on Single-walled Carbon Nanotube Films, *Chemistry Communication*, 47: 4980–4982.
5. Pradip G., Tetsuo S., Masaki T., Mohd Z., Takashi J., Ryo K. and Kenji S., 2009. Vertically Aligned Carbon Nanotubes from Natural Precursors by Spray Pyrolysis Method and Their Field Electron Emission Properties, *Appl. Phys. A*., 94: 51–56.
6. Geim A K. and Novoselov K.S., 2007. The Rise of Graphene, *Nature Materials*., 6: 183–191.
7. Usuki A., Kojima Y., Kawasumia M., Okada A., Fukushima, Y., Kurauchi T. and Kamigatio O., 1993. Synthesis of Nylon 6-clay Hybrid, *Journal of Materials Research*, 8: 1179.
8. Masoud S-N., Ghanbari D., 2011. Polymeric Nanocomposite Materials, in *Advances in Diverse Industrial Applications of Nanocomposites*, Boreddy Reddy (Ed.), IntechOpen.
9. Antonio M. and Giovanni M., 2014. Electrical Properties of Graphene for Interconnect Applications, *Applied Science*, 4(2): 305-317.
10. Deborah P., 2014. Edge Structures for Nanoscale Graphene Islands on Co (0001) Surfaces, *ACS Nano*., 8(6): 5765–5773.
11. Kuilla T., Bhadra S., Yao D., Kim N.H., Bose S. and Lee J.H., 2010. Recent Advances in Graphene Based Polymer Composites, *Progress in Polymer Science*, 35(11): 1350-1375.
12. Yuqi Y., Mohamed Asiri A., Tang Z., Du D. and Lin Y., 2013. Graphene Based Materials for Biomedical Applications, *Materials Today*, 16(10): 365-373.
13. Thomas S., Stephen R. (Eds.), 2009. *Rubber Nanocomposites: Preparation, Properties and Application*. John Wiley & Sons.
14. Koo J.H., 2006. *Polymer Nanocomposites: Processing, Characterization and Applications*, McGraw- Hill.
15. Hasmuni N.F., Abdul Kader A.Z., Sudin I., Aziz M., Mohd Yusop M.Z., 2017. Fabrication of Polymer-based Graphene Composite as Highly Conductive Polymer Electrode, Universiti Teknologi Malaysia.