Preparation and Characterization of Graphene Membrane Electrode Assembly

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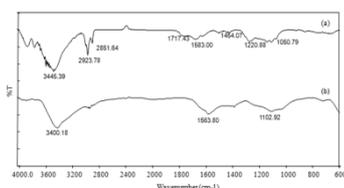
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Graphical abstract

Abstract

Fuel cell has been of great demand as power sources for electronic devices. However this has been delayed by the deficiency of catalyst material properties. The aim of this research is to design and synthesis graphene membrane electrode assembly (MEA) as catalyst support in direct methanol fuel cell (DMFC). Graphene was produced from pure graphite powder using chemical reduction method of graphene oxide aqueous solution with a reducing agent. The modified membrane electrode assembly of graphene sulfonated poly (ether ether ketone) (SPEEK) was fabricated for DMFC testing. After the reduction process, the FTIR spectrum showed the disappearance of the carbonyl group of graphene oxide. XRD spectrum showed a sharp peak at $2\theta = 26.4^o$ which can be assigned as 002 indexed peak with hexagonal crystal structure. The morphology of graphene observed is a uniform multi layer with crumple flakes and the product has conductivity of as high as 1.36×10^4 S/m. The characteristic of the synthesized graphene membrane electrode assembly suggest potential application in direct methanol fuel cell.

Keywords: Graphene; membrane electrode assembly; direct methanol fuel cell

■1.0 INTRODUCTION

Fuel cell has greater demand on power sources of electronic devices applications. Numerous researches come with new ideas achieving on extend fuel cells performance and an attempt to reduce the cost. However this has been delayed by the deficiency of possible catalyst material. Besides, fuel cell system encounter various difficulties related to the leading materials with good chemical resistance and high conductivity [1]. Resolution of this matters can be resolved in various way by decreasing electrocatalyst nanoparticle size, reduce electrocatalyst loading at electrodes, improving performance by carbonaceous catalyst support, and development of membrane electrode assembly (MEA) fabrication [2].

It been generally acknowledged, platinum are the most efficient used catalyst. However, by solely using platinum limits the application due to its high price [1]. Besides, previous research has proved that the catalyst with support material had improved stability and higher activity compared to unsupported catalyst [3]. There are two categories of materials been use as catalyst support which are carbonaceous material or non-carbonaceous material.

Catalyst materials can be employed in term of electrode electrocatalyst or catalyst support in MEA. Characteristics of good material for catalyst support should poses high electrical conductivity, good catalyst interaction, and mesoporous structure for electron transport. Nowadays, carbon based materials was greatly utilized as catalyst support because carbon is an important electrode assembling for maximizing fuel cell performance [4]. Besides, graphene is one of carbonaceous material that capable to conducts both electricity and heat due to its unique configuration of carbon atoms [5]. Thus, this research suggest fabrication of graphene in MEA for further study as supporting material believed to have excellent electronic transport and low cost of production.

■2.0 EXPERIMENTAL

2.1 Materials

Pure graphite powder (Thermo-Pure), concentrated sulphuric acid (H_2SO_4 98%, Qrec), potassium permanganate ($KMnO_4$, Qrec), hydrogen peroxide (H_2O_2 5%, Qrec), hydrochloric acid (HCl 35%, Qrec), sodium hydroxide pellets (NaOH, Merck) and sodium borohydrite ($NaBH_4$, Qrec) were used as received.

2.2 Preparation of Graphene Oxide

Modified Hummers method [6] was selected in preparation of graphene oxide powder. In ice bath, pristine graphite powder was placed into a flask of concentrated cold H_2SO_4 (5^oC) under constant stirred condition. Once graphite powder was dissolved, potassium permanganate was slowly added and continuously stirred for 1 hour. Temperature was controlled between $10\text{-}15^oC$. After 1 hour, the mixture solution was then stirred at 35^oC for 30 minutes and diluted drop-wise with distilled water. Subsequently, further dilution with distilled water and hydrogen peroxide and the solution colour was observed changed to dark chocolate colour. For complete

reaction, the mixture was allowed to stay for the night. Next day, the mixture solution was centrifuged, filtered, washed with HCl solution followed by distilled water for several times and be dried at 70°C for 24 hours to obtain the graphene oxide powder.

2.3 Preparation of Graphene

Reduction method was selected to synthesize graphene by introducing any potential reducing agent that may be able to exterminate the oxide during the reduction process [7]. Resultant graphene oxide powder was dispersed into water with ultrasonication for 30 minutes. In the meantime, sodium borohydrite solution was prepared as reducing agent. After finishing minutes, sodium borohydrite solution was added drop-wise and stirred at room temperature for 24 hours. Then, graphene powder was obtained after the mixture was filtered, rinsed with ethanol and distilled water continually and dried in an oven at 70°C for 24 hours.

2.4 Characterizations

FTIR spectra observed the frequency of each available bonding in the samples was determined through Perkin Elmer Spectrum One FT-IR with KBR pellet technique by prepared samples in potassium bromide pellets. XRD patterns identify the structure of element analysis via scanning with Bruker Advance D8 Siemens 500 diffractometer, using Cu Kα radiation (λ = 0.15418 nm, 40 kV, 40 mA). The scanning rate is 1 second with interval of 0.05°, 2θ range of 20°- 80° in the ambient temperature. TEM images recognize the morphology

of samples determined by transsmission electron microscope modelled Philips CM12. Four point probe technique was used to measure electrical conductivity of the samples and model been used was Four Probe Dfp-02.

■3.0 RESULTS AND DISCUSSION

FTIR spectrum was used to identify appearance of main functional groups in the structure. FT-IR spectra of all peaks band of graphene oxide and graphene was depicted in Figure 1. Graphene oxide spectrum (see spectrum (a)) shows different type of oxygen functionalities peaks which are allocated to O-H stretching, C=O stretching, and C-O stretching which has good agreement with previous works [1, 5, 8-9]. The broad peak at 3445.39 cm^{-1} and 1583.00 cm^{-1} are assigned to OH groups indeed of contained water in compound. Existence of two peaks at 2923.78 cm^{-1} and 2851.64 cm^{-1} showed sp^3 C-H bonding which indicated the product was produce in acidic phase which proved the presence of carboxylic acid in structure. The readings 1717.45 cm^{-1}, 1220.88 cm^{-1} and 1050.79 cm^{-1} are signified to C=O and C-O stretching due to carbonyl groups in the product. Compared to the graphene spectrum, obviously there is distinction in term of functional group. Peak at 1717.43 cm^{-1} in graphene oxide was found vanished from spectra (b) which enlighten success deduction of carbonyl group during the reduction process [9]. Besides, graphene peaks stipulate at 3400.18 cm^{-1} and 1563.80 cm^{-1} which is attributed to the C-OH bond respectively. Hence, confirmation of graphene oxide and graphene structure was validated by FT-IR study.
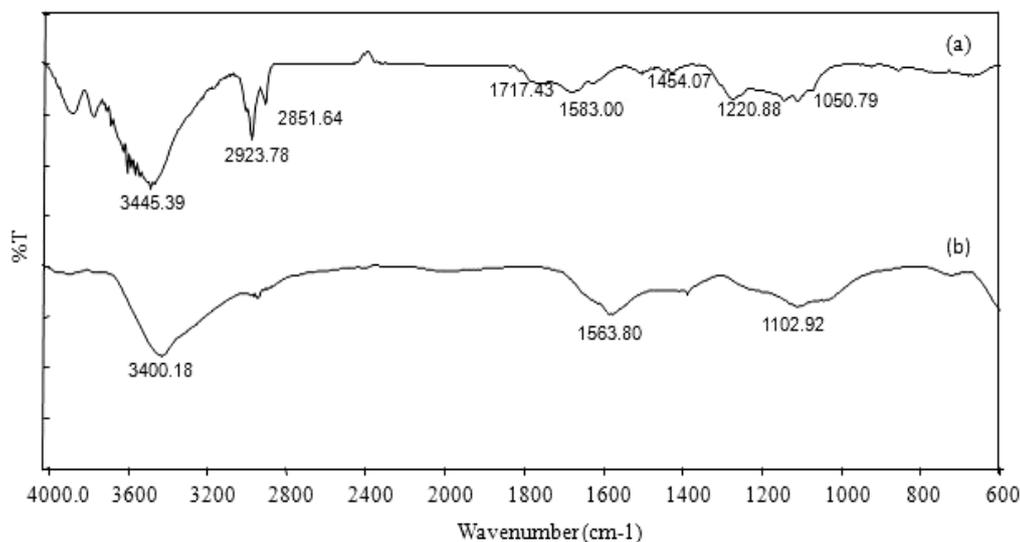

Figure 1 FT-IR spectra of (a) graphene oxide and (b) graphene

Crystallinity and verification of available of an oxide in layer structure of graphene oxide and graphene was determined through by X-Ray diffraction (XRD). XRD patterns of synthesized products were as shown in Figure 2. Graphene oxide spectrum (see spectrum (a)) figure out indexed *002* peak at *2θ* =17.2° which explain non uniform crystal structured with addition of oxygen functional group. This result be supported by FTIR spectrum of emergence of carbonyl and hydroxyl group and high layer distance of 0.779 nm [1, 10-11]. XRD data indicates d-spacing of graphene oxide is much higher than theoretical graphite may due to interlayer water trapped between the hydrophilic graphene

oxides [9]. This also proved the expandable of graphite layers was successfully oxidized.

It is different to graphene product, in which significant indexed *002* peak was at *2θ* = 26.4° and *004* at *2θ* = 54.2°. The peak appeared at 2θ = 26.4° indicates the same peak trend of graphite with uniform structured but different layer spacing at 0.341 nm. This spectrum confirmed structure exhibited an ordered crystal structured by the disappearance of diffraction peak at 17.2° [12]. Therefore, the distance between the interplanar of graphene is slightly larger than graphite, mainly due to deformed of graphite structure [13] and the subsistent of residual chemical groups between layers in the product [10]. Thus, it can be concluded that the degree of 2θ can be as

indicator of presence subtituent of oxygenated functional available between the graphene oxide and graphene layers.

The smaller the degree of angle, the more amounts of oxides trapped in layers and vice versa.
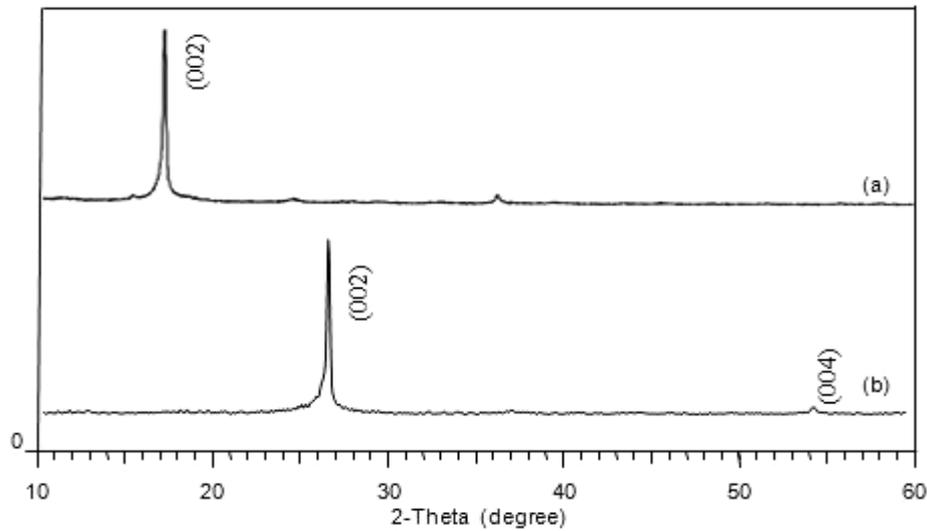

Figure 2 XRD pattern of (a) graphene oxide and (b) graphene

The surface studies on morphology properties of synthesized graphene oxide and graphene was examined by TEM micrograph as shown in Figure 3. A clear view of images observed the samples have more than one layers as material was produced in powder form. Graphene oxide image (see image (a)) emerged as semi transparent which describe the material is not stable under high energy beam in contrast with graphene, which stable nature under high energy electron with transparent figure. Morphology graphene oxide revealed a thick flat flake layers, rough surface, not crumpled and irregular shape with non uniform of particle size. Disordered and unwrinkled structured was owing to no removal of oxygen atoms and high degree of exfoliation during oxidation process [13]. Moreover, irregular shape and unorganized particle size was cause by cracking of structure occurred during oxidation process with uncontrollable temperature or amount of oxidant [14].

On the other hand, the image of graphene composed a thin flat flake and crumpled morphology consistent with previous reports [15-16]. The wrinkled flake structure was evidently observed alike graphene sheets thin film morphology. The thin multi layers and crumpled sheets was associated with exfoliation process in reduction and sonification medium cause by rapid elimination of intercalated oxygen and others functional groups between the layers [13]. Thus, exfoliation results induced the affect of disorder solid graphene structure in form of crumpled sheets. Therefore, by linked the results of morphology and structural properties of graphene at $2\theta = 26.4°$, it is proved that there is less existence or lack of oxygen functionality in the graphene composition.
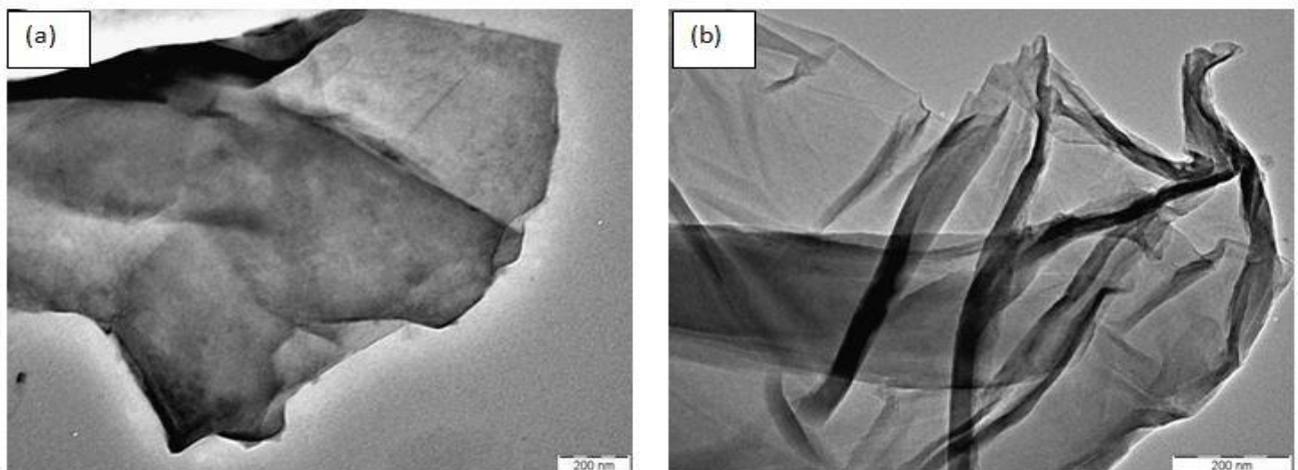

Figure 3 TEM images of (a) graphene oxide and (b) graphene

The quality of graphene material in membrane electrode assembly as supporting catalyst is evaluated through this characterization. Electronic properties study was done by measuring electrical conductivity of each sample with four point probe technique at room temperature. Conductivity measurement determines ability of material to carry out or transmit heat or electricity. Table 1 tabulated the electrical conductivity value of the samples.

Table 1 Electrical conductivity data of graphene oxide and grapheme

Material	Conductivity (S/m)
Graphene Oxide	3.5800×10^1
Graphene	1.3560×10^4

From the table, graphene oxide resulted conductivity of 3.58×10^1 S/m and graphene show conductivity at 1.36×10^4 S/m. Graphene experienced higher conductivity about three orders of magnitude better than graphene oxide due to no interference of restoring carbon sp^2 network [15]. Catalyst support material should present high conductivity for facilitate electron transport and easy recovery of the catalyst. Requirement as catalyst support material acquire minimum conductivity value in range of $1.25 \times 10^2 - 1.25 \times 10^3$ S/m, for that reason the synthesized graphene is suitable candidate for catalyst support in fuel cell where the conductivity value is higher than the range stated [17].

■4.0 CONCLUSION

In summary, graphene oxide and graphene was successfully synthesized by employing Hummer's method (oxidation process) and chemical reduction method (reduction process). Physiochemical properties of samples were studied from the results of FTIR spectra, XRD patterns, TEM images and conductivity measurement. The results shows graphene indicate more preferable in overall characteristic as compared to graphene oxide. Hence, the characteristic of synthesized graphene material as candidate for catalyst support material in membrane electrode assembly suggest the application in direct methanol fuel cell according to its structure and great electrical properties. Further works, modified membrane electrode assembly of graphene sulfonated poly (ether ether ketone) (SPEEK) was fabricated for DMFC testing.

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