

Sulfonated Graphene Oxide Polystyrene Ethylene Butylene Styrene as Membrane in Microbial Fuel Cell

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Article history:

Received 23 June 2019

Accepted 20 July 2019

GRAPHICAL ABSTRACT

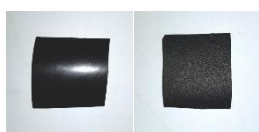


Image of GOPSEBS thin film (left) and sulfonated GOPSEBS composite thin film (right)

ABSTRACT

Microbial Fuel Cell (MFC) is the game changer for the search of renewable source of energy in this era for its eco-friendly and high output generation of energy nowadays. This study focused on the membrane in the MFC as the separator for both anode and cathode chamber and also as the ionic conduction in the fuel cell. This study was carried out to prepare and characterize the graphene oxide, composite of graphene oxide (GO) with polystyrene ethylene butylene styrene (PSEBS) and the sulfonated GOPSEBS as the membrane in the microbial fuel cell. GO-based was selected as filler in PSEBS because of its proton-conductive properties for applications in fuel cells which have unique graphitized plane structure, electric conductivity, and mechanical stability. The GO was synthesized using modified Hummer's Method. The sulfonation of this membrane composite shows a new significant improvement as the membrane in the microbial fuel cell. The GO, GOPSEBS and SGOPSEBS are characterized by using Attenuated Reflectance Fourier Transform Infrared (ATR-FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX) and Electrochemical Impedance Spectroscopy (EIS). The GO was successfully synthesized by the confirmation of IR spectrum which are assigned to O-H stretching, C=O stretching, C-OH stretching, and C-H stretching respectively. The EDX result for SGOPSEBS shows the peaks for carbon, oxygen and sulphur indicates the presence of the elements in the membrane composite. Lastly, from the SEM image, it shows that the GO has crumpled sheets with a folded appearance, without any pores or defects and in the GOPSEBS composite membrane the GO was expected to distribute uniformly in the PSEBS matrix and for SGOPSEBS, the crumpled sheet appear with some scratch like pattern on its surface.

Keywords: Graphene, graphene oxide, PSEBS, proton exchange membrane

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1. INTRODUCTION

Microbial fuel cell is an alternative for various kind of energy sources available nowadays. As the increase in demand for non-fossil-fuel-based energy production, this electrical energy generated from biochemical process by the microorganism in anaerobic condition [1] making this cell can be categories as a green energy. The biochemical process is involving the metabolisms of complex organic carbon substance [2] where used as a substrate that presence inside anode chamber the Microbial fuel cell. The biochemical process in the cell can generate electricity when a suitable substrate was used, thus initiates metabolisms of the immobilized biocatalysts on the electrode surface degrading substrate are resulting electrical energy where the electron produced flow when connected to a complete circuit. The abundance of wastewater that rich with substrate source for MFC such as domestic wastewater and factory wastewater available. MFC become the most alternative way to treat that wastewater as the great amount of energy also can be generated along with the treatment according to a study by Fornero [3].

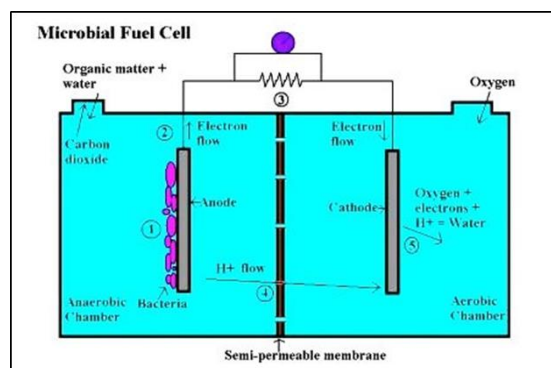


Figure 1 Structure of MFC. Adapted from ref. [8]

In MFC, the Proton Exchange Membrane (PEM) are one of the prior components that play significance role in overall energy efficiency that being produced by the cell. PEM is the part which allow the transfer of proton and also act as a barrier within chamber of cathodic and anodic [4]. There were a lot of PEM that have been manufactured and developed such as Nafion and Chitosan. Nafion is one of the common membrane that has been commercialized, but due to several drawback faced by the user of Nafion membrane, new foundation recently come out with a kind of polymer that can perform better than Nafion, which is polystyrene ethylene butylene styrene (PSEBS).

In order to obtain a good characteristic of PEM, some factors should be considered, such as membrane should have the high proton conductivity that will extend its application when it comes to energy production [5]. From time to time, the membrane developer are trying to improve and maximize the performance of their membrane to compete with others in the market. As a new generation of optimized alternative membrane, such as sulfonated graphene oxide polystyrene ethylene butylene styrene S(GO-PSEBS), have been recently introduced and have revealed the potential to achieve low-cost and high-performance of the microbial fuel cell membrane.

2. EXPERIMENTAL

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was produced using modified hummers method from pure graphite powder. In this method, 27 ml of sulfuric acid (H_2SO_4) and 3 ml of phosphoric acid (H_3PO_4) (volume ratio 9:1) were mixed and stirred for several minutes. Then 0.225 g of graphite powder was added into mixing solution under stirring condition. 1.32 g of potassium permanganate ($KMnO_4$) was then added slowly into the solution. This mixture was stirred for 6 hours until the solution became dark green. To eliminate excess of $KMnO_4$, 0.675 ml of hydrogen peroxide (H_2O_2) was dropped slowly and stirred for 10 minutes. The exothermic reaction occurred and let it to cool down. 10 ml of hydrochloric acid (HCl) and 30ml of deionized water (DIW) was added and centrifuged at 5000 rpm for 7 minutes. Then, the supernatant was decanted away and the residuals was then rewashed again with HCl and DIW for 3 times. The washed GO solution was dried using oven at 90 °C for 24 hours.

2.2. GO and PSEBS composite membrane fabrication

10 wt % of PSEBS solution was prepared by dissolving 10 g of PSEBS in 90 mL of N-Methylpyrrolidone (NMP). The solution was stirred continuously at 60°C for about hours to obtain a homogenous solution. On the other hand, 1 g of GO was added into 10 mL of NMP and also stirred for 3 hours to obtain homogenous solution. The mixture was then sonicated for another 3 hours in order to disperse the GO particles. The GO mixture was then added into PSEBS solution and was vigorously stirred for 24 hours at 70°C to homogenize the solution. The PSEBS and GO were fabricated using a dry-phase inversion method where both homogenous solutions were cast onto two different glass plates using a casting knife, dried at room temperature for 24 hours, followed by oven heating at 45°C for 48 hours and 60°C again for 48 hours. The thoroughly dried membranes were then immersed in deionized water and peeled from the glass plate. The treated membrane was washed with deionized water until the wash solution become neutral.

2.3. Sulfonation of Graphene Oxide PSEBS

5g of GOPSEBS was dried in a hot air oven at 100°C and then dissolved in 95 ml of concentrated (98%) sulphuric acid (H_2SO_4) at room temperature under vigorous stirring. The 98% H_2SO_4 was used for sulfonation of GOPSEBS. After completing the dissolution, the polymer solution was heated to 55°C and the reaction time was fixed for 24 hours. The sulfonation was terminated by cooling the solution to 0°C. Then, the composite was cast into thin film again on the glass plate before it was dried at 100°C for 24 hours in the oven. The thin film was then rinsed by de-ionized water until a neutral pH was reached.

3. RESULTS AND DISCUSSION

3.1. Preparation of graphene oxide, GOPSEBS and SGOPSEBS membrane

Graphene oxide was successfully synthesized from the graphite by using potassium permanganate, $KMnO_4$ as strong oxidizing agent as stated in the modified Hummer's method. The solution obtained after the oxidation of the graphite to graphene oxide is black showing that the graphene oxide was obtained after the reaction. There were no colour changes after the graphite has been oxidized as it remains as black for the graphene oxide. After the production of graphene oxide,

the composite polymer membrane is prepared by using PSEBS polymer in the NMP as solvent. The dope PSEBS solution is colourless because only polymer is used. After both is successfully synthesized and fabricate using dry-wet phase inversion method to make the membrane, the dope was cast onto a glass plane to obtain a uniform thickness of film. Figure 4.1 shows the films that have been produced. The colour still remains black as the colour of GO because the PSEBS dope is colourless. The product of GOPSEBS membrane is shining black in colour and dope GOPSEBS solution is black. For sulfonation of membrane, using 98% sulphuric acid, H_2SO_4 , for 24 hours, in order to introduce sulfonic group while avoiding degradation of the composite and a cross-linking reaction, which may occur when using 100% H_2SO_4 [6].

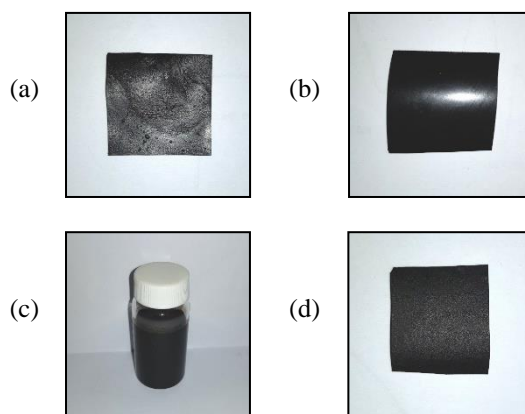


Figure 2. Images of (a) graphene oxide, (b) GOPSEBS thin film, (c) GOPSEBS dope liquid, and (d) sulphonated GOPSEBS thin film

3.2. Functional group GO, GOPSEBS and SGOPSEBS composite membrane

The attenuated reflectance Fourier transform infrared (ATR-FTIR) was used to determine the functional groups present in the GO, GOPSEBS and SGOPSEBS samples obtained. Figure 3 shows the spectra obtained for all the samples prepared. The simplicity and reliable result of this method making it being chosen to confirm the functional groups presence and confirmed the reaction. ATR-FTIR focus on the solid sample and thus it easy to perform the instrumentation as the product obtained also in thin film form. Table 4.1 summarize the important peaks in the FTIR spectra. When the GO, GOPSEBS and SGOPSEBS was characterized, the ATR-FTIR was expected to show some of the following peaks that represent the presence of GO peaks at $3400\text{-}2400\text{ cm}^{-1}$ for O-H stretching vibrations, $1800\text{-}1650\text{ cm}^{-1}$ for C=O and other peaks respectively [7]. In this study, the peaks found for the graphene oxide are at 3397.37 cm^{-1} , 2927.34 cm^{-1} , 1383.21 cm^{-1} and 1736.36 cm^{-1} which specifies to the O-H stretching, C-H stretching, C-OH stretching, and C=O stretching respectively. Therefore, all those peaks in the spectrum are a confirmation that the GO is successfully synthesized.

After the GO was fabricated with PSEBS dope to obtain GOPSEBS, the spectrum gives the peaks at the 3417.12 cm^{-1} , 2953.41 cm^{-1} , 1376.67 cm^{-1} and 1707.43 cm^{-1} are assigned for O-H stretching, C-C stretching, C-OH stretching, and C=O stretching respectively and as addition of PSEBS, the spectrum for hydrocarbon groups of =CH₂ stretching, -CH₃ stretching, and aromatic compound benzene, peaks appear at 3173.11 cm^{-1} , 2923.86 cm^{-1} and 1460.14 cm^{-1} respectively. The peak present is the same as the GO but since it has been fabricated, the peak of PSEBS also appear in the spectrum. Then GOPSEBS undergone sulfonation, the peak for S=O stretching appear at 1047.83 cm^{-1} while the peaks for other functional groups remain present. This peak was subjected as the presence of sulphonic group which ranged between 1030 cm^{-1} to 1200 cm^{-1} [8], SO₃, at the membrane composite was successfully obtained.

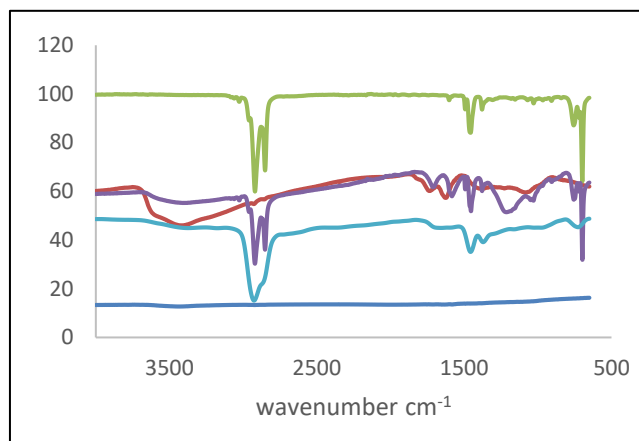


Figure 3. ATR-FTIR spectra of GOPSEBS and SGOPSEBS

3.3. Surface morphology and composition of GO, GOPSEBS and SGOPSEBS

The surface morphology of the samples obtained is characterized by using scanning electron microscope at an operating voltage of 10 kV through various scale of magnification. The SEM micrographs of graphene oxide (GO) is given in Figure 4. From Figure 4(a), it can be observed that GO has layered structure, which can form the ultrathin and homogeneous graphene oxide films and seems to be a bit wavy and fair surface compared to the composite membrane at Figure 4(b). The fabrication of GO with PSEBS making the surface a bit wrinkled and some area with crumpled appearance. This is due to the uniform distribution of GO in PSEBS structure. For SGOPSEBS, Figure 4(c) shows the surface became rougher than GOPSEBS [7]. This may indicate the effect of sulfonation caused the surface became more folded and the sharp edges results in scratch like pattern on the surface seems to be obvious than on GOPSEBS membrane surface.

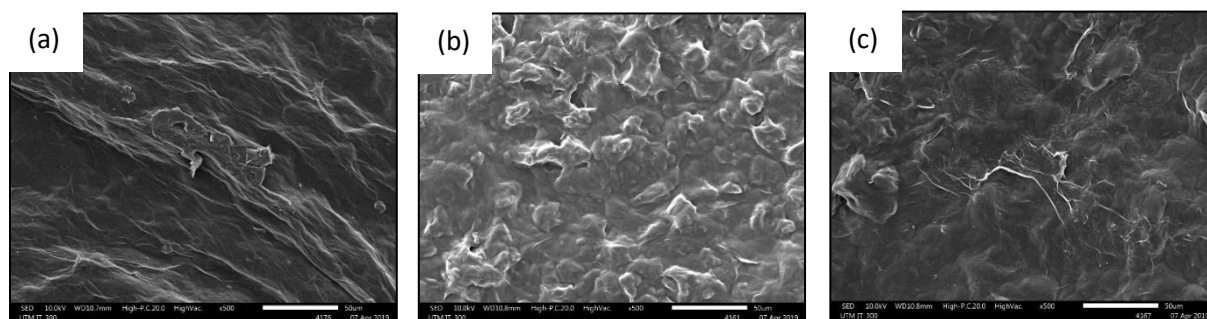


Figure 4. SEM images for (a) Graphite (b) GOPSEBS and (c) SGOPSEBS

From Table 1, EDX result shows that the sulphur content was presence in SGOPSEBS membrane composite as much as 2.23% wt. This might be due to the compatibility of sulphonic acid (SA) to the universal sulfonation method used in this study because of the structure of SA with substantial sulfonic groups that can induce the chemical bond with the GOPSEBS structure. EDX spectra provided convictive evidences of sulfonation of graphene oxide [9]. As a comparison to GOPSEBS, SGOPSEBS exhibited not only the signals of C and O but also the signal of sulphur element from sulfonated acid group, indicating the successful sulfonation of graphene oxide. This point was in good agreement with FTIR spectra.

Table 1. EDX elemental microanalysis of GOPSEBS and SGOPSEBS

Material / Sample	Element (wt %)		
	Carbon (C)	Oxygen (O)	Sulphur (S)
GOPSEBS	90.87	9.13	-
SGOPSEBS	80.78	16.99	2.23

3.4. Proton conductivity of GOPSEBS and SGOPSEBS

The conductivity of membranes was obtained by the value of resistance from EIS result as shown in figure 4.4. The value impedance of the lowest frequency is used to measure the maximum value for membrane resistance because at the lowest frequency, the phase angle was in maximum value. At this point, the constant phase element, nearly maximum for impedance, because impedance is inversely proportional to frequency [11]. The average value of resistance for GOPSEBS and SGOPSEBS are 261 M ohm and 560 k respectively. Then the values were to obtain the proton conductivity of both membrane which are $2.88 \times 10^{-11} \text{ Scm}^{-1}$ and $1.34 \times 10^{-8} \text{ Scm}^{-1}$ respectively.

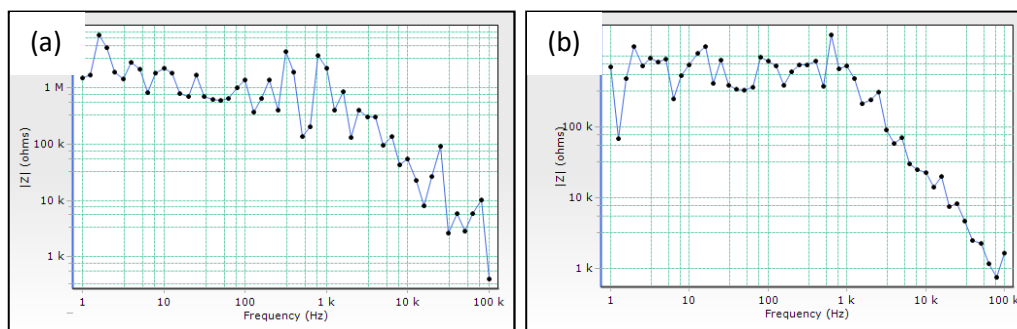


Figure 5. EIS spectra of (a) GOPSEBS and (b) SGOPSEBS

3.5 Water uptake

It is well known that water in proton exchange membrane plays an important role in proton conducting because adsorbed water can facilitate the transport of protons. The presence of acid group in the membrane and their capacity to dissociate in water determines the proton conductivity [10]. However, if too much value in water adsorption, it can cause the reduction in mechanical stability as well as swelling problem that can lead to a low membrane performance. Thus, the water uptake for GOPSEBS and SGOPSEBS membrane are 21.63% and 36.72% respectively as compared to Nafion117 which is 33% [10]. This indicate the addition of protogenic group into the composite influence the amount water uptake.

4. CONCLUSION

As the conclusion, graphene oxide was successfully synthesized using modified Hummer's method which of the solution is black in colour is being characterized using ATR-FTIR, SEM instrumentation. The ATR-FTIR gives the confirmation of GO which show the presence of the peak at 3397.37 cm^{-1} , 2927.34 cm^{-1} , 1383.21 cm^{-1} and 1736.36 cm^{-1} are assigned to O-H stretching, C-H stretching, C-OH stretching, and C=O stretching respectively. In addition, the surface morphology which is testing by using SEM shows that GO has thin sheets randomly aggregated, with minimal edges, wrinkled surfaces, and folding. For GOPSEBS membrane was successfully fabricated and characterized by using ATR-FTIR, SEM, EDX and EIS instrumentation. The IR spectrum shows a combination peak of GO and PSEBS indicate the bond between this material is successfully establish. The morphology for this composite is slightly differ from the GO as it is more wrinkled and crumpled. Oxygen and carbon are the element that contribute to the composition for this membrane as the result from EDX analysis. Lastly, SGOPSEBS also possibly being obtained and characterized by using ATR-FTIR, SEM, EDX and EIS instrumentation. The IR spectrum was different with the GOPSEBS for the peak of sulphonic group at 1047.83 cm^{-1} , SO_3 , thus indicates the sulfonation process is successfully undergone to introduce the functional group to this membrane structure. The EDX result also supporting the IR spectrum as the peak of sulphur were presence as much as 2.23% wt. The results for water uptake of membrane before and after sulfonation showing an increment value which indicate the presence of acid group in SGOPSEBS.

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