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Synthesis and Characterization of Sulfonated Graphene Oxide in Polystyrene Ethylene Butylene Polystyrene as Membrane for Microbial Fuel Cell

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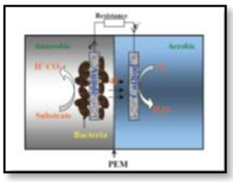
GRAPHICAL ABSTRACT



Schematic diagram of the microbial fuel cell

ABSTRACT

A microbial fuel cell (MFC) is a bio-electrochemical system which has gained a lot of attention in recent years as a mode of converting organic waste into electricity. Therefore, in this study a modification was carried out by fabricating n of sulfonated graphene oxide (SGO) with a polymer which is polystyrene ethylene butylene polystyrene (PSEBS) in order to improve the proton conductivity of the membrane. The graphene oxide (GO) was synthesized by using an *Improved Hummer's Method* and the SGO was successfully prepared by using sulphuric acid. The sulfonated GO and PSEBS membranes were fabricated using THF as a solvent. The properties of sulfonated GO and SGO-PSEBS were characterized by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR), Energy dispersive X-ray (EDX), X-ray fluorescence (XRF) and Scanning Electron Microscope (SEM). The SGO was successfully synthesized and confirmed by IR spectroscopy in which peaks corresponding to O=S=O appeared. Based on the EDX from SEM characterizations, they showed that the degree of sulfonation is 1.30%, and about 0.0139 mass% of the sulphur content in the membrane by using XRF. The proton conductivity value for SGO-PSEBS is 1.8634×10^{-7} Scm^{-1} obtained by using Electrochemical Impedance Spectroscopy (EIS) and showed about 25% of water uptake for this membrane.

Keywords: sulfonated graphene oxide, polystyrene ethylene butylene polystyrene, proton conductivity.

1. INTRODUCTION

A microbial fuel cell (MFC) is a bio-electrochemical system which have gained a lot of attention in recent years as a mode of converting organic waste into electricity. MFC is a novel knowledge that can be used to obtain bioenergy in the form of hydrogen and/or electricity directly from different organic and inorganic compounds while simultaneously treating biodegradable contaminants in wastewaters [1]. There are three main components in the MFC which are anode, cathode and proton exchange membrane (PEM). The performances of MFC may be enhanced through several important process parameters which are critical to its operation such as proton exchange membrane (PEM). PEM is one of the most important components in the cell because it allows the protons to pass and reach cathode to maintain the current in an MFC. In addition, it also act as barrier to separates the anode and cathode physically and prevent the substrate and the oxygen from go through the membrane.

Nafion is the most commonly used PEM due to highly selectivity permeability and conductivity to proton. But there are still number of problem associated with the use of Nafion such oxygen leakage and biofouling [3].Therefore one of the alternative membrane is fabrication sulfonated graphene oxide (SGO) with polystyrene ethylene butylene polystyrene (PSEBS) in order to overcome those drawbacks. The chemical resistance of PSEBS is similar to natural rubber and having excellent resistance. Therefore, it has excellent mechanical, chemical and thermal stability which makes it such an excellent material to use as the PEM of MFC.

However, the PSEBS need to composite with another compound for significant improvement in the performances of PEM in terms proton conductivity and fuel cross-over. Thus, a new way of composite sulfonated graphene oxide with PSEBS as a new approach since SGO was recognized as outstanding inorganic filler among the derivative of graphene [4].This is because it have SO_3H functional groups besides the existing amphiphilic structure of GO which showing potential to improve the properties of PEM especially on its proton conductivity [5].

2. EXPERIMENTAL

Graphene oxide was synthesized by the Improved Hummers Method. The first step consists on the oxidation of graphene using KMnO4 as the oxidizing agent. For this purpose, 360 mL of H2SO4 and 40 mL of H3PO4 were introduced into an Erlenmeyer flask with constant and vigorous shaking. 9 g KMnO4 and 3 g of graphite (3:1) was slowly added to the H2SO4/H3PO4 mixture. The reaction mixture was maintained at 50ºC for 12 hours. After the oxidation step, the resulting mixture was added to a beaker containing 400 g of flake ice and 3 mL of H2O2 in order to quench the reaction. The mixture was filtered under vacuum through a 10–20 μm filter. The resulting compact cake was washed twice (by vacuum filtration) with deionized water (200 mL), HCl (200mL) and ethanol (200 mL) to clean the oxidized graphite. Finally, the compact cake was slurred with dry diethyl ether (200 mL), filtered off and dried at 100ºC overnight.

The graphene oxide (50 mg) was added into 8 ml of 0.06 M sulfuric acid solution at 70°C. Under continuous stirring, 2 ml of 0.006 M sodium nitrite solution was added dropwise and kept at 70°C for 12 h. After the reaction, the solid part was collected by filtration and washed with deionized water several times until the pH became neutral. The SGO was then dried at 70°C for 24 h [6].

3wt% of PSEBS solution was prepared by dissolving 3 g of PSEBS in 87 mL of NMP. The solution was stirred continuously at 60°C for about hours to obtain a homogenous solution. On the other hand, 0.05 g of SGO 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 SGO particles. The SGO mixture was then added into PSEBS solution and was vigorously stirred for 24 hours at 70°C to homogenize the solution. The SGO-PSEBS 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. 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. They were kept in deionized water prior to use.

3. RESULTS AND DISCUSSION

3.1. Preparation of GO, SGO and SGO-PSEBS Membrane

Based on this experiment, the synthesis of graphene oxide (GO), sulfonated graphene oxide (SGO) were successfully done. The GO was prepared from graphite powder by using *Improved Hummers method* and the GO obtained is in the form of thin film. Then, GO was successfully sulfonated with the sulphuric acid. The sulfonation reaction was done by dissolving 0.05 grams of GO thin film with the 0.06 M sulphuric acid. The SGO obtained also in the form of thin film same as GO. After that, the fabrication of SGO and SGO-PSEBS membrane using the tetrahydrofuran (THF) as a solvent were done successfully. The SGO-PSEBS has black in colour due to the addition of SGO into PSEBS.

3.2. Characterizations

The GO, SGO and SGO-PSEBS were characterized using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR),Scanning Electron Microscopy (SEM) and X-ray Fluorescence (XRF) to study functional group of the compound, the morphology and composition of the membrane. The membrane properties which SGO-PSEBS were characterized by Eletrochemical Impedance Spectrosopy (EIS) and percentage of water uptake. The results of the characterization are discussed in the following sub-sections.

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR) of Graphite, GO and SGO

Functional group determination in graphite powder, graphene oxide and sulfonated graphene oxide was done by FTIR spectroscopy in order to confirm their synthesis as shown below**.** Figure 1 shows the spectra shows the wavenumber of each functional group for graphite, graphene oxide and sulfonated graphene oxide. The presence of oxygen and carbonyl group shows that the obvious change in sample which can be seen in the spectra after oxidation process occur and presence of sulfonic groups as sulfonation process occur.

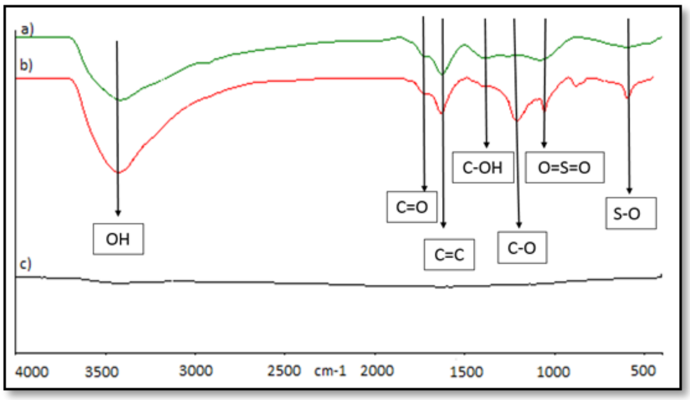


Figure 1. FTIR spectra (a) GO (b) SGO (c) Graphite

FTIR studies confirmed the successful oxidation of graphite to graphene oxide and sulfonated graphene oxide as shown in Figure 1. From the FTIR spectra shown the spectra for graphene oxide and sulfonated graphene oxide clearly shown the variation of peaks for different functional groups, such as hydroxyl, carbonyl groups and sulfonic acid groups. Thus, by comparing spectra of graphite (G), graphene oxide (GO) and sulfonated graphene oxide (SGO), it can be seen that there are obvious distinctions in terms of functional groups. The structure of graphene-based nanoparticles was characterized by FTIR spectroscopy.

From the FTIR spectra shown in Figure 1, graphite does not show any significant peak as no functional group can be detected while there is a strong and broad absorption at 3415.59 cm^{-1} and 3430.16 cm^{-1} due to O-H stretching vibration of the COOH groups in the spectrum of GO and SGO .The peak at 1713.5cm^{-1} and 1721.3 cm^{-1} was assigned to the C=O stretching vibration bands while peak at 1076.48 and 1205.50 associated with C-O stretching vibration bands of COOH in GO and SGO. The medium peak at 1625.63 cm^{-1} and 1628.61 cm^{-1} specifies the C=C stretching vibration in GO and SGO. The obvious peak observed in the FTIR spectrum of SGO is the absorption peaks corresponding to O=S=O and S-O appeared at 1055 cm^{-1} and 593.31 cm^{-1} which indicated the successful completion of sulfonation process while in GO spectrum is the absorption peaks at 1386.17 cm^{-1} which represents the O-H deformation of the C-OH group.

3.2.2. Morphological Structure of Graphene Oxide and Sulfonated Graphene Oxide by SEM

SEM was used to observe the surface state and structure of the samples using a scanning electron microscope Phenom Prox model with magnification was 2000x and 10 kV. EDX spectroscopy was used to measure the elemental analysis of the composites.

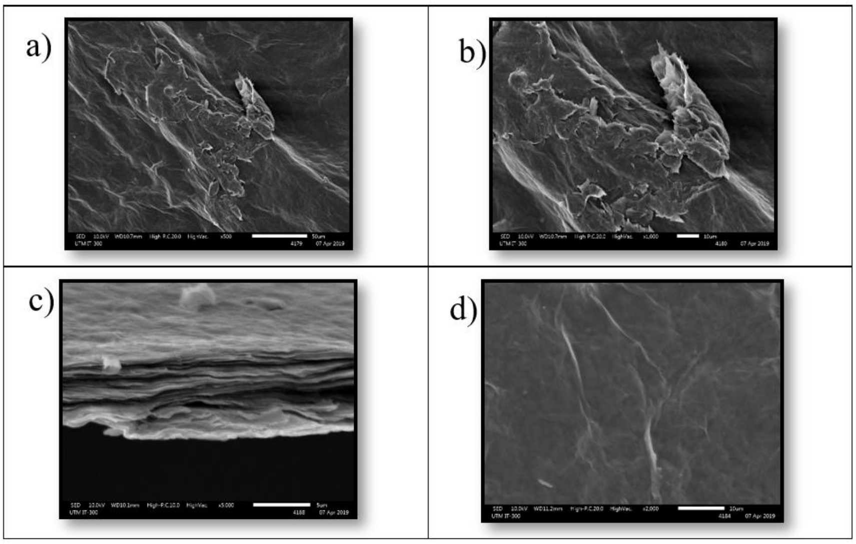


Figure 2. Morphology of the cross section of (a)(b) GO (c)(d) SGO

Figure 2 shows the SEM images of graphene oxide (GO) and sulfonated graphene oxide (SGO).From the result obtain obtained in Figure 2 (a) it shows that GO presence in form of layer. It also shows that there are wrinkles that form on the surface of GO. This observation is similar to studies conducted by Kellici (2014) and Liu (2011) [6]. The wrinkles formation will give the conducting characteristics to the GO [7]. Furthermore, the formation of the wrinkles and crumples like structure might be due to the existence of H_2O molecules and hydroxyl or carboxyl groups [8]. In addition, the formation of wrinkles on the surface of GO means that the sp^2-hybridized structure of the stacked graphene sheets has broken up [9].The bulky structure observed was due to the introduction of oxygen functional group in between graphite layer caused the expansion of the interlayer spacing while the exfoliated layered structure resulted from thermal exfoliation. In Figure 2 (b) shows that GO morphology resembled a fluffy appearance decreasing the number of layers in comparison with graphite due to the oxidation process.

The exfoliated SGO were centrifuged at 4000 rpm to remove the larger and unexfoliated SGO to ensure the quality of the initial material. The cross-section image of Figure 2 (c) revealed that the exfoliated SGO were easy to restack and formed layered structure. The SGO nanosheets also shows wavy and well exfoliated layered structure resulting from hydrophilic sulfonic acid group modification on the GO surface. As shown in Figure 2 (d) SGO exhibited smooth and thinner sheet structure compared to GO. The structural changes could be attributed to the dispersibility of SGO in aqueous solution increased by the introduction of hydrophilic –SO_3H groups, restricting the accumulation of SGO sheets.

Table 1. EDX elemental microanalysis of SGO

Material	**Carbon**	**Oxygen**	**Sulphur**
	wt%	wt%	wt%
SGO	57.7	41.0	1.30

The elemental analysis of SGO paper was performed by EDX on different areas of paper and an average of wt% data is presented in and Table 1. Graphite is composed of 98 wt. % carbon. The amount of carbon present in SGO samples was considerably lower (compared to graphite) due to the carbon replacements by oxygenated groups after the oxidation process but still higher compared with sulphur and oxygen content. The oxygen wt% is quite higher which demonstrated that oxygen is mostly present as hydroxyl, epoxy and carboxyl groups, which are located at the edges of the sheets and in the interior of the aromatic domains. The EDX result show in Table 1 shows the composition of sulphur suggested that –SO_3H groups were successfully grafted on GO after sulfonation. The sulphur content in SGO is about 1.30 wt%, therefore the degree of sulfonation is ~ 1.30%. The degree of sulfonation is directly proportional to the sulphur content [9].

3.2.3. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) PSEBS and SGO-PSEBS

Figure 3 (a) shows the IR spectrum of PSEBS. Appearance of peak around 1657cm^{-1} and 1456.08 cm^{-1} was assigned to the aromatic ring C=C. Appearance of peak around 1378cm^{-1} was assigned to the bending vibration which is due to the presence of aromatic ring backbone –CH– bending vibration. The peak at 2920.59 cm^{-1} is due to the stretching of C–H (sp^2) bond of aromatic hydrocarbon and at 2852.01 cm^{-1} due to the stretching of C-H (sp^3) bond. Appearance of peak around 698.26 cm^{-1} and 756.17 cm^{-1} was assigned to the aromatic ring out of plane C–H bending vibration. Appearance of these peaks confirmed the structure of PSEBS.

Figure 3 (b) shows an additional absorption peak in the IR spectrum of SGO-PSEBS due to composition of SGO into PSEBBS polymer. The absorption peak was observed at 1304.04 cm^{-1} and 1154.91 cm^{-1}, which were attributed to the stretching vibrations of C-SO_3H and S-O stretching vibration at 660.25 cm^{-1} were suggesting the successful fabrication of SGO into the PSEBS. In addition, the broad peaks at 3418.77 cm^{-1} were assigned to the the –OH stretching mode of absorbed.

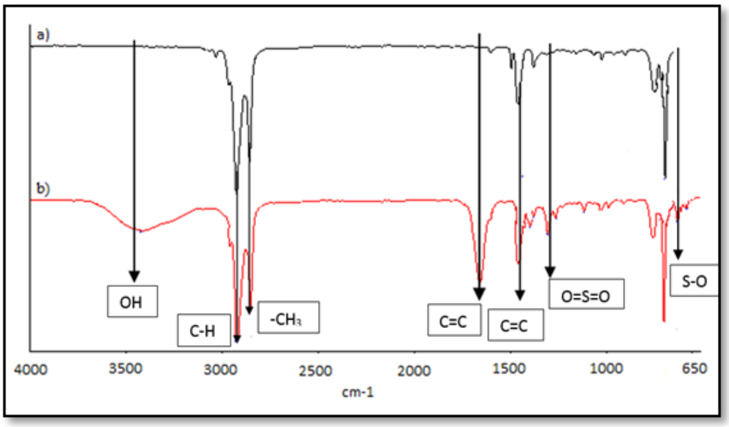


Figure 3. ATR-FTIR spectra (a) PSEBS (b) SGO-PSEBS

3.2.4. Morphological structure of SGO-PSEBS membrane by SEM

The morphology of the surface image of SGO-PSEBS composite membrane can be observed as in the Figure 4. The surface analysis of the SGO-PSEBS membrane shows that the surface of the membrane is clear and did not form any agglomeration which showing that SGO is homogeneously dispersed into the polymeric matrix finally. The cross-section analysis of the SGO-PSEBS membrane shows that it is nonporous membrane in Figure 5. Therefore, it observed to be a good membrane because membrane separator in MFCs should be non-porous which prevent oxygen and substrate crossover. In general, the use of porous membrane as a separator in MFC is discouraged due to its high oxygen and substrate crossover rate although it has low internal resistance compared with nonporous membrane. It was also observed that the SGO filler in the composite PEMs was well interconnected with the PSEBS substrates in SGO sample. Meanwhile, there was a more compact cross-section structure which indicates that SGO has better interface wettability, chemical compatibility and crosslink behaviour in the PSEBS substrate which it shows that the SGO is homogeneously dispersed into the polymeric matrix finally. The SGO showed to be more compatible and incorporated with the polystyrene matrix.

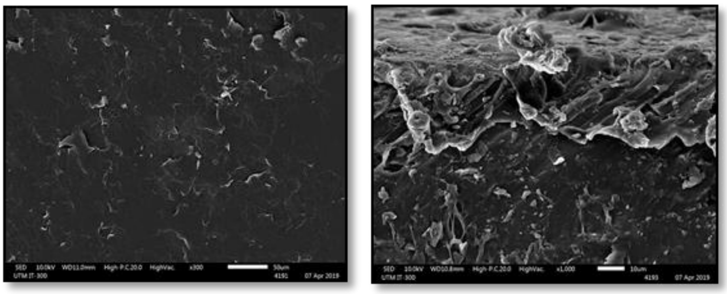


Figure 4. Morphology of the (a) surface image of SGO-PSEBS, and (b) cross section of SGO-PSEBS

3.2.5. X-Ray Fluorescence (XRF) of SGO-PSEBS

XRF was performed to know the chemical compositions of the sulphur that are present in the membrane. The data obtained shows that the sulphur are present in the membrane about 0.0139 mass% which indicates that SGO was successfully composite with PSEBS polymer. This confirms the chemical analysis of SGO-PSEBS membrane.

3.2.6. Proton conductivity and water uptake of GO-PSEBS and SGO-PSEBS

The proton conductivity is one of the key parameters of PEM which determines the efficiency of a fuel cell. It is complicated to establish a relation between the proton conductivity and structural properties of the membranes. Still, it is accepted that higher proton exchange groups consumed in the polymer and higher water uptake facilitate the migration of proton across the membrane and hence it helps to enhance the proton conductivity**.** The proton mobility across the membrane is highly dependent on the hydrophilic sulfonate groups present in the polymer matrices.

The SGO-PSEBS membranes with SD = 1.30% showed higher conductivity than the GO-PSEBS which $1.8634\text{x}10^{-7}$ Scm^{-1} (Table 1). Proton transfer enhances by presence the number of acid sites which enhances the proton transfer. The observed enhancement in conductivity could be explained by the increased SO_3H group content of the membrane due to the addition of SGO, which could possibly increase the number of channels available for proton transport by interconnecting some of the hydrophilic domains.

Table 2. Impedance, proton conductivity and water uptake of different membrane

Material	**Impedance (Ω)**	**Proton conductivity (σ)**	**Water uptake (%)**
GO-PSEBS	(1846±490)K	$1.625\text{x } 10^{-8}$	18
SGO-PSEBS	(161± 2)K	$1.8634\text{x}10^{-7}$	25

Sulfonation is known to enhance hydrophilicity by introducing the sulfonic acid groups. Therefore, the water uptake properties of the SGO-PSEBS and GO-PSEBS were also investigated. Table 2 shows that SGO-PSEBS have higher percentage of water uptake which 25% compared to GO-PSEBS which 18% .The presence of sulfonic groups in PSEBS polymers in the presence of water facilitates proton transfer and increases the conductivity of solid electrolytes. The enhancement of hydrophilicity by sulfonation of GO which composite with PSEBS polymer can be followed by water absorption of SGO-PSEBS membranes as a function of the degree of sulfonation [8].

These results show that the water absorption of SGO-PSEBS membranes increased linearly up to a DS of 1.30% .In the SGO-PSEBS, the density of SO_3H groups is high which may involve clustering or agglomeration. Clustered ionomers might be expected to absorb more water. Therefore, a large water uptake may be suggestive of the presence of ion-rich regions where proton transport is particularly fast. So, sulfonation not only increases the number of protonic sites SO_3H but also provides formation of water-mediated pathways for protons. . This active proton exchange group facilitates the water uptake capacity into the polymer due to their hydrophilic nature. The sulfonation of graphene oxide and composite with the PSEBS polymer could enhanced the conductivities and water uptake of the membrane. Due to these properties, it shows that they are suitable candidates for membrane in fuel cells.

4. CONCLUSION

As conclusion, graphene oxide was successfully synthesized by using *Improved Hummers method* while the sulfonated graphene oxide was a sulfonated by using sulphuric acid. Then both of this compound were fabricated to form a membrane which PSEBS-SGO. Graphene oxide and sulfonated graphene oxide are characterized by using ATR-FTIR and SEM instrumentation. The obvious peak observed in the FTIR spectrum of SGO is the absorption peaks corresponding to O=S=O and S-O appeared which indicated the successful completion of sulfonation reaction. After that, in the surface morphology which testing by using SEM shows SGO has smooth and thinner sheet structure compared to GO due to high dispersibility of SGO in PSEBS polymer. The degree of sulfonation of SGO is 1.30% which obtained by elemental analysis performed by EDX spectroscopy. In addition, PSEBS-SGO membrane was also successfully fabricated and characterized by using ATR-FTIR, SEM instrumentation and XRF. In FTIR spectrum of PSEBS-SGO shows significant peak due to fabrication of SGO into PSEBS. The absorption peak was observed which were attributed to the O=S=O and S-O functional group. In addition, there was about 0.0139 mass% of sulphur present in the membrane which suggesting the successful fabrication of SGO with PSEBS from the results obtained by using XRF. SEM image of PSEBS-SGO shows that the surface membrane of membrane is clear without any pores and have more compact cross section structure which indicate that SGO has better interface wettability and crosslink behaviour with PSEBS. Lastly, the membrane properties which PSEBS-SGO was investigated by using EIS and water uptake. From the data obtained, it show PSEBS–SGO has higher proton conductivity and water uptake compared with PSEBS-GO. Therefore, the fabrication of PSEBS-SGO composites is suitable candidates for membrane as it shows excellent approach to enhance the performances of PEM in MFC.

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