SEMARAK ILMU PUBLISHING

Semarak International Journal of Chemical Process Engineering

Journal homepage:
https://semarakilmu.my/index.php/sijcpe/index
ISSN: 3036-020X

Functionalized Graphene Oxide Incorporated in Sulfonated Poly Ether Ether Ketone for Proton Exchange Membrane Fuel Cell Application

Aressh[1], Nuor Sariyan Suhaimin[1], Juhana Jaafar[1,*]

[1] Advanced Membrane Technology Research Centre, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

ARTICLE INFO

Article history:
Received 26 June 2025
Received in revised form 24 July 2025
Accepted 30 July 2025
Available online 4 August 2025

Keywords:
Proton exchange membrane fuel cells; polymer electrolyte membrane; sulfonated poly ether ether ketone; nanomaterial; functionalized graphene oxide

ABSTRACT

As concerns grow over the depletion of fossil fuel sources and the effects of climate change, fuel cell technology has gained widespread attention for its excellent energy efficiency and low emissions. These devices operate as electrochemical systems that directly transform the chemical energy of fuels like hydrogen into electrical energy, bypassing the need for combustion. Proton exchange membrane fuel cells (PEMFCs) utilize polymer electrolyte membranes (PEMs) to facilitate proton transport. Among these, Nafion is one of the most widely used membrane materials in PEMFC applications. Nafion is one of the most commonly used polymer membranes in PEMFCs. However, Nafion presents several limitations, including relatively low proton conductivity, complex fabrication procedures, and a narrow operational window that demands elevated temperatures and continuous water regulation to maintain optimal performance. This study focuses on developing a composite membrane by incorporating sulfonated graphene oxide (SGO) into sulfonated poly (ether ether ketone) (SPEEK), aiming to improve the performance of single-cell PEMFCs when compared to the standard Nafion® 117 membrane by evaluating the membrane's physical and electrochemical properties. The fabrication of 10 wt. % of SPEEK and SGO/SPEEK dope solutions with different loading of GO & SGO (0.15, 0.20, 0.25 wt. %) via direct blending method followed by casting method. Scanning electron microscopy (SEM) was employed to identify the morphological structure of the filler incorporated membrane and several other test like ionic exchange capability and water uptake and FTIR was conducted to determine the ion capacity upon incorporation of SGO nanomaterial in SPEEK membrane. Hence via the functionalization of graphene oxide by sulfonation at 0.15 wt. % incorporated in SPEEK membrane proved to display better characteristics that suffice better as a PEM compared to bland SPEEK membrane and nonfunctionalized GO.

1. Introduction

With rising concerns about the depletion of fossil fuels and the impacts of climate change, fuel cell technology has gained significant attention for its high energy efficiency and low environmental

* *Corresponding author.*
E-mail address: juhana@utm.my

https://doi.org/10.37934/sijcpe.4.1.4658

impact. These devices generate electricity through electrochemical reactions, directly converting the chemical energy in fuels such as hydrogen into electrical power. Fuel cells are classified based on the type of electrolyte they utilize. They can achieve electrical conversion efficiencies of up to 60%, and when used for both electricity and heat generation, the overall efficiency can reach approximately 80%, all while cutting major pollutant emissions by over 90%. Although the concept of the fuel cell was first introduced in 1839 by Sir William Robert Grove, a lawyer who transitioned into science it took nearly a hundred years for the technology to find practical applications [1]. Fuel cells function similarly to batteries except they don't need to be recharged or run out of power. They generate heat and power constantly as long as fuel is available. An electrolyte separates the two electrodes that make up a standard fuel cell: the cathode, which is the positive electrode, and the anode, which is the negative electrode. The anode receives fuel, such as hydrogen, while the cathode receives air [2]. Hydrogen molecules are split into protons and electrons by a catalyst at the hydrogen fuel cell's anode, and these particles then proceed to the cathode via a number of different pathways. The electrons move across an external circuit, which results in the flow of electricity. Through the electrolyte, the protons travel to the cathode, where they mix with oxygen and electrons to produce water and heat.

Nafion emerged as the preferred membrane for DMFCs and PEMFCs. This is largely because the polymer backbone was perfluorinated, which significantly increased Nafion's chemical stability over its predecessors. However, deterioration from reactions with peroxide radicals produced during fuel cell operation still occurs [3]. Although Nafion currently dominates the commercial fuel cell market, it suffers from several critical design limitations that hinder its performance at elevated operating conditions. As its proton conductivity relies solely on the presence of adequate water channels within its hydrophilic regions, Nafion is ineffective at temperatures below 0 °C or above 100 °C. Furthermore, various intermediate products are always formed at the electrodes of redox reactions in fuel cells, which impacts their performance. For example, Nafion is stable against the generation of hydrogen peroxide (H2O2) up to 30% in solution. The decomposition of H_2O_2 into reactive radicals such as .OH and .OOH leads to the attack on hydrogen-containing terminal groups, accelerating the degradation of Nafion, particularly under low humidity and temperatures above 80 °C [4]. A vast majority agree that this is the main and most aggressive mechanism of deterioration. Additionally, by lowering the water content, the presence of foreign charged impurities (apart from H+) may also significantly reduce Nafion conductivity for this reason, the contaminating ions should be kept to a minimum during the membrane production process. At high temperatures, Nafion has poor thermal and chemical stability. Nafion experiences significant deterioration as a component of MEA and is vulnerable to numerous temperature and hydration or dehydration cycles. Moreover, mechanical stresses generated on the membrane's surface as a result of compression and external vibrations are the main reasons why PEMFC compact layers sustain mechanical degradation. Additionally, these pressures lead to layer delamination, crack initiation, and propagation, all of which can produce short circuit current [5].

Hybrid or composite polymer-inorganic PEMs have attracted significant attention due to their advantageous properties such as high chemical and mechanical stability, as well as high proton conductivity. These membranes combine the benefits of both polymer and inorganic materials, resulting in improved performance compared to neat polymer membranes [6]. One of the key factors contributing to the enhanced properties of hybrid or composite PEMs is the incorporation of fillers. Various types of fillers, including zeolites and mesoporous silica materials, have been utilized in the fabrication of these membranes. These fillers serve multiple purposes, such as reinforcing the membrane structure, providing additional proton conduction pathways, and enhancing the overall performance of the membrane. By incorporating zeolites or mesoporous silica materials into the

polymer matrix, the resulting hybrid or composite membranes exhibit improved mechanical strength and stability. This reinforcement helps prevent membrane deformation or degradation, making them suitable for demanding operational conditions. Additionally, the fillers contribute to the enhanced proton conductivity of the membrane by facilitating the movement of protons through their porous structures [7]. This improved proton transport property enables more efficient proton exchange in fuel cells or other electrochemical devices utilizing the PEMs. Furthermore, the incorporation of fillers can also contribute to other desirable properties, such as increased thermal stability, reduced methanol crossover in direct methanol fuel cells and enhanced water retention capacity. These factors further improve the overall performance and durability of the hybrid or composite PEMs [8].

GO is a single-layered, two-dimensional nanomaterial that is atomically thin. Thin flakes with a lateral width of several microns and a thickness of around 1 nm are typical characteristics of nanosheets [9]. GO is characterized by the presence of oxygen functional groups such as epoxy, hydroxyl, and carboxyl groups on the edges and basal planes[10]. Without the use of stabilisers or surfactants, the presence of these functional groups offers exceptional aqueous colloidal stability, making it simple to process and assemble GO for membrane construction [11]. Because of the sp3-bonded carbon atoms' internal distortions and wrinkles, these functional groups give the nanosheets amorphous properties even though the parent material graphene has a flawless hexagonal crystal structure [12]. Poor homogeneous dispersion inside the membrane matrix, which leads to excessive agglomeration, is the most frequent issue with graphene oxide use. This significantly lowers hydrophilicity, water flux, and ultimately membrane efficiency. Consequently, the aggregation issues on the membrane surface will be reduced by functionalising graphene oxide with more nanoparticles. Sulfonic groups on sulfonated graphene oxide create and maintain a water-thick layer, which raises the water flow flux [13]. Additionally, the sulfonic acid group surface in sulfonated graphene nanosheets with oxygen functional groups and sulfonated poly(ether ketone) offers a high interfacial hydrogen bond interaction, enhancing the composite proton exchange membranes' heat durability [14].

The goal of this research is to develop SGO/SPEEK membrane to enhance the effectiveness of single cell PEMFC compared to the pristine SPEEK and GO/SPEEK membranes through membrane's characteristics behaviour and to study the effect of different SGO loading on SPEEK membrane and the optimum formulation to obtain PEM with improved physio-chemical properties.

2. Methodology

2.1 Materials

Poly(ether ether ketone) (PEEK) polymer in powder form was provided by Victrex US Inc. Ltd, 1-Methyl-2-pyrrolidone (NMP) with purity (GC) ≥ 99.9% was obtained from Merck Co., Germany and Sulfuric acid (H2SO4, 95-97%) was supplied by QReC, Graphite powder with a purity of 99.99 wt% was obtained from Sigma Aldrich, the electrodes (platinum-ruthenium (40%) on carbon cloth and 40% platinum (40%) on carbon cloth) were acquired from Fuel cell earth. Sulfonilic acid, Sodium Nitrite, Sodium Hydroxide and Hydrochloric acid was obtained from AMTEC laboratory inventory.

2.2 Sulfonation of PEEK

1 L of sulfuric acid is poured into a 2 L beaker that has been placed on a hot plate. A thermometer and an automatic stirrer are placed within the beaker before closing with the aluminium foil. After that, 60 g of PEEK powder that has been dried overnight in an oven is added steadily into the beaker as the solution is mixed clearly at room temperature for an hour. After an hour, the temperature is

increased to 60℃ to heat up the mixture for 3 hours. After 3 hours, the mixture is precipitated in a water strainer filled with ice. Then the SPEEK precipitation is washed until the precipitation has been neutralized. The neutralized SPEEK precipitation is placed in an aluminium foil shaped as a cup and dried overnight in an oven at 80℃.

2.3 Sulfonation of GO

A mixture of 2% NaOH (5 mL) and 0.005 g of the acid was prepared in a 100 mL beaker and dissolved using a warm water bath. Once fully dissolved, 0.02 g of sodium nitrite ($NaNO_2$) at room temperature was added. This resulting solution was then transferred into 10 mL of ice-cold water, followed by the gradual addition of 1 mL of concentrated HCl with continuous stirring at 0 °C for 15 minutes to form a diazonium salt. The freshly prepared diazonium solution was then added dropwise to 50 mL of graphene oxide (GO) dispersion (1.1 mg/mL) while stirring constantly under reflux in an ice water bath for 4 hours. The resulting sulfonated graphene oxide (SGO) product was thoroughly rinsed with 550 mL of distilled water until a neutral pH was achieved and subsequently dried in an oven at 60 °C for future use.

2.4 Fabrication of SPEEK Membrane

To produce a 10 wt.% of SPEEK dope solution, 10 g of dried SPEEK precipitation is added to 90 g of 1-Methyl-2-pyrrolidone (NMP) with a magnetic stirrer and left overnight to dissolve completely. Next, 11 mL of dope solution is added into a 10 cm x 10 cm mold and it is placed into the oven at 80°C overnight. On the next day, the membrane is peeled off from the mold and stored in Deionised water till used during further testing.

2.5 Fabrication of SGO/SPEEK Membrane

To produce a 0.25 wt.% of GO/SPEEK dope solution, 10 g of dried SPEEK precipitation is added to 90 g of 1-Methyl-2-pyrrolidone (NMP) with a magnetic stirrer and left overnight to dissolve completely. Next, 11 mL of dope solution is added into a 10 cm x 10 cm petri dish and it is placed into the oven at 80°C overnight. On the next day, the membrane is peeled off from the mold and stored in Deionised water for membrane electrode assembly. The steps were repeated with 0.15 wt%, 0.20 wt%, 0.25wt% of SGO/SPEEK to produce dope solution and casting of membrane. The dope solution formulation of each membrane is shown in Table 1.

Table 1
Dope solution formulation of GO/SPEEK & SGO/SPEEK

Membrane Label	SPEEK	NMP	GO/SGO (wt%)
SPEEK			0
GO/SPEEK			0.25
SGO/SPEEK 1	10wt%	90wt%	0.15
SGO/SPEEK 2			0.20
SGO/SPEEK 3			0.25

2.5 Characterizations of Physio-Chemical Properties Of SGO/SPEEK Membrane

2.5.1 Morphology structure of membrane

To observe the morphology and dispersion of functionalized graphene oxide (GO) in the Sulfonated Poly (ether ether ketone) (SPEEK) membrane, Scanning Electron Microscopy (SEM) was employed. The membrane samples were immersed in liquid nitrogen for a brief period, causing them to fracture. Subsequently, the fractured samples were placed onto an aluminium stub. The observation was conducted after the membrane samples had been coated with platinum particles.

2.5.2 Water uptake test & swelling ratio

This step involved determining the water uptake of the hybrid membrane. The water uptake was obtained by finding the difference in weight of the membrane before and after wetting. The membrane was thoroughly dried in an oven and then cut into three samples of 1 cm x 1 cm. Once the weight of the dry membrane had been recorded, the membrane samples were submerged in Deionised Water for 24 hours. After that period, the membrane was patted with filter paper to extract surface-attached water onto the membrane. The weight of the wetted membrane (W_{wet}) was measured as quickly as possible. The water uptake was calculated using Eq. (1).

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

To calculate the swelling ratio of membrane. The thickness of all 3 samples of 1cm x 1cm was measured during wet and dry condition and the following Eq. (2) is used to calculate the swelling ratio.

$$\text{Swelling Ratio} = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100\% \quad (2)$$

2.5.3 Proton nuclear magnetic resonance (H-NMR)

The characterization of SPEEK was made by measuring the degree of sulfonation (DS) by H-NMR at a resonance frequency of 400.13 MHz and at room temperature. The DS is defined as the ratio of the number of the structural units containing sulfonic acid group to the total number of the structural units. The ratio between the peak area of the distinct signal (AH_f) and the integrated peak area of the signals corresponding to all other aromatic hydrogen ($AH_{a,b,c,d,e}$) is expressed in Eq. (3).

$$\frac{q}{(12-2q)} = \frac{AH_f}{\sum AH_{a,b,c,d,e}} \quad (3)$$

where q is defined as the ratio (the number sulfonated repeat units/the number of the entire repeat units) or the degree of sulfonation (DS%)

2.5.4 Fourier transform infrared spectroscopy (Ftir)

The FTIR spectra is performed to observe the chemical properties in the functionalized GO and all membrane samples (pristine SPEEK and SPEEK with SGO). The spectra are recorded using a Nicolet iS 10 spectrometer (Thermo Scientific) and ATR technique. The sample was placed in the scanner and

tightly sealed before undergoing scanning. The scanning rate will be set at 32, and the wavenumber will range from 4000 to 650 cm^{-1}. The process will be repeated for the other membrane samples.

2.5.5 Ionic exchange capacity

Ion exchange capacity (IEC) was determined through a titration method conducted at room temperature. This approach measures the amount of acidic functional groups present in the polymer electrolyte membrane. The membrane's proton conductivity and water absorption properties are strongly influenced by the concentration of ion-exchange sites, specifically sulfonic acid groups. During the procedure, membrane samples were soaked in a sodium chloride (NaCl) solution to displace the H^+ ions, which were then titrated using a 0.01 N NaOH solution. The IEC value was calculated based on the titration data using Eq. (4).

$$\text{Consumed ml of NaOH x} \frac{Normality\ of\ NaOH}{Weight\ Dried\ Membrane} \tag{4}$$

3. Results

3.1 Confirmation of Chemical Bonding

After the sulfonation procedure is completed, the FTIR-ATR spectroscopy investigation aims to qualitatively validate the parent polymer's sulfone synthesis. The PEEK polymer needed to be sulfonated in order to increase the proton conductivity of the SPEEK polymer and create a hydrophilic region. Through the use of FTIR spectroscopy, the different functional groups of PEEK and SPEEK were assessed. As seen in Figure 1, absorption bands were attributed to PEEK and the main chain of SPEEK were found in groups. The broad band in SPEEK, which was centred between 3707 cm−1 and 3124, was identified as the (O-H) vibration band from (SO3-) groups that interacted with H2O. Additionally, the hydroxyl group of vibration in the sulfonic acid group is accessible and reacting with absorbed water molecules, as indicated by the significant broad peak in the SPEEK spectrum that occurs between 3707 cm−1 and 3124. When the SO3H group is present in SPEEK membranes, more water molecules are absorbed, which increases the number of hydrogen bonds and enhances the hydrophilicity of the membrane [15]. The presence of the SO_3H group was clearly confirmed by a distinct peak, indicating its successful incorporation into the aromatic ring. The absorption band at 1635 cm^{-1} corresponds to the asymmetric stretching of carbonyl (–C=O) groups, while the peak at 1213 cm^{-1} is attributed to C–O stretching in hydroxyl (C–OH) groups. A signal near 1484 cm^{-1} is associated with the =CH group. Additionally, as shown in Figure 1, the peak observed around 1269 cm^{-1} is indicative of the sulfonic acid (O=S=O) functional group.

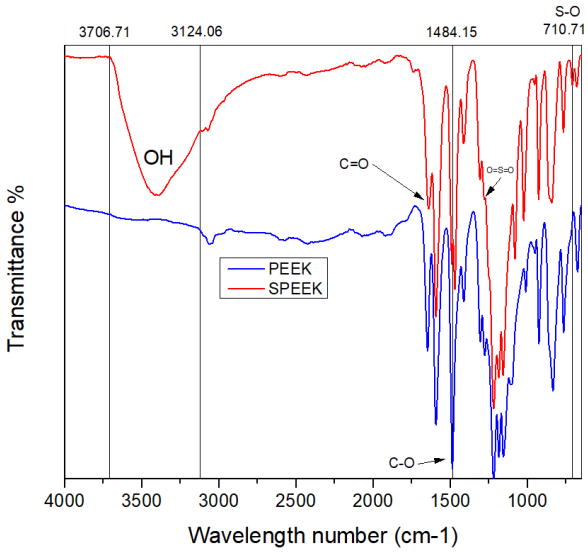


Fig. 1. FTIR spectra of PEEK & SPEEK polymer

Figure 2 illustrates the chemical modification of graphene oxide (GO). To monitor the conversion of GO to sulfonated graphene oxide (SGO), a comparative FTIR spectral analysis was conducted. Both GO and SGO samples showed a broad absorption band between 3700 and 2990 cm^{-1}, corresponding to the stretching vibrations of hydroxyl (–OH) groups. In the FTIR spectrum of unmodified GO, the signal at 1711 cm^{-1} is attributed to carboxylic groups prior to sulfonation, while the peak at 1257 cm^{-1} corresponds to C–OH bending vibrations. Additional peaks at 1613 cm^{-1}, 1261 cm^{-1}, and 1039 cm^{-1} are linked to C=C stretching, C–OH, and C–O stretching vibrations, respectively, confirming the full oxidation of graphite into GO. In contrast, the FTIR spectrum of SGO retained these characteristic peaks of GO and exhibited new signals related to sulfonic acid functionalization. Notably, the peak at 1216 cm^{-1} is due to O–S–O stretching vibrations, and the one at 1363 cm^{-1} is assigned to SO_3H stretching, confirming the successful introduction of sulfonic acid groups into the GO structure.

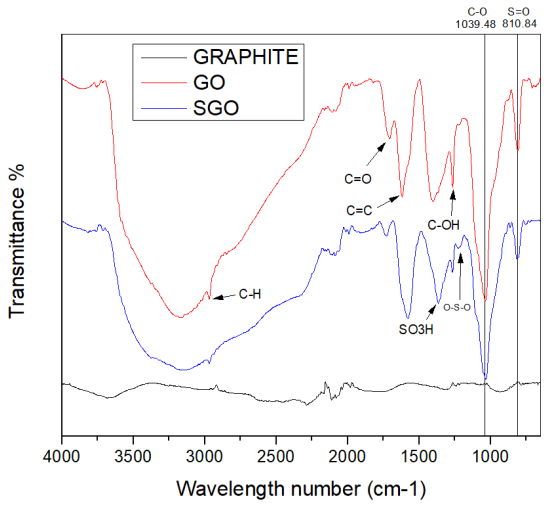


Fig. 2. FTIR spectra of Graphite, Graphene Oxide & Sulfonated GO nanomaterial

Figure 3 presents the FTIR spectra of both the pristine SPEEK membrane and the composite nanomaterial membranes. The unmodified SPEEK membrane exhibits distinct peaks at 1024 and 1080 cm^{-1}, which correspond to the symmetric and asymmetric stretching vibrations of the O=S=O

group from the sulfonic acid (SO_3H), confirming its successful incorporation into the polymer backbone. The FTIR profiles of all membranes appear largely similar, primarily because SPEEK constitutes the major component of the membrane, while the nanomaterial fillers are present only in small amounts. Hence the SPEEK characteristic and its vibration band overshadowing the GO and SGO nanomaterial filler present in the membrane.

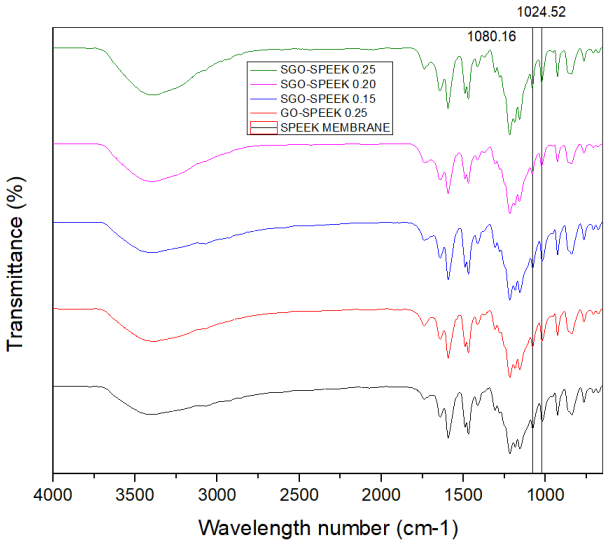


Fig. 3. FTIR spectra of SPEEK, GO-SPEEK & SGO-SPEEK membrane

3.2 H-NMR Structural Analysis

An electrophilic substitution reaction takes place when sulphuric acid is used to sulfonate PEEK, introducing sulfonic acid groups into the hydroquinone portion of the polymer backbone. This part of the chain is particularly reactive due to the presence of ether linkages, which promote electrophilic attack. The chemical and physical behavior of SPEEK is significantly influenced by the amount of sulfonic acid groups incorporated. In theory, a higher degree of sulfonation (DS) results in increased acidity. The incorporation of sulfonic groups and the degree of sulfonation can be analyzed using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The structure of sulfonated SPEEK was confirmed through ^{1}H-NMR analysis, and the aromatic proton signals for the SPEEK repeating unit are illustrated in Figure 4. A downfield shift to 7.523 ppm indicates the presence of the sulfonic acid group. The peaks observed at 7.272 and 7.115 ppm are doublets and correspond to the Hc and Hd protons on the hydroquinone ring [16]. The degree of sulfonation (DS) of SPEEK was calculated using ^{1}H-NMR analysis based on Eq. (3), as depicted in Figure 4, and was determined to be 64.95%. The H_f peak corresponds to the sulfonic acid group, while the remaining signals represent other hydrogen atoms within the repeating unit of the SPEEK structure. For optimal membrane performance in terms of ion exchange capacity and proton conductivity, the ideal DS range for SPEEK is typically between 60% and 80%. Within this range, the membrane provides an adequate number of ion exchange sites necessary for effective electrochemical reactions, enabling efficient operation as a proton exchange membrane in fuel cell applications.

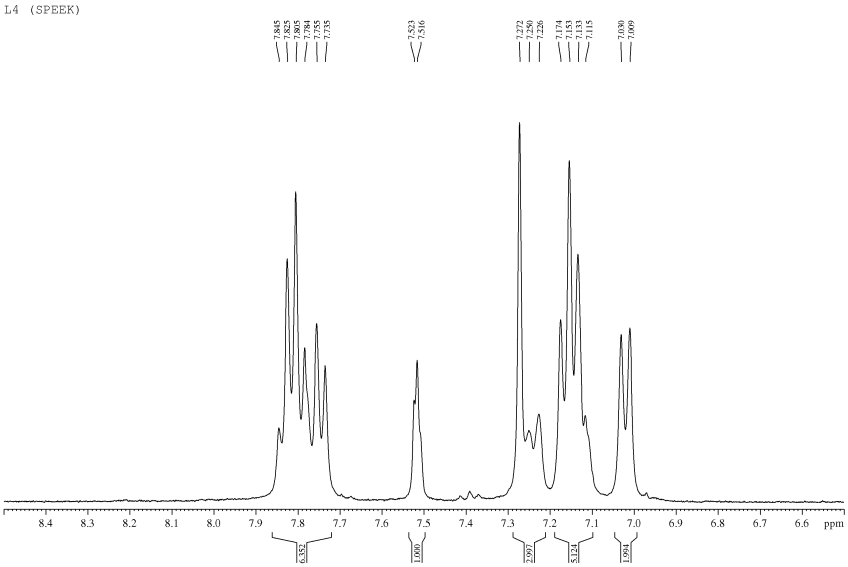
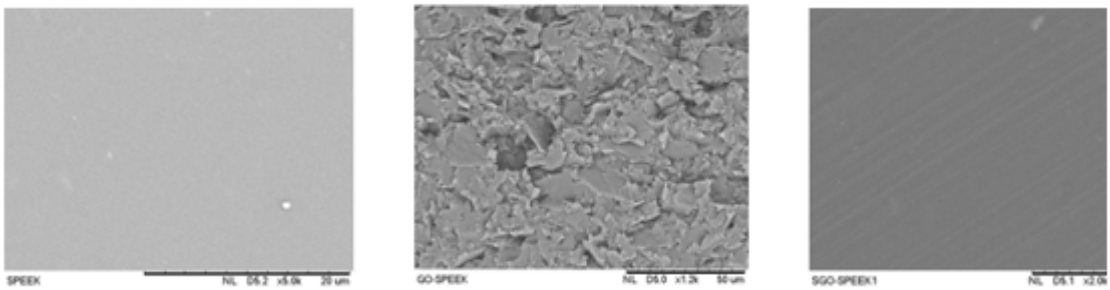


Fig. 4. H-NMR spectrum of SPEEK

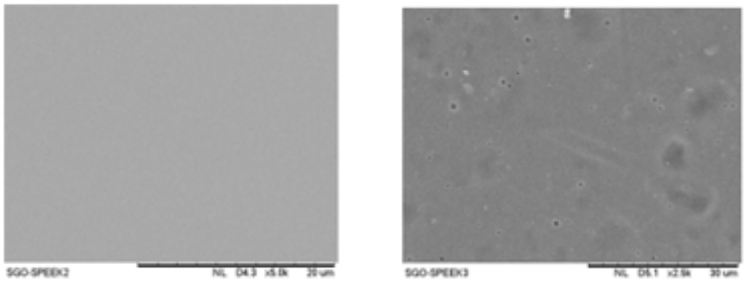
3.3 Surface Morphology of Functionalised GO/SPEEK Membranes

The cross section and surface morphology from SEM image of SPEEK, GO-SPEEK and SGO SPEEK membranes are depicted in Figure 5 (a,b,c,d,e), respectively. Pristine SPEEK membrane shows a smooth surface on the cross-section indicating the uniformity and well-dense structure. Meanwhile, Figure 5 (b) shows that the addition of GO in SPEEK has disrupted the continuous phase of SPEEK matrix and exhibited some sites with crumples proven the existence of GO nanoparticles.

Based on Figure 5 (c) the surface image of SGO-SPEEK (0.15wt%) it shows that the membrane has a smooth and uniform surface without any uneven spots indicating that the SGO filler incorporated in the membrane has dispersed evenly in the membrane which without clogging up the proton transport pathway which will further improve onto the proton conductivity of the specific membrane. We can also observe the black spots that appear in the CS image of SGO-SPEEK(0.25wt%) in Figure 5(e) which shows the presence of SGO nanomaterial present in the membrane. The appearance of the black spots indicates that the dispersion of SGO in the specific membrane might be slightly uneven due to the abundance of SGO. The introduction of sulfonic acid groups can lead to a compact structure which arises from the presence of polar functional groups, which may affect the spacing and arrangement of graphene sheets.



(a) (b) (c)



(d) (e)

Fig. 5. SEM images of a) pristine SPEEK, b) GO-SPEEK(0.25wt%) membrane c) SGO-SPEEK (0.15wt%) membrane d) SGO-SPEEK (0.20wt%) membrane e) SGO-SPEEK (0.25wt%) membrane

3.4 Water Uptake & Swelling Ratio of Functionalised SGO/SPEEK Membrane

Eqs. (1) and (2) were used to calculate the water intake and swelling ratio, respectively. Figure 6 displays the findings. It is determined that Pristine SPEEK has a water uptake of 15.88 percent. Compared to Pristine SPEEK, the produced GO-SPEEK and SGO-SPEEK had a greater water absorption. Water absorption and porosity typically rise when a nanomaterial filler is introduced to a polymer solution because the addition causes the thermodynamic instability of the polymer solution to increase. This trend can be explained by considering that the addition of 0.15 wt.% SGO filler raises the water uptake to 21.39%. However, further increasing the filler content leads to a reduction in water uptake, likely due to increased viscosity of the solution. The higher viscosity slows down the mass transfer between the solvent and nonsolvent, resulting in decreased water absorption. This decline becomes more evident as the SGO filler concentration in the SPEEK membrane continues to rise. Meanwhile when compared to GO-SPEEK membrane and SGO membrane it can be observed that SGO at a lower dosage possesses a higher water uptake than GO-SPEEK membrane at 0.15 wt. %. This occurrence is due to the fact that functionalization of GO tends to have improved dispersion in water or other polar solvents compared to untreated graphene oxide. Better dispersion can facilitate the interaction of the material with water and promote uniform water uptake throughout the membrane and increase the hydrophilicity of membrane which helps to improve the proton conductivity of membrane.

One of the crucial factors in assessing the dimensional stability of composite membranes is the swelling ratio. When a membrane swells too much in acid, its mechanical qualities deteriorate and its long-term performance is impacted. Based on figure 6 it is observed that SGO-SPEEK at 0.15 wt. % has the lowest swelling ratio at 2.91% and the swelling ratio gradually increases as the concentration of SGO in membrane increase. One possible explanation for the increase in swelling ratio alongside a decrease in water uptake could be the higher cross-linking density in the SGO-SPEEK membrane at elevated filler concentrations. This increased cross-linking leads to a more rigid and compact polymer network, which may limit water absorption despite the membrane's tendency to swell. Evaluating the swelling ratio offers valuable insight into how the membrane deforms under exposure to moisture, mechanical stress, and heat—particularly when these factors exceed the material's yield point, causing it to stretch or expand. Since polymers tend to deform permanently under such conditions, maintaining a low swelling ratio is advantageous to prevent structural defects like cracking and the formation of pinholes [17]. One sign that the SGO composite membrane is thinning due to stretching and high linear expansion is the detection of an increased swelling ratio.

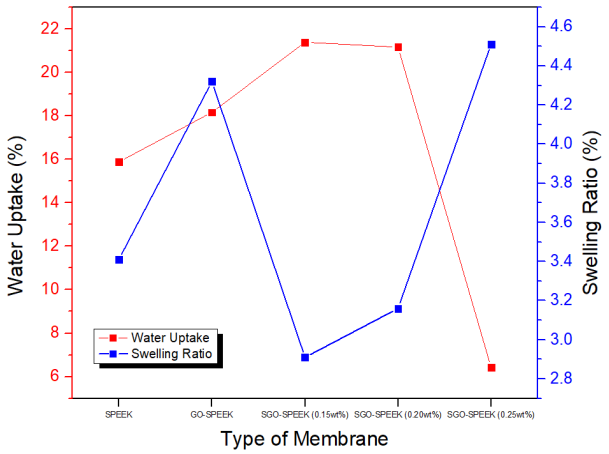


Fig. 6. Water Uptake & Swelling Ratio of Membrane

3.5 Ionic Exchange Capacity (IEC)

The IEC of fabricated membranes was calculated using back titration method using estimated 1cm x1cm of membrane sample immersed in NaOH for 24 hrs to allow the Na+ to be replaced by H+. IEC is the measure of a material's capability to displace ions formerly incorporated within its structure. The IEC of composite membranes with different fillers is shown in Figure 7. It is seen that SGO-SPEEK membrane at 0.15wt% has the highest IEC also directly indicating that membrane with SGO nanomaterial as filler at 0.15wt% will be able to further improve of proton conductivity of blank membrane. A higher IEC indicates more transport of protons (H+ ions) between the anode and cathode, allowing the electrochemical reactions to occur which shows that there a more ion exchange sites available in the membrane, which directly enhances the proton conductivity of the membrane [14]. It is also observed that all membranes incorporated with filler is able to possess a higher IEC than bland SPEEK membrane. The sulfonation of GO also further improves upon the IEC of membrane compared to non functionalized GO membrane and pristine SPEEK. The sulfonic acid groups provide active sites for ion exchange. As the density of these functional groups increases on the graphene oxide surface, the material gains a higher capacity to exchange ions. Excessive incorporation of SGO may disrupt the uniform distribution of the filler within the polymer matrix [18]. This can lead to reduced interactions between the polymer matrix and the sulfonated groups on SGO, affecting the ion exchange properties of the membrane.

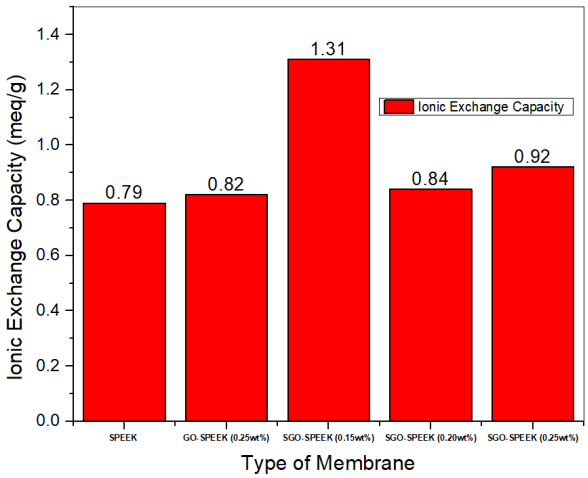


Fig. 7. Ionic Exchange Capacity of each membrane

4. Conclusions

SPEEK incorporated with sulfonated graphene oxide has showed desirable traits to act as polymer electrolyte membrane in PEMFC application. Through physiochemical test such as SEM SGO has displayed its ability to evenly disperse and further improve upon the morphological structure of pristine SPEEK membrane by increasing the surface area of membrane which provides more ion exchange sites. The water uptake percentage of SGO SPEEK at 0.15wt% showed better results than SPEEK which attributed from sulfonic acid group (SO3H) in both SGO and SPEEK. The lowest swelling ratio of membrane of 0.15wt% of SGO-SPEEK membrane further proves that 0.15wt% SGO-SPEEK membrane is the most suitable to act as a PEM as it manages to retain its shape and maintain its mechanical properties while also retaining the most amount of water. Through the FTIR analysis of nonfunctionalized polymer and nanomaterial compared to the functionalized SPEEK and SGO it is learned that the presence of SO3H groups in the membrane that consists of this material could exhibit higher proton conductivity compared to nonfunctionalized materials due to sulfonation of PEEK and GO creates pathways for protons to move through the composite membrane. The IEC of SGO incorporated membrane at 0.15wt% was higher compared to other membranes which indicates its benefits to act as PEM compared to Bland SPEEK and GO-SPEEK membrane which will translate into high proton conductivity which is desired for PEMFC. Overall SGO-SPEEK membrane at 0.15 wt% would act as a better PEM option compared to nonfunctionalized GO incorporated SPEEK membrane.

Acknowledgement

This work was financially supported by the Ministry of Education, Malaysia under Fundamental Research Grant Scheme grant code no: FRGS/1/2024/TK08/UTM/02/8 (R.J130000.7809.5F700).

References

[1] Chen, Ta-Yung, and Johna Leddy. "Ion exchange capacity of Nafion and Nafion composites." *Langmuir* 16, no. 6 (2000): 2866-2871. https://doi.org/10.1021/la991094x

[2] Demirbas, A. "Direct use of methanol in fuel cells." *Energy Sources, Part A* 30, no. 6 (2008): 529-535. https://doi.org/10.1080/15567030600817159

[3] Ahmad, Shahbaz, Tahir Nawaz, Asghar Ali, Mehmet Fatih Orhan, Ayesha Samreen, and Arunachala M. Kannan. "An overview of proton exchange membranes for fuel cells: Materials and manufacturing." *International Journal of Hydrogen Energy* 47, no. 44 (2022): 19086-19131. https://doi.org/10.1016/j.ijhydene.2022.04.099

[4] Tsuneda, Takao, Raman K. Singh, Akihiro Iiyama, and Kenji Miyatake. "Theoretical investigation of the H2o2-induced degradation mechanism of hydrated Nafion membrane via ether-linkage dissociation." *ACS omega* 2, no. 7 (2017): 4053-4064. https://doi.org/10.1021/acsomega.7b00594

[5] Pham, Tuyet Anh, Le Vu Nam, Eunho Choi, Min-Su Lee, Tea-Sung Jun, Segeun Jang, and Sang Moon Kim. "Mechanically Stable Thinned Membrane for a High-Performance Polymer Electrolyte Membrane Fuel Cell via a Plasma-Etching and Annealing Process." *Energy & Fuels* 35, no. 14 (2021): 11525-11532. https://doi.org/10.1021/acs.energyfuels.1c01225

[6] Zheng, Lanyue, Haixia Wang, Ruiting Niu, Yuxia Zhang, and Haifeng Shi. "Sulfonated poly (ether ether ketone)/sulfonated graphene oxide hybrid membrane for vanadium redox flow battery." *Electrochimica Acta* 282 (2018): 437-447. https://doi.org/10.1016/j.electacta.2018.06.083

[7] He, Yao, Cuiyan Tong, Lei Geng, Lingdi Liu, and Changli Lü. "Enhanced performance of the sulfonated polyimide proton exchange membranes by graphene oxide: Size effect of graphene oxide." *Journal of Membrane Science* 458 (2014): 36-46. https://doi.org/10.1016/j.memsci.2014.01.017

[8] Ch'Ng, Y. Y., K. S. Loh, W. R. W. Daud, and A. B. Mohamad. "Synthesis and characterization of sulfonated graphene oxide nanofiller for polymer electrolyte membrane." In *IOP Conference Series: Materials Science and Engineering*, vol. 160, no. 1, p. 012035. IOP Publishing, 2016. https://doi.org/10.1088/1757-899X/160/1/012035

[9] Yao, Kangkang, Peng Chen, Zhengwei Zhang, Jia Li, Ruoqi Ai, Huifang Ma, Bei Zhao et al. "Synthesis of ultrathin two-dimensional nanosheets and van der Waals heterostructures from non-layered γ-CuI." *npj 2D Materials and Applications* 2, no. 1 (2018): 16. https://doi.org/10.1038/s41699-018-0058-2

[10] Ahn, Eungjin, Houda Gaiji, Taehyung Kim, Manef Abderrabba, Hyun-Wook Lee, and Byeong-Su Kim. "Graphene oxide nanosheet as a two-dimensional polyelectrolyte: pH-responsive behavior of a multilayered nanomembrane." *Journal of Membrane Science* 585 (2019): 191-198. https://doi.org/10.1016/j.memsci.2019.05.035

[11] Basso Peressut, Andrea, Matteo Di Virgilio, Antonella Bombino, Saverio Latorrata, Esa Muurinen, Riitta L. Keiski, and Giovanni Dotelli. "Investigation of sulfonated graphene oxide as the base material for novel proton exchange Membranes." *Molecules* 27, no. 5 (2022): 1507. https://doi.org/10.3390/molecules27051507

[12] Yang, Gao, Lihua Li, Wing Bun Lee, and Man Cheung Ng. "Structure of graphene and its disorders: a review." *Science and technology of advanced materials* 19, no. 1 (2018): 613-648. https://doi.org/10.1080/14686996.2018.1494493

[13] Zahid, Muhammad, Anum Rashid, Saba Akram, HM Fayzan Shakir, Zulfiqar Ahmad Rehan, Talha Javed, Rubab Shabbir, and Mahmoud M. Hessien. "Fabrication and characterization of sulfonated graphene oxide-doped polymeric membranes with improved anti-biofouling behavior." *Membranes* 11, no. 8 (2021): 563.https://doi.org/10.3390/membranes11080563

[14] Cao, Ning, Chaofan Zhou, Yong Wang, Hong Ju, Dongyang Tan, and Jin Li. "Synthesis and characterization of sulfonated graphene oxide reinforced sulfonated poly (ether ether ketone)(SPEEK) composites for proton exchange membrane materials." *Materials* 11, no. 4 (2018): 516. https://doi.org/10.3390/ma11040516

[15] Yagizatli, Yavuz, Berdan Ulas, Alpay Sahin, and Irfan Ar. "Preparation and characterization of SPEEK–PVA blend membrane additives with colloidal silica for proton exchange membrane fuel cell." *Journal of Polymers and the Environment* 32, no. 9 (2024): 4699-4715. https://doi.org/10.1007/s10924-024-03263-z

[16] Arul Joseph Helen Therese, J. B., K. Selvakumar, R. Gayathri, M. Ramesh Prabhu, and P. Sivakumar. "In situ polymerization of poly aniline—SPEEK-PMA-based proton exchange membrane for DMFC application." *Journal of Thermoplastic Composite Materials* 34, no. 2 (2021): 221-237. https://doi.org/10.1177/0892705719835293

[17] Prakash, Shruti, William E. Mustain, and Paul A. Kohl. "Electrolytes for long-life, ultra low-power direct methanol fuel cells." In *Micro Fuel Cells*, pp. 1-50. Academic Press, 2009. https://doi.org/10.1016/B978-0-12-374713-6.00001-9

[18] Khomein, Piyachai, Wesley Ketelaars, Tijs Lap, and Gao Liu. "Sulfonated aromatic polymer as a future proton exchange membrane: A review of sulfonation and crosslinking methods." *Renewable and Sustainable Energy Reviews* 137 (2021): 110471. https://doi.org/10.1016/j.rser.2020.110471