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Sulfonated poly(aryl ether ketone) and graphene oxide nanocomposite membrane for microbial fuel cell

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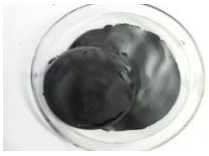
GRAPHICAL ABSTRACT



Synthesized GO

Synthesized SPAEK

ABSTRACT

Materials based on graphene oxide (GO) as inorganic fillers in polymer composites have been attracting attention as a result of the potential for applications in electronics and nanocomposites membrane, due to their high conductivity, high mechanical strength, unique graphitized plane structure and electrically insulating property. Thus, poly(arylene ether ketone) (PAEK) has been used in this research to synthesize the nanocomposite membrane that could be higher selectivity than most commercially proton exchange membrane, nafion. The structure of graphene oxide and the bond form with the polymer is important as a lead to final properties and stability of the membrane for microbial fuel cell. GO has been synthesized from graphite powder by using modified Hummer method which is an oxidation process of graphite to graphene oxide. The PAEK was undergo sulfonation process to synthesize sulfonated PAEK by dissolving the polymer into concentrated sulfuric acid. The composite membrane could be prepared by mixing the the 5%, and 10% of GO solution with 10% SPAEK solution which give ratio of 0.5:10 and 1:10 respectively. The GO synthesized then was characterized by using attenuated total reflectance-fourier transform infrared (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). While, the SPAEK was characterized by using only ATR-FTIR and SEM. The graphene oxide structure was confirmed with the presence of broad peak of O-H at 3202 cm^{-1}, C=O of carboxylic acid at 1718 cm^{-1} and C=C aromatic at 1615 cm^{-1} and 1371 cm^{-1}. The GO is successfully exfoliated from graphite due to intense peak showed by XRD pattern at two-theta is 11.285º. From micrograph of SEM, the image of GO have a bulky and flaky structure due to introduction of oxide in the graphite layer.

Keywords: Sulfonated Poly(aryl ether ketone), Graphene Oxide, nanocomposite membrane and proton exchange membrane.

1. INTRODUCTION

The most common commercially proton exchange membranes used are perfluorinated sulfonic acid ionomers, such as Nafion, which was developed by Dupont [1]. This is due to their high proton conductivity, and excellent stability. However, the high cost and gas crossover, low proton selectivity as well as the loss of the preferable properties at high temperature, have restricted the applications and stimulated the development of new alternatives for PEM materials [2] and [3]

Therefore, wide variety of chemical composition, acceptable manufacturing cost and high performance sulfonated aromatic polymers have been intensively studied as substitutes for Nafion [4]. Alternative inexpensive proton-conducting materials with superior properties are required, such as sulfonated poly- aryl ether ketone (SPAEK), which are being investigated due to their higher temperature capability and overall thermo oxidative and chemical stability performance [5]..

This studies involved synthesis and characterized GO, SPAEK and GO/SPAEK membrane. The success of formation of GO, SPAEK, and GO/SPAEK composite membranes was characterized for structural functional group using attenuated total resistance-fourier transform infrared (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) for the study of surface morphology. The properties of synthesized GO/SPAEK membrane were studied in term of membrane water uptake and ion exchange at different % of GO composite membrane.

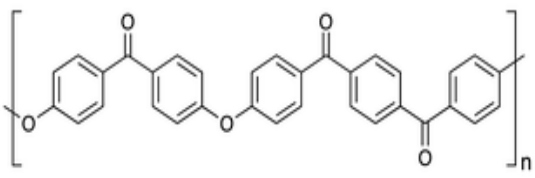
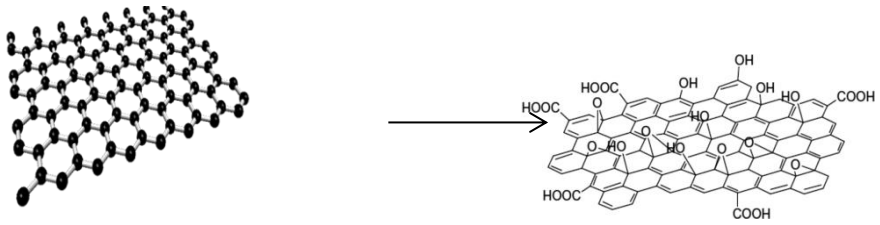


Figure 1 Molecular structure of PAEK

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the synthesized of graphene oxide by using modified Hummers method, synthesized sulfonated poly(aryl ether ketone) from poly(aryl ether ketone) undergo sulfonation process with sulphuric acid, and synthesized GO/SPAEK as nanocomposite membrane. The second stage was the characterization of successfully producr by using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The last stage supposedly was the study of membrane properties which the membrane should undergo several test such as water uptake, ion exchange capacity (IEC) and proton conductivity to identify the performance of membrane synthesized.



Scheme 1 Exfoliated Graphene Oxide from Graphene

3. RESULTS AND DISCUSSION

3.1. Preparation of GO and SPAEK

Graphene oxide was prepared from graphite powder by using modified Hummer's method. The colour changes from dark brown to yellowish brown at the end of step of Hummer's method indicate that graphene oxide was successfully exfoliated from the graphite. The crucial part at the very end of this method before the GO solution was casted on the petri dish was neutralization step of the GO. This because the process took a long period than proposed method in order to reduce acidity of GO and remove excess acid. This step of neutralization could be improve by improvise the method. The final desired GO was in thin dark film form of GO.

Figure 2: Graphene Oxide thin film

Next, sulfonated poly(aryl ether ketone) was successfully prepared by dissolving the PAEK which obtained from Sigma Aldrich into concentrated sulfuric acid. Initially, the PAEK was in the form of crystal and brownish in colour. Then after undergo sulfonation method, the SPAEK was successfully precipitated out from the dark orange mixture solution of SPAEK

Figure 3: a) PAEK b) SPAEK

3.2. Functional Group of GO and SPAEK

The significant oxygen functionalities in graphene oxide were established at broad and wide peak at 3202 cm^{-1} which is belong to the vibration of O-H with strong intensity. The vibration of C=O carboxylic acid present in graphene oxide was observed at 1718 cm^{-1}. While, the vibration of C=C aromatic graphene peaks show at 1615 cm^{-1} and 1371 cm^{-1}

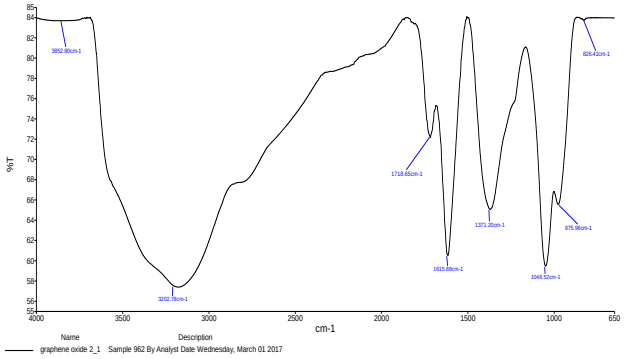


Figure 4: Functional Group of GO

The vibration of C=O ketone was observed at 1654 cm^{-1} and C-O peak was observed at 1235 cm^{-1} which are the significant peaks indicate the present of this polymer used. Next, the vibration of C=C aromatic which indicate the present of aryl group or benzene ring in this structure of polymer was observed at 1587 cm^{-1} and 1495 cm^{-1}. Hence, the presence of this C=C aromatic affect the vibration value of C=O ketone to be lower than 1705 cm^{-1} due to the delocalization of electron into the conjugated double bond of benzene. The vibration S=O of sulfonate was observed at peak value 1305 cm^{-1} and 1274 cm^{-1} which indicate PAEK was successfully sulfonated to SPAEK.

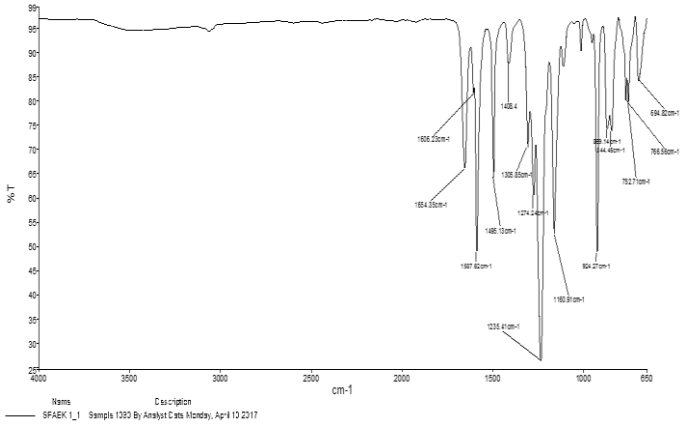


Figure 5: Functional Group of SPAEK

3.3. Structure of GO

The figure 6 shows the X-ray diffraction pattern of the graphene oxide that was successfully synthesized. The previous study state that the graphite show characteristic peak at 2θ = 26.51° and the graphitic peak shifts to 2θ = 10° was observed due to the intercalated of oxygen functionalities [6]. While, in the figure 6, the intense peak was observed at 2θ = 11.28° which indicate the successfully exfoliated graphene oxide.

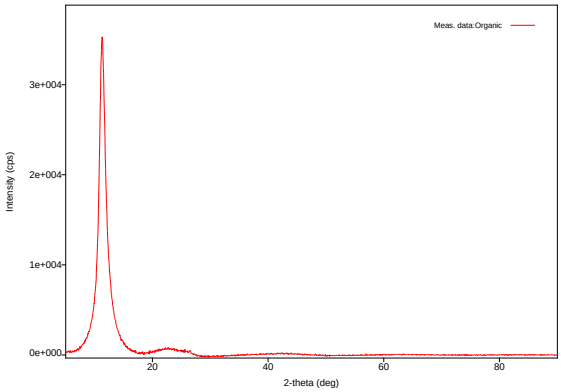


Figure 6: XRD Pattern of GO

3.4. Morphology of GO and SPAEK

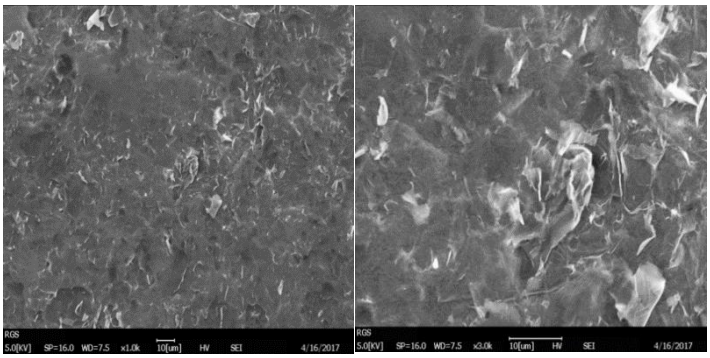


Figure 7: Morphology of Graphene Oxide at 1.0K and 3.0K magnificent

The figure 7 shows the graphene oxide under magnification of 1000x and 3000x with 10 µm of length. The magnification of surface morphology showed that GO exhibit crimpy and flaky surface structure due to the introduction of oxygen functionalities onto the graphite layer and caused the expansion of interlayer spacing. The previous study state that after the chemical oxidation, the layer distance was enlarges and GO was crimped, while the vander-waal forces between interlayer was decreased[7].

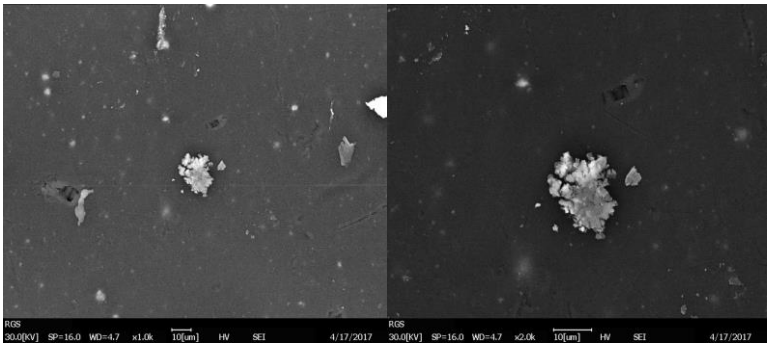


Figure 8: Morphology of PAEK at1.0K and 2.0K magnificent

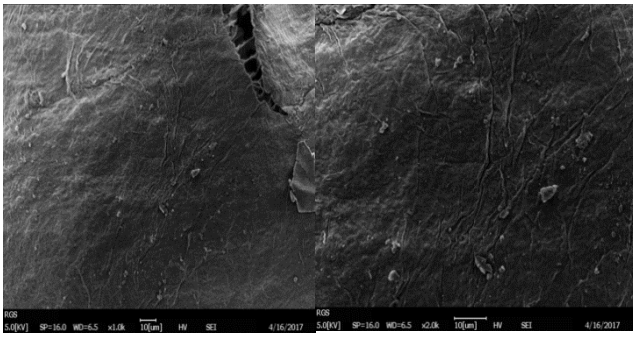


Figure 9: Morphology of SPAEK

The figure 9 shows the morphology of sulfonated poly(aryl ether ketone) at magnificent of 1000x and 2000x with 10µm length. The image obtained show the stretched and crimped surface layer of polymer compared to PAEK which is smooth on surface. This is may due to the successfully introduction of sulfonate (SO3-) to the structure of PAEK.

4. CONCLUSION

The graphene oxide was successfully synthesized from graphite through modified Hummers method was viscous and brownish in color while it wet but thin in film and black in color while it dry. The successfully sulfonated poly(aryl ether ketone) was precipitated out in the form of white foam.

From the observation of ATR-FTIR, the confirmation of GO was confirmed due to the present of wide and broad peak at3202 cm^{-1} which is belong to the vibration of O-H with strong intensity. The vibration of C=O carboxylic acid present in graphene oxide was observed at 1718 cm^{-1}. While, the vibration of C=C aromatic graphene peaks show at 1615 cm^{-1} and 1371 cm^{-1}.

The spectrum of ATR-FTIR for SPAEK show the vibration of C=O ketone was observed at 1654 cm^{-1} and C-O peak was observed at 1235 cm^{-1} which are the significant peaks indicate the present of this polymer used. Next, the vibration of C=C aromatic which indicate the present of aryl group or benzene ring in this structure of polymer was observed at 1587 cm^{-1} and 1495 cm^{-1}. The vibration S=O of sulfonate was observed at peak value 1305 cm^{-1} and 1274 cm^{-1} which indicate PAEK was successfully sulfonated to SPAEK.

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