

Synthesis and Characterization of Sulfonated Graphene Oxide Nanofiller for Polymer Electrolyte Membrane

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Abstract. In this study, sulfonated graphene oxide (SGO) nanocomposite were produced as potential nanofiller to improve the properties of polymer electrolyte membrane (PEM) for fuel cell applications. The GO is produced by modified Hummers's method and the as-synthesized GO was used to prepare SGO with three distinctive precursors, namely 3-mercaptopmethoxysilane (MPTMS), sulfanilic acid (SA) and butane sultone (BS). The SGO samples were characterized with several physical characterization techniques (XRD, FTIR, SEM-EDX and XPS) to provide the insights into the morphology; the state of homogenization; the crystallography and the functional groups. The experimental result indicated that the sulfonic acid group has been successfully incorporated with GO and can be used as filler in PEM.

1. Introduction

Fuel cell is a high efficiency electrochemical device that converts chemical energy into electrical energy. Fuel cell gains popularity through the clean emission from the electrochemical reaction, using hydrogen and oxygen or air as the fuel source, emitting only carbon dioxide and water molecules [1-3]. In fuel cell, the polymer electrolyte membrane (PEM) is vital to promote the transfer of proton from anode to cathode side besides acting as a barrier for the fuel [3,4].

The major drawback of current Nafion electrolyte used as PEM is the retention of water in membrane to maintain humidity for proton conduction when operated beyond 80 °C [5]. Many efforts have been made to improve the mechanical strength and chemical stability of the Nafion including the CO poisoning on the catalyst with the incorporation of nanofiller such as graphene oxide (GO) [6,7]. GO can be synthesized through the oxidation of graphene that weakens the Van der Waals forces between the carbon layers and bring in the carbonyl, peroxy and hydroxyl groups [8]. Despite using GO, sulfonated graphene oxide (SGO), owing of the SO₃H functional groups besides the existing unique amphiphilic structure of GO; showing potential to enhance the characteristics and properties of



PEM especially on its proton conductivity [9, 10]. Due to the compatibility of SGO with Nafion, the interface interaction increases the mechanical stability of the membrane as well as the electrochemical performance of the fuel cell [11]. The proton transport phenomena within PEM can be describe as vehicular where the hydronium ions flow according to the proton concentration gradient and hopping where the sulfonic group or proton move from one site to another with the sufficient water content [3].

In this study, the SGO nanofillers are synthesised for PEM using three distinct precursors: 3-mercaptopmethoxysilane (MPTMS), sulfanilic acid (SA) and butane sultone (BS). The as-prepared SGO are then characterized with X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared (FTIR) scanning electron microscopy-electron dispersive X-ray (SEM-EDX) to study on the effect of these precursors used for sulfonation.

2. Materials and Methods

2.1. Synthesis of Sulfonated Graphene Oxide (SGO)

Graphene oxide (GO) was synthesized according to the modified Hummers' method [12, 13]. To synthesize SGO, 0.2 g prepared GO was added into 250 ml of anhydrous THF and put into the ultrasonic bath until the solution was homogenized. Then, 1.5 g of sodium hydride (NaH) was added slowly to the mixture at 60 °C for 6 hours. 12.28 mmol of the precursor (MPTMS, SA or BS) was added slowly into the mixture and stirred 24 hours at 80 °C. The obtained product was soaked in 1:1 HCl:H₂O solution for 12 hours and rinsed with ethanol for few times to remove the residue of reactants. The product was then dried in vacuum oven at 80 °C for 24 hours [14].

2.2. Characterization of GO and SGO

An X-ray diffractometer (Bruker D8 Advance-XRD) was used to analyse the degree of crystallinity of samples. The Fourier transform infrared (FTIR) spectra of GO and SGO samples were obtained by using Thermoscientific Nicolet FTIR to investigate the functional groups. Scanning electron microscopy-electron dispersive X-ray (SEM-EDX) was performed with Zeiss EVO MA 10 to observe the morphology and composition of the GO and SGO samples. X-ray photoelectron spectroscopy (XPS) was performed on an Axis ultra DLD using Al-K α sources to analyse the surface chemistry of the samples.

3. Result and Discussion

Fig. 1 showed the successful transformation of graphite into graphene oxide through oxidation, indicating with the disappearance of peak at 26° of 2 θ in the XRD spectra [2, 15]. According to Marcano et al. [10], GO interlayer spacing is proportional to the degree of oxidation. The oxidation process has effectively caused the disappearance of graphitic structure on graphite due to the introduction of oxygen functionalities into the carbon basal plane [16, 17].

The incorporation of only GO into Nafion would decrease the proton conductivity of the membrane due to the lack of proton conductive groups (carboxylic acid and oxygen containing groups are not good proton conductor) despite the improved mechanical properties [11, 18]. This could lead to the decreased performance in fuel cell. Therefore, the incorporation of SGO into Nafion could be a better choice as SGO can facilitate the formation of homogenized membranes due to the compatibility of SO₃H groups between SGO and Nafion.

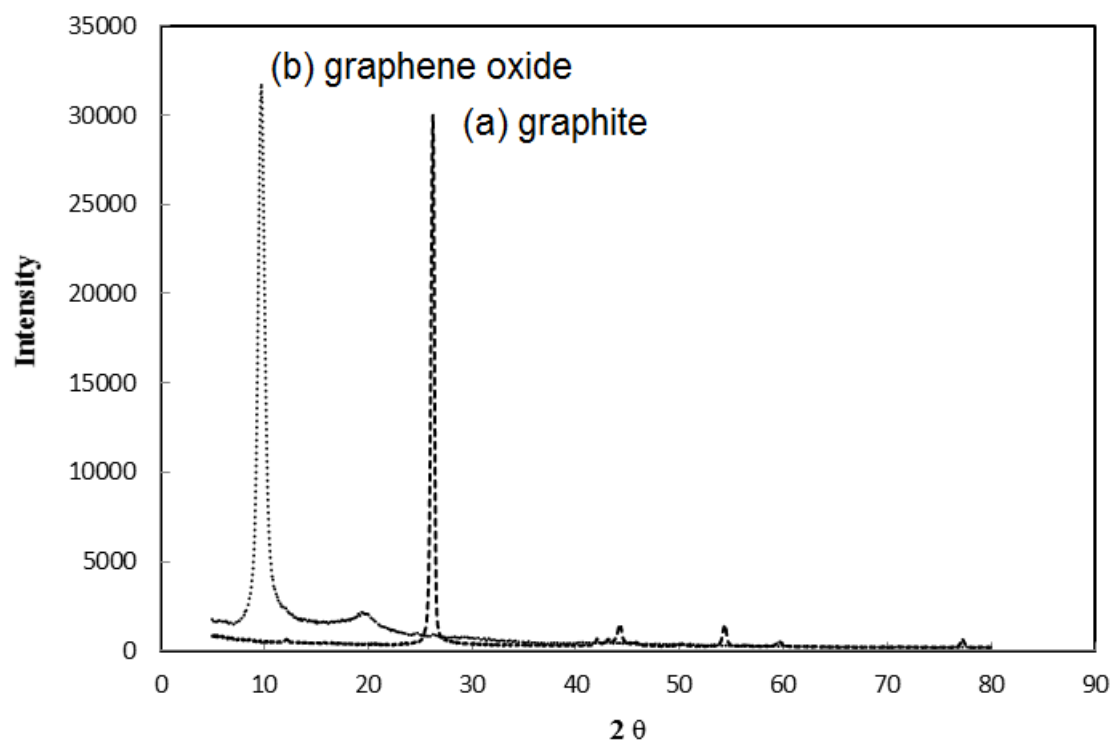


Fig.1 XRD spectra of (a) graphite and (b) graphene oxide.

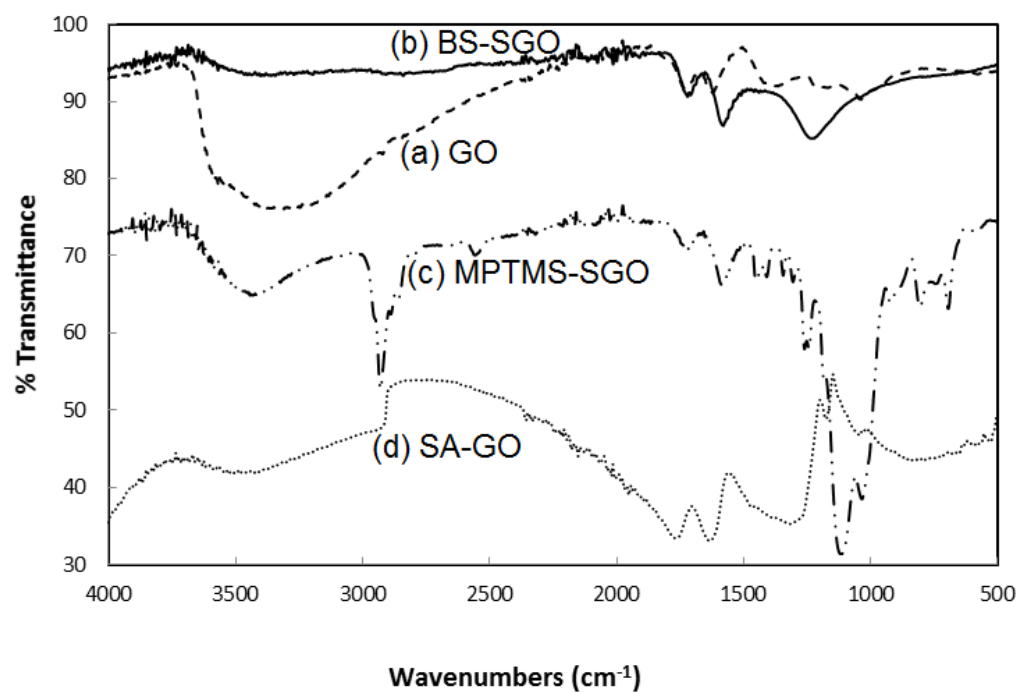


Fig.2 FTIR spectra of (a) GO; (b) BS-SGO; (c) MPTMS-SGO; and (d) SA-SGO

Table 1. Functional groups of GO and SGO samples from FTIR spectra.

Wavenumber (cm ⁻¹)	Functional group	GO	MPTMS-SGO	SA-SGO	BS-SGO
3400-2400	hydrogen-bonded O-H	√	√	-	-
3000-2850	C-H aliphatics (CH ₂) ₃	√	√	-	-
1800-1650	C=O	√	√	√	-
1680-1600	Amide NH ₂	-	-	√	-
1400-1070	Si-O	-	√	-	-
1440-1220	C-O,C-O-H	√	-	-	-
1260-1160	SO ₃ H	-	√	√	√

SGO from different precursors was characterized with FTIR and SEM-EDX to identify the functional groups present and to compare the morphology and element contain in SGO and GO. The FTIR spectra in Fig. 2 shows the respective peaks of SGO and GO samples, and their assignments are tabulated in Table 1. The FTIR spectra of GO shows the functional groups of the oxidized graphite. The existence of epoxy, hydroxyl, carboxyl and carbonyl functional groups indicated the successful oxidation of graphite. The presence of functional groups in SGO that were similar to that of the precursors (MPTMS, SA and BS) indicated the successful sulfonation of GO as compared to the original peaks. The diagnostic peak of MPTMS-SGO showed the presence of Si-O group and the presence of NH₂ shown in SA-SGO which was absent in GO indicating the incorporation of precursors on GO.

The morphology and elements contain in GO and SGO can be seen via SEM as shown in Fig. 3 and Table 2. It was observed that the surface morphology of SGO (Fig. 3b – 3d) was rougher than that of GO (Fig. 3a) because of the sulfonation [14]. The result from EDX shows that the sulfur content was highest in SA-SGO. This might be due to the compatibility of 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 grafting. On the other hand, the Si content in MPMTS-SGO and N contain in SA-SGO were confirmed via EDX where the result corresponds with FTIR spectra obtained.

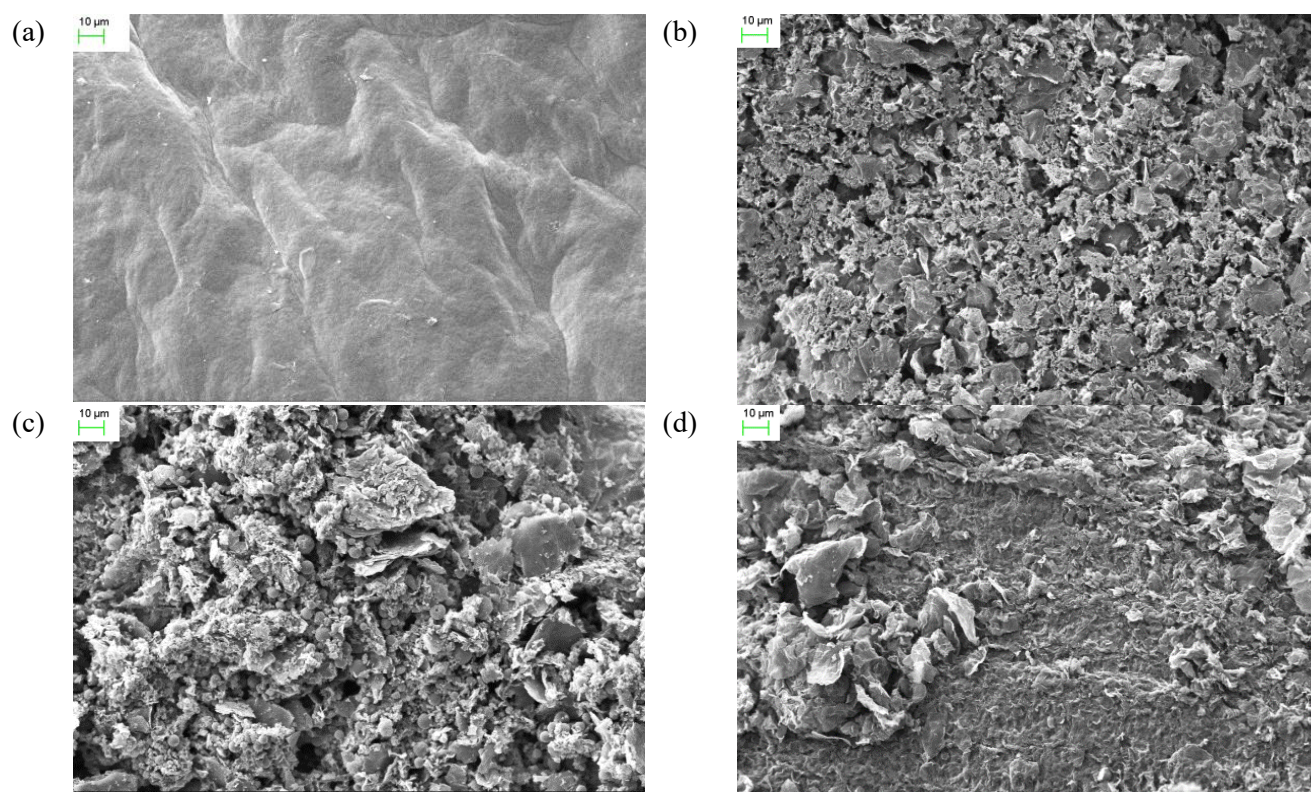


Fig. 3 SEM Images with the magnification of 500 \times for the sample (a) GO; (b) MPTMS-SGO; (c) SA-SGO; and (d) BS-SGO.

Table 2. Elemental content in GO and SGO samples via EDX.

Samples	C (% at.)	O (% at.)	N (% at.)	S (% at.)	Si (% at.)
GO	56.97	43.03	-	-	-
MPTMS-SGO	83.68	13.07	-	2.65	0.6
SA-SGO	48.06	25.42	4.65	21.87	-
BS-SGO	83.92	13.67	-	2.41	-

Besides, XPS was also used to confirm the sulfonation of GO as shown in Fig. 4 (a)-(d) where the new S2p peaks appear in the SGO due to the sulfonic groups that anchored on the backbones of GO [14, 19]. The original peaks of GO appeared at Fig. 4(a) at C-C (284.82eV), C-O (286.96eV), C=O (288.55eV) in C1s spectrum [18, 20]. The S2p peaks near 168eV attributed to the binding energy of sulfonic groups where these peaks were not seen in GO. These peaks confirmed the presence of sulfonic acid groups on the surface of GO [14]. XPS result was consistent with the FTIR and EDX results.

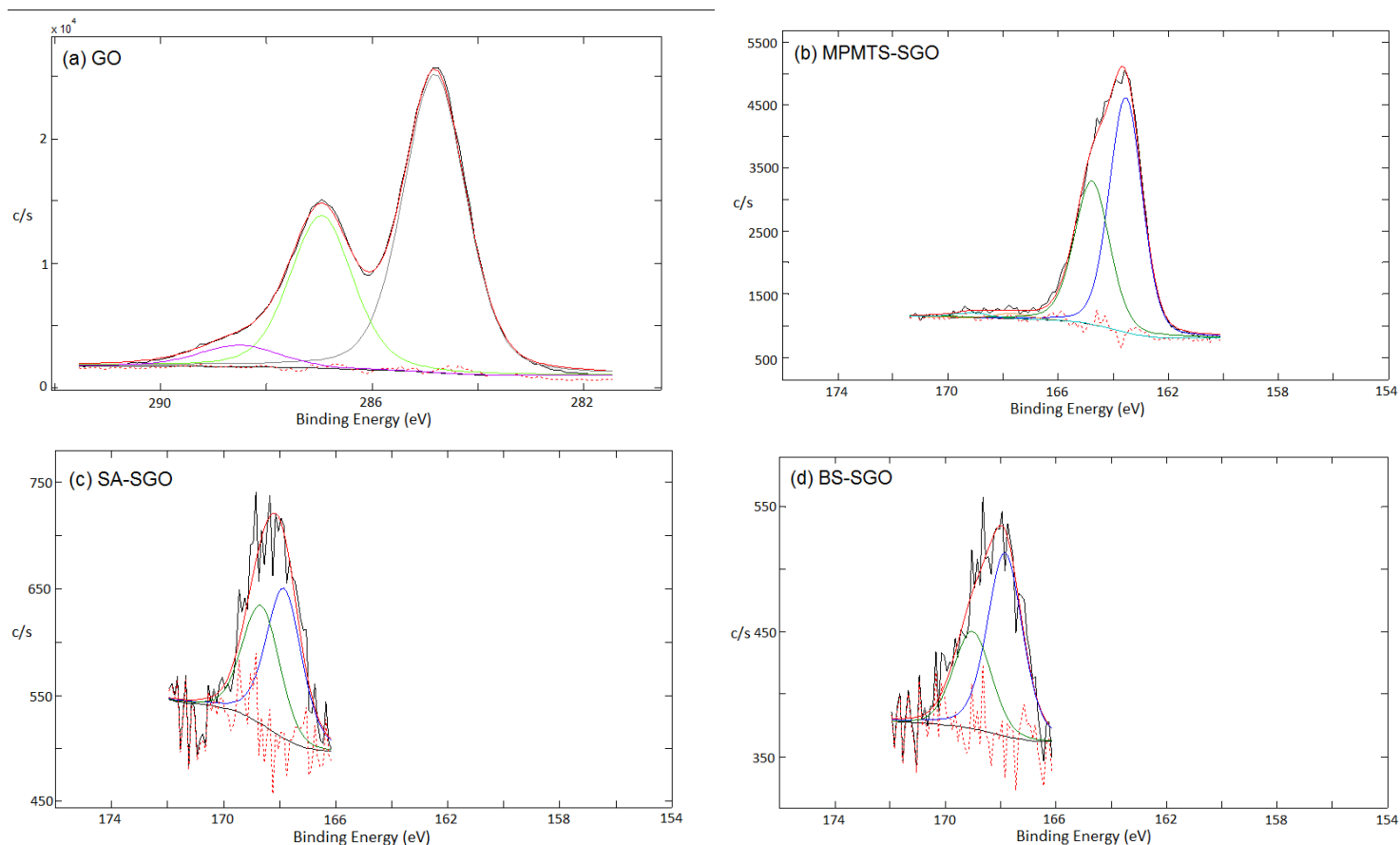


Fig. 4 XPS spectrum of (a) GO; (b) MPMTS-SGO; (c) SA-SGO and (d) BS-SGO.

4. Conclusion

In conclusion, GO was synthesized successfully with modified Hummers method. SGO samples with different precursors namely MPMTS-GO, SA-GO and BS-GO were prepared and characterized via FTIR, SEM, EDX and XPS analyses. The characterization result showed that the sulfonation groups have been introduced in the structure of GO. Further investigation of SGO as nanofiller in polymer membrane electrolyte will be study in its ionic conductivity and thermal properties.

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References

- [1] Kim D J, Jo M J and Nam S Y 2015 *J. Ind. Eng. Chem.* **21** 36
- [2] Wang R and Ji S 2008 *J. Power Sources* **180** 205
- [3] Wang Y, Mishler J, Cho S C and Adroher X C 2011 *Appl. Energy* **88** 981
- [4] Peighambardoust S J and Amjadi M 2010 *Int. J. Hydrogen Energy* **35** 9349
- [5] Zhang L, Hendren Z, Park J S and Wiesner M R 2012 *Chem. Eng. J.* **204-206** 87
- [6] Lee D C, Park S H and Kim W J 2013 *J. Memb. Sci.* **452** 20

- [7] Zhang J 2004 *Investigation of CO Tolerance in Proton Exchange Membrane Fuel Cells* (Worcester Polytechnic Institute-PhD Thesis)
- [8] Ban F Y, Huang N M and Lim H N 2012 *Int. J. Electrochem. Sci.* **7** 4345
- [9] Choi B G, Park Y C, Jung D H and Hong W H 2012 *Carbon* **50** 5395
- [10] Liu J and Dai L 2012 *J. Phys. Chem.* **3** 1928
- [11] Jiang Z and Manthiram A 2013 *Int. J. Hydrogen Energy* **38** 5875
- [12] Hummers J W S and Offeman R E 1958 *J. Am. Chem. Soc.* **80** 1339
- [13] Marcano D C, Kosynkin D V, Berlin J M, Sinitskii A, Sun Z, Slesarev A, Alemany L B, Lu W and Tour J M 2010 *ACS Nano* **4** 4806
- [14] Heo Y and Kim J 2012 *J. Membr. Sci.* **425-426** 11
- [15] Leng Y 2008 *Material Characterization: Introduction to Microscopic and Spectroscopic* (Singapore: John Wiley & Sons)
- [16] Chen C, Yang Q, Yang Y, Lv W, Wen Y, Hou P. Wang M and Cheng H 2009 *Adv. Mater.* **21** 3007
- [17] Gao Z, Yang W, Wang J, Yan H, Yao Y, Ma J, Wang B, Zhang M and Liu L 2013 *Electrochim. Acta* **91** 185
- [18] Chien H C, Huang C P, Kang C Y, Lin J N and Chang F C 2013 *Int. J. Hydrogen Energy* **38** 13792
- [19] Zarrin H, Jun Y, Chen Z and Fowler M 2011 *J. Phys. Chem.* **115** 20774
- [20] Lee K J and Young H. C 2014 *Vac.* **107** 269