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Synthesis and Characterization of Membranes from Sulfonated Polystyrene Waste and TiO_2 Fillers (PSS/TiO_2) as Proton Exchange Membranes

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Synthesis of sulfonated membrane from polystyrene waste and TiO_2 filler as proton exchange membrane has been carried out. The effect of variations in the concentration of polystyrene (10%, 15%, 20%) and the addition of TiO_2 was studied. The solvothermal synthesis results of TiO_2 confirmed by XRD showed the typical peaks according to standards. The membrane characterization was analyzed by FTIR, SEM-EDX and LCR meter. The success of sulfonation was evidenced by the presence of sulfonate groups at 1171.37 and 1170.67 cm^{-1} with degree of sulfonation (DS) of 10%, 15% and 20% PSS membranes of 32.02%, 40.03% and 48.04%, respectively. The insertion of TiO_2 filler into the membrane was confirmed by SEM-EDX and its effect could increase the conductivity value (σ). The results showed that this membrane has the potential to be developed as a proton exchange membrane fuel cell.

Keywords: Sulfonated polystyrene waste, TiO_2 Fillers, Membrane.

INTRODUCTION

Alternative energy sources and storage mechanisms such as fuel cells have gained a lot of attention in recent years [1]. Of the various types of fuels, proton exchange membrane fuel cells (PEMFC) have an advantage, as they produce high power and operate at low temperatures [2]. The quality of PEMFC performance is determined by the type of electrolyte membrane used. PEMFC uses a polymer as an electrolyte membrane to deliver H^+ ions from anode to cathode. Materials commonly used as electrolyte membranes in PEMFC are tetrafluoro ether (TFE) copolymerized nafion and perfluoro vinyl ether. However, TFE is carcinogenic and expensive, so alternative materials are needed that have the potential to replace nafion membranes [3].

Studies on membrane materials from several polymers have shown good results, such as polyether-ether ketone (PEEK), polyether sulfone (PES), sulfonatedpolysulfone (SPS), sulfonatedpolyaryl ether sulfone (SPAES), polyvinyl alcohol (PVA), chitosan (CS), polystyrene (PS) and other membranes [4-7]. Rani *et al.* [8] succeeded in synthesizing sulfonated polystyrene as direct methanol fuel cell (DMFC) membrane, but the resulting conductivity value is still low.

Organic-inorganic composites have been studied to improve membrane conductivity, and the addition of filler has shown promising outcomes. Composite membranes with zeolite [9], zirconium hydrogen phosphonate [10] and TiO_2 [11,12] have been investigated to improve the membrane quality. Therefore, in this study, membrane synthesis was carried out from sulfonated polystyrene (PSS) waste with TiO_2 filler. Characterization and performance of the resulting PEMFC membrane were studied in relation to concentration variation and TiO_2 filler.

EXPERIMENTAL

The materials used were polystyrene waste, titanium(IV) isopropoxide (97%, Sigma-Aldrich), isopropanol (Sigma-Aldrich p.a), acetic acid (96%, Sigma-Aldrich), sulfuric acid (Merck p.a), methanol (Merck p.a), chloroform (Merck p.a), dichloromethane (Merck p.a), nitrogen gas, ethanol (Merck p.a), sodium chloride (Merck p.a) and deionized water.

Synthesis of sulfonated polystyrene (PSS): Polystyrene (PS) dissolved in chloroform solution was added to 10%, 15% and 20% concentration of a sulfuric acid solution (96%) to obtain sulfonated polystyrene (PSS). The PSS solution was refluxed with 500 rpm stirring until homogeneous for 4 h. The solution was then heated in an oven at 60-65 °C to form a powder.

Synthesis of TiO_2: Synthesis of TiO_2 was carried out by the solvothermal method using titanium(IV) isopropoxide (TTIP) as a precursor. In brief, 10 mL of TTIP and 50 mL of isopropanol were mixed in a 250 mL beaker glass and stirred using a magnetic stirrer for 30 min. Then added CH_3COOH to pH 1 and sonicated for 5 min. Furthermore, it was carried out solvothermal at 150 °C for 4 h. The solvothermal product was washed with isopropanol 2-3 times and dried in an oven at 100 °C for 2 h.

Synthesis of sulfonated polystyrene/TiO_2: PSS powder was added with TiO_2 and dissolved in dichloromethane in a ratio of 2:1:3. The sulfonation process was dripped gradually into a two-necked flask driven by nitrogen gas. Then stirred until homogeneous. The solution was poured into a glass dish, then dried at room temperature for 1 day to obtain a PSS/TiO_2 composite membrane.

Characterization

Sulfonation degree (DS): The prepared PSS powder (0.1 g) was immersed in 10 mL of 0.1 M NaCl solution for 2 days. The mixture was filtered to obtain the filtrate which was then titrated with 0.02 M NaOH using phenolphthalein indicator. The degree of sulfonation was determined using eqn. 1:

$$\text{DS }(\%) = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}} \times Mr_{\text{styrene}}}{\text{Mass of sample}} \times 100 \qquad (1)$$

FTIR analysis: The polystyrene (PS) and sulfonated polystyrene (PSS) membranes were analyzed using a Perkin-Elmer Frontier FTIR spectrophotometer at a wavenumber range of 4000-500 cm^{-1}.

X-ray diffraction (XRD) analysis: The synthesized TiO_2, PSS and PSS/TiO_2 membranes were analyzed using a Shimadzu XRD-7000 diffractometer. Analysis was caried out with specifications of 45 kV, 30 mA, Cu$K\alpha$ + Ni filtered radiation at λ = 0.1540 nm. While the 2θ observation range was carried out in the range of 5-80° with a scan speed of 4°/min and a scan step of 0.026°.

Scanning electron microscope-energy despersive X-ray (SEM-EDX) analysis: Surface morphology analysis was done using the JEOL JSM-836OLA scanning electron microscope (SEM) instrument. The PSS/TiO_2 membrane sample was cut to a size of 0.8 × 0.8 cm and then plated with gold. The imaging process was carried out with a voltage of 20 kV and a resolution of 1280 × 960 pixels. The analysis was integrated with the Oxford-EDX IE 250 X Max 80 system for energy dispersion X-15ray (EDX) analysis.

Proton conductivity: The proton conductivity of PS and PSS/TiO_2 membranes were measured using impedance spectroscopy LCR-Meter-370. The membrane was conditioned in deionized water at 80 °C for 5 min. The membrane was cut 5.6 cm long, 0.8 cm wide and clamped between two carbon electrodes. The analysis was carried out at 25 °C with an open circuit potential in the frequency range of 300 kHz-100 mHz using a 10 mV sinusoidal signal. The value of the ionic conductivity (σ) was calculated according to eqn. 2:

$$\sigma = \frac{1}{R} \times \frac{1}{A} \qquad (2)$$

In eqn. 2, the value of the ionic conductivity (σ) is related to the film thickness (*l*), cross-sectional area (A) and the resistance of the material used (R).

RESULTS AND DISCUSSION

Acetic acid acting as chelating agent and bidentate ligand was used in the synthesis of titanium dioxide (TiO_2). Acetic acid also acts as a nucleophile which replace an isopropoxy group (Fig. 1a) to form $Ti(^{i}PrO)_3(OAc)$. Then there was a reaction of incorporation of $Ti(^{i}PrO)_3(OAc)$ monomers to form an acetate bridge, resulting in the isopropoxy group bound to Ti^{4+} being released and the acetate ligand remaining bound to Ti^{4+} (Fig. 1b). Furthermore, a dimer reaction occurs which forms a polymer chain (Fig. 1c).

The main part of the modification of $Ti(O^{i}Pr)_4$ with acetic acid is the reduction of the availability of hydrolyzable and condensable groups through the formation of $Ti(OCOCH_3)(O^{i}Pr)_2$ complex. The use of acetic acid as a modifier allows control of the degree of condensation and oligomerization leading to the preferential crystallization of TiO_2 in the anatase phase as confirmed by XRD analysis.

The aromatic electrophilic substitution reaction includes the sulfonation process that takes place in the polystyrene membrane. The reaction aims to substitute the H atom with group through chemical bonds on the carbon atom. The presence of a sulfonate group causes polystyrene to have a charged group that can donate proton [13]. The sulfonation reaction of polystyrene can occur in the alkyl chains in the *ortho*- and *para*-positions [14]. The sulfonation reaction is shown in Fig. 2.

Degree of sulfonation of PSS membrane: The amount of H atoms in benzene that can be changed into a sulfonate group is indicated by a value known as the degree of sulfonation. The degree of sulfonation increased with increasing concentrations of sulfonic acid used in 10%, 15% and 20% PSS membranes as shown in Fig. 3. The higher the degree of sulfonation, the greater the proton transport that occurs in the membrane. This result was also confirmed by the FTIR spectrum where the higher the PSS concentration, the higher the intensity of the sulfonate group.

FTIR studies: The main peaks of the polystyrene membrane are indicated by the wavenumber 3081.97, 3060.16, 3025.24 and 2924.19 cm^{-1}, which reveals the presence of a typical CH bond in the aromatic ring (Fig. 4a). In addition, there is also an aromatic C=C stretch at 1601.30 cm^{-1}. In the FTIR spectrum of sulfonated membranes (PSS) (Fig. 4b), it can be seen that the presence of sulfonate groups ($-SO_3$) at 1171.37 and 1170.67 cm^{-1} indicates that the membrane sulfonation process has successfully been occurred. The peaks at 1171.37 1170.67 cm^{-1} are attributed to a symmetrical $-SO_3$ stretching and S=O stretch vibrations, respectively. The presence of a sulfonate group is strengthened by the presence of hydroxyl absorption at 3435.02 cm^{-1}. In addition, it is also known that the higher the PSS concentration, the higher the absorption intensity.

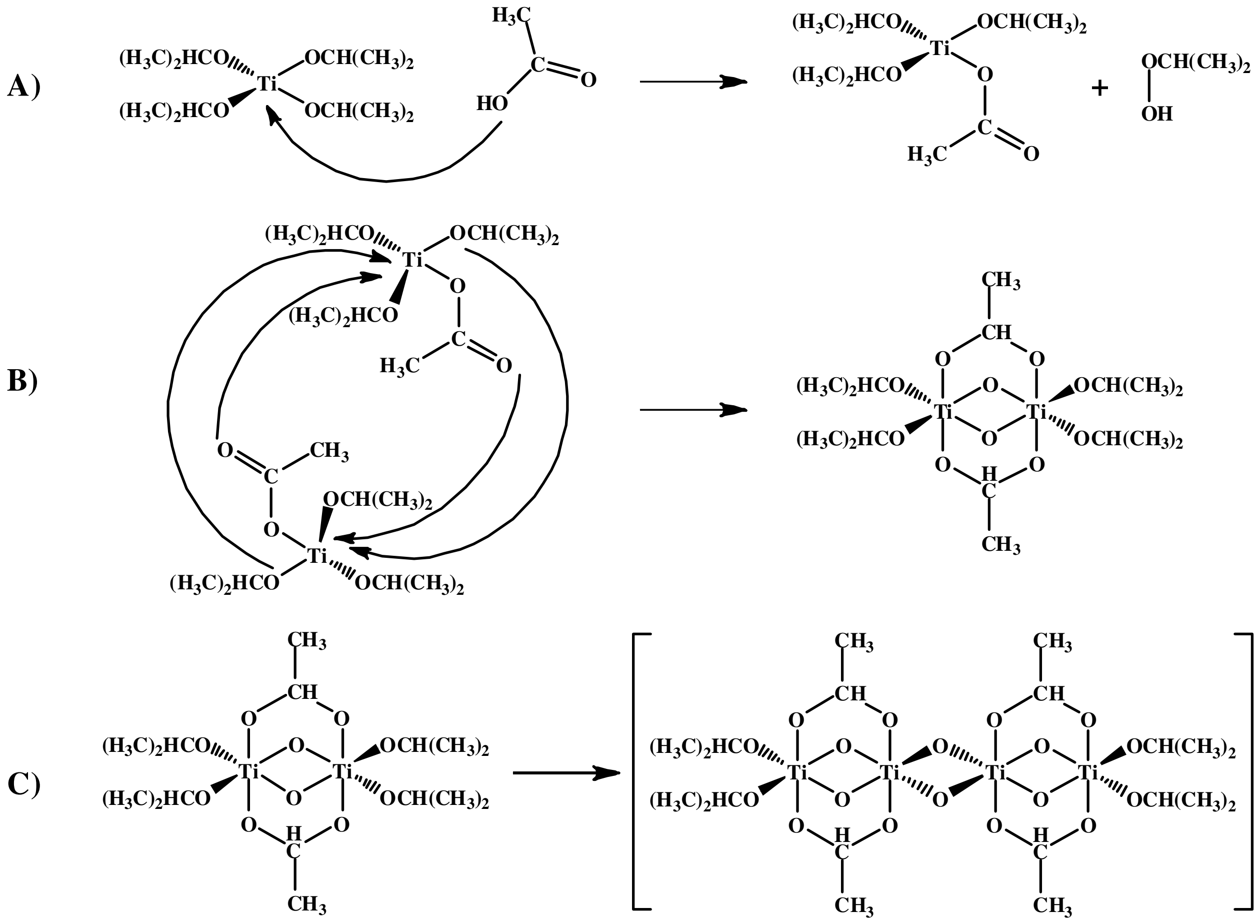

Fig. 1. Mechanism of the reaction for the synthesis of TiO_2 from TTIP

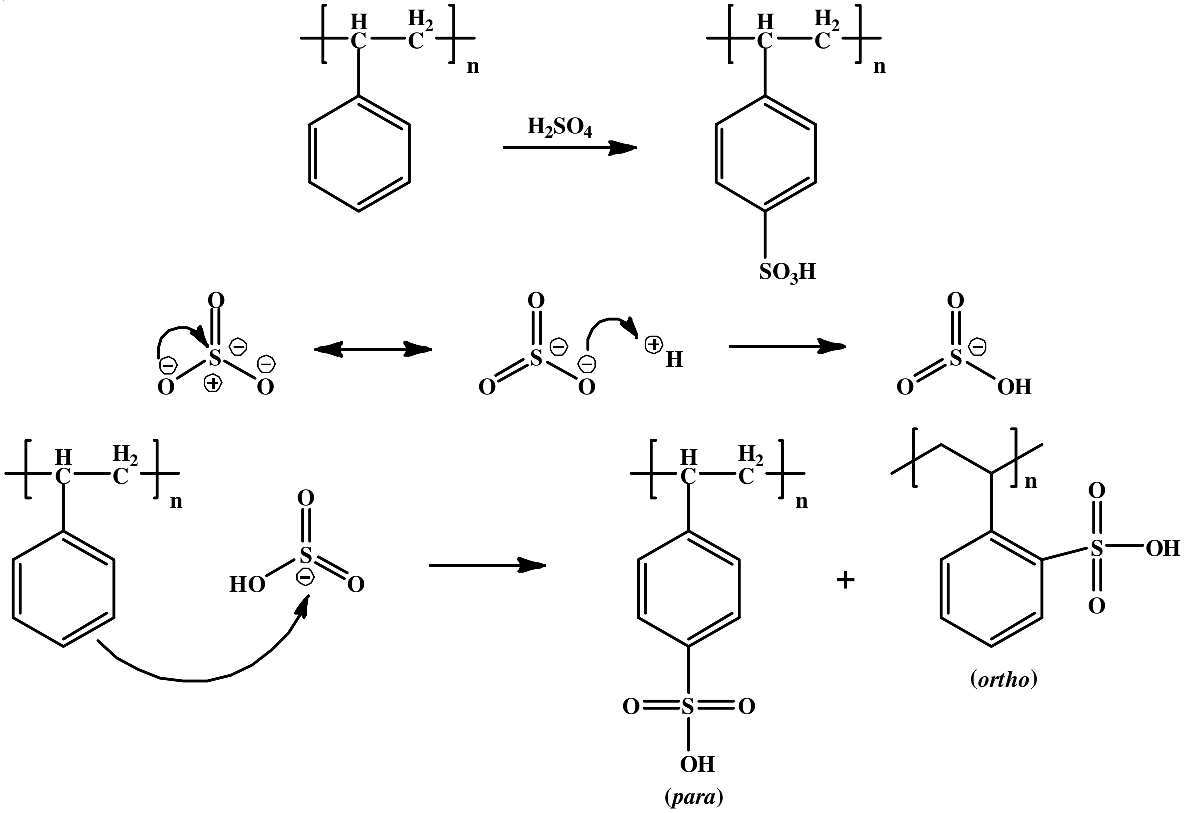

Fig. 2. Mechanism of the reaction for polystyrene sulfonation

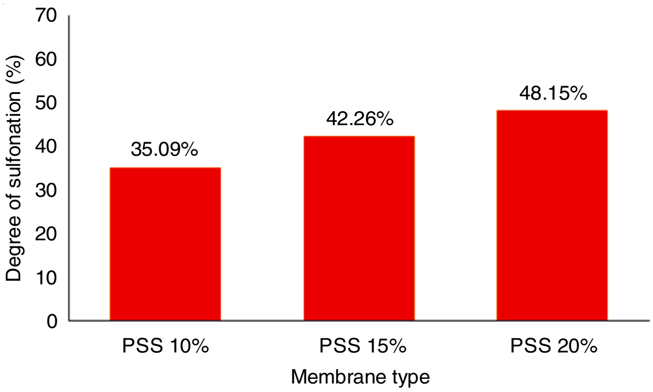

Fig. 3. Sulfonation degrees of PSS membrane

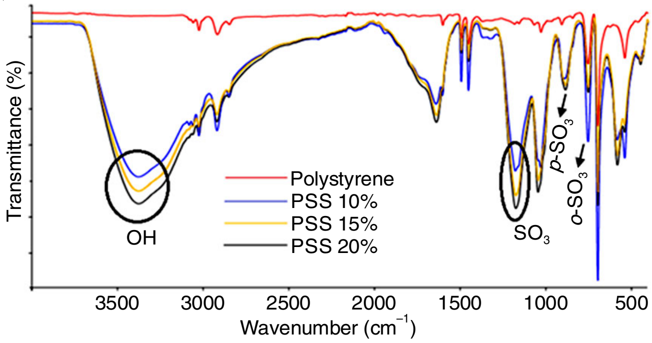

Fig. 4. FTIR results of polystyrene (PS) and sulfonated polystyrene (PSS) membrane

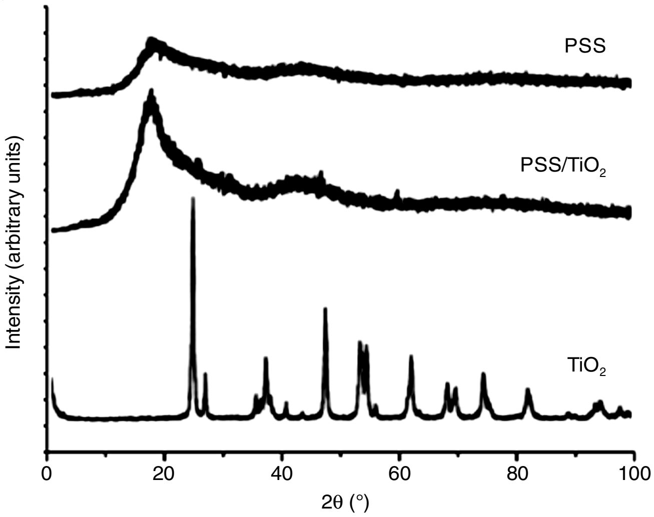

Fig. 5. XRD patterns of PSS, PSS/TiO_2 composite membranes and TiO_2

The sulfonation reaction that occurs is influenced by the alkyl substituents contained in the aromatic ring. This alkyl substituent is one of the electrons donating groups so that it can increase the electron density in the ring. Therefore, sulfonation reactions can occur in the *ortho* and *para* positions. The sulfonate group attached to substituted benzene is 1.4 (*para* position) as seen at 838.66 cm^{-1}, while the *ortho* position is indicated by the wavenumber 757.70 cm^{-1}. The absorption peak of *ortho* position is greater than that of *para* position, so the -SO_3 group is more likely to be bound to the *ortho* position.

XRD studies: Fig. 5 shows the XRD diffraction pattern of PSS, PSS/TiO_2 and TiO_2 composite membranes. The PSS membrane is known to be an amorphous polymer with a rigid polymer structure. The PSS/TiO_2 composite membrane pattern has three characteristic crystal peaks at 2θ, namely 26.15°, 38.23° and 48.95° in the crystal plane (110), (101) and (200), which indicate the formation of rutile TiO_2 phase. The observed results are matched with the JCPDS card No. 21-1276 [15]. Due to the low TiO_2 concentration in the PSS/TiO_2 composite membrane, only the characteristic amorphous peaks were seen in the XRD pattern. However, the peak is slightly shifted, when compared to the pattern of TiO_2 nanoparticles. The shift of characteristic peaks of TiO_2 on PSS/TiO_2 composite membranes suggests that there may be an interaction between the polymer and TiO_2 [16].

Surface morphology: The SEM analysis show that the surface morphology is not porous with TiO_2 appearing on the surface of the membrane as shown in Fig. 6a. The presence of TiO_2 is also confirmed by metal mapping in Fig. 6b, which is symbolized in green. According to the findings of Mulijani *et al*. [14], a non-porous membrane type of PSS/TiO_2 was successfully synthesized, which renders it appropriate for use in PEMFC.

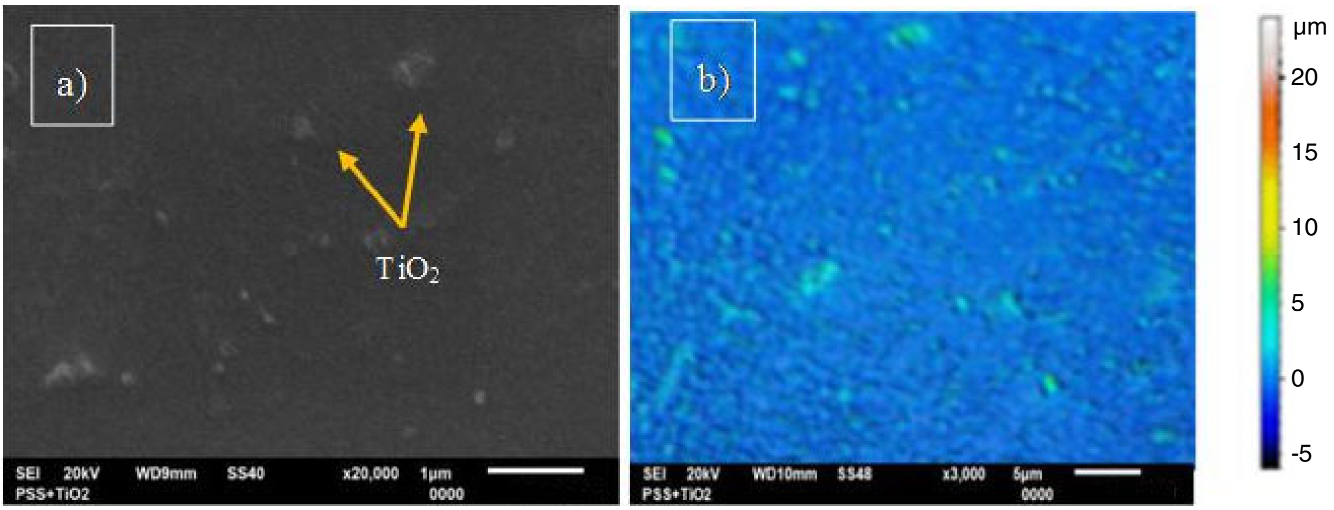

Fig. 6. Surface morphology (a) and composition mapping (b) of PSS/TiO_2 membrane

Measurement of the composition of the synthesized PSS-TiO_2 membrane was then carried out with EDX and the elemental counts are shown in Table-1. Fig. 7a shows the two peaks of elemental Ti (0.4 keV and 4.5 keV) and elemental O (0.5 keV), showing the characteristic constituents of TiO_2. In contrast, the peaks for elements C (0.2 keV), S (2.3 keV) and Na (1.0 keV) in Fig. 7b clearly represent PSS compositions. While the Au peak (2.1 keV) comes from the analytical preparation, which was sprayed and Si (1.7 keV) from the silicon substrate on the instrument.

TABLE-1
COMPARISON OF ELEMENTAL CONTENT OF PURE TiO_2 AND PSS/TiO_2 SYNTHESIZED

Sample	Elements content (wt.%)				
	Ti	O	C	S	Na
TiO_2	30.12	69.88	0	0	0
PSS-TiO_2	12.96	23.31	46.15	12.15	5.43

The elemental amounts shows that 30.12% Ti and 69.88% O were found in pure TiO_2. Meanwhile, in PSS-TiO_2, the total elements of Ti, O, C, S and Na were 12.96%, 23.31%, 46.15%, 12.15% and 5.43%, respectively. This clearly confirms the ratio in the TiO_2:PSS synthesis of 1:2 and shows a composition that is in agreement with the functional groups in the FTIR and XRD peaks as discussed earlier.

Proton conductivity: As shown in Table-2, the proton conductivity of the synthesized PSS membranes increase with increasing degree of sulfonation or sulfonic acid content with a maximum conductivity of 3.20×10^{-4} S/cm at 100% relative humidity and 90 ºC. This shows that proton transfer increases with the increasing number of sulfonic acid groups as proton exchangers. The addition of TiO_2 also has a synergistic role in increasing the conductivity compared to the results of the study of polystyrene without TiO_2 filler.

In comparison with other polymeric materials used, this work has better potential. However, when compared to the Nafion standard, this membrane still needs further improvement. Further research related to the mechanical properties and thermal stability analysis is important for further improvement as PEMFC membranes. The potential to use polystyrene waste material to generate renewable energy is an additional benefit of the present study.

TABLE-2
COMPARISON OF PROTON CONDUCTIVITY OF PSS/TiO_2 MEMBRANES

Membrane	Proton conductivity (S/cm)	Ref.
Polysytrene (PS)	2.04×10^{-5}	[17]
	3.54×10^{-7}	Present work
PSS 10%/TiO_2	1.47×10^{-6}	Present work
PSS 15%/TiO_2	7.48×10^{-6}	Present work
PSS 20%/TiO_2	3.20×10^{-4}	Present work
Polyphenylene sulfide/graphene	2.6×10^{-5}	[18]
Polyvinyl alcohol/graphene	2.54×10^{-5}	[18]
PBT/graphene	1.0×10^{-12}	[19]
Nafion 117	2.5×10^{-3}	[20]

Conclusion

Polystyrene sulfonated (PSS)/TiO_2 membrane has been successfully synthesized from polystyrene waste and TiO_2 filler. This is evidenced by FTIR analysis, namely the presence of sulfonate groups (-SO_3) at 1171.37 and 1170.67 cm^{-1} and the presence of hydroxyl peak at 3435.02 cm^{-1}. TiO_2 insertion was also confirmed by typical peak XRD and surface morphology by SEM. The higher the concentration variation will increase the degree of membrane sulfonation. Increasing the amount of TiO_2 in the membrane composition led to a higher conductivity, with 20% PSS/TiO_2 yielding the best results, which was 3.20×10^{-4} S/cm. So, it can be concluded that a sulfonated polystyrene membrane with TiO_2 filler has the potential as a proton exchange membrane fuel cell (PEMFC).

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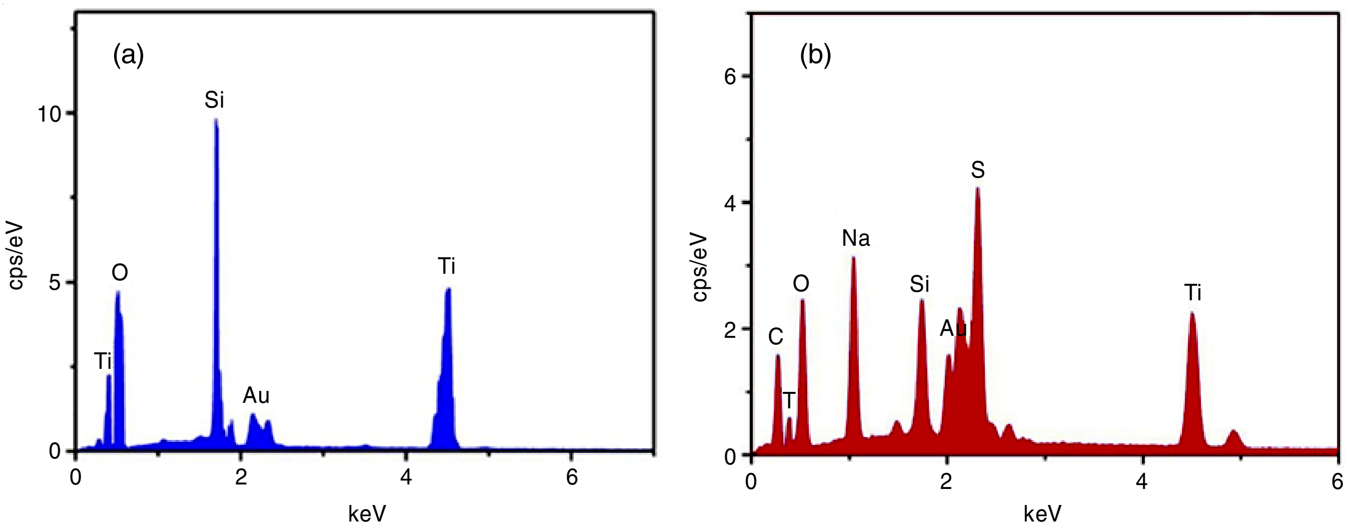

Fig. 7. EDX of TiO_2 (a) and PSS/TiO_2 membrane (b)

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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