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A comparative study on the performance of highly conductive sulfonated poly(ether ether ketone) PEM modified by halloysite nanotubes, sulfonated polystyrene and phosphotungstic acid

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Abstract−Proton transfer is the most important task of proton exchange membranes (PEMs) for application in fuel cells. One vital disadvantage of currently used commercial Nafion membranes is the low proton conductivity at high temperatures. Therefore, the objective of this research was to increase the proton conductivity of PEMs based on sulfonated poly (ether ether ketone) (SPEEK). Herein, modification of SPEEK-based PEM was carried out using polydopamine-coated halloysite nanotubes (HNT) alone and in combination with sulfonated polystyrene (SPS) and phosphotungstic acid (PWA). In this method, poly (ether ether ketone) sulfonation process was performed under optimum operating conditions to create more sulfonic acid groups on its chains. Here, polydopamine was doped on the outer surface of HNT (DHNT) and employed as the additive to create additional proton transferring pathways in the membrane. The hydrophilicity of the modified nanotube was enhanced through silanization (named as DHNTS). Moreover, SPS and PWA were applied to improve the ability of protons to transfer through the proton barrier channels in the membrane. Performing the sulfonation of polystyrene in the solution phase was a novel approach in this study, which led to significant increase in the degree of sulfonation. The results showed that the SPEEK/DHNTS|SPS and SPEEK/DHNTS|PWA membranes in the presence of 15% weight ratio additives and 100% relative humidity exhibited 109% and 90% higher proton conductivity than the neat SPEEK membrane, respectively. Furthermore, 20% and 10% higher proton conductivity was observed for the aforementioned membranes compared to the commercial Nafion117 membrane. Because of the strong acid-base bonding between DHNTS and SPEEK and the sticky nature of polydopamine, the chemical stability of the modified PEMs was higher than the neat membrane. In terms of fuel cell performance, there was little difference between Nafion117 membrane and DHNTS-modified PEM. These modified membranes are therefore suitable alternatives to address the commercial Nafion membrane's gap in the fuel cells.

Keywords: Proton Exchange Membranes, Proton Conductivity, SPEEK, Sulfonated Polystyrene, Halloysite Nanotubes, Phosphotungstic Acid

INTRODUCTION

The application of renewable energy as a substitute for fossil fuels has received much attention in recent decades. Recently, fuel cells, one of these alternatives, have come under the spotlight where the chemical energy is converted directly into electricity. The sole byproducts of this system are water and heat [1]. Therefore, fuel cells can promise pollution-free production of energy. Proton exchange membrane (PEM) fuel cells and microbial fuel cells (MFC) are two types of fuel cells that can generate electricity in vehicles. One of the main components of these apparatuses is the proton exchange membrane where its role is the transfer of H^+ from the anode to the cathode of the cell. The proton exchange membrane must further have acceptable chemical stability to ensure the efficient performance of the fuel cells for long-term operation [2]. The most common material that is applied for the fabrication of PEM is Nafion, a sulfonated tetrafluoroethylene copolymer that has high ability to transfer protons as a consequence of the presence of sulfonic acid groups in its structure [3]. However, due to the high fuel/liquid crossover, the strong hydrophobicity and low proton conductivity at higher temperature, researchers have been looking for suitable alternatives for Nafion [1]. Among the various options, sulfonated poly(ether ether ketone) (SPEEK), an aromatic hydrocarbon polymer, has received much attention [4]. Due to the presence of aromatic groups in the structure of SPEEK, the membranes based on this polymer have reliable mechanical strength to be applied in fuel cells [5]. Besides, the presence of the sulfonic acid groups in the matrix of SPEEK makes it a highly proton conductive compound. However, the high water adsorption ability of SPEEK lessens the chemical stability of the related PEMs. Therefore, different additives are employed to improve proton conductivity and physicochemical characteristics of the membrane that should be compatible with the base polymer [6,7]; otherwise, defects will be created in the structure of the membrane that reduce the performance greatly. Recently, nanotubes that are modified with hydrophilic and/or proton conductive materials have been used. It is proved that the tubular structure

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of the nanotubes increases the ionic barrier within the membrane. Besides, the strong bonding between the nanotube and SPEEK can reduce the membrane degradation by the free radicals.

Among these nanotubes, Halloysite nanotube (HNT) is the most suitable option because of its desirable dispersive properties and the presence of hydroxyl groups in its structure [8,9]. Furthermore, proton conductive materials, such as boron phosphate and phosphotungstic acid (PWA), have been used to create additional proton transfer pathways [10,11]. Utilizing both nanotubes and the conductive substances as the additive is an effective strategy to make highly stable PEM with excellent proton transportation ability.

Gong et al. [12] improved the SPEEK-based PEM using BPO_4-grafted carbon nanotubes (CNTs) as the additives. Polydopamine was first coated on the surface of the CNT. Then, BPO_4 which is a hydrophilic compound, was doped on the surface of the modified CNT. The application of BPO_4 reduced the risk of short-circuiting in the membrane. Furthermore, the number of the proton conductive sites was enhanced via the modification of the CNTs [12]. However, the strong molecular interactions in CNTs increase the possibility of the agglomeration within the fabricated PEM, which can negatively affect the membrane performance by disconnecting the proton transfer pathways. Titanate nanotubes (TNTs) modified with the sulfonic acid groups were incorporated to the SPEEK PEM in the study by Salarizadeh et al. [13], where the highly hydrophilic TNT significantly enhanced the number of the ion conductive sites within the PEM. However, TNTs are expensive for low cost membrane fabrication. Liu et al. [8] produced a SPEEK membrane using modified HNT as an additive. In this research, sulfonated HNT (SHNT) was employed to modify the properties of the base polymer. Polystyrene sulfonic acid (PSSA) was successfully doped onto the inner and outer surface of the HNT to enhance the ability to transfer protons [8]. In this research, dopamine was first doped on the surface of HNT. In fact, dopamine acts as a bonding agent between HNT and sulfonic acid groups. In addition, the presence of the amine groups in the structure of dopamine creates a strong acid-base bond between the SPEEK and the additive [14]. The application of modified HNT made significant increase in the hydrophilicity and proton conductivity of the fabricated membrane. They pointed out that the application of HNT would have profound benefits compared to the CNT that was utilized in the previous works. The van der Waals forces in the CNT particles make them difficult to disperse in the membrane, while HNT has suitable dispersibility. Moreover, unlike CNT, HNT is not an electron conductor. These properties make HNT an exclusive option for modifying the base polymer [8].

Rico-Zavala et al. [15] prepared SPEEK-based PEMs using PWA-modified HNTs as the additives. For this purpose, SPEEK was first synthesized through the reaction of PEEK and sulfuric acid at different reaction times and constant weight ratios. Subsequently, PWA was doped on the outer surface of HNT. The addition of PWA to the polymer solution improved the proton conductivity of the membrane. In addition, the presence of HNT increased the water uptake and thereby improved the proton conductivity of the membrane, compared to the neat SPEEK membrane [15]. Notably, the leaching of PWA is still a bottleneck in further utilization of this material for PEM development, which causes the diffusion of excess amounts of water into the membrane structure and thereby reduces its durability.

In our earlier research [16], the effects of soluble additives on SPEEK membrane were studied, which improved the performance of membrane and showed suitable compatibility with the base polymer to inhibit the creation of defects. In addition, our experimental studies showed that the addition of tubular nanoparticles (such as HNT) can increase the conductivity of the membrane, maybe through the introduction of channels for proton transport. The objective of this research was the fabrication of low cost PEMs with appropriate properties to be applied in the MFCs. Moreover, investigation of the influence of different types of additives, namely, DHNTS, DHNTS/sulfonated polystyrene (SPS) and DHNTS/PWA on the performance of PEM, is another objective of this research. Accordingly, PEEK was selected as the base polymer because of its high mechanical and chemical stabilities. To create additional channels for proton transferring, the sulfonation of PEEK was performed through a modified method to improve the degree of sulfonation. Furthermore, sulfonation of polystyrene was performed under optimal conditions and the sulfonated polymer was employed as a proton conductive additive to make more channels for proton transfer. The application of tetrahydrofuran (THF) as the solvent for polystyrene and performing the sulfonation process in the solution phase is the new approach in this research, which led to significant increase in the degree of sulfonation for SPS. Besides, polydopamine-doped HNT was used as another additive for polymer solution, which its hydrophilicity and dispersibility in the casting solution were improved via the silanization with trimethoxysilylpropylethylenetriamine. The application of HNT instead of other types of nanotubes was advantageous because of its desired dispersion, lower cost and the presence of hydroxyl groups on its surface. Phosphotungstic acid was further utilized as a soluble additive because of its high acidity and hydrophilicity. To facilitate he proton transport and improve the stability of PEM, modified HNT was blended with SPS or PWA. Subsequently, neat SPEEK and modified membranes were prepared through the casting solution method and characterized by different tests.

EXPERIMENTAL

1. Materials

Poly(ether ether ketone) (PEEK) was utilized as the base polymer for the membrane fabrication. Phosphotungstic acid ($H_3PW_{12}O_{40}$, purity: 95-99 wt%) and sulfonated polystyrene (polystyrene was industrial grade) were used as the additives to the polymer solution. Sulfuric acid (99 wt%) was applied as the sulfonation agent in the sulfonation process of PEEK and polystyrene. N-methyl-2-pyrrolidine (NMP) was used as the solvent to prepare the polymer solutions. In addition, tetrahydrofuran (THF) was used as the solvent for polystyrene in the sulfonation process. Sodium chloride and sodium hydroxide were applied in the titration process to measure the ion exchange capacity (IEC). Trimethoxysilylpropylethylenetriamine, a hydrophilic silane, was employed to improve the dispersibility of nanotubes in the polymer solution. Dopamine hydrochloride solution (40 mg/mL solution) and ammonia solution (25 wt%) were used for the modification of HNT particles. To make constant pH during the MFC test, K_2HPO_4 (>98 wt%) and KH_2PO_4 (>99 wt%) were utilized as the buffering agents. PEEK powder was obtained from Goodfellow Cambridge limited, UK. Sulfuric acid, tetrahydrofuran and sodium hydroxide were purchased from Ghatran Shimi Company (Iran). Phosphotungstic acid, NMP, trimethoxysilylpropylethylenetriamine, K_2HPO_4, KH_2PO_4 and HNT were supplied by Merck Company. Dopamine hydrochloride solution was provided by Caspian Tamin Company (Iran). Polystyrene was supplied by Tabriz Petrochemical Co. (Iran).

2. Sulfonation of PEEK

SPEEK was synthesized through a procedure described elsewhere [16]. PEEK was sulfonated by reaction of PEEK and H_2SO_4 at three different reaction times (2.5, 3 and 3.5 hrs) and under nitrogen atmosphere to investigate the influence of the reaction time on the DS of the final product. At first, a mixture containing 100 mL H_2SO_4 and 5 g dried PEEK was prepared in a 4-neck flask. Then, the flask was placed in a cold water bath to prevent any possible reaction between acid and the polymer. The mixture was magnetically stirred for 20 minutes and further sonicated for 20 minutes at room temperature to enhance the contact between the reagents. This process reduces the possibility of polymer agglomeration during the reaction. Then, the flask was placed in the hot water bath and the sulfonation reaction was carried out at 45, 55 and 60 °C and under nitrogen atmosphere.

To terminate the reaction, the flask temperature was decreased below 10 °C and the mixture was poured into large volume of DI water to precipitate the sulfonated polymer. Then, the precipitated solids (SPEEK) were washed several times with DI water to reach the neutral pH [17]. The amount of water in the washing step used was as low as possible to reduce the potential blockage of sulfonic acid groups by the cations present in the water. Finally, the synthesized SPEEK was dried in the oven at 43 °C for 24 hrs. Sulfonated PEEK (Fig. 1) was referred to as S-x (x: sulfonation time).

3. Sulfonation of Polystyrene

To enhance the contact between polystyrene and sulfuric acid, the sulfonation process was performed in the solution phase as described in our earlier research [16]. First, the polystyrene solution was prepared via dissolving 5 g polystyrene in 150 mL THF at 25 °C. Then, 20 mL H_2SO_4 (99 wt%) was slowly added to the solution under mixing and the solution was further stirred at 25 °C for 24 h and 48 h to perform the reaction between polymer and acid. Then, the solution was poured into large amounts of DI water to terminate the reaction and form the sulfonated product. The precipitated solids were washed several times with DI water to be neutralized. Finally, the sulfonated polystyrene (SPS) (Fig. 2) samples were oven dried at 60 °C and referred to as SPS24 and SPS48. Furthermore, 0.1 gr silver nitrate was used as the catalyst for the sulfonation reaction by the same procedure and the products were referred to as SPS24* and SPS48*.

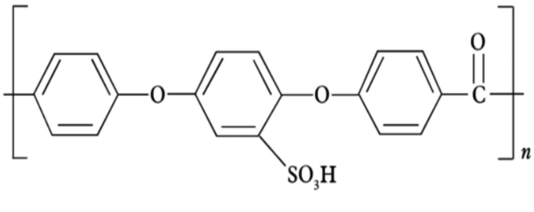

Fig. 1. Structure of SPEEK.

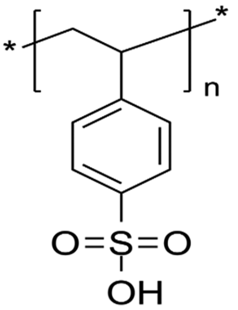

Fig. 2. Structure of sulfonated polystyrene.

4. Preparation of Polydopamine-coated Halloysite Nanotubes

HNT was modified through the self-polymerization of dopamine on its surface. At first, 1 g HNT was added to 100 mL DI water under mixing and ultrasonication to form the HNT suspension. Then, 15 mL dopamine hydrochloride solution was added and the mixture was sonicated for 30 minutes. 1 mL ammonia solution was added as the initiator and the mixture was further stirred at room temperature for 24 h to complete the polymerization. To terminate the reaction, the mixture was poured into large amounts of DI water. Finally, the obtained solids were filtered and washed several times with DI water to be neutralized. The solid was referred to as DHNT.

The coupling of the nanotube with the hydrophilic silane was performed to improve the dispersion of DHNT in the polymer solution. 1 g DHNT nanoparticles were dispersed in DI water. Then, 0.2 g trimethoxysilylpropylethylenetriamine was added and the mixture was stirred at room temperature for 24 hrs. Silane-modified DHNT nanoparticles (referred to as DHNTS) were collected through filtration and dried at 60 °C in the oven. The schematic diagram for the preparation of DHNTS is presented in Fig. 3.

5. Preparation of Neat SPEEK Membrane

All membranes in this study were fabricated via solution casting method. 5 g SPEEK was slowly dissolved in 42.6 g NMP to make 10.5 wt% polymer solution. The solution was sonicated for 30 minutes to remove the air bubbles and then cast on a clean glass sheet. Afterward, the glass sheet was placed in the oven at 43 °C for 18 h to form a thin skin layer and then into the DI water bath to form the thick sublayer of the membrane through the phase inversion process [18].

6. Preparation of the Modified SPEEK Membranes

To make SPEEK/DHNTS solution, certain amounts of DHNTS were dispersed in NMP. SPEEK was added and the mixture was stirred at room temperature to obtain a homogeneous polymer solution. The modified membranes were fabricated with the same procedure as the neat SPEEK membrane. For all fabricated membranes, the weight percent of the solid (SPEEK or SPEEK+additive) content was selected as 10.5. Furthermore, the weight ratio of DHNTS to SPEEK varied as 0.05, 0.10 and 0.15. The membranes were named S-2.5/DHNTS-x, where x is the weight ratio of DHNTS to SPEEK.

To prepare SPEEK/DHNTS|SPS and SPEEK/DHNTS|PWA

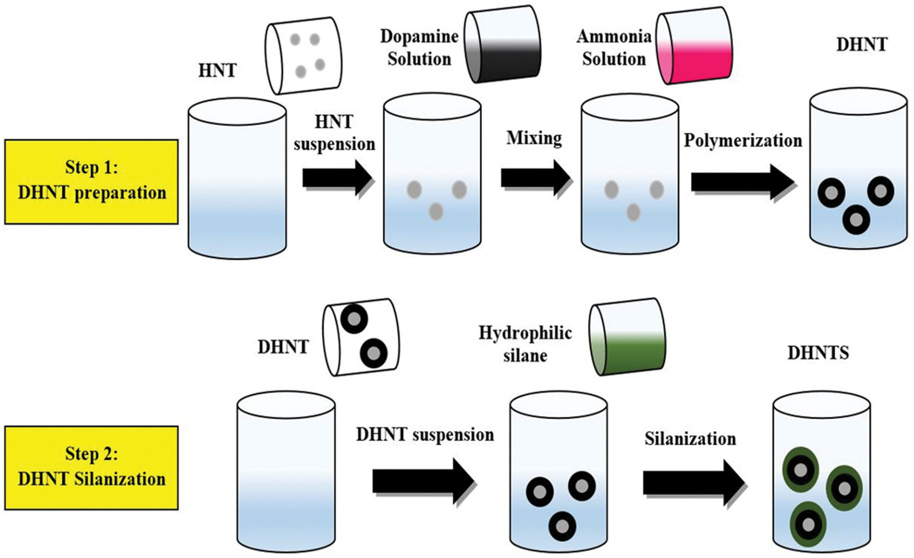

Fig. 3. Schematic of DHNTS preparation.

Table 1. Compositions of the polymer solutions for the preparation of the membranes

Sample name	SPEEK (g)		NMP (g)	SPEEK (wt%)	
S-2.5	0.7		5.96	10.5	
	SPEEK (g)	DHNTS (g)	NMP (g)	SPEEK+DHNTS (wt%)	DHNTS/SPEEK (g/g)
S-2.5/DHNTS-0.05	0.667	0.0330	5.96	10.5	0.05
S-2.5/DHNTS-0.1	0.636	0.0636	5.96	10.5	0.1
S-2.5/DHNTS-0.15	0.608	0.0912	5.96	10.5	0.15
	SPEEK (g)	DHNTS (g) or SPS48* (g)	NMP (g)	SPEEK+DHNTS+SPS48* (wt%)	(DHNTS+SPS48*)/ SPEEK (g/g)
S-2.5/DHNTS|SPS48*-0.05	0.666	0.0165	5.96	10.5	0.05
S-2.5/DHNTS|SPS48*-0.1	0.636	0.0320	5.96	10.5	0.1
S-2.5/DHNTS|SPS48*-0.15	0.608	0.0456	5.96	10.5	0.15
	SPEEK (g)	DHNTS (g) or PWA (g)	NMP (g)	SPEEK+DHNTS+PWA (wt%)	(DHNTS+PWA)/ SPEEK (g/g)
S-2.5/DHNTS|PWA-0.05	0.666	0.0165	5.96	10.5	0.05
S-2.5/DHNTS|PWA-0.1	0.636	0.0320	5.96	10.5	0.1
S-2.5/DHNTS|PWA-0.15	0.608	0.0456	5.96	10.5	0.15

membranes, certain amounts of DHNTS were dispersed in NMP. Then, equal amounts of SPS or PWA were added to the mixture and magnetically stirred at room temperature. Finally, SPEEK was added to the mixture. The modified membranes were fabricated according to the abovementioned procedure. The weight percent of the solids in the solution was 10.5, while the weight ratio of the additives to SPEEK varied as 0.05, 0.10 and 0.15. The membranes were named S-2.5/additive-x, where x is the weight ratio of additives to SPEEK. The compositions of the polymer solutions are presented in Table 1.

7. MFC test

A microbial fuel cell made in Babol Noshirvani University of Technology (Fig. 4) was employed to evaluate the performance of the prepared PEMs in the fuel cell applications. The anode and cathode compartments were made of Plexiglas and the two sides of the MFC were separated by PEM with an effective area of 9 cm^2. Before starting the test, the membrane was treated by immersing in DI water for 24 h to activate the ion conductive sites. The anode and cathode electrodes were carbon-paste and carbon paper, respectively. The pH of the cell should be controlled during the test. For this reason, K_2HPO_4 and KH_2PO_4 were utilized as the buffering agents. Besides, glucose was applied in the anode chamber as the sole carbon source for the growth of the microorganisms. The wastewater was oxidized by the microorganisms, which were mixed culture, and the electrons were released. The electrons were transferred to the anode electrode and reached the cathode chamber through an external current circuit, generating the electricity. The anaerobic condition was maintained during the whole process. Data

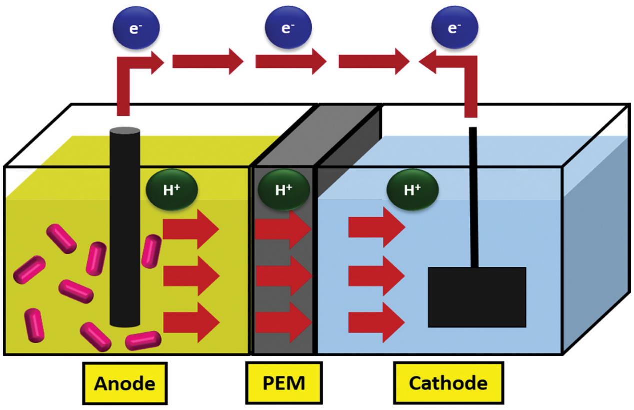

Fig. 4. Schematic of the microbial fuel cell.

logger was used to record the measured potential differences at different currents; then the power was calculated by multiplying these two parameters [19].

8. Characterization of the Fabricated Membranes

The presence of different bonds in the structure of the synthesized materials was investigated using the FTIR analysis (model: TENSOR 27-Brucker Co. (Germany)) in the wavenumber range of 4-4,000 cm^{-1}. Thermogravimetric analysis (TGA) was performed using Linseis's TGA apparatus (L8A1750, USA) to further confirm the grafting of polydopamine on HNT. SEM analysis (TESCAN Co. (Czech)), with 3 nm measurement accuracy, was used to observe the cross-section and top surface of the fabricated membranes. TEM analysis (model: EM 208S) was employed to observe the tubular structure of HNT. To perform the proton conductivity test, conductivity meter (model: MSTC-A1) manufactured by Asian Hydrogen Co. (Iran) with 0.0001 measurement accuracy was used.

The MFC made at the Babol Noshirvani University of Technology was applied to evaluate the performance of the membrane in the fuel cell. The specified data were gathered to evaluate the performance of the fabricated PEMs in the MFC by connecting the two electrodes to the data logger used for data recording. The potential difference values were measured at different currents. Then, the power values were obtained by multiplying the potential difference and the current.

The ultrafiltration setup was utilized to examine the possible water crossover of the membranes. A schematic diagram of the setup is shown in Fig. 5 where the feed water was pumped at 2 bars pressure to the cross-flow membrane module. The permeated water through the membrane can be collected at the outlet of the module to calculate the crossover flux.

The contact angle between the water drop and the surface of the membrane was measured using the sessile drop method. At least ten points on the membrane surface were used for contact angle measurement via Sharif Solar test device (model: CA-500M, Iran) and the results were averaged.

8-1. Proton Conductivity

Proton conductivity is mainly measured through the alternative current (AC) impedance method. At first, and to activate the ion conductive channels, the membrane was immersed in DI water for 24 h at room temperature. Then, the membrane's electrical resistant was measured at 60 °C and relative humidity of 60%, 80% and 100%. The proton conductivity of the membrane is calculated using Eq. (1):

$$\sigma = L/RA \tag{1}$$

where σ is the proton conductivity of the membrane (S/m), L is the thickness of the membrane (m), R is the membrane resistance (Ω) and A is the effective area of the membrane (m^2). In Fig. 6, the schematic of the cell for measuring the membrane's electrical resistance is shown [20].

8-2. IEC and DS

Ion exchange capacity (IEC) represents the amount of protons (in terms of mmol) per gram of the dry polymer and was measured by the titration method. Predetermined amounts of SPEEK (or SPS) sample were dispersed in 100 mL of 1 M sodium chloride solution and the resulting mixture was stirred for 24 h to exchange H^+ with Na^+. IEC was calculated by the titration of the mixture with 0.05 M sodium hydroxide solution in the presence

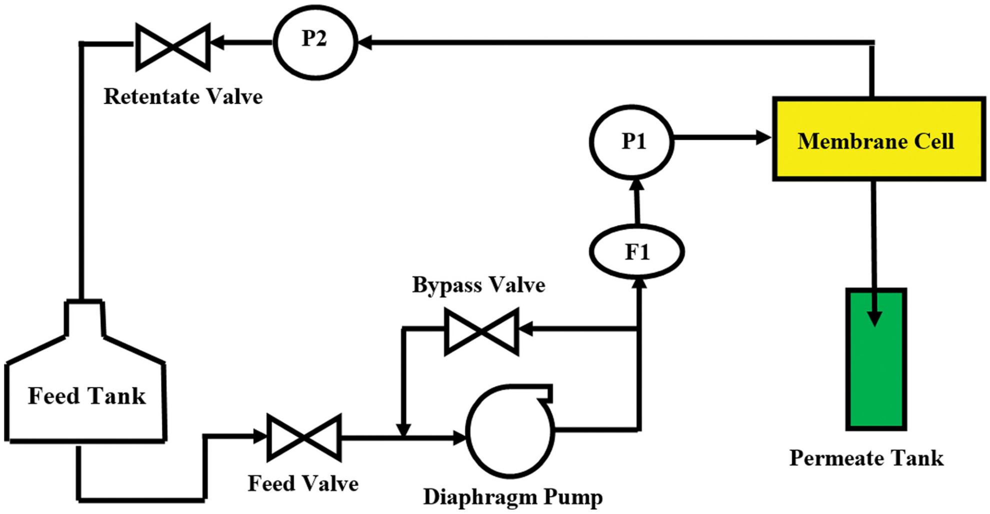

Fig. 5. Schematic of the ultrafiltration setup.

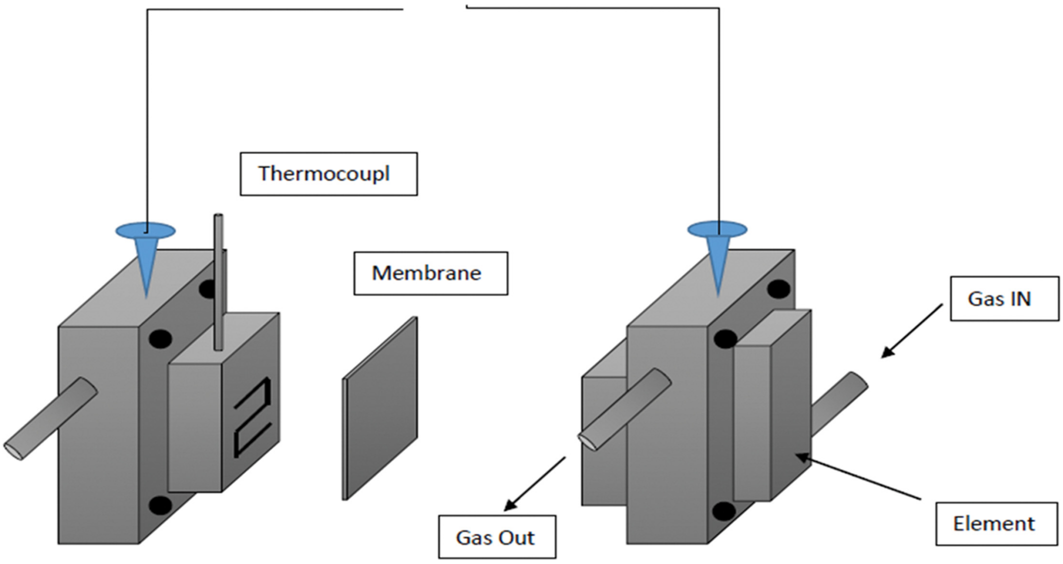

Fig. 6. Schematic diagram of the cell.

of phenolphthalein as the end-point indicator; according to Eq. (2):

$$\mathrm{IEC}=\frac{\mathrm{V}_{NaOH}\times\mathrm{M}_{NaOH}}{\mathrm{W}_{d}} \tag{2}$$

where W_d is the mass of the dry polymer (gr) and V_{NaOH} (mL) and M_{NaOH} (M) are the volume and molarity of NaOH titrant. The degree of sulfonation (DS), which expresses the number of SO_3H groups for a repeating unit of the polymer, was calculated by Eq. (3) [21].

$$\mathrm{DS}=\frac{\mathrm{M}_{p}\times\mathrm{IEC}}{(1000-81\ \mathrm{IEC})}\times100 \tag{3}$$

where M_p is the molecular weight of PEEK (or polystyrene) and 81 is the molecular weight of SO_3H groups [22].

8-3. Water Uptake

The water adsorption ability of the PEM is an important characteristic that positively affects proton conductivity. To perform this test, the membrane was immersed in DI water at room temperature for 24 hrs. Then, the weight of the wet membrane (W_{wet}) was measured after removing the excess water from the surface of the membrane. The membrane was dried at 100 °C for 24 h and the weight of the dry membrane (W_{dry}) was measured. The water uptake was calculated using Eq. (4) [23,24].

$$\text{Water uptake (\%)}=\frac{\mathrm{W}_{wet}\times\mathrm{W}_{dry}}{\mathrm{W}_{dry}}\times100 \tag{4}$$

8-4. Oxidation Stability

The oxidation stability test was performed to evaluate the durability of the PEMs for the MFC applications. In this test, the Fenton reagent (3 wt% H_2O_2 solution containing 4 ppm Fe^{2+}) was applied for membrane degradation where a piece of membrane was immersed in 100 mL Fenton reagent and the released free radicals interact with the membrane. Then, the chemical stability of the membrane was measured in terms of the time for the complete deterioration of the membrane [25,26].

RESULTS AND DISCUSSION

1. FTIR Test

The FTIR test results for HNT and DHNT are shown in Fig. 7. The bands at 1,033.57 cm^{-1} and 909.25 cm^{-1} in both spectra were related to the tensile vibration of Si-O-Si and Al-O groups in the HNT structure. The presence of polydopamine on the surface of HNT was further confirmed by the observation of the bands at 1,640.88 cm^{-1} and 1,498.75 cm^{-1}, corresponding to the tensile vibration of N-H and C-C groups in the structure of dopamine [8,9].

In Fig. 8, the FTIR spectra for polystyrene and SPS48* are presented where in the spectrum for polystyrene the peaks at 1,602.78 cm^{-1} and 3,095.62 cm^{-1} correspond to C=C and C-H bonds. On the other hand, the peaks for these bonds can be observed at 1,595.69 cm^{-1} and 3,023.94 cm^{-1} in the spectrum of SPS. In case of SPS48*, there are two peaks at 3,679.28 cm^{-1} and 1,023.30 cm^{-1} which are related to O-H and S=O bonds in the sulfonic acid groups [20,27].

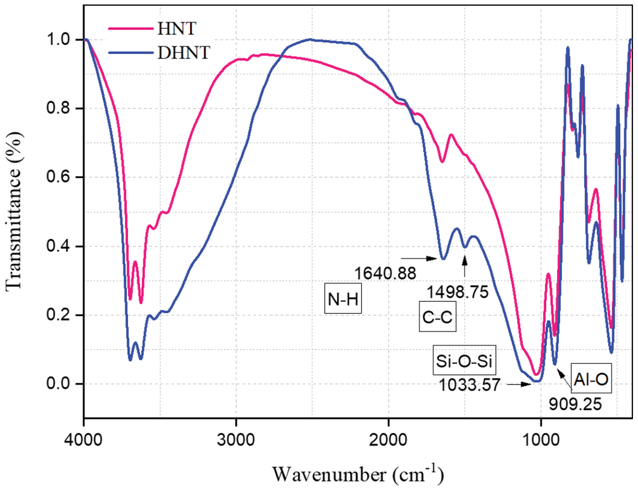

Fig. 7. FTIR test results for HNT and DHNT.

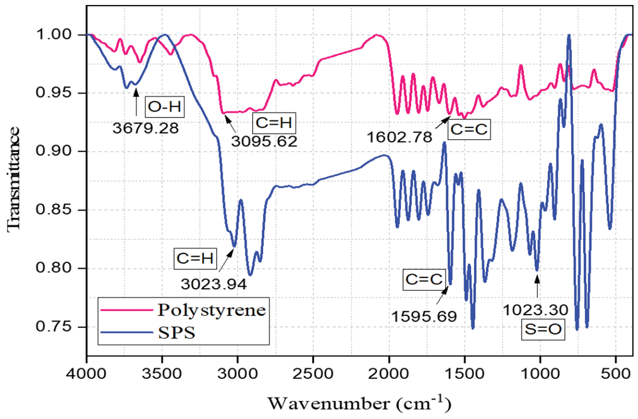

Fig. 8. FTIR test results for polystyrene and SPS48*.

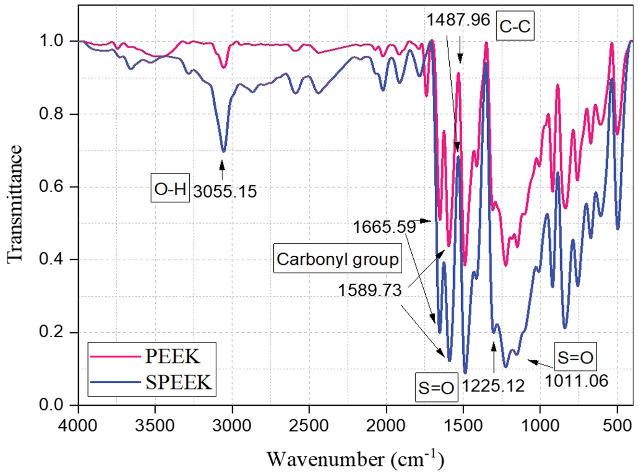

Fig. 9. FTIR test results for PEEK and SPEEK.

Therefore, the sulfonation of polystyrene is confirmed by observing the related peaks in the spectrum of SPS.

The FTIR test results for PEEK and SPEEK are reported in Fig. 9 where the bands at 1,589.73 cm^{-1} and 1,665.59 cm^{-1} are related to the carbonyl group and the band at 1,487.96 cm^{-1} is related to the tensile vibration of C-C group [20] in the structure of PEEK and SPEEK. In the case of SPEEK, the band observed at 3,055.15 cm^{-1} is attributed to O-H in the structure of sulfonic acid groups. The presence of sulfonic acid groups is further confirmed by the bands at 1,011.06 cm^{-1} and 1,225.12 cm^{-1} which are linked to the tensile vibration of S=O bond [20].

2. TGA Test

To investigate the thermal degradation of HNT and DHNT, a TGA test was carried out and the results presented in Fig. 10. Both HNT and DHNT started weight loss after 400 °C, indicating desired durability for the MFC applications. In addition, DHNT exhibited more weight loss between 400 °C to 750 °C, which can be linked to the polydopamine decomposition. Therefore, the successful grafting of polydopamine on HNT was confirmed through the FTIR and TGA test results. Note that the weight percentage of polydopamine on DHNT was estimated to be 2.8% based on the results of TGA analysis.

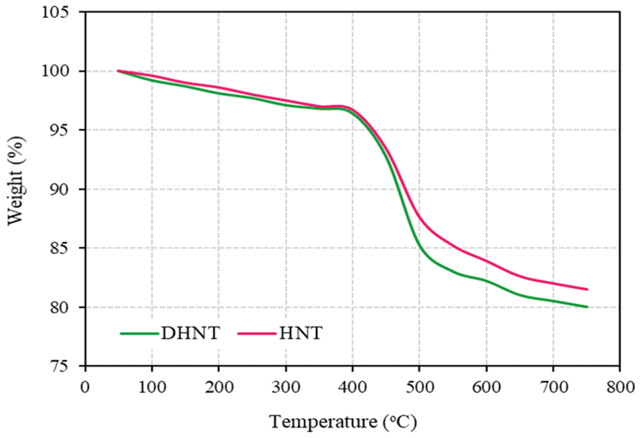

Fig. 10. TGA test results for HNT and DHNT.

3. IEC and DS

The IEC and DS of the synthesized SPEEK were studied and to recheck the obtained results. SPEEK was dispersed in 0.05 M hydrochloric acid for 24 h to reactivate the blinded proton barrier sites and after washing with DI water, IEC test was carried out in which the results did not differ from the former test. It was observed that the SPEEK prepared at T=45 °C and 2.5 h sulfonation time showed IEC equal to 2.1±0.1 mmol/g and 72%±2 degree of sulfonation. Furthermore, PEEK was sulfonated at T=60 °C/sulfonation time=2.5 h, T=55 °C/sulfonation time=3 h and T=45 °C/ sulfonation time=3.5 h to study the effect of various sulfonation conditions, but for these three cases the obtained SPEEEK was dissolved in water during the neutralization step. Thus, sulfonation reaction time and temperature more than 2.5 h and 45 °C would create highly hydrophilic SPEEK that can dissolve in water.

The comparison of the results obtained in this research for the synthesized SPEEK with other researches in this field shows higher IEC and DS, even though the sulfonation process was performed at lower temperature and/or lower reaction time. Xie et al. [28] sulfonated PEEK at H_2SO_4/PEEK equal to 20 mL/g, sulfonation time of 3 h and reaction temperature of 50 °C and the prepared SPEEK showed DS equal to 69.3%. In another study, Parnian et al. [5] synthesized SPEEK with IEC equal to 1.23 mmol/g and DS equal to 40.23% while they used the same sulfonation conditions as Xie et al. [28], except the reaction time was changed to 4 h. Gong et al. [12] synthesized SPEEK with IEC equal to 1.36 mmol/g and DS equal to 45.4% at reaction time of 2 h, reaction temperature of 50 °C and H_2SO_4/PEEK equal to 16.6 mL/g. The significant increase in IEC and DS values of the synthesized SPEEK in this study can be related to the following items:

A) Complete dispersion and ultrasonication of PEEK polymer in the H_2SO_4 before the reaction that increased the contact area between the reactants and prevented the agglomeration of PEEK in the acid. In addition, uniform reaction of PEEK particles could be expected.

B) Reducing the amount of water that was used during the washing step which diminished the blockage of sulfonic acid groups.

The IEC and DS test results for the synthesized SPS samples are presented in Table 2. It was observed that increasing the sulfona-

Table 2. IEC and DS test results for the synthesized SPS samples

Sample	Temperature (°C)	Sulfonation time (hr)	IEC (mmol g^{-1})	DS (%)
SPS24	25	24	1.22	14
SPS48	25	48	1.60	19
SPS24*	25	24	2.24	28
SPS48*	25	48	2.34	30

tion reaction time and temperature can lead to an extraordinary increase in the hydrophilicity of sulfonated polystyrene, which makes it soluble in water during the neutralization step. Due to the higher IEC and DS values for SPS48*, it was selected as the additive for the SPEEK membrane. Performing the sulfonation process in the solution phase resulted in the uniform dispersion of the sulfonic acid groups in SPS48*. The latter was confirmed by implementing several IEC tests for the synthesized sample in which the results did not differ.

The IEC and DS of SPS48* compared to those of other researches in Table 3. De Leon-Condes et al. [29], Fukuhara et al. [30], and Peng et al. [31] applied extreme operating conditions (higher temperature and H_2SO_4/polystyrene ratio) to the polystyrene sulfonation and achieved much lower IEC or DS compared to this work. This can be related to the novel and optimized sulfonation method that was performed in this research as is mentioned below:

A) The enhancement of the contact between polymer and acid by conducting the sulfonation process in the solution phase.

B) Accelerating the reaction between reagents by the application of silver nitrate as the catalyst.

C) Increasing the sulfonation time instead of higher temperature and more H_2SO_4/polystyrene ratio. It is proved that the effect of sulfonation time is more pronounced.

4. Water Uptake

In PEM, the protons are transferred by the help of proton conductive sites which are active in the presence of water. Therefore, higher water uptake of the membrane can ensure the desired proton transportation ability. The results of the water uptake test for the fabricated membranes are shown in Fig. 11, which generally the addition of the hydrophilic compounds (such as DHNTS) increased the water uptake of the modified SPEEK membranes [32]. Furthermore, increasing the weight percent of the additives improved the water uptake, e.g., the water uptake of S-2.5/DHNTS-0.05 was 33.3% higher than the neat S-2.5 membrane. The higher water uptake can be related to the hydroxyl and amine groups in the structure of polydopamine, as well as the surface modification of DHNT by a hydrophilic silane. In addition, the tubular structure of HNT (Fig. 12) can provide more space for water adsorption. However, the water adsorption of the S-2.5/DHNTS-0.15 membrane was reduced 12% compared to the S-2.5/DHNTS-0.1 membrane, which can be attributed to increasing the viscosity of the polymer solution, which makes less porosity in the structure of the membrane. In addition, the agglomeration of the nanoparticles may result in the reduction of the polar groups for bonding with the water molecules [14].

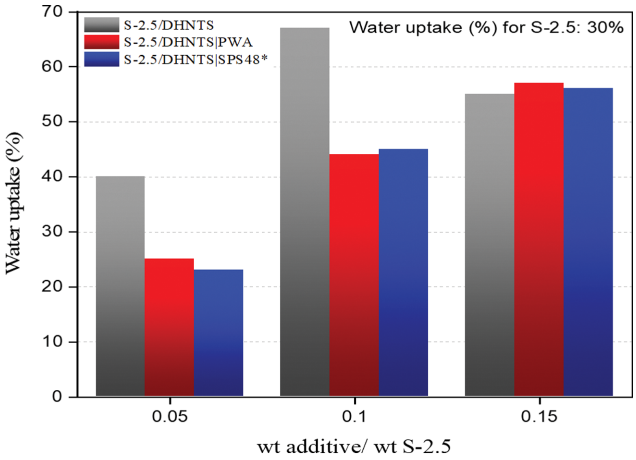

Fig. 11. Water uptake test results for the fabricated membranes.

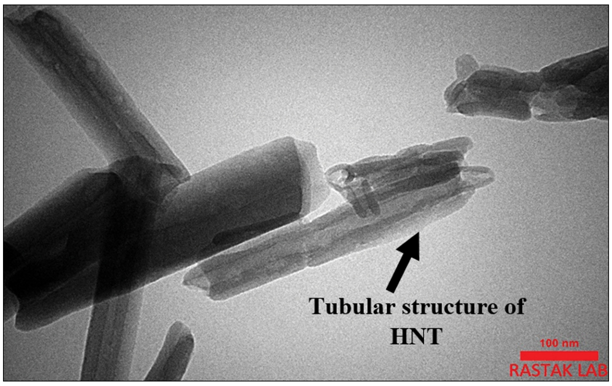

Fig. 12. TEM photograph of HNT.

On the other hand, the addition of PWA or SPS48* to the S-2.5/DHNTS membrane improved the water uptake of the modified membranes compared to the neat membrane at higher concentrations of the additives. Furthermore, their water uptake was less than

Table 3. Comparison of IEC and DS of the synthesized SPS48* with those of other studies

Author	Temperature (°C)	Sulfonation time (hr)	H_2SO_4/Polystyrene (ml/g)	IEC (mmol g^{-1})
This work	25	48	4	2.34
De Leon-Condes et al. [29]	95	1.5	16	1.2
Fukuhara et al. [30]	30	5	NA	1.5
Peng et al. [31]	30	4	40	0.75

Table 4. Comparison of the water uptake for S-2.5 membrane with the neat SPEEK membrane in other researches

Author	DS (%)	Water uptake (%)
This work	72±2	30
Parnian et al. [5]	40.2	6
Ayaz et al. [34]	53	16.3
Zhang et al. [9]	62.7	17
Parnian et al. [35]	65	20

the corresponding membrane in the S-2.5/DHNTS group, i.e., the water uptake of S-2.5/DHNTS|SPS48*-0.1 and S-2.5/DHNTS|PWA-0.1 was 49% and 52% lower than the water uptake of S-2.5/DHNTS-0.1. It seems that the effect of DHNTS on the water uptake of the modified membranes was more pronounced. Blending PWA or SPS48* in the polymer solution provided more hydrophilic groups for adsorption of water molecules but enhanced the viscosity of the polymer solution, which decreased the membrane porosity and water uptake [26,33]. Besides, the addition of PWA or SPS may block the inlets of the HNT tubular structure and reduced its water adsorption. It seems that the effect of hydrophilic groups was more pronounced at higher concentrations of PWA or SPS48*.

The water uptake of commercial Nafion117 membrane was reported as 12.41% [5], which in comparison to the neat SPEEK membrane and modified membranes was much lower, e.g., the water uptake of S-2.5/DHNTS|PWA-0.15 membrane was 57% that was almost five times more. The ability of the S-2.5 membrane to adsorb more water than Nafion can be linked to its inherent hydrophilicity, while Nafion is more hydrophobic [21]. Moreover, the ionic bonding between the water molecules and the sulfonic acid groups on the surface of SPS48*, the presence of hydrophilic groups in the structure of DHNTS and its tubular form, and the strong acidity and cage structure of PWA significantly increased the water uptake of the modified membranes. In Table 4, the water uptake of the S-2.5 membrane is compared with the neat SPEEK proton exchange membranes in other researches. Higher DS means the presence of more SO_3H groups in the matrix of the membrane and that enhances the ability to adsorb water.

5. Proton Conductivity

The proton conductivity of the fabricated membranes is presented in Table 5 where the same trend as the water uptake was observed, i.e., the proton conductivity of the S-2.5/DHNTS membrane showed a maximum while the other two had a minimum. Furthermore, the proton conductivity increased as the relative humidity increased. Janik et al. [36] reported that the activation energy for proton migration in phosphotungstic acid decreased from 103.3 kJ mol^{-1} in the anhydrous form to 11.2 kJ mol^{-1} when the acid adsorbed water [36]. Higher relative humidity makes a rise in the number and size of the proton transfer channels in the structure of the membrane and improves the ability of the membrane to transfer protons [5].

The powerful acid-base ionic bonds between the sulfonic acid groups in SPEEK and the amine groups in DHNTS facilitated the proton hopping between ion conductive sites, thereby increasing the proton conductivity of the S-2.5/DHNTS membrane compared to the neat S-2.5 membrane. Furthermore, the application of HNT, which has suitable dispersibility in the polymer solution, led to uniform distribution of proton conductive channels through the bulk of membrane structure and facilitated the transport of protons [9]. At higher concentration of DHNTS, reduction of proton conductivity was observed, which may be related to the agglomeration of particles and decrease in water uptake. Reduction in porosity of the membrane due to the presence of large amounts of DHNTS can decrease the number of polar groups for bonding with the water molecules.

The addition of PWA or SPS48* to the polymer solution resulted in significant increase in the proton conductivity of the S-2.5/DHNTS|SPS48* and S-2.5/DHNTS|PWA compared to S-2.5/DHNTS and neat S-2.5 membranes at the higher concentrations of the additives. It can be concluded that the presence of PWA and SPS48* compensated the negative effect of high concentration of DHTNS and enhanced the proton conductivity of the fabricated membranes [37]. The hydrophilic character of PWA and the presence of sulfonic acid groups in the structure of SPS48* increased the ability of membrane to adsorb water, as well as the ease of separation and transfer of protons [37]. However, the positive effect of DHNTS was more pronounced than PWA and SPS48* at lower concentrations where the proton conductivity of S-2.5/DHNTS-0.05 was 80% and 98% higher than that of S-2.5/DHNTS|SPS48*-0.05 and S-2.5/DHNTS|PWA-0.05 at RH=100% and that may be related to the less agglomeration of the nanotubes at lower concentrations.

As presented in Table 5, the presence of SPS48* provided more sulfonic acid groups in the structure of the membrane and resulted in the creation of more proton transfer barriers [27]. In addition, the acid-base linkage between the alkaline groups in DHNTS and

Table 5. Proton conductivity of the prepared membranes at different concentrations of the additives; cell temperature: 60 °C

Membrane	Proton conductivity (S/m)								
	RH: 60%			RH: 80%			RH: 100%		
S-2.5	1.10			1.62			2.59		
	Additives/SPEEK: 0.05			Additives/SPEEK: 0.1			Additives/SPEEK: 0.15		
	RH: 60%	RH: 80%	RH: 100%	RH: 60%	RH: 80%	RH: 100%	RH: 60%	RH: 80%	RH: 100%
S-2.5/DHNTS	3.55	3.60	4.22	2.22	2.26	2.81	1.38	1.41	1.68
S-2.5/DHNTS|SPS48*	1.95	2.07	2.35	3.92	4.11	4.68	4.53	4.75	5.42
S-2.5/DHNT|PWA	1.77	1.86	2.13	3.55	3.74	4.25	4.12	4.32	4.94

Table 6. Comparison of proton conductivity for S-2.5 membrane with the neat SPEEK membrane in other researches (relative humidity: 100%)

Author	Cell temperature (°C)	DS (%)	Proton conductivity (S/m)
This work	60	72±2	2.59
Chen et al. [39]	60	65	1.9
Wang et al. [38]	25	68.7	1.22
Zhang et al. [9]	25	62.7	1.50
Parnian et al. [5]	60	40.2	2.10

Table 7. Comparison of the proton conductivity for the modified membranes in this study with those of the other studies

Reference	DS (%)	Additive/SPEEK (wt%)	Additive type	Cell temp. (°C)	Proton conductivity (S/m)
This work	72	0.15	DHNTS|SPS48*	60	5.42
This work	72	0.15	DHNTS|PWA	60	4.94
This work	72	0.05	DHNTS	60	4.22
Rico-Zavala et al. [15]	70	0.15	PWA-coated HNT	25	2.70
Chen et al. [32]	64.9	0.05	Sulfonated HNT	55	4.50
Zhang et al. [9]	62.7	0.10	Sulfonated HNT	25	2.50
Zhang et al. [9]	62.7	0.05	Neat HNT	25	1.10
Rico-Zavala et al. [15]	70	0.15	Neat HNT	25	2.50

acidic groups in SPEEK was improved, thereby increasing the intensity of the proton transfer in S.2.5/DHNTS|SPS48* membrane. The proton conductivity of the S-2.5/DHNTS|SPS48*-0.05 and S-2.5/DHNTS|SPS48*-0.15 was 2.35 S/m and 5.42 S/m, respectively. Furthermore, the addition of DHNTS|PWA not only made additional proton transfer pathways in the membrane structure, but also the strong acidity of PWA increased the ease of proton separation and transfer. The strong acid-base bond in the presence of more nanotubes further resulted in the increase in the proton conductivity of the S-2.5/DHNTS|PWA from 2.13 S/m (additives/SPEEK=0.05) to 4.94 S/m (additives/SPEEK=0.15). Notably, S-2.5/DHNTS|SPS48* membrane exhibited higher conductivity than S-2.5/DHNTS|PWA membrane, which can be linked to the presence of hydrophilic and proton conductive groups (sulfonic acid) in the structure of SPS48*.

The proton conductivity of the Nafion117 membrane was measured as 4.50 S/m [5], which was 74% and 168% higher than the conductivity of neat SPEEK and S-2.5/DHNTS-0.15 membranes at RH=100%, respectively. This was related to the extraordinary hydrophilic/hydrophobic phase separation of Nafion that facilitated the proton transfer through its structure [5,12]. On the other hand, it is interesting that the proton conductivity of S-2.5/DHNTS|SPS48*-0.15 and S-2.5/DHNTS|PWA-0.15 membranes was 20% and 10% higher than Nafion117 membrane, respectively; that was connected to the additional proton transfer pathways that DHNTS, PWA and SPS made in the matrix of the membrane.

Comparison of the proton conductivity for the neat S-2.5 membrane and the synthesized neat SPEEK membrane in other researches at RH=100% is shown in Table 6 with the temperature of the cell and DS of the membrane as two effective factors. Higher DS means the presence of more sulfonic acid groups in the structure of the SPEEK, leading to the higher number of proton conductive sites in the membrane. The proton conductivity of the S-2.5 membrane was higher than that of Parnian et al. [5], Wang et al. [38], Chen et al. [39] and Zhang et al. [9] because of the higher DS. In addition, the higher temperature of the cell enhanced the molecular mobility in the membrane and caused more proton transport through the water molecules [5]. The difference in the cell temperature of this research (60 °C) and those of Zhang et al. [9] and Wang et al. [38] (25 °C) may lead to 73% and 112% variation in the proton conductivity, respectively.

The proton conductivity (as a performance index for PEMs) of the modified membranes in this work was compared with the results in other studies (Table 7). In the case of modified SPEEK PEMs with neat HNT [9,15], the fabricated PEMs in this study achieved much higher proton conductivity. This can be connected to the surface modification of HNT with polydopamine, which improved the water storage within the membrane. On the other hand, Rico-Zavala et al. [15], Chen et al. [32], and Zhang et al. [9] coated HNT with hydrophilic compounds such as PWA and sulfonic acid groups. However, S-2.5/DHNTS|SPS48*-0.15 and S-2.5/DHNTS|PWA-0.15 membranes exhibited higher conductivity com-

Table 8. Oxidation stability test results for the selected membranes

Membrane	Degradation time (min)
S-2.5	207
S-2.5/DHNTS-0.15	380
S-2.5/DHNTS|SPS48*-0.15	340
S-2.5/DHNTS|PWA-0.15	230
SPEEK/Fe$_2$TiO$_5$ [17]	62
SPEEK/sulfonated ZrO$_2$ [41]	102
SPEEK/graphene oxide|TiO$_2$ [42]	71

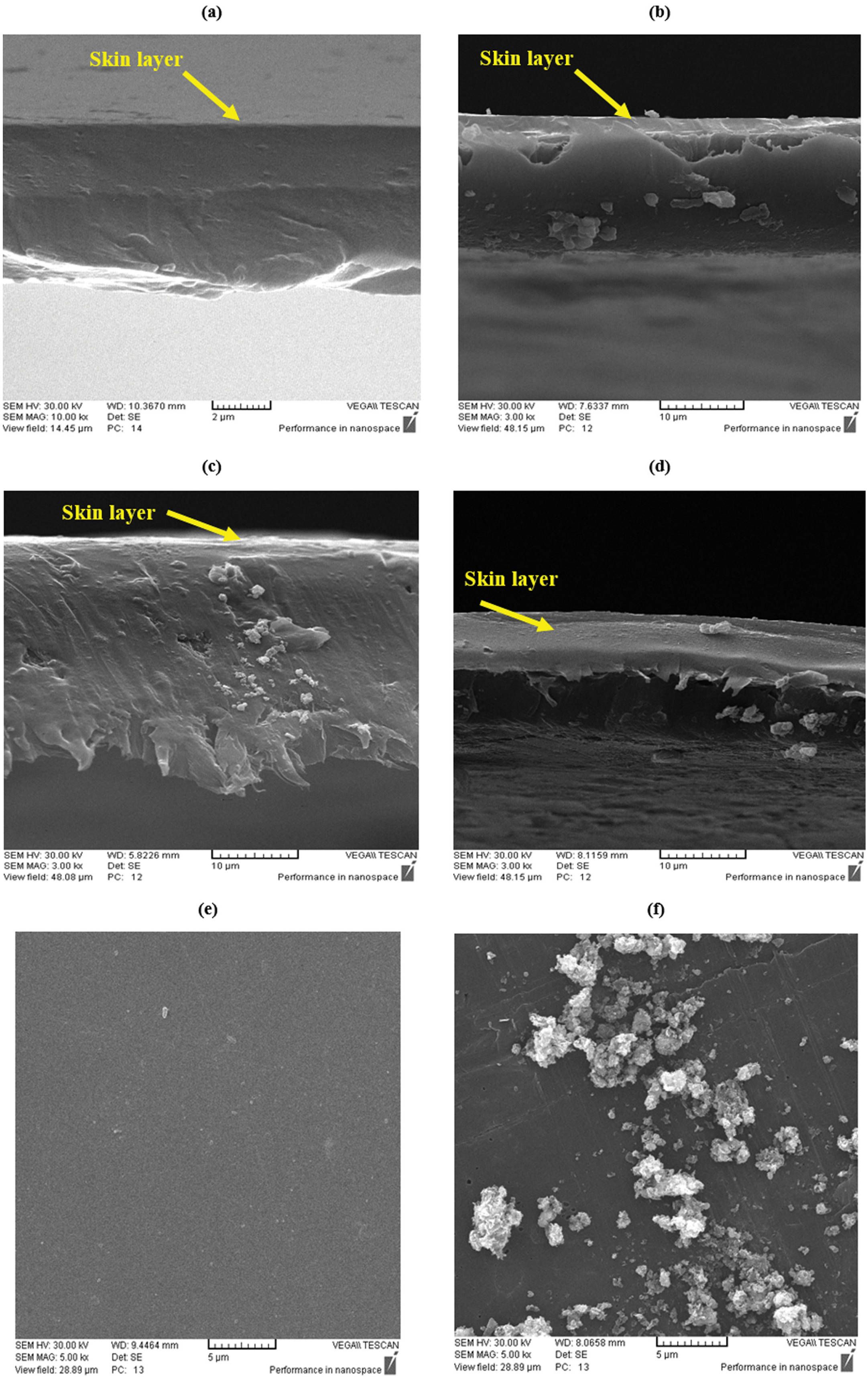

Fig. 13. Cross sections SEM micrographs for (a) S-2.5, (b) S-2.5/DHNTS-0.1, (c) S-2.5/DHNTS|SPS48*-0.1 (d) S-2.5/DHNTS|PWA-0.1 and SEM micrographs from the surface of (e) S-2.5, (f) S-2.5/DHNTS-0.1.

pared to the aforementioned membranes. This can be related to (a) higher DS of SPEEK in this research due to the modified sulfonation process in this study; (b) the silanization of DHNT, which led to the more uniform distribution of proton transfer sites in the PEM, and (c) higher operating temperature that facilitated the proton transportation by enhancing the mobility of the water molecules.

6. Oxidation Stability

An oxidation stability test was conducted to investigate the durability of the fabricated membranes. From the reaction of H_2O_2 and Fe^{2+}, two radicals [HO· and HOO·], which cause the membrane degradation in the fuel cell, are released [25]. Therefore, this test can measure the chemical stability of the membrane. The results of the test for the membranes with higher proton conductivity are presented and compared with those of other studies in Table 8 where the selected membranes exhibit acceptable oxidation stability to be used in the fuel cells. The creation of the strong acid-base bond between the sulfonic acid groups at SPEEK and the alkaline groups in the DHNTS structure and the sticky nature of polydopamine enhanced the chemical stability and increased the degradation time of the S-2.5/DHNTS membrane compared to the neat S-2.5 membrane [8]. However, the lower oxidation stability of S-2.5/DHNTS|SPS48*-0.15 and S-2.5/DHNTS|PWA-0.15 compared to S-2.5/DHNTS-0.15 can be linked to the instability of polystyrene and increased reactivity of SPEEK in presence of PWA. The complete degradation time for the Nafion117 membrane was reported as 450 min [40], which was higher than those of the selected membranes in this work; that is linked to the hydrophobic tetrafluoroethylene backbone of Nafion. As indicated in Table 8, different types of additives, namely metal oxides, sulfonated compounds, and blended fillers, were used in PEMs, but the achieved oxidation stabilities are much lower than the ones in this study; that may be related to the application of nanotubes in this study. The strong interaction between DHNTS and SPEEK as well as the tubular structure of HNT reduced the reaction between the free radicals and the polymer chains.

7. SEM

The SEM micrographs for the selected PEMs are illustrated in Fig. 13 where uniform skin layers were observed related to the adaptability of the additives [43,44], and the membrane fabrication method with solvent evaporation step, making slow phase inversion that allows the skin layer to develop. Thin and uniform skin layer further leads to the lower electrical resistance of the membrane [45]. Furthermore, the presence of DHNTS in the skin layer of the membranes is clearly visible in Fig. 13(b), (c), (d). The formation of the thin and uniform skin layer further shortened the proton transferring pathways and enhanced the proton conductivity. As can be seen in Fig. 13(f), agglomeration of DHNTS occurred in the structure of the S-2.5/DHNTS-0.1 membrane. In comparison, there was no observable agglomeration in the S-2.5 membrane (Fig. 13(e)). Agglomeration causes the deactivation of active proton transferring channels. It can be introduced as the main drawback of using nanotubes for the PEM application. However, the silanization of DHNT in this research reduced the possibility of agglomeration in the modified membranes.

8. MFC Test

The MFC test results for the selected membranes are reported in Fig. 14. Accordingly, the MFC equipped with S-2.5 and Nafion117 membranes produced the powers equal to 6.96 mW/m^2 and 8.20 mW/m^2, as the maximum produced power. Furthermore, for the cell equipped with S-2.5/DHNTS-0.05 membrane, the power equal to 7.67 mW/m^2 was obtained as the highest value, which was slightly less than Nafion117 membrane. The differences in the power values can be attributed to the difference in the proton conductivities of the membranes. More proton conductivity actually means higher ability to transmit protons and produce more power [46]. For instance, the conductivity of S-2.5/DHNTS-0.05 membrane was 62% higher than that of neat S-2.5 membrane. This can be the reason for the better MFC performance of the membrane, modified with DHNTS compared to the neat S-2.5 membrane. However, the power density was reduced with a sharp drop in the voltage at higher current values. In fact, V is the potential difference between the two electrodes which decreases at higher current values due to the activation of the electrodes [28].

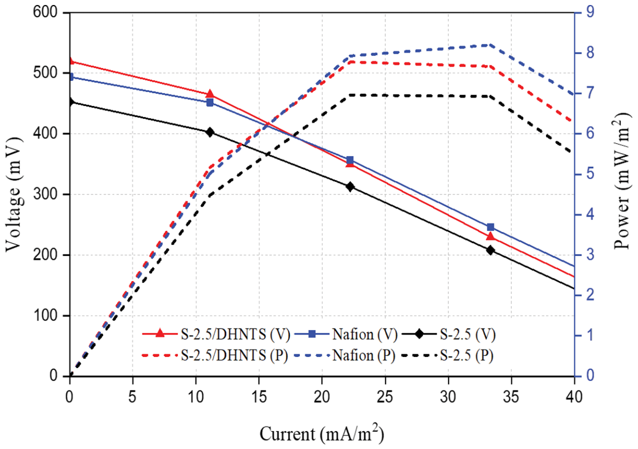

Fig. 14. MFC performance test results: V, voltage; P, power.

9. Water Crossover

One of the main drawbacks of Nafion is its considerable water crossover which negatively affects the MFC performance in the long term operation. Therefore, it is important that PEM prevents water diffusion through its structure. Accordingly, a water crossover test for the membranes with the highest proton conductivities (S-2.5/DHNTS-0.05, S-2.5/DHNTS|SPS48*-0.15 and S-2.5/DHNTS|PWA-0.15) was performed using the ultrafiltration setup at the pressure of 2 bars. The results demonstrated that there was no permeation of water through the membranes, which confirms the nonporous skin layer of the membrane.

10. Contact Angle

The results of the contact angle test for the selected membranes are reported in Table 9. For all fabricated membranes, the average contact angle was lower than the neat S-2.5 membrane, which was because of the hydrophilic additives. Furthermore, the contact angle of the S-2.5/DHNTS-0.1 membrane was lower than that of the S-2.5/DHNTS|SPS48*-0.1 and S-2.5/DHNTS|PWA-0.1 membranes; that can be linked to the less surface roughness of the membrane [47]. The contact angle of the Nafion117 membrane was reported as 89° [47]; higher than the contact angle of the fabricated membranes in this research. This is related to the hydrophobicity

Table 9. Contact angle test results for the selected membranes

Membrane	Contact angle (°)
S-2.5	87.7±2.8
S-2.5/DHNTS-0.1	82.7±2.3
S-2.5/DHNTS|SPS48*-0.1	85.2±2.7
S-2.5/DHNTS|PWA-0.1	83.5±3.4

of the Nafion117 membrane, which can affect the water retention ability and the proton conductivity of the Nafion-based membranes.

CONCLUSIONS

Proton exchange membranes were prepared based on the SPEEK polymer. The sulfonation of PEEK was through a modified method to assess higher degree of sulfonation. Polydopamine-coated HNTs alone and blended with the sulfonated polystyrene and phosphotungstic acid were used to create additional proton transfer pathways in the SPEEK membrane and to increase proton conductivity. Blending nanotubes with hydrophilic compounds was an effective strategy to fabricate highly conductive and durable PEMs. Performing the sulfonation of polystyrene in the solution phase was a novel approach in this research, which led to higher and uniform hydrophilicity of the sulfonated sample. The results showed higher proton conductivity of the modified membranes because of the presence of sulfonic acid groups in the structure of sulfonated polystyrene (SPS), strong acid-base bonding between DHNTS and SPEEK as well as the high acidity of phosphotungstic acid (PWA). Furthermore, the membranes containing PWA and SPS showed higher proton conductivity compared to the Nafion117 membrane. 20% and 10% higher conductivities were observed for SPS- and PWA-coated PEMs compared to the Nafion117 membrane, respectively. The presence of DHNTS in the modified membranes further caused significant improvement in the durability and MFC performance, compared to the neat S-2.5 membrane. For instance, the degradation time for S-2.5/DHNTS-0.15 was 380 min, while in case of neat S-2.5 membrane, this was 207 min. Besides, nearly equal maximum power was produced by both Nafion117 and DHNTS-modified PEM. Therefore, the oxidation stability and MFC test results confirm that the modified membranes are suitable candidates for MFC applications.

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NOMENCLATURE

Symbols & Abbreviations

PEEK : poly(ether ether ketone)
SPEEK : sulfonated poly(ether ether ketone)
SPS : sulfonated polystyrene
PWA : phosphotungstic acid
HNT : halloysite nanotubes
DHNTS : polydopamine-coated HNT modified by silane
MFC : microbial fuel cell
PEM : proton exchange membrane
NMP : N-methyl-2-pyrrolidine
THF : tetrahydrofuran
IEC : ion exchange capacity [mmol g^{-1}]
DS : degree of sulfonation [%]
σ : proton conductivity of the membrane [S/m]
L : thickness of membrane [m]
R : membrane resistance [Ω]
A : effective area of the membrane [m^2]
W : mass of the polymer/membrane [gr]
M_{NaOH} : molarity of NaOH titrant [M]
V_{NaOH} : volume of NaOH titrant [ml]
M_p : molecular weight [g mol^{-1}]

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