Investigation of MIL-53(Fe)-(COOH)₂ as a Filler in Sulfonated Polystyrene/Polyethylene Membrane for Application in Direct Methanol Fuel Cell

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ABSTRACT: *Some of the main challenges of direct methanol fuel cell membranes are proton conduction and high selectivity required. In the present study, new proton exchange membranes were developed using sulfonated polystyrene (SPS), polyethylene (PE), and a type of metal-organic framework (MOF) used in the direct methanol fuel cells (DMFCs). MIL-53(Fe)-(COOH)₂ is a metal-organic framework prepared in this study, and it was used as a filler in manufacturing the membranes. Characterization of these membranes was performed by SEM, FTIR, and TGA. SEM images showed that the MIL-53(Fe)-(COOH)₂ particles have a porous surface without any agglomeration. Also, the conductivity of proton, methanol permeability, oxidation resistance, and ion conductance tests were performed on membranes to evaluate membrane performance. The effect of MIL-53(Fe)-(COOH)₂ content in membranes was also studied. The embedding of MIL-53(Fe)-(COOH)₂ in SPS/PE membrane increases proton conductivity and selectivity factor. Finally, the prepared membranes were applied to the direct methanol fuel cell, and the performance of the membranes was examined. The result was a maximum peak power density of 23.61 mWcm⁻² with a maximum current density of 138.46 mAcm⁻².*

KEYWORDS*: MIL-53(Fe)-(COOH)₂; Metal-organic framework; Sulfonated polystyrene; Proton exchange membrane; Proton conductivity.*

INTRODUCTION

Polymer electrolyte membrane fuel cells are electrochemical devices that offer a greener future for advancing universal energy resources with environmental and economic benefits. The fuel cell is one of the renewable sources that has attracted the attention of many researchers in recent years. Fuel cells convert chemical energy into electrical energy. One type of fuel cells is the Proton-Exchange Membrane Fuel Cell (PEMFC) [1-3]. PEMFC has received a lot of attention because of its high efficiency, high power density, low-temperature operation, low environmental pollution, low noise pollution, easy maintenance, etc. [4-5]. A PEMFC is formed by several components. The main components of PEMFC include are an anode, a cathode, a catalyst employed in electrodes and a membrane. The membranes used in the fuel cells are among the main components of the proton-exchange fuel cell, which are responsible for conducting the protons from the anode side where oxidation takes place towards the cathode side, where reduction reactions are going to occur [6-9]. The anodic and cathodic reactions in direct methanol fuel cells are seen below:

Anodic reaction: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathodic reaction: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
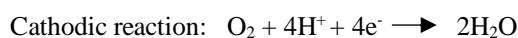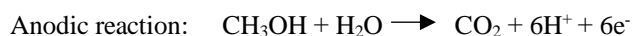
DMFCs use regenerative methanol as fuel. One of the significant barriers to the broad commercial use of DMFCs on a large scale is Methanol CrossOver (MCO). Methanol penetration from the anode to the cathode using the polymer electrolyte membrane can severely degrade the activity of the cathode catalyst, which limits the use of PEMs in DMFCs. Given the above, researchers have made great efforts to develop the PEMs to minimize the methanol crossover problem [10-11]. These membranes must be capable of conducting protons and preventing electrical and chemical particles from passing through. Many membranes have been prepared and studied for this purpose in recent years, including Nafion-based membranes, polyetherether ether ketone (PEEK), polysulfone, polyvinyl chloride, polystyrene, etc. [12-15].

In recent years, perflurosulfonated based membranes such as Nafion are most popular membranes in Direct Methanol Fuel Cell (DMFC) applications due to high proton conductivity as well as excellent mechanical, chemical and thermal stability [16-17]. However, Nafion membranes have some drawbacks such as noticeable rate of methanol crossover, low proton conductivity at temperatures above 80 ℃ and high cost. In this regard, the main challenge for DMFC development is improving proton conductivity with a parallel reduction of methanol crossover [18]. Incorporation of inorganic additive to polymer matrix and blending of two suitable membranes are important ways for preparing alternative membranes.

In recent years, our research team has developed polystyrene-based membranes. Since adding proper fillers can help the membranes in their primary task, we decided to use them. A Metal-Organic Framework (MOF) is a group of organic-metallic materials studied recently for many applications [19, 20]. One application of this group is their use as fillers in preparing membranes. These materials have been used by researchers because they can form strong bonds with polymers and prevent cracks and fissures in the produced membranes. MOFs are a large group of organic-metallic compounds [21-23]. MIL-53(Fe)-$(COOH)_2$ is one of the MOFs, which can assist the membranes of proton-exchange fuel cells in conducting protons from the anode to the cathode because it contains carboxyl functional groups. Therefore, in the present study, first MIL-53(Fe)-$(COOH)_2$ was synthesized, and then sulfonated polystyrene was prepared. Finally, some membranes for direct methanol fuel cells were produced by prepared sulfonated polystyrene, MIL-53(Fe)-$(COOH)_2$, and polyethylene. Characterization of these membranes was performed by Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FT-IR) Spectroscopy, and ThermoGravimetric Analysis (TGA) methods. Also, the conductivity of proton, methanol permeability, oxidation resistance, and ion conductance tests were studied to evaluate the performance of the membrane. The effect of MIL-53(Fe)-$(COOH)_2$ content in membranes was also studied. Finally, the prepared membranes were applied to the DMFC, and the performance of the membranes was investigated.

EXPERIMENTAL SECTION
Materials

Dichloromethane, acetic anhydride, HF, sulfuric acid 98%, $FeCl_2 \cdot 4H_2O$, 1, 2, 4, 5-benzenetetracarboxylic acid, N, N′-dimethylformamide, p-Xylene, and polystyrene (PS) were obtained from Merck, Germany. Linear low-density polyethylene (LDPE) was bought from Bandar Imam petrochemical company, Iran (ρ = 0.92 g/cm³, water adsorption 0.01 %, and melting temperature range 120-160 ℃).
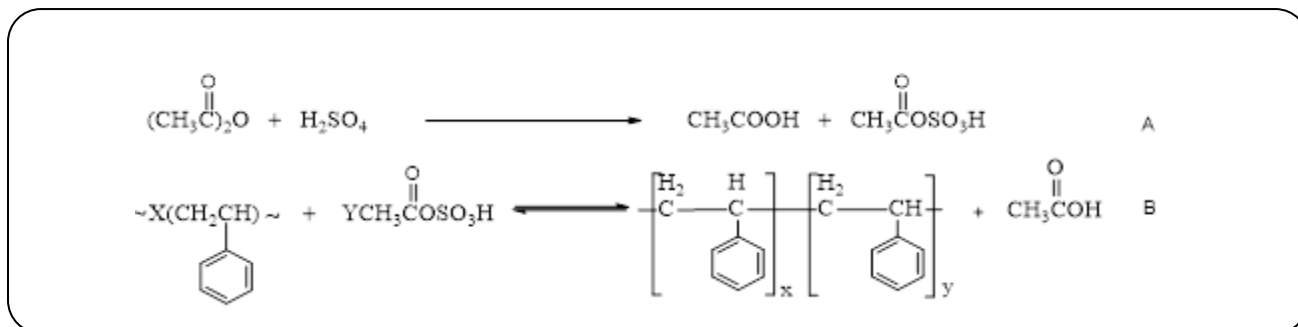
Fig. 1: Schematic reaction of A) acetylsulfate generation and B) SPS generation

Instrumentation

A JASCO-460 FT-IR spectrometer was applied for recording FT-IR spectra. The spectral range was 4000-400 cm^{-1}.

MIRA3 TESKAN & MIRA2 TESKAN SEM were used to observe surface morphology and the status of the sample. Dry membranes were manually fractured after cooling in the liquid nitrogen. Samples were sputter-coated with gold (15 nm thickness), and the images were taken by SEM at 5kV.

TGA was obtained by a TGA/DSC 1 (TGA Q50) at a heating rate of 10 K min^{-1} under an N$_2$ atmosphere at a flow rate of approximately 50 mLmin^{-1}.

A four-probe method by electrochemical impedance spectroscopy (EIS) with a Zahner potentiostat/galvanostat electrochemical workstation model PGSTAT over a frequency range of 4 MHz - 1 Hz with an oscillating voltage of 5 mV was applied to measure the proton conductance of the membrane.

Preparation and characterization
SPS preparation

Makowski et al. method [24-25] was used for preparing the SPS. Herein, first, the acetyl sulfate solution 2.0 M (50 mL) was prepared by mixing a constant amount of acetic anhydride and dichloromethane under the nitrogen atmosphere. It was chilled to 273 K, and sulfuric acid (98 %) was gradually added. It was stirred at room temperature till transparent and a homogeneous solution was achieved. An excess amount of acetic anhydride was used to clear any trace of water, if present. If any trace of water was observed, acetic anhydride has been added to omit it.

For the sulfonation reaction, 20.0 g of polystyrene was dissolved in 500 mL of CH$_2$Cl$_2$ in a round-bottomed flask. Then, it was heated to 313 K to gain total solubilization of polystyrene, and it was purged with nitrogen (40 min).

Then, a fresh acetyl sulfate solution was added. It was stirred for 2 h at 313 K. After adding the sulfonating agent, a clear yellow solution was provided. By adding an extra amount of 2-propanol for 30 min and chilling at room temperature, the reaction was finished. Then, the SPS was isolated. A schematic of the two-step SPS production can be observed in Fig 1. [26].

Synthesis of MIL-53(Fe)–(COOH)$_2$

MIL-53(Fe)–(COOH)$_2$, was prepared according to Ref. [25]. 1.13 g of FeCl$_2$·4H$_2$O, 0.71 g of 1,2,4,5-benzenetetracarboxylic acid, and HF (0.21 mL) and 48 mL of water were added to a 100 mL Teflon-lined steel autoclave. The autoclave was heated in an oven at 473 K for two days. After filtering and washing with water, orange crystals of MIL-53(Fe)–(COOH)$_2$ were obtained. Fig. 2 shows the synthesis method of MIL-53(Fe)–(COOH)$_2$.

Polymer electrolyte membrane (PEM) preparation

Polymer electrolyte membrane (PEM) was prepared similar to previous work [27]. LDPE (1.0 g) was liquefied in 30 mL p-Xylene. It was stirred for 2.0 h and 373 K at 300 rpm to obtain a homogeneous solution. Then, SPS (1.0 g) and MIL-53(Fe)–(COOH)$_2$ (0.25 g) were added. Then, p-Xylene was used to obtain an orange polymer solution. It was cast on different glass plates and dried at 318 K for 24 h and then at 348 K in a vacuum for 12 h. The provided membrane was nominated as SPS-PE- MIL-53(Fe)–(COOH)$_2$. It was converted to the H$^+$ form before using in DMAFC, by boiling first in deionized water (30 min) and in 1.0 M H$_2$SO$_4$ (24 h). Then, remained sulfuric acid was omitted by rinsing and boiling in deionized water. Fig. 3 shows the preparation method of SPS-PE-MIL-53(Fe)–(COOH)$_2$ membrane.
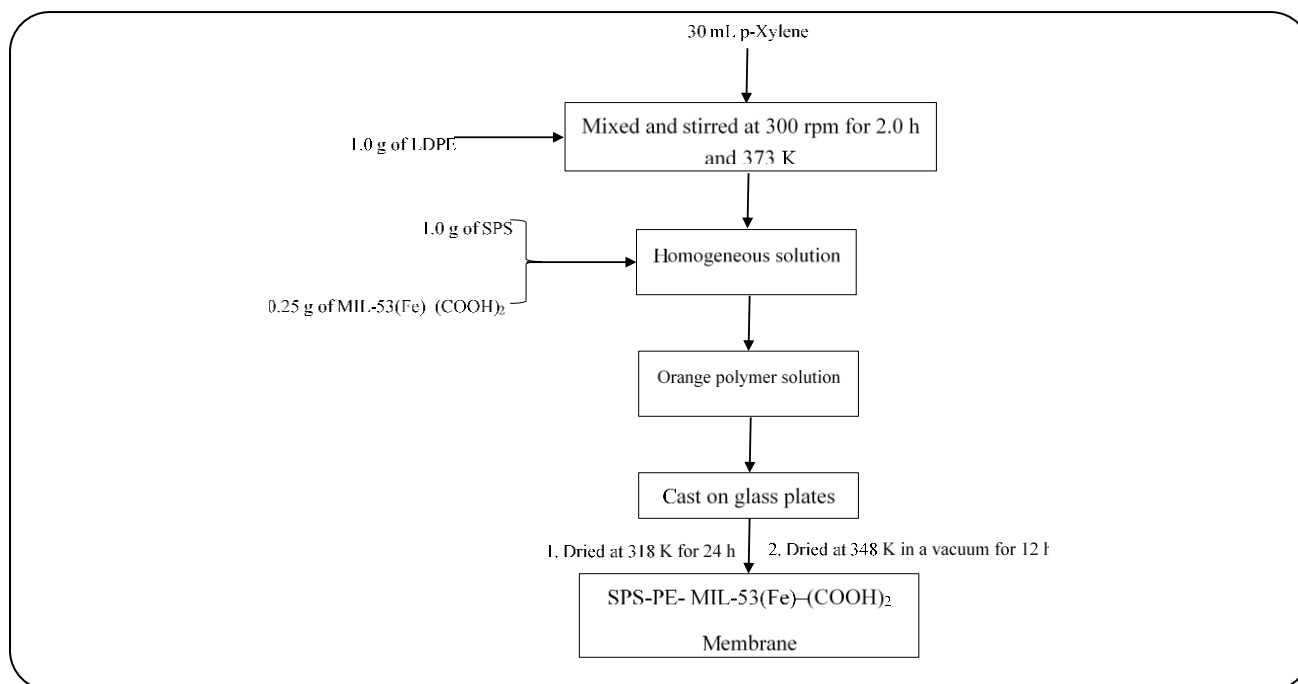
Fig. 3: schematic of synthesis method of SPS-PE- MIL-53(Fe)–(COOH)₂ membrane

Physico-chemical properties of the membrane

To assess PEM performance, it is necessary to investigate various properties of the membranes, including the rate of water uptake, the capacity of ion exchange, methanol permeability, and the selectivity factor.

A water uptake investigation measured the membrane's wet and dry weights. Therefore, the membrane was initially immersed and saturated in the deionized water (24 h). After clearing the surface water, the weight of the membrane was rapidly measured to specify the weight of the wet membrane (W_w). After 2 hours of drying at 373 K, the weight of the dry membrane (W_d) was calculated [28]:

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100 \qquad (4)$$

Acid-base titration was used to estimate the membranes' experimental ion exchange capacities. The membrane sample was initially dried until it reached a constant weight. Then, it was immersed in a solution of saturated NaCl for 24 hours to allow proton exchange from the membrane to the solution. Using phenolphthalein as the indicator and a 0.01 M NaOH solution as the titrant, the ion-exchanged solution was titrated. Equation (5) determined the Ion Exchange Capacity (IEC):

$$\text{IEC} = \frac{V_{NaOH} \times N_{NaOH}}{W_{dry}} \qquad (5)$$

Where V_{NaOH} is the volume of NaOH solution used during titration, N_{NaOH} is the NaOH solution normality, and W_d is the membrane's dry weight.

To test the membrane persistence against free radical species, a piece of the membrane was immersed in Fenton's reagent for 1 hour at 80 °C while stirring (3% aqueous solution of H_2O_2 with 2ppm $FeSO_4$). The oxidative durability of the membrane was determined by monitoring the time it took to dissolve and checking the membrane's weight after 2 hours in the reagent.

Impedance measurements in a Zahner potentiostat/galvanostat electrochemical workstation PGSTAT (4MHz-1Hz frequency range, 5 mV oscillating voltage) were used to measure the conductivity of proton of the membranes under fully humidified conditions at different temperatures after equilibration for 1 h. Two inner Pt wires (diameters = 0.2 mm) acted as the sensors of voltage, while two outer Pt wires (same diameter) acted as AC injectors in this four-probe technique. Sandwiched the membrane sample (ca. 3×1.0 cm^2) between two Teflon blocks, using nylon screws to keep it in place. The membranes were plunged in HCl solution (1.0 M) for activation before testing (12 h). Afterward, it was washed using deionized water to pH = 7. Equation (6) was used to calculate the conductivity of proton from the impedance data [29]:
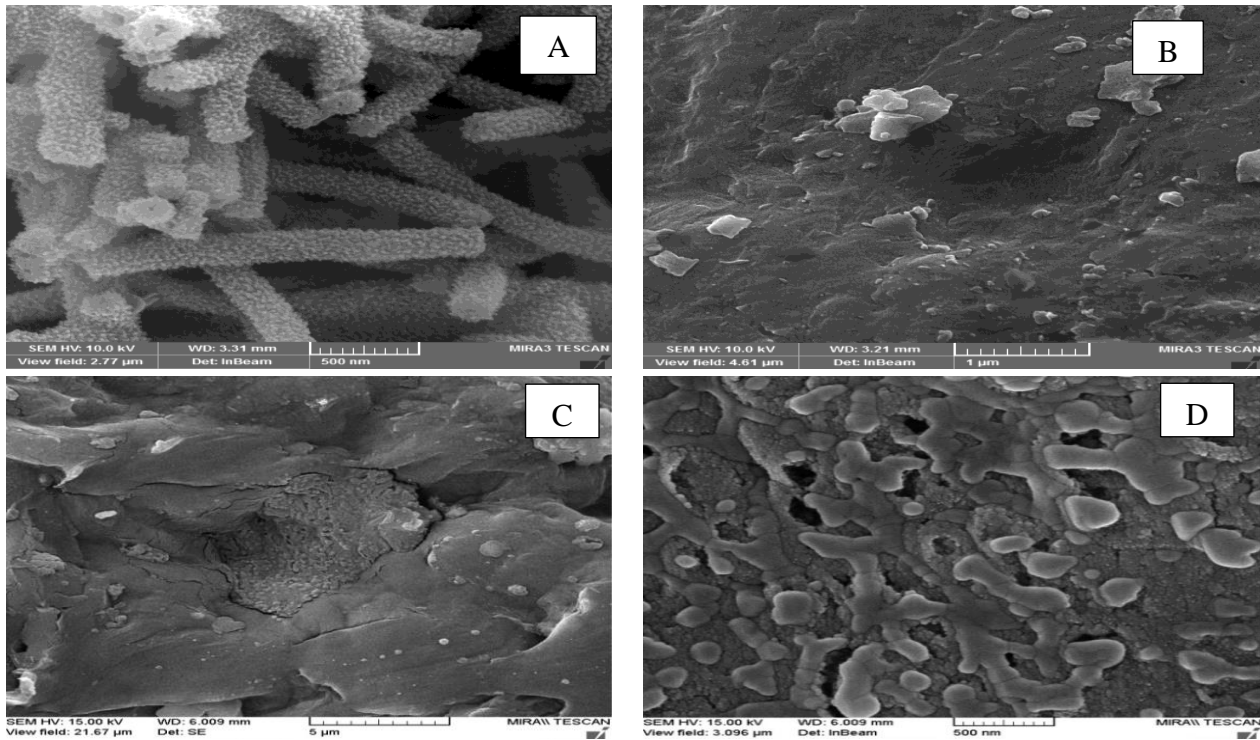
Fig. 4: SEM images for (A) MIL-53 particles (B) SPS-PE-MIL-53 membrane (C and D) SPS-PE membrane [27]

$$\sigma = \frac{L}{RA} \tag{6}$$

where σ is the conductivity of proton (S/cm), L is the distance between potential-sensing electrodes (cm), R is the resistance of the membrane ionic conductivity from the impedance data (Ω), A is the cross-sectional area of the membrane.

A custom-built two-compartment diffusion cell was applied to investigate the permeability of methanol. The setup consisted of 2 chambers, and 5 M methanol was poured into chamber A (the feed compartment). The receiving one (chamber B) had deionized water, and continuously stirred it at various temperatures while there was a membrane between the chambers. Equation (7) was used to calculate the permeability of membrane [29]:

$$P = \frac{1}{CA}\left(\frac{\Delta C_{B(t)}}{\Delta t}\right)\left(\frac{LV_B}{A}\right) \tag{7}$$

Where P is the membrane diffusion permeability for methanol (cm^2/s), C_A is the concentration of methanol in cell A (mol/L), $\Delta C_{B(t)}/\Delta t$ is the slope of methanol's molar concentration variation in cell B as a function of time (mol/(L.s)), V_B is each diffusion reservoir's volume (cm^3), A is the area of the membrane (cm^2), and L is the thickness of the membrane (cm).

Equation (8) was used to calculate the selectivity factor (the ratio of the conductivity of proton to the methanol permeability) [29].

$$\text{Selectivity} = \frac{\sigma}{P} \tag{8}$$

Where σ is the conductivity of the proton and P is the methanol permeability.

RESULTS AND DISCUSSION
SEM characterization

The surface morphology of the synthesized membranes has been displayed in Fig. 4 (A) and 4 (B), respectively. Fig. 4 (C and D) shows the surface image of SPS-PE membrane without of MIL-53. Fig. 4 (A) shows the surface image of particles of MIL-53, and Fig. 4 (B) shows the top view of the SPS-PE-MIL-53 membrane surface. MIL-53 particles have a porous surface without any agglomeration. More functional groups are included in the network due to the porosity of MIL-53 (the metal-organic framework). The functional groups (COOH) and (NH$_2$) will make the transport of protons across the membrane easier. The harmony between the polymer and the particle provides a dense homogeneous surface for the membranes, which supplies a straightforward path for the conductivity
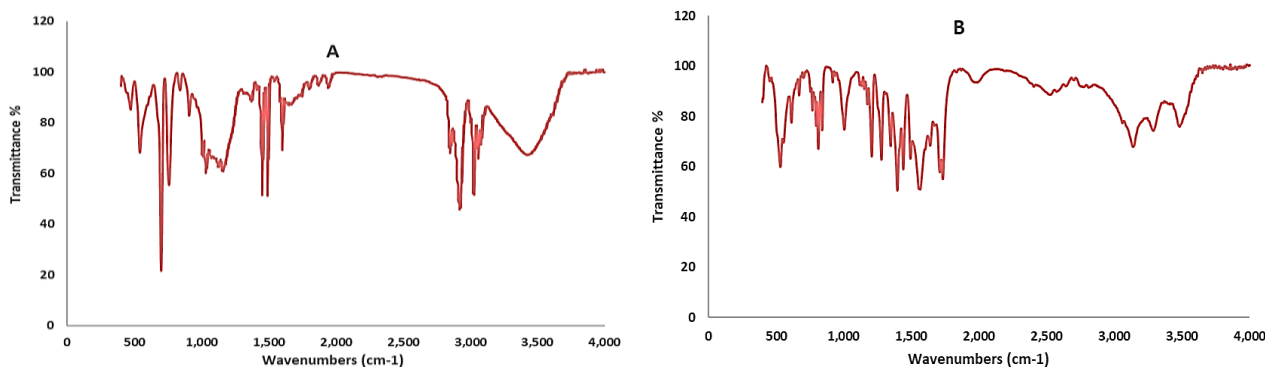
Fig. 5: FTIR spectra of (A) MIL-53 (B) SPS-PE-MIL-53 membrane

of proton via the ionic channels in the matrix of the polymer. When MIL-53 was not used in the membrane construction, fine cracks were observed in the membrane construction, while the use of MIL-53 in the membrane caused the bonding between the functional groups of MIL-53 and the membrane, leading to the production of a uniform membrane (See Figs. 4 (B) and 4 (C)). Also, the presence of MIL-53 prevents agglomeration on the membrane surface, while the absence of MIL-53 causes a little agglomeration.

FT-IR characterization

FT-IR spectra of the MIL-53, and SPS-PE-MIL-53 are presented in Fig. 5. FT-IR important bands of the PE and SPS have been explained in our previous work [29-30]. Fig. 5 (A) shows the FT-IR of MIL-53, the very strong bands centered at $3420 \, cm^{-1}$ can be assigned to O-H and N-H stretching vibrations of the -COOH and -NH$_2$ functional groups. The width of this peak indicates the significant presence of these functional groups in the structure of the MIL-53. They can absorb some water by forming hydrogen bonds. The membrane water content in a direct methanol fuel cell is a key factor because it shows the amount of membrane proton conduction. The strong bands at $1737 \, cm^{-1}$ are attributed to the C=O stretching of COOH groups, and the bands at $1434 \, cm^{-1}$ are assigned to the O–H deformation of C–OH groups. Fig. 5 (B) shows the FT-IR bands of the SPS-PE-MIL-53 membrane. According to Fig. 5 (B), the strong bands centered at $3480 \, cm^{-1}$ can be assigned to O-H and N-H stretching vibrations of the -COOH and -NH$_2$ functional groups. The bands at 3060-$3286 \, cm^{-1}$ are assigned to the aliphatic C-H stretching of methane and methylene groups in the main chain. SO$_2$ asymmetric stretching can be found at $1347 \, cm^{-1}$.

The bands at $1732 \, cm^{-1}$ are attributed to the C=O stretching of COOH groups, the bands at 1564 and $1493 \, cm^{-1}$ are associated with the O–H deformation (in C–OH). The sharp bands at $1004 \, cm^{-1}$, $1180 \, cm^{-1}$, $1207 \, cm^{-1}$, $1279 \, cm^{-1}$ are due to the symmetric stretching of SO$_3$.

Water uptake

One of the important properties of a fuel cell membrane is proton transport from the anodic side to the cathodic side. Therefore, the water uptake is a significant parameter for fuel cell membranes as their participation helps in conducting protons from the anode part to the cathode part, affecting the conductivity of the proton. Water absorbed by the membrane, on the one hand, causes the transfer of protons by the membrane. On the other hand, excessive water absorption can cause swelling in the membrane and affect its mechanical properties. Fig. 6 depicts the water uptake of the synthesized composite membranes equilibrated with 100% relative humidity in the air at 25 °C and immersed in water at 25 °C. According to Fig. 6, the membrane water uptake order is as SPS-PE-MIL-53 (1:1:0.5 w:w:w) > (1:1:0.25 w:w:w) > (1:1:0.1 w:w:w). Fig. 5 shows that greater water is absorbed by higher amounts of MOF content. Due to the hydrogen bonding, they can form with water. COOH, NH$_2$, and other functional groups can cause more water absorption by the membrane. Therefore, the more functional groups on the membranes, the more water must be absorbed.

Proton conductivity

The membranes used in the direct methanol fuel cells must easily transfer protons from the anodic part to the cathodic part. Thus, this research focused on employing materials containing functional groups that can simplify
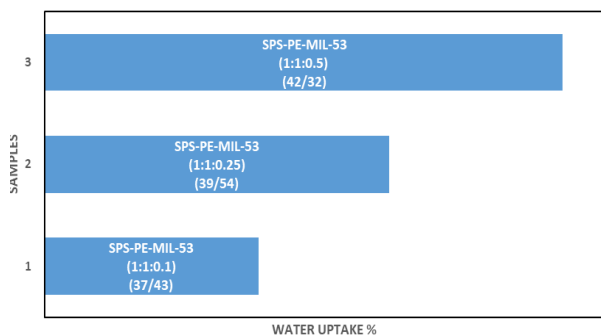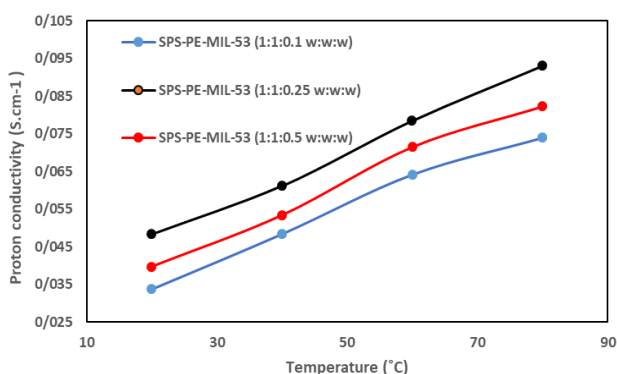
Fig. 6: Water uptake of composite membranes

Fig. 7: Proton conductivity of composite membranes

the proton transfer through the membrane. Functional groups such as SO_3H, NH_2, and COOH are the important groups result the best proton transfer (as studied here). Due to the hydrogen bonding between the groups and water molecules, these functional groups can absorb more water on the membrane, thereby improving the transfer of protons through the membrane. The presence of MIL-53 in membranes was expected to increase proton transfer by the membrane and increase its amount to increase proton transfer by the membrane. Fig. 7 shows the proton conductivity for different membranes at different temperatures. As can be seen in Fig. 7, the conductance of the proton has increased with increasing temperature from 20 °C to 80 °C. Also, the conductivity of the proton increased by increasing the amount of MIL-53 in the membranes (0.1-0.25 g), maybe due to the increasing number of COOH and NH_2 within the membrane. However, the conductivity of the proton decreased as the value was increased in the range of 0.25 - 0.5 g. The development of bonds between the sulfonic groups of polystyrene and COOH and NH_2 of MIL-53 may enhance the resistance to mass transfer of proton across the membrane when the membrane MIL-53

content is increased above a particular level. 0.25 g is the best amount of MIL-53 selected in the present study.

***Investigation of membrane properties***

The composite membranes' IEC, the conductivity of proton (σ), the methanol permeability (P), selectivity (σ/P), and oxidative stability are shown in Table 1. The IEC is a measure of the membrane's ability to transport protons from the anodic to the cathodic sides in the DMFC. It is a reliable value for finding the aggregation of and the proton conductivity of the membranes and proton exchangeable groups. Based on the guidelines, the capacity of ion exchange was measured for the produced membranes. All-composite membranes have high ion exchange capacity values, as evidenced by the results of measurements. The high value of IEC shows that the membranes can transfer protons well.

At 20°C and 100% relative humidity, the proton conductivity of membrane samples was determined. For 24 h, the composite membranes were tested with water. The composite membranes showed strong conductivity of proton, as can be seen in Table 1. A 5M methanol solution was used to test the membrane methanol permeability at ambient temperature. The values of methanol permeability of the membranes are tabulated in Table 1. The order of permeability of methanol in the studied membranes is: SPS-PE-MIL-53 (1:1:0.5 w:w:w) > (1:1:0.25 w:w:w) > (1:1:0.1 w:w:w). The higher the amount of MIL-53, the higher the methanol permeability of the membrane; however, the methanol permeability values were extremely similar to each other. For DMFC, a membrane with a low permeability of methanol is ideal. Because the purpose of DMFC membranes is to rise the conductivity of proton while lowering the methanol permeability, the ratio of proton conductivity to methanol permeability (the selectivity factor) may be used as a reference for generating the improved DMFC membrane properties. Better DMFC performance causes a higher selectivity factor (see Table 1).

Table 1 tabulated the oxidation stability of the studied membranes in Fenton's reagent at 80 °C. These membranes displayed proper stability, as evidenced by the fact that more than 98% of their weight was preserved after 1 hour. The crosslinking network, which was formed between the functional group of the metal-organic

Table 1: Ion exchange capacity, the conductivity of proton, the methanol permeability, selectivity and the composite membranes oxidative stability factor

Membrane	IEC (meq.g^{-1})	σ (S.cm^{-1})	P (cm^2.s^{-1})	σ / P (S.s.cm^{-3})	Oxidative stability (Wt %)
SPS-PE-MIL-53 (1:1:0.1 w:w:w)	0.96	3.37×10^{-2}	6.13×10^{-7}	5.50×10^4	> 98
SPS-PE-MIL-53 (1:1:0.25 w:w:w)	0.97	4.83×10^{-2}	6.46×10^{-7}	7.48×10^4	> 98
SPS-PE-MIL-53 (1:1:0.5 w:w:w)	0.96	3.97×10^{-2}	6.43×10^{-7}	6.17×10^4	> 98
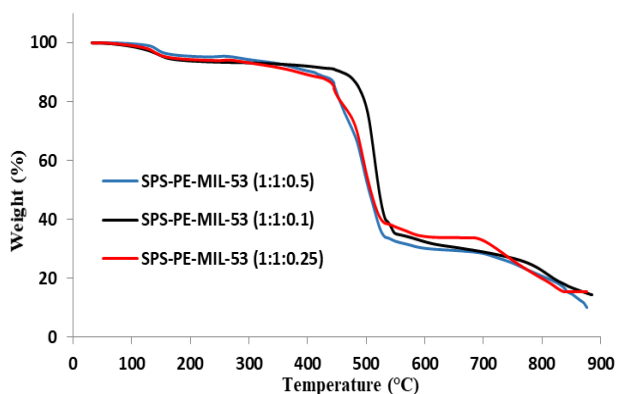
Fig 8: TGA analysis of the membranes in a temperature range from 30 to 900 °C

framework (MIL-53) and the SPS-PE, led to the membrane's good oxidative stability.

TGA characterizations

The TGA curves for membranes developed by SPS-PE-MIL-53 are shown in Fig. 8. All three produced membranes had excellent thermal resistance, and they were pretty similar in this regard (see Fig. 8). The heat resistance of the membranes diminished gradually as the content of MIL-53 in the samples increased. The weight-loss area-related parameters show the degradation of 4 weight zones for all membranes. As shown in Fig 8., the initial weight loss occurred around 100–190°C. Because membranes absorb much water, this weight loss may be because of the absorbed water loss. The next weight loss was located between 370 and 570. Weight losses of around 65% occurred in this area. This weight loss was related to the largest mass loss, and so it was called the main stage. So, this one has been ascribed to the thorough thermodegradation of the composite's skeletal chain structure. Weight loss within a range of 570–720 °C for SPS-PE-MIL-53 membranes could occur due to eliminating the organic moieties. The weight loss above 720 °C was because of the polystyrene and MIL-53 decomposition.

Single-cell performances

To understand the performance of the proposed membrane, single-cell tests for the composite membranes for CH_3OH/O_2 were performed. The effectiveness of the electrochemical reaction at the interface between the liquid and gas phases in the anode and cathode sides and the solid phase of electrodes, the fuel cell temperature, the fuel's flow rate, and the carrier stream's methanol concentration, all had major effects on the proposed single-cell system performance, which itself depends on the membrane composition.

Fig. 9 shows the results of single-cell testing using Membrane Electrode Assembly (MEA) prepared with 3 different compositions within oxygen in the cathode and methanol (2M) in the anode side at 80 °C with flow rate of 1 mL/min. The direct methanol fuel cell based membrane had a The maximum peak power density of the one composed with on SPS-PE-MIL-53 (1:1:0.25 w:w:w) was 23.61 mWcm^{-2} and 138.46 mAcm^{-2} was its maximum current density. At the same time, corresponding values for the ones prepared with the SPS-PE-MIL-53 (1:1:0.5 w:w:w) and the SPS-PE-MIL-53 (1:1:0.1 w:w:w) were 23.02 mW/cm^2 and 117.43 mA/cm^2, and 20.14 mW/cm^2 and 102.60 mA/cm^2, respectively. Due to the increased selectivity in the studied membrane, methanol proton exchange and permeability through the membranes directly influenced the Open Circuit Voltage (OCV) in direct methanol fuel cells. The OCV in SPS-PE-MIL-53 (1:1:0.25 w:w:w) membrane (0.96V) was found to be the same as membrane (1:1:0.5 w:w:w) and higher than membrane (1:1:0.1 w:w:w).

Table 2 tabulated a comparison between the studied DMFC with some other fuel cells in the literature. The proposed DMFCs provide better and satisfactory results.

CONCLUSIONS

For the first time, SPS composites with different MIL-53(Fe)-$(COOH)_2$ particle weight percentages in PE were

Table 2: Comparing the proposed DMFC (with SPS-PE-MIL-53 membrane) with other DMFCs (with different membranes)

Membrane	Membrane size / cm^2	Anode loading/ $mg.cm^{-2}$	Cathode loading/ $mg.cm^{-2}$	Temperature/°C	Methanol concentration/ M	Power Density/ $mW.cm^{-2}$	Ref.
Nafion 117	4	8- Pt/Ru	8- Pt	RT	5	8.6	[32]
Nafion-ZP [a]	3	1-1.25- Pt/Ru	5- Pt	RT	1	6-8	[32]
Nafion-Mordenite	4.5	1- Pt/Ru	1-60% Pt/C	70	2	37	[33]
SDMFC [b]	4	3- 40% Pt/20% Ru/C	1.75- 40% Pt/C	60	1	9.4	[34]
Nafion- Polyaniline - Silica	5	4- 80 wt% Pt/Ru on carbon	4- Pt	40	2	8	[35]
PANI (5%)- SPSD -PE	5	4.0-PtNPs-0.6-CNT/CC-DL	2- Pt	80	2	35	[29]
SPS-PE	5	4.0-PtNPs-0.6-CNT/CC-DL	2- Pt	80	2	18	[30] This work
SPS-PE-MIL-53 (1:1:0.1 w:w:w)	5	4.0-PtNPs-0.6-CNT/CC-DL	2- Pt	80	2	102	This work
SPS-PE-MIL-53 (1:1:0.25 w:w:w)	5	4.0-PtNPs-0.6-CNT/CC-DL	2- Pt	80	2	138	This work
SPS-PE-MIL-53 (1:1:0.5 w:w:w)	5	4.0-PtNPs-0.6-CNT/CC-DL	2- Pt	80	2	117	This work

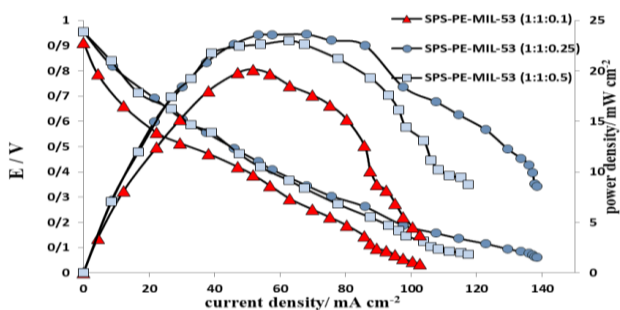[a] zirconium phosphate (ZP), [b] special-shaped direct methanol fuel cell.

Fig. 9: Current density-potential (I-V) and power density curves of the DMFC assembled with different prepared membranes at 80 ºC

produced by a simple method. These new membranes were characterized by SEM, FTIR, and TGA. The membrane conductivities were relatively increased with increasing the weight percent of MIL-53(Fe)-(COOH)$_2$ in SPS-PE composites and the temperatures of fuel cells. 0.25 g of MIL-53(Fe)-(COOH)$_2$ in the polymer matrix provides an improvement in conductivity. All produced membranes possessed proper thermal resistance, which could be attributed to the retardation effect of MIL-53(Fe)-(COOH)$_2$ as barriers for the degradation of SPS-PE composites. In comparison with other fuel cells, the studied DMFCs provide better a nd satisfactory results.

Acknowledgments

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