



Preparation and Characterization of New Composite Membranes containing Polyvinylpyrrolidone, Polyvinyl alcohol, Sulfosuccinic acid, Silicotungstic acid and Silica for Direct Methanol Fuel Cell applications

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Abstract

A novel ionic polymer membranes of different thicknesses (50-450 μ m) based on polyvinylpyrrolidone(PVP), polyvinylalcohol(PVA),sulfosuccinicacid and silicotungstic acid (SiWA) with or without silica have been synthesized for polymer electrolyte membrane fuel cells (PEMFCs). The chemical characterization of the membranes has been studied by Fourier Transform Infrared Spectroscopy (FT-IR). The thermal stability of the membranes has been studied using the techniques of thermogravimetric analysis (TGA) between room temperature and 600°C.The water uptake, ionic conductivity, ionic exchange capacity of these membranes were determined. Water uptake of these membranes ranged between 35% to 75%. The ionic conductivities of these membranes ranged between $1.025 \cdot 10^{-3}$ S/cm to $7,55 \cdot 10^{-3}$ S/cm. The best water uptake and ionic conductivity were those of the membrane based on PVA, PVP, SSA, 10.30 wt. % of SiWA and 5,15 wt.% of Silica .Whereas, the highest ion exchange capacity was 3.67 mmol/g. Therefore, it can be concluded that the membrane was a potential candidate for application in PEMFC

1. Introduction

Recent decades have seen an increase in interest in proton exchange membrane fuel cells (PEMFC), the global energy production was mainly based on fossil fuel such as oil, coal, and natural gas. Nowadays, the very high global population growth, the global economic development, and the environmental issues such as greenhouse gas emissions related to the use of fossil fuels are pushing the researchers to develop new forms of energy that are more respectful of our environment. Because when the polymer electrolyte membrane fuel cell functions to convert chemical energy into electrical energy, water is the only waste rejected by the stack, the fuel cell (PEMFC) is considered today as a clean promising source of energy especially in the automotive sector. In fact, Polymer electrolyte membrane fuel cell was adopted by some automotive suppliers as the electrochemical converter for future light vehicles. PEMFCs requires membranes with high proton conductivity, high water hydration, good mechanical, chemical and thermal stability. However, the high cost of the most available membranes, with the required properties prevents, actually a large commercialization of the fuel cells in areas of major energy consumers such as the automotive sector. Researchers developed various perfluorinated membranes such as Nafion[®] membranes developed by Dupont is the most commonly used proton exchange membrane in DMFC owing to its excellent chemical stability and high proton conductivity [1]. However, Nafion[®] is currently employed in fuel cells though it has limitations like decreased conductivity at low humidity and/or at elevated temperatures, fuel crossover and instability at temperatures of operation higher than 353K [2]. Therefore it is essential to find novel proton conductive membranes with low cost and low methanol permeability. For the above objects, many kinds of proton exchange membranes have been developed. The development of a PVA membrane for DMFC applications is of interest because the polymer has been used to separate alcohol from water in a pervaporation process [3]. Although these membranes have good ionic conductivities and high performances in a fuel cell, the cost remains high. So, different membranes have been developed based on, low cost, non fluorinated polymers such as membranes based on Polyvinyl alcohol [4-5], poly (arylene ether phosphine oxide) [6], and polyimides (PI) [7-10]. However, the membranes based on these materials have low ionic conductivities compared to membranes based on perfluorinated materials or partially fluorinated mentioned above, hence the importance of the work of various research teams is to try to improve the ionic conductivity properties of this type of membranes.

Recently, polymers incorporated with inorganic materials have been extensively studied in order to develop new fuel cell membranes. Kim et al [11] synthesized organic-inorganic hybrid membranes based on poly(vinyl alcohol), containing sulfonic acid groups. The PVA/sulfosuccinic acid (SSA) /silica hybrid and PVA/SSA that did contain any silica were investigated regarding their proton conductivity. It was found that these properties were very dependent on the SSA content .

Incorporation of heteropolyacids such as (PMA) $H_3PMo_{12}O_{40}$, (PTA) $H_3PW_{12}O_{40}$, and (SWA) $H_4SiW_{12}O_{40}$ into PVA/SSA polymer has also been studied. Ga et al [12] studied the PVA/SSA/HPAS, the results have clearly showed that the proton conductivity of PVA-SSA-HPAs composite membranes improved at low HPA concentration (5-10 wt.%), while those properties decreased as HPA concentration increased over 10 wt.%. Among synthetic polymers, both poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) have been intensively studied as biomaterials. Researchers have found for the former that it is very useful in pharmacy and medicine due to its outstanding absorption and complex abilities [13]. Both polymers are water soluble [14]. An important property for processing, although this characteristic could be a disadvantage when being used as a long-term implant. Blends, on the other hand, might represent an appropriate solution for material design. They have been investigated in order to satisfy the needs of specific sectors within the polymer industry. Generally, they show superior performance in relation to the individual components and, as a result, the range of applications grows continuously for this class of materials [15].

Thus, in this context, this work focuses on the development and the characterization of new inexpensive solid polymer electrolyte membranes based on polyvinyl alcohol, sulfosuccinic acid, polyvinylpyrrolidone and silicotungstic acid, with or without silica. The effect of the weight percentage of SiWA and SiO_2 nanoparticles in the preparation of composite membranes on the water uptake and proton conductivity of the membranes has been investigated. The effect of membrane thicknesses has also been studied. Ion exchange capacity and fixed ion concentration have been studied for PVA- SSA- PVP, PVA-SSA-PVP-xSiWA and PVA-SSA-PVP- SiWA-y SiO_2 membranes. The prepared composite polymer electrolyte membranes have been characterized by various TGA and F.T.I.R.

2. Experimental

2.1. Membrane preparation

0.5 g of PVA (with 30000-70000 average weight from Sigma Aldrich was dissolved in deionized water at 60°C and stirred at 60°C for 4 hours. 0.12 g of a commercial 70% Sulfosuccinic acid solution (from Aldrich) was added to the mixture and stirred at room temperature for 24 hours. 0.20 g of polyvinylpyrrolidone was added to the resulted solution and stirred for 2 hours at 80°C. silicotungstic acid (from Panreac) was subsequently added to the above solution at 80°C under stirring for 2 hours in the appropriate concentration to produce PVA-SSA-PVP-xSiWA membrane solutions (A). x: (from 0 g to 0.40 g). This preparation composition varies (from 0 wt.% to 33 wt.%). Silica (60A, from sigma) was added to the above solution (A) to produce PVA-SSA-PVP-SiWA-y SiO_2 membranes, y(from 0g to 0.18 g). This preparation composition varies (from 0 wt.% to 16.36 wt.%). Membranes of various thicknesses were made by solvent evaporation for different amount of solution in a Teflon glass beaker with flat bottom. After 24 hours solvent evaporation at room temperature, the membranes were peeled of the beaker and dried at 60°C for 16 hours and then in the oven at 140°C for 1 hour .

2.2. Water uptake

The membranes were first dried in an oven at 60°C for 24 hours. They were then equilibrated in boiling water for 24 hours, after which the total amount of water inside the membranes was determined by weighing them and subtracting the weight of the dried membrane from that of the humidified membrane. The water uptake percentage (τ) was calculated using the following equation:

$$\tau = \frac{W_{wet} - W_{dry}}{W_{dry}} * 100 \quad (1)$$

W_{wet} and W_{dry} are the weight of the PVA-SSA-PVP-xSiWA or PVA-SSA-PVP-SiWA-y SiO_2 hydrated membranes .and the PVA-SSA-PVP-xSiWA or PVA-SSA-PVP-SiWA-y SiO_2 dry membranes respectively.

2.3. Ionic conductivity

The cell used for measuring conductivities is shown in Fig .1. The ionic conductivity of membranes of various thicknesses was determined by polarization. The potential drop between the two reference electrodes (Fig.1) was measured following application of a constant direct current. Different values, ranging from 0,5 to 5 mA,

using a potentiostat-galvanostat–Amel instrument (70-50).The ionic conductivity of the membranes was determined in 1M NaCl solution. The proton conductivity (σ) was obtained using the following equation:

$$\sigma = \frac{e}{RS} \quad (2)$$

Where σ is the proton conductivity in S/cm, and e is the distance between the electrodes used to measure the potential (e cm). R is the impedance of membrane in Ω , S is the surface area of the membranes (cm^2).

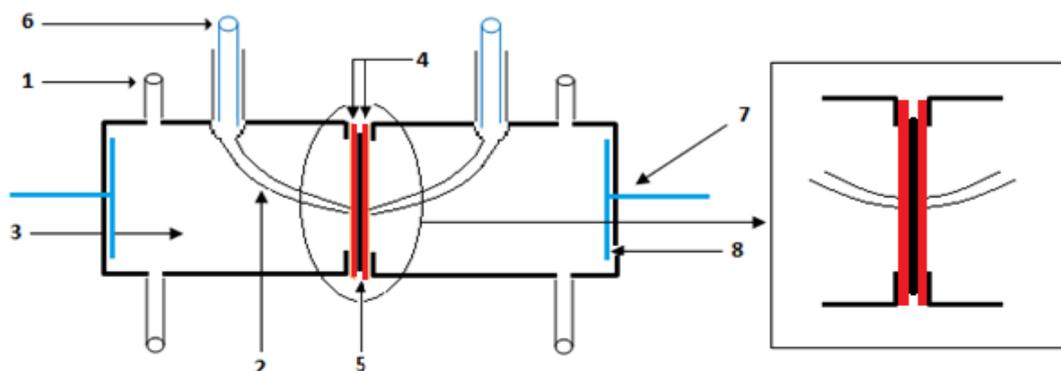


Figure 1: Ionic conductivity measurement cell.

The membranes were pre-treated by emerging in boiling water for 1 hour and then stored in deionized water. For conductivity determination in 1M NaCl, the membranes were immersed in 1M NaCl.

- 1: Capillary (allow entry and exit of the solutions).
- 2: Capillary Luggin .
- 3: Electrolyte.
- 4: Teflon gaskets.
- 5 Membrane.
- 6: Reference electrodes.
- 7: Stem platinum.
- 8: Platinum electrodes.

2-4 FTIR spectroscopy

The FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$), resolution 4 cm^{-1}) were recorded on a MVP2 STAR ART DIAMANT.

2.5 Thermal gravimetric analysis (TGA)

The PVA-SSA-PVP, PVA-SSA-PVP-10.30SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membrane were analysed using a thermogravimetric analyser (TA 60 SHIMADZU TG-DTA). Curves of weight loss and derivatives of weight loss versus temperature were determined for each membrane between 25°C and 600°C using a heating rate of 20°C/min.

2.6. Ion exchange capacity (IEC)

Ion exchange capacity (IEC) of PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP-SiWA-5.15 SiO₂ membranes were determined by titration method. About 0,465g to 0,850 g of the sample was immersed in a beaker containing 250 ml of 1 M HCl solution stirring gently for 1 hour to change them into the H⁺ form. The samples were then washed with deionized water to remove excess HCl, and then equilibrated with 250 ml (230 ml of 0,1M NaCl+20 ml of 0,1M NaOH) solution for 24 hours at room temperature, to allow exchange between protons and sodium ions. After that, 25 ml of the solution was titrated with 0,1M HCl solution to evaluate the amount of HCl generated from the exchange process. From the titration, the IEC value was then calculated by using the following equation:

$$IEC = \frac{n(H^+)}{(W_{dry})} \quad (3)$$

Where $n_{(H^+)}$ is the Number of moles of protonic sites present in the membrane .and W_{dry} , the weight of the dry membrane

3. Results and discussion

3.1 Thermal gravimetric analysis (TGA)

The PVA-SSA-PVP, PVA-SSA-PVP-10.30SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membrane were analysed using a thermogravimetric analyser (TA 60 SHIMADZU TG-DTA). Curves of weight loss and derivatives of weight loss versus temperature were determined for each membrane between 25°C and 600°C using a heating rate of 20°C/min.

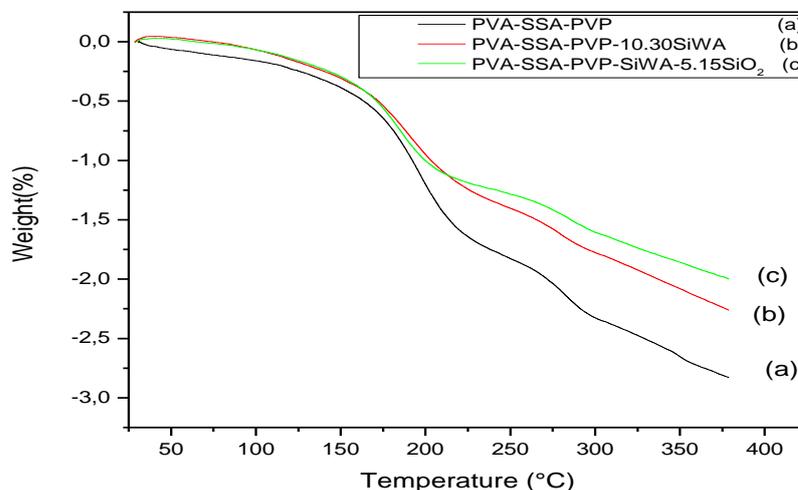


Figure 2: TGA plots for PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and, PVA-SSA-PVP- SiWA -5.15 SiO₂

The TGA curve of the membranes were fitted using three weight –loss stages due to thermal dehydration, thermal desulfonation, and thermal decomposition of the membranes. The figure 2 shows the weight loss and weight loss derivatives of the membranes. The first weight loss is observed between 50 and 200 ° C, and was associated with the loss of absorbed water molecules formed after the esterification reaction of the membranes. The value of the corresponding mass loss is equal to 18. The peaks of the weight derivatives are around 100 ° C for each of these membranes. Most of the absorbed water molecules in the membranes are supposed to exist in a bound state rather than in the free molecules state. The water molecules seem to have been bound directly to the polymer chains and /or the –SO₃H groups via hydrogen bonds. The second weight loss between 180°C-300°C is due to the loss of sulfonic acid due to the desulfonation of SSA and the resulting breakage of cross-linked bonds. In the third weight loss region (at temperatures > 300°C, the polymer residues were further degraded at 300°C, which corresponds to the decomposition of the main chains of the PVA and SiWA.

3.2. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SS A-PVP- SiWA -5.15 SiO₂ membranes are shown in Fig 3. The spectrums of all the studied membranes exhibit peaks at 3389 cm⁻¹, 1417, cm⁻¹, 2926 cm⁻¹ which are respectively attributed to the OH groups in PVA, CO groups in PVA and –CH groups. The peaks observed at 1032,cm⁻¹, 1211, cm⁻¹, and 1714 cm⁻¹ are attributed respectively to SO₃⁻ groups in SSA, C=O bands, and the ester groups C-O stretch mode. Ester group formation is caused by ester bands (C-O-C) between the PVA alcohol groups and SSA carboxyl groups. The absorption band at 1035 cm⁻¹ arose from –SO₃H group. The peak observed at 1647 cm⁻¹ correspond to the stretching vibration of hydrogen banded carbonyl group (C=O) on PVP [16].This absorption confirms the intermolecular interactions between the hydroxyl groups on PVA and carboxyl groups on penetrating PVP in membranes [17]. For the PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP- SiWA-5.15 SiO₂ membranes showed bands at 981, 916, 876 and 790 cm⁻¹, which agree with reported in literature [18,19] for silicotungstic acid the peak at 981 cm⁻¹ characteristic to the stretching vibrations of W=O_t terminal bonds and the bond at 916 cm⁻¹ corresponds to stretching of Si-O_a bond. The bands at 876, and 790 cm⁻¹ are attributed to the W-O_b-W and the striching vibration of W-O_c-W respectively. This confirms the presence of SiWA in the synthesized membranes. The peaks observed at 1080 cm⁻¹ and 1220 cm⁻¹ are characteristic of asymmetric (Si-O-Si) stretch band. This confirms the presence of silica in PVA-SSA-PVP-SiWA-5.15 SiO₂ synthesized membranes. P. Staiti had reported that the increase of conductivity of membranes based on polybenzimidazol, silicotungstic acid and silica was attributed to the presence of silica probably by increasing the water absorption thus facilitating proton motion [20].

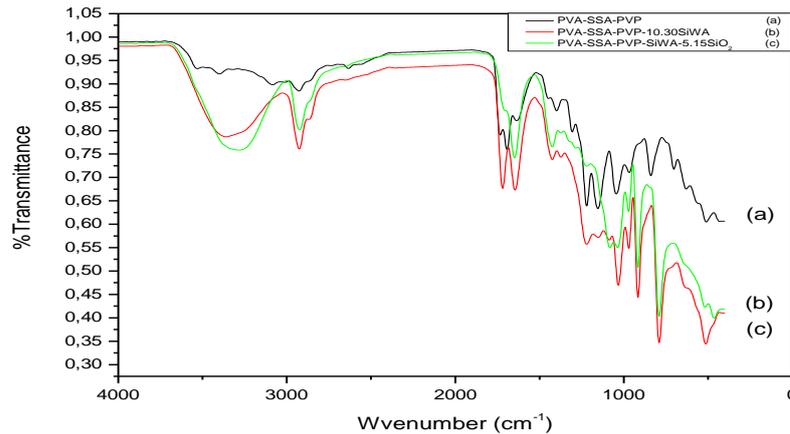


Figure 3: FTIR spectra of PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP-SiWA-5.15 SiO₂ membranes.

3.4. Water uptake and Conductivity

Fig. 4 shows a plot of the water uptake of the membranes as function of the SiWA content. The water uptake varies from 35% to 60%. As shown in Fig. 4(a), the water uptake increases with the increase of SiWA, and the maximum is obtained for 10.30 wt.% of SiWA. After that, the increase of SiWA in the membrane leads to a decrease of water uptake. This trend in behavior was the same as that observed for the water uptake content behavior Fig. 4(b).

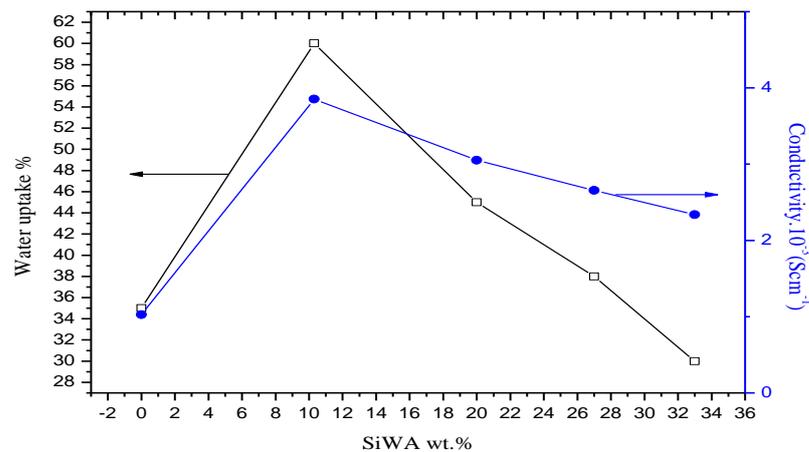


Figure 4: water uptake (a) and ionic conductivity (b) of the membranes PVA-SSA-PVP-x SiWA (0 wt.% ≤ x ≤ 33 wt.%) with different amounts of SiWA.

The proton conductivities of the membranes PVA-SSA-PVP-xSiWA increases with the increase of SiWA and reaches a maximum value for the membrane containing 10.30 wt % weight of SiWA, and decreases when the SiWA content exceeds 10.30 wt. %. The water uptake of the membranes PVA-SSA-PVP-SiWA-y SiO₂ as function of SiO₂ content, (0 wt.% ≤ y ≤ 16.36 wt.%). The water uptake varies from 60% to 75%. As shown in Fig. 5 (c). We notice that the water uptake varies with the silica percentage. Hence, the maximum which is equal to 74% , was obtained for the membrane PVA-SSA-PVP-SiWA-5.15 SiO₂ .Thus, over 5.15 wt.% in silica ,the water uptake of this membrane starts decreasing. As shown in Fig. 5(d), the ionic conductivity of PVA-SSA-PVP-SiWA-ySiO₂ membranes was in the range 3,132 to 7,554.10⁻³ Scm⁻¹.The ionic conductivity increase with SiO₂ percentage goes from 0 wt.% to 5.15 wt. % and decreases when SiO₂ percentage exceeds 5.15 wt. %. So, the maximum ionic conductivity is attributed to the membrane PVA-SSA-PVP- SiWA-5.15SiO₂ and is equal to 0,755 .10⁻² S/cm.This figure shows that the ionic conductivities of PVA-SSA-PVP- SiWA-ySiO₂ membranes increases with the increase weight of SiO₂ percentage.The ionic conductivities goes from 0,3857. 10⁻² S/cm. for the membrane without SiO₂ to 0,757 .10⁻² S/cm for the membrane containing SiO₂ (Table1). The ionic conductivity of the membrane based on PVA, SSA, PVP,SiWA and 5.15 wt.% SiO₂ increases from 0 wt.% to 15.36 wt.% and reaches a maximum value 0,755.10⁻² S/cm for the membrane containing 5.15 wt.% weight of

SiO₂, and decreases when the SiO₂ content exceeds 5.15 wt.%. This value was higher than that of the Nafion[®]112 membrane ($5,9 \cdot 10^{-3} \text{ S cm}^{-1}$) [21]. This is in agreement with the results which show that the latter membrane also has the best hydration rate.

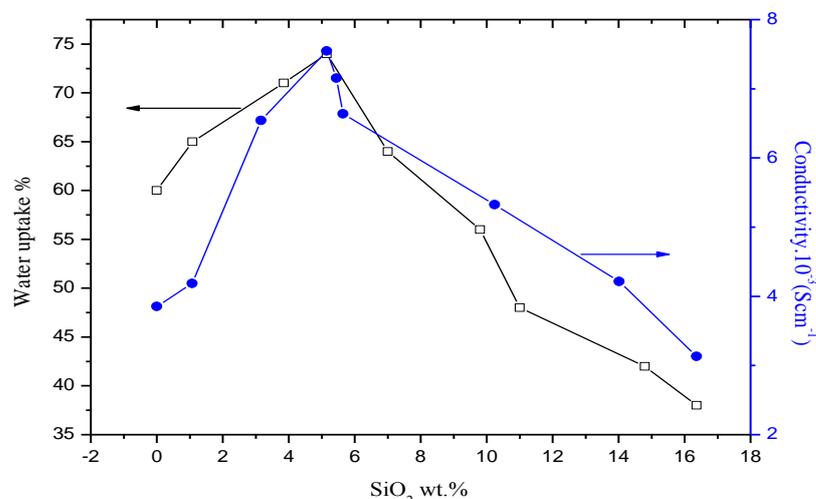


Figure 5 : water uptake (c) and ionic conductivity (d) of the membranes PVA-SSA-PVP-SiWA-y SiO₂ (0 wt.% ≤ y ≤ 16.36 wt.%) with different amounts of SiO₂

Table 1: Ionic conductivities (S/cm) for PVA-SSA-PVP, PVA-SSA-PVP-10.30SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membranes in 1M NaCl.

Membranes	(a) PVA-SSA-PVP in 1M NaCl	(b) PVA-SSA-PVP-10.30SiWA in 1M NaCl	(c) PVA-SSA-PVP-SiWA- 5.15 SiO ₂ in 1M NaCl
Ionic Conductivity (S/cm)	$0,1235 \cdot 10^{-2}$	$0,3857 \cdot 10^{-2}$	$0,755 \cdot 10^{-2}$

3.5. Ion exchange capacity and fixed ion concentration.

The IEC and water uptake of PVA-SSA-PVP, PVA-SSA-PVP-10.30SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membranes are given in table 2. The IEC values of 2.13 mmol/g obtained with PVA-SSA-PVP is 2.17 times higher than that of Nafion[®]112, (0.98 mmol g⁻¹), 2.15 times higher than that of Nafion[®] 115 (0,99mmol g⁻¹) and 2.29 times higher than that of Nafion[®] 117 membrane (0,93mmol g⁻¹) [22]. The IEC values of 3.45 mmol/g obtained with PVA-SSA-PVP-10.30SiWA is 3.52 times higher than that of Nafion[®] 112, 3.48 times higher than that of Nafion[®] 115 (0,99mmol g⁻¹) and 3,71 times higher than that of Nafion[®]117 membrane [22].

Table 2: IEC and Water uptake of PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP-SiWA-5.15 SiO₂ membranes.

Membranes identification	Water uptake%	IEC(mmol/g)	Ion concentration sites
PVA-SSA-PVP	35	2,13	6.10
PVA-SSA-PVP-10.30SiWA	60	3.45	4.95
PVA-SSA-PVP-SiWA-5.15SiO₂	75	3.67	4,89

The IEC values of 3.67 mmol/g obtained with PVA-SSA-PVP- SiWA-5.15SiO₂ is 3.74 times higher than that of Nafion[®]112(0.98 mmol g⁻¹), 3.70 times higher than that of Nafion[®]115 (0,99mmol g⁻¹) and 3.95 times higher than that of Nafion[®]117 (0,93mmol g⁻¹) membrane [22]. The ion concentration sites, X, expressed as the number of ionic sites (IEC) divided by the membrane water uptake, of 6.10, 4.95 and 4.89 are respectively obtained with PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membranes. Those

results show that the ion concentration sites of the PVA-SSA-PVP- SiWA-5.15SiO₂ membrane is lower than that of the PVA-SSA-PVP-10.30 SiWA membrane which is lower than that of the PVA-SSA-PVP membrane. Even if the IEC values of PVA-SSA-PVP- SiWA-5.15SiO₂ membrane is higher than that of the PVA-SSA-PVP-10.30 SiWA membrane which is higher than that of the PVA-SSA-PVP membrane, this result is obtained because of the water uptake obtained with PVA-SSA-PVP-SiWA-5.15SiO₂ membrane (0.75), compared to those obtained with PVA-SSA-PVP-10,30SiWA membrane (0.60) and PVA-SSA-PVP membrane (0.35) .

Conclusion

This paper has attempted to investigate the elaboration and characterization of new composite membranes based on PVA, SSA, PVP, SiWA with or without silica. The studies of FTIR has confirmed the formation of crosslinked networks and the intermolecular interactions between the hydroxyl groups of PVA and carbonyl groups on penetrating PVP in membranes. The FTIR has also confirmed the presence of silicotungstic acid and silica. The studies of TGA has demonstrated that these membranes are stable at temperatures higher than 180°C. Ionic conductivities of PVA-SSA-PVP-10.30SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ synthesized membranes in contact with 1M NaCl solution are about $0,3857 \cdot 10^{-2}$ and $0,755 \cdot 10^{-2}$ S/cm respectively. The ion exchange capacities of PVA-SSA-PVP, PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP-SiWA-5.15SiO₂ membranes have presented the following results: 3.45 mmol/g and 3.67 mmol/g 115 membrane respectively. These values of ion proton conductivities and exchange capacities of the new synthesized membranes (PVA-SSA-PVP-10.30 SiWA and PVA-SSA-PVP- SiWA-5.15 SiO₂) has proved to be higher than that the standard values of Nafion[®]112 commercial membrane. Therefore, it can be concluded that the new composite polymer membranes PVA-SSA-PVP-10.30 SiWA, PVA-SSA-PVP- SiWA- 5.15 SiO₂ have the potential application in PEMFC.

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