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Research Article

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Synthesis and characterization of new composite membranes based on polyvinylpyrrolidone, polyvinyl alcohol, sulfosuccinic acid, phosphomolybdic acid and silica

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ABSTRACT

Several new composite proton conducting polymer membranes of different thicknesses (50-500μm) based on polyvinylpyrolidone (PVP), polyvinyl alcohol (PVA), sulfosuccinic acid (SSA) and phosphomolybdic acid (PMA) with or without silica have been developed for polymer electrolyte membrane fuel cells (PEMFCs). The chemical characterization of the membranes has been studied by Fourrier Transform Infrared Spectroscopy (FT-IR). The thermal stability of the membranes has been studied using the techniques of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) between room temperature and 600°C.The water uptake, ionic conductivity and ionic exchange capacity of these membranes were determined. Water uptake of these membranes ranged 25 % to 93 %. The ionic conductivities of these membranes ranged between 4, 65.10^{-3} S/cm to 1.33.10^{-2} S/cm. The best water uptake and ionic conductivity were those of the membrane PVA-SSA-PVP-PMA-7.69SiO_2 *based on 45.25 wt% of PVA, 10.86 wt% of SSA, 18.1 wt % PVP , 18.1 wt % PMA and 7.69 wt % SiO_2 and the membrane* PVA-SSA-PVP-19,61PMA *containing 49.02 wt % of PVA, 11.76 wt% of SSA, 19.61 wt % PVP and 19.61 wt % of PMA. The membrane* PVA-SSA-PVP-19,61PMA *gave ionic conductivity of about 4, 65 10^{-3} S/cm in 1M NaCl media and 4, 95 10^{-3} S/cm in 1M H_2SO_4 media. The membrane* PVA-SSA-PVP-PMA -7.69SiO_2 *gave ionic conductivity of about 8.07 10^{-3} S/cm in 1M NaCl media and reach 1.35 10^{-2} S/cm in 1M H_2SO_4 media. The ion exchange capacity of the PVA-SSA-PVP-19.61PMA and PVA-SSA-PVP-PMA7.69 SiO_2 membranes were 2.92 and 3.79mmol/g respectively.*

Keywords: Polymer electrolyte membranes fuel cell, Polyvinylpyrrolidone, Polyvinyl alcohol, Sulfosuccinic acid, Phosphomolibdic acid, Ionic conductivity, Silica.

INTRODUCTION

For several decades, 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 require membranes with high proton conductivity, high water hydration, good mechanical, chemical and thermal stabilities. 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 per fluorinated membranes such as Nafion® membranes developed by Dupont or similar ones supplied by Dow, Asashi and some other companies [1]. Nafion®

is highly chemically and mechanically resistant acidic; and can absorb large quantities of water .If it is well hydrated, then H^+ can move quite freely within the material and for this reason it is a good protonic conductor [2]. Modified membranes have been developed based on Nafion® and heteropolacids. They exhibit better protonic conductivitises and performances in a fuel cell than Nafion 117 membranes .Those improvements were attributed to heteropoliacids insersion into the membranes [3,4] Others modified Nafion® -Silica composition membranes exhibit hight affinity to water enabling proton even at elevated temperature and low relative humidity values [5].

Even if Nafion based membranes have good proton conductivities and performances in a fuel cell, they have limitation due, especially to their hight cost. Due to the limitations of the commercially available membranes. The developments of alternative membrane materials to commercially available nafion include various new modified partially per-fluorinated membranes [6-7].

A common problem of fluorine-free membrane such as sulfonated phenol formaldehyde [8] , the polystyrene based membranes that are designed by radio-grafting followed by sulfonation [9,12], and homogeneous partially sulfonated arylene main chain-polymers[10-11] is that they are too swelling in water and lose their mechanical property. 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 polybenzimidazole (PBI) [13-15], poly(ether Ketone),(PEEk) [16-18] , poly(Oxyethylene), (POE)[19-20], poly (Phenylquinoxaline) [21], poly (ether sulfone) [22-23], polyvinyl alcohol [24-25], poly (arylene ether phosphine oxide) [26], and polyimides (PI) [27-29]. 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 [30] 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. The proton conductivity and methanol permeability of the hybrid membranes were studied with changing SSA content from 5 to 25 wt%. It was found that the proton conductivity was dependent on the SSA content. Up to an SSA content of about 20wt% the proton conductivity decrease, and above this SSA content. The methanol permeability through the PVA/SSA silica membranes were proportional to the proton conductivities of the membranes were in the range 10^{-3} to 10^{-2} S/cm.

Incorporation of heteropolyacids such as (PMA) $H_3PMo_{12}O_{40}$, (PTA) $H_3PW_{12}O_{40}$, and (STA) $H_4SiW_{12}O_{40}$ into PVA/SSA polymer has also been studied. Bhat et al [31] studied the PVA/SSA/HPAS, the results have clearly showed that the incorporation of certain inorganic fillers in PVA/SSA provide effective DMFC performance with high power density. Huang et al [32] prepared a series of membranes consisting of PVA/SSA and poly(vinylpyrrolidone (PVP). The results showed that the water uptake increases as the PVP increases and the proton conductivity increases as the PVP content increases from 10% to 20%, reaching a maximum value of 0,01S/cm when the PVP content reaches 20%. These membranes then experience a decrease in proton conductivity when the PVP content exceeds 20%.

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 phosphomolybdic acid, with or without silica. The effect of the weight percentage of PMA 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 capacities have been studied for PVA- SSA- PVP, PVA-SSA-PVP-19.61PMA and PVA-SSA-PVP-19.61PMA-7.69SiO_2 membranes. The prepared composite polymer electrolyte membranes have been characterized by various TGA, DTA and FTIR.

EXPERIMENTAL SECTION

Membrane preparation

0.5g of PVA (with 30000-70000 average weight from Sigma Aldrich was dissolved in deionized water at 60°C and stirred at 60°C for 24 hours. 0.12g of a commercial 70% Sulfosuccinic acid solution (from Aldrich) was added to the mixture and stirred at room temperature for 24 hours. 0.20g of polyvinylpyrrolidone was added to the resulted solution and stirred for 2 hours at 80°C. Phosphomolibdic acid (from Panreac) was subsequently added to the above solution at 80°C under stirring for 24 hours in the appropriate concentration to produce PVA-SSA-PVP-xPMA membranes solutions (A); x(from 0 g to 35 g). This preparation composition varies from 0 wt. % to 29.91wt.%. Silica (60A, from sigma) was added to the above solution A (containing 0.2g of PMA) to produce PVA-SSA-PVP-

PMA-ySiO$_2$ membrane solutions (B); y (from 0 g to 0.15g). This preparation composition varies from 0 wt.% to 12.82wt.%. 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 24 hours and then in the oven at 140°C for 2 hours .

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:

$$\tau = \frac{\mathrm{Wwet} - \mathrm{Wdry}}{\mathrm{Wdry}} * 100 \qquad \textbf{(1)}$$

W_{wet} and W_{dry} are the weight of the PVA-SSA-PVP-xPMA or PVA-SSA-PVP-xPMA-ySiO$_2$ hydrated membranes and the PVA-SSA-PVP-xPMA or PVA-SSA-PVP-xPMA-ySiO$_2$ dry membranes respectively.

Ionic conductivity

The cell used for measuring conductivities is shown in Fig .1. The ionic conductivity of the membranes of various thicknesses was determined by polarization. The potential drop between the two reference electrodes (Fig.1) was measured in 1M H_2SO_4 and 1M NaCl solution, using a potentiostat-galvanstat –Amel instrument (70-50), following application of a constant direct current (values ranging from 0,5 to 5 mA). The proton conductivity (σ) was obtained using the following equation:

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

Where σ is the proton conductivity in S/cm, e is the membrane thickness in cm, R is the impedance of the membrane in Ω and S is the surface area of the membranes in cm^2.

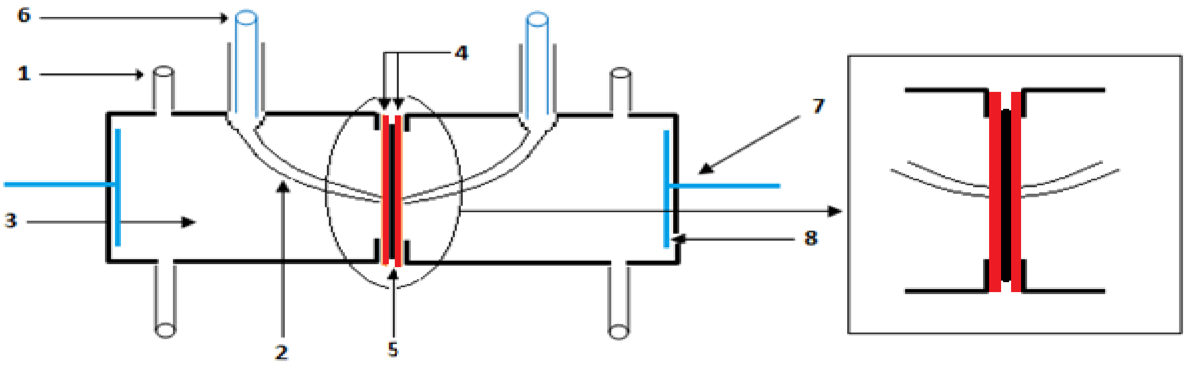


Fig 1: Ionic conductivity measurement cell

The membranes were pre-tread by emerging them in boiling water for 1 hour and then stored in deionized water. For conductivity determination in 1M H_2SO_4 or 1M NaCl, the membranes were immersed in 1M H_2SO_4 or 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.

FTIR spectroscopy

The FTIR spectra of the PVA-SSA-PVP , PVA-SSA-PVP-PMA and. PVA-SSA-PVP-PMA-7.69SiO_2 membranes .The spectrum was recorded over wave numbers ranging from 4000 to 400 cm^{-1}, resolution 4 cm^{-1} were recorded on a MVP2 STAR ART DIAMANT.

Thermal gravimetric analysis (TGA)

The PVA-SSA-PVP, PVA-SSA-PVP-PMA and. PVA-SSA-PVP-PMA-7.69SiO_2 membranes were analyzed using a thermogravimetric analyzer (TA 60 SHIMADZU TG-DTA). Curves of weight loss versus temperature were determined for each membrane between 25°C and 600°C using a heating rate of 20°C/min.

Ion exchange capacity (IEC)

Ion exchange capacity (IEC) of PVA-SSA-PVP, PVA-SSA-PVP-19.61PMA and, PVA-SSA-PVP-PMA -7.69 SiO_2 membranes were determined by titration method. About 0,375g to 0,765 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:

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

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

RESULTS AND DISCUSSION

Thermal gravimetric analysis (TGA)

The PVA-SSA-PVP, PVA-SSA-PVP-19.61PMA (containing 19.61 wt.% of PMA) and , PVA-SSA-PVP-PMA-7.69SiO_2 (containing 18.1 wt.% of PMA and 7.69 of SiO_2) membranes were analyzed using a thermogravimetric analyzer (TA 60 SHIMADZU TG-DTA). Curves of weight loss versus temperature were determined for each membrane between 25°C and 600°C using a heating rate of 20°C/min.

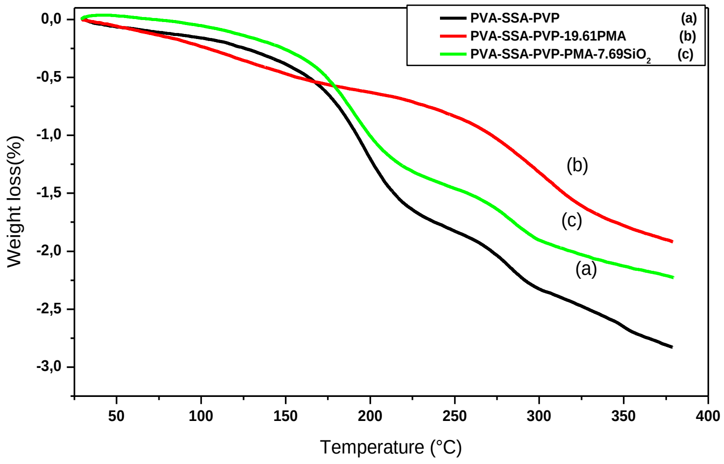


Fig 2: TGA plots for PVA-SSA-PVP , PVA-SSA-PVP-19.61PMA and , PVA-SSA-PVP-PMA -7.69 SiO_2

The TGA curves of the membranes were fitted using three weight loss stages due to thermal dehydration, thermal desulfonation, and thermal decomposition of the membranes. The first weight loss occurred at temperatures above 100°C, and was associated with the loss of absorbed water molecules formed after the esterification reaction of the 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 –SO_3H groups via hydrogen bonds [30]. The second weight loss between 150°C-250°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 > 250°C) the polymer residues were further degraded at 250°C, which corresponds to the decomposition of the main chains of the PVA and PMA.

Fourier transform infrared spectroscopy

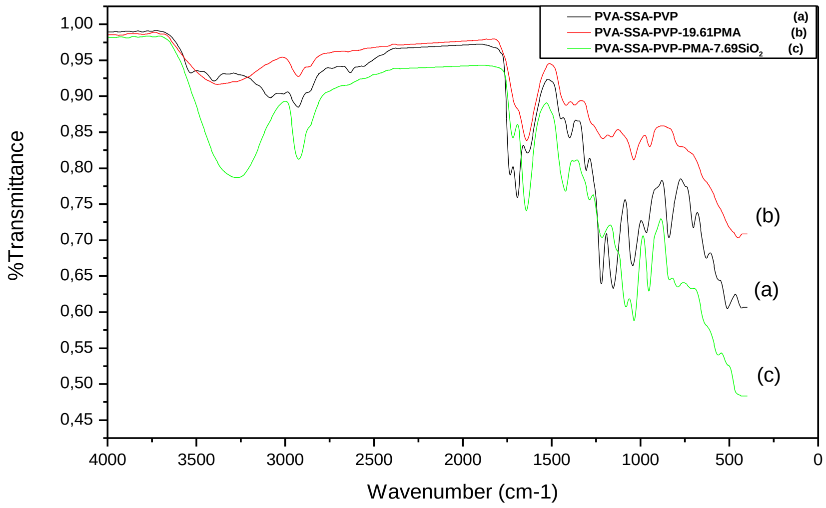


Fig 3: FTIR spectra of PVA-SSA-PVP, PVA-SSA-PVP-19.61PMA and PVA-SSA-PVP- PMA -7.69 SiO_2 membranes

The FT-IR spectra of PVA-SSA-PVP, PVA-SSA-PVP-19.61PMA and, PVA-SSA-PVP-PMA -7.69 SiO_2 membranes are shown in fig 3. The spectrums of all the studied membranes exhibit peaks at 3389 cm^{-1}, 1417, 97 cm^{-1}, 2926,38 cm^{-1} which are respectively attributed to the OH^- groups in PVA, CO^- groups in PVA and –CH groups. The peaks observed at 1032,66cm^{-1}, 1211,24 cm^{-1}, and 1712 cm^{-1} are attributed respectively to SO_3^- 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 1037cm^{-1} arose from $-SO_3H$ group. The peak observed at 1634 cm^{-1} correspond to the stretching vibration of hydrogen banded carbonyl group (C=O) on PVP. This absorption confirms the intermolecular interactions between the hydroxyl groups on PVA and carboxyl groups on penetrating PVP in membranes [32]. For the PVA-SSA-PVP-19.61PMA and , PVA-SSA-PVP-PMA-7.69 SiO_2 membranes, the peak observed at 964,12 cm^{-1} is attributed to the stretching vibrations of (Mo=O) [31] Thus confirms the presence of PMA in the synthesized membranes. For the PVA-SSA-PVP-PMA-7.69SiO_2 membrane, the peaks observed at 793 cm^{-1} and 952 cm^{-1} are respectively attributed to the symmetric (Si-O-Si) stretch band and to the (Si-OH) groups. The peaks observed at 1080 cm^{-1} and 1220 cm^{-1} are characteristic of asymmetric (Si-O-Si) stretch band. Thus confirms the presence of silica in PVA-SSA-PVP-PMA-7.69SiO_2 synthesized membrane. 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 [33].

Water uptake

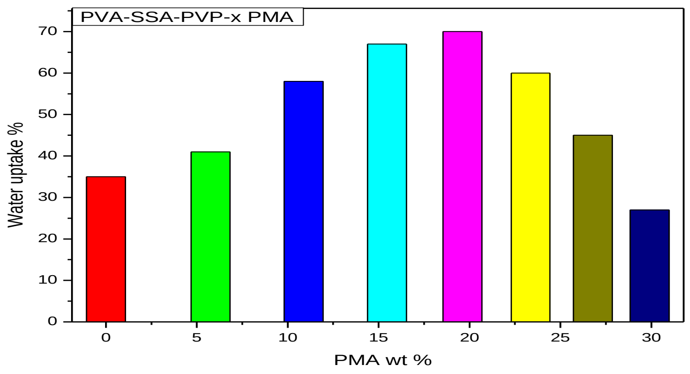


Fig 4: Water uptake of the PVA-SSA-PVP-xPMA membranes (0 wt%≤x≤30 wt%)

Fig. 4 shows the water uptake of the PVA-SSA-PVP-xPMA membranes (0 wt%≤x≤ 30 wt%). The water uptake goes up with the increase of PMA, and the maximum value of about 70% is obtained for the membrane containing 19.61 weight percent of PMA. After that the increase of PMA in the membrane leads to a decrease of Water uptake.

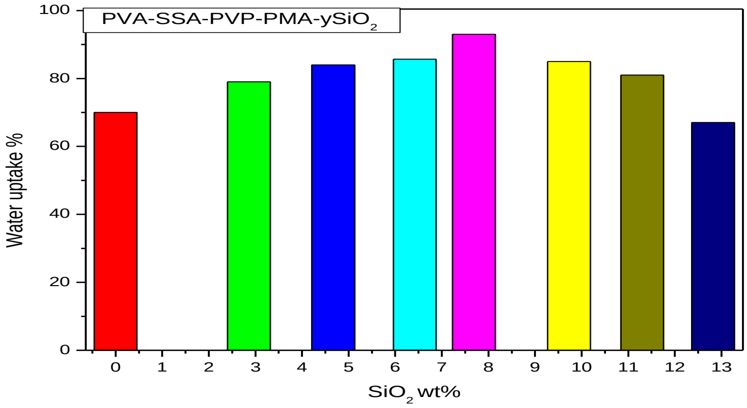


Fig 5: Water uptake of the PVA-SSA-PVP-PMA-ySiO_2 membrane (0 wt%≤y≤12,82 wt%)

Fig. 5 shows the water uptake of the PVA-SSA-PVP-PMA-y SiO2 membrane (0 wt. %≤y≤12, 82 wt. %). This figure shows that the Water uptake goes up with the increase of PMA, and reaches a maximum of 93% for the membrane PVA-SSA-PVP-PMA-7.69SiO_2 containing 19.61 wt.% of PMA and 7.69 wt.% of SiO_2. After this value, an increase of PMA in the membrane leads to a decrease of Water Uptake.

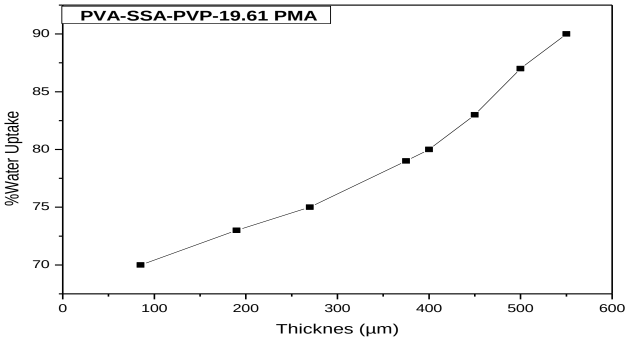
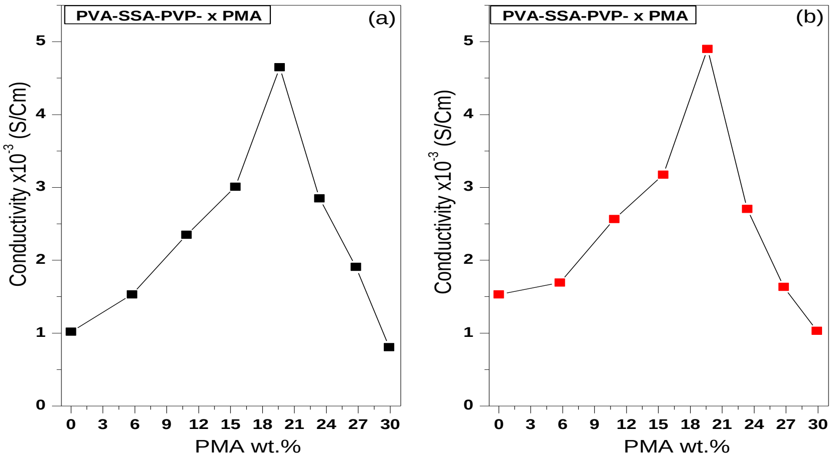


Fig 6 : Water uptake of PVA-SSA-PVP-19.61PMA membrane with membrane thickness

Fig. 6 shows the water uptake of PVA-SSA-PVP-19.61 PMA membrane versus thickness. This fig shows that the maximum water uptake of the PVA-SSA-PVP-19.61PMA membrane increases with membrane thickness. It goes from 70% for the PVA-SSA-PVP-19.61PMA membrane 85μm thick to 90% for PVA-SSA-PVP-19.61PMA membrane 550 μm thick.

Proton conductivity

Fig: 7 represents the ionic conductivities PVA-SSA-PVP-xPMA membranes versus PMA content (0 wt%≤x≤ 29,91 wt%). The figures 7 (a and b) show that the proton conductivity of the PVA-SSA-PVP-xPMA membranes increases with the increase of PMA content and reaches a maximum value for the membrane containing 19.61% weight of PMA and decreases when the PMA content exceeds 19.61%. In NaCl media (figure 7.a) the maximum ionic conductivity (of about 4,65 .10^{-3} S/cm) is attributed to the membranes PVA-SSA-PVP-xPMA containing 19.61 wt % of PMA. This value is higher than that of the membrane based on polyvinyl alcohol and phosphomolibdic acid measured in the same condition (4,25.10^{-3} S/cm) [34]. In H_2SO_2 media (figure 7.b), the maximum ionic conductivity (of about 4,95.10-3 S/cm) is attributed to the membrane PVA-SSA-PVP-xPMA containing 19.61wt%.



(a) : in 1M NaCl solution **(b):in 1M H_2SO_4 solution**

Fig 7: Proton conductivity of the PVA-SSA-PVP-xPMA with PMA content

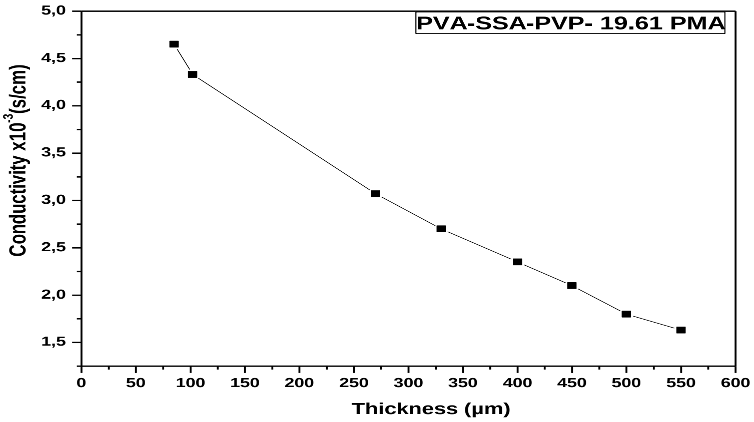


Fig 8: Proton conductivity of the PVA-SSA-PVP-19.61 PMA membrane with membrane thickness

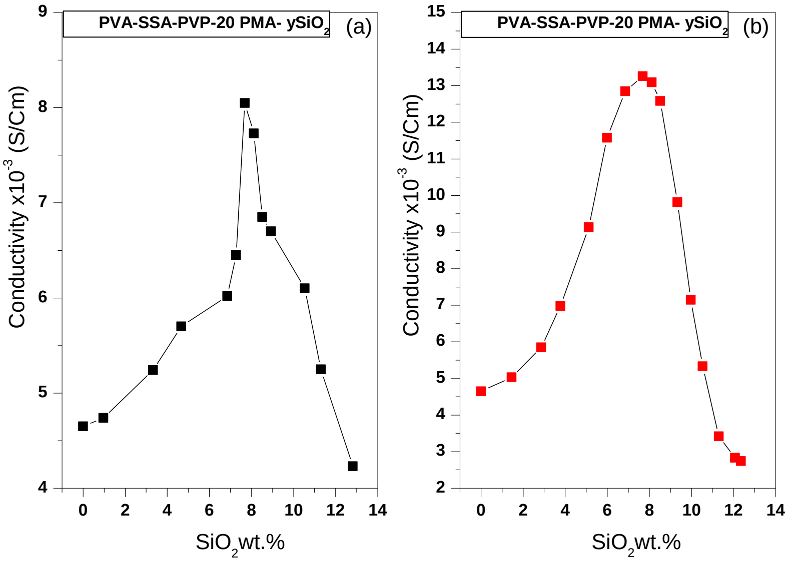


Fig 9: Ionic conductivities of PVA-SSA-PVP- PMA-ySiO_2 with SiO_2 wt%

Figure 8 represents the ionic conductivity of the PVA-SSA-PVP-19,61PMA membrane versus membrane thickess. This figure shows that the ionic conductivity of the membrane decreases when the membrane thickness increases. Ionic conductivity goes from 1, 63.10^{-3} S/cm for PVA-SSA-PVP -19,61PMA membrane (550 µm thick) to 4,65 10^{-3} S/cm for PVA- SSA- PVP- 19,61PMA membrane (85µm thick).

Fig. 9 represents the ionic conductivity of PVA-SSA-PVP- PMA-ySiO_2 membranes in 1M NaCl (fig 9.a) and 1M H_2SO_4 (fig 9.b). This figure shows that in both, 1M NaCl and 1M H_2SO_4, the ionic conductivities increases with SiO_2 and reaches a maximum for PVA-SSA-PVP-PMA-7.69 SiO_2 membrane containing 7.69% of SiO_2 wt%. When SiO_2 exceeds 7.69%, the ionic conductivities of the membranes PVA-SSA-PVP-PMA-ySiO_2 starts to decrease. Table 1 represents the ionic conductivities of PVA-SSA-PVP-19.61PMA and PVA-SSA-PVP-PMA-7.69 SiO_2 membrane in 1M NaCl and 1M H_2SO_4. The ionic conductivities of PVA-SSA-PVP- PMA-7.69 SiO_2 in 1M NaCl and 1M H_2SO_4 are 0,85 .10^{-2} S/cm and 1,35.10^{-2} S/cm respectively. Those values are higher than that of the Nafion®, 112 membrane (5, 9 10^{-3} S / cm) [35].

Table1: Ionic conductivities (S/cm^{-1}) for PVA-SSA-PVP-20PMA and PVA-SSA-PVP-20PMA-ySiO_2 membranes in 1M H_2SO_4 and 1M NaCl

Membranes	(a) PVA-SSA-PVP-19.61PMA in 1M NaCl	(b) PVA-SSA-PVP-19,61PMA in 1M H_2SO_4	(c) PVA-SSA-PVP-PMA-7,69 SiO_2 in 1M NaCl	(d) PVA-SSA-PVP-PMA-7,69 SiO_2 in 1M H_2SO_4
Maximum ionic Conductivity (S/cm)	4,645.10-3	4,957.10-3	8,0714.10-3	1,3504.10-2

Ion exchange capacity

Table 2 shows the IEC values of PVA-SSA-PVP, PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2 membranes**.** The IEC values of 2.13 mmol/g obtained with PVA-SSA-PVP is 2.17 times higher than that of the 112 Nafion®, 115 and 1135 Nafion® membranes (0.99 mmol g-1) and 2,29 times higher than that of the Nafion® 1135 (0,93mmol g-1) membrane[36]. The IEC values of 2.972 mmol/g obtained with PVA-SSA-PVP-19,61PMA is 3.03 times higher than that of the112 Nafion® 112, 115 and Nafion® 1135 membranes and 3,2 times higher than that of Nafion® 1135 membrane [36]. The IEC values of 3.79 mmol/g obtained with PVA-SSA-PVP-19,61PMA-ySiO2 is 3.87 times higher higher than that of Nafion® 112 , 115 and Nafion® 1135 membranes (0.99 mmol g-1) and 3.94 times higher than that of Nafion® 1135 (0,93mmol g-1) membrane[36].

Table 2: IEC values of PVA-SSA-PVP, PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2 membranes

Membrane	IEC(mmol/g)
PVA-SSA-PVP	2,13
PVA-SSA-PVP-19,61PMA	2.97
PVA-SSA-PVP-PMA-7,69SiO_2	3.79

CONCLUSION

This work reports the elaboration and characterization of new composite membranes based on PVA, SSA, PVP, PMA with or without silica. The FTIR studies confirmed the formation of crosslinked networks and the intermolecular interactions between the hydroxyl groups of PVA and carbonyl groups on penetrating PVP in membranes. FTIR confirms also the presence of phosphomolybdic acid and silica. A TGA and TDA study confirms that theses membranes are stable at temperatures higher than 180°C. Ionic conductivities of PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2 synthesized membranes in contact with 1M NaCl solution are about 4,65.10^{-3} and 8,07.10^{-3} S/cm respectively. Ionic conductivities of PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2 synthesized membranes in contact with 1M H2SO4 solution are about 4, 96.10-3and 1, 35.10^{-2} respectively. The ion exchange capacities of PVA-SSA-PVP-19,61PMA, PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2 membranes are 2.972 mmol/g and 3.79 mmol/g 115 membrane. These values of proton conductivities and ion exchange capacities of the new synthesized membranes (PVA-SSA-PVP-19,61PMA and PVA-SSA-PVP-PMA-7,69SiO_2) are higher than that of the standard values of Nafion112, Nafion® 115 and 1135 Nafion commercial membranes. Therefore, it can be concluded that the new composite polymer membranes PVA-SSA-PVP-19,61PMA, PVA-SSA-PVP-PMA-7,69SiO_2 shows potential application in PEMFC.

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