Synthesis and characterization of PVA /sPTA proton exchange membranes for fuel cell applications

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Abstract. Using the casting method, proton exchange membranes PEMs for fuel cell were prepared by thermal cross-linking of polyvinyl alcohol (PVA) with sulfophthalic acid (sPTA). The membranes were prepared with different cross-linking temperatures with thickness ranged between 100 to 150 µm. The prepared membranes were characterized by different techniques such as ion exchange capacity, thermal analyses, water uptake and proton conductivity. The prepared membranes showed proton conductivity between 8.46-32.7 mS/cm. Increasing the cross-linking temperature increased the cross-linking density, resulting in an enhancement in the tensile strength and thermal stability of the prepared membranes. The membrane hole sizes were obtained using positron annihilation lifetime spectroscopy (PALS) measurements. Cross-linked PVA/sPTA membranes showed a strong correlation between the free volume hole size with the mechanical stability and methanol permeability of the membranes.

1. Introduction
Proton exchange membrane fuel cells (PEMFC) have attracted attention because of their low operating temperature and fast startup process. One of the essential problems of the fuel cell is the high material costs, in particular, the membrane and the catalysts In order to become commercially available, Low coast and high efficient membranes should be prepared. The standard material used commercially throughout the world is the Nafion. It has several drawbacks because it is unstable at high temperatures and has high fuel permeability, resulting in deterioration of the performance of the fuel cell and a reduction in the life of the cell[1]. Therefore, many researchers are focusing on finding an alternative membrane to Nafion[2-9]. The membrane should have some requirements such as high proton conductivity and high mechanical, thermal and chemical stability[10]. In general, it is believed that the fuel permeability through the PEMs correlates with the structure of the membrane and the open spaces or holes in the PEM material[11-14], so that the structure with less free volume is desirable for PEM. In order to develop the advanced PEM materials with low fuel permeability, It is important to have a deep insight into the hole nanostructures to get more information about the size and distribution of the holes.

The size and distribution of membrane nanopores can be accurately determined using positron annihilation lifetime spectroscopy (PALS), a nondestructive and very sensitive technique. The basic idea of PLAS is to measure the difference between the implantation time and the time of annihilation a positron with an electron. Upon entry into the material, the positron can be directly annihilated with one of the free electrons of the material emitting two gamma rays each of them has energy 511 kev, or it can be located at free volume spaces that form positronium (Ps), which is then annihilation after a longer time (142 ns). Positron annihilation lifetime spectra in polymer usually comprise three or more lifetime
components $\tau_1$, $\tau_2$ and $\tau_3$ with corresponding intensity $I_1$, $I_2$ and $I_3$, respectively. The third component orthopositronium (o-Ps) is in the range of 1 to 10 ns in the matter and correlates with the radius of the holes in the membranes according to this equation[15]:

$$\tau_3 = 0.5\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right)^{-1}$$  (1)

Here, $R_0 = R + \Delta R$ is the radius of an infinitely deep square well potential and $\Delta R = 0.166$ nm is the homogeneous electron layer thickness [16]. The volume can be calculated by:

$$V_h = \frac{4}{3}\pi R^3$$  (2)

Modification of the membranes using cross-linking such as chemical cross-linking and thermal cross-linking is a promising method for improving the various properties of the polymers [17-19], including thermal, chemical and mechanical stability. Many researchers are currently focusing on thermal and chemical cross-linking in which the polymer reacts with the cross-linking agent to form a network structure with the aid of a catalyst. In comparison between thermal and chemical cross-linking, Lee et al. [20] concluded that thermal cross-linking can improve the thermal and chemical stability of the polymer membrane more efficiently than chemical cross-linking because of the ability of thermal cross-linking to form a stable three-dimensional network structure after cross-linking.

In this study, PVA was sulfonated with sPTA and then thermally cross-linked at different cross-linking temperatures. The influence of the cross-linking temperature on the various properties is investigated. In addition, the structure of the free volume was studied and correlated with the different properties of the membranes.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, extra pure, Mw =1,25,000 g/mol, from Alpha Chemika), Sulfophthalic acid (sPTA, 50% w/w aqueous solution, from Alfa Aesar, Germany). Sodium chloride (NaCl) and sodium hydroxide (NaOH) were used for titrimetric analysis and purchased from Adwic, Egypt. All chemicals used without further purification.

2.2. Preparation of the Proton Exchange Membranes (PEMs)
The PEM has been prepared using casting technique by heating of (10 % PVA) in an aqueous solution for 6 h at 70°C. After the solution becomes clear, sPTA with concentration 20 wt.% was added to the PVA solution. The PVA/sPTA solution was stirred under the room conditions for 1 day. Then, the solution was poured into a Teflon Petri-dish to avoid the adhesion of the membranes and left for 24 hours to evaporate the excess water. After the evaporation of the excess water, solid membranes were removed from the petri-dish. Finally, the PVA/sPTA membranes were thermally cross-linked for 1 h at different temperatures between 100-120 °c and stored in a desiccator until further testing. The thickness of the prepared membrane ranged from 100 to 150µm.

3. Membrane characterization

3.1. Thermal stability

The thermal stability of pure PVA and PVA / sPTA with different cross-linking temperatures was investigated using a Thermogravimetric Analyzer (TGA) (Model Q50, USA). The TGA spectra were investigated between 35 and 700 °C at a heating rate of 10 °C min -1 under a nitrogen atmosphere.

3.2. Water uptake

The water uptake is the tendency of the membranes to absorb water, which can be determined by calculating the percentage weight difference between wet and dry membrane. The water uptake for
PVA/sPTA with different cross-linking temperature was measured at room temperature. The wet membranes were weighted after 24 hours immersion in deionized water and wiped their surface with a tissue paper. The various membranes were then dried in a vacuum oven at 60 °C for 24 hours and weighted several times under vacuum until the weight became constant to obtain the dry weight of the membranes. The water uptake (WU) of the membranes was calculated according to the following formula:

\[
\text{Water uptake } \% = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100
\]

where \(w_{\text{wet}}\) and \(w_{\text{dry}}\) are the weight of the wet and dry membrane.

3.3. Ion Exchange Capacity (IEC)
IEC gives information about the concentration of the active groups in the PEMs (SO₃ groups). The IEC of the sulfonated membranes was carried out by back-titration technique. The synthesized membranes were weighted after drying at 60 °C for 1 day under vacuum and then soaking in 30 ml of 1 M NaCl solution for 24 hours at room temperature. During the titration process, H⁺ ions in the PEMs are replaced by Na⁺ ions. This solution was titrated with 0.05 M NaOH with phenolphthalein as an indicator to determine the concentration of exchanged H⁺ ions picked up by the membrane. The NaOH was added to the solution until the color changed to pink color. The IEC values, in units of mmole per gram, were calculated according to the following equation [21]:

\[
\text{IEC} = \frac{0.05 \times V_{\text{NaOH}} \times n}{w_{\text{dry}}} \left( \frac{\text{mmol}}{\text{g}} \right)
\]

where \(V_{\text{NaOH}}\) is the NaOH volume used for titrating, \(n\) is the quotient of volume the NaCl solution in which the membranes were immersed to the volume of NaOH used for titration and \(w_{\text{dry}}\) is the dried weight of the membranes.

3.4. Methanol permeability
A homemade side-by-side diffusion cell is used to study the methanol permeability through the PEM[22]. The PEM was sandwiched between two identical glasses reservoirs (A and B). At room temperature, reservoir (A) was filled with 150 ml of 4M methanol while reservoir (B) was filled by distilled water and the two were magnetically stirred at room temperature. Using refractometer, the refractive index of the methanol concentration in the reservoir (B) was measured as a function of time and compared with the calibration curve of the refractometer. Finally, the methanol permeability could be calculated from the concentration versus time curve according to the following equation[23]:

\[
P = \frac{K \times V_{B} \times L}{A \times C_A} \left( \frac{\text{cm}^2}{\text{s}} \right)
\]

where \(C_A, K, V_B, L, A\) and \(C_A\) are slope of concentration-time curve, volume of distilled water, thickness of membrane, effective area of permeability and methanol concentration respectively.

3.5. Mechanical properties
The tensile testing of the dried membranes was performed under room conditions (the temperature is about 24 °C and the relative humidity between 30 and 35%) using a universal material testing machine (Lloyd model LR5K-Plus) at 0.5 mm / min as a constant crosshead speed.

3.6. Proton conductivity
The synthesized membranes were immersed for 24 h in deionized water and were cut into small sections (2×2 cm²). The ionic conductivity of the cross-linked membranes is obtained at room temperature by the AC impedance spectroscopic technique using HIOKI-3532 LCR Hi-tester over a frequency range from 50 Hz to 1 MHz and an oscillating voltage between 50 and 500 mV. The in-plane ionic conductivity (\(\sigma\)) of the samples was calculated from the respective impedance data according to the following relation:
\[ \sigma = \frac{L}{R \times A} \left( \frac{S}{cm} \right) \]  

(6)

Where \( L \) is the distance between the two electrodes, \( R \) is the membrane resistance which was taken at the minimum imaginary impedance response in Col-Col plot and \( A \) is the cross-sectional area of the membrane.

3.7. \textit{Positron Annihilation Lifetime Spectroscopy (PALS)}

Positron annihilation lifetime (PAL) measurements are performed using \(^{22}\text{NaCl}\) radioactive material as a positron source. Kapton film has enveloped the source. The source activity is approximately 0.297 MBq. The source is placed between 10 layers of the membrane with a total thickness of 1 mm on each side to ensure that the positrons are completely annihilated inside the membrane. A fast-fast coincidence spectrometer with a time resolution of 370 ps was used to collect spectra with more than 2 million counts at room temperature for PVA/sPTA with different cross-linking temperature.

4. \textbf{Results and discussion}

4.1. \textit{Thermal Stability}

Figure 1 shows the TGA curves for pure PVA and cross-linked PVA/sPTA. The pure PVA showed three weight loss regions with increasing the temperature. The first region between 50–200 °C is caused by the loss of absorbed water molecules while the second one between 200–340 °C is related to the loss of water bound to the polymer matrix. The third region between 340-450 °C is associated with the decomposition and carbonization of the polymer. Contrary, PVA/sPTA showed four regions for weight loss. The first region between 40-150 °C was belonging to the loss of the bounded and free water. The second ranged between (150-210) °C was due to loss of bounded water. The third region (210-450 °C) is attributed to the degradation of the functional groups. Finally above 450 °C, the last loss is the decomposition of the polymeric backbone. It is interesting to find that weight loss values decrease with increasing the cross-linking temperature. Increasing the cross-linking density leads to an increase in the interaction between polymer chains and it is needs more energy to loss. Finally, it is found that increasing the thermal cross-linking temperature for PVA/sPTA is leads to enhancement in thermal stability for the prepared membrane.

4.2. \textit{Water uptake}

Figure 1. TGA curves for pure PVA and cross-linked PVA/sPTA.
The hydration of the membrane has a very important function for transporting the protons through the PEM which can reflect the fuel cell performance. There are two types of absorbed water molecules in the membranes. The first type is the free water, which is easy to lose, the second type is bounded water, which interacts with the material itself and requires more energy to lose. The water uptake was determined for the membranes with a different cross-linking temperature of PVA/sPTA and varied between 142 and 40 %, as shown in figure 2. It is obvious that the resulting water absorption values decrease with increasing cross-linking temperature. This behaviour can be attributed to the effect of increasing cross-linking density with increasing the temperature. Hydroxyl groups are responsible for the hydrophilicity of the PVA material, which is known as a highly hydrophilic material due to having a high OH content. Cross-linking limited the concentration of the hydroxyl groups in PVA/sPTA membranes which leads to decreasing the hydrogen bonds interactions, resulting in a decrease in the water uptake of the membranes[7]. The thermal cross-linking leads to creating a three-dimensional cross-linking network which restricts the mobility of the chains due to the decrease of the internal free volume space in the structure of the membranes. As a consequence, little water can be trapped in the membrane resulting in lower water uptake.

4.3. Ion Exchange Capacity (IEC)
IEC is an important parameter affects many properties of the PEMs [24] and gives information about the number of functional groups in the membrane that can be considered the way of gaining the membrane the property of proton conductivity [25]. As shown from figure 3, the IEC values of PVA/sPTA decreased with increasing the cross-linking temperatures. This reduction of the IEC is due to forming a hard cross-linking network by thermal cross-linking which reduces the movements of the sulfonic acid molecule and limits the exchange between the ions.

![Figure 2. Water uptake of cross-linked PVA/sPTA with different cross-linking temperature.](image1)

![Figure 3. IEC of cross-linked PVA/sPTA with different crosslinking temperature.](image2)
4.4. Mechanical Properties

The mechanical stability is one of the requirements of the PEM since it is subjected to a high hot-press pressure to prepare the anode-membrane-cathode which called membrane electrode assembly (MEA)[26]. The membrane should have high mechanical stability to can survive after the hot press process. The tensile testing was performed at room temperature for pure PVA and the PVA/sPTA membranes with the different cross-linking temperature. The obtained results which are presented in figure 4 showed that the cross-linked membranes have higher tensile strength values than that of the pure PVA. The tensile strength values of the prepared membranes ranged between 38 to 80 MPa while it is about 30 MPa for the pure PVA. Moreover, it is clear that with raising the cross-linking temperature, the tensile strength was enhanced. This behaviour can be explained as: when the thermal cross-linking takes place, the polymeric chains connected to each other strongly makes the membrane more rigid. Higher cross-linked temperature leads to stronger polymer chains and lower elongation at break percentages. From the results of PALS, thermal cross-linking leads to a decrease in the dimensions of the holes. The reduction in the size of the holes enhances the interaction between polymer chains and it is become stronger, which is reflected in the increase in tensile strength of the cross-linked membranes. It should be noted that the thermally cross-linking PVA / sPTA membranes exhibited a stronger mechanical property than the commercially available Nafion 117 membrane having tensile strength values of about 10 MPa [27].

![Figure 4. Tensile strength of pure PVA and cross-linked PVA/sPTA with different cross-linking temperature.](image)

![Figure 5. Methanol permeability of cross-linked PVA/sPTA with different cross-linking temperature.](image)

4.5. Methanol permeability

The methanol permeability of PEMs is one of the keys to confirming whether PEMs can be used for long-term operation in fuel cells. High methanol crossover is one of the disadvantages of PEM and affects its properties. It was responsible for reducing the performance of the fuel cell [28]. Figure 5 shows the correlation between the methanol permeability and the cross-linking temperature. It is clear from the figure that increasing the cross-linking temperature of PVA/sPTA membranes leads to decrease the methanol permeability. The methanol permeability values are ranged between (1.2-1.36) x10-6 cm2s-1 as shown in figure 5 which is lower than the permeability of Nafion membrane (1.65 x10-6 cm2s-1)[29]. The results show that the thermal cross-linking reaction can significantly improve the methanol permeability of the membranes, which can cause the polymer to form cross-linking structures. After thermal cross-linking, the membranes have a dense structure that effectively limits the presence
of the hydrophilic domains and inhibits swelling of the membranes [30]. In addition, the cross-linking leads to a narrowing of the transport channels of the methanol and plays a strong role as a barrier to methanol permeation. This behaviour is confirmed by reducing the size of the holes in the membrane obtained by PALS results. Decreasing the free volume decrease the interaction between polymers chains leading to enhancement in the tensile strength of the cross-linked membranes.

4.6. The proton conductivity
The proton conductivity of the PEM is the ability of passes the protons from anode to cathode. It is strongly dependent on the water uptake and IEC of the membrane [31]. The proton conductivity was calculated using the in-plane method impedance spectroscopy. The resistance of the membranes obtained from the intersection with the x-axis from the Col-Col diagram (figure 6). The proton conductivity was calculated using Eq. (6) and presented in figure 7 as a function of the cross-linking temperature. It is clear from the figure 7, the proton conductivity of the cross-linked PVA / sPTA membranes decreases with increasing the cross-linking temperature as a behaviour of water absorption and as values of IEC. Decreasing the IEC means decreases the number of active groups (SO₃) in the membrane which is responsible for the conduction of the proton through the membranes. Moreover, a diminution in the size of the free volume and their concentrations with increasing the cross-linking temperature leads to a reduction in the mobility of the charge carrier and is clearly reflected in the reduction of the conductivity values after cross-linking.

4.7. Positron Annihilation Lifetime spectroscopy PALS
The free volume size is studied for cross-linked PVA/sPTA with increasing the cross-linking temperature. Figure 8 shows the o-Ps lifetime τ₃ and its intensity I₃ as a function of the cross-linking temperature, including on the right axis of the upper figure, the free volume hole V₃ calculated using Eqs. (1) and (2). From figure 8, it is clear that there is no significant change in the o-Ps lifetime, which translates into constant free volume. In contrast, I₃ is dramatically decreased with increasing the cross-linking temperature indicating that the concentration of the holes is decreased. Increasing the cross-linking temperature leads to increasing the density of the cross-linking. After thermal cross-linking, the polymer chains become shorter, which leads to a minimization of the interactions between the polymer molecules, therefore the hole concentration becomes lower. Resulting in an increase in cross-linking density, which reduces the concentrations of the holes without affecting their radius. The reduction in
free volume concentrations is reflected in the improvement in thermal and mechanical properties. On the other hand, this leads to a lessening in water absorption and conductivity. It is important to mention that the average size of the holes in Nafion 117 is about 0.18 nm³[32], which is larger than the cross-linked PVA / sPTA membranes (0.074 nm³), which have a good correlation with the permeability results.

Figure 8. The o-Ps lifetime τ₃ and its intensity I₃ of PVA with concentration 20 wt.% membrane as a function of cross-linking temperature

5. Conclusion
PEM was successfully prepared by thermal cross-linking of PVA /sPTA by casting method. Detailed investigation of PVA/sPTA with different cross-linking temperatures has shown that its thermal and mechanical properties have been improved due to the reduction in the free volume of the membranes with increasing the cross-linking temperature. In addition, the prepared membranes showed methanol permeability less than Nafion membrane. The proton conductivity of the prepared membranes is decreased with increasing the cross-linking temperature and ranged between 8.46-32.7 mS/cm. The increase in the cross-linking density in PVA / sPTA leads to a reduction in the number of holes in the
membranes without affecting the size of the holes. It has been observed that there is a strong correlation between water uptake, ionic conductivity, tensile strength, methanol permeability, and free volume holes.

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