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STUDY OF WATER MANAGEMENT IN SOLID POLYMER ELECTROLYTES

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Abstract: The variety of polymeric materials with distinct chemical structures that precisely control the molecular architecture underlies the numerous industrial uses of polymers over the past few decades. Polymer electrolytes or gel-type polymer electrolytes, for example, are interesting alternatives to substitute liquid electrolytes in different systems such as fuel cells (FC) and dye-sensitized solar cells (DSSC). For application in FC, the Nafion electrolyte is the most widely studied. However, this material is highly dependent on hydration and operating temperature. To a certain extent, concepts and models of proton conductivity in bulk water carry over to proton conductivity in Nafion and other polymer electrolyte membranes. To understand how water acts on these systems, in this work we conducted a study to identify the kind of interaction between the adsorbed water and the electrolyte structure of membrane. Differents copolymers were synthesized from styrene as the main comonomer and characterized chemically and thermally. Membranes were prepared by casting, hydrated and the Water Uptake (WU) and Water Content (WC) were determined. Differential Scaning Calorimetry (DSC) was used to determine the kinds of present water. We observed that several compositions absorb a lot of water and do not showed conductivity because it is basically free water and does not interact with the copolymer. For other side, when the copolymer structure allows strong interaction with water, the kind of water present also changes and this is reflected in the ionic properties of the membrane.

Keywords: Polystyrene membranes; water management; solid electrolyte; Fuel cells

Introduction

Water is considered the most important compound on earth, being found in different physical states, both solid and liquid and vapor [1]. Compared to other common liquids, water is characterized by high boiling, melting and critical temperatures, high specific heat and high surface tension, among other properties [2]. The variety of polymeric biomaterials with distinct chemical structures that precisely control the molecular architecture underlies the numerous industrial uses of polymers over the past few decades. For example, sulfonated aromatic copolymers, due to their high thermal stability, strength, cost competitiveness, and strong resistance to membrane decomposition in an acidic water medium, these materials have been considered a promising alternative to Nafion [3–6]. However, particularly when the membranes from these materials have a high degree of sulfonation, to increase proton conductivity, they tend to suffer from poor performance in reducing methanol crossover and water uptake. Meanwhile, considering the fact that protons in fuel cell membranes move forward via water channels, the management of water molecules in water-swollen membranes is said to be crucial in determining transport properties such as proton conductivity, methanol permeability, and selectivity. Therefore, control and understanding of the state of water in polymers structure must be essential in breaking through the technical limits of the water-swollen proton conductors.

For this purpose, various terms have been used to characterize the water adsorbed in materials, mainly in membranes where water plays an important role in different processes in which they are used. Bound

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water, imbibed water, water of constitution, adsorbed water, saturation point are some of the terms that have been used to describe the water in membranes. The origin of each term can be traced to either theoretical considerations or to the experimental method of measurement. Bound water has been the most popular term used to describe the associated water. Bulk water or free water is that portion of water not associated (or not bound) with the membrane.

There are different techniques that can be used to determine the kind of water present in membrane, but two techniques are especially important to quantified and identify the different kind of water present in membrane, these are thermal analysis techniques.

Thermogravimetric analysis: A wet membrane sample is heated under controlled conditions to obtain the mass loss curve. The loss of mass at temperatures below 200 °C is associated with the water content in the membrane. The loss of mass rates is highly dependent upon the diffusion rates and the geometry of the sample.

Differential Scanning Calorimeter analysis: When a wet membrane sample is cooled well below 0 °C, the free water freezes but the bound water remains in the non-frozen state. When the frozen sample is heated in a calorimeter, the heat required to melt the frozen water can be measured. Non-frozen water, which is defined as the bound water, is the difference between the total water and the frozen water. The freezing of free water and non-freezing of bound water are thermodynamic phenomena, so the measurement is absolute, but as the bound water is calculated by difference, the measurement is indirect. The bound water is measured only at the freezing point [7-9].

In this work, we describe the methodology used to quantify and qualify the different types of water present in a polymeric electrolyte. The results demonstrate that there may be a relationship between the kind of water present in the membrane and ionic properties related to these.

Materials and Methods

Preparation of membranes

The membranes used were the same as those used in a previous experiment [10-11] i.e., styrene copolymers (in different concentrations of comonomers) prepared by casting in DMF. For comparison, the styrene-acrylonitrile copolymer (StAN, 50:50) was prepared as a comparison parameter. This system has an acrylonitrile group, quite hygroscopic, but it does not have ionizable hydrogen, which does not allow ionic conductivity. The **Table 1** shows the composition ($\%_{St}$) weight average molecular weight (Mw) and dispersity (Mw/Mn) of the membranes StCo-1, StCo-2, StCo-3, StCo-4 and StAN.

Sample	**$\%_{St}$ (moles)**	**Mw (Daltons)**	**Mw/Mn**
StCo-1	60.0	45,345	4.543
StCo-2	70.0	45,193	3.818
StCo-3	80.0	33,634	2.628
StCo-4	90.0	56,784	3,742
StAN	50.0	58,670	3.573

Table 1. Percentage of styrene ($\%_{St}$) and molecular weight (Mw) of used the copolymers.

Determination of the states of water

Before starting the water characterization tests, the different compositions were used to prepare membranes by casting. After, the membrane were dried in a vacuum oven at 50 °C for 24 hours, and than, immersed in deionized water for 24 hours for hydration.

- ***Using DSC*** (Q2000, TA Instruments): The fully hydrated sample was placed in an alumina sample pan For scanning, the sample was cooled to – 80 °C at 20 °C/min and then kept at – 80 °C for 5 min before heating to 40 °C at 2.0 °C/min under a nitrogen atmosphere.

- ***Using TGA*** (STA PT1000, Linseis): The measurements were made in an alumina pan. For scanning, the sample was heated to 50 °C and kept for 5 min before heating to 250 °C at 10.0 °C/min under a nitrogen atmosphere.

Results and Discussion

Thermogravimetric analysis (TGA) was achieved at a heating rate of 10 °C/min under nitrogen atmosphere (**Fig. 1** and **Fig. 2**) and the results are listed in **Table 2**.

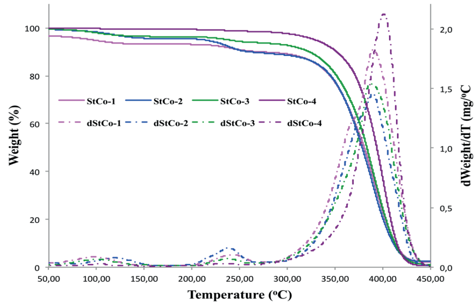

Fig. 1. TGA and DTG curves of copolymers StCo-1, StCo-2, StCo-3 and StCo-4.

It is observed that all copolymers have three stages of thermal decomposition. The first stage occurs at temperatures below 200 C, the second stage occurs at temperatures between 200 and 280 C and the third stage occurs at temperatures between 290 and 450 C. The Table 1 shows the temperature range for each mass loss stage. The first stage of mass loss is associated with the polymer dehydration process (Fig. 2). This way, knowing the mass used in the analysis and the percentage of loss that occurs up to a temperature of 180 °C, it is possible to determine the total amount of water present in the polymer. The amount of water determined by TGA was called Total Water (**W_T**).

Water Content (WC) and Water Uptake (WU) are two denominations for total water absorbed in a sample determined by using an analytical balance. Then, water uptake (*WU*) and water content (*WC*) can be calculated as follows:

$$\text{WU (\%)} = [(W_{wet} – W_{dry})/W_{dry}] \text{ x } 100 \quad (1)$$

$$\text{WC (\%)} = [(W_{wet} – W_{dry})/W_{wet}] \text{ x } 100 \quad (2)$$

Where, W_{wet} and W_{dry} correspond to the weight of wet membrane and weight of dry membrane, respectively.

The **W_T**, **WU** and **WC** values obtained for the prepared membranes from different copolymers are shown in **Table 3**. The **W_T** values were determined based on the TGA spectra (Fig. 2), observed at temperatures below 180 degrees. For this test, TGA equipment has been programmed to stabilize the sample at 40 °C for 10 min and heated at a rate of 10 °C/min, in a nitrogen

Copolymer	Loss mass 1		Loss mass 2		Loss mass 3	
	$T_{initial}$ (°C)	**T_F (°C)**	**$T_{initial}$ (°C)**	**T_F (°C)**	**$T_{initial}$ (°C)**	**T_F (°C)**
StCo-1	54.3	168.0	204.2	279.4	278.4	389.8
StCo-2	53.4	172.2	192.4	270.6	280.8	387.3
StCo-3	75.4	161.2	175.4	278.4	287.3	389.4
StCo-4	68.1	139.0	200.1	270.8	270.7	400.8

Table 2. Results of TG/DTG analysis of the copolymers **StCo-1**, **StCo-2**, **StCo-3** and **StCo-4**.

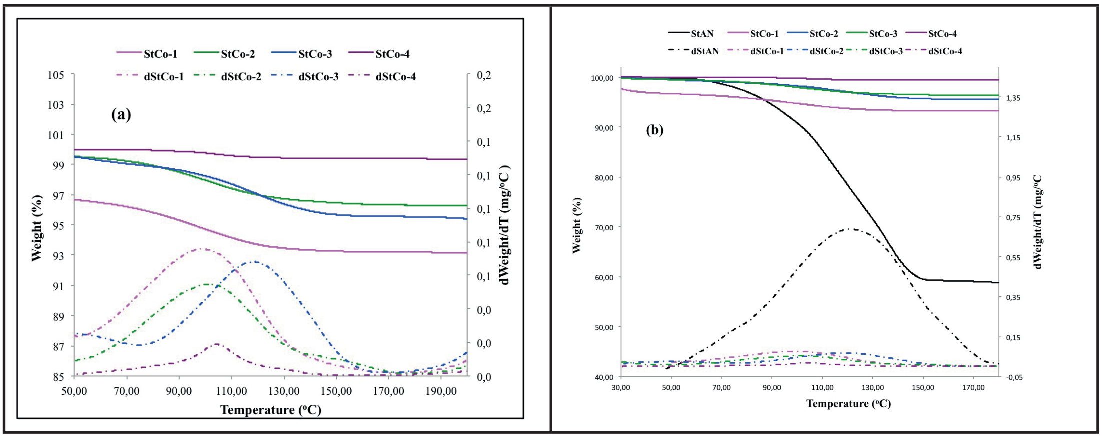

Fig. 2. TGA and DTG curves of copolymers. (a) StCo-1, StCo-2, StCo-3 and StCo-4 expanded in the region between 50 and 200C; (b) StCo-1, StCo-2, StCo-3, StCo-4 and StAN expanded in the region between 50 and 200C;

atmosphere, up to temperature of 200 °C. To determine WC and WU, the dry membrane was weighed before being hydrated (W_{dry}) and after hydrating (W_{wet}).

Copolymer	WU (%)	WC (%)	W_T (%)
StCo-1	25.90	20.50	8.35
StCo-2	48.10	32.50	8.30
StCo-3	26.60	20.90	7.60
StCo-4	7.50	6.20	2.88
StAN	2.80	6.99	49.51

Table 3. Water uptake (**WU**), water content (**WC**) and total water (**W_T**) for copolymers **StCo-1**, **StCo-2**, **StCo-3, StCo-4** and **StAN**.

It is observed that the amount of water absorbed (**WU**) and the water content (**WC**) are different values and different of total water (**W_T**) value. **W_T** was obtained by TGA analysis while **WU** and **WC** were obtained by difference in mass between the vacuum dried membrane and the hydrated membrane. Considering that to weight of wet membrane (**Wwet**), the determination depends a lot on how the experiment is carried out, since the excess water present on the membrane surface must be discarded, it is possible that part of the excess water is still present in the **Wwet** value. Parameters such as porosity and sample dimensions should also influence in **W_{wet}** determination. For the purpose of interpretation of results, the amount of total water present will be used the value of $\mathbf{W_T}$.

The amount and interaction mechanism of water with the polymer structure could be an important factor to understand the behavior of these materials. Considering the membrane hydration process, the water present could be classified in three states according to mobility that could be described as ***linked water***, an ordered water structure in the vicinity of different surfaces, due to its low molecular mobility. Considering the membrane hydration process, the water present could be classified in three states according to mobility. This parameter allows to classify the water in: ***linked water*** - an ordered water structure in the vicinity of different surfaces, that have low molecular mobility; ***free water*** - water with higher mobility; ***intermediated water*** - water that behaves similarly to linked water. ***Linked water*** is tightly bound to the surface and theses interactions are very strong, while water–water interactions are very weak. ***Intermediate water*** interacts moderately with the surface (stronger than free but weaker than Linked water) involving both water--surface and water–water interactions. ***Free water*** hardly interacts with the surface and there is mainly water–water interaction. According to the difference of intermolecular hydrogen bonding, including water/polymer bonding, weakened water/water bonding, and normal water/water bonding, the structure of hydrated polymer network could be represented by **Fig. 3**.

When a sample of hydrated copolymer is cooled well below 0°C, the free water and intermediated water freezes but the linked water remains in the non-frozen state. When the frozen sample is heated in a calorimeter, the heat required to melt the frozen water can be measured (**Fig. 4**). Non-frozen water, which is defined as the linked water, is the difference between the total water (water content) and the frozen water.

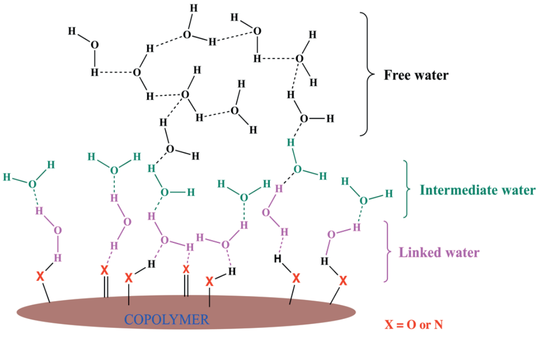

Fig. 3. Schematic representation of the water in the copolymer network.

The frozen water (W_{fs}) could be determined using equation 4.

$$W_{fs}\,(\%) = \frac{\Delta H_{\text{polymer hydrated}}}{\Delta H^{o}_{m\ water}} \times 100 \qquad (4)$$

Where: $\Delta H^{0}_{m,\ water} = 333.5(J/g)$ and $\Delta H_{\text{polymer hydrated}}$ is the summation of all the melting enthalpy in the heating trace of DSC of hydrated copolymer.

The linked water (W_{liked}) could be determined by difference between water content (W_T) and frozen water (W_{fs}) using the equation 5.

$$W_{liked}\,(\%) = W_T - W_{fs} \qquad (5)$$

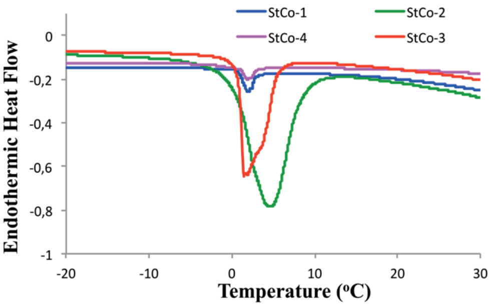

Fig. 4. Differential thermal analysis thermograms of a StCo-1, StCo-2, StCo-3 and StCo-4 composites.

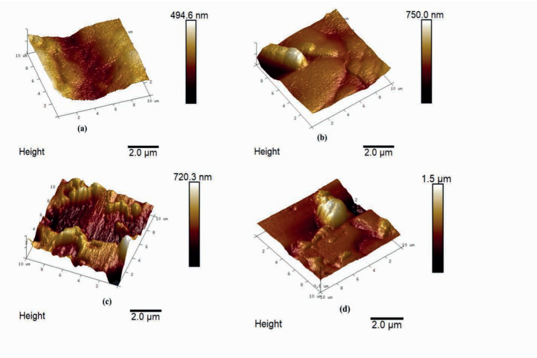

Fig. 5. AFM pictures of (a) StAN dry, (b) StAN hydrated, (c) StCo-1 dry and (d) StCo-1 hydrated.

Copolymer	W_T (%)	$\Delta H_{\text{polymer hydrate}}$ (J/g)	W_{fs} (%)	W_{liked} (%)
StCo-1	8.35	3.40	1.02	7.33
StCo-2	8.30	22.93	6.87	1.43
StCo-3	7.60	10.42	3.12	4.48
StCo-4	2.88	0.87	0.26	2.62

Table 4. Water content (W_T), melting enthalpy ($\Delta H_{\text{polymer hydrated}}$), frozen water ($W_{fs}$) and linked water ($W_{liked}$) for copolymers **StCo-1**, **StCo-2**, **StCo-3** and **StCo-4**.

It is observed that the StAN copolymer is the material that absorbs the largest amount of water (> W_T) and also the one that has the lowest amount of linked water (< W_{linked}). All the water absorbed in StAN is in the form of free or intermediate water.

AFM was used for the determination of phase morphology, heterogeneity, or homogeneity of the membranes. In addition, the surface roughness of the membranes was too determined. The selected AFM images of membranes are presented in **Fig. 5**. In the comparison, it is possible to differentiate the morphology between the two types of materials, StAN and StCo-1.

Conclusion

Styrene copolymers were synthesized and characterized. Membranes of these copolymers were prepared by casting. theses membranes were hydrated and the amount of water that each type of material absorbs was determined by thermal analysis. The results demonstrate that there is a difference in how water is in the membrane and how much water is directly linked to the material surface. Complementing this study is necessary, but it is possible that there is a direct relationship between the type of water present in the material and properties as ionic conductivity, which is highly dependent on the presence of water in the membrane.

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