A new solid polymer electrolyte membrane based on cross-linking of water soluble monomers

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A free radical polymerization was conducted to prepare a diblock copolymer based on two water soluble monomers 4-styrenesulfonic acid sodium salt and 4-vinylpyridine with a high molecular weight. For the polymer synthesis was used as an initiator sodium persulfate and the polymerization was conducted at 70ºC. A new membrane was obtain by cross linking with 1,10-dibromodecane and the resulting membrane SSA-4VP2 exhibits good hydrophilic stability and higher proton conductivity (0.136 S/cm) at 25 ºC .

1. Introduction

The ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of the ionic groups attached to the membrane matrix. The cation exchange membranes contain negatively charged groups, such as $-SO_3^-$, $-COO^-$, $-PO_3H^-$, $-PO_3^{2-}$, $-C_6H_4O^-$, fixed on the membrane backbone allowing the passage of cations but rejecting anions. While anion exchange membranes contains positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, $-SR_2^+$, fixed to the membrane backbone which allow the passage of anions but reject cations [1-4]. According to the connection way of charged groups to the matrix or to their chemical structure, the ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. However, most of the practical ion exchange membranes are rather homogenous and composed of either hydrocarbon or fluorocarbon polymer films hosting the ionic groups [3, 4].

The proton exchange membrane fuel cells, also called polymer electrolyte fuel cell or solid polymer electrolyte fuel cells use a proton exchange membrane, which acts as a solid electrolyte between the anode and cathode electrodes [5]. The proton exchange membranes in these fuel cells consist of copolymer materials which include proton conductor units. Usually sulfonic acid groups are utilized. The current state of art for proton exchange membranes is Nafion (perfluorinated ionomer). Nafion™'s poly (perfluorosulfonic acid) structure imparts exceptional oxidative and chemical stability, which is also important in fuel cell applications. Moreover, Nafion™ shows high proton conductivity. However, it suffers from

high methanol permeability and also relatively low glass transition temperatures. The operating temperature of proton exchange membrane fuel cells has been reported between 60 and 130 °C, but mostly at 80 ºC.

Generally, proton exchange membrane (PEM) contains cationic exchange groups such as SO_3^- group. For PEM materials, poly(styrene sulfonic acid) (PSSA) and its copolymers have been widely studied because of their synthetic easiness and higher conductivities [6], and many studies used PSSA in the forms of random copolymers, block or graft copolymers.

Acid-based blends are considered a class of fuel membrane design, which use basic polymers, such as poly (ethylene oxide) (PEO) [7, 8, 9], poly (vinylalcohol) (PVA), poly (acrylamide) (PAAM), poly (vinylpyridine), or poly (vinylpyrrolidone) (PNVP) complexed with strong acids, such as sulfuric acid or phosphoric acid. These blends possess low proton conductivities (~ 0.1 S/cm) in both their dehydrated and hydrated states. In order to get sufficient conductivity it is usually necessary to load the membrane with a high acid content; however, this can result in poor mechanical stability especially at temperatures above 100 °C. Another concern is the tertiary C-H bond stability in the oxidative environment of fuel cells. The approaches to improving the polymer's mechanical strength have included: (1) cross-linking; (2) use of high temperature polymers such as polybenzimidazole (PBI) and poly (oxadiazole); and (3) adding inorganic filler or/and a plasticizer [10].

The cross-linking can be accomplished chemically [11] or by irradiation. Chemical cross-link is accomplished by heat induced reaction between the polymers and a cross-linking agent [12]. When the polymer chains are linked together by cross-links, they lose some of their ability to move as individual polymer chains. In general, the mechanical characteristics are improved, especially at

higher temperatures. It results in improved resistance to stress cracking and better fluid resistance. The chemical covalent cross-links are mechanically and thermally stable, so once formed are difficult to be broken. The cross-linked materials can't dissolve in solvents, because all the polymer chains are covalently tied together. But they can absorb solvents.

The vinyl monomers may be polymerized via free-radical polymerization, a type of chain growth reaction. One of the most common free radical generation methods is achieved by a redox reaction of organic or inorganic compounds. This method is well known for its high effectiveness in mild conditions [13]. Also, because the components of the redox couple are stable when they are separated, the initiator feed can be controlled very easily and the catalyst can be delivered in a long period of time if needed.

Polymers derived from 4-vinylpyridine (4VP) have been quaternized with alkyl halides [14, 15] to form cross-linked polymers for use in anion-exchange membranes [16,17]. 4-Vinylpyridine is known to polymerize spontaneously at higher temperatures and it is more reactive than styrene under the conditions of free radical polymerization [18].

The direct polymerization of sulfonated monomers provides the means of control over the position, number, and distribution of proton conducting groups along the polymer backbone, unlike the polymer sulfonation.

In particular, the block copolymers based on an inexpensive monomer sodium styrene sulfonate, SSNa, are of great practical interest, as they are used in several applications, including ion exchange or fuel cell membranes [19, 20].

In this work, we present the results related to a diblock copolymer free radicals synthesis based on two water soluble monomers 4-styrenesulfonic acid sodium salt and 4-vinylpyridine with a high molecular weight.

2. Experimental part

2.1 Materials

The materials used for membrane synthesis are 4-Styrenesulfonic acid sodium salt ($H_2C=CHC_6H_4SO_3Na$), from Alfa Aesar, 4-vinylpyridine (C_7H_7N) containing 100 ppm hydroquinone as inhibitor, 95% from Aldrich, and sodium persulfate ($Na_2S_2O_8$), 1,10-dibromodecane ($Br(CH_2)_{10}Br$), acetone, methanol, dimethylsulfoxide (DMSO) from Merck.

2.2 Copolymer synthesizes

The copolymer (styrenesulfonic acid-co-vinylpyridine) was synthesized using a free radical polymerization in distilled water at 70ºC under nitrogen atmosphere and 8h continuous mixing.
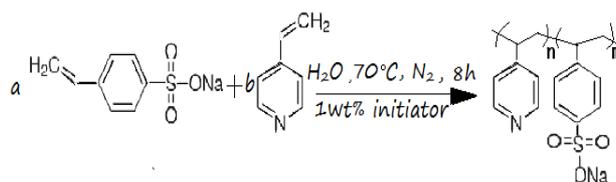

Fig. 1 Synthesis of poly(styrene sulfonic acid-co-4-vinylpyridine) copolymer through free radical polymerization ; a-mol of 4-NaSSA, b-mol of 4-VP

The reaction conditions were: the monomer mole ratio [NaSS]:[4VP]= [a]:[b], monomer weight was 10wt% and the initiator was ~ 1wt % of monomers.

We put in a flask the monomers (NaSSA and 4VP) with distillated water and then they were mixed with a magnetic stirrer at room temperature and under N_2 for 30 minutes before heating the solution to 70ºC. After the solution reached 70ºC, we added the initiator ($Na_2S_2O_8$) dissolved in H_2O and stirred for 8 h under N_2.

Table 1. Copolymers - initial monomer feed ratio

Sample	Monomer feed ratio [mol]: [mol]	
	4NaSS	4VP
NaSSA-4VP 1	1	1
NaSSA-4VP 2	1.5	1
NaSSA-4VP 3	2	1
NaSSA-4VP 4	3	1
NaSSA-4VP 5	5	1

The resulting solution was precipitated in acetone then filtered and washed three times with acetone. The precipitated solution was yellow and had the consistence of a rubber. Then we put it into the vacuum drier at 80 ºC for 11h.
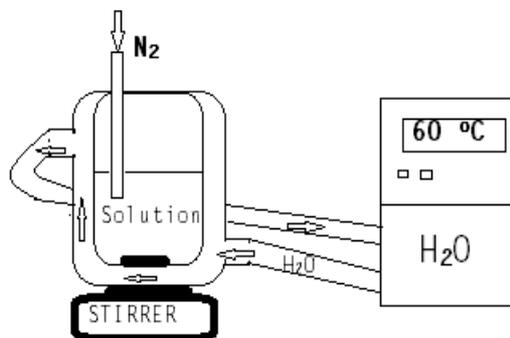

Fig. 2. Installation scheme of free radical polymerization.

The obtained copolymer was characterized by infrared spectroscopy (PerkinElmer spectrophotometer) and by pyridine content. The mid-IR spectra were measured using a PerkinElmer spectrophotometer using 32 scans with a spectral resolution of 1 cm^{-1}. The KBr pellets were prepared by a standard technique when 3-5 mg of a sample was compounded and pressed with 300 mg of KBr.

2.3 Cross-linking and casting the membrane

A desired amount of copolymer and the haloalkyl cross-linker 1,10-dibromodecane ((molar ratio of copolymer's pyridine groups to $(Br(CH_2)_{10}Br)$ was 2:1 molar) were dissolved in DMSO using an amount of 10%wt solute at room temperature which was then mixed up for 2 h with a magnetic stirrer. The resulting solution was cast onto a glass plate and heated at 60 ºC for 72 h in order to complete the cross-linking reaction. The resulting membrane was soaked in methanol to remove the solvent and then washed with water and put it in HCl 2M for 2 days for acidification.

2.4 Ion exchange capacity and water uptake

The ion exchange capacity (IEC) was determinate by potentiometric titration. The sample membrane in H$^+$ form (W$_{dry}$) was equilibrated in a solution of 1M NaCl for 24 h to release H$^+$ ions. The membrane sample was extracted, easily wiped with filter paper to remove the excess of NaCl and weighted (W$_{Naform}$). The solution was titrated with 0,1035M KOH using a pH-meter to register the change in pH. The titration was done with Cerko Lab System (CLS) instruments which allow a precision potentiometric titration and it was connected to a PC which registered the change in pH and plot the titration curve. Then, from the first derivative $\Delta pH/\Delta V$ it was determined the equivalence point from the peak of the curve which corresponded with the inflection point.

$$IEC\left[\frac{meq}{g}\right] = \frac{C_{KOH} \times V_{KOH}}{W_{dry}}, \qquad (1)$$

The water uptake was measured after the membrane in H$^+$ form was immersed in water for two days before being wiped and quickly weighted (W$_{wet}$). The mass of the dry membrane was obtain after being dried in the heating cabinet at 100ºC for 10h until there was noticed no change in weight (W$_{dry}$).

$$WU[\%] = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%, \qquad (2)$$

2.5 Proton conductivity

The proton conductivity was measure under atmospheric pressure and in membrane thickness, using as electrolyte HCL 1M in a cylindrical glass holder at 25ºC. The proton conductivity was calculated by

measuring the impedance R (ohm) of the membrane using a LCR meter [21].
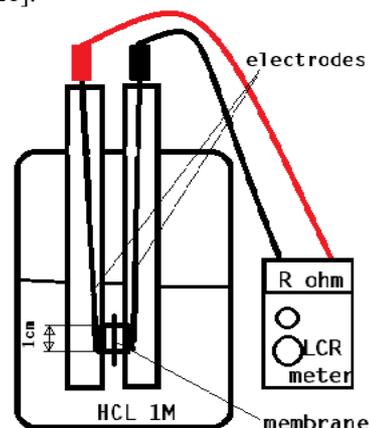

Fig. 3 Proton conductivity measurement installation scheme

The membrane was put between two wire electrodes (sandwich like) which were directly connected to a LCR meter. The proton conductivity of the membrane was calculated by:

$$\sigma = \frac{L}{R \times A}, \qquad (3)$$

Where: σ is the proton conductivity [Scm^{-1}], L is the membrane thickness[cm] , A is the membrane section area [cm^2], namely 0.786 cm^2, as the membrane diameter is 1 cm diameter and R is the impedance [ohm]. The impedance was measured overlaying an a.c. potential perturbance of 7.5 mV at a constant 1 KHz frequency over the direct current carrier.

The membrane was equilibrated prior to any measurement for at least 30 minutes.

$$R = Rmemb - Rel, \qquad (4)$$

R$_{el}$ is the impedance of the electrolyte and R$_{memb}$ is the impedance of the equilibrated membrane.

3. Result and discussions

Copolymer characterization

The content of pyridine was determinate using a potentiometric titration with Hal 0.05M and the values are shown in Table 2.

Table 2. Copolymer's pyridine content

Sample	Pyridine content [%]
NaSSA-4VP 1	49.7
NaSSA-4VP 2	37.3
NaSSA-4VP 3	28.7
NaSSA-4VP 4	21.2
NaSSA-4VP 5	12.1

3.1 MIR

Fourier transform infrared spectroscopy is a powerful tool used to characterize the functional groups in a material. In Figure 4 is presented an IR spectra for copolymer NaSSA-4VP2 and the resulting membrane SSA-4VP2.

It was noticed a significant band at the 1639 cm^{-1} C=C bond in the vinyl monomer. For instance, since they all have C=C double bond, all spectra presented a band within 1660-1630 cm^{-1} range. In order to understand whether they polymerized with other monomers we needed to determine their characteristic bands.

It could be observed that after cross-linking and acidification the intensity of the band increased at 1639 cm^{-1}. This peak could be assigned to the pyridine action du to the C=N bond which has the absorption bands at 1690 and 1620 cm^{-1}.

The styrene sulfuric acid spectrum had a series of bands within the range 1200-1120 cm^{-1} due to the suffocate group attached to the phenyl ring. This side group presented the most significant band of the monomer at 1188 cm^{-1}. By using all these data from the characteristic bands' position it was possible to get very quickly a basic idea about addition of the monomers to polymer.

The SO$_3^-$ group's asymmetric and symmetric vibration adsorption bands could be assigned to the bands at 1038 and 1009 cm^{-1}. The bands at 1188 and 1128 cm^{-1} could be assigned to the in-plane skeleton vibration of the benzene ring and in-plane bending vibration of the benzene ring.
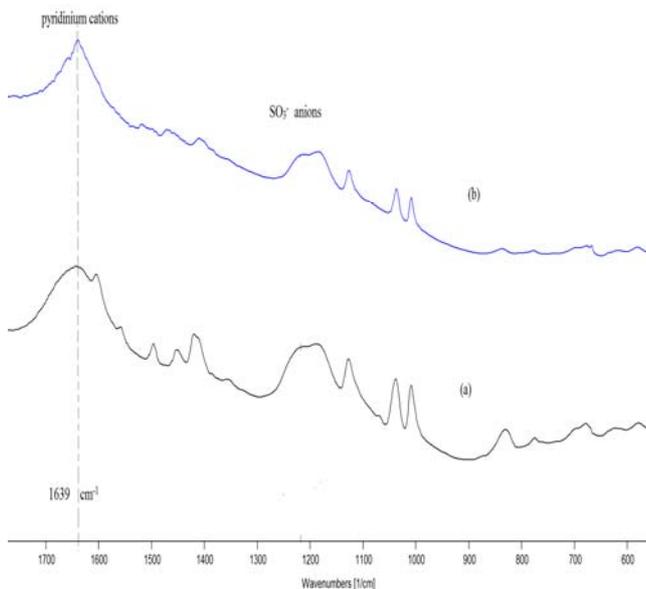

Fig. 4 MIR spectra (a) Copolymer NaSSA-4VP2,
(b) Membrane SSA-4VP2

The peaks at 1378 cm^{-1} and 828 cm^{-1} were assigned to the bending vibration of aliphatic -CH$_3$ groups.

3.2 Ion exchange capacity and water uptake

The ion-exchange capacity (IEC) indicates the density of ionisable hydrophilic groups in the membrane matrix, which are responsible for the ionic conductivity. IEC is a quantification of the ion-exchangeable sulfonic acid groups ($-SO_3^-H^+$) and pyridinium salts in the membranes. The measured IEC for the cross-linked membranes SSA-4VP ranges from 0.09meq/g to 3.95meq/g. The increase in IEC values was caused by the increase in the overall of sulfonic acid content.

The water sorption of the polymeric materials has a profound effect on the proton conductivity and mechanical properties of the PEMs, so an excessively high water uptake (WU) could conduct to membrane fragility and dimensional changes, which could also lead to poor mechanical properties.

The WU was determined from the ratio of the weight of the water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. As IEC increased, there were more ionic groups to interact with water.

3.3 Proton conductivity

A good proton conductivity of a proton exchange membrane is clearly one of the most important properties when referring to applications. The magnitude of the specific conductivity is determined by a combination of charge carrier density and the charge carrier mobility [22]. The charge carrier is the proton and it is depending, to some extent, on the number of pendent sulfonic acid groups along the polymer chain. The conductivities for the cross-linked membrane ranged from 0.081 S/cm to 0.593 S/cm which are higher than those of Nafion 117 (0.105 S/cm) [23]. In PEM fuel cells, the proton conductivity of the membrane is particularly important since it plays a significant role in the performance of fuel cells. To achieve a good conductivity, a high acid loading is desirable.
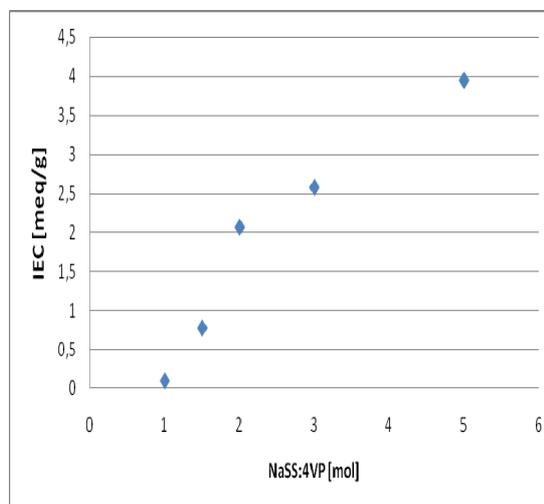

Fig. 5. Ion exchange capacity function of copolymer
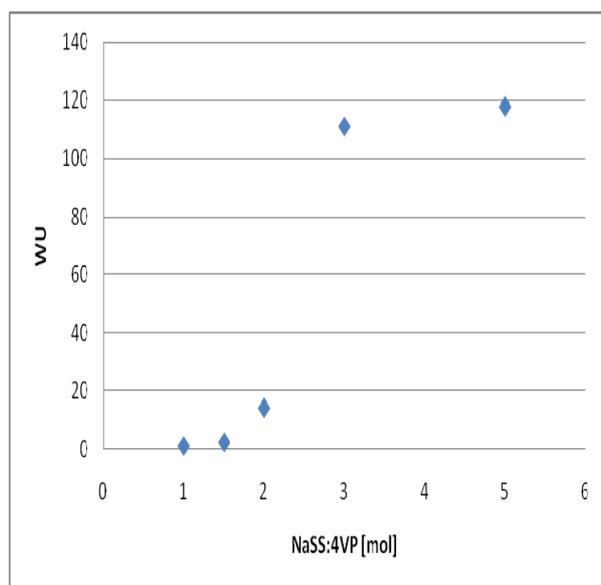*NaSSA-4VP initial monomers mole ratio*

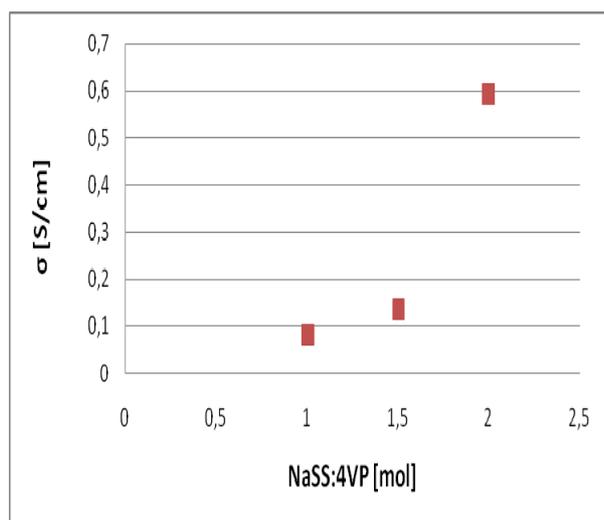*Fig. 6 Water function of copolymer NaSSA-4VP initial monomers mole ratio*

Fig. 7 Proton conductivity function of copolymer NaSSA-4VP initial monomers mole ratio

Nevertheless, for linear PEM materials, this is achieved by compromising the mechanical integrity and an excessive swelling. Through chemically cross-linked systems, we have maximized the acid loading of the PEM materials to reach higher proton conductivity. As the proton conductivity is determined by the product of charge carrier density and charge carrier mobility, it is expected that the high ion content of PEMs will result in an increase of proton carriers.

From figure 5, figure 6 and figure 7 it could be observed the ion exchange capacity, water uptake and proton conductivity increase with the content of the styrenesulfonic acid in membrane.

Table 3. SSA-4VP2 membrane characteristics.

	IEC [meq/g]	σ [S/cm]
SSA-4VP2	0.78	0.136
Nafion 117 [18]	0.91	0.105 *

*in water at 30 ºC

3.4 Hydrolytic and mechanical stability

Usually, the proton conducting polymer for fuel cell application, especially at high temperature, must meet a number of criteria such as good film forming, highly proton conductivity, chemically stable to acid/free radicals, thermally and hydrolytic stability in the presence of water.

The membrane SSA-4VP1 was too rigid and easily to be broken and the membrane SSA-4VP3, SSA-4VP4 and SSA-4VP5 with a smaller content of pyridine looked like gels and suffered changes in shape and dimension.

The best membrane obtained was the membrane SSA-4VP2 due to a 40% pyridine content, with a good stability in water (25 ºC); even after one month it did not suffer any changes in dimension, conductivity, appearance and shape.

4. Conclusion

Our work proved that a new copolymer poly (styrene sulfonic acid-co-4-vinylpyridine) could be prepared through direct free radical polymerization of styrene sulfonic acid sodium salt and 4-vinylpyridine in water. Cross-linked SSA-4VP membranes were conducted with a haloalkyl cross-linker. The cross-linked SSA-4VP2 membrane demonstrated an excellent hydrolytic stability with only slight changes in weight and proton conductivity after one month of testing in water at 25ºC. The proton conductivity (0.136 S/cm) was superior to that of Nafion 117(0.105 S/cm) and the IEC (0.78 meq/g) was comparable to that of Nation 117(0.91 meq/g).

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