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Polyelectrolyte Membranes Based on Sulfonated Syndiotactic Polystyrene in Its Clathrate Form

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Summary: Recently, more and more attention has been focused on new techniques for energy production also in view of environmental problems. A noticeable device is small fuel cell that converts chemical energy into electric energy by electrochemical reaction of hydrogen with oxygen, and exhibits a high-energy efficiency. Conventional small fuel cells have been classified into phosphoric acid-type fuel cells, molten carbonate-type fuel cells, solid oxide-type fuel cells, solid polymer type fuel cells, etc., according to the type of electrolyte used. The target of this work is the development of a new process to build up polyelectrolyte membranes, for polymer type fuel cell (PEM), by sulfonating syndiotactic polystyrene in its clathrate form. The polyelectrolyte membranes of this paper are inexpensive and exhibit good long-term stability and ion exchange capability.

Keywords: clathrate form; fuel cell; polyelectrolyte membranes; sulfonation; syndiotactic polystyrene

Introduction

Application of solid polymer electrolyte membranes spans a variety of electrochemical technologies: low-temperature fuel cells, batteries, electrodialyzers, chlor-alkali cells, sensors, electrochromic devices, and supercapacitors. Nafion® is a perfluorinated ionomer which has been investigated extensively [1–3], and largely utilized as a membrane material, particularly in fuel cells and in the chlor-alkali process. The proton-conducting membrane is the key component of a fuel cell system. The main function of the membrane in the cell is to transport protons from the anode to the cathode. Further, the membrane should provide a gas barrier and physically separate the electrodes. In order to fulfil these functions, the membrane should be prepared from a polymer having excellent mechanical, thermal, hydrolytic, oxidative and reductive stability. These high demands require the use of very stable polymers, which normally limits the materials choice to perfluorinated or partially fluorinated polymers [4,5]. However also these materials show some

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shortcomings such as unacceptable methanol cross-over and water transport rates, high cost, around 800 US$/m^2 [6], and involvement of production processes with high toxicity and environmental impact.

A recent development in the field of proton-conductive polymer membrane is the sulfonation of atactic and syndiotactic polystyrene. Carretta et al. [7] have partially sulfonated commercially non cross-linked atactic polystyrene to various extents, obtaining a homogeneous distribution of the sulfonic acid groups in the polymer. Since the resulting materials are not cross-linked, high quality membranes were easily obtained by evaporation casting from appropriate solvents. The level of sulfonation was tailored to maximize the proton conductivity, while preventing the membrane from becoming soluble in water. The most extensively sulfonated membrane exhibited a conductivity equal to that of Nafion. In fact a conductivity of $5 \cdot 10^{-2} \Omega^{-1} cm^{-1}$ was measured for a degree of sulfonation of 20%. Very recently, styrenic polymers with syndiotactic configuration (e.g. syndiotactic polystyrene, sPS) have been sulfonated [8]. Sulfonation has been performed in solution, and once sulfonated, sPS polyelectrolyte membrane was produced by solution-cast. Syndiotactic polystyrene is a rigid semicrystalline material with a glass transition temperature close to 80-90°C and a high melting temperature close to 270°C and, unlike the corresponding isotactic polymer, crystallizes rapidly upon cooling from the melt. Several structural studies have shown a very complex polymorphic behaviour for this polymer [9-11]. Different polymorphic forms of sPS are characterized by widely different conformation. In fact, two crystalline forms include chains with a *trans*-planar conformation while two crystalline forms include chains with sequences of dihedral angles corresponding to a s(2/1)2 helical symmetry. Different modes of packing in different unit cells exist for the *trans*-planar chains of sPS in the so called α and β forms, for which hexagonal and orthorhombic unit cells have been described, respectively. Instead the chains with s(2/1)2 symmetry are present in the two crystalline forms named γ and δ. In particular, the term "δ-form" has been used to indicate different clathrate structures, which include molecules of solvent [9-11].

Object of the present work is to realize a polyelectrolyte membrane by sulfonating a film of syndiotactic polystyrene (sPS) while being in its clathrate form [12]. The presence of clathrate regions is essential for the proposed functionalization process: in fact the basic idea is that the swollen crystalline phase supplies regular sulfonation patterns inside the crystalline phase.

Experimental procedures

Sulfonation procedure. A sulfonation procedure, to introduce the ion exchange groups into a sPS membrane, has been employed. Several sulfonating agent can be used for this propose (sulfuric acid, chlorosulfonic acid, etc.). The reaction mechanism is described from the following equation:

$$Ar + H_2SO_4 \rightarrow ArSO_3H + H_2O$$

The sPS membrane was first produced by casting a polymer-choloroform solution onto a glass substrate to form a film. The solution was prepared by mixing 0.5 g of syndiotactic polystyrene pellets in 40 ml of chloroform (99,9% HPLC grade, Aldrich Chemicals) and then heating up to about 100°C for 1.5 hours until complete polymer dissolution. The solution was subsequently cooled adown to room temperature and then poured into a Petri's dish allowing partial evaporation of the solvent. By this procedure a sPS film, in its clathrate form, was obtained with a thickness of about 100 μm.

Next step was sulfonation of the sPS membrane in clathrate form, by soaking it in a solution of chloroform and chlorosulfonic acid (99%, Aldrich Chemicals) at room temperature for 4 hours. The reaction mechanism for chlorosulfonic acid is described from the following equation [13,14]:

$$2\,HOSO_2Cl \leftrightarrow H_2^+O\text{-}SO_2Cl + SO_3 + Cl^- \leftrightarrow {}^+SO_2Cl + HCl + HSO_4^-$$

$$Ar + {}^+SO_2Cl + HSO_4^- + HCl \rightarrow ArSO_2Cl + H_2SO_4 + HCl$$

Overall reaction: $Ar + 2\,HOSO_2Cl \rightarrow ArSO_2Cl + H_2SO_4 + HCl$

After the desired time reaction, the membrane was washed with deionized water to remove residual sulfonating reagent from functionalized sPS membrane. The sulfonated membrane was then placed in a stirred solution 1 M NaOH (Sodium hydroxide 97% 20-40 Mesh bead, Aldrich Chemicals) at room temperature to hydrolyze the sulfonyl chloride to sulfonic group according to:

$$ArSO_2Cl + NaOH \rightarrow ArSO_3H + NaCl$$

Finally, the membrane was washed with distilled water and then dried in an oven under vacuum at 60°C for 1 hour.

Characterization methods. FT-IR spectroscopy was used to detect the presence of sulfonated groups attached to the phenyl. Infrared spectra were obtained with a Thermo Nicolet Nexus FT-IR on potassium bromide pellets.

The thermal properties of the syndiotactic polystyrene and sulfonated sPS were determined using a TA Instrument 2910 Differential Scanning Calorimeter (DSC) equipped with a nitrogen purge.

Thermal stability of sPS and sulfonated sPS was studied using a TA Instrument 2950 Termogravimetric balance (TGA) equipped with a nitrogen purge. A heating rate of 10°C/min. Evaluation of water absorption was performed by immersing the membrane in distilled water for 24 hours, or longer, at room temperature. Then, samples were carefully blotted and their weight, W_1 (g), was measured using a Mettler-Toledo analytical balance mod.AB204-S, with a sensitivity of 0.0001g. After that, the membrane was dried at 120°C for 4 hours and the dry weight, W_2 (g), measured. The water content C(%) of the membrane was hence calculated as:

$$C(\%) = [(W_1 - W_2)/ W_2] \times 100$$

Proton conductivity of membranes was determined from lateral resistance of membrane that was measured using a four-point-probe electrochemical impedance spectroscopy technique [15] using a BekkTech Conductivity Cell. The cell was equipped with two platinum foil outer current-carrying electrodes and two platinum wire inner potential-sensing electrodes. The inner electrodes had a diameter of 0.75 mm and were placed at a distance of 0.425 cm. The Conductivity Cell, with membrane sample loaded, was fitted between the anode and cathode conduction plates of Fuel Cell Technologies Hardware. Impedance measurement was made using a Solartron SI 1280B electrochemical impedance analyser. The instrument was used in galvanostatic mode with AC current amplitude of 0.01 mA over a frequency range from 0.1 to 20,000 Hz. Before measurement, membrane samples were cut into strip approximately 1.0 cm wide, 2 cm long and 0.02 cm thick and immersed in distilled water for 2 hours at room temperature. Then it was blotted and finally mounted in the Conductivity Cell.

Results and discussion

The first step of polyelectrolyte membrane formation consists in forming an sPS film by solution-casting using a proper solvent (chloroform, methylene chloride, o-dichlorobenzene, toluene). In fact, the solvent has to be the selected among those able to form clathrates into sPS [16]. During solution densification which precedes by solvent evaporation the polymer solvent mixture first forms a gel and then a solid film made of amorphous and crystalline regions. Inside the film the solvent is partly dissolved into the amorphous domains and partly hosted into regularly spaced nanocavities present in the crystalline phase, forming so-called inclusion compounds. The presence of clathrate regions is essential for the proposed functionalization process: in fact the basic idea is that the swollen crystalline phase supplies regular sulfonation patterns inside the crystalline phase. Possibly, this can induce the anchoring of ionic groups in a regularly spaced arrangement along the polymer backbones included in the crystalline domains. It is worth noting that attempts of sulfonating semicrystalline sPS membranes in α form was not as successful: in fact sulfonation was found to occur only on the surface. There are examples in the literature [7,8] of sulfonation of sPS but in those cases sulfonation was performed in bulk starting from dilute solutions. As a consequence aim of the present contribution was, on one side, to try to obtain a regularly sulfonating structure likely characterized by higher proton conduction efficiency and, on the other side, to set up at the same time a simpler manufacturing protocol. The present procedure presents advantages also as compared to the case of sulfonation of atactic PS. In fact, although atactic polystyrene is easily and effectively sulfonated, it cannot be sulfonated above certain limits due to occurrence of water solubility.

The sulfonation of sPS film in its clathrate form introduces the sulfonic groups in the polymer forming an electrolyte membrane with ion exchange capability. The degree of sulfonation is controlled by the chlorosulfonic acid concentration; the conditions used for about 0.3 g of polymer are given in Table 1. In the last column is reported the theoretical maximum degree of sulfonation that would be obtained in the purely hypothetical case that all the chlorosulfonic acid present in the solution is effective for sulfonation.

Table 1. Sulfonation condition

Sample	**sPS (g)**	**Chlorosulfonic acid (mL)**	**Reaction time (h)**	**Maximum theoretical degree of sulfonation (%)**
A	0.4494	0.15	4	25
B	0.3514	0.14	4	30
C	0.2703	0.13	4	37
D	0.3155	0.18	4	44
E	0.3144	0.18	72	44

The figure 1a shows the FTIR spectra of the samples of pure and sulfonated sPS. The spectra have been normalized to absorbance value at 2850cm^{-1} relating to the stretching of metilene group (-CH_2-) invariant respect to the sulfonation reactions.

In the spectra of the neat sPS sample the peaks at 1278, 934 and 943cm^{-1} correspond to vibrational modes of the crystalline s(2/1)2 helices [17] while the two peaks at 1160cm^{-1} and

1130cm^{-1} correspond to vibrational modes in the plane of the ring C-H bonds. It is worth to note that these peaks are observed also in the spectra of the sulfonated samples, even though as shoulders. The absorptions due to the bending of ring C-H bonds have been strongly reduced by the substitution's reactions in the benzene rings. Furthermore the peaks of the vibrational modes of the sulfonated anion, in particular in the range 1150-1300cm^{-1}, are overlapped to the absorptions of the crystalline phase. These evidences highlight that the conducted sulfonation reaction does not destroy completely the crystalline structure of the membranes of sPS.

The most prominent bands for confirming sulfonation on sPS are observed at 1175 cm^{-1} and 1040 cm^{-1} and correspond respectively to the asymmetric and symmetric stretching vibrations of the sulfonated anion group (SO_3^-) [18]. Also the strong absorption band at 1009 cm^{-1} has been attributed to a vibrational mode of sulfonated anion attached to a benzene rings [19]. Further evidence of sPS sulfonation is gained by observing the peak at 1128cm^{-1} and the shoulder at 1097cm^{-1}. These absorptions, which are absent in the spectrum of the unsulfonated sPS, have been attributed to in plane skeletal vibrations of the disubstituted benzene rings [20]. The occurrence of these absorption bands proved qualitatively the presence of groups $-SO_3H$ attached in polymeric chains. In figure 1b, the FTIR spectra of sulfonated samples A, C, D and E show the enhanced content of sulfonic group in the sPS samples with the increase of the theoretical degree of sulfonation.

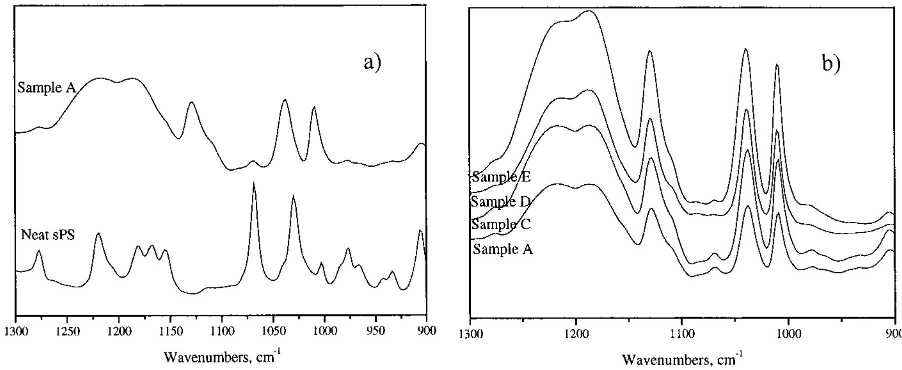

Figure 1. Infrared spectra of (a) pure and sulfonated sPS membranes; (b) sulfonated sPS samples.

To characterize the pure and sulfonated sPS membrane (sample A), the samples were first heated to 300°C and then rapidly cooled (-150°C/min) to the starting temperature of 25°C (first scan). A second heating scan was then performed up to 300 °C at 10°C/min: results are reported in figure 2 for unfunctionalized syndiotactic polystyrene membrane obtained by solution-cast with $CHCl_3$ and for sulfonated sPS membrane (sample A). The glass transition temperature (T_g) of pure sPS is about 100°C, the melting temperature (T_m) is 271°C and ΔH_f is 24.0 J/g (corresponding to a weight percent crystallinity of 29% based on theoretical heat of fusion for sPS with 100% crystallinity, i.e. ΔH°_f= 82.6J/g [21]).

During the first scan the sulfonated sPS membrane shows a broad peak around 120°C witnessing desorption of a significant amount of water solubilized in the sample associated to the presence of sulfonic groups. In this case the glass transition temperature (T_g) is still about 100°C, but the melting temperature (T_m) is now 264°C and ΔH_f is now 7.3 J/g (corresponding to a weight percent crystallinity of 9%). Therefore the sulfonation promotes a significant structural change which induces a depression of melting temperature and a reduction of crystallinity. Literature studies [20,24] on sPS sulfonated in solution report significant alteration of the crystallization behavior of sulfonated sPS as compared to neat sPS in terms of depression of degree of crystallinity and melting temperature as well as crystallization rate. Our experimental observation are, hence, consistent with an effective sulfonation of crystalline domains [22,23].

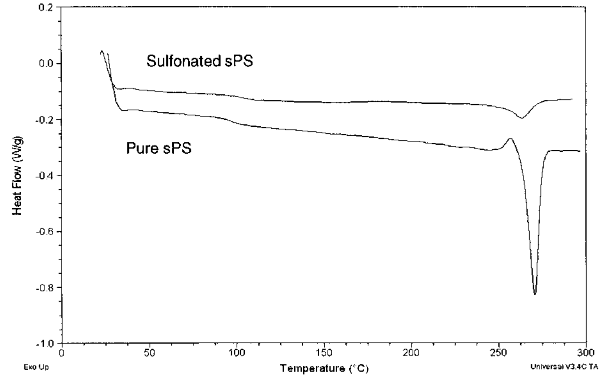

Figure 2. DSC curves of pure sPS membrane and sulfonated sPS membrane (Sample A).

Thermogravimetric analysis performed on unfunctionalized sPS membrane, obtained by solution-cast with $CHCl_3$, indicates that the polymer is stable up to 370°C, and at around 400°C begins its degradation. Sulfonated sPS displays weight loss below 370°C likely due to loss of absorbed water and, in a minor extent to other low molecular weight compounds. Also in this case significant degradation and associated weight loss occurs above 400°C.

The equilibrium water content of sulfonated sPS membranes was measured utilizing the procedure described in the experimental section. In table 2 are reported the results for membranes with different levels of sulfonation. As expected the water content increases with increasing theoretical sulfonation degree and reaction time.

Table 2. Water content of sPS membranes obtained

Sample	**Water content** (%)
A	125
B	331
C	400
D	416
E	746
Nafion 117	24

Proton conductivity is affected by the ability of membrane to retain water. Then, proton conductivity of samples B and D were measured at 21°C versus water content. In figure 3 are shown the results of proton conductivity measurements performed on sample B and D at different water content. In this figure are reported similar measurements for a commercial Nafion 117 membrane (Quintech), used as reference, performed in the same experimental conditions as for samples B and D.

A decreasing behaviour of conductivity with decreasing water content is evident for the Nafion's membranes. In contrast the sPS membranes show a linear increase of the conductivity with the water content until to about 100%. Then the conductivity values are constant within the error bars. That is probably due to an overflowing of the ionic structure that doesn't contribute to increase the conductivity. In Table 3 are listed the conductivity values for different membranes of sPS and Nafion 117. These were obtained at 21°C just after the water attached on the surface of the samples was removed and they were placed in the cell, i.e. in highest hydration condition.

Table 3. Proton conductivity of sPS and Nafion 117 membranes

Sample	Proton conductivity (mS/cm)
A	9 ± 2
B	13 ± 2
C	21 ± 2
D	23 ± 3
E	26 ± 4
Nafion 117	56 ± 1

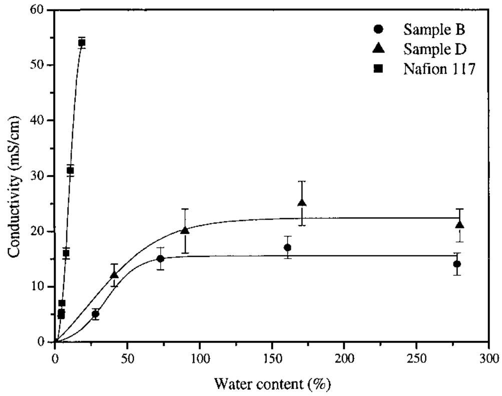

Figure 3. Proton conductivity versus water content (Sample B, D and Nafion 117).

As expected, the conductivity increases with sulfonation degree and with reaction time.

The preparation of the polyelectrolyte membrane according to this work is simpler and requires less working steps compared to the membrane develop by Idemitsu Petrolchemical Co. [8]. In fact the introduction of ion-exchange groups is carried out on an already formed film containing syndiotactic polystyrene in its clathrate form. Instead the Idemitsu process for obtaining the polyelectrolyte membrane is quite complicated and requires several working steps due to the fact that it is necessary to perform reagent used for the sulfonation of the polymer. In addition, the sulfonation degree and reaction time of polyelectrolyte membrane developed in this work could be increase to obtained higher conductivity. Instead the proton conductivity, at room temperature, of ionomeric membranes based on partially sulfonated atactic polystyrene develops by Carretta et al. [7] is very close to the conductivity of Nafion ($5 \cdot 10^{-2} \Omega^{-1} cm^{-1}$). In principle, a still higher conductivity could be attained, by further sulfonating the polymer, but the atactic polystyrene would then become water-soluble. Generally, when precipitated in water from the reaction solution, the sulfonated atactic polystyrene formed particles that could be easily separated by filtration. For this reason, Carretta et al. did not attempt to prepare polymers with higher degree of sulfonation. Finally novel membrane developed in this work, compared to the membrane of Nafion that are commercially available today, exhibits high proton conductivity and lower cost.

Conclusion

Polyelectrolyte membranes were produced by sulfonating syndiotactic polystyrene in its clathrate form to introduce ion-exchange groups into film, with a variety of density of the sulfonic acid groups. The sPS membranes obtained were characterized by FT-IR spectroscopy and by DSC differential scanning calorimeter to ascertain the presence of sulfonated groups attached to the aromatic rings and to study their thermal properties. The most extensively sulfonated membrane exhibited conductivity equal to that of Nafion. We have measured for a degree theoretical of sulfonation of 44% a conductivity of 26 mS cm^{-1}, very close to that one of the Nafion. These results are promising to produce very low-cost of sPS.

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