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Characterization of Electrolyte Polyester Membranes for Application in PEM Fuel Cells

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Summary: One of the factors that limits the lifetime of proton exchange membrane fuel cells (PEMFC) is the chemical stability of the polymeric membrane electrolyte operating at cell conditions. This work studies the thermal stability of a novel family of electrolyte membranes for use in fuel cells. The membranes were prepared by two different methods: Firstly, the MEB series were prepared by the addition of sodium dodecyl sulphate (SDS) to the resin obtained from the polymerization of terephthalic and adipic acid with glycerol. Secondly, the MP series were prepared from the polymerization of maleic acid and glycerol, phosphotungstic acid (PWA) was afterwards added to this material. The composites were processed in a reactor and shaped by hot pressing, yielding homogeneous and flexible slabs with an excellent surface finish. The materials were characterized by Thermo-gravimetric analysis (TGA), Scanning-electron microscopy (SEM), and electric conductivity measurements. The developed materials showed good properties as electrolytes for PEM fuel cells operating at temperatures above 100 °C.

Keywords: conducting material; fuel cells; PWA; sodium dodecyl sulfate; thermal stability

Introduction

The clean production of energy from renewable sources is one of the major concerns of modern society. Fossil fuels, near depletion, have damaged the environment and threatened human health with high emissions in their production, processing, distribution and usage. Furthermore, the use of fossil energy with accompanying greenhouse gases and pollutant emissions has impelled the scientific community to seek alternative energy sources.[1] In this scenario, fuel cells can be seen potentially to play a remarkable role in the development of non-polluting electric vehicles and more efficient generation of distributed energy. However, this technology is still not well established, and at present cannot be used as alternative for large scale sources of energy.[2]

Much research is being directed at the development of fuel cells for applications in mobile and portable equipment.[3,4] The most promising technology for this purpose is the Polymer Electrolyte Fuel Cell (PEMFC) which uses a polymeric electrolyte.[5–7] The principal technological barrier to PEMFC is its high cost;[8] however, there are currently intense efforts to reduce costs as well as to solve other problems in PEMFC technology, such as membrane dehydration. This phenomenon results in the reduction of membrane ionic conductivity and may be prevented by operating the cell at lower temperatures; however, this operating condition increases the sensitivity of the cell electro-catalysts to contamination by carbon monoxide in the hydrogen fuel. The water transport through the membrane, the maintenance of optimum moisture conditions and the proton transport in hydrated membranes are of

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great importance in the efficient performance of PEM type fuel cells.[9]

The polymeric electrolytes are usually comprised of a polymer matrix to which ionic conducting groups are added. These groups typically require the presence of a conducting medium, such as water, to enable membrane conductivity.[10] The most commonly used electrolytes are based on perfluorosulfonic acid, Nafion® stands out among them as the most effective. Nevertheless, its high cost and stability problems at high temperatures suggest the need to look for a new generation of materials for use as PEMFC electrolyte.[11]

The method most commonly used for the development of polymeric electrolytes is by the incorporation of specific conductive additives to the polymeric matrix. Such additives may be organic salts, sulfonic groups, as well as intrinsically conductive polymers. Already synthesized polymeric materials doped with conductive groups, such as sodium dodecyl sulphate (SDS) have shown values of electrical conductivity as high as 0.1 Scm^{-1}.[12] Another conductor additive that has been well studied is phosphotungstic acid, $H_3[P(W_3O_{10})_4]$ (PWA), a heteropoly acid known for being an excellent proton conductor.[13–15] Channels that may contain more than 29 water molecules are formed in its structure, leading to the formation of different protonic species.[16]

The proton exchange membrane in the PEMFC is subject to particularly aggressive conditions: chemically oxidizing environment on the cathode side and chemically reducing environment on the anode side. In addition to this, peroxy and hydroperoxy radicals formed in the fuel cell attack the polymer and lead to chain scission and thus membrane degradation. Furthermore, temperatures above 100 °C have several advantages for PEMFC and these conditions would reduce cooling requirements and dramatically decrease the cell tendency to fuel contamination. Unfortunately, polymer membrane degradation rapidly increases with temperature.[17–20]

Polyesters have several advantages over other polymers, especially due to their low cost and ease of processing. Nevertheless, polyesters are chemically degraded by hydrolytic cleavage of backbone ester bonds. Hydrolysis is catalyzed by either Brønstedt acids or bases, for example, poly(lactic acid) shows higher degradation rates at lower pH. Chain scission results in the formation of carboxylic end-groups that, given their acidic nature, will enhance the rate of further hydrolysis in an autocatalysis mechanism.[21,22] Nevertheless, the pH inside a PEMFC is not particularly harsh for polyesters. Pozio et al.[23] observed that the pH of water leaving a PEMFC varied from four to six, depending on the end plate materials. By using SS316L end plates, the average pHs for the cathode and anode water were 3.7 and 4.1, respectively. In contrast, by mounting aluminum end plates, the pH increased to 5.5 for the cathode and 5.4 for the anode. Furthermore, to prevent membrane degradation, several ionic fillers, such as sodium dodecyl sulphate (SDS), may show neutral pH[24] and some buffer action.[25]

This work aims to study the properties of composite materials prepared from polyesters with the addition of ionic conductors, in particular SDS or PWA added to a polymeric matrix of polyester obtained from the co-polymerization of glycerol and dicarboxylic acids.

Experimental Part

Materials

This work used terephthalic acid, kindly donated by Rhodiaco Ind. Chem. Ltda., adipic acid, maleic acid, both from Vetec, ammonium hydroxide from Merck, glycerol from Labsynth and dibutyl tin dilaurate from Sigma-Aldrich, as a catalyst. Sodium dodecyl sulfate (SDS)* from Qeel and phosphotungstic acid (PWA) from Merck were used as conducting agents.

Furthermore, in order to identify the SDS effect on the pH, it was observed that an aqueous solution of SDS (30% weight) presented a pH of 7.31; in agreement with reported data.[24] Moreover, the addition of

1.5 mL of 0.1 M HCl to this solution changed its pH to 6.06. In comparison, adding the same acid solution to pure water changed its pH from 7.80 to 2.60. This result agreed with the observation of the buffer action of SDS.[25]

Synthesis and Functionalization of Polymers and Membrane Production

MEB Series: SDS Immobilization

The copolymers were synthesized from terephthalic and adipic acids with glycerol in the proportion shown in Table 1, composited with SDS in the following proportions: 0, 5, 10, 13 and 15% by weight of the polymer matrix.

The material was processed in a reactor with a high-torque stirrer for 90 minutes at 165 °C and molded by hot pressing. Homogeneous, flexible and thin slabs were obtained with an excellent surface finish.

MP Series: PWA Immobilization

The polyester was prepared by adding glycerol and maleic acid in stoichiometric ratio (1:1.5), with three different proportions of PWA (Table 2). The material was synthesized in a Teflon® beaker using dibutyl tin dilaurate as catalyst, under constant agitation. The glycerol and maleic acid mixture was heated to 120 °C then the catalyst was added, 0.15% by weight, and the temperature was increased to 165 °C. The PWA was added to the polymerization reactor as soon as the material showed a gelatinous consistency, indicating that the polymerization was occurring. The resulting material was pressed at 150 °C and dried in a vacuum oven, producing the MP series.

Table 1.
Monomer molar ratio and SDS weight percentage in MEB series.

Sample	SDS (%)
MEB 0	0
MEB 5	5
MEB 10	10
MEB 13	13
MEB 15	15

glycerol: phthalic: adipic acid molar ratio = 1: 0.5: 1

Table 2.
PWA contents in MP series, as weight percentage.

Sample	PWA (%)
MP 0	0
MP 5	5
MP 10	10

Techniques used in Material Characterization

Thermo-Gravimetric Analysis (TGA)

The tests were performed in a TGA (Shimadzu TG-50) thermo-balance operating at a scanning rate of 20 °C/minute in the range of 25 to 600 °C under nitrogen flow. The analysis data were obtained directly from the software provided by the TGA manufacturer.

Scanning Electron Microscopy (SEM) Analysis

The surface analyses of the synthesized materials were performed in a Shimadzu scanning electron microscope, model SS-550. The samples were previously dried under vacuum and coated with gold in a Shimadzu IC-50 ion coater.

Electric Conductivity Measurements

The conductivity tests were performed in a measurement system composed of an electrical circuit with two multimeters, two variable resistance boxes, and a source of continuous voltage.[12] Data were collected with the aid of the software provided by the multimeter manufacturer. The electrolyte under study was previously hydrated in a 0.1 molar solution of hydrochloric acid. The membrane separated two

Figure 1.
Overall view of the home-made apparatus for conductivity measurements.

compartments containing a 0.5 molar solution of hydrochloric acid, the contact electrodes were connected to the measurement system using carbon glue to adhere contact electrode (platinum screens) to both sides of the membrane (Figure 1). All electrochemical tests were performed at room temperature.

Results and Discussion

Thermo-Gravimetric Analysis (TGA) Results

MEB Series

Figure 2 shows the TGA curves for MEB series electrolytes including the pure SDS curve for comparison. For this material there was a significant weight loss between 200 and 300 °C which can be attributed to the decomposition of the material organic fraction, leaving a residual mass of approximately 30%. On the other hand, the pure polymer matrix (MEB0) presented the main degradation step occurring at temperatures higher than 300 °C, with a residual mass of less than 15%. The increase in the percentage of SDS caused a slight decrease in the thermal stability of the polymer matrix, as measured by the reduction of the material decomposition temperature. For all composites, it was observed that the profile of mass loss was very close to that of the polymer matrix and well above the SDS profile, suggesting that SDS was thermally stabilized after its incorporation in the polymeric matrix. Furthermore, the thermal profile of the MEB series membranes indicated that they presented enough thermal stability for use as electrolyte fuel cells.

Figure 3 shows the curves of the derivative of thermal decomposition profile for the MEB series related to the TGA curves presented in Figure 2. The temperatures of maximum degradation rate for the polymer matrix and SDS were 458 and 248 °C, respectively. SDS addition to the matrix did not significantly change the temperature of the maximum mass loss rate. However, for these materials a second peak appeared between 300 and 400 °C, the temperatures of this peak depending on SDS concentration in the composite. This peak might be associated with the material decomposition at temperatures significantly higher than that of the pure material. This result agrees with the observation that SDS was thermally stabilized when incorporated into the polymer matrix.

MP Series

The pure membrane MP0 was thermally stable up to 200 °C. The maximum degradation rate of the materials occurred from 260 to 470 °C, increasing with the PWA contents. The residual mass percentage ranged from 15 to 30% at 600 °C and was proportional to the filler amount (Figure 4). The mass loss that occurred in the region

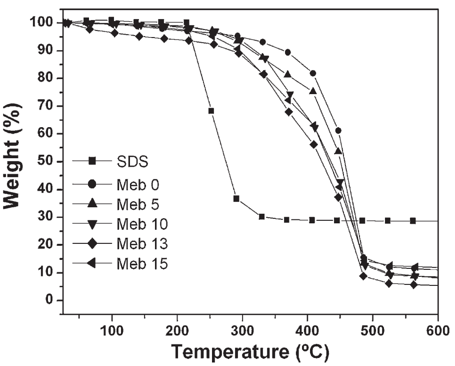

Figure 2.
TGA curves for the MEB series in nitrogen atmosphere.

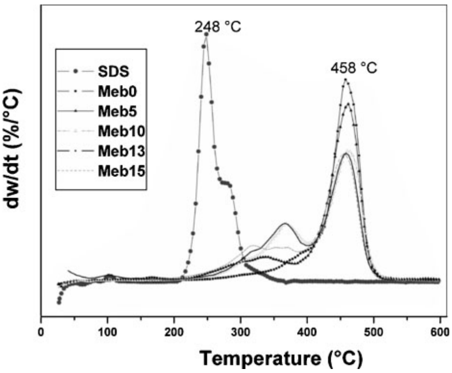

Figure 3.
Derivative curve of thermal decomposition profile for the MEB series.

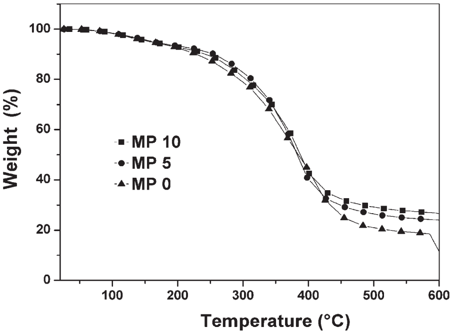

Figure 4.
TGA curves for the MP series in nitrogen atmosphere.

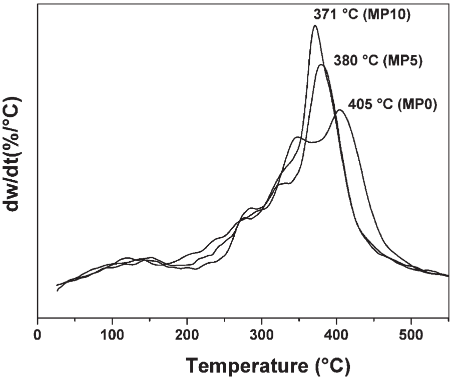

Figure 5.
Derivative curve of thermal decomposition profile for the MP series.

below 200 °C might be attributed to the desorption of hydration water present in the conductor species, which was hygroscopic.[26] Zhang et al.[27] showed that pure PWA presented negligible mass loss in TG analysis under nitrogen up to 600 °C. The membrane decomposition ceased at temperatures ranging from 410 to 475 °C. A more detailed analysis of the mass loss rate curves for the matrix indicates that the material decomposition occurs in three stages, corresponding to the peaks of maximum weight loss rate at about 280, 340 and 405 °C (Figure 5). The PWA addition to the polymer matrix in general maintained the three decomposition step behavior, but with peaks which shifted to lower temperatures. The high temperature peak became more prominent with the increase in PWA contents, occurring at 380 and 371 °C for samples MP5 and MP10, respectively. However, the curve of the MP10 sample suggested that PWA induced the matrix decomposition at temperatures below 200 °C, indicated by the disappearance of the minimum in the derivative curve around this temperature, especially when compared with the pure polymer matrix profile. The matrix stability loss with the addition of PWA might be caused by the acid property of the additive, causing its attack to the polymer chains.

Scanning Electron Microscopy (SEM) Results

MEB Series

The SEM micrographs of the matrix used for the MEB series revealed a relatively flat and uniform surface with very small lumps, probably formed by material with different molecular mass (Figure 6A). The

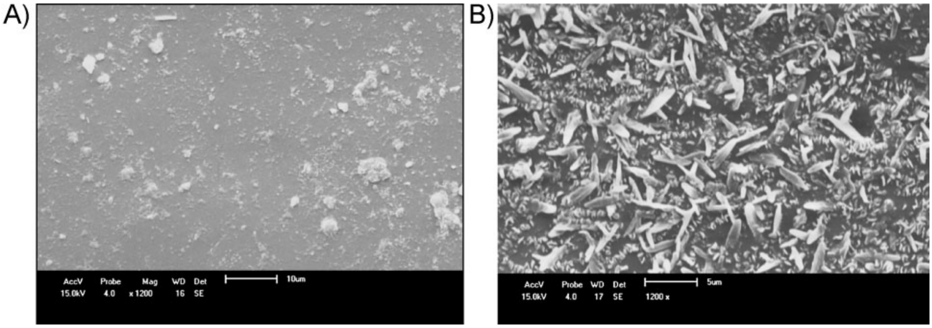

Figure 6.
SEM micrographs of the membranes: (A) MEB0; (B) MEB15.

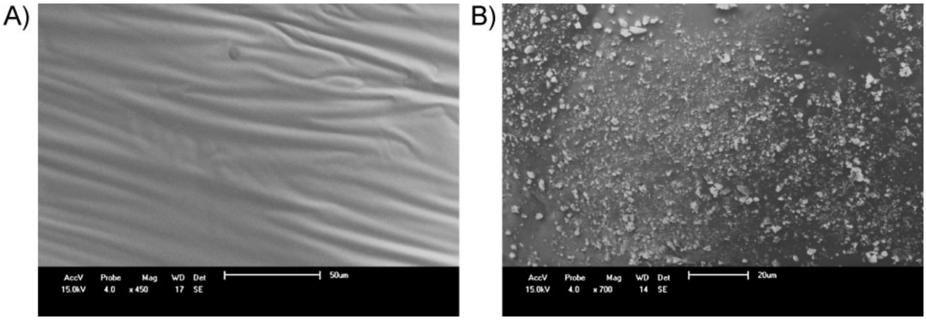

Figure 7.
SEM micrograph of surface samples: A) MP0; B) MP10.

membrane with 15% SDS showed a uniform superficial dispersion of the dopant (Figure 6B).

MP Series

The SEM micrographs of the pure copolymer matrix showed a very flat and uniform surface with smooth wave-like structures, probably formed in the hot molding processing (Figure 7A). The MP10 membrane showed a morphology characterized by the presence of PWA clusters, covered by the polymer matrix uniformly dispersed on the surface (Figure 7B).

Electric Conductivity Measurements

MEB Series

The conductivity of polymers is governed by the ion flow along an almost immobile matrix, with a highly insulating property. The transport of ions occurs in the solvation sites which are covalently linked to the polymer chain by loose bounds; the chain mobility is very important to the effective ionic transport. Armand et al.[28] observe that the conduction of ions in polymeric materials is a solvation-desolvatation process along polymer chains. As ion solvation occurs, there is a separation between cations and anions, which move in opposite directions. Armand[29] has shown that conductivity, in predominantly amorphous polymers, increases with temperature, suggesting that the amorphous phase is essential for the transport of ions in these materials. The addition of SDS to the polymeric matrix increases the material's crystallinity, consequently might stiffen the polymer chain and lower the conductivity

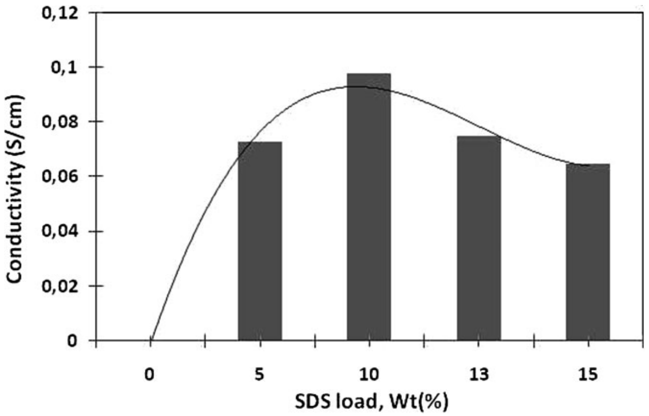

Figure 8.
Electrical conductivity curves *versus* SDS contents, for the MEB series.

of the material. Therefore, it is of great importance the optimization of the ratio between conductor and polymer matrix.

The electrical conductivity of MEB series in relation to SDS content is shown in Figure 8. The pure polymer matrix is an electrical insulator, while the composite shows conductivity of about 0.1 S/cm. This value was comparable to the conductivity of commercial polymeric electrolytes, such as Nafion®.[7,30] The conductivity profile shows a maximum at around 10% by weight of SDS, decreasing slightly from this concentration. This effect was probably due to the stiffening of the polymer chain with increasing SDS concentration, thereby reducing the synergetic effect between molecular vibration of the polymer chain and proton transport of the solvation sites.

Conclusion

Electrolytes are thermally stable up to 200 °C, and their micrographs show a good distribution of SDS and PWA in the polymeric matrix. SDS is thermally stabilized when incorporated into the matrix; otherwise PWA induced a slight thermal decomposition of the matrix. Composites of polyester (glycerol, therephthalic and adipic acids) and SDS present high electrical conductivity. These properties give the synthesized materials great potential for application in PEM fuel cells operating at temperatures above 100 °C.

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