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New proton conducting polymer membranes based on EPDM and branched HPBS

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Abstract

In this study, research was undertaken to obtain new proton conducting polymer blends based on hydrogenated poly(butadiene–styrene) (70/30) block copolymer (S-HPBS) and ethylene–propylene diene monomer (EPDM), in order to utilize them as membranes in polymer electrolyte membrane fuel cells (PEMFC). Blends become conducting by a sulfonation reaction, in heterogeneous phase, which inserts $-SO_3H$ groups into the macromolecular chain.

As is known, there exists a direct relationship between the level of sulfonation and proton conductivity. Sulfonation results, however, in a simultaneous and direct loss of membrane stability, and this latter fact constitutes a very important limitation.

Hence we decided to prepare membranes based on both polymers, incorporating, however, an additional component, i.e. polypropylene (PP) polymer with excellent mechanical and processing properties.

First, all membranes were characterized from a structural point of view through techniques, such as: FT-IR, DSC, DMA, dynamic crystallization and complex impedance analysis. Then, we selected one membrane among all the blends studied, with the aim of determining its qualities as a membrane in a direct methanol fuel cell (DMFC). To this purpose we analyzed polarization curves and water and methanol crossover.

The obtained membranes present good perspectives especially regarding the methanol permeability and physical stability, though the values of conductivity and power density need to be improved.

Keywords: Polyblends; Sulfonation; Crossover; Glass transition; FT-IR

1. Introduction

Polymer electrolyte based fuel cells, including direct methanol fuel cells, are an extremely attractive energy conversion system suited for use in many industrial applications, including transportation and on-site power plants, due to their inherently higher efficiency rates and lower emission values, when compared to those of internal combustion engines. The main impediment to the introduction of fuel cells [1–6] in vehicles [7–11] today is their high cost [12], to which the proton conducting polymer membrane contributes considerably. In fact, commercially available fuel cells are based on Nafion (Dupont) or similar expensive perfluorsulfonic polymers.

In addition, application of Nafion membranes in direct methanol fuel cells is affected by significant crossover levels (which reduce fuel efficiency) and loss of dimensional stability.

Within this scope, it is the goal of this research to develop new low-cost membranes possessing a high conductivity and showing no leakage and tear formation. To achieve this aim, we have chosen, as starting materials, commercial and cheap polymers and, in addition, for the preparation of membranes we have used conventional techniques in the industrial processes of polymeric materials.

The main function of the membrane in the cell is to transport protons from the anode, where they are formed through

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hydrogen gas oxidation, to the cathode, where the oxygen gas reacts with the protons and electrons to form water. Furthermore, the membrane should provide a gas barrier and physically separate the electrodes. In order to cover these functions, the membrane should be prepared from a polymer with excellent mechanical, thermal, hydrolytic, oxidative and reductive stability [13]. These high demands require the use of very stable polymers.

Therefore, in this work several proton exchange membranes are synthesized by incorporating varying numbers of sulfonic groups into very stable polymer systems based on the blend of two different thermoplastics: branched hydrogenated poly(butadiene–styrene) (S-HPBS) and ethylene–propylene diene monomers (EPDM).

In the light of our previous research, it is legitimate to assume that the sulfonation of EPDM [14] and S-HPBS [15] in solution yields materials that possess excellent proton conductivity but a low thermal and dimensional stability. This explains why heterogeneous sulfonation was the method of choice in membrane manufacturing. Moreover, and in order to get thin and uniform films, 20% of polypropylene was incorporated into the blends, due to its good processing properties.

Two consecutive steps were followed in the preparation of polymer materials. First, blends based on EPDM and S-HPBS were obtained by physically blending both components with equal proportion in weight, and subsequently 20% polypropylene was incorporated. In the second step, sulfonated polymer membranes were obtained from the already prepared films, by means of heterogeneous sulfonation of the latter. All blends were studied through different techniques such as: FT-IR, DMA, DSC, isothermal crystallization and complex impedance.

Afterwards the membranes exhibiting the most promising properties were studied as to their behavior as an integral component of fuel cell systems, determining power density and *I*–*V* curves. Water and methanol crossover were also studied in view of the possibility of using these types of membrane in DMFC's. The results obtained were compared to those known for Nafion membranes.

2. Experimental

2.1. Materials and procedures

The polymers used in this study were a selectively hydrogenated poly(butadiene–styrene) block copolymer (S-HPBS); the polymer commercially known as Calprene CH-6120, which contains 30 wt.% styrene units, was supplied by Repsol. The same company supplied the polypropylene, trade name Isplen (PP). Ethylene–propylene–5-ethylidine-2-norbonene (60/29/11) EPDM (Vistalan 9500) was provided by Exxon Chemical. Chlorosulfonic acid and 1,2-dichloroethane were obtained from Aldrich and Scharlau, respectively. De-ionized water used for washing purposes was Milli-Q quality. The commercial membrane used as a reference was Nafion 117 from DuPont.

The manufacture of the films was carried out in three steps. The first one consisted of preparing a pre-mix of EPDM and S-HPSB on a two roll rubber mill at room temperature. During a second step polypropylene was incorporated into this blend in an internal mixer, type Brabender Plasticorder, at the melting temperature of PP. Finally thin films (∼0.9 mm) of these materials were obtained in a hydraulic press.

The sulfonation of these films was carried out by placing them in organic chlorosulfonic acid/dichloroethane solutions at different concentrations: 0.1, 0.2 and 0.3 M of sulfonating agent. These concentrations were chosen in such a way that the maximum theoretical degree of sulfonation reached were of 10, 20 and 30%, respectively. The reaction went on for at room temperature and pre-set times selected in order to improve the conductivity and preserve the physical integrity of the membranes. Then the experimental samples were washed several times with acetone and Milli-Q water until obtaining neutral pH.

2.2. Techniques

Sulfonation of the membranes was verified by FT-IR spectroscopy using the technique of total attenuated reflection (ATR). The equipment used was a Perkin Elmer Spectrum One.

Glass transition temperatures were measured by DSC analysis using a Mettler TA 4000 Differential Scanning Calorimeter. Samples were molten at 230 °C for 5 min in order to delete any previous thermal history and rapidly quenched in liquid nitrogen. Thermograms were then recorded at a heating rate of 10 °C/min. The inflection point of the slope of the heat capacity plot was taken as the glass transition temperature.

Dynamic-mechanical measurements were conducted by utilizing a 983 Dynamic Mechanical Analyzer TA Instrument at 0.1 Hz. The temperature ranged from −100 to 100 °C and the heating rate was 5 °C/min. The glass transition temperature was obtained from E'' determination. It has been shown that E''-maximum relates much better to the value obtained by DSC than tan δ [16].

The crystallization kinetics in non-isothermal conditions were measured by using a Mettler TA300 Differential Scanning Calorimeter. All the samples were heated to 240 °C for 10 min, in order to remove all structural antecedents, and immediately afterwards they were allowed to crystallize at different cooling rates.

A computer-assisted Hewlett Packard 4192A Impedance Spectroscopy Analyzer was used for impedance spectroscopy of the samples. Complex impedance measurements were carried out in the two-electrode ac impedance mode, at ambient temperature, frequency range 0.01–10000 kHz and 0.1 V amplitude of the signal applied. To measure the conductivity, we have designed a special cell composed of two silver electrodes of 0.07 cm^2 of surface. The electrode surfaces were kept clean