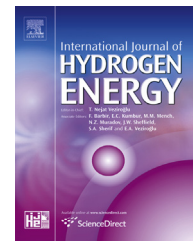




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Plasma-treated phosphonic acid-based membranes for fuel cell

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ABSTRACT

In the highly competitive market of fuel cells, proton exchange membrane fuel cells operating in the range 80–150 °C seem quite promising. One of the main hurdles for emergence of such a technology is the development of phosphonic acid-based membranes characterized by high conductivity and stability beyond 80 °C. In this work, new polymer blend membranes mixing a fluorinated polymer (poly(VDF-co-CTFE)) and a phosphonated polymer (poly(CTFE-alt-DEVEP)) have been prepared at low cost. High proton conductivity (40 mS m⁻¹ at 80 °C, 100% HR) and good thermal stability, directly related to the specific structuration of membranes, have been demonstrated. Due to cross-linking effect, argon plasma treatment of blend membranes has enabled to improve their thermal stability and fuel retention without altering their morphology, chemical composition and proton conductivity. Plasma-treated blend membranes appear as good candidates for PEMFC, as shown by preliminary fuel cell tests.

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Introduction

Fuel cells have received an increasing interest for many years. Proton Exchange Membrane Fuel Cells (PEMFC), considered as one of the most attractive fuel cells [1,2], commonly use perfluorosulfonic membrane commercialized by Dupont society (Nafion[®]) as electrolyte membrane. Several specific advantages of Nafion[®] have been demonstrated such as excellent chemical, mechanical, and thermal stabilities as well as high proton conductivity (90–120 mS cm⁻¹ in the range 25–80 °C) [3–5]. However, the dependence of Nafion[®] proton transport

mechanism on water causes its poor conductivity at temperature above 80 °C. Now membrane operating at temperature higher than 80 °C could enable to overcome some fuel cell limitations such as the monoxide carbon poisoning, and to improve the kinetic of the oxydo/reduction reaction at the surface of electrodes. So many research efforts currently concern the development of a membrane which combines high proton conductivity and chemical stability at high temperature (>80 °C) or under low relative humidity [6–8]. Membranes based on phosphonic acid groups are good candidates for fuel cells operating at intermediate temperatures

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(80–150 °C) [9]. Indeed $-\text{PO}_3\text{H}_2$ groups are amphoteric and possess a relatively high dielectric constant. The combination of these properties leads to a high degree of autodissociation which favors the formation of a hydrogen-bonding network making the proton conductivity independent on temperature and relative humidity, which eventually allows the proton transport through an anhydrous conduction mechanism, also known as the Grotthuss mechanism [10]. So the main interest of phosphonic acid-based electrolyte membranes is their high proton conductivity in dry conditions that is to say at intermediate temperatures (80–150 °C) and low relative humidity, which are suitable conditions for the intended application [11].

During these last years, different works have been carried out on the synthesis of different polyaryolphosphonic acid functionalized [12–17] or polystyrene derivative carrying phosphonic acid groups [18,19]. However, the quantity of works concerning the membranes carrying phosphonic acid groups is limited. Indeed, very few phosphonated monomers are commercially available and their polymerization is difficult, especially because of the radical attractor character of phosphonate groups [20]. The post-phosphonation of non-functionalized polymers could be an interesting alternative, but this step is also much more limiting than in the case of sulfonic acid as functional group. Previous works performed by our team have aimed at proposing original and competitive approaches to synthesize phosphonic acid-based polymers [21–24]. One approach has consisted in a multistep synthesis of partially fluorinated copolymers bearing phosphonic acid groups [21–23]. Due to much high molar mass (about $20,000 \text{ g mol}^{-1}$), these polymers exhibit poor mechanical properties which greatly limit their use in dry conditions. An easier and less expensive approach offering the possibility to improve the mechanical properties of phosphonic acid-based membranes is the blend approach. It consists in the combination of polymers whose complementary properties enable to match the whole requirements for any intended application. Fluorinated polymers are commonly used to perform blend membranes, because these polymers show very high mechanical [25,26] and chemical properties [27–29]. So, it looks promising to perform fuel cell membranes mixing a polymer bearing protogenic groups, allowing the proton transport, and a fluorinated polymer for providing the mechanical, thermal and chemical properties. This promising approach is precisely the subject of this study which partly deals with the preparation of blend membranes composed of a phosphonated polymer, i.e. poly(chlorotrifluoro ethylene-alt-diethyl vinyl ether phosphonated) (poly(CTFE-alt-DEVEP)) with 47wt.% of phosphonic groups, mixed with a low cost fluorinated polymer, i.e. poly(vinylidene fluoride-co-chlorotrifluoro ethylene) (poly(VDF-co-CTFE)). Several blend membranes have been elaborated with different contents of both polymers. Glass transition and crystallinity properties of blend membranes have been investigated through thermal analysis.

The low mechanical and thermal stability is not the only limitation of conventional phosphonic acid-based polymers. They also suffer from low fuel retention and poor compatibility with electrodes as many polymer electrolytes do usually. Now such limitations could be overcome enhancing the cross-

linking of the polymer surface using a surface treatment method. Among all surface treatment techniques, plasma treatment presents many advantages in comparison to conventional chemical modification methods. Firstly, it is a clean and dry technique, using no harmful effluents. In addition, it modifies only the outermost surface (a few nanometers deep) without altering the properties of the core material. Finally, it is a quick treatment method; indeed a few minutes are enough to modify a polymer surface. In the specific case of plasma treatment using neutral gas (typically argon), the main effect is the physical cross-linking of the material surface, eventually coupled to grafting of hydroxyl groups (inducing hydrophilization) and/or etching [30]. Plasma treatment using argon has currently attracted the attention of some studies that have shown that plasma-modified polymer electrolyte membranes (essentially Nafion® [31–34] but also anionic conductive membranes [35,36]) can display superior properties required for PEMFC applications such as enhanced chemical and mechanical stability, reduced fuel permeability, better compatibility with electrodes and even improved ion conductivity in some cases [37].

The current study offers to investigate the surface plasma modification of the synthesized blend membranes. Argon has been chosen as a non-condensable plasma gas likely to essentially cross-link the membrane surface (although some etching and grafting could happen simultaneously), in order to improve the membrane properties (stability and fuel retention essentially) and performance in a PEMFC stack. The virgin and plasma-treated membranes have been characterized in terms of surface morphology and roughness by Atomic Force Microscopy, thermal stability by ThermoGravimetric Analysis, ion exchange capacity, water uptake and hydration number properties, and also proton conductivity by Electrochemical Impedance Spectroscopy. In addition, measurements of diffusion permeability to methanol and ethanol (as potential fuels for fuel cell) have been performed. Lastly, the best plasma-modified membranes have been tested in a fuel cell. Correlations between the plasma conditions, the physico-chemical characteristics of the modified materials (morphology, roughness, thermal stability, IEC, water uptake, hydration number) and their functional properties (proton conductivity, fuel permeability, global fuel cell performance) have been discussed.

The aim of this work is to demonstrate on the one hand the feasibility to prepare original phosphonic acid-based blend membranes, and on the other hand the competitiveness of plasma treatment to improve the physico-chemical and functional properties as well as the fuel cell performance of these membranes.

Experimental section

Materials and synthesis procedure for the preparation of blend membranes

Polymers used for matrix were the poly(vinylidene fluoride-co-chlorotrifluoro ethylene) as fluorinated polymer and the poly(chlorotrifluoro ethylene-alt-diethyl vinyl ether phosphonated) as phosphonated polymer. The poly(VDF-co-CTFE)

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