



Methanol and gas crossover through modified Nafion membranes by incorporation of ionic liquid cations

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ABSTRACT

Nafion membranes were modified by incorporation of ionic liquid (IL) cations, at controllable degrees, in order to assess the influence of this modification in both the methanol and gas crossover. The effect of using different degrees of incorporated IL cations, as well as the type of IL cation incorporated, in the transport of gases and methanol was studied in detail. The results obtained were compared with those obtained with an unmodified Nafion membrane. Depending on the IL cation incorporated, a reduction in methanol crossover in the range of 60–600 times was obtained in this work, when compared with a Nafion-112 membrane. This reduction was related both with the type of cation incorporated and its incorporation degree which determine the amount of water retained by the membrane and its degree of structuring inside the membrane. Pure H₂, O₂, N₂ and CO₂ permeabilities were also determined, and a lower gas crossover through all of the modified Nafion/IL cation membranes was obtained when compared with those obtained through the unmodified membrane (Nafion/H⁺). It was concluded that the electric properties, methanol and gas crossover as well the stability at high temperatures of these membranes can be tuned by controlling the degree of incorporation as well as the type of cation incorporated. The best compromise between all these properties has to be found in order to consider their use in direct methanol fuel cells (DMFCs).

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1. Introduction

Direct methanol fuel cells (DMFCs) have been widely studied in the literature over the last years [1–3] since they can be regarded as a potential energy power source due to their simple design and mode of operation, their ability to operate at relatively low temperatures (up to 150 °C), and their easy fuel storage, when compared with fuel cell systems using H₂ as a fuel. Energy is produced in a DMFC by the catalytic oxidation of liquid methanol at the anode, thereby producing protons, electrons and carbon dioxide. The protons produced are transported by diffusion to the cathode compartment through a polymer exchange membrane (PEM). In this compartment, the protons react with oxygen and electrons to produce water. One of the key elements that determine the performance and life-time of a DMFC is the polymer exchange membrane. The PEMs used in this type of devices should exhibit a low methanol and gas crossover, a high proton conductivity as well as a high chemical, mechanical and thermal stability at temperatures above 80 °C [4].

The PEM material most studied in DMFCs is Nafion. This polymer consists of a polytetrafluoroethylene (PTFE) backbone with sulphonic acid side-groups arranged in intervals along the chain, as illustrated in Fig. 1 [5,6].

This membrane is widely used in fuel cell studies because it fulfils most of the required properties. Nafion has a high proton conductivity, which depends strongly on its water content, and it also exhibits good mechanical, thermal and chemical stabilities at temperatures up to 80 °C. However, above this temperature a decrease in its water content is observed lowering the proton conductivity and leading to a loss of the spatial coherence of the membrane. Additionally, when used in a DMFC system, a relatively high methanol and gas crossover is observed [1–4].

A number of works are available in the literature where Nafion membranes were modified in order to overcome the problem of methanol crossover. Wang et al. [7] modified a Nafion membrane by a direct polymerization of a protonated polyaniline (PANI), in order to obtain a composite membrane. PANI was chosen due to its electrochemical conductivity and stability in corrosive environments. In that work a reduction of 59% on the methanol crossover was observed. In the work developed by Li and Zhang [8] Nafion was modified by an *in situ* chemical polymerization of 3,4-ethylenedioxythiophene, and the methanol crossover of the membranes produced was reduced by 30–72% when compared with unmodified membranes. There is also a number of works

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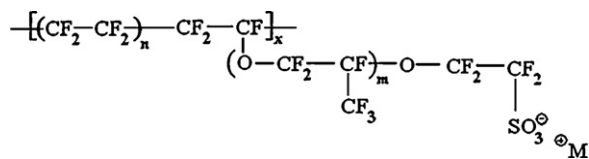


Fig. 1. Chemical structure of Nafion.

that report the development of organic–inorganic composite membranes [9,10], where reductions in methanol crossover between 50% and 80% were obtained. In the work developed by Nguyen and Wang [11] a porous polyimide film was synthesized and used as a matrix to construct a Nafion-infiltrated composite membrane. Porous polyimide was chosen in that work due to its high mechanical strength, as well as to its compatibility with Nafion and inertness to methanol. A methanol crossover reduction of 80 times, when compared with a Nafion membrane in the protonated form, was obtained. Instead of modifying the Nafion membrane material, other authors prepared less expensive membrane materials as alternatives to Nafion. Examples of such materials are the sulfonated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) membranes, where a reduction of about two orders of magnitude of the methanol crossover was obtained in comparison with Nafion-117 [12], and the sulfonated poly(ether ether ketone) (sPEEK) membranes, where a reduction of 92% on the methanol crossover was observed [13].

Gas crossover in Nafion membranes is relatively well documented in the literature [14–21]. Despite the fact that crossover of gases, present as reagents and/or reaction products in DMFCs, may be also considered as an important factor influencing the efficiency of a DMFC, strategies to reduce gas crossover have attracted a relatively lower attention when compared to methanol crossover. Strategies for gas crossover reduction were studied for alternative membrane materials with modest results [12,13,22,23]. Drioli et al. [12] studied the permeability of the sulfonated PEEK-WC membranes towards O₂, N₂, CO₂, He and H₂, and obtained lower permeabilities than those obtained with Nafion-117 for the gases O₂, N₂ and CO₂. In the work developed by Silva et al. [13] the permeability of Nafion-112 for N₂, O₂ and CO₂ was determined and compared with a sulfonated poly(ether ether ketone) membrane with different sulfonation degrees. Depending of the sulfonation degree, permeability reductions in the ranges of 43–57, 20–57 and 12–39 were obtained for N₂, O₂ and CO₂, respectively when compared with a Nafion membrane. Gosalawit et al. [22] tested two types of membranes, the sulfonated PEEK-WC and Krytox-Si-Nafion, and determined the permeability of H₂ and O₂. A reduction in gas crossover was observed for both membranes when comparing with Nafion-117, with a maximum reduction of 91% for H₂ and 42% for O₂.

The approach followed in this work was the design of modified Nafion membranes by partially replacing their protons with ionic-liquid (IL) cations, in order to assess the influence of this modification in both the methanol and gas crossover. It is expected that the introduction of these bulky IL cations will modify the way water is structured and involved in solvation processes, improving the stability of Nafion at high temperatures and, hopefully, reducing methanol and gas crossover. On the other hand, it is important to identify the best compromise that allows for developing highly stable membranes with sufficiently good proton mobility.

Ionic liquids (ILs) are compounds consisting entirely of ionic species comprising an organic cation and an inorganic or organic anion [24], and they present a good electrical conductivity, a high ionic mobility and good thermal and chemical stability [25,26]. Due to these unique properties ILs have already been studied as potential electrolytes in batteries and fuel cells, double-layer capacitors,

dye-sensitive fuel cells, and actuators. The potential of using ILs or ILs incorporated into cation-exchange membranes, as Nafion, in fuel cell applications has been reported in the literature [6]. Fuel cells systems based on imidazolium ILs, such as [BMIM][PF₆] and [BMIM][BF₄] have been studied and a 67% overall cell maximum efficiency was obtained [27]. Another approach described in the literature is the modification of Nafion membranes using ionic liquids, where ILs have been assumed to behave as solvents instead of electrolytes. Doyle et al. [28] studied the incorporation of different ionic liquids in Nafion, where it was shown that these membranes have the ability to swell in contact with ionic liquids, which resulted in membranes with an excellent stability and proton conductivity in the range of 100–200 °C, while retaining the low volatility of the ionic liquid. Tigelaar et al. [29] studied the incorporation of protic ionic liquids into different polymers, including Nafion, evaluating the resulting mechanical and thermal properties, and the uptake of water. It was observed that the conductivity of the modified membranes was mainly dependent from the relative amount of the ionic liquid inside the membrane. Schmidt et al. [30] studied the effect of impregnating different ionic liquids in Nafion 117 on the mechanical properties, thermal stability, ion exchange capacity, swelling and conductivity of the resulting membranes.

In a previous work [31], the incorporation of IL cations into a Nafion-112 membrane was studied. The IL cations tested were phenyltrimethylammonium (TPMA⁺), *n*-dodecyltrimethylammonium (DTA⁺), hexadecyltrimethylammonium (CTA⁺), 1-*n*-butyl-3-methylimidazolium (BMIM⁺), and 1-*n*-octyl-3-methylimidazolium (OMIM⁺). After incorporation into Nafion their distribution was characterised by X-ray photoelectron spectroscopy (XPS). Additionally, the electrical properties of the modified membranes, with different degrees of cation incorporation, were determined by electrochemical impedance spectroscopy (EIS). The stability of the modified membranes with increasing temperature was determined by thermogravimetric studies, which allowed to establish a plausible relation between the membrane stability at high temperatures with its water content and type of water structuring. The results obtained show that, depending on the incorporated IL cation in the Nafion structure, the ionic conductivity and consequently the proton mobility of the modified membranes can either decrease or increase. Even though for some of the IL cations incorporated the ionic conductivity of the modified Nafion/IL membranes obtained was compromised, it was observed that all membranes studied remained stable at temperatures up to 200 °C due to their ability to retain water at higher temperatures, which is attributed to water structuring effects within the membrane and water involvement in additional solvation of the incorporated cation.

This work discusses the design of Nafion membranes, modified with different degrees of incorporation of ionic liquid cations, and evaluates the effect of this modification on methanol and gas crossover, comparing it with an unmodified Nafion-112 membrane.

2. Experimental

2.1. Materials

The membrane used as a reference material was Nafion 112 in the protonated form (equivalent molecular weight of 1100 g mol⁻¹ and a thickness of 51 μm), obtained from Dupont (USA).

Different ionic liquid (IL) cations were incorporated within the Nafion 112 membranes. The compounds used as source materials for the cations are listed below:

- tetramethylammonium chloride, TMA⁺ Cl⁻ from Fluka (Germany);

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