Influence of ionic liquids on the properties of sulfonated polymer membranes

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HIGHLIGHTS

- Increasing immersion time increases the incorporation of the BMI$^+$ cations.
- Increase of the amount of the BMI$^+$ cations there decrease in water absorption.
- The increase of the conductivity in the SPEEK, makes it attractive for use in PEMFC.

ARTICLE INFO

ABSTRACT

Two types of sulfonic acid membranes perfluorinated (Nafion) and poly(ether–ether-ketone) (SPEEK) were modified by impregnation with the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF$_4$). The ionic exchange between the butyl-methylimidazolium (BMI) cation and the sulfonic acid groups of the polymers are limited by diffusion into the membrane pores and can be controlled via the time of contact with the IL solution. Infrared (IR) and thermogravimetric (TGA) analyses confirmed the incorporation of the BMI$^+$ cations into the polymers. The polymer electrolyte membranes modified with ILs exhibit enhanced conductivity at a relative humidity of 70% and at elevated temperatures despite their reduced absorptive capacity.

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1. Introduction

Fuel cell (FC) technology is generally accepted as one of the most attractive approaches to the production of clean energy because fuel cells can convert the chemical energy of a clean fuel directly into electric power with high efficiency and without emission of environmentally hazardous gases [1]. An important segment of FC technology is the study of polymer proton exchange membranes (PEM), which are responsible for ionic transport between the cathode and anode of certain types of fuel cells. Despite a large variety of PEMs, the Nafion membranes have shown promising performance in FC applications, these membranes were commercialised by DuPont. Nafion consists of a polytetrafluoroethylene backbone functionalised with sulfonic acid groups. It exhibits good thermal, mechanical and chemical stabilities as well as high proton conductivity, but only when it is fully hydrated, which is difficult to achieve at elevated temperatures [2,3]. The transport of protons in a PEM is a water-mediated process [4]. Therefore, FCs are preferably operated at temperatures lower than the boiling point of water, normally less than 80 °C, at which the poison of the anode Pt catalyst by CO becomes inevitable [5].

The development of high-temperature membranes that remain conductive at low relative humidity has become an important topic of the research in the proton exchange membrane fuel cell (PEMFC) domain. In recent years, much attention has been focused on sulfonated poly(ether–ether-ketone) (SPEEK) membranes due to their good chemical stability and mechanical properties [6]. However,

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the conductivity of pure SPEEK membranes also decreases with temperature when their hydration is low [7]. Therefore, the modification of the polyelectrolyte to enhance the water retention and thereby preserve the high proton conductivity at elevated temperatures is a topical issue.

One approach to this technical challenge involves partial substitution of water into the pores of a hydrated polymer using ionic liquids (ILs) as efficient proton-transporting media. In fact, the choice of ILs as electrolytes is motivated by their properties, which include good thermal and chemical stability, high ionic conductivity and negligible vapour pressure [8–10].

Some ionic liquids have been used in FCs [11,12]. For example, the ion exchange of Nafion with imidazolium cations improved the thermal stability and the water retention capacity of a membrane [13].

The literature contains few systematic studies concerning the modification of Nafion by exchange with IL cations. Most of these works have been focused on the modification of membrane properties, whereas the dependence of the PEM conductivity on the time of contact between the membrane and the IL remains unexplored [14]. Herein, we present a study of the incorporation of an ionic liquid into Nafion and SPEEK membranes, where we examine the effects of contact time on the properties of these membranes.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium tetrafluoroborate (BMI·BF$_4$) was synthesised as previously described [15–18]. Nafion-117 was purchased from DuPont (EW 1100, thickness 183 μm). Poly(-ether−ether-ketone), PEEK 450 PF was from Victrex PLC USA. Sulphuric acid 95−98% and hydrochloric acid 32−33% were of analytical grade and used as received.

2.2. Preparation of membranes

The Nafion membranes were treated in aqueous hydrochloric acid solutions in accordance with procedures reported in the literature [19].

The SPEEK membranes were prepared dissolving 25 g of Poly(ether−ether ketone) in 500 mL of sulphuric acid (95−98%), and the resulting solution was vigorously stirred at room temperature for 19 h. Then the polymer solution was precipitated with a large excess of deionised ice water under continuous mechanical stirring. The precipitated polymer (SPEEK) was washed several times until the pH of the wash water was 5. The polymer was subsequently dried in air at room temperature for 48 h and then dried in an oven at 60 °C for 48 h, which resulted in clear, nonporous films [20,21].

2.3. Modification of membranes with the ionic liquid BMI·BF$_4$

We prepared modified membranes by immersing them into 50 mL of ultrapure water (2 μS cm^{-1}) containing 5 mmol of BMI·BF$_4$, *i.e.*, a concentration of 0.1 mol L^{-1} at room temperature, as previously described [22], and subsequently washing then with deionised water to remove any residual IL. This procedure was used because the IL can be incorporated by different processes, including cation exchange and physical adsorption [12].

2.4. Characterization of membranes

The degree of sulphonation (DS) of the obtained SPEEK polymer was determined by ^{1}H NMR spectroscopy [23,24], on a Varian Inova

spectrometer at a resonance frequency of 300 MHz. In this analysis, a 2 wt% polymer solution was prepared in DMSO-d_6 and tetramethylsiloxane (TMS) was used as the internal standard.

The degree of exchange was calculated as the molar ratio (λ) between the IL cations and the sulfonic acid functional groups of Nafion. The Nafion membranes were dried under vacuum at 70 °C for 6 h prior to and after the IL treatments [12].

The structure of the membranes was analysed by infrared spectroscopy using a Bruker Alpha-P FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q-50 apparatus in the temperature range from 20 to 350 °C under nitrogen at a heating rate of 10 °C min^{-1}. The scanning electronic microscopic (SEM) of the membranes was taken using a SEM EVO-50 Carl Zeiss.

Water uptake (WU) of the membranes at different temperatures was determined by the weight difference between the fully hydrated membrane and the completely dry membrane [7,25]. The membrane specimens were dried at 70 °C under vacuum for 6 h, weighed and then immersed in deionised water for 24 h. The membranes were then wiped with blotting paper to remove the surface water and were quickly weighed. Water uptake, WU, was calculated gravimetrically:

$$\text{WU}(\%) = \frac{W_s - W_d}{W_d} \cdot 100 \tag{1}$$

where W_s and W_d are the weights of the wet and dry membranes, respectively.

The cation exchange capacity was determined at room temperature. The membrane samples were placed in a beaker containing an excess of 0.1 mol L^{-1} BMI·BF$_4$ solution. The degree of incorporation of the BMI cations into the polymer was controlled while the membrane was in contact with the solution and was gravimetrically determined after the samples were thoroughly washed with deionised water and dried at 70 °C for 6 h.

The proton conductivity (σ) of the membranes was determined as a function of temperature (from 23 to 100 °C) at a relative humidity of 70% by AC impedance spectroscopy over a frequency range of 10 Hz−100 kHz; an Autolab PGSTAT30 potentiostat was used for the measurements. A sample of each membrane was placed in a test cell with controlled temperature and humidity, where it was clamped between two stainless steel block electrodes. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data according to the relation [26]:

$$\sigma = \frac{d}{RS} \tag{2}$$

where d and S are the thickness and face area of the sample, respectively; R was derived from the low intersection of the high-frequency semicircle on a complex impedance plane with the Re(Z) axis.

Degradation of the membranes in Fenton's reagent is builds in the properties strongly oxidizing a solution of the hydrogen peroxide and ions Fe (II). Using this reagent, many organic molecules may be oxidized easily without recourse to high pressures, high temperatures and complex equipment. In the Fenton's test, the peroxyl or hydroxyl radicals can be formed through the reaction of hydrogen peroxide with Fe (II):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$$
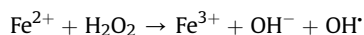
For this test we used 3% H$_2$O$_2$ solution and 5 ppm of Fe (II) [27]. The membranes were cut into pieces in size of 0.5 cm $\times$ 2.0 cm