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SPEEK based composite PEMs containing tungstophosphoric acid and modified with benzimidazole derivatives

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ABSTRACT

Composite SPEEK based PEMs, containing tungstophosphoric acid (TPA) and modified with benzimidazole derivatives as cross-linking spacers, were prepared and characterized by a number of physico-chemical methods. It was observed, that the cross-linking agents strongly affect membrane properties, reducing their swelling, but at the same time decreasing their proton conductivity. However the cross-linkers provided a better retention of the TPA particles embedded within the composite membranes. The TPA particles enhanced the polymer conductivity to values overpassing that of the non-modified membranes. The performance of the PEMs was tested in hydrogen/air FC and found to be superior to that of Nafion 212 commercial PEM. The stability of the composite PEMs was adequate at least for 2 days, during which no degradation of the performance was observed.

1. Introduction

Starting from the 1980s worldwide research activity in the development of proton exchange membranes has been growing exponentially, with the number of peer-reviewed publications on PEM exploding from some units published yearly until 1990, to about two hundred in 2000, which since then was tripled reaching about 700 papers in 2006 and 2007 [1].

The interest in these materials is mostly stimulated by the need for efficiency improvement and cost reduction of PEM fuel cells, which are considered to be an innovative alternative to existing power sources. The most commonly utilized perfulorinated PEMs, such as Dupont Nafion, are inherently expensive, which impedes their large scale commercialization as a FC component [2–4]. Consequently, widespread efforts are currently being spent on developing a non-perfluorinated, purely hydrocarbon based electrolyte membrane with better performance and lower cost.

Four approaches to this goal have been discussed [5] in the literature: (1) development of membranes based on new ionomers with desired characteristics; (2) solubilizing of suitable oxygenated acids (phosphoric or sulfuric) within polymer matrix bearing basic groups (e.g. poly-benzimidazole); (3) composites based on non-conductive polymeric matrix, filled with ionomers or inorganic solids of high proton conductivity; (4) composite membranes where the particles of solid oxides or acids with low solubility are embedded within the ionomeric matrix. One more approach must be added to this list, namely: (5) chemical modification of known ionomers in order to make them more suitable (often - more mechanically stable) for FC application.

Generally, the proton conductivity of sulfonated poly-hydrocarbons rises with the degree of their sulfonation (DS), which at the same time makes the PEM more prone to swelling under hydrothermal conditions of FC. Thus, the mechanical stability of such ionomers tends to deteriorate with DS [6] due to excessive swelling, making questionable their long- and even short-term stability. The mechanical weakness of sulfonated polymers has initiated a number of attempts to prepare more stable and mechanically stronger cross-linked PEMs. A series of studies focused on the development of covalently and ionically cross-linked poly-arylenes has been reported in Refs. [7–9]. It was observed that tough covalent cross-linking, accomplished through sulfonate groups, often brings about impractically brittle membranes. In contrast with this, the mild polar cross-linking of the polymers by blending with basic (aminated) polymers in binary and ternary compounds, usually does not affect membranes flexibility, but reduces their swelling with insignificant sacrifice in conductivity [8,9]. This was also observed in our previous works [10,11] where simple polyatomic alcohols were used as cross-linking agents, and in Refs. [12,13] where basic nitrile groups were introduced into the polymer backbone.

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In the present study both the 4th and 5th of the above mentioned approaches were employed. Composite membranes were prepared by incorporation of an inorganic filler into a polymer matrix, where the former is tungstophosphoric acid (TPA) and the latter is sulfonated poly-ether-ether ketone (SPEEK). However, similar composites have already been studied in our laboratory [14] as well as by other researchers [15], and it was found that embedding a fast proton conductor such as TPA ensures only temporary improvement of the PEM properties. When swollen in the FC hydrothermal environment the composite membranes lose the second phase, gradually transforming into their initial form. As was denoted in Ref. [16] "to maintain high conductivities, a technique must be developed to trap the acids inside the membranes". Such a technique, employing a mild polar cross-linking of SPEEK main chains by benzimidazole derivatives, which allowed to reduce swelling and better retain TPA particles within a sulfonated polysulfone matrix, was tested previously [17]. The observed significant improvement in PEM's conductivity was attributed to the high loading of extremely conductive hydrated TPA, which was found to be much less prone to leaching out of the composite due to restricted mobility of polymer chains, interconnected by the basic links of the cross-linking agent.

In the present study the polymer matrix was SPEEK with different degrees of sulfonation (DS). The solid filler was TPA with loading from 5 to 30 wt.% and as a cross-linking agent various bezimidazole derivatives were blended with the matrix at different ratios.

It should be mentioned that the cross-linking molecule obviously affects interchain distances and therefore may also play a role of a spacer between polymer chains, thus allowing to some extent to adjust the polymer structure. For this purpose the nature of the benzimidazole derivatives was chosen in such a way as to ensure a variety of spacer lengths.

The proton conductivity, water uptake, thermal properties, morphology, chemical structure examined by FTIR were monitored and the performances in the hydrogen/air FC were tested for these composite membranes in order to reveal a consistent pattern for the SPEEK cross-linking and its effect on the properties of the composite PEMs.

2. Experimental

2.1. Materials

Poly (ether ether ketone), PEEK 450PF was from Victrex USA. The chemicals used in this work were sulfuric acid 95–98%, NaOH, ethanol and dichloromethane (Nuclear); polyethylene glycol (PEG 400), tetraethylene glycol and benzimidazole (Merck); butane dibromide, decane dibromide, N-methyl pyrrolidone (NMP) and phosphotungstic acid (PTA) (Aldrich). All materials were analytical grade and used as received.

2.2. PEEK sulfonation

The sulfonation of PEEK (Victrex PLC) was performed using concentrated sulphuric acid according to the procedure described elsewhere [10,11]. Twenty-five grams of polymer dissolved in 500 ml of sulfuric acid at 25 or 50 °C and vigorously stirred during the period of time needed to reach the desired degree of sulfonation (DS). To terminate the sulfonation reactions, the polymer solutions were decanted into a large excess of ice-cold water under continuous mechanical agitation. The polymer precipitate was filtered and washed several times with distilled water until pH 5. The resulting SPEEK was dried at room temperature under vacuum, until the polymer changed its color from white to yellow. DS was evaluated by titration with 0.1 M NaOH from SPEEK directly dissolved in *n*-methyl-pyrolidinone (NMP) and by ^{1}H NMR. Three SPEEK samples were prepared with DS = 40, 56 and 65%.

2.3. Synthesis of benzimidazole derivatives

Table 1 shows the structure and designations of benzimidazole derivatives synthesised in this study and used for PEM modification. The compounds B and D were synthesised directly from butane and decane dibromides obtained from Aldrich. PE and TE compounds were first brominated as follows.

Polyethylene glycol or tetraethylene glycol was first dissolved in dichloromethane at 40 °C and then phosphorous tribromide was added and stirred for 48 h. The solution was then cooled down to 0 °C by adding ice from deionised water and an oily liquid containing dibromide compounds was separated from the water soluble fraction and condensed in a rotary evaporator. FT-IR spectra confirmed substitution of OH by Br in polyethylene and tetraethylene glycols.

All four brominated compounds were transformed into benzimidazole derivatives following a similar route. First benzimidazole was dissolved in KOH/EtOH solution and then the dibromide compound was added to the reaction mixture. It was refluxed for 3 h, cooled and KBr was filtered out. The filtrate was dried in a rotary vacuum evaporator, dissolved in chloroform and purified with by extraction in NaOH aqueous solution. The oily component was then separated and treated with anhydrous sodium sulphate to trap water. After filtration the resulting benzimidazole derivatives were crystallized from acetonitrile solutions and dried under vacuum. All benzimidazole derivatives where characterized by ^{1}H NMR, ^{13}C NMR and CG–MS to confirm their chemical structure.

2.4. PEM preparation

Membranes containing SPEEK, benzimidazole derivatives and TPA were prepared by casting 10 wt.% solutions in *n*-methyl-pyrolidinone (NMP). TPA was dissolved in NMP separately which then was added to the casting solution. The solutions were heated to 60 °C and stirred for 24 h, then filtered through a 0.5 μm Millipore filter into Petri dishes with flat bottoms. The cast membranes were dried at 60 °C for 12 h, under flowing nitrogen and then at 80 °C under vacuum for 2 days resulting in clear non-porous films.

2.5. Membrane characterization

Thermal analysis was carried out using a TGA Q50 (TA Instruments) under nitrogen atmosphere. The ~10 mg samples were heated from room temperature up to 800 °C at 20 °C/min. The weight loss and its derivative were used to evaluate the thermal stability and degradation behaviour of the membranes.

The conductivity of the polymer membranes was measured by AC impedance spectroscopy as previously described in Refs. [10,18] both in transversal and longitudinal directions. Measurements across the membrane were carried out on 13 mm diameter discs placed in an open temperature controlled cell, between two stainless steel electrodes. There was no external humidification provided for the samples in these measurements and they serve as estimation of the conductivity of dry membranes. A longitudinal scheme was used for measurements at 100%RH. For this purpose a stripe 10 mm × 20 mm was cut from a membrane and placed in a closed frame cell with some water on the bottom of the chamber. The sample was clamped between two pairs of stainless steel electrodes and the conductivity was measured along membrane surface. Tests were carried out at controlled temperature and 100%RH. The impedance data were corrected for the contribution from the empty and short-circuited cell.