



Epoxides cross-linked hexafluoropropylidene polybenzimidazole membranes for application as high temperature proton exchange membranes



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ABSTRACT

Covalently cross-linked hexafluoropropylidene polybenzimidazole (F₆PBI) was prepared and used to fabricate high temperature proton exchange membranes with enhanced mechanical strength against thermoplastic distortion. Three different epoxides, i.e. bisphenol A diglycidyl ether (R₁), bisphenol A propoxylate diglycidyl ether (R₂) and poly(ethylene glycol) diglycidyl ether (R₃), were chosen as the cross-linkers to investigate the influence of their structures on the properties of the cross-linked F₆PBI membranes. All the cross-linked F₆PBI membranes displayed excellent stability towards the radical oxidation. Comparing with the pure F₆PBI membrane, the cross-linked F₆PBI membranes showed high acid doping level but less swelling after doping phosphoric acid at elevated temperatures. The mechanical strength at 130 °C was improved from 0.4 MPa for F₆PBI membrane to a range of 0.8–2.0 MPa for the cross-linked F₆PBI membranes with an acid doping level as high as around 14, especially for that crosslinking with the epoxide (R₃), which has a long linear structure of alkyl ether. The proton conductivity of the cross-linked membranes was increased accordingly due to the high acid doping levels. Fuel cell tests demonstrated the technical feasibility of the acid doped cross-linked F₆PBI membranes for high temperature proton exchange membrane fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) operating above 100 °C, i.e. high temperature PEMFCs, have exhibited superiority for automotive and stationary applications due to the minimization of precious metal loading, simple water and better thermal managements [1,2]. Up to now, the most promising electrolytes for the high temperature PEMFCs are widely considered as phosphoric acid (PA) doped polybenzimidazole (PBI) membranes, just as stated in the DOE Fuel Cells Technical Plan of 2012 [3,4]. The advantages of the PBI-based PEMFCs include working under low humidity conditions, high CO tolerance, better heat utilization and possible integration with fuel processing units [1,5]. The PBI is a kind of heterocyclic polymers with excellent thermal and mechanical properties. One of the most widely investigated PBIs is poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (*m*PBI), which has been proposed as the electrolyte material for the high temperature PEMFC since 1995 [6]. Basically, *m*PBI

based membranes exhibit high proton conductivities when they possess a high acid doping level (ADL, the mole number of PA per molar repeat unit of the polymer) [6–8]. However, the high proton conductivity is normally at the expense of mechanical strength of membranes due to the strong plasticization of PA [1,7,8]. Therefore, a trade-off between the conductivity and mechanical strength has become one of the critical issues for attaining an effective performance of the *m*PBI-based high temperature PEMFC. In order to improve the mechanical strength without or with less sacrifice of the proton conductivity, various approaches have been developed. The resultful explorations include increasing molecular weight of the *m*PBI polymer [9,10], synthesis of PBI variants or copolymers [11–19], fabrication of composite membranes with nano inorganic compounds [10,20], ionically and covalently crosslinking [6,21].

Among a number of PBI variants, the polymer containing hexafluoropropylidene groups, termed as F₆PBI, has high stability towards the attack of radical oxidants and good solubility in the normally used organic solvents comparing with those of the pristine *m*PBI [21–25]. However, the flexible spacer groups (-C(CF₃)₂-) containing in the main chain of F₆PBI result in less rigidity of the polymer against the plastification of doped PA,

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which brings about significant thermoplastic deformation of the membranes at elevated temperatures, such as 130 °C [25]. To reinforce the F₆PBI membrane with high ADLs, crosslinking has been demonstrated as an effective method [21,24,25]. The covalent cross-linking of PBI membranes is normally performed between imidazole groups of PBI and electrophilic cross-linking agents containing two or more active groups. In our previous work, covalent crosslinking of F₆PBI with a polymeric cross-linker, chloromethylated polysulfone, was proposed by means of “polymer covalently crosslinking polymer” [25]. The results indicated that the macromolecule crosslinked F₆PBI membranes displayed superior mechanical strength at elevated temperatures while maintaining high PA contents, which resulted in a better fuel cell performance and a long term fuel cell durability. In the meanwhile, other macromolecule cross-linkers including poly(vinylbenzyl chloride) [26], polybenoxazine [27] and bromomethylated poly(aryl ether ketone) [28] were also employed to prepare the cross-linked PBI membranes. It is seen that the used macromolecule cross-linkers to the PBIs are aromatic polymers, which profit the PBI maintaining its stability. Compared to macromolecules, the small molecule reagents such as halide [24,29,30] and epoxide [31–33] are more frequently used cross-linkers for improvement of the membrane properties. In addition, several other methods were also explored to obtain cross-linked PBI membrane electrolytes, which include free radical polymerization of the side chain of cross-linker (i.e. vinylbenzyl [34]), polycondensation of trimesic acid [35] or aniline monomer [36], and thermal curing [37].

For improvement of properties of the PBI-based high temperature membrane electrolyte, the chemical stable F₆PBI polymer was chosen as the base material to prepare proton conducting membranes. To solve the thermoplastic distortion of the acid doped F₆PBI membrane at elevated temperatures, three different epoxides having different sizes with and without rigid groups of benzene rings were used as cross-linkers to enhance the mechanical properties of the F₆PBI membrane by the covalent cross-linking, meanwhile to better understand the influence of the structure of the cross-linkers on the properties of the cross-linked membranes. Physicochemical properties of the cross-linked F₆PBI membranes were investigated, including high temperature fuel cell tests.

2. Experimental

2.1. Fabrication of crosslinked F₆PBI membranes

The F₆PBI polymer was synthesized by condensation polymerization of 3,3'-diaminobenzidine tetrahydrochloride dehydrate (Applichem, USA) and 2,2-bis(4-carboxyphenyl) hexafluoropropane (Sigma-Aldrich), with a molar ratio of 1:1 in polyphosphoric acid (Sigma-Aldrich), as reported previously [25]. The intrinsic viscosity of the obtained polymer was around 0.73 dL g⁻¹ which was measured in 96 wt% sulfuric acid with a concentration of 5 g L⁻¹ at 30 °C.

As shown in Fig. 1, the cross-linked F₆PBI membranes were fabricated from F₆PBI and three different epoxides, which were bisphenol A diglycidyl ether (R₁), bisphenol A propoxylate diglycidyl ether (R₂) and poly(ethylene glycol) diglycidyl ether (R₃) (Sigma-Aldrich), respectively. The corresponding membranes are denoted as F₆PBI-x%R_y (R_y = R₁, R₂ and R₃), where x% was termed as the theoretical cross-linking degree estimated from the initial ratio of the reactants by assuming complete conversion. The cross-linked F₆PBI-R_y membranes were prepared as following. The polymer of F₆PBI and the cross-linker of R_y were separately dissolved in *N,N'*-dimethyl acetamide (DMAc, Sinopharm Chemical Reagent Co., Ltd) with a concentration of 2 wt%. The solutions of the polymer and the cross-linker were mixed together according to the

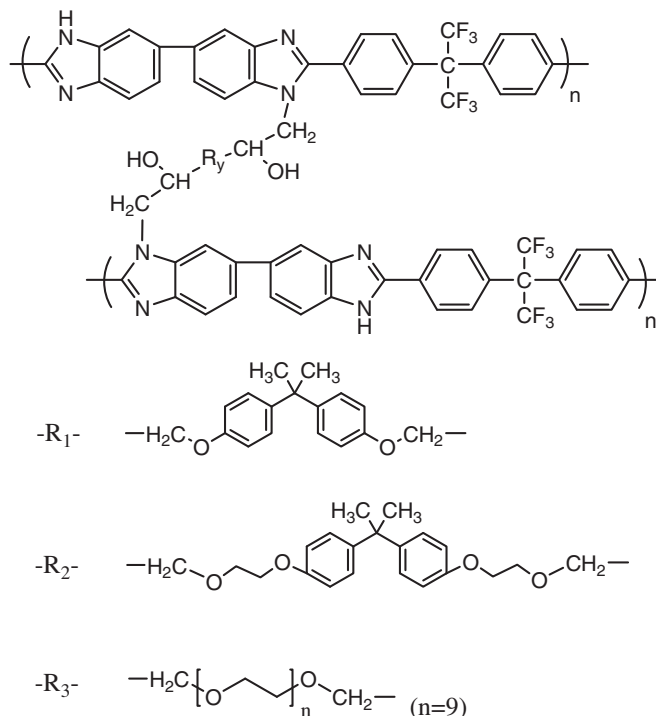


Fig. 1. Schematic illustration of the cross-linked F₆PBI membranes.

theoretical cross-linking degrees of 5%, 10% and 20%, respectively. The mixtures were ultrasonicated for 1 h at room temperature and then poured onto Petri dishes, respectively. The solvent was evaporated at 60 °C for 24 h and at 120 °C for 8 h. The resulting membranes were peeled off and soaked in demineralized water at 80 °C for 1 h and further dried in an oven at 180 °C for 1 h.

2.2. Acid doping and swelling

The acid doping of the membranes were performed by immersing membranes in 85 wt% PA solution at room temperature, or at an elevated temperature (60 °C or 80 °C) for a certain time in order to obtain the desired ADLs. The ADL of a membrane, defined as the mole number of PA molecules per mole F₆PBI repeat unit, was calculated based on the mass gains of the membrane samples by the process of the acid doping. The membrane swellings were determined accordingly by measuring the membrane dimension changes.

2.3. Characterizations

The cross-linking of the membranes was characterized by measuring their solubilities in DMAc. The membranes were immersed in DMAc at 80 °C under magnetic stirring, and a 0.5 wt% polymer solution would be obtained if complete dissolution of the membrane occurred. At different time intervals during the test, the undissolved membrane samples were collected by filtration and weighted after washing and drying. The dissolution level of the membranes in DMAc was calculated from the weight losses of the membranes. Fourier transform infrared spectra (FT-IR) of membranes were taken on a Bruker VERTEX70 spectrometer equipped with a DTGS detector and a ZnSe crystal as attenuated total reflection (ATR) accessory. FTIR spectra of cross-linkers (R₁, R₂ and R₃) were recorded on the above FTIR spectrometer as filming a KBr disk. Thermogravimetric

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