Graft-type polymer electrolyte membranes for fuel cells prepared through radiation-induced graft polymerization into alicyclic polybenzimidazoles

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ABSTRACT

Graft-type sulfonated polybenzimidazole was prepared through radiation-induced graft polymerization of styrenes into an alicyclic polybenzimidazole film and subsequent sulfonation. The alicyclic polybenzimidazole, ChPBI, was prepared from *trans*-1,4-cyclohexanedicarboxylic acid and 3,3′-diaminobenzidine using typical polycondensation. Anisotropic domains with a size of several tens of micrometers were found in the ChPBI films casted from LiCl-containing *N,N*-dimethylacetamide. Irradiation of the ChPBI membranes with a 220 kGy dose of γ-rays created radical species with mean lifetimes of two days. The treatment of this membrane with a 50/50 (v/v) mixture of 1-propanol and styrene produced polystyrene graft chains. Sulfonation of the resulting grafted membrane with ClSO$_3$H occurred selectively on the polystyrene grafts. The sulfonated films showed proton conductivity on the order of 10^{-3}–10^{-2} S/cm with an ion exchange capacity between 2.1 and 2.9 mmol/g. SEM-EDX analysis of the membrane indicated the presence of macrophase separated domains up to 1 μm in diameter. The proton conductivity of the membrane did not decrease for 600 h at 120 °C in liquid water.

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1. Introduction

Over the past several decades, polymer electrolyte membrane fuel cells (PEMFCs) have received worldwide attention due to their potential as a clean power source for many applications, such as electrical vehicles or portable electronic devices [1]. In particular, proton exchange membranes (PEMs) have been studied intensively because they are directly related to the efficiency and longevity of PEMFCs under hostile conditions (i.e., temperature and relative humidity). In addition to high proton conductivity, PEMs are required to show high mechanical, chemical, and thermal stability [2,3].

Among the numerous types of PEMs, sulfonated perfluoropolymers such as Nafion® show excellent stability and high proton conductivity (0.06 S/cm at the fully hydrated states at room temperature). However, they are strongly restrictive in PEMFC applications because of their low stability when the operating temperature is raised above 80 °C [4]. As an alternative, sulfonated hydrocarbon polymers, such as polyimides [5], polysulfones [6], poly(ether ether ketone)s [7], and polybenzimidazoles (PBIs) [8], have been studied [9]. Among them, PBI is regarded as the most attractive polymer backbone due to its excellent stability to hydrolytic decomposition under acidic conditions at high temperature [10].

PBIs for PEM applications are mainly divided into the following categories: phosphoric acid (H$_3$PO$_4$)-impregnated PBIs, PBIs doped with other organic/inorganic proton conductors, and sulfonated PBIs (sPBIs) [11]. H$_3$PO$_4$-impregnated PBIs are known to show a high σ value even at temperatures greater than 100 °C. However, these PBIs and other doped PBIs have the inevitable drawback of low stability under ambient conditions due to leaching of the dopant. Therefore, the use of sPBI is considered a better approach for the development of PEM for use over broad temperature ranges [12]. The sPBIs can be prepared through the thermal treatment of PBI films impregnated with sulfuric acid [13,14], the alkylation of the imidazole nitrogens on the PBI chain by electrophiles that have sulfonate groups [15,16], or polycondensation using sulfonated dicarboxylic acids [17,18]. However, all the reported sPBIs suffer from low proton conductivity of 10^{-5}–10^{-3} S/cm, regardless of the ion exchange capacity (IEC), which denotes the amount of sulfonic acid (SA) per unit mass of the dry polymer. The low proton conductivity has been attributed to the interaction between the SA and

imidazole (Im) groups, which leads to salt formation and trapping of the protons [19–22]. This trapping should cause some of the SA groups to be useless for proton conduction.

In this respect, Kreuer et al. have pointed out that the molar balance of SA and Im strongly affected the proton conductivity in the solution phase [23]. They had shown that higher proton conductivity can be realized in an imbalanced mixture of the two components than at either an equimolar composition or a pure solution of single components. This observation indicates that highly localized SA groups in a PBI matrix are expected to show high proton conductivity, as illustrated in Fig. 1.

In order to realize highly localized SA, a graft polymerization of styrene into a PBI polymer backbone and the subsequent sulfonation of the phenyl groups of the polystyrene grafts might be one of the choices [24–26]. For that purpose, a well-established radiation-induced graft polymerization technique that includes the radiation mediated generation of radical species and the subsequent radical graft polymerization of styrene might be suitable. However, because typical PBIs with aromatic structures are known to show resistance to radiation, generating the radicals in the films would be difficult.

In this context, some of the authors have found that a polyimide having 1,4-*trans*-cyclohexylene groups in the main chain successfully underwent radiation-induced graft polymerization of styrene, while a fully aromatic polyimide did not show reactivity with radiation at all [27]. Thus, we envisaged that an alicyclic PBI (ChPBI) derived from *trans*-1,4-cyclohexanedicarboxylic acid should show similar reactivity as alicyclic polyimides toward radiation. Here, we report on the preparation of sPBIs via radiation-induced graft polymerization and the evaluation of their performance as PEMs.

2. Experimental section

2.1. Materials

3,3′,4,4′-Tetraaminobiphenyl (TAB) from Sigma–Aldrich Chemical was purified by re-crystallization just before use. Dicarboxylic acids, *trans*-1,4-cyclohexanedicarboxylic acid (CDA) and isophthalic acid (IPA) both purchased from Tokyo Chemical Industry, and polyphosphoric acid (PPA) from Sigma–Aldrich Chemical were used as received. *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), lithium chloride (LiCl), sodium bicarbonate (NaHCO₃), styrene monomer (St), toluene, 1,4-dioxane, 1-propanol (1-PrOH), 2-propanol (2-PrOH), chlorosulfonic acid (ClSO₃H), and 1,2-dichloroethane (ClCH₂CH₂Cl) were purchased from Wako Pure Chemical Industries Ltd., and used as received. For sulfonation, a solution of 0.05 M of ClSO₃H in ClCH₂CH₂Cl was prepared just before use. Sodium chloride (NaCl),

sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Wako and used for titrimetric analysis. Ultra-pure water was obtained using a Millipore Mill-Q purification system.

2.2. Preparation of PBI membranes

2.2.1. Synthesis and characterization of PBIs

2.2.1.1. Synthesis of ChPBI. A 300-mL two-neck round-bottomed flask equipped with a mechanical stirrer and a nitrogen inlet were charged with TAB (2.1427 g, 10.00 mmol) and 100 g of PPA. After the TAB was completely dissolved, CDA (1.7218 g, 10.00 mmol) was added to this flask, and the reaction mixture was stirred at 120 °C for 4 h, at 140 °C for 5 h, and finally at 160 °C for 2 h to create a highly viscous solution. Then, the solution was slowly poured into water with stirring to give fibrous products. The fibers were washed with water several times and kept overnight in aqueous NaHCO₃ to remove residual PPA. After being washed with water several times, the fibers were dried in a vacuum oven at 140 °C for 14 h. Yield: 99%. ¹H NMR (DMSO-*d6*, ppm): 7.65 (br, 2H), 7.59 (br, 2H), 7.41 (br, 2H), 2.22 (br, 4H), 1.93 (br, 4H), FT-IR (KBr, cm⁻¹): 3350–2750 (N–H), 1620 (C=N), 1585, 1445, 1290 (benzimidazole ring), TGA: $T_d > 500$ °C, GPC; 160 kDa (M_n), 2.5 (PDI).

2.2.1.2. Synthesis of poly[2,2′-(m-phenylene)-5,5′-bibenzimidazole] (mPBI). The monomers were mixed in the same way as above, and the reaction mixture was stirred at 170 °C for 5 h, then at 200 °C for 24 h. Isolation of the product was carried out in the same way as above. Yield: 98%. ¹H NMR (DMSO-*d6*, ppm): 9.16 (s, amine proton), 8.34 (d, 4H), 8.04 (s, 1H), 7.84 (br, 2H), 7.62 (br, 3H), FT-IR (KBr, cm⁻¹): 3350-2750 (N–H), 1620 (C=N), 1585, 1445, 1290 (benzimidazole ring), TGA: $T_d > 500$ °C, GPC; 80 kDa (M_n), 2.3 (PDI).

2.2.2. Fabrication of PBI films

PBI was dissolved in DMAc containing LiCl (2 equiv. of the total amount of the repeating unit of PBI) at 80 °C. The solution was concentrated using a rotary evaporator, filtered through a Whatman 5 μm filter membrane, and then cast onto a clean glass substrate. The solvent was evaporated at 60 °C overnight under nitrogen flux to give a film, then the temperature was gradually increased up to 200 °C and kept at that temperature for 1 h. After cooling down to room temperature, the film was peeled off by soaking the glass substrate in water. The obtained film was repeatedly immersed in water and 2-PrOH, and then dried under vacuum for 5 h at 120 °C.

2.3. Preparation of sPBI

As shown in Scheme 1, a ChPBI film with a dimension of 3 cm × 5 cm was introduced into a glass ampoule. The ampoule was purged with argon and sealed. Then this ampoule was irradiated with a dose of 220 kGy (at a dose rate of 10 kGy/h) using γ-rays from a ⁶⁰Co source (Takasaki, JAEA) at ambient temperature. The irradiated film was immersed in bulk styrene or solutions of styrene in organic solvents (50/50 v/v) at temperatures ranging from room temperature to 80 °C to create a polystyrene grafted ChPBI (ChPBI-*g*-PSt) film. After that, the resulting film was washed with 5 ml of toluene and 5 ml of hexane to remove the homopolystyrene and residual St monomer. The degree of grafting (DG) was calculated from the following equation, where W_0 (g) and W_g (g) are the film weight before and after the graft polymerization, respectively.

$$DG(\%) = ((W_g - W_0)/W_0) \times 100 \tag{1}$$

Then sulfonation of the ChPBI-*g*-PSt film was performed by immersion in 40 ml of 0.05 M ClSO₃H in ClCH₂CH₂Cl at 0 °C for 4 h.
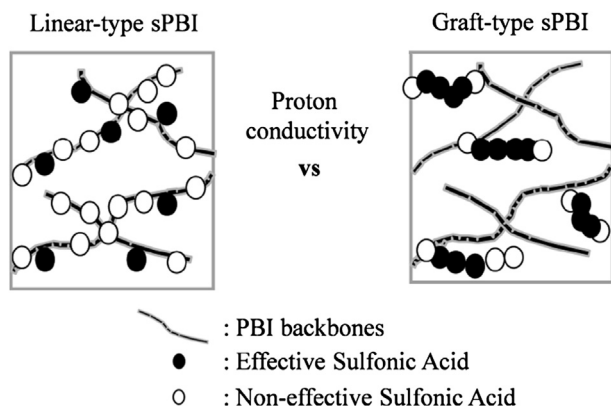

Fig. 1. 2D comparison of proton conductivity between linear-type and graft-type sPBI.

Linear-type sPBI Graft-type sPBI

Proton conductivity vs

〰 : PBI backbones
● : Effective Sulfonic Acid
○ : Non-effective Sulfonic Acid