Sulfonated polyimide nanofiber framework: Evaluation of intrinsic proton conductivity and application to composite membranes for fuel cells

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ABSTRACT

A series of proton conductive nanofibers were fabricated by an electrospinning method from various sulfonated polyimides bearing different polymer structures, such as block, graft, and block/graft structures. Except for S-*b*-PI and S-*bg*-PI that showed low solubility in the appropriate solvent, the four types of SPIs gave uniaxially-aligned nanofibers along with the nanofibrous mat, which is applicable as nanofiber framework for the composite membranes. The intrinsic proton conductivities of the uniaxially-aligned nanofibers were evaluated to discuss the influence of polymer structures on proton conductivity of the nanofibers. In accord with the result of this study, the S-*r*-PI nanofiber was selected to fabricate nanofiber framework composite membrane by composing with S-*bg*-PI that shows high proton conductivity and low gas permeability. The nanofiber framework composite membrane showed good proton conductivity as well as improved gas barrier property and membrane stability. The nanofiber framework composite membrane has a high potential for achieving high proton conductivity, gas barrier property, and membrane stability for future fuel cell application.

1. Introduction

Proton exchange membrane (PEM) is one of the key components in polymer electrolyte fuel cells (PEFCs), which have attracted considerable attention for stationary, portable, and automotive applications because of their high efficiency and low emissions of pollutants [1]. In order to improve performance and durability of the PEFCs, PEMs are required to have better characteristics including higher proton conductivity, higher chemical and physical stabilities, and lower gas permeability [2–4]. Although perfluorinated sulfonic acid (PFSA) aliphatic polymers, such as Nafion (Du Pont), have been widely used for PEMs due to their excellent proton conductivity and durability, the PFSA membranes have several critical issues on their low thermal stability and high gas permeability as well as environmental unadaptability and high production cost. Therefore, non-fluorinated alternative proton conductive membranes have been strongly desired. Recently, much effort has directed to the development of aromatic hydrocarbon polymer electrolyte membranes because of their advantages on low environmental load and production cost in addition to their high thermal and mechanical stabilities [5–12]. In past decades, there have been actively studied on sulfonated aromatic hydrocarbon polymers, such as sulfonated polyimides (SPIs) [5–7], sulfonated poly(arylene ether sulfone)s (SPAEs) [8–10], and sulfonated polyphenylenes (SPPs) [11,12]. Recent researches on the novel synthesis of these aromatic

hydrocarbon polymer electrolytes provided PEMs comparable or superior to the PFSA membranes in their proton conductivity. Most of them, however, contain a large number of sulfonic acid groups to enhance the proton conductivity, resulting in an unfavorable swelling of the membranes and a dramatic loss in their mechanical properties. Besides, they have critical problems in realizing both high proton conductivity and low gas permeability at the same time. Hydrogen and oxygen crossovers through the membrane are an undesirable diffusion because they lead to the following problems. First, the hydrogen crossover reduces fuel efficiency by depressing anode and cathode potential. Second, reactive oxygen species (ROS), which are believed to attack not only the catalyst but also the membrane causing their significant degradation, could be formed by the gas crossovers [13–15]. Therefore, one of the important objectives for designing the polymer electrolyte membranes is the development of new polymer membranes that simultaneously satisfy high proton conductivity, good membrane stabilities, and low gas permeability.

In recent years, much attention has been focusing on nanofibers fabricated through an electrically charged jet of a polymer solution/melt (electrospinning method) [16,17]. The electrospun nanofibers with their diameters in nanometer range possess many unique properties including a large specific surface area, superior mechanical properties, and fast materials transport properties [18,19]. Most recently, proton conductive nanofibers have been applied to polymer electrolyte
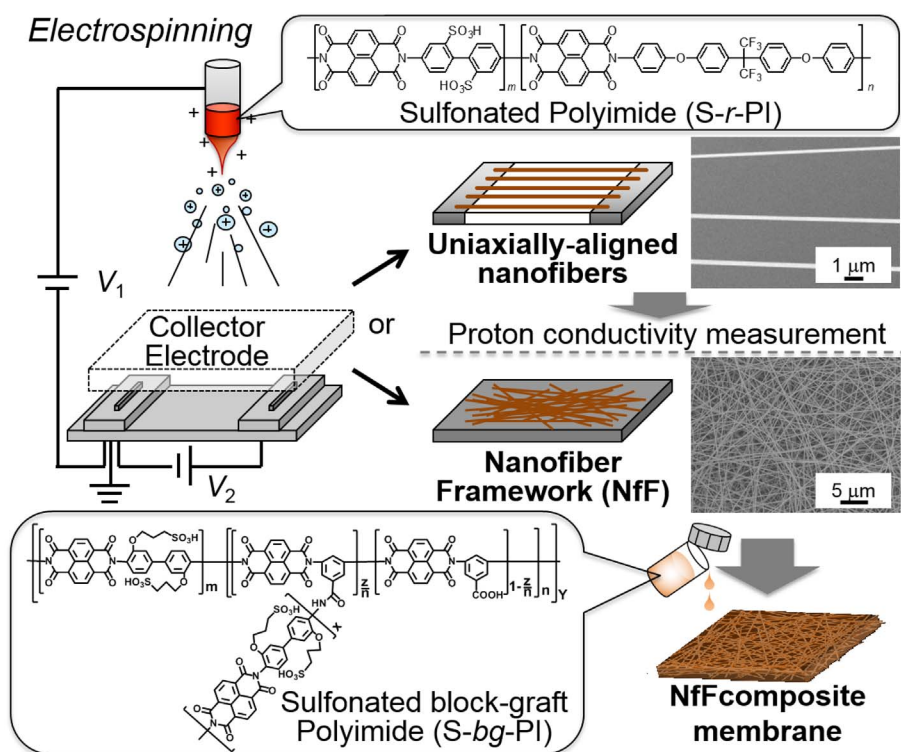
Fig. 1. Schematic illustration of the sulfonated polyimide (SPI)-based Nanofiber Framework (NfF): Evaluation of intrinsic proton conductivity and application to composite membranes for fuel cells.

composite membranes to break the conventional trade-off relationship between proton conductivity and gas barrier property. The first study on the proton conductive polymer nanofiber composite membranes was reported by J. Choi and co-workers in 2008 [20]. The following study by P. N. Pintauro et al. reported improvement of proton conductivity, durability, and fuel cell performances by fabricating nanofibers form perfluorosulfonic acid polymers and sulfonated polysulfones [21–24]. Snyder and Elabd also reported on the improvement of fuel cell performance by using Nafion nanofibers for composite membranes [25]. Our group has developed SPI-based nanofiber composite membranes to show better fuel cell performances than the corresponding SPI membrane prepared by a conventional solvent-casting method due to their improved proton conductivity and enhanced gas barrier property [26–28]. Furthermore, the membrane containing uniaxially-aligned SPI nanofibers showed higher in-plane proton conductivity along the fiber direction, indicating the SPI nanofibers have higher proton conductivity than the corresponding SPI membranes. Indeed, several studies have indicated that scaling down polymer electrolytes to the nanometer size scale may impact its properties and subsequently its fuel cell performance. Elabd et al. reported that the proton conductivity of a single Nafion nanofiber with 400 nm-diameter reached 1.5 S/cm at 30 °C and 90%RH, which is much higher than the conventional Nafion film (~ 0.1 S/cm) [29]. Similar extremely high proton conductivity on electrospun nanofibers was reported by J. Zhu and co-workers [30]. We also revealed that the electrospun SPI nanofibers showed ultra-high proton conductivities above 1 S/cm, which were one or two orders of magnitude higher than those of the corresponding SPI cast membranes [31]. In addition, we revealed that such ultra-high ion conductivity was observed not only in proton conductive nanofibers but also in anion conductive nanofibers [32].

Although there is growing interest in proton conductive electrospun polymer nanofibers for PEFC applications, only a few papers have been published on the proton conductive characteristics of the nanofibers [29–32]. The combination of nanofiber and matrix electrolyte were widely studied by many groups, and P. Pintauro and co-workers or D. Jones and co-workers revealed that the optimum membrane morphology is a network of reinforcing nanofibers made from Poly

(benzimidazole) or poly(vinylidene fluoride) that are surrounded by ionomer [16,24]. However, optimal combinations of the proton conductive nanofibers, such as SPI nanofibers, and the matrix polymer electrolyte, such as SPI matrix, for fuel cell membrane are still unclear. In this study, we attempted to fabricate various proton conductive nanofibers from six types of SPIs possessing diverse polymer structures. Then, the intrinsic proton conductivities of the nanofibers were evaluated to discuss the structure-property relationship on the electrospun SPI nanofibers. Furthermore, the best one in the series of SPI nanofibers was attempted to "Nanofiber Framework (NfF)", which is a new keyword that we proposed for three-dimensional electrospun nanofiber network structures prepared from functional polymers [33], for a polymer composite membrane. Based on our previous study [34,35], sulfonated *block*-graft polyimide (S-*bg*-PI) that possessed distinguished proton conductivity and gas barrier properties was selected as an appropriate polymer matrix for the NfF composite membrane. The proton conductivity, gas permeability, and other properties of the NfF composite membrane were investigated for future PEFC applications (Fig. 1).

2. Experimental

2.1. Materials

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) and 3.5-diaminobenzoic acid (DABA) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). DABA was refluxed in boiled water in the presence of activated carbon and was recrystallized from the filtrate. 2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-bis(4-aminophenyl) hexafluoropropane (6FAP) were purchased from Central Glass (Saitama, Japan). 6FDA was purified by sublimation before use. 6FAP was recrystallized twice from an ethanol solution before use. 2,2-Bis[4-(4-amino phenoxy)phenyl]-hexafluoropropane (APPF) was purchased from the Wako Pure Chemical Industries Co. (Osaka, Japan) and was recrystallized twice from an ethanol solution prior to use. 3,3'-Bis(3-sulfo-propoxy) benzidine (BSPB) was prepared using the same method reported by Watanabe et al. [36]. All other