Development of ion conductive nanofibers for polymer electrolyte fuel cells

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Electrospun polymer nanofibers have been actively studied in both academic and applied research. Ion conductive nanofibers in particular have attracted considerable attention owing to their unique characteristics and potential applications in electrochemical devices. This Focus Review summarizes our recent work on the development of ion conductive nanofibers and their application to polymer electrolyte fuel cell membranes. Recent research trends on ion conductive nanofibers are described along with a brief overview of the fabrication, properties and applications of polymer nanofibers. In our recent studies, we succeeded in evaluating the intrinsic proton and anion conductivity of electrospun nanofibers and revealed their distinguished ion conductive properties, which were quite different from those of the corresponding polymer membranes. These ion conductive nanofibers have potential utility as polymer electrolyte membranes to improve fuel cell performance by utilizing efficient ion conduction both inside and at the surfaces of nanofibers.

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INTRODUCTION

Nanomaterials such as nanoparticles, nanotubes and nanofibers are being actively studied due to their unique characteristics, which are quite different from those of conventional bulk materials.^{1,2} Among them, nanofibers with diameters $< 1 \,\mu m$ (1000 nm) are an important class of one-dimensional nanomaterials that has attracted considerable attention in both academic and industrial research.³ In recent decades, an enormous amount of research has focused on the fabrication, characterization and applications of nanofibers.^{4–6} We have also engaged in fundamental and practical research on polymer nanofibers. For example, we have reported on the morphological control of nanofibers during the fabrication process,⁷ the evaluation of mechanical properties of a single nanofiber⁸ and the application of nanofibers in a catalysis system,⁹ as described in the next section. Above all, we have been particularly focused on ion conductive nanofibers as academically interesting and practically useful novel materials.

This Focus Review summarizes our recent work on the development of ion conductive nanofibers and their applications to polymer electrolyte fuel cell membranes (Figure 1). The next section provides a brief overview of the fabrication, properties and applications of polymer nanofibers. In the context of our work, recent research trends on ion conductive nanofibers are also mentioned. Then, our original study on the intrinsic conductivity evaluation of ion conductive nanofibers is described. A series of nanofibers showed distinguished proton and anion conductive characteristics compared with the corresponding polymer membranes. Subsequently, these ion conductive nanofibers were applied to the development of polymer electrolyte membranes for fuel cell applications.

POLYMER NANOFIBERS: FABRICATION, PROPERTIES AND APPLICATIONS

Several techniques are being used to fabricate nanofibers, including melt-spinning,¹⁰ molecular assembly¹¹ and chemical vapor deposition.¹² Among them, electrospinning (ES) is one of the most useful and convenient approaches for the fabrication of various types of organic and/or inorganic nanofibers at ordinary temperatures and pressures.⁴⁻⁶ A typical procedure for the fabrication of polymer nanofibers by ES is as follows: first, a polymer solution is charged in a syringe, and a high voltage is applied between the syringe nozzle and a collector electrode. By ejecting the solution from the syringe at a constant slow speed, an electrically charged jet is sprayed from the nozzle. Although the sprayed jet is electrically attracted to the collector electrode, it stretches and sometimes splits into narrower jets owing to the electrostatic attractive and repulsive forces, respectively. The majority of the solvent evaporates from the jet before arriving at the collector electrode, resulting in the formation of non-woven nanofibers. Because of the electrostatic forces applied to the spray jet, the ES method is capable of producing ultrafine fibers with diameters in the nanometer range. The diameter and morphology of electrospun nanofibers are controllable by the ES parameters, including the applied voltage, flow rate, viscosity and electrical conductivity of the polymer solution, as well as the temperature and humidity inside the apparatus. For example, uniform non-beaded fluorinated polyimide nanofibers with diameters of ~ 30 nm have been obtained by optimizing the ES parameters.^{13,14} In addition to uniform nanofibers with smooth fiber surfaces, nanoporous or hollow nanofibers have also been reported.15,16 Recently, we reported the fabrication of core/shell and branch-structured nanofibers from polymer blend solutions that

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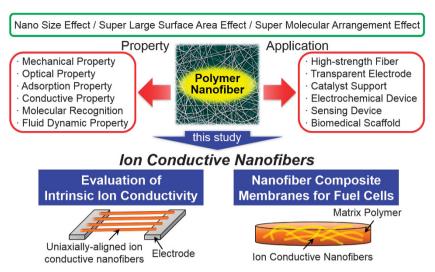


Figure 1 Unique characteristics of polymer nanofibers and the concept of our study on ion conductive nanofibers.

underwent a phase separation phenomenon during the ES process.⁷ Furthermore, the configuration of the nanofiber assembly can also be controlled from non-woven nanofibrous membranes to aligned nanofibers.⁴ Novel uniaxially and biaxially aligned nanofibers have successfully been fabricated by using specially designed collector electrodes.¹⁷

Electrospun polymer nanofibers are known to possess unique characteristics owing to the following three primary effects: (1) the 'nano-size effect' (major reduction in light scattering and fluid resistance), (2) the 'super surface area effect' (extremely high specific surface area to volume ratio) and (3) the 'super molecular arrangement effect' (polymer chain orientation along the nanofiber axis).4-6 These nanofibers often exhibit distinctive properties, which are quite different from corresponding bulk materials. For example, it was shown that single nanofibers prepared by the ES method with a rotary drum collector had extremely high mechanical strength owing to their molecular arrangement, namely the stretching and/or packing of the polymer chains.¹⁸ Most recently, we succeeded in evaluating the mechanical properties of single electrospun nanofibers prepared using specially designed parallel collector electrodes. It was clearly demonstrated that the elastic modulus of a single fluorinated polyimide nanofiber reached up to 2.9 GPa, which was almost twice as large as that of a membrane prepared from the same polymer.8 The distinguished mechanical properties and other unique characteristics of nanofibers are advantages for their practical application.

In recent decades, a number of applications of polymer nanofibers have been explored, including additives for reinforcement,¹⁹ filtration membranes,²⁰ transparent electrodes,²¹ electrochemical devices²² and scaffolds for tissue regeneration.²³ We have also reported on functional nanofibers, such as catalytically active nanofibers containing cationic manganese–porphyrin with superoxide dismutase activity⁹ and electrically conductive nanofibrous membranes prepared by an ion-beam irradiation technique.^{24–26} Although the production of nanofibers by ES is occasionally seen as a limitation for practical applications, the ES method can supply industrial processes by using rotary drum collectors and/or nozzle-less type spinnerets to efficiently fabricate large nanofibrous membranes.^{4,5,27}

RECENT RESEARCH TRENDS IN ION CONDUCTIVE NANOFIBERS

In the past, the fabrication of nanofibers by ES has been attempted using a variety of polymers. Among them, ion conductive nanofibers prepared from ionic polymers have been strongly desired for their potential applications in electrochemical devices.²⁸ However, ES of ionic polymer solutions is often challenging because electrically charged ion exchange groups, such as a sulfonic acid group, can cause instability of the spray jet when high voltages are applied to the solution. Consequently, no group has succeeded in fabricating electrospun nanofibers form the perfluorosulfonated polymer, Nafion, which is well known as an excellent proton conductor and is utilized in polymer electrolyte membranes in fuel cells. In addition to the instability of spray jet, it is difficult to obtain nanofibers by the ES of Nafion solutions owing to poor entanglement of the polymer chains and micelle formation due to the hydrophilic/hydrophobic amphipathic property of the polymer. To solve this problem, it has been common to add small amounts of spinning aids to Nafion solutions. Pintauro and colleagues reported electrospun Nafion nanofibers by adding a small quantity of poly(ethylene oxide) with high molecular weight $(M_W = 300\ 000\ \text{or}\ 1\ 000\ 000\ \text{g}\ \text{mol}^{-1})$.²⁹ The influence of the molecular weight and amount of poly(ethylene oxide) on nanofiber formation was carefully studied in the paper. Jones and colleagues partially investigated the effects of the solvent species and the sidechain length of perfluorosulfonated polymers on the ES process.³⁰ Poly(vinyl alcohol),³¹ poly(acrylic acid),³² poly(vinyl pyrrolidone),³³ polyethersulfone³⁴ or polyacrylonitrile³⁵ have also been utilized as additives to produce electrospun Nafion nanofibers. Electrospun nanofibers from sulfonated aromatic hydrocarbon polymers, which have been developed as alternatives to perfluorosulfonated polymers owing to their low cost and excellent thermal and mechanical stability, have also been actively investigated. Mather and colleagues succeeded in fabricating sulfonated poly(arylene ether sulfone) nanofibers by the ES method without any additives.³⁶ Our group has focused on sulfonated polyimides (SPIs) to fabricate nanofibers by the ES method.37-39 SPIs are typically presumed to be difficult to fabricate into nanofibers because of their limited solubility in specific solvents, such as dimethylsulfoxide and N-methylpyrrolidone. However, several SPIs containing fluorine groups have sufficient solubility in N, N-dimethylformamide to form nanofibers by the ES method.

Our recent study on the influence of SPI structure on the formation and ion conductivity of nanofibers is described in one of the following sections. In addition to these polymers, there have been many reports on various types of proton conductive nanofibers, including sulfonated polystyrene,^{40–43} sulfonated poly(phenylene oxide)⁴⁴ and sulfonated poly(arylene ether)s.^{45–48} Most recently, hybrid nanofibers composed of nonionic polymers and sulfonated inorganic materials have also been reported.^{49,50}

EVALUATION OF THE INTRINSIC ION CONDUCTIVITY OF ELECTROSPUN NANOFIBERS

As mentioned above, proton conductive nanofibers have been actively studied by many groups. However, most of the studies have focused primarily on the fabrication and applications of proton conductive nanofibers, there has been limited research on the characterization of the nanofibers themselves, specifically with regards to their intrinsic proton conductivity. In addition, the conductive characteristics of other ion species in the electrospun nanofibers have rarely been investigated. This section presents our recent fundamental study on ion conductive nanofibers.

Elucidating the intrinsic ion conductivity of nanofibers is of interest from an academic perspective to reveal the unique characteristics of the nanomaterial, but it also provides useful practical information for the development of novel ion conductive nanofibers for fuel cells and other electrochemical devices. In a previous study, it was predicted that electrospun proton conductive nanofibers have diverse conductive characteristics that are distinct from conventional membranes prepared from the same proton conductive polymer.³⁷ However, the proton conductive properties of the electrospun nanofibers themselves were not addressed due to the difficulty of measuring ion conductivity in the nanofiber assembly, owing to their nanofibrous structures that have many void gaps. Before our recent study, only one paper reported

the proton conductive characteristics of an electrospun nanofiber itself.⁵¹ The innovative research by Elabd and colleagues first succeeded in measuring proton conductivity of a single Nafion nanofiber using microfabricated electrodes. The electrospun Nafion nanofiber with a diameter of 400 nm showed an extremely high proton conductivity of up to $1.5 \,\mathrm{S \, cm^{-1}}$ at 30 °C and 90%RH, which was an order of magnitude greater than the bulk Nafion membrane (~0.1 S cm⁻¹).

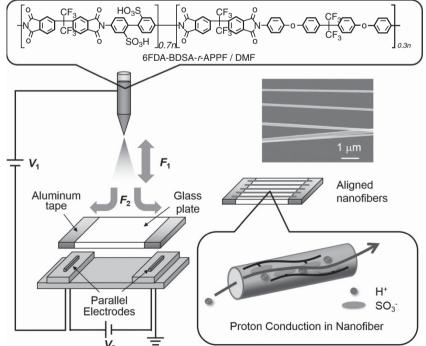
In our recent study, we focused on SPI nanofibers and revealed their intrinsic proton conductivity according to the following procedure.⁵² First, uniaxially aligned SPI (6FDA-BDSA-r-APPF) nanofibers with diameters of ~100 nm were prepared by the ES method using parallel collector electrodes, separated by a distance of 3 cm. In our specially designed ES apparatus, a high voltage (V_2) can be applied between the parallel electrodes, in addition to the conventional high voltage (V_1) applied between the syringe nozzle and the collector electrodes. Uniaxially aligned nanofibers were collected on a glass plate that bridged across the two parallel electrodes by means of the electrostatic attractive force (F_2 ; Figure 2). The uniaxially aligned nanofibers on the collector electrodes were then pressed against another micro-gap gold electrode with a 75-µm-wide linear gap to measure the conductivity. Then, their proton conductive characteristics were evaluated by performing alternating-current impedance measurements at various temperatures and humidity. Finally, the nanofiber diameters and the number of nanofibers between the micro-gap electrodes were analyzed by scanning electron microscopy. The intrinsic proton conductivity (σ) was calculated from equation (1):

$$\sigma = \frac{d}{(a \times N) \times R} \tag{1}$$

where *d*, *a*, *N* and *R* are the distance between the micro-gap electrodes (75 μ m), the cross-sectional area of a single nanofiber calculated from

Figure 2 Schematic illustration of the preparation and proton conductivity measurements performed on SPI (6FDA-BDSA-*r*-APPF) nanofibers.⁵² Reproduced

by permission of The Royal Society of Chemistry. SPI, sulfonated polyimide. A full color version of this figure is available at Polymer Journal online.



the average fiber diameter, the number of nanofibers between the micro-gap electrodes and the impedance obtained from the alternating-current impedance measurements, respectively.

The intrinsic proton conductivity of the SPI nanofibers (fiber diameter = 108 ± 22 nm, obtained by a V₂ voltage of 3.0 kV) was estimated to be 7.1 and 0.082 S cm⁻¹ at 90 °C, 95%RH and 90 °C, 30%RH, respectively (Figure 3). These proton conductivities were one or more orders magnitude greater than those of the corresponding SPI and Nafion membranes.⁵² This result agreed with the previous study by Elabd and colleagues,⁵¹ which clearly demonstrated that the proton conductivity of Nafion nanofibers increases sharply with decreasing fiber diameters. Our recent study suggested that the activation energy of proton conductivity in SPI nanofibers is smaller than that of the corresponding membrane. It is assumed that the quasi-onedimensional narrow conduction pathway inside the thin nanofibers permits rectilinear fast proton transport. Furthermore, it was also revealed for the first time that the proton conductivity of the SPI nanofibers was enhanced by increasing the V_2 voltage (Figure 2) during the ES process.⁵² Higher V₂ voltage is expected to facilitate molecular orientation in the electrospun nanofibers, thereby

> а Temperature / °C 90 30 60 at 95% RH 10¹ Proton conductivity / S cm⁻¹ 10⁰ 10⁻¹ Nafion 10-2 Membrane SPI mbrane 10⁻³ SPI Nanofiber (=3.0 kV SPI Nanofiber SPI Nanofiber 0.5 10-4 2.8 3.0 3.2 3.4 1000 T⁻¹ / K⁻¹ b at 90°C 10¹ Proton conductivity / S cm⁻¹ 10⁰ 10-1 10⁻² SPI membrane 10⁻³ Nafion Membrane 10-4 SPI Nanofiber $= 3.0 \, kV$ Nanofiber Nanofiber SPI .5 10⁻⁵ 30 50 20 40 60 70 80 90 100 Relative humidity / %

enhancing their proton conductivity. A similar phenomenon has also been observed in stretched membranes, in which material transport is enhanced along the extended axis owing to molecular orientation.53 We attempted polarized attenuated total reflection Fourier transform infrared spectroscopy to verify the molecular orientation in the SPI nanofibers (Figure 4).52 Unlike in the case of the SPI membranes (Figure 4a), the uniaxially aligned SPI nanofibers showed greater peak intensities for polarized measurements parallel to the fiber axis (P polarization) compared with those from the perpendicular measurements (S polarization), as shown in Figure 4b. It is known that the intensity of P polarization is greater than that of S polarization when the polymer backbone is oriented along the nanofiber axis.54 Therefore, this result indicated molecular orientation of the SPI backbone along the nanofibers. Furthermore, the P polarization spectra of uniaxially aligned nanofibers prepared using different V₂ voltages (3.0, 1.0 and 0.5 kV) revealed that higher V2 voltages led to increased molecular orientation in the electrospun nanofibers (Figure 4c).⁵² These results clearly supported that the enhancement of proton conductivity in the uniaxially aligned SPI nanofibers, and especially in the nanofibers prepared using higher V_2 voltages, was owing to the effects of molecular orientation in the nanofibers.

Most recently, a series of SPIs with different chemical structures, including naphthalene(N)- and fluorinated(F)-type polymers with block and/or graft structures that promote hydrophilic/hydrophobic microphase separation (Figure 5), have been synthesized to produce nanofibers by the ES method. The influence of the chemical structure

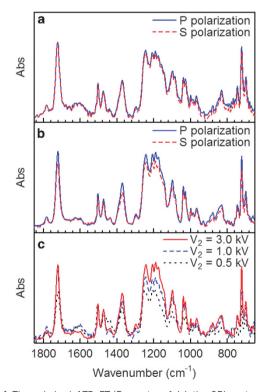


Figure 3 (a) Temperature dependence (at 95%RH) and (b) relative humidity dependence (at 90 °C) of proton conductivity of the SPI nanofibers prepared from different electrospinning condition ($V_2 = 0.5$, 1.0 and 3.0 kV), the SPI cast membrane and the Nafion membrane.⁵² Reproduced by permission of The Royal Society of Chemistry. SPI, sulfonated polyimide. A full color version of this figure is available at *Polymer Journal* online.

Figure 4 The polarized ATR FT-IR spectra of (**a**) the SPI cast membrane, (**b**) the uniaxially aligned SPI nanofibers prepared from V_2 voltage of 3.0 kV and (**c**) P polarization spectra of the uniaxially aligned SPI nanofibers prepared from different electrospinning conditions (V_2 =0.5, 1.0 and 3.0 kV).⁵² Reproduced by permission of The Royal Society of Chemistry. ATR FT-IR, attenuated total reflection Fourier transform infrared; SPI, sulfonated polyimide.

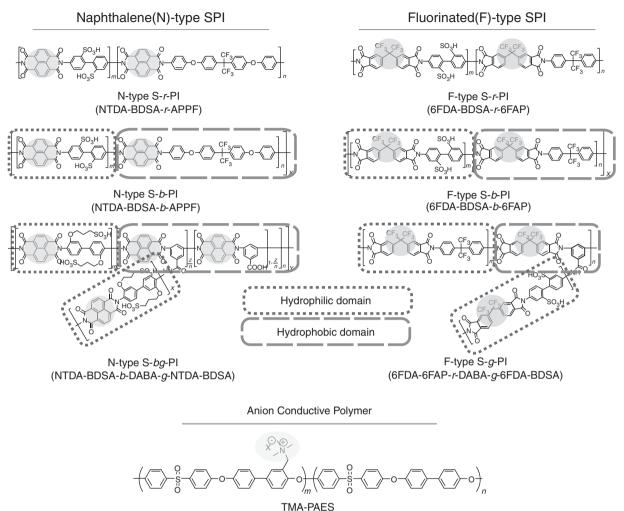


Figure 5 Chemical structures of SPIs and TMA-PAES used to fabricate ion conductive nanofibers. SPI, sulfonated polyimide; TMA-PAES, tetramethylammonium-substituted poly(arylene ether sulfone). A full color version of this figure is available at *Polymer Journal* online.

on the proton conductivity of these nanofibers was carefully investigated to demonstrate that the chemical structure strongly affects their proton conductive characteristics. Briefly, the F-type S-*b*-PI nanofibers showed higher proton conductivity than the F-type S-*r*-PI and S-*g*-PI nanofibers, especially at low relative humidity. It is believed that the block structure in the F-type S-*b*-PI nanofibers may contribute to the formation of an effective proton conduction pathway compared with other nanofibers with random and graft structures.⁵⁵ The N-type S-*b*-PI and S-*bg*-PI did not give nanofibers by the ES method under any conditions, presumably owing to their low solubility in solvents appropriate for ES and micelle formation. The details of this study will be published elsewhere.

Up to this point, the conducting ion in nanofibers had been limited to protons. We were strongly interested in the conductivity of other ions in the electrospun nanofibers. To the best of our knowledge, there have been no studies on the anion conductive characteristics of electrospun polymer nanofibers. The anion conductive polymer, tetramethylammonium-substituted poly(arylene ether sulfone) (TMA-PAES, Figure 5), was synthesized on the basis of the author's previous research.^{56–58} The ES method gave uniaxially aligned

nanofibers with diameters of ~120 nm from the TMA-PAES solution under the appropriate ES conditions. Similar to the proton conductivity measurements of the SPI nanofibers, anion (chloride, bromide and hydroxide ions) conductivity in the TMA-PAES nanofibers was successfully evaluated over a wide range of temperatures and humidity. The anion conductivity of the TMA-PAES nanofibers was suitably one order of magnitude higher than that of the corresponding membranes.⁵⁹ Details of our study on the influence of IEC, anion species and molecular orientation in nanofibers will soon be reported elsewhere.

NANOFIBER COMPOSITE MEMBRANES FOR POLYMER ELECTROLYTE FUEL CELLS

Polymer electrolyte fuel cells (PEFCs) have attracted considerable attention as alternative power sources for stationary, portable and automotive applications because of their high efficiency, compact size and low operating temperature.⁶⁰ Although residential fuel cells and fuel cell vehicles are being introduced to the market in several countries, further improvements in performance characteristics and reductions in the manufacturing cost are strongly desired to realize

broader applications of PEFCs. Polymer electrolyte membranes are an essential component of fuel cell systems, in which the membrane is sandwiched between anode and cathode electrodes to conduct ions and to prevent electrical shortage and fuel crossover (that is, permeation of hydrogen through the membrane).^{61–63} PEFCs are categorized into three major types: proton exchange membrane fuel cells (PEMFC),⁶¹ anion exchange membrane fuel cells (AEMFC)⁶² and phosphoric acid fuel cells.⁶³ In all three types of PEFCs, polymer electrolyte membranes require technical advancement in terms of their performance, including reducing the membrane resistance by increasing the ion conductivity and/or by reducing the membrane thickness, suppressing unexpected fuel crossover, improving long-term durability and reducing the manufacturing cost.^{61–63}

The application of proton conductive nanofibers to polymer electrolyte membranes is one of the major trends in recent PEFC research.^{37–39,42–50} Electrospun non-woven nanofibers embedded in a polymer electrolyte matrix can improve the mechanical strength of the membranes and prevent excessive swelling, which often leads poor dimensional stability in polymer electrolyte membranes. Some nanofiber composite membranes have shown improved fuel cell performance, mainly owing to the suppression of fuel crossover through the nanofiber composite membrane.^{37,44–46,48} We have developed a series of nanofiber composite membranes not only for PEMFC but also for other types of PEFCs. More specifically, proton conductive nanofiber composite membranes, anion conductive nanofiber composite membranes and acid-doped nanofiber composite membranes were prepared for PEMFC, AEMFC and phosphoric acid fuel cell applications, respectively.

In the case of PEMFCs, our group has reported that the fuel cell performance with a proton conductive SPI nanofiber composite membrane was superior to that with the corresponding SPI membrane without nanofibers (Figure 6).³⁷ On the basis of our fundamental study on the intrinsic proton conductivity measurements of a series of SPIs (Figure 5),^{52,55} we optimized the combination of proton conductive nanofibers and the matrix polymer electrolyte to create a novel nanofiber composite membrane. A notable advantage of the nanofiber composite membranes is the diverseness of the combinations of nanofibers and matrix polymers, which can be leveraged to give the appropriate properties to each component. In our preliminary

work, one of the best combinations of N-type S-*r*-PI nanofibers and N-type S-*bg*-PI matrix polymer (Figure 5) led to an exquisite nanofiber composite membrane that outperformed conventional membranes of SPI and other sulfonated hydrocarbons.

In the same way, anion conductive nanofibers have potential application in composite membranes for AEMFC. The fuel cell costs can be reduced in AEMFCs compared with PEMFCs because of ability to use non-precious metals as catalysts. However, the performance of AEMFCs is not currently suitable for practical fuel cell operation because of extremely low anion conductivity and insufficient stability of the electrolyte membranes currently being used. Therefore, the use of anion conductive nanofibers in polymer electrolyte membranes for AEMFCs is expected to overcome such conventional issues. In our study, a nanofiber composite membrane consisting of anion conductive TMA-PAES nanofibers and the same polymer electrolyte matrix (IEC = 1.32 meg g^{-1}) showed higher chloride anion conductivity (0.49 mS cm⁻¹ at 90 °C at 95%RH) than the corresponding TMA-PAES membrane without nanofibers (0.27 mS cm⁻¹ under the same conditions).58 This result clearly demonstrated that anion conductive nanofibers in the membrane can improve the performance of polymer electrolyte membranes for AEMFCs. Recent work on the successful preparation of anion conductive nanofiber composite membranes with higher anion conductivity will be reported elsewhere.

Finally, a new type of nanofiber composite membrane is presented here. In our past study, we revealed that the ternary combination of sulfonated polymer (SPI), basic polymer (PBI, polybenzimidazole), and phosphoric acid (PA) constructed new proton conduction pathways via interactions between the sulfonic acid and phosphoric acid groups in the composite membrane under low temperature and low relative humidity conditions.64-66 PA-doped PBI membranes are widely used as polymer electrolyte membranes in phosphoric acid fuel cells. However, these membranes are generally utilized at an unhumidified high temperature, and their proton conductivity drastically drops at a low temperature due to the high activation energy of proton conductivity via proton hopping among phosphoric acid groups. On the other hand, PA-SPI/PBI membranes have multiple proton conducting pathways and can even conduct protons at low temperatures. This concept was recently applied to nanofiber composite membranes (Figure 7).67 For example, an acid-doped nanofiber

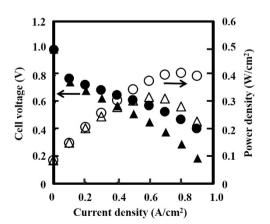


Figure 6 Cell voltage (close plots) and power density (open plots) of composite membrane containing 10 wt% aligned nanofibers and membrane without nanofiber under fully humidified conditions at 80 °C. (\bullet , \bigcirc), composite membrane containing 10 wt% aligned nanofibers; (\blacktriangle , \triangle), membrane without nanofiber.³⁷ Reprinted with permission from Tamura and Kawakami.³⁷ Copyright 2010 American Chemical Society.

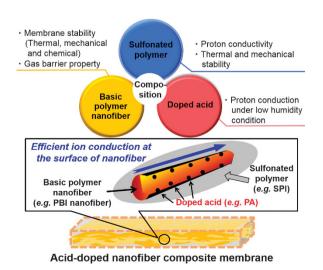


Figure 7 Schematic diagram of acid-doped nanofiber composite membranes. PBI, polybenzimidazole; SPI, sulfonated polyimide.

composite membrane was prepared by combining electrospun PBI nanofibers (PBINF), SPI as a sulfonated matrix polymer and PA as an acid dopant. The PA-SPI/PBINF membrane showed higher proton conductivity than a PA-doped SPI/PBI blend membrane with similar composition but without nanofibers, especially at low relative humidity. Interestingly, a composite membrane containing uniaxially aligned PBINF showed improved in-plane proton conductivity parallel to the nanofiber axis compared with perpendicular to the nanofiber axis. Presumably, an efficient proton conduction pathway was constructed at the surface of the PBINF by the aggregation of sulfonic acid groups with the basic nanofibers owing to acid-base interactions. Cross-sectional scanning transmission electron microscopy supported the aggregation of acid groups at the interface of the PBINF and SPI matrix in the nanofiber composite membrane. On the basis of these results, we conceived utilizing nanofiber surfaces to construct an efficient proton conduction pathway through three-dimensionally connected network structures to achieve high proton conductivity in the through-plane direction of the nanofiber composite membranes. We are now studying these novel nanofiber composite membranes and their performance in fuel cells under the support of a grant from the New Energy and Industrial Technology Development Organization for practical PEFC applications.

CONCLUSION

This Focus Review provides an overview of our recent study and related work on ion conductive polymer nanofibers and their applications in PEFCs. Ion conductive polymer nanofibers have unique characteristics and extremely high ion conductivity in particular, which is quite different compared with conventional bulk membranes. In some inorganic nanomaterials, similar unusual phenomena related to ion conduction are known as 'Nanoionics'.68,69 Fast ion conduction has been observed in inorganic planar heterostructures at the nanometer scale and high temperatures.⁶⁸ Recently, similar high ion conductivity has also been reported in ion-conducting liquid crystalline materials⁷⁰ and organic-inorganic hybrid nanomaterials.⁷¹ The author considered that the ultra-fast ion conduction inside and at the surface of electrospun ion conductive nanofibers in our study was a type of nanoionics and has proposed the term 'Organic Nanoionics' to reflect the similarity to conventional nanoionics in inorganic nanomaterials. In fact, full details regarding the fast ion conduction mechanism in the nanofibers have not been enclosed here. Further fundamental studies on ion conductive nanofibers are required for precise spectrographic and morphological analyses. The ion conductive nanofibers are attractive materials from both practical and academic perspectives and are expected to be useful for novel applications in the future.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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