Fabrication and Characterizations of Polymer Electrolyte Composite Membranes Consisted of Polymer Nanofiber Framework Bearing Connected Proton Conductive Pathways

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Nanofiber Framework (NfF)-based polymer electrolyte membranes were investigated for polymer electrolyte fuel cells. New processes, including the hot-pressing and vapor-welding, were attempted to the polybenzimidazolone nanofibers (PBNFs) to increase the fractions and connectivity of the Nfs. The phytic acid (Phy)-doping to the NFs and the followed composition with Nafion gave hot-pressed NfF (HPNfF)/Nafion and vapor-welded NfF (VWNfF)/Nafion composite membranes. These new composite membranes showed higher proton conductivity than a conventional NfF composite membrane by forming connected effective proton conductive pathways at the interface of the three-dimensionally connected Nfs and the matrix polymer electrolyte. The mechanical and gas barrier properties were also evaluated to reveal the effectiveness of the new processes.

Keywords: Composite Membrane, Electrospinning, Nanofiber, Polymer Electrolyte Fuel Cell, Proton conductivity

1. Introduction
Polymer Electrolyte Fuel Cell (PEFC), which generates electricity using hydrogen and oxygen without the carbon dioxide emission, is one of the key technologies for the carbon-neutral society [1]. For further popularization of PEFCs, higher efficiency, more extended durability, and lower cost of the PEFC components and system are required [2, 3]. The fuel cell operating at high temperatures (120°C or above) without humidification is the promising approach to improve the catalyst activity, leading to higher efficiency and lower cost [4, 5]. However, high temperatures and low- or non-humidification are severe conditions for polymer electrolyte membranes (PEMs). In conventional PEMs, protons can dissociate from sulfonic acid groups and diffuse by hydration in the membranes. In addition, other essential characteristics, including gas barrier properties and membrane stability, generally decrease at high temperatures. Therefore, novel PEMs that achieve high proton conductivity at low relative humidity, low gas permeability, and sufficient membrane stability are strongly desired.

Over the past decades, there have been enormous numbers of reports on PEMs to achieve higher proton conductivity and better electrolyte characteristics. In addition to the optimization of chemical structures of proton conductive polymers, the composition of polymer electrolytes with functional additives is an expected approach to achieve high-performance PEMs [6-8]. One of the promising materials for composite membranes includes polymer nanofibers (Nfs) prepared from an electrospinning method [9-13]. In particular, proton conductive Nfs fabricated from sulfonated polymers, such as Nafion, sulfonated poly (ether sulfone), and sulfonated polyimide, can enhance proton conductivity along with the improvement of gas barrier properties and membrane stabilities [14-20]. Instead of sulfonated polymer Nfs, we focused on acid-doped Nfs, in which polybenzimidazolone (PBI) and phytic acid (Phy) that has six phosphoric acid groups were selected as a polymer for Nfs and a doped acid, respectively. The nanofiber framework
(NfF) was combined with matrix polymer electrolytes, such as Nafion, to give composite membranes[21, 22]. The NfF/Nafion composite membrane showed improved electrolyte characteristics and fuel cell performances, especially at low humidity [21]. Based on our previously proposed concept, in which the combination of sulfonic acid and phosphoric acid realized efficient proton conduction at low humidity [23], the Phy-doped PBINfs formed sulfonic and phosphoric acids-concentrated areas at the interfaces between the Nfs and the matrix electrolyte.

Most recently, we revealed that the compression of Nfs is a practical approach to achieve higher proton conductivity and other properties by increasing nanofiber fractions and connectivity among Nfs in the composite membranes [24]. In this study, we proceed this idea to further improve the electrolyte characteristics by the hot-pressing and the followed vapor-welding (Fig. 1). Pressing the Nfs under heating conditions is expected to make tighter the Nfs than the previous pressing at room temperature. Also, exposure to good solvent vapor can soften and swollen the Nfs, and then the Nfs weld to each other after cooling and drying. The construction of connected proton conductive pathways is expected to enhance the proton conductive characteristics. The influence of these processes was investigated by forming three types of NfF composite membranes and evaluating their mechanical strength, proton conductivity, and gas barrier properties.

2. Experimental

All the commercially available chemicals, such as phytic acid (50wt% aqueous solution, TCI Co., Tokyo Japan) and Nafion DE 520 dispersion (Sigma-Aldrich Co., St. Louis, USA), were used without purification. Polybenzimidazole nanofibers (PBINfs) fabricated by an electrospinning nanofibers (PBINfs) fabricated by an electrospinning method were supplied from Japan Vilene Company, Ltd. The fiber diameters, fibrous membrane thickness, and porosity were ca. 200 nm, 15 µm, and 90%, respectively.

Hot Pressed Nanofiber Framework (HPNfF) was prepared by pressing the pristine PBINF with 10 MPa at 120°C for 1 hour. Vapor Welded Nanofiber Framework (VWNfF) was obtained by exposing the HPNfF in N,N-dimethylformamide (DMF) vapor at 60°C for 10 min, and then dried under vacuum. All the NfFs, including conventional pristine PBINFs, were doped with Phy by immersing the NfFs in 50wt% Phy aqueous solution at room temperature for 1 hour. The Phy-doped NfFs were repeatedly washed in hot water at 80°C for total 24 hours to remove unreacted Phy that was not chemically doped on NfFs. Then, each Phy-doped NfF was put in a petri dish, and an appropriate volume of Nafion dispersion was poured. The volume of Nafion dispersion was calculated to fill the voids among the Nfs with Nafion after slowly evaporating

Fig. 1. Fabrication procedure of three types of NfF composite membranes.
solvent in air. Three types of obtained Phy-PBINF composite membranes, including conventional NfF/Nafion, HPNfF/Nafion, and VWNfF/Nafion, were dried under vacuum at 80°C for 24 hours.

The nanofiber and membrane morphologies were observed by JEOL JXP-6100P scanning electron microscopy (SEM). The mechanical strength of the NfFs and membranes were measured by a tensile testing machine (AGS-X5kN, Shimadzu Co., Tokyo, Japan). The proton conductivity of the electrolyte membranes was evaluated by the electrochemical impedance analyzer (3532-50, Hioki Co., Tokyo, Japan) in a temperature- and humidity-controlled chamber. Proton conductivity $\sigma$ (S cm$^{-1}$) was determined from the equation: $\sigma = d / (R \cdot A)$, where $d$, $R$, and $A$ represent the distance between two platinum electrodes (cm), impedance value (Ω) in measured by the analyzer, and cross-sectional area of the membrane (cm$^2$), respectively. Water uptake was evaluated by the thickness change after immersing a membrane in hot water at 80°C for 24 hours. Oxygen gas permeability coefficients $P_{O2}$ and water vapor permeance $Q_{H2O}$ were measured according to our previous study [21,24] using a gas permeability apparatus (RGP-3000Z, Round Science Inc., Kyoto, Japan).

### 3. Results and discussion

#### 3.1. NfF fabrication

Three types of NfFs were fabricated according to the procedures shown in Fig. 1. The hot-pressed PBINF was obtained by pressing the pristine PBINF with 10 MPa at 120°C for 1 hour. The thickness of the nanofibrous mat reduced from 30 μm to 24 μm after the process (Fig. 2). Although the nanofiber diameters maintained their original values (200±20 nm), the porosity also reduced from 90% to 85% by the compression. The vapor welded PBINF was prepared by exposing the hot-pressed PBINF in DMF vapor at 60°C for 10 min. Since DMF is a good solvent for the PBI, the PBINFs softened and swelled with DMF and welded each other after evaporating DMF from the Nfs. The average fiber diameter estimated by SEM slightly increased from 200±20 nm to 220±30 nm after the welding. The thickness and porosity also reduced to 19 μm and 82%, respectively. Then, each Nf, including conventional PBINF, hot-pressed PNINF, and vapor-welded PBINF, was doped with Phy and was washed with hot water to yield NfF, HPNfF, and VWNfF, respectively. Finally, pouring the Nafion dispersion onto each NfF and the followed evaporating solvent provided the NfF/Nafion, HPNfF/Nafion, and VWNfF/Nafion composite membranes.

#### 3.2. Mechanical property

Fig. 3(a) shows the mechanical strength of the three types of NfFs. In this figure, the tensile force...
(N) was used as a Y-axis instead of stress (MPa) because the cross-sectional area of the NfFs was unclear due to the porous nanofibrous mat structures. As expected, the HPNfF and VWNfF showed higher tensile force than the conventional NfF. It indicates the hot-pressing and vapor-welding processes are effective ways to increase the mechanical strength of the NfFs. The mechanical strengths of a series of NfF/Nafion composite membranes were also depicted in Fig.3(b). The HPNfF/Nafion composite membrane indicated higher maximum stress (29.2 MPa) and elastic modulus (0.42 GPa) than those of the NfF/Nafion composite membrane (26.4 MPa and 0.39 GPa) and the recast-Nafion membrane (17.8 MPa and 0.34 GPa), respectively. However, the mechanical strength of the VWNfF/Nafion composite membrane was slightly inferior to that of the NfF/Nafion composite membrane. It may result from the insufficient densification of the VWNfF/Nafion composite membrane. As shown in Fig. 2 (g) and (h), The VWNfF formed densely welded structures that could patricianally inhibit the filling of Nafion to the void space of the nanofibrous mat. Future study for denser composite membranes from the VWNfF has the potential to achieve higher mechanical strength.

3.3. Proton conductivity

Proton conductivity is an essential characteristics of polymer electrolyte membranes. In particular, high proton conductive characteristics at low relative humidity are desired. Fig. 4 demonstrates the relative humidity and temperature dependency...
of the proton conductivity on the NfF composite membranes. The HPNfF/Nafion and VWNfF/Nafion composite membranes showed higher proton conductivity than the conventional NfF composite membrane using pristine PBINFs and the recast-Nafion membrane without Nfs. Besides, the activation energy ($E_a$) of the proton conductivity at 40%RH on the HPNfF/Nafion and VWNfF/Nafion composite membranes were both 19 kJ mol$^{-1}$, which were much lower than those of the NfF/Nafion composite ($E_a = 39$ kJ mol$^{-1}$) and the recast-Nafion ($E_a = 45$ kJ mol$^{-1}$) membranes. These results mean that increase of the Nf fraction and the connectivity in the composite membranes is significantly effective for proton conduction, especially at low relative humidity. As is the case with mechanical strength, the VWNfF/Nafion composite membrane showed lower proton conductivity than the HPNfF/Nafion composite membrane. One possible reason is insufficient densification of the VWNfF/Nafion composite membrane, as described before. Another reason includes the difference in water uptake between the two composite membranes. After water uptake (in water at 80°C for 24 hours), a thickness change of the VWNfF/Nafion composite membrane was only 2%. In contrast, the HPNfF/Nafion and NfF/Nafion composite membrane showed their thickness change of 4.1 and 9.4% under the same conditions, respectively. The three-dimensionally connected VWNfF prevented the water swelling which may lead to lower proton conductivity of the VWNfF/Nafion composite membrane than the HPNfF/Nafion composite membrane.

3.4. Gas and water vapor permeability

High gas barrier property, that is to say low gas permeability, is required to polymer electrolyte membranes. In the fuel cell operation, gas crossover through the membrane is problematic because such gas crossover decreases the open circuit potential and the power generation efficiency. Besides, gas crossover increases the risk of decomposition of the membrane and the catalyst electrodes by forming hydrogen peroxide and radical spieces from the permeated hydrogen and oxygen on the precious metal catalyst. On the other hand, sufficient water vapor permeability is required for membranes to utilize generated water by the oxygen reduction reaction effectively. As shown in Fig. 5 (a), the NfF composite membranes, especially the HPNfF/Nafion composite membrane, showed significantly lower oxygen gas permeability than the recast-Nafion membrane. The low gas permeable PBINFs can reduce gas diffusion in the composite membranes. By contrast, all the NfF composite membranes indicated similar water vapor permeance to the recast-Nafion membrane without nanofibers (Fig. 5 (b)). At this moment, the water vapor diffusion pathways are not clearly understood. However, based on our previous study [21], it is considered that adequate water vapor diffusion pathways were constructed at the interface between the Phy-doped PBINFs and the matrix electrolyte.

4. Conclusion

The new NfF-based polymer electrolyte membranes were developed for future PEFC applications operated under high temperatures and low- or non-humidity conditions. The hot-pressing and vapor-welding processes on PBINFs increased the nanofiber fractions and connectivity among the
Nfs. The HPNfF/Nafion and VWNfF/Nafion composite membranes showed higher proton conductivity than a conventional NfF/Nafion composite membrane. It indicates that the construction of three-dimensionally connected NfF is a promising approach to form effective proton conductive pathways in PEMs. Furthermore, mechanical strength and gas barrier property were also improved by the new NfFs. Although the VWNfF/Nafion composite membrane did not reach the expected performances due to its insufficient densification, further study on compacted and connected NfFs will promise to achieve significant characteristics to apply to future PEFCs.

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