

Aligned electrospun nanofiber composite membranes for fuel cell electrolytes

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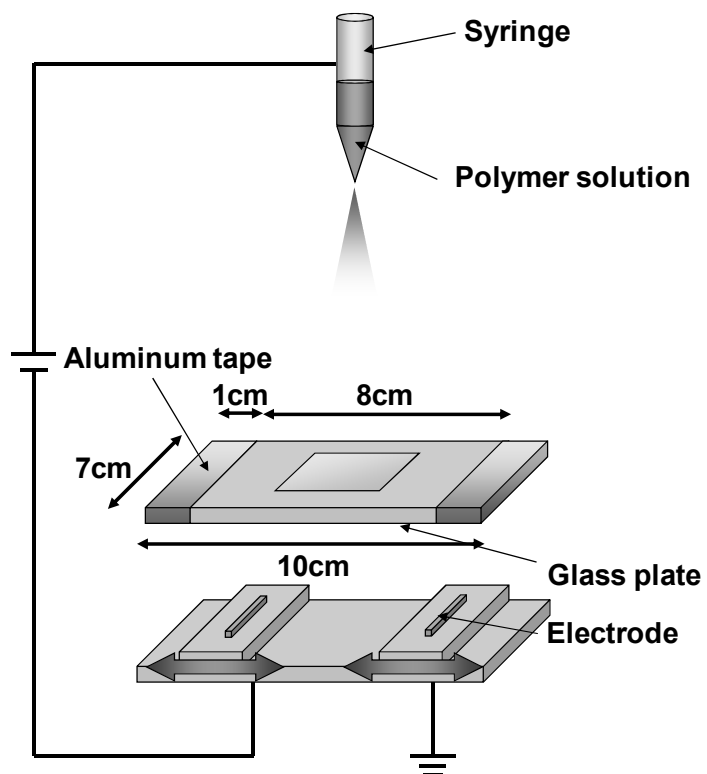
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MATERIALS

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) was purchased from the Sigma-Aldrich Co., Tokyo, Japan. 4,4'-Diamino-biphenyl 2,2'-disulfonic acid (BDSA) was purchased from the Tokyo Kasei Co., Tokyo, Japan, and was purified by dissolution in a triethylamine aqueous solution and then precipitated in 1 N H₂SO₄. Finally, the BDSA was dried in a vacuum oven at 70 °C for 12 h. 2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (APPF) was purchased from the Wako Pure Chemical Industries Co., Osaka, Japan, and then was recrystallized twice from an ethanol solution prior to use. Nafion[®] 117 was used in this study as the control membrane. The membranes were obtained from the DuPont Co., Ltd. (Tokyo, Japan). The sulfonated random copolyimide, NTDA-BDSA-r-APPF, was synthesized by the same method as described in previous papers.¹

METHODS

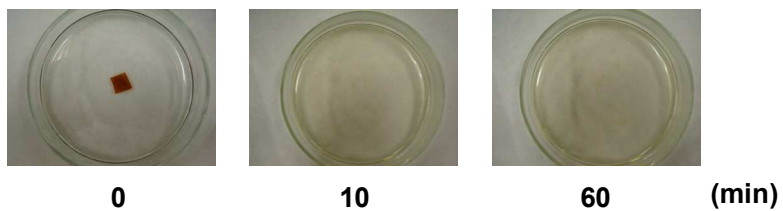
The experimental set-up used for the preparation of the uniaxially aligned nanofibers are shown in the Supplementary Information. The membranes were fabricated using an electrospinning apparatus (Fuence, Co., Ltd., ES-1000, Tokyo, Japan). NTDA-BDSA-r-APPF was dissolved in DMF. The typical electrospinning parameters were as follows: The polymer solution with a 11 wt% concentration was loaded into a 1 ml syringe as the spinneret. A syringe pump was used to squeeze out the polymer solution at the speed of 0.12 ml/h through a needle with an inner diameter of 0.21 mm. A voltage of 24 kV was applied between the syringe and the collector, and a voltage of 1 kV was applied between the two aluminum plates as the electrode. The distance between the spinneret and the grounded plate was 10 cm. Uniaxially aligned nanofibers were deposited on the glass plate (7cm×7cm), located on the collector by the electrospinning method. The composite membranes containing uniaxially aligned sulfonated polyimide nanofibers were prepared using a solvent-cast method.



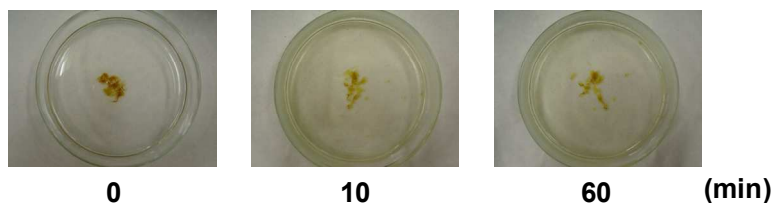
Supplementary figure 1. Preparation of aligned nanofiber with proton conductivity.

Figure 1 shows an electrospinning apparatus (Fuence, Co., Ltd., ES-1000, Tokyo, Japan) and specially designed collector.

a) Membrane



b) Nanofiber



Supplementary figure 2. Solubility of membrane without nanofiber and nanofibers.

Figure 2 a and b show the solubility of the polyimide membrane and nanofiber for DMSO solution at 110°C. The membrane was prepared with the solvent-cast method from NTDA-BDSA-r-APPE. The nanofiber hardly dissolved for 60 minutes, while the membrane completely dissolved during several minutes. We believe that the oriented or aggregated polyimides within the nanofiber inhibited the solvent diffusion through the nanofiber so that the solubility of the nanofiber for the solvent significantly decreased. Therefore, the nanofiber which does not easily dissolve in DMSO solution may be introduced into the composite membrane with maintaining of the form of nanofiber at the membrane preparation.

Preparation of composite membrane with uniaxially aligned nanofiber:

The experimental set-up used for the preparation of the uniaxially aligned nanofibers are shown in the Supplementary Information. The membranes were fabricated using an electrospinning apparatus (Fuence, Co., Ltd., ES-1000, Tokyo, Japan). NTDA-BDSA-r-APPF was dissolved in DMF. The typical electrospinning parameters were as follows: The polymer solution with a 11 wt% concentration was loaded into a 1 ml syringe as the spinneret. A syringe pump was used to squeeze out the polymer solution at the speed of 0.12 ml/h through a needle with an inner diameter of 0.21 mm. A voltage of 24 kV was applied between the syringe and the collector, and a voltage of 1 kV was applied between the two aluminum plates as the electrode. The distance between the spinneret and the grounded plate was 10 cm. Uniaxially aligned nanofibers were deposited on the glass plate (7cm×7cm), located on the collector by the electrospinning method.

The composite membranes containing uniaxially aligned sulfonated polyimide nanofibers were prepared using a solvent-cast method. After uniaxially aligned sulfonated polyimide nanofibers were fabricated by electrospinning, the nanofibers were fixed by the glass ring because of the maintain uniaxially aligned structure and the nanofibers were acidified with HCl solution. The resulting nanofibers were dried in a vacuum oven at 80 °C for 24 h. Then the sulfonated polyimide solution was poured to the nanofibers, and, in addition, dried in a vacuum oven at 100°C for 24 h. The composite membrane containing uniaxially aligned nanofibers were acidified with 0.1 M HCl solution, and finally washed with deionized water. The resulting membranes were dried in a vacuum oven at 80 °C for 24 h. The thickness of the membrane was approximately 50 μm.

Ionic-exchange capacity (IEC) and water uptake:

The ionic-exchange capacity (IEC) was measured by classical titration using NaOH and HCl solutions.¹ The water uptake of the sulfonated random copolyimide was gravimetrically measured from the dried and humidified membranes.¹ The sulfonated random copolyimide membranes were dried in a vacuum oven at 80 °C for 10 h and then immersed in liquid water at room temperature. After 24 h, the membrane was then wiped dry and quickly weighed. The water uptake was calculated with the following equation.

$$W = \frac{(W_s - W_d)}{W_d} \times 100(\%)$$

Chemical stability and proton conductivity:

The stability of the sulfonated copolyimide to oxidation was investigated by immersing the membranes in Fenton's reagent (2ppm FeSO₄ in 3% H₂O₂) at 80 °C. The thickness of the membranes was approximately 50 μm.

The proton conductivity of the membrane was measured by electrochemical impedance spectroscopy over the frequency range from 50 Hz to 50kHz (Hioki 3532-50, Tokyo, Japan) as reported in previous papers.¹ The membrane (1.0 x 3.0 cm²) and two blackened platinum plate electrodes were placed in a Teflon cell. The distance between the two electrodes was 1.0 cm. The cell was placed in a thermocontrolled humidity chamber to measure the humidity dependence of the proton conductivity. The experiments were carried out at more than three times. Data are expressed as mean ±SD.

Gas permeability:

The gas permeability coefficients of oxygen were measured with a high vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan).² The gas permeation measurements of the sulfonated copolyimide membranes were

carried out at 35 °C and 76 cmHg. The permeation parameters, D and S, of the sulfonated copolyimide membranes were calculated from

$$P=DS$$

and

$$D = \frac{L^2}{6\theta}$$

using the time lag , θ .

cc

Fuel cell performance:

We evaluated cell performance. MEA were prepared as follows. A slurry of Pt catalyst supported on carbon black (Pt/CB cathode: TEC10E50E, anode: TEC61E54, Tanaka Kikinzoku Kogyo K.K.), containing commercial NafionR solution (DE-521, DuPont) and a solvent (2-propanol/water = 1/1 by weight) were mixed. The electrolyte (binder) in the catalyst layer was NafionR for both cells, with the composite membrane and the membrane without nanofiber NRE212 being used as membranes. The mass ratio of Nafion to CB was adjusted to 0.7. The mass ratio of PTFE (D-1E, Daikin) to CB was adjusted to 0.3. The mixed solution was sprayed to the commercial carbon paper (24BC, SGL Carbon AG). The carbon paper was dried in vacuum oven at 80° C. The geometric electrode area was 5 cm² and the Pt loading amount in the electrodes was 0.50 mgcm⁻². The membrane and electrode assembly (MEA) was prepared by hotpressing the composite membrane or the membranes without nanofibers sandwiched between two identical gas diffusion electrodes for 5 min at 150 °C and 50 kg/cm².

References

- 1) T. Nakano, S. Nagaoka, and H. Kawakami, Polym. Adv, Technol. 16, 753-757 (2005).
- 2) H. Kawakami, M. Mikawa, and S. Nagaoka, J. Membr. Sci., 163, 167 (1999)