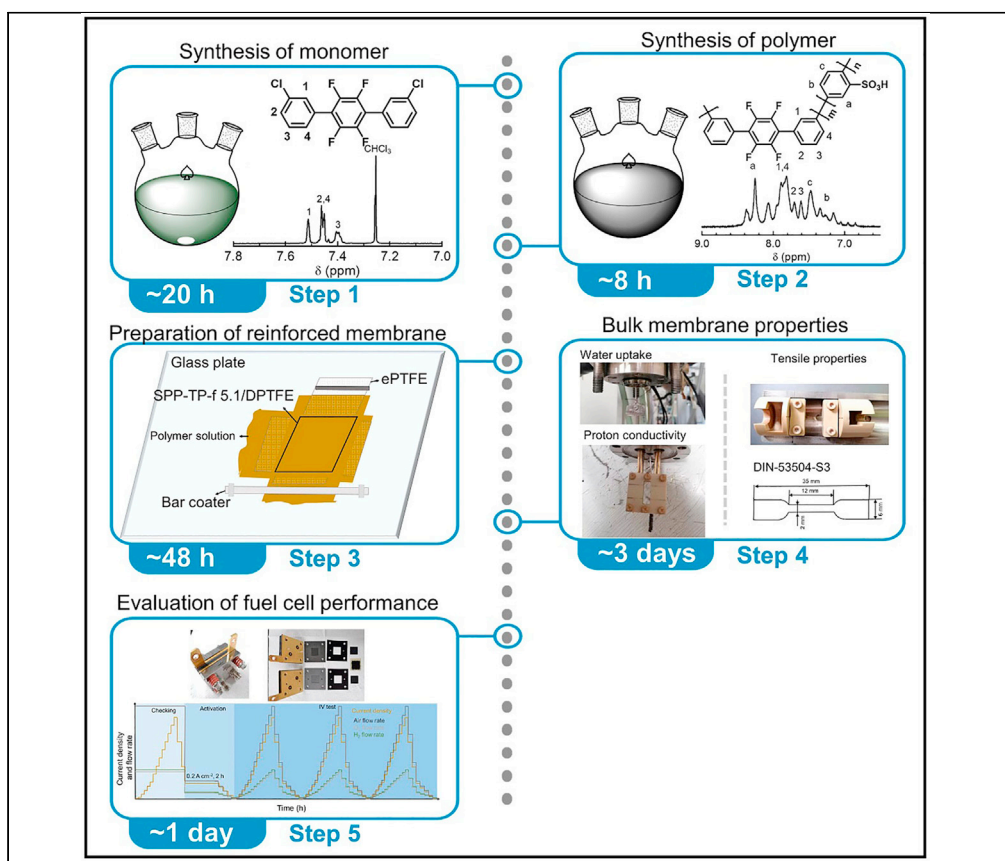# STAR Protocols

Protocol

Protocol for synthesis and characterization of ePTFE reinforced, sulfonated polyphenylene in the application to proton exchange membrane fuel cells

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Highlights

Detailed protocol for preparation of ePTFE-reinforced sulfonated polyphenylene membranes

Characterization technique of proton exchange membranes

Fabrication of membrane electrode assembly (MEA) and its evaluation in PEMFCs

Sulfonated polyphenylenes (SPPs) are one of the most promising polymers as proton exchange membranes for fuel cells (PEMFCs) because of their high proton conductivity, gas impermeability, and chemical and thermal stability. Mechanical stability needs further improvement for practical applications. Here we describe a protocol for the preparation and characterization of tetrafluorophenylene-containing SPP (SPP-TP-f) membranes reinforced with double porous ePTFE (expanded polytetrafluoroethylene) thin layers. The protocol also includes performance and durability evaluation of fuel cells using the reinforced membranes.

Protocol

Protocol for synthesis and characterization of ePTFE reinforced, sulfonated polyphenylene in the application to proton exchange membrane fuel cells

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SUMMARY

Sulfonated polyphenylenes (SPPs) are one of the most promising polymers as proton exchange membranes for fuel cells (PEMFCs) because of their high proton conductivity, gas impermeability, and chemical and thermal stability. Mechanical stability needs further improvement for practical applications. Here we describe a protocol for the preparation and characterization of tetrafluorophenylene-containing SPP (SPP-TP-f) membranes reinforced with double porous ePTFE (expanded polytetrafluoroethylene) thin layers. The protocol also includes performance and durability evaluation of fuel cells using the reinforced membranes.

For complete details on the use and execution of this protocol, please refer to Long and Miyatake (2021a).

BEFORE YOU BEGIN

Sulfonated polyphenylenes (SPPs) composed solely of phenylene groups as a rigid backbone are a promising candidate as a proton exchange membrane in the application of high-temperature fuel cells due to its thermal and oxidative stability as well as high proton conductivity. An SPP containing tetrafluorophenylene and high sulfonic acid concentration (SPP-TP-f 5.1) has been synthesized to render good solubility into lower alcohols and reinforced with expanded polytetrafluoroethylene (ePTFE) (SPP-TP-f 5.1/DPTFE) to improve the mechanical robustness. In this protocol, we present the preparation of SPP-TP-f 5.1/DPTFE and the evaluation of bulk membrane properties, and their fuel cell performance and durability. The protocol can in principle be applied for a variety of ion conductive composite membranes containing aromatic ionomers and mechanically robust porous substrates, aiming at high temperature and low humidity operation of the proton exchange membrane in fuel cells.

KEY RESOURCES TABLE

REAGENTS or RESOURCES	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
1,2,4,5-Tetrafluorobenzene	TCI	CAS: 327-54-8
Palladium(II) Acetate	TCI	CAS: 3375-31-3
Di-tert-butyl(methyl)phosphonium tetrafluoroborate	Sigma-Aldrich	CAS: 479094-62-7
1-Bromo-3-chlorobenzene	TCI	CAS: 108-37-2

(Continued on next page)

Continued

REAGENTS or RESOURCES	SOURCE	IDENTIFIER
K_2CO_3	KANTO Chemical	32323-00
N,N-Dimethylacetamide	KANTO Chemical	10306-00
Chloroform	KANTO Chemical	07278-70
Methanol	KANTO Chemical	25183-70
Dichloromethane	KANTO Chemical	10158-70
2,5-Dichlorobenzenesulfonic acid	TCI	CAS: 88-42-6
2,2'-Bipyridyl	TCI	CAS: 366-18-7
Dimethyl sulfoxide	KANTO Chemical	10380-05
Toluene	KANTO Chemical	40500-05
Bis(1,5-cyclooctadiene)nickel(0)	KANTO Chemical	CAS: 1295-35-8
Hydrochloric acid	KANTO Chemical	18078-70
Sodium chloride	KANTO Chemical	37144-86
Lead(II) acetate trihydrate	KANTO Chemical	24038-30
Pt/CB catalyst	Tanaka Kikinzoku Kogyo K. K.	TEC10E50E
Nafion dispersion	Du Pont	D-521
Gasket	Maxell Kureha Co., Ltd.	SB50A1P
Gas diffusion layer	SGL Carbon Group Co., Ltd.	29BC
ePTFE substrate	Valqua LTD.	http://www.valqua.com/
Software and algorithms		
ChemDraw 18.1	PerkinElmer	https://perkinelmerinformatics.com/products/research/chemdraw/
Other		
Nuclear magnetic resonance (NMR)	JEOL JNM-ECA 500 spectrometer	N/A
Gel permeation chromatography (GPC)	Jasco 805 UV with a Shodex K-805L column	N/A
Transmission electron microscopy (TEM)	Hitachi H-9500	N/A
Scanning electron microscope (SEM)	Hitachi S-3000N	N/A
Ion exchange capacity (IEC)	Kem Kyoto automatic potentiometric titrator AT-510	N/A
Water uptake and proton conductivity	Bel Japan Solid electrolyte analyzer system MSBAD-V-FC	N/A
Dynamic mechanical analysis (DMA)	ITK dynamic viscoelastic analyzer DVA-225	N/A
Tensile properties	Shimadzu universal testing instrument AGS-J 500N attached with a Toshin Kogyo Bethel-3A temperature/humidity-controllable chamber	N/A
Catalyst-coated membranes (CCMs)	Nordson pulse-swirl-spray instrument	N/A
Planetary ball mill	Fritsch P-6	N/A
Pot mill rotary stand	Nitto Kagaku ANZ-61S	N/A
Heat pressure machine	Toho Kogyo., Co. Ltd.	N/A
Fuel cell stand	Panasonic Production Technology FCE-1 equipped with an electronic load (PLZ-664WA, Kikusui Denshi) and a digital AC milliohmmeter (1 kHz, Model 3566, Tsuruga Denki)	N/A

MATERIALS AND EQUIPMENT

Instruments (for Structural Characterization)

Technique	Condition
Nuclear magnetic resonance (NMR)	Resonance frequency: 500 MHz for ^1H spectra and 471 MHz for ^{19}F spectra
Gel permeation chromatography (GPC)	Eluent: DMF containing 0.01 M LiBr Temperature: 50°C Molecular weight was calibrated with standard polystyrene samples
Transmission electron microscopy (TEM)	Accelerating voltage: 200 kV
Scanning electron microscope (SEM)	Acceleration voltage: 20 kV

Instruments (for Membrane Properties Measurement)

Property	Conditions
Ion exchange capacity (IEC)	25 ± 5 mg of the dry membrane was immersed in 2 M NaCl aqueous solution for 24 h at r.t., and then released HCl was titrated with standard 0.01 M NaOH aqueous solution.
Water uptake and proton conductivity	As shown in the step-by-step method details.
Dynamic mechanical analysis (DMA)	For temperature dependence: heating rate of $1°C$ min^{-1} from r.t. to $100°C$ at 60% RH or from r.t. to $120°C$ at 20% RH. For humidity dependence: humidification rate of 1% RH min^{-1} from 0 to 90% RH at $80°C$
Tensile properties	As shown in step-by-step method details.

Instruments (for application of fuel cell)

Technique	Condition
Catalyst-coated membranes (CCMs)	As shown in step-by-step method details.
Planetary ball mill	Mill for 30 min at 270 rpm
Pot mill rotary stand	Mill overnight at 125–150 rpm
Heat pressure machine	Hot-press the CCM at $140°C$ and 1.0 MPa for 3 min
Fuel cell stand	As shown in the step-by-step method details.

STEP-BY-STEP METHOD DETAILS
Synthesis of 3,3''-dichloro-2',3',5',6'-tetrafluoro-1,1':4',1''-terphenyl (TP-f)

⏱ Timing: ~20 h

TP-f was synthesized via Pd-catalyzed coupling reaction of 1,2,4,5-tetrafluorobenzene and 1-bromo-3-chlorobenzene under the alkaline conditions, where $Pd(OAc)_2$ and $P^tBu_2Me-HBF_4$ were the catalyst and ligand, respectively, and K_2CO_3 provided alkaline conditions, as shown in Figure 1A.

1. Add a magnetic bar, 1,2,4,5-tetrafluorobenzene (20.0 mmol, 3.00 g), 1-bromo-3-chlorobenzene (42.0 mmol, 8.04 g), $Pd(OAc)_2$ (1.1 mmol, 0.24 g), K_2CO_3 (46.2 mmol, 6.38 g), and DMAc (30 mL) to a 100 mL three-necked flask.
2. After equipping with a reflux condenser and an N_2 inlet/outlet, place the flask into an oil bath and stir at r.t. with purging N_2 to exclude air.
3. After stirring at r.t. for > 10 min, add $P^tBu_2Me-HBF_4$ (2.1 mmol, 0.52 g) to the flask and stir the mixture at $100°C$ for 18 h.

   ⚠ CRITICAL: The reaction time (18 h) may be shortened but it is recommended to ensure complete consumption of 1,2,4,5-tetrafluorobenzene via ^{19}F NMR spectra before quenching the reaction.

4. Cool the mixture to r.t. and dilute with $CHCl_3$.
5. After filtration to collect the filtrate, extract the residue with $CHCl_3$.
6. Wash the combined organic layer with water and then dry over Na_2SO_4.
7. Remove the solvent by evaporation under reduced pressure to obtain a crude product.
8. Wash the crude product with MeOH and $MeOH/CH_2Cl_2$ (3:1) to obtain a pure monomer (TP-f) at 73% yield.

   ⚠ CRITICAL: If the yield is lower than 65%, repeat step No. 5 (i.e. extracting the residue with $CHCl_3$) because the solubility of the TP-f monomer in $CHCl_3$ is not very high.

9. Confirm the chemical structure of the TP-f monomer by ^1H and ^{19}F NMR spectra, as shown in Figures 1B and 1C.
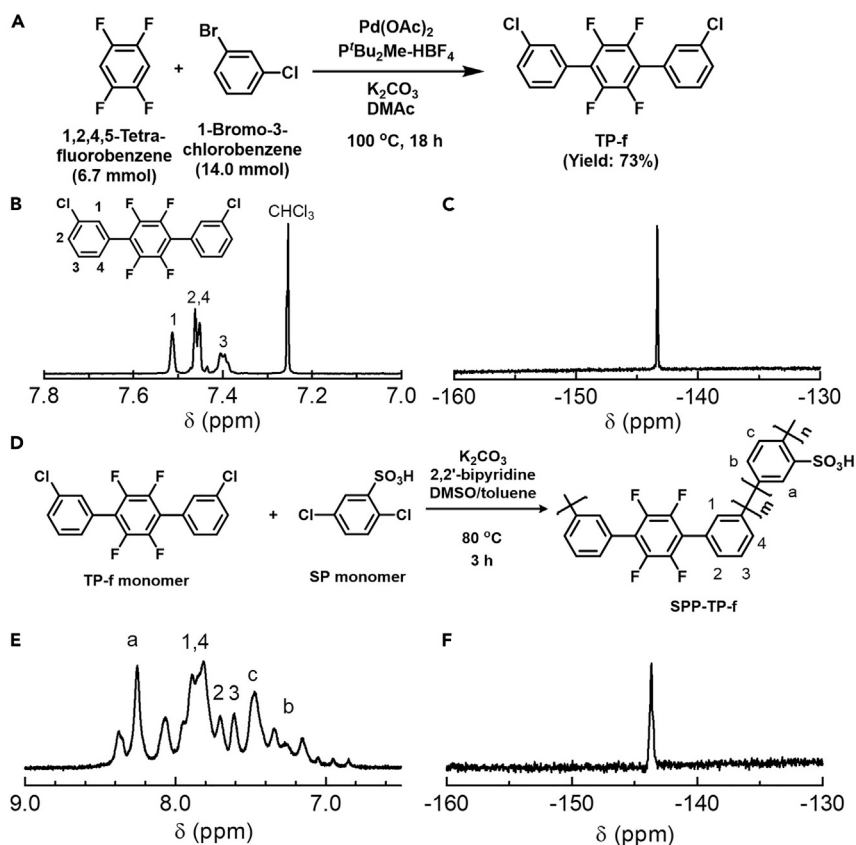
Figure 1. Preparation of TP-f monomer and SPP-TP-f polymers

(A) Preparation of TP-f monomer.

(B) ^{1}H NMR spectrum of TP-f monomer in CDCl$_3$ at r.t.

(C) ^{19}F NMR spectrum of TP-f monomer in CDCl$_3$ at r.t.

(D) Preparation of SPP-TP-f polymers.

(E) ^{1}H NMR spectrum of SPP-TP-f 5.1 polymer in DMSO-d_6 at 80°C.

(F) ^{19}F NMR spectrum of SPP-TP-f 5.1 polymer in DMSO-d_6 at 80°C.

Synthesis of sulfonated polyphenylene-based polymers (SPP-TP-f)

⏱ Timing: ~8 h

SPP-TP-f polymers were synthesized by Ni(0)-mediated polymerization of TP-f and 2,5-dichloroben-zenesulfonic acid (SP) under alkaline conditions, where Ni(cod)$_2$ and 2,2′-bipyridine were polymerization promoter and ligand, respectively. K$_2$CO$_3$ neutralized SP and provided alkaline conditions, as shown in Figure 1D. SPP-TP-f with different ion exchange capacity (i.e., feed IEC = 3.1, 4.1, and 5.1 mequiv g^{-1}) was synthesized by changing the feed composition of TP-f and SP monomers.

10. Add SP monomer (1.342 g, 5.10 mmol), TP-f monomer (0.252 g, 0.68 mmol), K$_2$CO$_3$ (0.846 g, 6.12 mmol), 2,2′-bipyridine (2.275 g, 14.57 mmol), dehydrated DMSO (28.9 mL) and dehydrated toluene (15 mL) to a 100 mL four-necked flask.

⚠ CRITICAL: The commercial SP monomer was 2,5-dichlorobenzenesulfonic acid dehydrate, therefore the mixture should be thoroughly dried by an azeotropic dehydration with toluene prior to the polymerization.

11. After equipping with a mechanical stirrer, a Dean-Stark trap and an N_2 inlet/outlet, place the flask into an oil bath and stir at 170°C for > 2 h with purging N_2 to remove water.

> △ CRITICAL: The mechanical stirrer can be replaced by a magnetic stirrer, however, the molecular weight of the resulting polymers from a mechanical stirrer was usually higher than that from a magnetic stirrer, which affected the membrane-forming capability and the tensile properties of the resulting membranes.

12. After removing water, stir the mixture at 170°C for another > 1 h to remove toluene completely.
13. Cool the mixture to 80°C and then, add Ni(cod)$_2$ (3.566 g, 13.87 mmol) to the flask. Stir the mixture at 80°C for 3 h.
14. After cooling to r.t., pour the mixture into 6 M HCl to precipitate the polymer product. Collect the polymer by filtration.
15. Wash the recovered polymer with 6 M HCl twice and with water thrice, and dry at 80°C in vacuo to obtain SPP-TP-f 5.1 in 96% yield.

> △ CRITICAL: An anion-cation test paper (Tokyo Roshi Kaisha, Ltd.) was used to ensure complete removal of the Ni catalyst.

16. Confirm the chemical structure of SPP-TP-f polymer by NMR spectra, as shown in Figures 1E and 1F.

Preparation of SPP-TP-f 5.1/DPTFE membranes

⏱ Timing: ∼48 h

To reduce excess swelling and improve the mechanical durability of SPP-TP-f 5.1, a reinforcement strategy was adopted. The ePTFE substrate exhibited anisotropic tensile properties (or a large difference in the tensile properties) between longitudinal-direction (LD) and transverse-direction (TD). In particular, the maximum stress was very low (< 0.2 MPa) for the transverse direction. Therefore, a reinforced membrane SPP-TP-f 5.1/DPTFE containing two vertical ePTFE sheets was designed as shown in Figure 2.

17. Preparation of a solution of SPP-TP-f 5.1 in ethanol (10 wt%). Add 0.5 g of SPP-TP-f 5.1 polymer and 4.5 g of ethanol to a 10 mL vial. Stir the mixture on a hot plate (50°C–70°C) to obtain a homogeneous solution.

> △ CRITICAL: The obtained SPP-TP-f 5.1 polymer at No. 15 was dissolved into ethanol to obtain 2-3 wt% solution and pre-filtered with a PTFE syringe filter (with 1.0 μm pore size). The filtrate was spread onto a petri dish at 80°C to obtain a flexible membrane, which was used in No. 17 to prepare a solution of SPP-TP-f 5.1 in ethanol (10 wt%). Ethanol can be replaced with isopropanol if the room temperature is so high that the solvent is easily evaporated. Polar aprotic solvents, such as DMSO and DMAc, were less suitable because of the poor compatibility with the ePTFE substrate.

18. Cut two pieces of ePTFE and hold them in the vertical position with a double-sided tape, as shown in step (1) of Figure 2A.
19. Keep the bar coater close to the double-sided tape and pour the solution of SPP-TP-f 5.1 in close proximity to the bar coater, as shown in step (2) of Figure 2A.
20. Spread the solution of SPP-TP-f 5.1 over a glass plate using a bar coater (gap size = 50 μm) and then, place the ePTFE substrate carefully over the solution layer, as shown in steps (3 and 4) of Figure 2A.
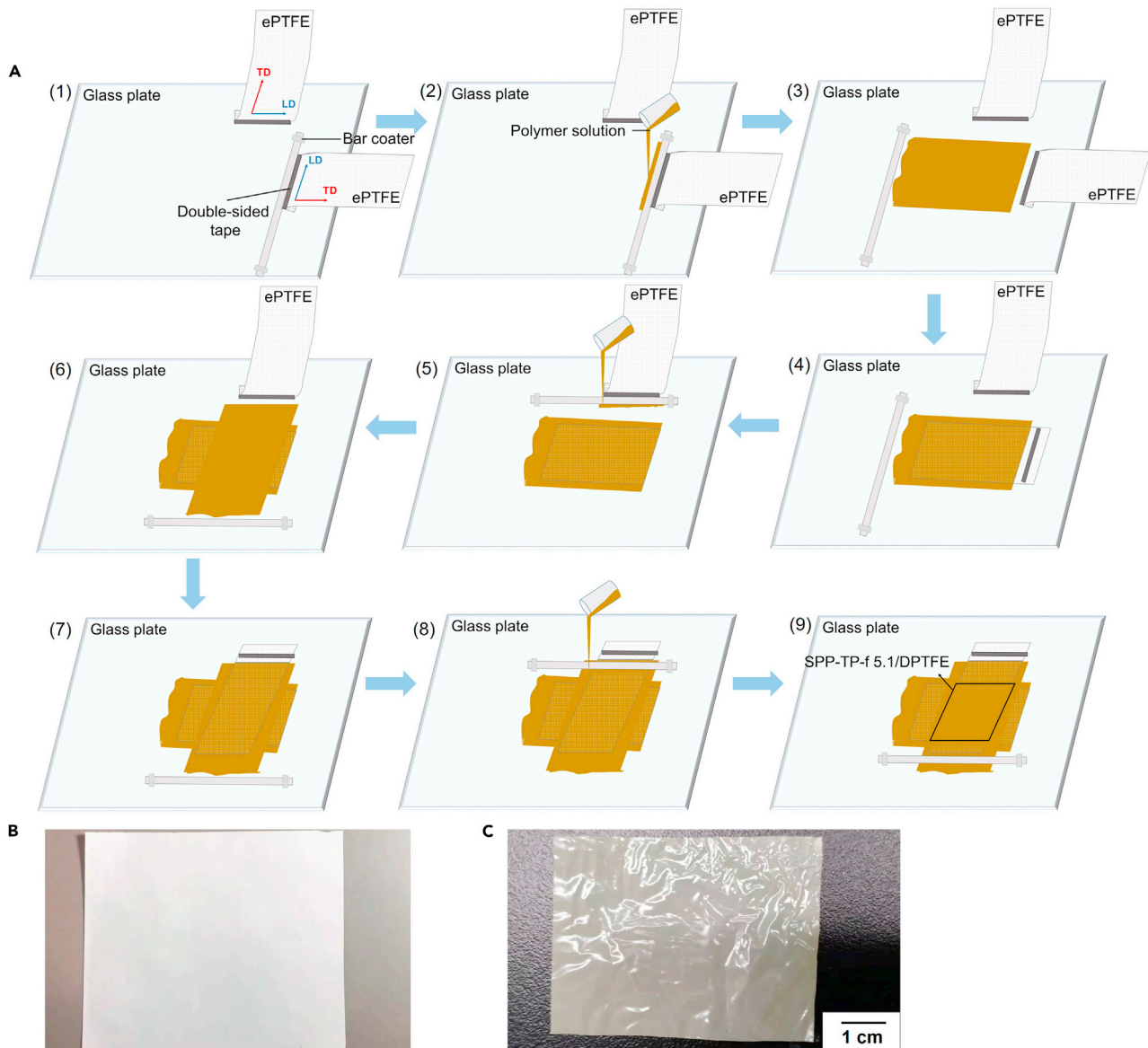
Figure 2. Preparation and photograph of SPP-TP-f 5.1/DPTFE
(A) Preparation of SPP-TP-f 5.1.
(B) Photograph of ePTFE substrate.
(C) Photograph of SPP-TP-f 5.1/DPTFE.

21. Cut the above-mentioned ePTFE along the double-sided tape and remove the top stuck with the double-sided tape. Keep the bar coater close to another double-sided tape and pour the solution of SPP-TP-f 5.1 in close proximity to the bar coater (gap size = 125 μm), as shown in step (5) of Figure 2A.
22. Spread another portion of SPP-TP-f 5.1 and then, place another ePTFE substrate carefully over the solution, as shown in steps (6–7) of Figure 2A.
23. Put the bar coater back to the initial position and pour the solution of SPP-TP-f 5.1 in close proximity to the bar coater (gap size = 175 μm). Spread another portion of SPP-TP-f 5.1 solution over the ePTFE substrate, as shown in step (8–9) of Figure 2A.
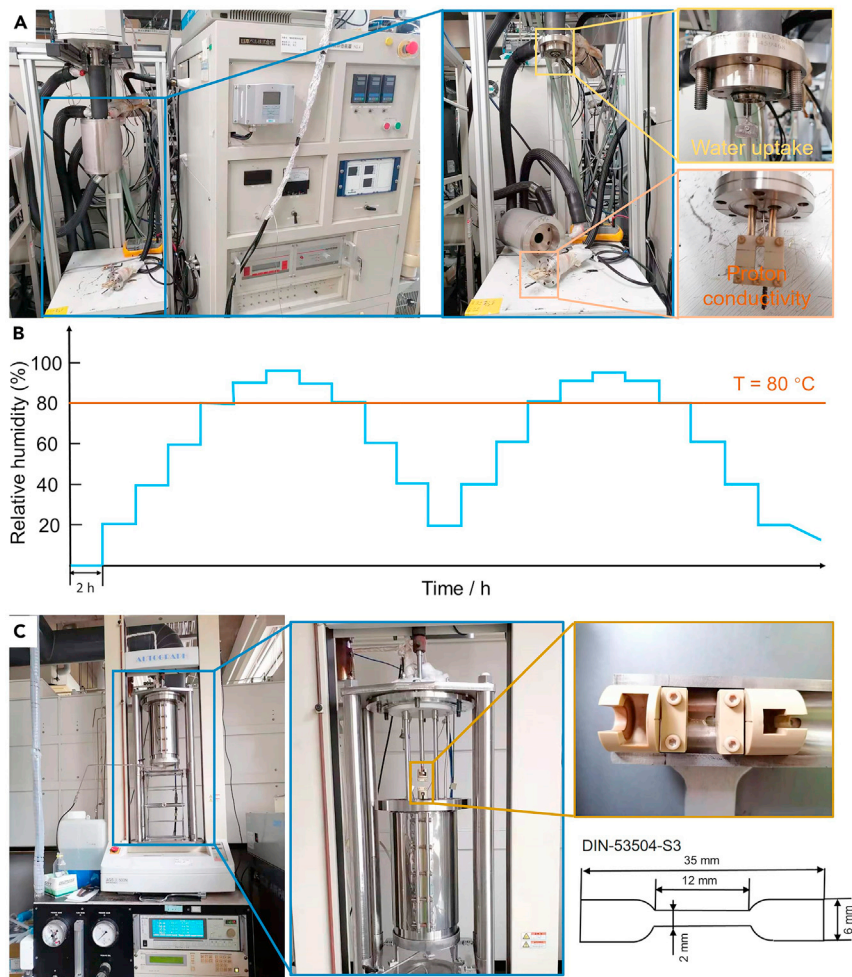
Figure 3. Evaluation of bulk membrane properties

(A) Solid electrolyte analyzer system to measure the temperature/humidity dependence of the proton conductivity and water uptake.

(B) Humidity program at 80°C for solid electrolyte analyzer system.

(C) Tensile testing machine attached with a temperature/humidity-controllable chamber.

24. After drying at r.t. for > 12 h, cut the resulting membrane containing two ePTFE substrates and immerse in 2 M HCl over 24 h and then, wash with water thoroughly to obtain the target SPP-TP-f 5.1/DPTFE membrane with a typical thickness of 22 μm after drying.

Evaluation of water uptake and proton conductivity

⏱ Timing: ~48 h

Water uptake and in-plane proton conductivity of the membranes were measured simultaneously at 80°C, 100°C and 120°C with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature/humidity-controllable chamber, as shown in Figure 3A. The weight was measured by a magnetic suspension balance. The in-plane proton conductivity was tested with a four-probe conductivity cell connected with an AC impedance analyzer (Solartron 1255B and 1287, Solartron Inc.). The ohmic resistance of the membrane was obtained from the Niquist plot in the frequency range from 1 to 10 kHz.

25. Cut a membrane piece with 1 × 3 cm^2 for in-plane proton conductivity and another piece with > 25 mg for the water uptake.

   ⚠ CRITICAL: The reinforced membrane SPP-TP-f 5.1/DPTFE possessed anisotropy in water swelling, i.e. 21% for the in-plane and 163% for the through-plane. Therefore, the ohmic resistance of the fuel cell could not accurately be estimated from the in-plane proton conductivity of the membrane.

26. Set the membranes to the testing holders of water uptake and proton conductivity, respectively.

   ⚠ CRITICAL: After placing the membrane into the test holder for the proton conductivity measurement, open circuit potential (< 0.1 V) should be measured to confirm the sufficient contact between the gold wire electrodes and the membrane. If the open circuit potential is higher than 0.1 V, the holder should be re-assembled.

27. Set the holders in the temperature/humidity-controllable chamber and lag the chamber.
28. Start the measurement at 80°C under the humidity of 20%, 40%, 60%, 80%, 90%, 95% RH, at 100°C under the humidity of 20%, 30%, 40%, 60%, 80% RH and at 120°C under the humidity of 20%, 30%, 40% RH, respectively.

   ⚠ CRITICAL: Prior to the measurement, the dry weight of the membrane should be measured via drying at 80°C in vacuo for > 2 h. Furthermore, the water uptake and proton conductivity should be measured after exposing the membranes to the testing humidity for > 2 h. The humidity program at 80°C is shown in Figure 3B.

29. Calculate the water uptake (wt%) from the equation: (wet weight - dry weight)/dry weight × 100. Calculate the proton conductivity (δ (S cm^{-1})) from the following equation: $\delta = l/(A \times R)$, where l (cm) is the distance between the two reference electrodes, A (cm^2) is the cross-sectional area, and R (Ω) is the ohmic resistance. For the detailed results, refer to our previous report (Long and Miyatake, 2021a).

Evaluation of tensile properties

   ⏱ Timing: ∼5 h

The tensile property was measured with a Shimadzu AGS-J 500N universal testing instrument attached with a Toshin Kogyo Bethel-3A temperature/humidity-controllable chamber, as shown in Figure 3C.

30. Cut a membrane piece into a dumbbell shape [DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)], as shown in Figure 3C.
31. Set the dumbbell-shaped membrane to the holder and then, set the holder to the testing instrument.
32. Assemble the temperature/humidity-controllable chamber and then, set the testing conditions (i.e., temperature and humidity). In this paper, tensile properties were tested under three conditions, i.e., 80°C and 60% RH, 80°C and 20% RH, and 120°C and 20% RH, respectively.
33. After equilibrating under the test conditions for > 2 h, measure the stress-strain curves at a stretching rate of 10 mm min^{-1}. The detailed results are shown in our previous report (Long and Miyatake, 2021a).

Preparation of the catalyst-coated membrane
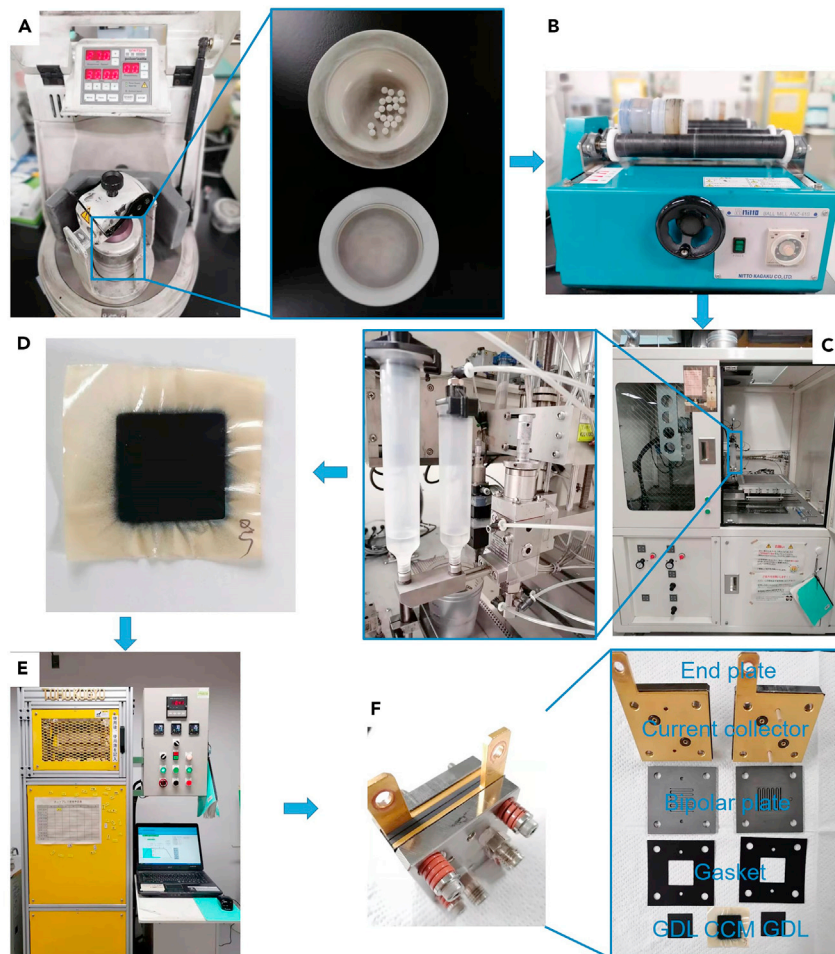
   ⏱ Timing: ∼24 h

Figure 4. Preparation of the catalyst-coated membrane
(A) Photograph of the planetary ball mill.
(B) Photograph of the mill.
(C) Photograph of the pulse-swirl spraying machine.
(D) Photograph of the catalyst-coated membrane.
(E) Photograph of the hot-press machine.
(F) Photograph and components of the single fuel cell hardware.

The catalyst paste was prepared by mixing Pt/C catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo K. K.), Nafion dispersion (IEC = 0.95–1.03 meq g^{-1}, D-521, Du Pont), deionized water and ethanol. Catalyst-coated membranes (CCMs) were prepared by spraying the catalyst paste on both sides of the membrane by the pulse-swirl-spray (PSS) technique. The geometric area of the electrodes was 4.41 cm^2.

34. Place 0.6 g of Pt/C into a ZrO$_2$ jar.
35. Place 2.5 g of water into the jar.

> ⚠ CRITICAL: The water should wet the Pt/C thoroughly before adding ethanol to prevent burning.

36. Place 4.9 g of ethanol into the jar.
37. Set the jar in the planetary ball mill (P-6, Fritsch Co., Ltd.) and mill for 30 min at 270 rpm, as shown in Figure 4A.

38. Add 4.5 g of Nafion solution (5 wt.%) to the jar.

> △ CRITICAL: The mass ratio of Nafion ionomer to the carbon support (I/C) was adjusted to 0.7.

39. Set the jar in the planetary ball mill and mill for 30 min at 270 rpm.
40. Move the mixture into a plastic jar and place it onto a pot mill rotary stand (ANZ-61S, Nitto Kagaku Co., Ltd.) to mill for 10–18 h at 125–150 rpm, as shown in Figure 4B, to obtain the catalyst paste.
41. Fill the catalyst paste into the pulse-swirl spraying machine (Nordson, Figure 4C).
42. A thin film was placed onto a hot plate of the pulse-swirl spraying machine at 80°C to measure the Pt loading for a single shot of the spray.

> △ CRITICAL: There were no special requirements for the above-mentioned thin film, such as materials and thickness. A catalyst layer should be prepared by spraying within 10 times. The Pt loading amount was 0.50 ± 0.05 mg cm^{-2} for both electrodes, therefore the Pt loading of a single shot should be regulated to ca. 0.05 mg cm^{-2}.

43. Place the ionomer membrane onto a hot plate of the pulse-swirl spraying machine at 80°C via a vacuum pump. Cover the membrane with a film having a square hole with 2.1×2.1 cm^2 in the center to regulate the electrode area. Prepare CCMs by spraying the catalyst paste on both sides of the membrane by the pulse-swirl-spray (PSS) technique.
44. Place the CCM (Figure 4D) into an oven at 60°C for 24 h to completely remove the remaining solvent in the catalyst layer.
45. Hot-press the CCM at 140°C and 1.0 MPa for 3 min, as shown in Figure 4E.
46. Assemble membrane electrode assembly (MEA) and mount it into a single fuel cell hardware (Figure 4F) in the order, end plate, current collector, bipolar plate, gasket (200 μm of silicone/poly(ethyl benzene-1, 4-dicarboxylate/silicone gaskets, SB50A1P, Maxell Kureha Co., Ltd.), gas diffusion layer (29BC, SGL Carbon Group Co., Ltd.), CCM, gasket, gas diffusion layer, bipolar plate, current collector, end plate. Fasten the hardware at 10 kgf cm^{-2} with four springs.

> △ CRITICAL: If the Pt loading was changed, the thickness of the gasket should also be changed. Typically, the thickness of the gasket was slightly smaller (10–20%) than the total thickness of the catalyst layer and the gas diffusion layer.

47. Check the airtightness of the electrodes. Connect the input and output of one-sided electrode with N$_2$ supply and manometer, respectively. Pump N$_2$ to the hardware and keep the pressure at 0.2 MPa. Make sure that the manometer keeps at a constant pressure (i.e., no obvious decrease) after turning off the N$_2$ supply, indicating that the electrode is pressure-tight. Check the airtightness of another electrode in the same manner.

Evaluation of fuel cell performance

> ⏱ Timing: ∼ 1 day under one testing condition

The fuel cell performance included hydrogen permeability, current/cell voltage (IV) curves and durability, and was evaluated by the fuel cell stand (FCE-1, Panasonic Production Technology) equipped with an electronic load (PLZ-664WA, Kikusui Denshi) and a digital AC milliohmmeter (1 kHz, Model 3566, Tsuruga Denki), as shown in Figure 5A. The detailed evaluation flow is shown in Figure 5B, namely activating and cleaning the electrode, IV curve test and durability test. In the present case, the IV curves were evaluated at 80°C and 100% RH, 80°C and 30% RH, 100°C and 30% RH, 100°C and 53% RH, and 120°C and 30% RH. The detailed results and discussions are shown in our previous report (Long and Miyatake, 2021a).
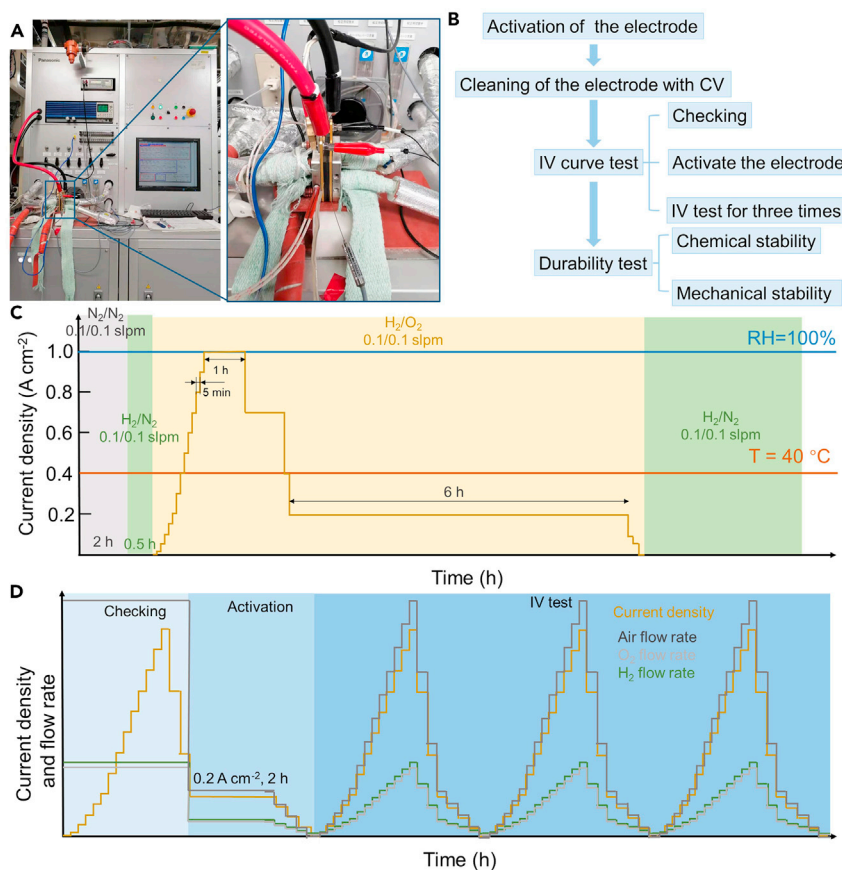
Figure 5. Evaluation of fuel cell performance
(A) Photograph of the fuel cell evaluation stand.
(B) Evaluation flow diagram.
(C) Current density program in the activation of the electrode.
(D) Performance test program; current density, air/O_2 and H_2 flow rates.

48. Assemble the fuel cell hardware to the fuel cell stand (i.e., connection of gas input/output, heater, thermocouple, voltage and current connecting lines), as shown in Figure 5A.

49. Activation of the electrodes. Supply N_2 (0.1 slpm) to both electrodes, set the cell temperature and humidity at 40°C and 100% RH and equilibrate the membrane electrode assembly for > 2 h. After supplying H_2 (0.1 slpm) to the anode for 0.5 h, supply O_2 (0.1 slpm) to the cathode and then, discharge from < 0.01 A cm^{-2} to 1 A cm^{-2}. After discharging at 1 A cm^{-2} for 1 h, 0.75 A cm^{-2} for 1 h, and 0.2 A cm^{-2} for 6 h, decrease the current density slowly to 0 A cm^{-2} and then, supply N_2 (0.1 slpm) to the cathode. The activation program is shown in Figure 5C in detail.

50. Set the cell temperature and humidity at 80°C and 100% RH and equilibrate the membrane electrode assembly for > 2 h.

51. Cleaning the electrode via cyclic voltammetry (CV). Connect the cell and potentiostat (PGST30 Autolab System, Eco-Chemie), i.e., connect the reference electrode with the anode, the working and counter electrodes with the cathode, respectively. Measure CV from 0.07 to 1.0 V at a sweep rate of 20 mV s^{-1} for 40 cycles.

⚠ CRITICAL: CV was measured after the cell potential became lower than 0.2 V.

52. Linear sweep voltammetry (LSV) test to evaluate hydrogen permeability. Connect the cell and potentiostat, while the gas supply and test conditions were the same as those in the electrode cleaning. Sweep the cathode potential from 0.15 to 0.6 V at a rate of 0.5 mV s^{-1}.

⚠ CRITICAL: The negative current can be often observed at 100% RH for such a small cell (4.41 cm² of the electrode area) probably because oxygen in the cathode was hard to be completely removed. However, the LSV curve with the positive current can be easily obtained at low humidity, such as 30% RH.

53. TheIV curve test contains three steps, as shown in Figure 5D.
    a. Find the highest current density (< 1.5 A cm^{-2}) with the potential higher than 0.4 V. Supply H$_2$ (0.1 slpm) to the anode and O$_2$ (0.1 slpm) or air (0.3 slpm) to the cathode, respectively. Increase the current density from 0 to 1.5 A cm^{-2} as long as the potential is higher than 0.4 V.
    b. Activation. Decrease the current density to 0.2 A cm^{-2}. After keeping at 0.2 A cm^{-2} for 2 h, decrease the current density to 0 A cm^{-2}.
    c. IV test. Set the current density, flow rate based on the current density and gas utilization (70% for H$_2$ and 40% for O$_2$ or air) in the continuous and automatic program. In general, repeat the IV test three times.
54. Set conditions at 80°C and 30% RH, 100°C and 30% RH, 100°C and 53% RH, and 120°C and 30% RH in the order and equilibrate the membrane electrode assembly for > 2 h. Repeat steps 52 and 53 to collect LSV and IV data.

55. The membrane durability test contains chemical durability and mechanical durability, and combined durability of both.
    a. Measure the chemical stability by open-circuit voltage (OCV) hold test, namely, the monitoring time dependence of the OCV at 80°C and 30% RH.

⚠ CRITICAL: The above-mentioned conditions (80°C and 30% RH) were general and used in our previous reports (Long et al., 2019, 2020a, 2020b, 2020c). To further examine the chemical stability of the membranes, severer conditions (100°C and 30% RH) were tried in our recent report (Long and Miyatake, 2021a, 2021b).

    b. Measure the mechanical durability by a humidity cycling test based on the protocols of US-DOE (U.S. Department of Energy; https://www.energy.gov/). Supply H$_2$ (2 L min^{-1}) and N$_2$ (2 L min^{-1}) to the anode and cathode at 80°C, respectively. Switch the dry and wet gases every 2 min.
    c. Measure the combined durability by humidity cycling test under OCV conditions based on the protocols of US-DOE (U.S. Department of Energy; https://www.energy.gov/; Mukundan et al., 2018). In this paper, the cell was operated at 90°C supplying H$_2$ and air at a flow rate of 60 mL min^{-1} to the anode and cathode, respectively. The wet-dry cycling test was conducted by switching dry gas (0% RH) for 2 s and wet gas (100% RH) for 15 s.

⚠ CRITICAL: The detailed conditions (i.e., flow rate, the interval of dry gas and wet gas) for the combined durability should be regulated based on the electrode size to ensure > 2.5 times difference in the ohmic resistance between the wet and dry conditions.

EXPECTED OUTCOMES

This protocol allows for the preparation of the sulfonated aromatic polymers and their reinforced membranes (composites with porous, expanded polytetrafluoroethylene: ePTFE), and their application in proton exchange membrane fuel cells. As aromatic polymers, sulfonated polyphenylenes solely composed of phenylene and sulfonic acid groups are preferable in terms of high proton conductivity and chemical stability (Miyake et al., 2017; Shiino et al., 2019, 2020). Furthermore, tetrafluorophenylene groups are incorporated to provide polymers (SPP-TP-f) with high concentration of the sulfonic acid groups, solubility in lower alcohols (ethanol and isopropanol), and enhanced compatibility with ePTFE substrate (Long and Miyatake, 2021a). The partially fluorinated sulfonated polyphenylenes and porous ePTFE give thin composite membranes (SPP-TP-f 5.1/DPTFE), that achieve high proton conductivity (ca. 70 mS cm^{-1} at 120°C and 40% RH, Figure 6) and mechanical properties (elongation > 80%).
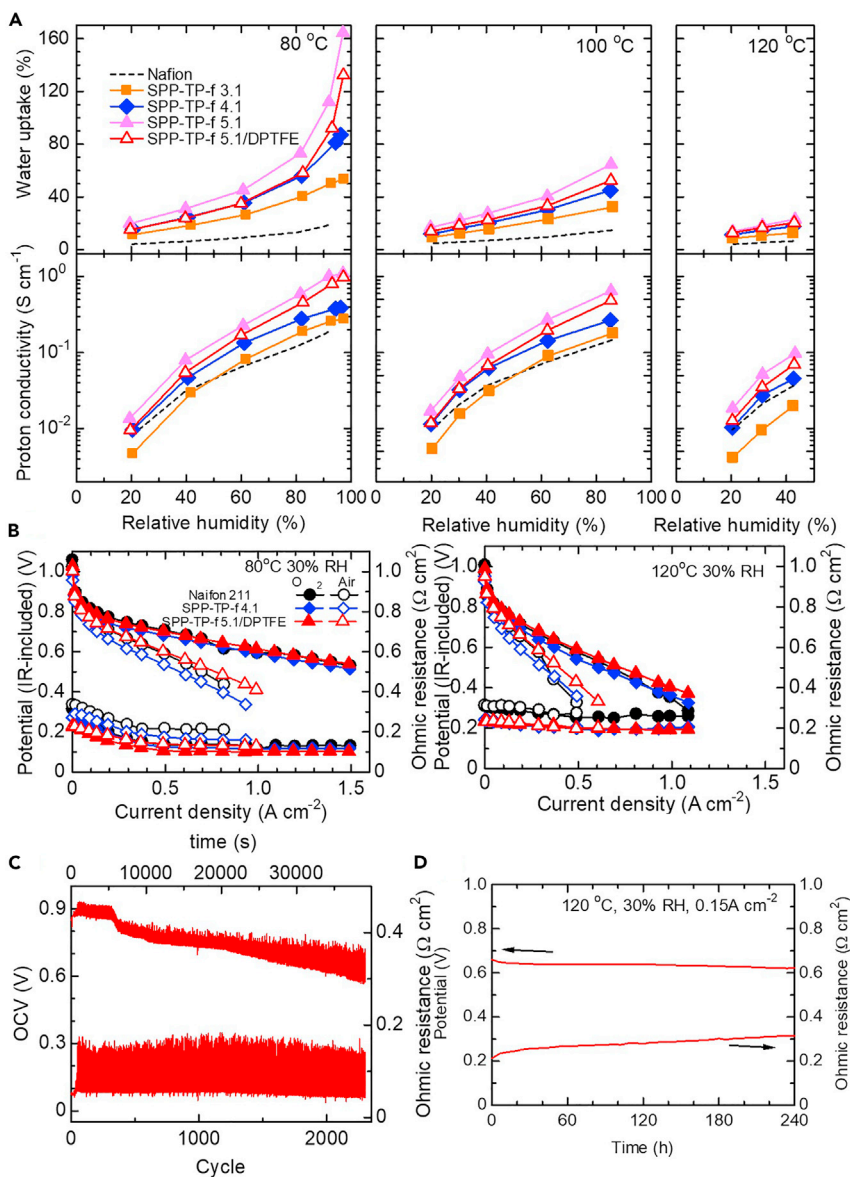
Figure 6. Performance of SPP-TP-f membranes and SPP-TP-f 5.1/DPTFE reinforced membrane

(A) Relative humidity dependence of water uptake and proton conductivity at 80°C, 100°C and 120°C.

(B) Polarization curves and ohmic resistance of Nafion 211, SPP-TP-f 4.1 and SPP-TP-f 5.1/DPTFE membranes at 80°C and 30% RH and 120°C and 30% RH.

(C) The combined chemical and mechanical durability test of SPP-TP-f 5.1/DPTFE.

(D) The durability test at 120°C and 30% RH at a constant current density (0.15 A cm^{-2}) with supplying hydrogen (0.1 L min^{-1}) and air (0.1 L min^{-1}).

Figure reprinted with permission from Long and Miyatake (2021a).

For fuel cell application, the reinforced membranes are mounted in a single cell together with catalyst layers. The reinforced membranes have an affinity with fluorinated ionomer-based catalyst layers and achieve fuel cell performance (ca. 400 mW cm^{-1}) at 120°C and 30% RH, outperforming state-of-the-art fuel cell membranes (Long and Miyatake, 2021a, 2021b). The membranes endure a combined accelerated stability test (humidity cycling test under open circuit voltage conditions) for 2,300 cycles without obvious chemical degradation (Long and Miyatake, 2021a, 2021b). Furthermore, the durability at high temperature is confirmed at a constant current density (0.15 A cm^{-2})

test at 120°C and 30% RH. Such membrane properties and fuel cell performance/durability have not been achieved for sulfonated aromatic polymer membranes (Long and Miyatake, 2021a, 2021b).

LIMITATIONS

This study deals with proton conductive membranes that enable the operation of proton exchange membrane fuel cells at higher temperatures (80°C–120°C) than that of the current fuel cells (60°C–80°C). The catalyst layers (both for the anode and cathode) utilize conventional perfluorosulfonic acid (PFSA) ionomers (D521, Du Pont) as binders and proton conductors needed for the electrochemical reactions. The PFSA ionomers are not thermally stable with glass transition temperatures typically lower than 100°C (depending on the water content). For practical fuel cells, alternative proton conductive binders that overcome the shortcomings of PFSA ionomers will be needed. In addition, since fuel cells are operated under a wide variety of conditions (temperature, humidity, gas pressure, cell voltage, and current density, etc.) in particular for automobile applications, the membrane materials should be evaluated further in other durability protocols.

TROUBLESHOOTING

Problem 1
Lower yield of the TP-f monomer than 65% (step 8).

Potential solution
Repeat step 5 (i.e., extracting the residue with $CHCl_3$) because of the low solubility of TP-f monomer in $CHCl_3$.

Problem 2
Amount of $Ni(cod)_2$ in the polymerization reaction (step 13).

Potential solution
In our previous cases (Long et al., 2019, 2020a, 2020b, 2020c; Miyake et al., 2017), the amount of $Ni(cod)_2$ was set to be 1.2–1.8 equimolar of terminal -Cl groups in the monomer; however, 1.0 and 1.2 equimolar was used to prepare SPP-TP-f 4.1 and SPP-TP-f 5.1 because of the higher polymerization reactivity of TP-f monomer. An excess amount of $Ni(cod)_2$ was tried expecting a further improvement of the molecular weight; however, it ended up with insoluble products of the resulting polymers. In addition, the amount of $Ni(cod)_2$ may need to be optimized if the source is different from ours since the minor difference in the purity often affects the polymerization reaction.

Problem 3
The obtained reinforced membrane is not homogeneous in thickness (step 24).

Potential solution
The push coating method using silicone sheets (Ikawa et al., 2012; Miyake et al., 2021) may be useful to obtain homogeneous reinforced membranes.

Problem 4
The negative current is obtained for the LSV test (step 52).

Potential solution
The negative current in the LSV test indicates that the cathode is not fully purged with N_2 and some O_2 remains. In that case, N_2 purge should be prolonged until a positive current is obtained. N_2 flow may be ceased during the LSV measurement.

Problem 5
In the combined durability test, the difference of ohmic resistance between low RH and high RH is smaller than 2.5 times (step 55).

Potential solution

Regulate the gas flow rate and duration time of wet/dry gas depending on the different electrode sizes and hardware. In general, the duration time of wet conditions should be slightly longer than that of dry conditions to make the membrane fully wet (so that the ohmic resistance should be comparable to that in the polarization test at 100% RH).

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Kenji Miyatake (miyatake@yamanashi.ac.jp).

Materials availability

All unique/stable reagents generated in this study are available from the lead contact without restriction.

Data and code availability

The published article includes all datasets/code generated or analyzed during this study.

AUTHOR CONTRIBUTIONS

Z.L. and K.M. developed the concept and designed the experiments. Z.L carried out the synthesis, measurement of membrane properties, and fuel cell evaluation. K.M. and Z.L. discussed the results and wrote the manuscript. K.M. supervised the whole project administration.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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