

SUPPORTING INFORMATION

New Proton Conducting Membrane with High Retention of Protic Ionic Liquids

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Experimental Section

4,4'-(Propane-2,2-diyl)bis[(prop-2-ynyloxy)benzene](PBPB)

In a three-neck, round-bottomed flask equipped with a condenser, sodium hydroxide solution (200 mL), bisphenol A (10 g, 43.8 mmol), and tetra-n-butylammonium bromide (1.37 g, 4.20 mmol) were mixed for 1 h at room temperature. Propargyl bromide (10.15 g, 85.2 mmol) was added dropwise over 3 h and then the mixture was maintained at 70 °C for 10 h. The reaction product was washed several times with deionized water to remove tetrabutylammonium bromide and the salts formed in the reaction. The product was recrystallized from EtOH (yield 87%).

M.p. 78 °C; ¹H NMR (d₆-DMSO): δ 1.68 (e), 2.53 (a), 4.68 (b), 6.89 (c), 7.17 (d) ppm. (Figure 1a); ¹³C NMR (d₆-DMSO): δ 31.54 (C-CH₃), 42.26 (Ar-C-CH₃), 55.99 (C-C-O), 75.68 (C≡), 79.25 (C≡C-C), 114.47 (C-CH-CH), 128.20 (CH-CH-C), 144.37 (CH-C-C), and 155.61 ppm (O-C-CH).

Potassium 2,5-bis(prop-2-ynyloxy)benzenesulfonate(PBPBS)

Potassium 2,5-dihydroxybenzenesulfonate (10 g, 43.8 mmol), potassium carbonate (7.1 g, 50 mmol) and dimethylformamide (DMF) 200 mL were added into a three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, and a N₂ gas inlet tube and then the system was heated to 70 °C. Propargyl bromide (11.9 g, 100 mmol) was added drop-wise over 1 h and then the mixture was maintained at 70 °C for 24 h. After cooling to ambient temperature and filtering to remove most of the salt, the solution was poured into 500 mL of ethanol. The precipitate was filtered, washed with ethanol, and then recrystallized from ethanol/water (yield 65%).

¹H NMR (d₆-DMSO): δ 3.51 (a), 4.72, 4.77 (b), 6.96 (d), 7.04 (e), 7.34 ppm (c). (Figure 1a); ¹³C NMR (d₆-DMSO): δ 56.08 (C-C-O), 57.37 (C-C-O), 78.09 (C≡), 79.70 (C≡C-C), 115.65 (CH-CH-C), 116.03 (C-CH-CH), 116.72 (C-CH-CH), 137.57 (CH-C-SO₃K), 148.57 (C-C-O), and 150.83 ppm (O-C-CH).

Ionic Liquid (BMIm-BF₄)

The imidazolium tetrafluoroborates with unsaturated aliphatic side chains were prepared according to a modified procedure described elsewhere. In brief, to a stirred solution of 1-methylimidazole (8.91 g, 100 mmol) in acetonitrile (70 mL) was added 1-bromobutane (17.1 g, 110 mmol) in acetonitrile (100 mL) dropwise at 0 °C. The reaction mixture was stirred for 48 h at 30 °C. Removal of the solvent under reduced pressure gave crude

1-butyl-3-methylimidazolium bromide (BMIm-Br), which was recrystallized from petroleum ether. To a solution of the BMIm-Br in acetone (100 mL) was added sodium tetrafluoroborate (10.9 g, 100.0 mmol). The reaction mixture was filtered through a pad of aluminum oxide to remove the sodium salt and color. Evaporation of the solvent under reduced pressure gave the corresponding 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF₄) (yield 89%). The Na content of all imidazolium tetrafluoroborates prepared in the present study was < 0.08 wt% by ICP and their water contents < 0.03 wt% by Karl-Fischer titration.

¹H NMR (d₆-DMSO): δ 0.87-0.90 (t, -CH₂-CH₃), 1.23-1.28 (m, 2H, -CH₂-CH₂-CH₃), 1.74-1.80 (m, 2H, -CH₂-CH₂-CH₂-), 3.85 (s, 3H, N-CH₃), 4.17 (t, 2H, -N-CH₂-CH₂-), 7.63 (s, 1H, -N-CHCH-N-), 7.70 (s, 1H, -N-CHCH-N-), 9.00 ppm (s, 1H, -N-CH-N-); ¹³C NMR: δ 13.2 (-CH₂-CH₃), 18.8 (-CH₂-CH₂-CH₃), 31.4 (-CH₂-CH₂-CH₂-), 35.7 (N-CH₃), 48.7 (-N-CH₂-CH₂-), 122.3 (-N-CHCH-N-), 123.6 (-N-CHCH-N-), and 136.5 ppm (-N-CH-N-).

Proton Conductivity

The proton conductivity of the membrane was determined with an ac electrochemical impedance analyzer (PGSTAT 30), and the experiments involved scanning the ac frequency from 100 kHz to 10 Hz at a voltage amplitude of 10 mV. The membrane (1 cm in diameter) was sandwiched between two smooth stainless tungsten-copper alloy disk electrodes in a cylindrical PTFE holder. The cell was placed in a thermally controlled chamber for measurement. At a given temperature, the samples were equilibrated for at least 20 min before repeated measurements were taken at 10 min intervals until no more changes in conductivity were observed. The proton conductivity of the membrane was calculated from the observed sample resistance from the relationship:

$$\sigma = \frac{L}{RA} \quad (1)$$

where: σ is the proton conductivity (in S cm⁻¹), L is the distance between the electrodes used to

measure the potential, R is the impedance of the membrane (in ohms) measured at the frequency that produced the minimum imaginary response, and A is the membrane section area (in cm^2)

Table S1 Quantity of ionic liquid uptake, IL loss after centrifugal test and thermal decomposition temperature of membranes.

Curing Time	Cross-linking degree (%) ^a	Measured IL uptake (wt%) ^b	Loss after centrifugal test (wt%)
30 min	49.5	53.9	20.3
60 min	69.5	48.6	16.8
120 min	84.3	44.3	13.7
240 min	100	40.4	11.5

^a Determined from DSC.

^b Calculated from TGA, using pristine polymer compared with composite membrane.

The cross-linking degree of the membrane was calculated from the integral area of exothermic peak from the DSC instrument:

$$\text{Cross-linking degree} = (A_I - A_T) \times 100 / A_I (\%) \quad (\text{S1})$$

where: A_I is the integral area of the membrane before curing process (J g^{-1}), A_T is the integral area of the membrane after designed time cross-linking process (J g^{-1}).

Fabrication of membrane electrode assembly (MEA) and a single-cell test

A membrane electrode assembly (MEA) was fabricated by sandwiching a composite membrane between two gas diffusion electrodes (E-TEK GDL, LT140EW; 30% Pt on Vulcan XC-72, 0.5 mg cm^{-2} , and ionomer free) and hot-pressed by applying a pressure of 20 kgf cm^{-2} at 120 °C for 3 min. The MEA was tested in a single-cell with a serpentine-shaped gas flow field and an active area of 3 cm^2 at ambient pressure. The H_2/O_2 fuel cell polarization curves were determined at 100 °C by using an Eiwa Corp. FC test station. Anhydrous H_2 (99.99%) and O_2 (99.6%) gases were supplied to the test station at gas utilization ratios of 30 % and 15 % without any humidification.

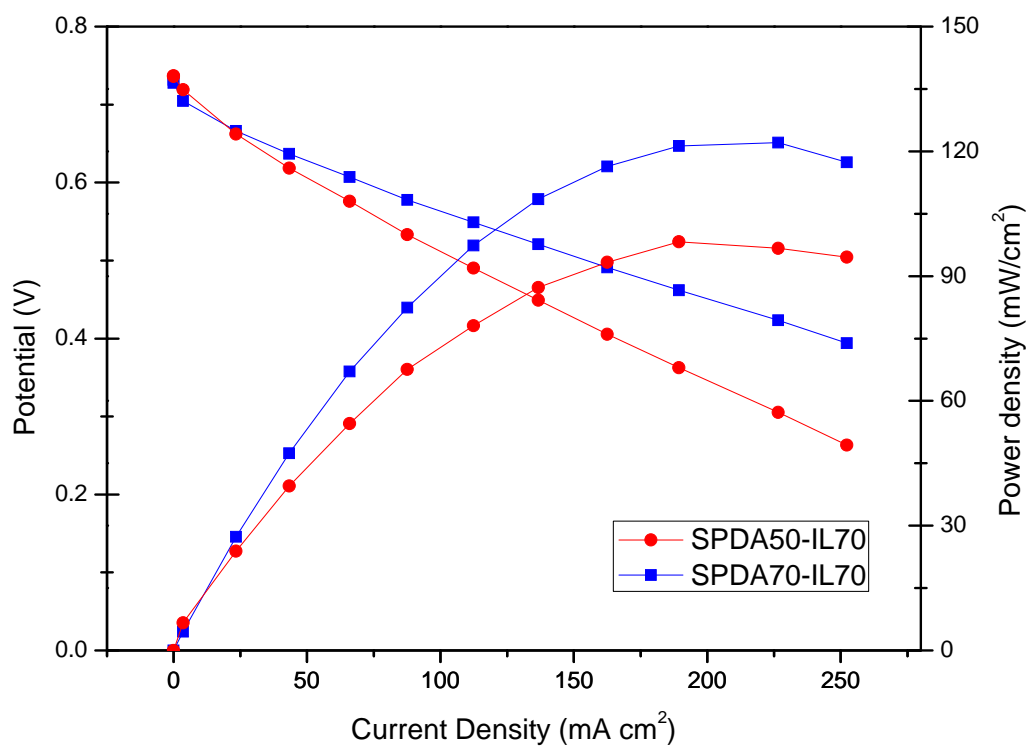


Figure S1. Polarization curves of a H₂/O₂ fuel cell using a SPDA50-IL70 and SPDA70-IL70 composite membranes without humidification at gas utilization ratios of 30 % for H₂ and 15 % for O₂ operation at 100 °C.