



Organic solvent-free preparation of electrolyte membranes with high proton conductivity using aromatic hydrocarbon polymers and small cross-linker molecules



Satoshi Matsushita^a, Je-Deok Kim^{a,b,*}

^a Polymer Electrolyte Fuel Cell Group, Global Research Center for Environmental and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^b Hydrogen Production Materials Group, Center for Green Research on Energy and Environmental Materials, NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Keywords:

Organic solvent-free electrolytes
Sulfonated poly(phenylsulfone)
Cross-linker
Cross-linked sulfonated poly(phenylsulfone) membrane
Proton conductivity
Polymer electrolyte fuel cell

ABSTRACT

We prepared proton exchange membranes of sulfonated poly(phenylsulfone) [SPPSU] cross-linked with ethylene glycol (EG) or glycerol (GL). The cross-linking reaction was performed in an SPPSU aqueous solution including 0–12 molecules/repeating unit; R.U. of the cross-linker at 180–200 °C to afford water-insoluble SPPSU membranes even in boiling H₂O. The characteristic properties of the SPPSU membranes, such as the number of cation exchange sites, water retention abilities, mechanical properties, and proton conductivities, can be easily optimized by selecting the amount and type of cross-linkers and the reaction temperature. The SPPSU membranes had tensile strengths of up to 43.5 MPa, moduli of up to 1.9 GPa, and elongations at break of up to 30.2%. An SPPSU membrane prepared at 180 °C using EG as a cross-linker exhibited a maximum proton conductivity of 0.23 S/cm at 120 °C and 90% relative humidity (RH), and the value remained at 0.11 S/cm even at 40 °C. A maximum residual weight of 98% was achieved for SPPSU membranes prepared at 200 °C using GL as the cross-linker under oxidation conditions at 80 °C for 1 h, and they exhibited good chemical stability.

1. Introduction

In materials science, because of their applicability in the field of polymer electrolyte fuel cells (PEFCs) and electrolyzers, many types of polymer electrolyte membranes (PEMs) have been produced using various synthetic techniques for use in practical applications to satisfy future societal demands. Currently, poly(perfluorosulfonic acid) [PFSA] membranes, like Nafion membranes, are widely used as PEMs for practical applications in PEFCs because they have high proton conductivities and excellent mechanical properties, as well as excellent chemical stabilities derived from their poly(tetrafluoroethylene) [PTFE]-based molecular structure. However, there are still some issues with the fluorinated polymers that need to be improved, such as a decrease in mechanical and proton conductive properties above their glass-transition temperatures (T_g), complex synthetic procedures resulting in high production cost, environmental incompatibilities, high gas permeabilities, and poor processabilities [1–6]. Recently, many aromatic hydrocarbon polymers with functionalized sulfo groups as alternatives to PFSA have been synthesized for use as proton conducting membranes for applications in PEFCs. Since sulfonated

aromatic hydrocarbon polymers have high processabilities, environmental friendliness (if no fluorinated moieties are included) and thermal stabilities based on their relatively high T_g compared with common vinyl polymers, they are good starting materials for advanced PEMs. In addition, the ease of synthesis and the introduction of sulfo groups into aryl building blocks via an electrophilic sulfonation reaction broadens the number of available structures of sulfonated aromatic hydrocarbon polymers. For example, the following aromatic hydrocarbon polymers with sulfo groups have been reported: poly(phenylene) [PP] [7–12], poly(imide) [PI] [13–16], poly(benzimidazole) [PBI] [17], poly(arylene sulfide) [PAS] [18–20], and poly(arylene ether) [PAE], such as poly(ether ether ketone) [PEEK] [21–26] and poly(phenylsulfone) [PPSU] [24,27–30]. One of the disadvantages of utilizing aromatic polymers for PEM applications is that, although the intrinsically rigid molecular chain structures of the polymers provides high thermal stabilities, their proton conductivities are generally lower than those of PFSA with flexible main chains. This is probably due to the inhibition of a proton channel formation in the PEM consisting of rigid aromatic polymer chain structures.

Kaliaguine et al. have recently reported the preparation of cross-

* Corresponding author at: Hydrogen Production Materials Group, Center for Green Research on Energy and Environmental Materials, NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

E-mail address: kim.jedeok@nims.go.jp (J.-D. Kim).

<https://doi.org/10.1016/j.ssi.2017.12.033>

Received 30 October 2017; Received in revised form 24 December 2017; Accepted 25 December 2017

0167-2738/ © 2017 Elsevier B.V. All rights reserved.

linked PEMs using mono-sulfonated PEEK (SPEEK) as a starting material and polyatomic alcohols as cross-linkers [21,22]. Although the SPEEK membranes show remarkable proton conductivities at room temperature, their absolute conductivities are considered to be limited due to their relatively small number of sulfo groups per polymer R.U. of < 1.0, and for SPEEK, the conductivity is even lower because of the cross-linking. To maximize the usefulness of this synthetic approach, it should be extended to multi-sulfonated aromatic hydrocarbon polymers. On the other hand, we have recently reported the preparation of multi-sulfonated PPSU-based PEMs through thermal cross-linking of sulfonated PPSU (SPPSU), producing water-insoluble cross-linked SPPSU membranes [28–30]. The cross-linker-free fabrication process of the SPPSU membrane requires organic solvents, such as dimethyl sulfoxide (DMSO), 1-propanol, and 2-propanol, and thermal cross-linking between sulfo groups ($-\text{SO}_3\text{H}$) can produce undesirable by-products, such as sulfur dioxide (SO_2), during the formation of the sulfone bonds ($-\text{SO}_2-$), resulting in the need for a time-consuming washing process to fully purify SPPSU membranes. If an SPPSU membrane can be produced using H_2O as a solvent, the environmentally green chemical process would be advantageous for the preparation of advanced PEMs.

Here we present a facile preparation of electrolyte membranes based on aromatic hydrocarbon polymers with high proton conductivities. The membranes were prepared via a thermal cross-linking reaction of an SPPSU cast film using ethylene glycol (EG) or glycerol (GL) as a cross-linker. The sulfonic ester bond ($-\text{SO}_3\text{RSO}_3-$) is expected to behave as a flexible alkyl spacer in comparison to the relatively rigid sulfone bond ($-\text{SO}_2-$), leading to a decrease in the intrinsic rigidity of aromatic polymer membranes and, thus, PEMs with high proton conductivities. We discuss the advantages of the present synthetic method from the viewpoints of the chemical and thermal stabilities and proton conductivities of the membranes.

2. Experimental

2.1. Materials and measurements

The chemical compounds were purchased from commercially available sources and were used as received. Hydrogen peroxide (H_2O_2), sodium chloride (NaCl), and sulfuric acid (H_2SO_4) were purchased from Nacalai Tesque, Inc. GL, iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), and nitric acid (HNO_3) were purchased from Wako Pure Chemical Industries, Ltd. A dialysis tubing cellulose membrane (molecular weight cut-off; MWCO = 14,000), DMSO, and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich Co., Ltd. EG was purchased from Tokyo Chemical Industry Co., Ltd. *N,N*-Dimethylformamide (DMF) was purchased from Kanto Chemical Co., Inc. Deuterated DMSO ($\text{DMSO}-d_6$) was purchased from Cambridge Isotope Laboratories, Inc. PPSU (Solvay Radel R-5000 NT) ($M_n = 2.6 \times 10^4$; $M_w = 5.0 \times 10^4$; $M_w/M_n = 1.9$) was purchased from Solvay Specialty Polymers Japan K.K. [Glass transition temperature (T_g) = 220 °C]. A DuPont™ Nafion® PFSA membrane (NR-212) was purchased from DuPont (USA). The Nafion212 membrane was pretreated by immersing in 10 vol% aqueous HNO_3 at room temperature for > 2 h, followed by rinsing in deionized (DI) H_2O before the measurements. Conductive carbon paint was purchased from SPI Supplies.

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in $\text{DMSO}-d_6$ using JNM-ECA400 NMR spectrometers. Chemical shifts are represented in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard.

The molecular weights of the polymers were determined by using gel permeation chromatography (GPC) on a TOSOH HLC-8220 system, and the system was calibrated using a polystyrene standard. The measurements were performed at 40 °C using DMF as an eluent.

The thermal behaviors of PPSU, SPPSU, cross-linked SPPSU, and

Nafion212 membranes were investigated in heating runs performed up to 1000 °C at a heating rate of 10 °C/min under flowing nitrogen (> 99.9999%) or oxygen (> 99.8%) gas (20.0 mL/min) using a thermogravimetric–differential thermal analysis (TG–DTA) apparatus (STA 8000, Perkin Elmer) with alumina pans. The samples were dried at 80 °C for > 24 h before the measurement.

The film thickness was measured using Mitutoyo 547-401 ABSOLUTE Digimatic Thickness Gauge.

Through-plane proton conductivities of the SPPSU and Nafion212 membranes were measured as a function of relative humidity (RH, 20%–90%) at 40–120 °C using a 740 membrane test system (MTS, Scribner Associates, Inc.) with a phase sensitive multimeter (model PSM1735, Newtons4th Ltd.) combined with an impedance analysis interface. The frequency range of 10^0 – 10^6 Hz under a peak-to-peak voltage of 10 mV was used in the impedance measurements. The samples were equilibrated in a temperature and humidity chamber at specified temperatures and relative humidities (RHs) for 30 min before the measurement. The chamber was pressurized at 130 kPa for the measurement at a temperature in the range 100–120 °C. The proton conductivities (σ) were calculated using the following equation: σ (S/cm) = λ/RA , where t_{wet} (cm) is the thickness of the wet membrane (0.0058–0.0166 cm), R (Ω) is the resistance, and A is the cross-section area (0.5 cm^2). The apparent activation energy (E_a) for proton conduction was estimated by fitting the data in the temperature range 40–80 °C using $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ (S/cm) is the proton conductivity, σ_0 is the pre-exponential factor, E_a (kJ/mol or eV) is the activation energy of proton conduction, R is the universal gas constant, and T (K) is the absolute temperature.

Infrared (IR) absorption spectra of PPSU, SPPSU, the SPPSU and Nafion212 membranes were acquired in film form on a Thermo Scientific Nicolet 6700 spectrometer in an attenuated total reflection (ATR) mode. The samples were dried at 80 °C for > 24 h before the measurements.

The ion exchange capacity (IEC) of SPPSU, the SPPSU, and Nafion212 membranes were calculated using the following equation: IEC (meq/g) = cv/w_{dry} , where c (mmol/L) is the concentration of the standardized NaOH aq. used for titration (0.01 mol/L), v (L) is the volume of the standardized NaOH aq. used for titration, and w_{dry} (g) is the mass of the dry membrane. The samples were dried at 80 °C for > 24 h and were dipped in 2 M NaCl aq. at room temperature for > 24 h before the measurements.

The degree of sulfonation (D.S.) of SPPSU and the SPPSU membranes was calculated using the following equation: D.S. (Sulfonic acid group/repeating unit; R.U.) = $[\text{IEC}/1000 \times \text{Fw}(\text{R.U.})] / [1 - (\text{IEC} / 1000 \times \text{Fw}(\text{SO}_3))]$, where $\text{Fw}(\text{R.U.}) = 400.45$ and $\text{Fw}(\text{SO}_3) = 80.06$.

The water-uptake (W.U.) of the SPPSU and Nafion212 membranes at room temperature was calculated using the following: W.U. (%) = $[(w_{\text{wet}} - w_{\text{dry}}) / w_{\text{dry}}] \times 100$, where w_{wet} is the mass of the wet membrane. The SPPSU membranes were immersed in boiling DI H_2O for > 1 h before the measurements.

The swelling ratios (S.R.) along the lengths of the SPPSU and Nafion212 membranes were calculated using the following: S.R. (l) (%) = $[(l_{\text{wet}} - l_{\text{dry}}) / l_{\text{dry}}] \times 100$, where l_{wet} is the length of the wet membrane and l_{dry} is the length of the dry membrane. The S.R. values in relation to the thickness of the membranes were calculated using the following: S.R. (t) (%) = $[(t_{\text{wet}} - t_{\text{dry}}) / t_{\text{dry}}] \times 100$, where t_{wet} is the thickness of the wet membrane and t_{dry} is the thickness of the dry membrane. The SPPSU membranes were immersed in boiling DI H_2O for > 1 h before the measurements.

The λ values for the SPPSU and Nafion212 membranes were calculated using the following: λ ($[\text{H}_2\text{O}] / [\text{SO}_3\text{H}]$) = $[1000(w_{\text{wet}} - w_{\text{dry}})] / 18w_{\text{dry}}\text{IEC}$.

The degrees of cross-linking (cross-link rate, $D_{\text{cross-link}}$) in the SPPSU membranes were calculated using the following: $D_{\text{cross-link}}$ (%) = $[(\text{IEC}_{\text{before annealing}} - \text{IEC}_{\text{after annealing}}) / \text{IEC}_{\text{before annealing}}] \times 100$.

All SPPSU aqueous solutions were prepared with purified water

Download English Version:

<https://daneshyari.com/en/article/7744532>

Download Persian Version:

<https://daneshyari.com/article/7744532>

[Daneshyari.com](https://daneshyari.com)