

Article

Synthesis and Characterization of Sulfonated Poly(Phenylene) Containing a Non-Planar Structure and Dibenzoyl Groups

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Abstract: Polymers for application as sulfonated polyphenylene membranes were prepared by nickel-catalyzed carbon-carbon coupling reaction of bis(4-chlorophenyl)-1,2-diphenylethylene (BCD) and 1,4-dichloro-2,5-dibenzoylbenzene (DCBP). Conjugated *cis/trans* isomer (BCD) had a non-planar conformation containing four peripheral aromatic rings that facilitate the formation of π - π interactions. 1,4-Dichloro-2,5-dibenzoylbenzene was synthesized from the oxidation reaction of 2,5-dichloro-*p*-xylene, followed by Friedel-Crafts reaction with benzene. DCBP monomer had good reactivity in polymerization affecting the activity of benzophenone as an electron-withdrawing group. The polyphenylene was sulfonated using concentrated sulfuric acid. These polymers without any ether linkages on the polymer backbone were protected from nucleophilic attack by hydrogen peroxide, hydroxide anion, and radicals generated by polymer electrolyte membrane fuel cell (PEMFC) operation systems. The mole fraction of the sulfonic acid groups was controlled by varying the mole ratio of bis(4-chlorophenyl)-1,2-diphenylethylene in the copolymer. In comparison with Nafion 211[®] membrane, these SBCDCBP membranes showed ion exchange capacity (IEC) ranging from 1.04 to 2.07 meq./g, water uptake from 36.5% to 69.4%, proton conductivity from 58.7 to 101.9 mS/cm, and high thermal stability.

Keywords: PEMFC; π - π interaction; proton conductivity; carbon-carbon coupling; nickel catalyst

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are widely regarded as a potential future renewable source because of their advantages of high efficiency, high power density, and eco-friendliness [1]. Commercial perfluorinated copolymer membranes, such as Nafion[®] and Flemion[®], have good chemical and mechanical stability, and proton conductivity at relative humidity (RH) and low temperature conditions [2]. Despite their advantages, these membranes have several drawbacks, such as high cost, high methanol crossover, and insufficient thermomechanical properties above 80 °C, which limit their PEM applications. Recently, demand has risen for alternative non-fluorinated polymeric materials that are more conductive, operable at high temperatures (>120 °C), environmentally benign, and inexpensive [3–7]. Polyphosphazenes [8,9], polybenzimidazole [10], poly(ether sulfone)s [11,12], and poly(ether ketone)s [13–15] have been used to prepare membranes for fuel cell applications. These polymers have received much attention because of their high thermal, oxidative, and chemical stability in fuel cell environments, and their performance close to Nafion's [16].

However, their chemical stability cannot reach that of Nafion, because the ether linkage with acid functional groups was attacked by hydrogen peroxide or peroxide radicals generated during PEMFC operation [17]. Carbon-carbon linked polymer structures, such as Parmax, are commercially useful inventions containing a side benzoyl group, which affects the surface properties including the surface morphology and other properties [18]. Polyphenylene structures without ether linkages are interesting candidate materials for polymer membranes. According to our previous works and other literature studies, polyphenylene containing pendant benzoyl groups has great advantages, such as good durability, high performance amorphous thermoplastic, thermooxidative stability, excellent chemical and physical properties, and good solubility [19–22].

This work represents an attempt to synthesize polyphenylene without ether linkages by Ni(0)-catalyzed polymerization. The sulfonation reaction was controlled by varying the mole ratio of bis(4-chlorophenyl)-1,2-diphenylethylene (BCD) monomers in the synthesized copolymer. BCD consists of a 4:6 ratio of *cis* and *trans* forms. Conjugated *cis/trans* isomer-based BCD has a non-planar conformation containing four peripheral aromatic rings that facilitate the formation of π - π interactions. Moreover, polymers with pendant benzoyl group have reactivity because of their electron-withdrawing groups. The proposed polymer membranes without ether linkage structure are promising units with good chemical stability and proton conductivity. The polymer membranes are easily soluble in aprotic organic solvents and the presence of double benzophenone groups induces high reactivity for improving the molecular weight. The resulting polymer membranes were studied by ^1H and ^{13}C -NMR spectroscopy, thermogravimetric analysis, water uptake, ion exchange capacity (IEC), proton conductivity, and atomic force microscopic (AFM) image investigation.

2. Experimental

2.1. Materials

2-5-Dichloro-*p*-xylene, potassium permanganate, pyridine, zinc powder, aluminum chloride, thionyl chloride, benzene, dimethylacetamide (DMAc), nickel bromide, triphenylphosphine, and sulfuric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA) and JUNSEI (Tokyo, Japan) and were used without purification. Nickel bromide, zinc powder, and triphenylphosphine were stored under nitrogen in a glove box. Commercial solvents, such as dimethylsulfoxide (DMSO), carbon disulfide, ethyl acetate, dichloromethane, methanol, acetone, ethanol, hexane, and distilled water were used without further purification. The bis(4-chlorophenyl)-1,2-diphenylethylene was prepared according to a previously reported procedure [23].

2.2. Characterization of Membrane

The dissolved membranes in DMSO were prepared to 25 μm thickness by using 2×2 silicon frame with flat glass at 80 $^\circ\text{C}$ and were then washed thoroughly with distilled water before casting the film. The ^1H -NMR analysis was recorded on a DRX (400 MHz) spectrometer (Bruker, Billerica, MA, USA). The spectra of the monomer and polymers were obtained from a 3% solution (w/v) in DMSO- d_6 and CDCl_3 with tetramethylsilane (TMS) as an internal standard. The thermogravimetric analyses were performed using a TGA-N 1000 analyzer (Scinco, Chicago, IL, USA). About 3–4 mg of the samples was measured at 30–800 $^\circ\text{C}$ with a scan rate of 20 $^\circ\text{C}/\text{min}$ under air conditions. To measure the water uptake, the membranes were vacuum-dried at 100 $^\circ\text{C}$ for 24 h. Then, the membranes were placed in deionized water up to equilibrium at 30 and 80 $^\circ\text{C}$ for 24 h. The blotted membranes were quickly weighed and the water uptake of the membranes is reported in weight percent as follows:

$$\text{Water uptake} = \{(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}\} \times 100 \quad (1)$$

Here, W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. In addition, the dimensional change of the membranes was measured by soaking them into distilled water at 80 $^\circ\text{C}$ for 24 h. Thickness (Δt) and length (Δl) were measured by comparing the swell-degree before and after

membrane state. Ion exchange capacity (IEC) of the membranes was determined by titration method. After casting the film, 0.3 g of dried membranes was immersed in a 1.0 M NaCl solution for 24 h to convert the protons into sodium salt ions. Then, the exchanged H^+ ions within the solutions were titrated with a 0.05 N NaOH solution and phenolphthalein indicator. The titrated IEC values were evaluated by the following equation:

$$IEC = (C_{NaOH} \times V_{NaOH})/W_{mem} \quad (2)$$

Here, C_{NaOH} is the concentration of NaOH solution, V_{NaOH} the titrated volume of NaOH solution, and W_{mem} the weight of dried membrane. The proton conductivity of the membranes and reference sample was measured according to the electrochemical impedance spectroscopy (EIS) method. Samples of the electrolyte membranes were prepared to a rectangular shape of 1 cm \times 3 cm and a measured thickness of the membranes. The measurement conditions were varying temperature (40–80 °C) under fixed 90% relative humidity (RH), and fixed temperature (80 °C) under varying RH (30%–90%). Alternating current potential occurs at the center of the electrolyte membrane sample while constant alternating current was applied to the both ends thereof. A MTS 740 through-plane membrane test system (Scribner Associates Inc., Southern Pines, NC, USA) was used for measuring the proton conductivity with a Newtons 4th Ltd. (N4L) impedance analysis interface (PSM 1735). EIS was conducted at the open circuit condition by applying a small alternating voltage (10 mV) and varying the frequency of the alternating voltage from 1 to 1×10^5 Hz. The surface morphologies of the polymer membranes were observed by AFM. Tapping mode AFM observations were performed with a Nanoscope (R) IIIA (Digital Instrument, Milano, Italy), using microfabricated cantilevers with an amplitude set point of 0.7785 V. The chemical degradation of membrane was conducted in Fenton reagent (4 ppm Fe^{2+} , 3% H_2O_2) at 75 °C. The weight of membrane was measured from a solution of iron (II) sulfate heptahydrate in pure water (45 mL), and heated to 75 °C. And then 5 mL of 30% H_2O_2 was added to the solution. The degradation reaction was stopped after a certain period of time, the sample washed in deionized water, and weighed without aqueousity. After assembling the single cell, the MEAs were fully hydrated by feeding a fully humidified N_2 into the single cell for 2 h. During the operation, fully humidified H_2 and air at 70 °C were fed into the anode and cathode, respectively. The stoichiometry of hydrogen and to air was maintained to be 1.5/2.0 and the relative humidity 100/100%. After the activation procedure, polarization curves were measured with a commercial test station (Scitech Inc., Kwangju, Korea) at the temperature of 70 °C and ambient pressure. Polarization measurements were started at open circuit voltage (OCV) and the cell was operated in the galvanostatic mode with a scan rate of 36 mA/s for each step.

2.3. Synthesis of 1,4-Dichloro-2,5-dibenzoylbenzene

1,4-Dichloro-2,5-dibenzoylbenzene was synthesized in a setup comprising a stirring bar, nitrogen inlet, and 500 mL 2-neck round bottom flask. 2,5-Dichloro-*p*-xylene (5.2 g, 21 mmol) was dissolved pyridine (81 mL, 1024 mmol) and room temperature distilled water (25 mL) and potassium permanganate (27.2 g, 177 mmol) was added. The purple solution was stirred for 12 h at 100 °C. The manganese oxide was filtered off while the suspension was still hot and hot water was poured over it twice on a filter funnel. The white suspension was acidified with hydrochloric acid to a pH of 1. The white solid was filtered and dried in an oven at 60 °C. Dried dichloroterephthalic acid (4.3 g, 18.5 mmol) was stirred under reflux condition for 24 h with thionyl chloride (15 mL, 195 mmol) and pyridine (0.018 mL, 0.18 mmol). The solution was evaporated to afford a yellow solid that was immediately dissolved in carbon disulfide (15 mL). Benzene (4.9 mL, 55.5 mmol) and aluminum chloride (12.34 g, 92.5 mmol) in carbon disulfide (60 mL) were placed in a 250 mL two-neck flask and the yellow solution dropped in over a period of 1 h. The mixture was stirred at 40 °C for 24 h and the residue was cooled by pouring into ice water with hydrochloric acid. The product was dissolved in methylene chloride

and washed twice with water. The organic layer was separated, evaporated, and recrystallized with ethanol before drying in an oven at 60 °C [24].

2.4. Synthesis of Polymers

The polymer was synthesized by placing nickel bromide (0.11 g, 0.51 mmol), zinc powder (2 g, 30.71 mmol), and triphenylphosphine (1.07 g, 4.09 mmol) in a 100 mL three-neck flask with flowing nitrogen. In another 50 mL round-flask, bis(4-chlorophenyl)-1,2-diphenylethylene (0.45 g, 1.12 mmol) and 1,4-dichloro-2,5-dibenzoylbenzene (1.6 g, 4.48 mmol) were added. All catalysts and monomers were prepared in a glove box under a nitrogen atmosphere. During the mechanical stirring, care was taken to prevent any ingress of oxygen or moisture. DMAc was added via a syringe in the catalyst flask and stirred at 80 °C for 20 min. After that, dissolved monomers in DMAc were injected by syringe into the catalyst flask slowly. The reaction was allowed to proceed for 24 h at 100 °C, after which the polymer was poured in water with 30% hydrochloric acid. After drying in an oven at 60 °C, the polymer was redissolved in DMAc, re-precipitated in 10% HCl aqueous solution and washed with 5% hydrochloric acid several times to give complete removal of zinc and catalyst. The bright yellow solid was then filtered and washed with methanol and water before drying in an oven at 60 °C.

2.5. Synthesis of Sulfonated Polymers

To a 50 mL flask, dried polymer (0.5 g) and concentrated sulfuric acid (12 mL) were added and the mixture was stirred at 40 °C for 24 h. The mixture was then poured into distilled water and washed several times to remove any residual acid. The product was dried at 60 °C in an oven for 24 h. The sulfonation reaction was controlled by the contents of the BCD monomer.

2.6. MEA Fabrication and Testing

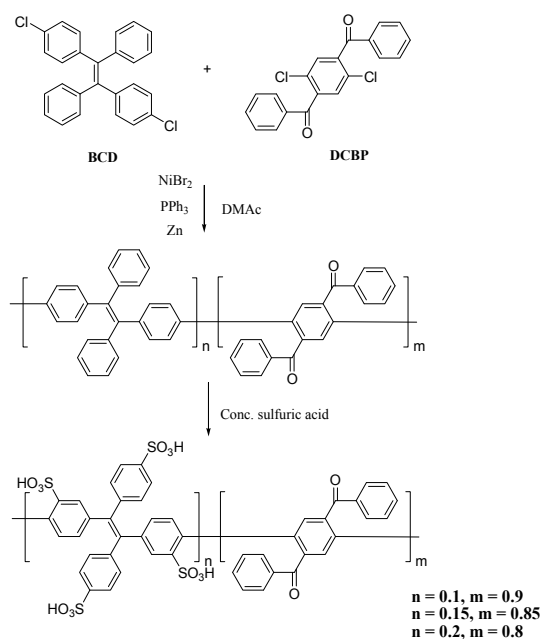
Membrane electrode assemblies (MEAs) with an active area of 3 cm × 3 cm were prepared using a decal method based on a catalyst coated membrane (CCM). A 20 wt % wet-proofed Toray carbon paper (TGPH-060, Toray Inc., Tokyo, Japan) of 190 mm in thickness was employed as a gas diffusion layer (GDL) for the anode and cathode sides. Carbon-supported Pt (Hispec 13100, Johnson Matthey Inc., London, UK) was used as catalyst for both anode and cathode. The loading of the catalyst layer in this work was 0.2 mg Pt/cm² for the anode and cathode. Then, the catalyst layer was transferred on the membrane at 130 °C and 10 MPa for 5 min by decal method to form the CCM. Cell performance was performed by PEMFC test station (Scitech Inc., Kwangju, Korea).

3. Results and Discussion

3.1. Preparation of the Polymers

The two most common methods of carbon-carbon coupling research are metal catalyst coupling and superacid polymerization. Superacid polymerization products have high molecular weight without moisture but are easily crosslinked due to the high reactivity [25]. The nickel-catalyzed coupling reaction is more sensitive to moisture than the acid reaction but it is possible to have stable reaction products with high molecular weight. The polymers were synthesized using nickel–triphenylphosphine ligand and zinc powder with bis(4-chlorophenyl)-1,2-diphenylethylene and 1,4-dichloro-2,5-dibenzoylbenzene (Scheme 1). Tetraethylene was used to increase the molecular weight and flexibility. Sulfonation was performed using concentrated sulfuric acid and the sulfonation level was controlled by the amount of BCD monomer. The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The molecular weight was measured according to the general procedure using pure THF. The polymers showed a weight average molecular weight (*M_w*) ranging from 71,500 to 91,200, and those of the sulfonated polymers are shown from 65,700 to 86,400. The prepared polymers have higher molecular weight than that previously reported, which

was attributed to the Parmax structure (2,5-dichlorobenzophenone) [20]. These polymers have more reactivity because of the symmetric benzophenone in the vicinity of chloride.



Scheme 1. Synthesis of BCDCBP and SBCDCBP.

Figure 1 shows the chemical structure of BCDCBP polymer by ^1H - and ^{13}C -NMR. The characteristic peaks of the polymer that are observed at 6.76–8.00 ppm are due to the dense aromatic rings. After sulfonation, the proton peak nearby the sulfonic acid group was shifted downfield, and the resulting broad and lumpy peaks indicated the sulfonated polymer structure. The peaks of the C=C double bond in were observed in the ^{13}C -NMR spectrum at 127–138 ppm which are the right positions, and they are broad peaks because the polymer is high molecular weight.

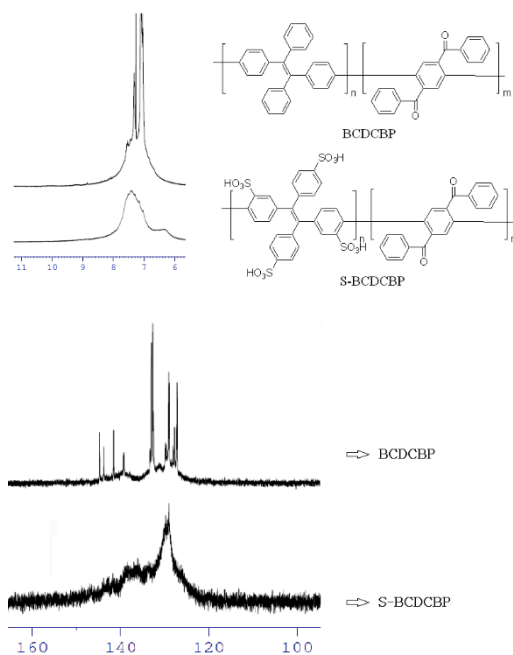


Figure 1. ^1H -NMR and ^{13}C -NMR spectra of SBCDCBP polymers.

3.2. Properties of the Membranes

The thermooxidative stabilities of the sulfonated membranes (SBCDCBPs) provide information about the starting point of degradation of the sulfonated polymer and the main polymer chain (Figure 2). The normal polymer with side benzoyl ketone and backbone started to degrade at 460 °C. The sulfonated polymer shows a two-step weight loss above 600 °C. The first step represents the degradation of sulfonic acid groups around 220 °C and the second the degradation of the side benzoyl ketone and the main chain of the polymer around 510 °C.

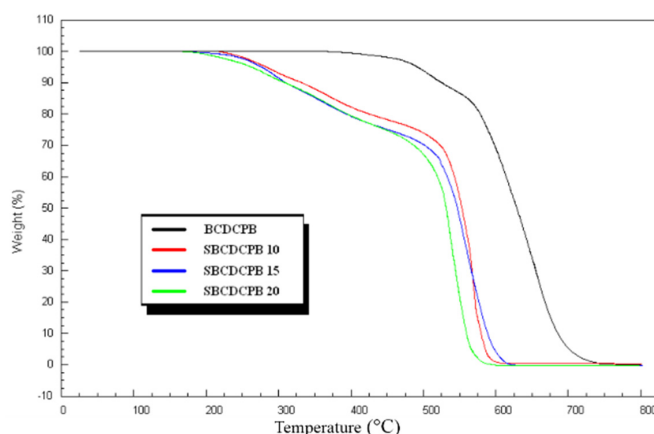


Figure 2. Thermooxidative stabilities of the sulfonated polymer membranes.

The IEC was decided by the sulfonation level and is a factor that influences the proton conductivity. The IEC values of the SBCDCBP membranes varied according to the degree of the sulfonic acid groups. The IEC values of SBCDCBP were in the range of 1.04–2.07 meq./g, compared to 0.91 meq./g for Nafion 211[®], as shown in Figure 3. The theoretical and titrated IECs were in reasonable agreement. Table 1 exhibits the water uptake, dimensional stability, and proton conductivity of the SBCDCBP membranes as a function of the sulfonation level. The water uptake of SBCDCBP increased in the range from 36.5% to 69.4% with increasing IEC, compared to 32.1% for Nafion 211[®] at 80 °C. The dimensional stabilities of the SBCDCBP membranes were evaluated by comparing their through-plane (Δt) and in-plane (Δl) dimensional changes in their hydrated and dry states. The dimensional changes of the SBCDCBP membranes were Δt values of 6.7%, 12.3% and 14.9%, and Δl values of 10.5%, 14.1% and 17.8%, respectively.

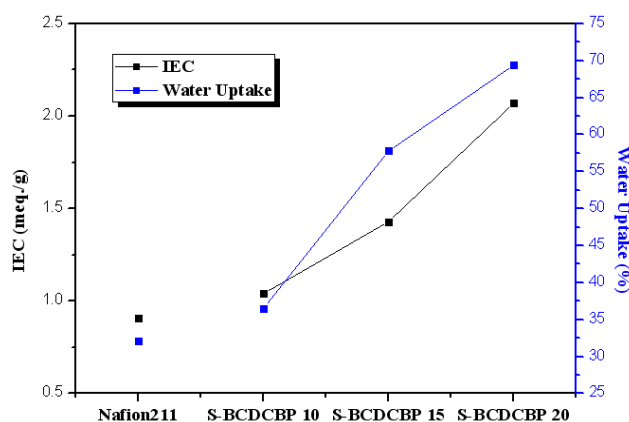


Figure 3. Ion exchange capacities (IECs) and water uptakes of sulfonated polymers.

Table 1. Properties of polyphenylene membranes.

Polymer	Theoretical IEC (meq./g)	Titrated IEC (meq./g)	Water Uptake ¹ (%)	Proton Conductivity ² (mS/cm)
SBCDCPB 10	1.24	1.04	36.5	58.7
SBCDCPB 15	1.76	1.43	57.8	83.4
SBCDCPB 20	2.23	2.07	69.4	101.9

¹ Water uptake at 80 °C; ² Proton conductivity at 80 °C under 100% RH.

Interestingly, the SBCDCBP membranes showed very low dimensional change values, which may have been due to their rigid structure consisting of a conjugated moiety with π - π interactions but without any ether linkage. The small through-plane dimensional change with high proton conductivity is desirable behavior for maintaining dimensional stability during PEMFC stack operation.

The proton conductivities of the SBCDCBP membranes were measured as a function of the mole fraction of the sulfonic acid groups. The measurement conductions were temperature fixed at 80 °C over an RH range of 40%–90% RH (Figure 4), and RH fixed at 90% over a temperature range of 40–80 °C (Figure 5).

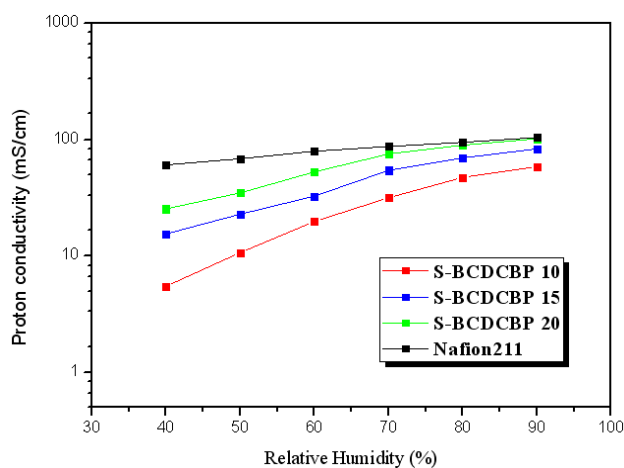


Figure 4. Proton conductivity of SBCDCBP membranes and Nafion 211[®] at 80 °C and varying relative humidity (RH).

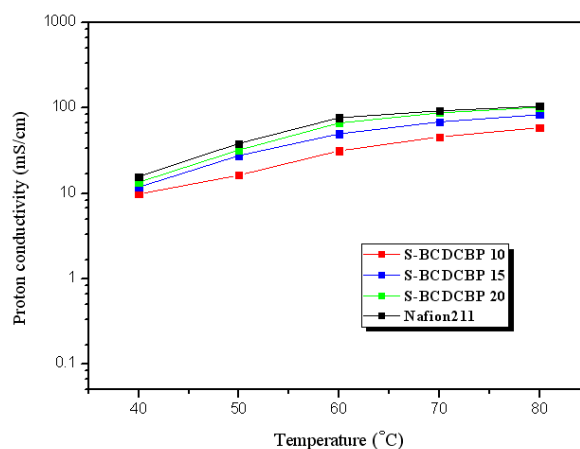


Figure 5. Proton conductivity of SBCDCBP membranes and Nafion 211[®] at varying temperatures and 90% RH.

All conductivity results are presented in Figures 4 and 5 in comparison with Nafion 211[®]. The proton conductivities of SBCDCBP 10, 15, and 20 were 58.7, 83.4 and 101.9 mS/cm at 80 °C with 90% RH, compared to 104.5 mS/cm for Nafion 211[®] at the same conditions. The proton conductivity of the SBCDCBP membranes increased sharply at 80 °C as RH was increased. The conductivities of all the samples increased as the temperature was increased, and the proton conductivity of the membrane SBCDCBP 20 was similar to that of Nafion 211[®] at the same conditions.

Figure 6 shows representative tapping-mode phase images of the surface features of the membranes, which were taken under ambient conditions on a scale of 1 $\mu\text{m} \times 1 \mu\text{m}$. Assessment of the images revealed that the surface pattern reflecting the phase separation of the hydrophilic and hydrophobic domains was strongly dependent on the chemical structure. The AFM images clearly distinguished the surface morphology with a worm-like shape. The brightly colored hydrophobic domains lie between the dark brown hydrophilic domains due to the cluster formation of sulfonic acids and water [4]. These conformations with four sulfonic acid groups on a tetraphenylethylene moiety provide good phase separation of the hydrophilic/hydrophobic domains and wide channels, thereby enhancing the cell performance and dimensional stability.

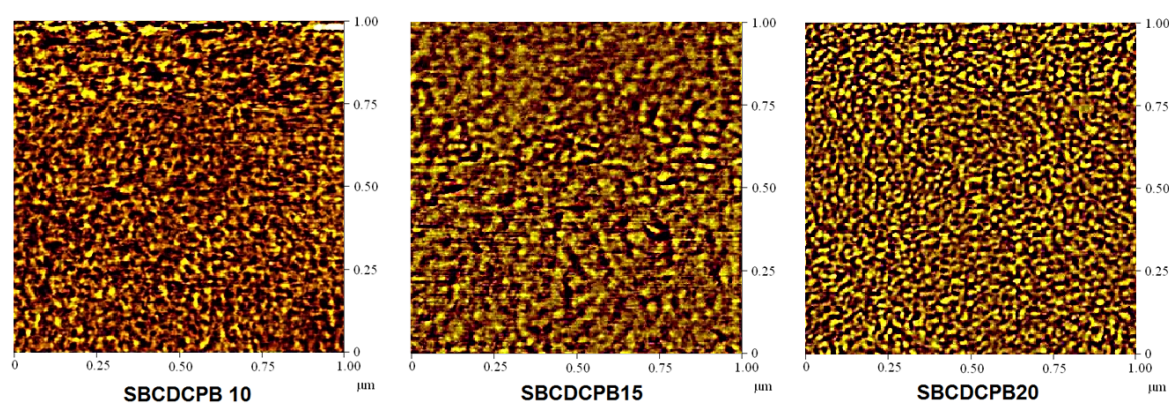


Figure 6. Atomic force microscopic (AFM) images of sulfonated membranes.

Hydrogen peroxide tests were carried out for all membranes, SBCDCPB membranes, Nafion 211[®], and SPES 40 (SPES40: sulfonated linear poly(ether sulfone) containing 40 mol % of 4-biphenol, IEC = 1.53 meq./g) at the same temperature. The tests were evaluated in hot Fenton reagent for 8 h as an accelerated chemical degradation test of membranes. Weight loss of the membranes after the testing are presented as the remaining mass of membranes a function of time, and shown in Figure 7. The resulting SBCDCPB membrane was more degraded than Nafion, but less than SPES 40 containing ether linkages on the polymer chain. As the result, this stability is attributed to the phenylene and planar structure polymer main chain, which is protected or reduced the probability of radical attack. Figure 8 displays a comparison of measured polarization and power density curves for SBCDCPBs under different inlet humidity conditions (RH_a/RH_c :100%/100%). The maximum power densities of SBCDCBP 10, 15, 20, and Nafion 211 are roughly 0.42, 0.48, 0.56 and 0.61 W/cm², respectively.

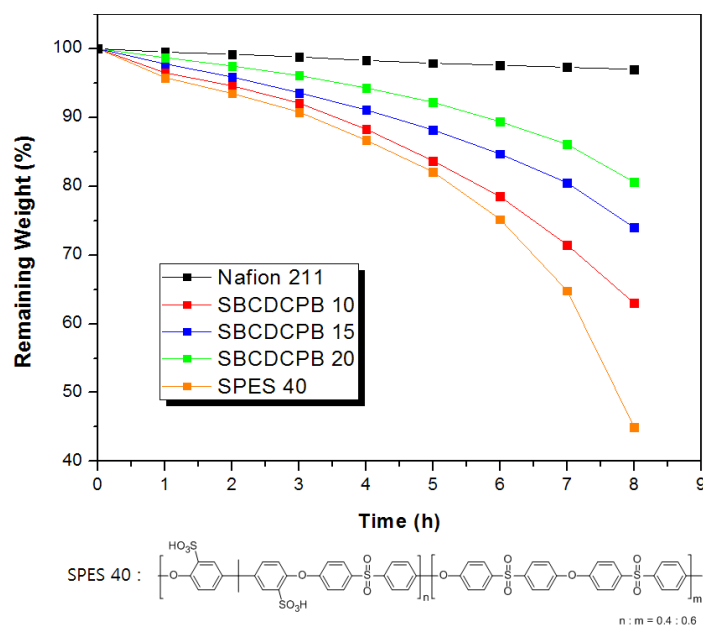


Figure 7. Fenton' reagent (4 ppm) test of membranes.

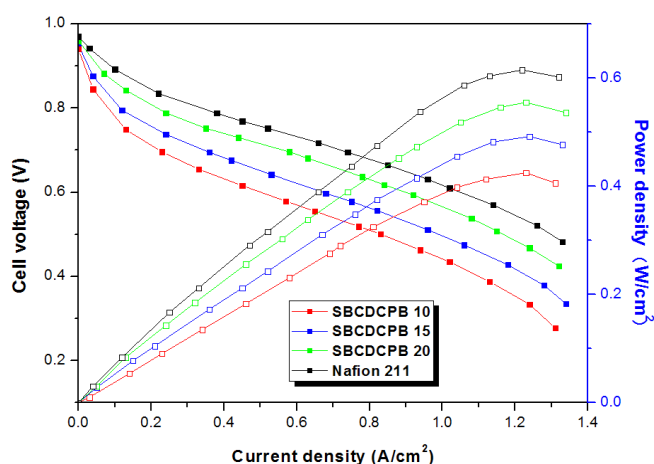


Figure 8. Cell test of sulfonated membranes.

4. Conclusions

A series of sulfonated polyphenylene membranes containing conjugated tetraphenylethylene moieties were synthesized via Ni(0) catalyzed polymerization and the sulfonation was carried out with concentrated sulfuric acid. Compared with Nafion 211[®] membrane, these SBCDCBPs showed rational IECs from 1.04 to 2.07 meq./g, water uptake from 36.5% to 69.4%, proton conductivity from 58.7 to 101.9 mS/cm, and high thermal stability. The proton conductivity was similar to Nafion 211[®]. These results showed that the morphology of polymer matrix greatly affected the membranes properties and stability. Membranes including conjugated segments without ether linkage also provided good dimensional stability in spite of high IEC values. Overall, the polyphenylene membranes demonstrated properties suitable for use in fuel cells and can possibly contribute to improvements of fuel cells' performance.

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Author Contributions: Hohyoun Jang and Sabuj Chandra Sutradhar conceived and designed the experiments; Hohyoun Jang, Jiho Yoo and Jaeseung Pyo performed the experiments; Chaekyun Lee and Taewook Ryu analyzed the data; Jaeseong Ha contributed reagents/materials/analysis tools; Whangi Kim wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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