



공학박사 학위논문

Fabrication of Nanocomposite and Cross-linked Membranes Using Sulfonated Aromatic Hydrocarbon Polymers for Proton Exchange Membrane Fuel Cell Applications 술폰산기가 도입된 방향족 탄화수소계 고분자를 활용한 나노복합

및 가교막의 제조 그리고 이의 양성자 교환막 연료전지로의 응용

2023년 2월

서울대학교 대학원

화학생물공학부

이 현 희

Fabrication of Nanocomposite and Cross-linked Membranes Using Sulfonated Aromatic Hydrocarbon Polymers for Proton Exchange Membrane Fuel Cell Applications

by

Hyunhee Lee

Adviser: Professor Jong-Chan Lee, Ph. D.

Submitted in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

February, 2023

School of Chemical and Biological Engineering College of Engineering Graduate School Seoul National University

술폰산기가 도입된 방향족 탄화수소계 고분자를 활용한 나노복합 및 가교막의 제조 그리고 이의 양성자 교환막 연료전지로의 응용

Fabrication of Nanocomposite and Cross-linked Membranes Using Sulfonated Aromatic Hydrocarbon Polymers for Proton Exchange Membrane Fuel Cell Applications

지도교수 이 종 찬 박사 이 논문을 공학박사학위 논문으로 제출함 2023년 2월 서울대학교 대학원 화학생물공학부 이 현 희

이현희의 박사학위논문을 인준함.

2023년 2월

<u>위</u> 원	<u></u> 신장	(인)
<u>부</u> 우	비원장	(인)
위	원	(인)
위	원	(인)
위	이건	(인)

Abstract

This study presents the synthesis of sulfonated aromatic hydrocarbon polymers for fabrication of nanocomposite and cross-linked membranes for proton exchange membrane fuel cell (PEMFC) applications. First, sulfonated poly(arylene ether sulfone) (SPAES) composite membranes were prepared using graphene oxide (GO) and sulfonated poly(arylene thioether sulfone)-grafted graphene oxide (SATS-GO) as fillers for proton exchange membrane fuel cell applications. SATS-GO was synthesized by grafting poly(arylene thioether sulfone) (SATS) on GO surface using a mild reaction condition (50 °C and 5 h). When GO and SATS-GO were mixed with SPAES to form the composite membranes, dimensional stability, chemical stability, and mechanical strength were improved. The composite membranes containing SATS-GO especially showed higher proton conductivity than the pristine SPAES and the composite membrane containing GO because highly sulfonated polymer (SATS) introduced on GO surface can increase the water uptake, while lower the barrier of proton transfer. Furthermore, the sulfonic acid groups in SATS-GO can increase the compatibility between the filler and matrix polymer due to strong hydrogen bonding and interfacial interactions with the sulfonic acid groups in SPAES.

Second, cross-linking technology has been considered as one of the effective strategies for improving the physicochemical stability of proton-exchange membranes (PEMs) for fuel cell applications. However, the complicated procedure, which consists of various reagents and multiple steps to form the proton-conducting cross-linked membranes, has been known to be disadvantageous to increasing the application of the cross-linking method. In this study, we present a simple and effective cross-linking technology for the development of high-performance crosslinked PEMs without any tedious chemical processes and catalysts or additives. A series of cross-linked membranes could be prepared by a simple one-step stage of casting and heating the mixture of sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly(arylene ether sulfone) (SPAES) in dimethyl sulfoxide (DMSO) solution, where DMSO works as the solvent and the reagent at the same time without any tedious chemical reaction steps. By controlling the cross-linking density, cross-linked membranes having tunable physicochemical stabilities and mechanical properties with outstanding proton conductivity could be obtained. The fuel cell performance of the membrane electrode assembly employing the crosslinked membrane with the optimum cross-linking density and composition ratio showed a maximum power density of 0.70 W cm⁻², which was superior to that employing Nafion 212 (0.58 W cm⁻²) at 80 °C under fully humidified H₂/air condition.

Keywords: Sulfonated poly(arylene ether sulfone), Sulfonated poly(ether ether ketone), Graphene oxide, Composite membranes, Cross-linking, Proton exchange membrane, Fuel cell

Student number: 2017-28196

TABLE OF CONTENT

Abstract	i
List of Tables	vii
List of Figures	viii

Chapter 1

Introduction

1.1. Proton exchange membrane fuel cell (PEMFC)	2
1.2. Proton exchange membrane (PEM) based on sulfonated aromatic	hydrocarbon
polymers (SAHPs)	4
1.3. Motivation	6
1.4. References	9

Chapter 2

Highly Sulfonated Polymer-Grafted Graphene Oxide Composite Membranes for Proton Exchange Membrane

Fuel Cells

2.1. Introduction	17
2.2. Experimental	20
2.3. Results and Discussion	29
2.4. Conclusions	40
2.5. References	42

Chapter 3

Simple and Effective Cross-Linking Technology for the Preparation of Cross-Linked Membranes Composed of Highly Sulfonated Poly(ether ether ketone) and Poly(arylene ether sulfone) for Fuel Cell Applications

3.1. Introduction	74
3.2. Results and Discussion	77
3.3. Conclusions	89
3.4. Experimental	91
3.5. References	100

Abstract in Korean

133

List of Tables

Table 2.1 CHNS elemental analysis results for GO and SATS-GO.	49	
Table 2.2 Chemical stability and mechanical properties of the SPAES	and	
composite membranes.	50	
Table 2.3 IEC and proton conductivities of the SPAES and composite membranes		
at 80 °C.	51	
Table 3.1 Solubility test of samples using DMAc at 80 °C for 24 h.	106	
Table 3.2 IEC _w , hydration number, and proton conductivities of membranes.	107	
Table 3.3 Oxidative stability and mechanical properties of CM-Xs.	108	
Table 3.4 Proton conductivity of various cross-linked membranes at	mid	
temperatures (70-80 °C) under different RH conditions.	109	
Table 3.5 Fuel cell performance of MEAs operating from 60 to 100 °C.	111	

List of Figures

Figure 2.1 Schematic illustration of (a) sulfonated poly(arylene ether sulfor	ne)
(SPAES) and (b) sulfonated poly(arylene thioether sulfone) (SATS).	52
Figure 2.2 ¹ H-NMR spectrum of SPAES.	53
Figure 2.3 ¹ H-NMR spectrum of SATS.	54
Figure 2.4 Preparation of sulfonated poly(arylene thioether sulfone)-graft	ìted
graphene oxide (SATS-GO).	55
Figure 2.5 FT-IR spectra of GO, SATS, and SATS-GO.	56
Figure 2.6 XPS analysis of GO and SATS-GO: (a) GO, (b) SATS-GO, and (c) S	2p
spectra of SATS-GO.	57
Figure 2.7 XPS analysis of GO and SATS-GO. (a) Survey spectrum of GO, (b)) S
2p spectra of GO, (c) C 1s spectra of GO, (d) survey spectrum of SATS-GO, (e	:) S
2p spectra of SATS-GO, and (f) C 1s spectra of SATS-GO.	61
Figure 2.8 TGA curves of GO, SATS, and SATS-GO.	62
Figure 2.9 Average lateral size of (a) GO and (b) SATS-GO confirmed by dynam	nic
light scattering (DLS) results	63

Figure 2.10 Cross-sectional (left) and surface (right) SEM images of the membranes: (a) SPAES, (b) SPAES/GO-2.0, (c) SPAES/SATS-GO-1.0, (d) SPAES/SATS-GO-2.0, and (e) SPAES/SATS-GO-3.0. Scale bar, 1 μ m. The circles indicate the agglomerated domains. 64

Figure 2.11 (a) Water uptake and (b) swelling ratio behavior of the SPAES and composite membranes at various temperatures.

Figure 2.12 Area-based dimensional change of SPAES and composite membranes after being immersed in deionized water at 25 °C and 80 °C for 1 h: (a) SPAES, (b) SPAES/GO-2.0, (c) SPAES/SATS-GO-1.0, (d) SPAES/SATS-GO-2.0, and (e) SPAES/SATS-GO-3.0. 66

Figure 2.13 Chemical stability of the SPAES and composite membranes. 67

Figure 2.14 Stress-strain curves of the SPAES and composite membranes. 68

Figure 2.15 Proton conductivities of the SPAES and composite membranes at 80 °Cas a function of relative humidity.69

Figure 2.16 Schematic illustration for the fabrication and the structure of the SATS-GO composite membrane. 70

Figure 2.17 AFM phase images of the membranes: (a) SPAES, (b) SPAES/GO-2.0, and (c) SPAES/SATS-GO-2.0. 71

Figure 3.1 ¹H-NMR spectra of (a) SPEEK88 and (b) SPAES90. 112

Figure 3.2 Schematics of possible mechanism of (a) $-SO_2^+$ formation from $-SO_3H$ by DMSO, (b) electrophilic aromatic substitution reaction between $-SO_2^+$ in SPEEK88 and electron rich positions of SPEEK88 or SPAES90, and (c) crosslinking reaction via aromatic sulfonic anhydride.

Figure 3.3 Schematics of ion exchange reaction of SPAES90, $-SO_2^+$ formation from $-SO_3H$ by DMSO, and electrophilic aromatic substitution reaction between $-SO_2^+$ in SPAES90 and electron rich positions of SPEEK88 or SPAES90. 114

Figure 3.4 (a) Before and (b) after solubility test of membranes using DMAc at 80 °C for 24 h.

Figure 3.5 FT-IR spectra of SPEEK88, SPAES90, CM-33, and rCM-33. 116

Figure 3.6 FT-IR spectra of (a) CM-100 (black line) and SPEEK88 membrane (blue line) and (b) difference spectrum between CM-100 and SPEEK88 membrane [(black line) – (blue line)]. SPEEK88 membrane (blue line) composed of linear structure was prepared using a casting solvent of DMAc instead of DMSO. 117

Figure 3.7 Contents of SPEEK88 used for the CM-Xs preparation and gel fraction of CM-Xs.

Figure 3.8 Surface (left) and cross-sectional (right) SEM images of CM-Xs: (a) CM-100, (b) CM-67, (c) CM-50, (d) CM-33, and (e) CM-25. The scale bars of surface and cross-sectional SEM images are 1 and 10 μ m, respectively. Photo images of each membrane are included.

Figure 3.9 ¹H-NMR spectra of SPAES90 and filtrates of CM-25 and CM-50 collected at various temperatures. 120

Figure 3.10 (a) Water uptake and (b) volume swelling ratio of membranes at various temperatures.

Figure 3.11 Area-based dimensional change of CM-X after being immersed in deionized water at 25 and 70 °C for 4 h: (a) CM-100, (b) CM-67, (c) CM-50, (d) CM-33, and (e) CM-25. Area-base dimensional change of CM-33 and CM-25 at 70 °C could not be measured due to the excessive swelling. 122

- Figure 3.12 Stress-strain curves of CM-Xs. 123
- Figure 3.13 Proton conductivity of the membranes. 124

Figure 3.14 Cross-section TEM images of (a) CM-100 and (b) CM-50.

Figure 3.15 Comparison of proton conductivity change between CM-50 and CM-100 with humidity cycling (*i.e.*, under repeated hydration (=80 °C, 98% RH for 1 h) and dehydration (=80 °C, 20% RH for 1 h)).

Figure 3.16 Cell performance of MEAs employing CM-50 and Nafion 212 at 80 °C and 100% RH condition.

Figure 3.17 Schematics of (a) sulfonated poly(ether ether ketone) (SPEEK88) and (b) sulfonated poly(arylene ether sulfone) (SPAES90). 129

Figure 3.18 (a) Schematic of CM-X preparation and (b) photo image of CM-50 including the cross-linked network structure formed by SPEEK88 and SPAES90. The weight ratios of SPEEK88 and SPAES90 used for the CM-X preparation are described.

Figure 3.19 (a) TGA thermogram of CM-50 and (b) isothermal TGA of CM-50 performed at 160 °C for 12 h.

Chapter 1

Introduction

1.1. Proton exchange membrane fuel cell (PEMFC)

Fuel cell is an electrochemical device that can directly convert the chemical energy in an oxidizing agent and fuel into electrical energy by a pair of redox reactions [1]. Among the several types of fuel cells, proton exchange membrane fuel cell (PEMFC) has attracted tremendous attention as a promising replacement for conventional Carnot cycle-based engine for the following reasons: the great potential for low weight and volume, fast start-ups and long stack life, operation at a high current density and low temperature [2, 3]. PEMFC consists of a sandwich-like structure containing the anode and the cathode flow field plates, catalyst layers (CLs), gas diffusion layers (GDL), and the membrane electrode assembly (MEA) as shown in Figure 1.1 [4].

Proton exchange membrane (PEM) is a key component of MEA where the electrochemical reaction occurs and electricity is produced [4]. Especially, the performance of PEM plays a key role in determining the output of fuel cell because it transfers the proton from anode to cathode as well as separates the oxidant and the hydrogen fuel in the PEMFC system [3]. Therefore, PEM should meet the following characteristics: high proton conductivity and impermeability of the fuel and oxidant, excellent physicochemical and hydrolytic stabilities, flexibility with

various fuels, good dimensional stability during the operation of the PEMFC, and high cost competitiveness [5]. Perfluorinated sulfonic-acid (PFSA) ionomers, such as Nafion, are the most widely used PEM materials. Nafion is a random copolymer comprised of hydrophobic polytetrafluoroethylene (PTFE) backbone and randomly tethered perfluoroether side-chains terminated with a hydrophilic sulfonic acid group (Figure 1.2). This dissimilar nature between polymer backbone and sidechains can induce highly phase-separated structures resulting in high proton conductivity in hydrated state [6, 7]. Nevertheless, Nafion suffers from several drawbacks including proton conductivity loss under high temperature and high production cost and fuel crossover [8]. Therefore, a lot of efforts have been made to overcome these shortcomings through the several strategies including incorporation of inorganic fillers, preparation of reinforced composite membrane using a porous support matrix, and development of alternative PEMs based on sulfonated hydrocarbon polymers (SHPs) [9, 10].

1.2. Proton exchange membrane (PEM) based on sulfonated aromatic hydrocarbon polymers (SAHPs)

To overcome the drawbacks of PFSA ionomers as a materials for PEM, numerous studies have been conducted to develop sulfonated aromatic hydrocarbon polymers (SAHPs) such as sulfonated poly(arylene ether sulfone) (SPAES) and sulfonated poly(ether ether ketone) (SPEEK) as alternatives to conventional PFSA ionomers due to their advantageous properties for the PEM as follows: 1) hydrocarbon polymers are cheaper than PFSA ionomers and a variety of materials are commercially available, 2) they have high thermal stabilities and excellent mechanical properties, and 3) their chemical structure can be easily controlled through various chemical modifications [11-14].

Typically, SPAES is synthesized through the step growth polymerization using aromatic dihalide monomers (4,4'-difluorodiphenyl sulfone (DFDPS) and 3,3'disulfonate-4,4'-difluorodiphenyl sulfone (SDFDPS)) and aromatic dihydroxy monomer (4,4'-dihydroxybiphenyl (BP) under an anhydrous condition as shown in Figure 1.3. In this case, degree of sulfonation (DS), the average degree of polymer repeating unit containing sulfonic acid group, can be easily adjusted by controlling the molar ratio of DFDPS and SDFDPS [15]. On the other hand, SPEEK can be prepared from the electrophilic substitution reaction through the post-sulfonation process of poly ether ether ketone (PEEK) using concentrated sulfuric acid or the chlorosulfuric acid (Figure 1.4). The DS of the product after post-sulfonation process can be regulated by changing the reaction temperature or time [16].

Despite the various advantageous properties of SAHPs, there are lot of skepticism about the direct application of SAHPs to PEMFCs due to their drawbacks. The main drawback is that the PEMs based on SAHPs have the relatively low proton conductivity compared to the PEMs composed of PFSA ionomers because their proton-conducting channels are tortuous and narrow originating from less developed phase-separated structures between hydrophilic and hydrophobic domains. Therefore, the SAHPs necessitate high ion exchange capacity (IEC) value to retain a required proton conductivity. Unfortunately, the PEMs with high IEC value show excessive dimensional change and poor physicochemical stability because they tend to absorb too much water [11]. Therefore, a lot of attempts have been made to overcome this trade-off relationship between the proton conductivity and physicochemical stability through introduction of inorganic filler materials, cross-linked structure in PEMs, and modification of chemical structure of SAHPs. Previous researches recently proposed an effective strategy to improve the PEM performance such as proton conductivity as well as physicochemical properties through the surface modification of GO.

1.3. Motivation

The development of PEMs using SAHPs with excellent physicochemical stability and proton conductivity is one of the critical issues to replace the commercial PEM based on PFSA ionomer. Considering the practical application and long-term use of PEMFC in stationary, portable, and transportation power generation, it is very important to overcome the trade-off relationship between physicochemical stability and proton conductivity of PEMs [12].

One of the effective approaches to enhance the physicochemical stability without the much loss of the proton conductivity is to introduce inorganic/organic fillers such as SiO₂, TiO₂, ZrO₂, Ce (III), and mineral nanofiber into the polymer matrix. Among the several inorganic fillers, graphene oxide (GO) has attracted much attention because of its extraordinary reinforcing efficiency of mechanical properties on the PEM [17, 18]. Moreover, GO can enhance the oxidative stability of the PEM since lattice defects such as oxygen functional groups and lattice vacancies on its surface can scavenge the oxidative radicals. However, the direct incorporation of pristine GO into the PEM without any modification cannot effectively improve the proton conductivity due to the blocking-effect by GO sheet and/or poor dispersion of GO [19]. Previous researches recently proposed an effective strategies to improve the PEM performance such as proton conductivity as well as physicochemical stability through incorporation of surface modified GO [20]. Therefore, we designed a surface modified GO having highly sulfonated polymer and studied its efficacy on the PEM properties as a filler material. Highly sulfonated polymer could be introduced on GO surface by the reaction of the epoxy group on GO and the thiolated group in highly sulfonated polymer under mild condition without any catalysts [21, 22]. The highly sulfonated polymer-grafted GO nanocomposite membrane showed significantly enhanced proton conductivity compared to the pristine SPAES membrane due to the increased water uptake capability and sulfonic acid group of surface modified GO. Nevertheless, dimensional stability of the nanocomposite membranes was found to be superior to that of pristine SPAES membrane. Moreover, the namocomposite membranes also have better chemical stability and mechanical strength than the pristine SPAES membrane.

Introduction of cross-linking structure in PEM has also been reported as effective way to improve the physicochemical stability as well as lower the fuel crossover of PEM [23-25]. However, this technology is typically accompanied by several elaborate and complicated procedures such as polymer modification to introduce the cross-linkable junction point [26, 27]. Such a complexity is a main impediment to widespread use of this technology. Therefore, we designed a simple and effective

cross-linking method without any tedious chemical processes, catalysts, and additives for the preparation of the cross-linked PEMs showing high-performance. A series of cross-linked membranes could be fabricated from one step casting and heating the dimethyl sulfoxide solution mixtures containing SPEEK and SPAES in a certain ratio. The cross-linked network structure was introduced through the electrophilic substitution reaction between $-SO_2^+$ groups in SPEEK formed during the heating process and the electron rich positions of aromatic groups in SPEEK and/or SPAES [28, 29]. The obtained cross-linked PEM exhibited excellent proton conductivity and physicochemical stability. Moreover, the single cell performance of the MEA employing the cross-linked PEM was better than that employing the Nafion 212, commercialized PFSA membrane, at 80 °C and 100% RH condition.

1.4. References

[1] S. Mekhilef, R. Saidur, A. Safari, Renew. Sustain. Energy Rev., 16 (2012) 981-989.

- [2] O.Z. Sharaf, M.F. Orhan, Renew. Sustain. Energy Rev., 32 (2014) 810-853.
- [3] J.-H. Wee, Renew. Sustain. Energy Rev., 11 (2007) 1720-1738.
- [4] D.-h. Ye, Z.-g. Zhan, J. Power Sources, 231 (2013) 285-292.
- [5] M. Vinothkannan, A.R. Kim, D.J. Yoo, RSC advances, 11 (2021) 18351-18370.
- [6] A. Kusoglu, A.Z. Weber, Chem. Rev., 117 (2017) 987-1104.
- [7] A. Kusoglu, D. Kushner, D.K. Paul, K. Karan, M.A. Hickner, A.Z. Weber, Adv.Funct. Mater., 24 (2014) 4763-4774.
- [8] K. Feng, L. Liu, B. Tang, N. Li, P. Wu, ACS Appl. Mater. Interfaces, 8 (2016)11516-11525.
- [9] S. Jang, Y.S. Kang, J. Choi, J.H. Yeon, C. Seol, M. Choi, S.M. Kim, S.J. Yoo, ,
 J. Ind. Eng. Chem., 90 (2020) 327-332.
- [10] Y. Li, M. Hoorfar, K. Shen, J. Fang, X. Yue, Z. Jiang, Electrochim. Acta, 232

(2017) 226-235.

- [11] T. Higashihara, K. Matsumoto, M. Ueda, Polymer, 50 (2009) 5341-5357.
- [12] W. Harrison, M. Hickner, Y. Kim, J. McGrath, Fuel cells, 5 (2005) 201-212.

[13] B. Liu, G.P. Robertson, D.-S. Kim, M.D. Guiver, W. Hu, Z. Jiang, Macromolecules, 40 (2007) 1934-1944.

[14] M. Rikukawa, K. Sanui, Prog. Polym. Sci., 25 (2000) 1463-1502.

[15] T. Ko, K. Kim, B.-K. Jung, S.-H. Cha, S.-K. Kim, J.-C. Lee, Macromolecules, 48 (2015) 1104-1114.

[16] R. Huang, P. Shao, C. Burns, X. Feng, J. Appl. Polym. Sci., 82 (2001) 2651-2660.

[17] Y. Devrim, A. Albostan, Int. J. Hydrogen Energy, 40 (2015) 15328-15335.

- [18] M.-Y. Lim, K. Kim, Polymers, 10 (2018) 569.
- [19] H. Yang, W. Lee, B. Choi, W. Kim, J. Membr. Sci., 504 (2016) 20-28.
- [20] M. Feng, Y. Huang, Y. Cheng, J. Liu, X. Liu, Polymer, 144 (2018) 7-17.

[21] H.R. Thomas, A.J. Marsden, M. Walker, N.R. Wilson, J.P. Rourke, Angew. Chem. Int. Ed. Engl., 53 (2014) 7613-7618. [22] H.R. Thomas, D.J. Phillips, N.R. Wilson, M.I. Gibson, J.P. Rourke, One-step grafting of polymers to graphene oxide, Polym. Chem., 6 (2015) 8270-8274.

[23] F. Ding, S. Wang, M. Xiao, Y. Meng, J. Power Sources, 164 (2007) 488-495.

[24] M. Han, G. Zhang, Z. Liu, S. Wang, M. Li, J. Zhu, H. Li, Y. Zhang, C.M. Lew,H. Na J. Mater. Chem., 21 (2011) 2187-2193.

[25] P. Mukoma, B. Jooste, H. Vosloo, J. Power Sources, 136 (2004) 16-23.

[26] W. Mabrouk, L. Ogier, S. Vidal, C. Sollogoub, F. Matoussi, J. Fauvarque, J.Membr. Sci., 452 (2014) 263-270.

[27] S. Gu, R. Cai, Y. Yan, Chem. Commun., 47 (2011) 2856-2858.

[28] M. Di Vona, E. Sgreccia, M. Tamilvanan, M. Khadhraoui, C. Chassigneux, P. Knauth, J. Membr. Sci., 354 (2010) 134-141.

[29] B. Maranesi, H. Hou, R. Polini, E. Sgreccia, G. Alberti, R. Narducci, P. Knauth,M. Di Vona, Fuel Cells, 13 (2013) 107-117.

[30] A.P. Soleymani, L.R. Parent, J. Jankovic, Adv. Funct. Mater., 32 (2022)2105188.



Figure 1.1 Cross-sectional schematic representation of PEMFC [30].

PFSA Ionomers: General Chemical Structure



Figure 1.2 General chemical formula for the PFSA ionomers of various forms [6].



Figure 1.3 Schematic illustration of sulfonated poly(arylene ether sulfone) (SPAES).



Figure 1.4 Schematic illustration of sulfonated poly(ether ether ketone) (SPEEK).

Chapter 2

Highly Sulfonated Polymer-Grafted Graphene Oxide Composite Membranes for Proton Exchange Membrane Fuel Cells

2.1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been studied intensively in recent years as clean and efficient energy converting devices for stationary, transportation, and portable applications [1–3]. The proton exchange membrane (PEM) is a key component of PEMFCs because it can transport proton from anode to cathode and separate the fuel and oxidant in the PEMFC system [4]. Perfluorosulfonic acid (PFSA) ionomers, such as Nafion, have been widely used as a commercial benchmark for the PEMFC applications due to their high proton conductivity and excellent chemical stability [5]. Nevertheless, PFSA ionomers generally suffer from several drawbacks, including low operating temperature, high fuel crossover, and high manufacturing cost [6–8]. Consequently, a lot of studies have been conducted on the application of sulfonated aromatic hydrocarbon polymers, including sulfonated poly(arylene ether sulfone) (SPAES) in an attempt to overcome these drawbacks [9, 10] because of their advantages such as excellent thermomechanical stability, low fuel crossover, and relatively inexpensive production cost [5, 11].

However, the membranes based on hydrocarbon polymers have lower proton conductivity than the PFSA ionomer-based membranes because they have less developed phase separated hydrophilic domains [12]. To address this issue, hydrocarbon-based polymers with a high degree of sulfonation (DS) have been widely studied and developed [13, 14]. However, the high DS in such polymers makes PEM highly swellable or even soluble under the fuel cell operating conditions, which limits their direct applications in PEMFC systems [15]. For practical applications, therefore, the limitation of the membranes with a high DS should be overcome and the incorporation of inorganic fillers into the matrix polymer has been regarded as one of the promising solutions [16, 17].

Therefore, numerous studies have been reported on the polymer composite membranes containing inorganic fillers such as zeolites, mineral nanofiber, graphene, and Ce (III) to improve the performances of PEMFCs [18–22]. Among these inorganic materials, graphene oxide (GO) has attracted tremendous attention due to its robust characteristics and the oxygen functional groups that can impart the ability to interact with matrix polymer and improve thermochemical and mechanical properties of the membranes [8, 23]. However, when pristine GO was mixed with polymer to produce PEMs, the proton conductivity was not effectively improved [24]. Furthermore, the aggregation and stacking behavior of GO sheets often cause poor performance of the membrane [25]. Recently, studies have shown that modification of the GO using functional groups or polymers can effectively improve the membrane performance such as proton conductivity and also the physicochemical properties [26, 27].

Herein, highly sulfonated polymer-grafted graphene oxide (SATS-GO) was prepared by the reactions of the functional groups in GO with the thiolate group in sulfonated poly(arylene thioether sulfone) (SATS) [28, 29]. To the best of our knowledge, this is the first study to introduce a highly hydrophilic polymer with a DS of 100 on GO for use as filler materials for PEMFC applications. SATS-GO was found to effectively improve the proton conductivity, physicochemical stability, and mechanical strength of the membrane by the grafted polymer chains having sulfonic acid group on GO. The detailed synthetic approaches for preparation of the SATS-GO and SPAES composite membranes and their properties such as water absorption and mechanical properties, oxidative stability, and proton conductivity are fully discussed.

2.2. Experimental

Materials

4,4'-Difluorodiphenyl sulfone (DFDPS, 99.0%, Aldrich) was recrystallized using toluene. 3,3'-disulfonate-4,4'-difluorodiphenyl sulfone (SDFDPS) was prepared by the sulfonation of DFDPS as described by Harrison et al. (yield: 82%) [30]. 4,4'-dihydroxybiphenyl (BP, 97.0%, Aldrich) was recrystallized using methanol. Potassium carbonate (K₂CO₃, 99.0%, Aldrich) was dried in a vacuum for 48 h before use. *N*,*N*-dimethylacetamide (DMAc, 99.0%, Junsei), *N*-methyl-2-pyrrolidone (NMP, 99.0%, Junsei), and toluene (99.5%, Junsei) were stored over molecular sieves under nitrogen. Sulfuric acid (H₂SO₄, 95.0%, Daejung), hydrogen peroxide (H₂O₂, 30.0%, Daejung), acetone (99.5%, Dajung), isopropyl alcohol (IPA, 99.5%, Daejung), tetrahydrofuran (THF, 99.0%, Daejung), ethyl alcohol anhydrous (99.5%, Daejung), iron(II) sulfate heptahydrate (FeO₄S·7H₂O, 99.0%, Aldrich), and 4,4'-thiobisbenzenethiol (TBBT, 98.0%, Aldrich) were used as received. GO was purchased from Promico Co. Ltd. (purity: >99 wt%, thickness: 1.1–1.3 nm, and lateral dimension: >20 µm). Nafion[®] perfluorinated membrane (Nafion 117) was purchased from Aldrich.
Synthesis of sulfonated poly(arylene ether sulfone) (SPAES)

Sulfonated poly(arylene ether sulfone) (SPAES) was synthesized using dihydroxy and difluoro monomers as described in our previous report (Figure 2.1 (a)) [31]. 1.271 g (5.00 mmol) of DFDPS, 2.292 g (5.00 mmol) of SDFDPS, 1.862 g (10.00 mmol) of BP, and 1.590 g (11.50 mmol) of K₂CO₃ were added into the 250 mL three neck round bottom flask containing 12.3 mL of NMP and equipped with an overhead stirrer, a Dean-Stark apparatus, and nitrogen inlet and outlet. 6.15 mL of toluene (NMP/toluene = 2/1 v/v) as an azeotropic agent was added slowly dropwise to the solution in the reactor, and then temperature of the reaction mixture was maintained at 150 °C for 5 h to dehydrate the system. After removing toluene, the reaction, the resulting viscous solution was cooled to room temperature and filtered for the removal of the salt. White polymer powder resulted from precipitation in ethanol was washed, and then purified by Soxhlet extraction with deionized water, respectively. An 85% yield of final product was obtained after drying at 80 °C for 24 h in a vacuum oven.

Synthesis of sulfonated poly(arylene thioether sulfone) (SATS)

Sulfonated poly(arylene thioether sulfone) (SATS) was synthesized using

SDFDPS and TBBT. The typical procedure is illustrated in Figure 2.1 (b). Synthesis of the polymer was performed in the 100 mL three neck round bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, reflux condenser, and nitrogen inlet and outlet. The reaction mixture composed of 1.375 g (3.00 mmol) of SDFDPS, 0.751 g (3.00 mmol) of TBBT, 0.912 g (6.60 mmol) of K₂CO₃, 2.5 mL of toluene, and 12.9 mL of DMAc was stirred sequentially at 140 °C for 6 h and 160 °C for 2 h for azeotropic dehydration of the system and polymerization, respectively. After cooling to room temperature, the reaction solution was precipitated in IPA to obtain a light-yellow polymer and it was washed with THF to remove unreacted TBBT completely. The resulting product was dried under vacuum at 80 °C for 24 h.

Preparation of sulfonated poly(arylene thioether sulfone)-grafted graphene oxide (SATS-GO)

0.3 g of GO was added into the 100 mL round bottom flask and dispersed in 15 mL of DMAc using sonication for 30 min. 0.6 g of SATS was dissolved in 7.5 mL of DMAc in the 20 mL glass vial. After stirring each solution at room temperature for 2 h, the SATS solution was poured into the homogeneously dispersed GO suspension. The mixture was then stirred at 50 °C for 5 h. After cooling, the crude product was washed repeatedly by 4 cycles of centrifugation using DMAc and acetone at 9,000 rpm for 20 min for the purpose of removing unreacted SATS and DMAc, respectively. The resulting product, named SATS-GO, was obtained after drying in a vacuum oven at 80 °C for 24 h.

Preparation of the SPAES composite membranes

The SPAES composite membranes containing the GO derivatives were fabricated using a solution-casting method. A given amount of SATS-GO was dispersed in 2.7 g of DMAc using sonication for 30 min to get a homogeneous dispersion and kept under stirring overnight. 0.3 g of SPAES was added to the SATS-GO suspension. After dissolving SPAES completely, the resulting solution was cast onto a flat glass plate using a doctor blade and heated from 60 to 120 °C at a heating rate of 10 °C h⁻¹ and maintained at 120 °C for 12 h to obtain the smooth and tough membrane. The membrane in salt form (K⁺) was peeled off from the glass plate by immersion in a water bath. Acid form (H⁺) membrane was obtained by treating the salt form membrane with 1 M H₂SO₄ at room temperature for 24 h, followed by several washing cycles with deionized water for removing residual acid. The resulting membrane was named SPAES/SATS-GO-X, where X (X = 1.0, 2.0, and 3.0) denotes the weight percent of SATS-GO to SPAES. For comparison, the pristine SPAES and SPAES/GO-2.0 (containing 2 wt% of GO to SPAES) membranes were also fabricated through the same method of preparing the SPAES/SATS-GO composite membranes. All the membranes were stored in a vacuum oven before use. Thicknesses of the membranes ranged from 20 to 29 μ m.

Characterization

Fourier transform infrared (FT-IR) spectra of the samples were obtained from Nicolet 6700 (Thermo Scientific, USA) in the attenuated total reflectance (ATR) mode within a frequency range from 650 to 4000 cm⁻¹. The spectra were acquired as an average of 32 scans made at a 4 cm⁻¹ resolution. Proton nuclear magnetic resonance (¹H-NMR) spectra were collected using Avance-400 (Bruker, Germany) with a proton frequency of 400 MHz in deuterated dimethylsulfoxide (DMSO-*d*₆). The chemical shifts were calibrated to tetramethylsilane (TMS) at 0 ppm as an internal standard. CHNS elemental analysis was performed with an element analyzer TruSpec[®] Micro (Leco, USA). X-ray photoelectron spectroscopy (XPS) was recorded on a KRATOS AXIS-HSi (Kratos Analytical Ltd., UK) with a Mg K α (1254.0 eV) as a radiation source. Dynamic Light Scattering (DLS) was performed by ELS Z-1000 (Otsuka portal). Gel permeation chromatography (GPC, Waters[®], USA), containing a Waters 1515 isocratic HPLC pump at 40 °C, a Waters 2414 refractive index detector, and three columns (Styragel HR 2, Styragel HR 3, Styragel HR 4), was used to determine the molecular weights (M_n and M_w). The flow rate of HPLC grade DMAc with LiBr was 1.0 mL min⁻¹. Calibration was conducted using polystyrene standards.

Atomic force microscopy (AFM) was carried out by MFP-3D (Asylum Research, USA) to investigate the morphology of the membranes. A silicon probe, PointProbe[®] Plus (Nanosensors, Switzerland), with a force constant from 1.2 to 20 Nm^{-1} was used. All the membranes were dried for 2 h in a vacuum oven before use. The transmission electron microscopy (TEM) images were obtained from a Talos F200S (FEI, USA) with 200 kV accelerating voltage. The samples were stained using 1.0 M lead acetate solution by ion exchange of the sulfonic acid groups. The stained samples were embedded in epoxy resin, cut into 80 nm-thick sections, and then placed on copper grids. The morphologies of the membranes were inspected by JSM-6700F (JEOL, Japan) using a field emission scanning electron microscope (FE-SEM). For the inspection of cross-sectional morphology, samples were prepared by cutting the liquid nitrogen-quenched membranes.

The mechanical properties of PEMs were investigated by Lloyd-LS1 (Lloyd, UK). ASTM standard D638 (Type V specimens) was used to prepare dumbbell specimens. The test was performed at room temperature under 45% relative humidity (RH) at a gauge length and a cross head speed of 15 mm and 5 mm min⁻¹, respectively. The average values were obtained through at least more than 10 tests

for the samples. Thermogravimetric analysis (TGA) was performed using a Q-5000IR (TA instruments, USA) from 120 to 700 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The samples were pre-heated at 120 °C for 20 min to evaporate the absorbed moisture. The oxidative stability of the membranes was measured by Fenton's test from observing the decomposition behavior of the samples after being submersed in Fenton's reagent (4 ppm FeSO₄ in 3 wt% H₂O₂ aqueous solution) at 80 °C. The times at which the samples began to decompose (τ_1) and were completely decomposed (τ_2) were recorded. Each measurement was made at 20 min intervals.

The weight-based ion exchange capacity (IEC_w) of the membranes was measured by back-titration method. The dry membranes in the proton form were immersed in 1.0 M NaCl solution at 80 °C for 24 h to substitute the protons of the sulfonic acid groups with sodium ions, and then released protons were titrated with 0.01 M NaOH solution. The IEC_w value was calculated using the following equation:

$$IEC_w = (C_{NaOH} \cdot \Delta V_{NaOH} / W_s) \times 1000$$

where C_{NaOH} , ΔV_{NaOH} , and W_s are the concentration and the consumed volume of NaOH solution and the weight of the dry membrane, respectively.

Water uptake and swelling ratio values of the membranes were determined by measuring the changes in weight and volume in the dry and wet states. The predried membranes were cut into $1 \text{ cm} \times 2 \text{ cm}$ and their weights and volumes were measured. After that, the membranes were immersed in deionized water at various temperatures for 1 h. After the membranes were removed from the water and wiped, their weights and volumes were quickly measured. The water uptake and swelling ratio values of the membranes were calculated using the equations below.

Water uptake = $(W_w - W_d) / W_d \times 100$

Swelling ratio = $(V_w - V_d) / V_d \times 100$

where W_w and W_d indicate the weights of the wet and dry membranes, and V_w and V_d indicate the volumes of the wet and dry membranes, respectively.

The proton conductivity of PEMs was estimated using the four-probe method [32] under various RH conditions at 80 °C. The impedance of the membranes was measured from the IM-6ex impedance analyzer (ZAHNER-elektrik GmbH & Co. KG, Germany) with a perturbation amplitude of 10 mV within the frequency range from 1 Hz to 1 MHz in potentiostat mode. For accurate measurement, the membranes were placed in the chamber for at least 1 h in each condition before measurement to reach equilibrium. The proton conductivity (σ) was calculated using the equation below.

 $\sigma = d / RS$

where d, R, and S indicate the distance between the sensing electrodes and reference, the ohmic resistance, and the cross-section area (thickness × width) of the sample, respectively.

2.3. Results and Discussion

Synthesis of sulfonated poly(arylene ether sulfone) (SPAES)

Sulfonated poly(arylene ether sulfone) (SPAES) was successfully synthesized *via* the step growth polymerization of dihydroxy monomer (4,4'-dihydroxybiphenyl (BP)) and aromatic dihalide monomers (4,4'-difluorodiphenyl sulfone (DFDPS) and 3,3'-disulfonate-4,4'-difluorodiphenyl sulfone (SDFDPS)). In order to obtain high molecular weight polymers, the polymerization should proceed under an anhydrous condition [30]. Accordingly, the reaction was performed with toluene as a refluxing agent for the purpose of removing water present in the reaction system by azeotropic distillation. Successful synthesis of SPAES was demonstrated by ¹H-NMR spectrum, as shown in Figure 2.2. When the degree of sulfonation (DS) of SPAES exceeds 50, physical instability due to excessive swelling is unacceptable for the PEM applications [30]. Thus, SPAES with a DS of 50 was intentionally prepared by controlling the molar ratio of SDFDPS and DFDPS to 1:1. However, the DS value calculated from ¹H-NMR spectrum was found to be about 48. This slight difference could be ascribed to the slightly lower reactivity of the more sterically hindered sulfonated aromatic dihalide monomer (SDFDPS) compared to that of DFDPS [30, 33]. The number average (M_n) and the weight average (M_w) molecular weights of SPAES obtained from the result of GPC analysis were 147,000 and 201,000 g mol⁻¹, respectively.

Synthesis of sulfonated poly(arylene thioether sulfone) (SATS)

Sulfonated poly(arylene thioether sulfone) (SATS) was synthesized *via* the polycondensation of SDFDPS and TBBT at 160 °C for 2 h. A short reaction time was intentionally used to synthesize a polymer with small molecular weight to introduce SATS onto GO more effectively [34]. The chemical structure of SATS was confirmed by ¹H-NMR [35] as shown in Figure 2.3. It is well known that bisthiophenol monomers such as TBBT are usually unstable in air because it can be easily oxidized to form disulfide bonds even at room temperature [36]. Thus, the polymer obtained by precipitation in IPA was further washed with THF to remove remaining TBBT. TBBT with disulfide bonds is not soluble in IPA but is soluble in THF. The average molecular weight (M_n) of SATS was 9,100 g mol⁻¹, calculated by comparing the peak integrations of the main-chain protons (peak d) with the end-group protons (peak l) in the ¹H-NMR spectrum.

Characterization of sulfonated poly(arylene thioether sulfone)grafted graphene oxide (SATS-GO) Sulfonated poly(arylene thioether sulfone)-grafted graphene oxide (SATS-GO) was prepared as illustrated in Figure 2.4. Herein, SATS could be successfully introduced on GO by the reactions of the thiolate group in SATS with various functional groups such as the epoxy group and double bond in GO [28, 29]. SATS could also be introduced on GO by the non-covalent interaction (*e.g.*, π – π interaction). The chemical structures of GO and SATS-GO were confirmed by FT-IR spectroscopy (Figure 2.5). In the FT-IR spectrum of GO, a C=O stretching vibration band of a carboxyl group at 1732 cm⁻¹, a C=C stretching vibration band of an aromatic group at 1620 cm⁻¹, an OH stretching vibration band at 1414 cm⁻¹, and C–O and C–O–C stretching vibration bands of epoxy group at 1043 cm⁻¹ and 1220 cm⁻¹ can be observed [8, 37, 38]. After the modification of GO to SATS-GO, the appearance of new peaks at 1057, 1231 cm⁻¹ (sulfonic acid groups) [38], 1163, 1108, and 1017 cm⁻¹ (two ν_{s-o} and one $\nu_{s-phenyl}$) [37] clearly demonstrates the successful grafting reaction of SATS on GO.

The XPS spectra of GO and SATS-GO are presented in Figures 2.6 and 2.7. In Figure 2.6 (b), the spectrum of SATS-GO shows a new S 2p peak at 168 eV. In the S 2p spectra of SATS-GO (Figure 2.6 (c)), two major peaks at 168.2 and 169.4 eV are assigned to 2p3/2 and 2p1/2, respectively, from sulfur in highly oxidized state such as sulfonic acid group ($-SO_3^-$), and two minor peaks at 167.6 and 168.8 eV are assigned to 2p3/2 and 2p1/2, respectively, from sulfur in lower oxidized state

such as SO₂ and S–C [39]. Other new peaks in the spectrum of SATS-GO such as K 2s and K 2p appearing at 376.5 and 293.0 eV from –SO₃K groups in SATS are also shown.

The CHNS elemental analysis of GO and SATS-GO was performed and the average weight percentages of the characteristic atoms are presented in Table 2.1. The sulfur content of SATS-GO is larger than that of GO by 4.3 wt%. These results of the XPS and CHNS elemental analyses support the successful introduction of SATS on GO. The content of SATS in SATS-GO calculated using the elemental analysis is 18.8 wt%. In addition, the weight loss values for GO, SATS, and SATS-GO observed from TGA curves at 700 °C are 58.0%, 36.6%, and 53.6% respectively (Figure 2.8). On the basis of this result, the content of SATS in SATS-GO was calculated to be 20.6 wt%. This is in good agreement with the result calculated using elemental analysis. The average lateral size values of GO and SATS-GO determined with DLS are 852.0 ± 182.9 and 671.6 ± 123.4 nm, respectively (Figure 2.9). The slightly smaller average lateral size value of SATS-GO than GO can be attributed to the sonication step known to decrease the lateral size of GO.

Morphology of the SPAES and composite membranes

Nanofillers should be well dispersed in the matrix polymer to make PEM having

good mechanical properties [40]. Cross-sectional and surface SEM images were used to investigate the morphology of the membranes with various filler contents (Figure 2.10). The image of the pristine SPAES membrane shows a smooth and uniform surface and a cross-section image without any cracks or pinholes. However, as the filler content increases, the morphology becomes rougher because of the aggregation of the GO derivatives and the mutual interactions between themselves and with the SPAES matrix [41]. In particular, agglomerated domains are observed in the SPAES/GO-2.0 membrane due to the poor dispersion and/or the aggregation of the fillers, while any agglomerated domains are not observed in both crosssectional and surface SEM images of the SPAES/SATS-GO-2.0 membrane. This is because the highly sulfonated polymer chains grafted on GO effectively increase the contact area with the SPAES matrix by the strong hydrogen bonding and interfacial interactions with the sulfonic acid groups in the SPAES matrix, thus increasing the interfacial compatibility between SATS and the SPAES matrix [41], [42]. However, when the SATS-GO content is larger than 2.0 wt%, agglomerated sites are also observed from the composite membranes because of the aggregation of SATS-GO.

Water uptake and swelling ratio

An increase of water absorption in the membranes can increase the proton conductivity through both the vehicle and grotthuss mechanisms [43, 44]. Water uptake values of the membranes were measured after immersing them in deionized water for 1 h at various temperatures (Figure 2.11). The SPAES/GO and SPAES/SATS-GO composite membranes exhibit higher water uptake than the pristine SPAES membrane. For instance, the water uptake values of the SPAES/GO-2.0 and SPAES/SATS-GO-2.0 membranes at 80 °C are 60.9% and 77.7% respectively, and that of SPAES membrane at 80 °C is 46.7%. The SPAES/SATS-GO-2.0 membrane having larger water uptake value than the SPAES/GO-2.0 membrane should have more hydrophilic nature because it has the sulfonic acid groups in SATS-GO [45]. It was found that the water uptake value of the SPAES/SATS-GO-2.0 membrane is larger than that of SPAES/SATS-GO-3.0 membrane although the SPAES/SATS-GO-3.0 membrane contains more hydrophilic SATS-GO nanofiller because it cannot effectively absorb water by aggregation and/or poor dispersion in the matrix polymer as reported previously [42, 46]. As expected, the water uptake of all the membranes gradually increases with increasing temperature. The swelling ratio behavior of the membranes (Figures 2.11 and 2.12) is similar to the water uptake behavior because the volume expansion of the membranes by water is directly affected by the hydration of the hydrophilic groups [47]. However, all the composite membranes show smaller swelling ratio values than the SPAES membrane even though they have larger water uptake values because the hydrogen bonding interactions formed between the SPAES matrix and nanofillers can effectively inhibit volume expansion of the membranes [24, 38, 48]. In addition, chain entanglements between SATS and matrix polymer chains might further improve dimensional stability of the SATS-GO composite membranes [42]. Therefore, the SPAES/SATS-GO composite membranes can absorb more water, while swell less by the hydration, which is beneficial for the PEMFC applications [49, 50].

Oxidative stability

The oxidative and chemical stabilities of the sulfonated hydrocarbon membranes are not as good as the perfluorosulfonic acid membranes because radical \cdot OH radical can attack the hydrocarbon structure more easily [51, 52]. Therefore, oxidative instability of the sulfonated hydrocarbon membrane is one of the drawbacks for the fuel cell applications. The oxidative stability of the prepared membranes was assessed using Fenton's reagent (4 ppm Fe²⁺ in 3 wt% H₂O₂ aqueous solution) at 80 °C. Fenton's test has been widely used to produce hydroxyl or peroxy radicals by the following process and those reactive oxygen species (ROSs) cause polymer chain scission (*e.g.*, unzip and midpoint scissions) of sulfonated hydrocarbon PEMs [8, 53].

 $H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+}$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+$$

The elapsed times for membranes to start to break into pieces (τ_1) and dissolve completely (τ_2) in Fenton's reagent are presented in Table 2.2 and Figure 2.13. As expected, all the composite membranes exhibit better oxidative stability than the pristine SPAES membrane. For example, τ_1 and τ_2 of the SPAES membrane are 60 and 140 min, respectively, whereas τ_1 and τ_2 of the SPAES/GO-2.0 membrane are 140 and 220 min, respectively, and those of SPAES/SATS-GO-2.0 membrane are 80 and 180 min, respectively. Therefore, the oxidative stabilities are in the order of SPAES/GO-2.0 > SPAES/SATS-GO-2.0 > SPAES. Obviously GO having a lot of sp²-carbon domains on its basal surface can effectively scavenge the radicals. In addition, its sheet-like structure can further increase the antioxidant property [54]. The oxidative stability of the SPAES/SATS-GO composite membranes is poorer than that of the SPAES/GO composite membrane because the reaction of SATS with GO can make SATS-GO have more hydrophilic groups than GO and it increases ion exchange capacity of the membrane. These features have been known to decrease the oxidative stability [55-57].

Mechanical properties

The mechanical properties of the pristine SPAES and composite membranes were investigated using UTM at room temperature under 45% RH (Table 2.2 and Figure 2.14). The addition of GO or SATS-GO increases the tensile strength and Young's modulus of the membranes, which can be ascribed to the interaction between sulfonic acid groups of SPAES and the functional groups (oxygen or sulfonic acid groups) in the GO derivatives as well as the π - π interactions between aromatic rings in SPAES and unsaturated C-C bonds in GO [50]. On the other hand, when the GO derivatives are added, the elongation at break value of the membrane decreases because the polymer chain mobility decreases by the interaction between SPAES and the GO derivatives [8, 58]. Compared with the SPAES/GO-2.0 membrane, the SPAES/SATS-GO-2.0 membrane has larger mechanical strength and elongation at break value because SATS-GO having sulfonic acid group is much more compatible with SPAES having sulfonic acid group than GO having only oxygen functional groups [16, 42]. However, when the SATS-GO content is larger than 2.0 wt%, the mechanical properties get deteriorated due to the phase separation between fillers and matrix polymer [50, 59]. For example, the tensile strength and elongation at break values of the SPAES/SATS-GO-2.0 membrane are 62.2 MPa and 36.8%, respectively, while those of SPAES/SATS-GO-3.0 membrane are 46.6 MPa and 17.7%, respectively. It is well known that agglomerated domains of the fillers in the composite membrane act as defects that decrease the mechanical strength of the membrane [42, 60].

Proton conductivity

The proton conductivity (σ) values of the membranes including Nafion 117 were measured at 80 °C under various RH conditions from 40% to 90% (Table 2.3 and Figure 2.15). Proton conductivities of all the membranes increase with increasing RH because water molecule acts as a proton carrier and bridge between the sulfonic acid groups [61]. Overall, the pristine SPAES and composite membranes exhibit higher RH dependence than Nafion 117. As expected, the proton conductivity values over the entire RH range for all the SATS-GO composite membranes are larger than those of SPAES membrane. The proton conductivities of the SPAES/SATS-GO composite membranes are in the order of SPAES/SATS-GO-2.0

> SPAES/SATS-GO-1.0 > SPAES/SATS-GO-3.0 and the highest conductivity of

131.43 mS cm⁻¹ is observed from the SPAES/SATS-GO-2.0 membrane at 80 °C and 90% RH. This result can be ascribed to the additional hydrogen bonding networks and increased water uptake capability by the sulfonic acid group in SATS-GO [37]. In addition, excellent compatibility between SATS-GO and the SPAES matrix can effectively lower the barrier of proton transfer [24], as illustrated in Figure 2.16.

However, when the SATS-GO content is larger than 2.0 wt% such as 3.0 wt%, the proton conductivity value becomes smaller. Poor dispersion or aggregation of SATS-GO is likely to cause this behavior, as already demonstrated by SEM images (Figure 2.10) [24, 50]. The SPAES/GO-2.0 membrane, interestingly, has smaller proton conductivity value than the SPAES membrane below 80% RH although it has larger water uptake value than the SPAES membrane because the sheet-like structure of GO disconnects the hydrophilic channels and can interfere with proton transfer [62]. In order to further explain the high proton conductivity behavior of the SATS-GO composite membranes, AFM analysis was performed. Figure 2.17 shows the tapping mode AFM images of the SPAES, SPAES/GO-2.0, and SPAES/SATS-GO-2.0 membranes. The dark and bright domains correspond to the hydrophilic and hydrophobic regions, respectively [63]. Well-developed and larger ionic clusters can be observed from the SPAES/SATS-GO-2.0 membrane compared with other membranes because SATS-GO has additional sulfonic acid groups. TEM images of SPAES and SPAES/SATS-GO-2.0 are in good agreement with this result (Figure 2.18). These well-defined hydrophilic ionic clusters provide continuous and larger proton transport channels, which contributes to the relatively high conductivity of the SPAES/SATS-GO-2.0 membrane [64].

2.4. Conclusions

Sulfonated poly(arylene ether sulfone) (SPAES) composite membranes containing highly sulfonated SATS-grafted graphene oxide (SATS-GO) were prepared. Since the sulfonic acid groups in SATS-GO can effectively increase the interfacial interaction of the SPAES matrix with the filler and the GO units are able to scavenge the oxidative radicals, the mechanical strength and dimensional stability as well as the oxidative stability of the SPAES/SATS-GO composite membranes were found to be superior to those of the pristine SPAES membrane. The proton conductivities of the SPAES/SATS-GO composite membranes were higher than those of SPAES and SPAES/GO composite membranes over the entire range of RH because hydrophilic SATS-GO filler can effectively lower the proton transfer barrier and increase the water uptake capability of the membrane. In particular, 2.0 wt% of SATS-GO was found to be the optimum content to give the best membrane properties including mechanical strength and proton conductivity for the SPAES/SATS-GO composite membrane. Therefore, we believe that the incorporation of proper amount of SATS-GO with highly sulfonated polymers is an effective strategy to simultaneously improve the physicochemical stability and proton conductivity of sulfonated hydrocarbon-based PEMs for practical fuel cell applications.

2.5. References

- [1] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev., 104 (2004) 4587-4612.
- [2] C.H. Park, S.Y. Lee, D.S. Hwang, D.W. Shin, D.H. Cho, K.H. Lee, T.-W. Kim,T.-W. Kim, M. Lee, D.-S. Kim, Nature, 532 (2016) 480-483.
- [3] K. Kim, P. Heo, J. Han, J. Kim, J.-C. Lee, J. Power Sources, 401 (2018) 20-28.
- [4] K. Kim, B.-K. Jung, T. Ko, T.-H. Kim, J.-C. Lee, J. Memb. Sci., 554 (2018) 232243.
- [5] G. Wang, K.H. Lee, W.H. Lee, D.W. Shin, N.R. Kang, D.H. Cho, D.S. Hwang,Y. Zhuang, Y.M. Lee, M.D. Guiver, Macromolecules, 47 (2014) 6355-6364.
- [6] H. Xie, D. Tao, X. Xiang, Y. Ou, X. Bai, L. Wang, J. Memb. Sci., 473 (2015)226-236.
- [7] H. Zhang, P.K. Shen, Chem. Rev., 112 (2012) 2780-2823.
- [8] K. Kim, J. Bae, M.-Y. Lim, P. Heo, S.-W. Choi, H.-H. Kwon, J.-C. Lee, J. Memb. Sci., 525 (2017) 125-134.
- [9] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, J. Memb. Sci.,

197 (2002) 231-242.

- [10] Y.S. Kim, F. Wang, M. Hickner, S. McCartney, Y.T. Hong, W. Harrison, T.A. Zawodzinski, J.E. McGrath, J. Polym. Sci., B 41 (2003) 2816-2828.
- [11] N. Li, C. Wang, S.Y. Lee, C.H. Park, Y.M. Lee, M.D. Guiver, Angew. Chem.,123 (2011) 9324-9327.
- [12] H.-S. Lee, O. Lane, J.E. McGrath, J. Power Sources, 195 (2010) 1772-1778.
- [13] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, J. Memb. Sci., 219 (2003) 113-121.
- [14] M.-Y. Lim, K. Kim, Polymers, 10 (2018) 569.
- [15] T. Higashihara, K. Matsumoto, M. Ueda, Polymer, 50 (2009) 5341-5357.
- [16] T. Ko, K. Kim, S.-K. Kim, J.-C. Lee, Polymer, 71 (2015) 70-81.
- [17] D. He, H. Tang, Z. Kou, M. Pan, X. Sun, J. Zhang, S. Mu, Adv. Mater., 29(2017) 1601741.
- [18] Y. Devrim, A. Albostan, Int. J. Hydrogen Energy, 40 (2015) 15328-15335.
- [19] F. Xu, S. Mu, M. Pan, J. Memb. Sci., 377 (2011) 134-140.
- [20] H. Lee, M. Han, Y.-W. Choi, B. Bae, J. Power Sources, 295 (2015) 221-227.
- [21] M. Wei, M. Jiang, X. Liu, M. Wang, S. Mu, J. Power Sources, 327 (2016) 384-

393.

[22] D. He, Z. Kou, Y. Xiong, K. Cheng, X. Chen, M. Pan, S. Mu, Carbon, 66 (2014)312-319.

[23] M.-Y. Lim, H.J. Kim, S.J. Baek, K.Y. Kim, S.-S. Lee, J.-C. Lee, Carbon, 77(2014) 366-378.

[24] X. Qiu, T. Dong, M. Ueda, X. Zhang, L. Wang, J. Memb. Sci., 524 (2017) 663-672.

[25] J.-Y. Wang, S.-Y. Yang, Y.-L. Huang, H.-W. Tien, W.-K. Chin, C.-C.M. Ma, J. Mater. Chem., 21 (2011) 13569-13575.

[26] M.-Y. Lim, Y.-S. Choi, J. Kim, K. Kim, H. Shin, J.-J. Kim, D.M. Shin, J.-C. Lee, J. Memb. Sci., 521 (2017) 1-9.

[27] M. Feng, Y. Huang, Y. Cheng, J. Liu, X. Liu, Polymer, 144 (2018) 7-17.

[28] H.R. Thomas, A.J. Marsden, M. Walker, N.R. Wilson, J.P. Rourke, Angew. Chem. Int. Ed. Engl., 53 (2014) 7613-7618.

[29] H.R. Thomas, D.J. Phillips, N.R. Wilson, M.I. Gibson, J.P. Rourke, Polym. Chem., 6 (2015) 8270-8274.

[30] W.L. Harrison, F. Wang, J.B. Mecham, V.A. Bhanu, M. Hill, Y.S. Kim, J.E.McGrath, J. Polym. Sci. A: Polym. Chem., 41 (2003) 2264-2276.

- [31] K. Kim, S.-K. Kim, J.O. Park, S.-W. Choi, K.-H. Kim, T. Ko, C. Pak, J.-C. Lee,J. Memb. Sci., 537 (2017) 11-21.
- [32] S.-K. Kim, T. Ko, S.-W. Choi, J.O. Park, K.-H. Kim, C. Pak, H. Chang, J.-C. Lee, J. Mater. Chem., 22 (2012) 7194-7205.
- [33] M. Sumner, W. Harrison, R. Weyers, Y. Kim, J. McGrath, J. Riffle, A. Brink,M. Brink, J. Memb. Sci., 239 (2004) 199-211.
- [34] K. Mühlbach, V. Percec, J. Polym. Sci. A: Polym. Chem., 25 (1987) 2605-2627.
- [35] M.S. Jung, T.-H. Kim, Y.J. Yoon, C.G. Kang, D.M. Yu, J.Y. Lee, H.-J. Kim,Y.T. Hong, J. Memb. Sci., 459 (2014) 72-85.
- [36] I. In, S.Y. Kim, J. Polym. Sci. A: Polym. Chem., 43 (2005) 2021-2027.
- [37] H. Beydaghi, M. Javanbakht, E. Kowsari, Ind. Eng. Chem. Res., 53 (2014)16621-16632.
- [38] Z.-J. Jiang, Z. Jiang, X. Tian, L. Luo, M. Liu, ACS Appl. Mater. Interfaces, 9(2017) 20046-20056.
- [39] M.M. Nasef, H. Saidi, Appl. Surf. Sci., 252 (2006) 3073-3084.
- [40] Y. Jin, S. Qiao, L. Zhang, Z.P. Xu, S. Smart, J.C.D. da Costa, G.Q. Lu, J. Power Sources, 185 (2008) 664-669.

[41] L. Zhao, Y. Li, H. Zhang, W. Wu, J. Liu, J. Wang, J. Power Sources, 286 (2015)445-457.

[42] D. Liu, J. Peng, Z. Li, B. Liu, L. Wang, J. Power Sources, 378 (2018) 451-459.

[43] S. Peighambardoust, S. Rowshanzamir, M. Amjadi, Int. J. Hydrogen Energy, 35 (2010) 9349-9384.

[44] S.-K. Kim, T. Ko, K. Kim, S.-W. Choi, J.O. Park, K.-H. Kim, C. Pak, H. Chang,J.-C. Lee, Macromolecular Res., 20 (2012) 1181-1190.

[45] L. Lin, Z. Chen, Z. Zhang, S. Feng, B. Liu, H. Zhang, J. Pang, Z. Jiang, Polymer, 96 (2016) 188-197.

[46] H.-C. Chien, L.-D. Tsai, C.-P. Huang, C.-y. Kang, J.-N. Lin, F.-C. Chang, Int.J. Hydrogen Energy, 38 (2013) 13792-13801.

[47] H.Q. Li, X.J. Liu, J. Xu, D. Xu, H. Ni, S. Wang, Z. Wang, J. Memb. Sci., 509(2016) 173-181.

[48] T. Cheng, M. Feng, Y. Huang, X. Liu, Ionics, 23 (2017) 2143-2152.

[49] J.-R. Lee, N.-Y. Kim, M.-S. Lee, S.-Y. Lee, J. Memb. Sci., 367 (2011) 265-272.

[50] T. Ko, K. Kim, M.-Y. Lim, S.Y. Nam, T.-H. Kim, S.-K. Kim, J.-C. Lee, J. Mater. Chem. A, 3 (2015) 20595-20606. [51] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Chem. Mater., 15 (2003) 4896-4915.

[52] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Lee, Prog. Polym. Sci., 36 (2011) 1443-1498.

[53] S. Mu, C. Xu, Q. Yuan, Y. Gao, F. Xu, P. Zhao, J. Appl. Polym. Sci., 129 (2013)1586-1592.

[54] Y. Qiu, Z. Wang, A.C. Owens, I. Kulaots, Y. Chen, A.B. Kane, R.H. Hurt, Nanoscale, 6 (2014) 11744-11755.

[55] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, Chem. Rev., 107 (2007) 3904-3951.

[56] H. Liu, H. Gasteiger, A. Laconti, J. Zhang, ECS Trans., 1 (2006) 283-293.

[57] L. Wang, Y. Meng, S. Wang, X. Li, M. Xiao, J. Polym. Sci. A: Polym. Chem.,43 (2005) 6411-6418.

[58] C.Y. Tseng, Y.S. Ye, M.Y. Cheng, K.Y. Kao, W.C. Shen, J. Rick, J.C. Chen, B.J. Hwang, Adv. Energy Mater., 1 (2011) 1220-1224.

[59] Y.-L. Liu, J. Memb. Sci., 332 (2009) 121-128.

[60] B.-X. Yang, J.-H. Shi, K. Pramoda, S.H. Goh, Compos. Sci. Technol., 68 (2008) 2490-2497. [61] A. Goni-Urtiaga, D. Presvytes, K. Scott, Int. J. Hydrogen Energy, 37 (2012) 3358-3372.

[62] B.G. Choi, Y.S. Huh, Y.C. Park, D.H. Jung, W.H. Hong, H. Park, Carbon, 50(2012) 5395-5402.

[63] X. Zhang, Z. Hu, L. Luo, S. Chen, J. Liu, S. Chen, L. Wang, Macromol. Rapid Commun., 32 (2011) 1108-1113.

[64] H. Hu, M. Xiao, S. Wang, Y. Meng, Int. J. Hydrogen Energy, 35 (2010) 682-689.

Sample	C (%)	H (%)	S (%)
GO	54.8	3.1	0.3
SATS-GO	39.0	1.8	4.6

Table 2.1 CHNS elemental analysis results for GO and SATS-GO.

Table 2.2 Chemical stability and mechanical properties of the SPAES and composite membranes.

Samples	Fenton's test		Mechanical properties			
	$ au_1^a$ (min)	$ au_2^b$ (min)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	
SPAES	60	140	37.9±2.3	3078±417	57.2±3.7	
SPAES/GO-2.0	140	220	53.5±2.3	4279±168	23.2±4.7	
SPAES/SATS- GO-1.0	100	200	53.5±8.8	3723±819	49.2±2.6	
SPAES/SATS- GO-2.0	80	180	62.2±3.0	4994±34	36.8±3.7	
SPAES/SATS- GO-3.0	60	160	46.6±1.2	4621±837	17.7±2.8	

^a The elapsed time when the membranes start to break into pieces in Fenton's reagent at 80 °C.

^b The elapsed time when the membranes dissolved completely in Fenton's reagent at 80 °C.

Table 2.3 IEC and proton conductivities of the SPAES and composite membranes at 80 $^{\circ}$ C.

Samples	IEC_w^a (meq g ⁻¹)	Proton conductivity (σ) (mS cm ⁻¹)					
		40%	50%	60%	70%	80%	90%
		RH	RH	RH	RH	RH	RH
SPAES	2.02	2.68	7.93	18.33	38.57	67.22	97.91
SPAES/GO- 2.0	1.96	2.05	6.28	16.20	35.35	67.01	114.90
SPAES/SATS- GO-1.0	2.00	3.28	9.25	21.97	44.19	80.59	123.71
SPAES/SATS- GO-2.0	2.00	4.63	12.24	27.37	52.66	90.00	131.43
SPAES/SATS- GO-3.0	1.97	3.18	9.03	21.60	42.96	77.74	118.,91
Nafion 117	-	12.70	22.57	35.70	53.05	75.73	107.98

^a Measured by a back-titration method.



Figure 2.1 Schematic illustration of (a) sulfonated poly(arylene ether sulfone) (SPAES) and (b) sulfonated poly(arylene thioether sulfone) (SATS).



Figure 2.2 ¹H-NMR spectrum of SPAES.



8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2

Figure 2.3 ¹H-NMR spectrum of SATS.



Figure 2.4 Preparation of sulfonated poly(arylene thioether sulfone)-grafted graphene oxide (SATS-GO).



Figure 2.5 FT-IR spectra of GO, SATS, and SATS-GO.


Figure 2.6 XPS analysis of GO and SATS-GO: (a) GO, (b) SATS-GO, and (c) S 2p spectra of SATS-GO.







Figure 2.7 XPS analysis of GO and SATS-GO. (a) Survey spectrum of GO, (b) S 2p spectra of GO, (c) C 1s spectra of GO, (d) survey spectrum of SATS-GO, (e) S 2p spectra of SATS-GO, and (f) C 1s spectra of SATS-GO.



Figure 2.8 TGA curves of GO, SATS, and SATS-GO.



Figure 2.9 Average lateral size of (a) GO and (b) SATS-GO confirmed by dynamic light scattering (DLS) results



Figure 2.10 Cross-sectional (left) and surface (right) SEM images of the membranes: (a) SPAES, (b) SPAES/GO-2.0, (c) SPAES/SATS-GO-1.0, (d) SPAES/SATS-GO-2.0, and (e) SPAES/SATS-GO-3.0. Scale bar, 1 μ m. The circles indicate the agglomerated domains.



Figure 2.11 (a) Water uptake and (b) swelling ratio behavior of the SPAES and composite membranes at various temperatures.



Figure 2.12 Area-based dimensional change of SPAES and composite membranes after being immersed in deionized water at 25 °C and 80 °C for 1 h: (a) SPAES, (b) SPAES/GO-2.0, (c) SPAES/SATS-GO-1.0, (d) SPAES/SATS-GO-2.0, and (e) SPAES/SATS-GO-3.0.



Figure 2.13 Chemical stability of the SPAES and composite membranes.



Figure 2.14 Stress-strain curves of the SPAES and composite membranes.



Figure 2.15 Proton conductivities of the SPAES and composite membranes at 80 °C as a function of relative humidity.



Figure 2.16 Schematic illustration for the fabrication and the structure of the SATS-GO composite membrane.



Figure 2.17 AFM phase images of the membranes: (a) SPAES, (b) SPAES/GO-2.0, and (c) SPAES/SATS-GO-2.0.



Figure 2.18 Cross-section TEM images of SPAES and SPAES/SATS-GO-2.0.

Chapter 3

Simple and Effective Cross-Linking Technology for the Preparation of Cross-Linked Membranes Composed of Highly Sulfonated Poly(ether ether ketone) and Poly(arylene ether sulfone) for Fuel Cell Applications

3.1. Introduction

As a promising replacement for traditional combustion engine systems, the proton-exchange membrane fuel cell (PEMFC) has attracted much attention in recent years due to its high energy conversion efficiency and eco-friendly operation [1, 2]. The proton-exchange membrane (PEM), which allows the proton to be transported from the anode to the cathode and separates fuel and gas, is recognized as a main component of the PEMFC [3, 4]. The current state-of-the-art PEMs based on perfluorosulfonic acid (PFSA) ionomers (e.g., Nafion and Flemion) have been adopted in the PEMFC from 1960s [5]. The PFSA ionomers composed of hydrophobic perfluorinated backbones and flexible side chains containing hydrophilic sulfonic acid groups can induce the highly phase-separated (hydrophilic/hydrophobic) structures producing high proton conductivity especially under high relative humidity (RH) condition, while the proton conductivity of the PEMs based on PFSA ionomers is not high enough under low RH condition [6]. Nevertheless, the PEMs based on PFSA ionomers typically suffer from several drawbacks such as limited operating temperature (0-80 °C) due to their low glasstransition temperatures and high cost of production [7-9].

To overcome these shortcomings, significant efforts have been made to develop

alternative PEMs based on sulfonated hydrocarbon polymers (SHPs) including sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly(arylene ether sulfone) (SPAES) due to their low fuel crossover, high thermal stability, and high mechanical strength [10-13]. However, the PEMs based on SHPs reveal relatively low proton conductivity compared to those based on PFSA ionomers due to the narrow and tortuous proton-conducting channels originating from their less developed phase-separated structures [14]. Meanwhile, the PEMs based on SHPs having a high degree of sulfonation (DS) can achieve comparable proton conductivity to those based on PFSA ionomers because high DS can lead to welldefined hydrophilic domains and sufficiently high concentration of ion-conducting groups for proton transportation [15]. However, considering the long-term operation, the poor physicochemical stability of the PEMs based on SHPs with high DS has impeded their direct utilization in the PEMFC system [9]. The introduction of the cross-linked structure has been considered as one of the effective strategies for improving the physicochemical stabilities of PEMs based on SHPs with high DS [16-20]. However, this technology is typically accompanied by a series of elaborate and complicated procedures such as polymer modification steps to introduce the cross-linkable junction groups [10, 21, 22]. In addition, the optimization process to choose the proper cross-linker having the desirable chemical structure, good solubility in the precursor solution, and optimum amount of cross-linker to get the membrane having the desired chemical and physical properties has been known to not be easy [23, 24].

Di Vona's group reported that SPEEK or polyphenylsulfone (SPPSU) could be self-cross-linked by thermal treatment in the presence of dimethyl sulfoxide (DMSO) acting as a catalyst and reactant [14, 25, 26]. In this study, we could successfully prepare cross-linked PEMs with high proton conductivity and physicochemical stability by cross-linking SPAES with the potassium sulfonate (K⁺) form using SPEEK with the proton (H⁺) form by the thermal treatment method developed by Di Vona's group. The cross-linking density of the PEMs could be easily controlled by adjusting the composition of SPEEK and SPAES. The preparation method of the cross-linked membranes and their PEM properties such as water absorption behavior, oxidative stability, mechanical properties, and proton conductivity are fully discussed. Furthermore, the fuel cell performance of the membrane electrode assembly (MEA) employing the cross-linked membrane consisting of the optimum composition of SPEEK and SPAES is also compared with that employing the commercialized PEM based on PFSA ionomer, Nafion 212, at 80 °C and under 100% RH condition.

3.2. Results and Discussion

Synthesis of sulfonated poly(ether ether ketone) and sulfonated poly(arylene ether sulfone)

Sulfonated poly(ether ether ketone) (SPEEK) was obtained by post-sulfonation of PEEK using concentrated H₂SO₄. The DS of SPEEK calculated from the ¹H NMR spectrum by comparing the integration of H3' and other peaks is about 88 mol % (Figure 3.1 (a)) [27,28]. SPEEK with a DS of 88 mol % (SPEEK88) was used in this study.

Sulfonated poly(arylene ether sulfone) (SPAES) was synthesized from the nucleophilic aromatic substitution reaction between the dihalo monomers (4,4'-difluorodiphenyl sulfone (DFDPS) and 3,3'-disulfonate-4,4'-difluorodiphenyl sulfone (SDFDPS)) and the dihydroxy monomer (4,4'-dihydroxybiphenyl (BP)). SPAES with a DS of 90 mol % (SPAES90) was intentionally prepared by adjusting the molar ratio of DFDPS to SDFDPS to 1:9 for the development of cross-linked PEMs that can show high proton conductivity. The chemical structure of SPAES90 with the potassium sulfonate (K⁺) form was characterized by the ¹H NMR spectrum (Figure 3.1 (b)). The DS of SPAES90 calculated from the ¹H NMR spectrum is

about 88 mol %, which is close to the DS value obtained from the feed molar ratio of DFDPS to SDFDPS. The number (M_n) and weight (M_w) average molecular weights of SPAES90 measured by the GPC analysis are 58,000 and 85,000 g mol⁻¹, respectively.

Preparation of cross-linked membranes

A series of cross-linked membranes (CM-Xs) was fabricated in one step, simultaneously casting and heating the mixture solution in DMSO composed of SPEEK88 with sulfonic acid (H⁺) groups and SPAES90 with potassium sulfonate (K⁺) groups. During the thermal treatment, some of the sulfonic acid groups in SPEEK88 were consumed by the reaction with DMSO forming the $-SO_2^+$ groups; then, the electrophilic aromatic substitution reaction between $-SO_2^+$ in SPEEK88 and the electron-rich positions of aromatic rings (*e.g.*, -O-Ar-O- and -O-Ar-Ar-O-) in both SPEEK88 and SPAES90 occurred, as shown in Figure 3.2 (a, b) [14, 16, 26]. The cross-linking reaction could also occur via the formation of aromatic sulfonic anhydride as an intermediate where DMSO enhances the reactivity of the benzenesulfonate anion (Figure 3.2 (c)) [26]. Since pK_a values of SPEEK88 and SPAES90 are not much different, proton and potassium ions can be easily exchanged each other; then, $-SO_2^+$ groups could be also formed from the potassium sulfonate (K^+) groups in SPAES90 in the presence of DMSO during the thermal treatment (Figure 3.3). The solubility test performed to systematically investigate the reaction conditions for the solvent-induced electrophilic aromatic substitution reaction in the CM-X system demonstrated that the cross-linked structure can only be constructed from polymer in the proton form (H^+) under the thermal treatment over 160 °C (Table 3.1 and Figure 3.4).

The cross-linked structure of CM-X was confirmed by comparing the FTIR spectra of SPEEK88, SPAES90, CM-33, and the remaining portion of CM-33 (rCM-33) after the gel fraction test using DMAc at 80 °C for 24 h (Figure 3.5). The absorption peaks of both SPEEK88 (at 1650 cm⁻¹ from C=O stretching vibration) and SPAES90 (at 690 and 1090 cm⁻¹ from O–S–O stretch and 1,2,4-substituted phenyl rings, respectively) observed from the spectrum of rCM-33 indicate that SPEEK88 and SPAES90 are involved in the formation of the cross-linked structure, CM-X system, together [23, 29, 30]. In addition, the formation of the cross-linked structure via $-SO_2$ – linkages could be confirmed by comparing the FTIR spectra of CM-100 and the SPEEK88 membrane. The increased intensity of the absorption peaks of 1,2,4-substituted phenyl rings at 1080 and 1220 cm⁻¹ and O=S=O stretching vibration of PhSO₂Ph at 1160 cm⁻¹ are observed in the difference spectrum between CM-100 and the SPEEK88 membrane in Figure 3.6 [25].

Since the amount of cross-linkable -SO2+ group is highly affected by the

contents of SPEEK88 in the mixture solution, the gel fraction of CM-Xs indicating the fully cross-linked portion in the membrane increases with the increase in SPEEK88 contents and the value is in the range from 62.2 wt % in CM-25 to 99.8 wt % in CM-100 (Figure 3.7). The gel fraction values of CM-Xs are larger than the SPEEK88 contents used to make the CM-X system. This result also supports that although the ortho-positions of phenylene groups located between electrondonating ether linkages in SPEEK88 have greater nucleophilicity than those in SPAES90 for the electrophilic aromatic substitution reaction, the nucleophilicity of those in SPAES90 is enough to participate in the electrophilic aromatic substitution reaction to form the cross-linked linkages during the membrane preparation procedure. Furthermore, since the potassium sulfonate groups in SPAES90 could be easily changed to sulfonic acid groups by the ion exchange, $-SO_2+$ groups could be formed from SPAES90 and they can also participate in the cross-linking reaction.

Morphology

The polymer miscibility is one of the critical issues for the preparation of blend membranes composed of more than two polymers because the phase-separated domains caused by the immiscibility of polymers can produce a physically unstable state and brittleness problems [31, 32]. Figure 3.8 shows the surface and crosssectional SEM images as well as photo images of CM-Xs. The transparent photo images of CM-Xs indicate that SPEEK88 and SPAES90 are miscible in the range of visible light wavelength size because they have the same sulfonated groups and a similar aromatic structure although they are cross-linked [24, 33-35]. The surface SEM images of CM-50, CM-67, and CM-100 exhibit a uniform structure without any pinholes, while those of CM-25 and CM-33 containing SPAES90 larger than 50 wt % show a nonuniform structure with small pinholes, although all the crosssectional SEM images of CM-Xs show a dense structure without any cracks or pinholes. Since the uncross-linked polymer chains located on the membrane surfaces can first diffuse into solvents, the nonuniform and small pinholes observed by the surface SEM images of CM-25 and CM-33 can be ascribed to the dissolution of the uncross-linked moieties of SPEEK88 and/or SPAES90 during the membrane preparation process [36]. To verify the dissolved materials from the surface of CM-25 and CM-33, the filtrates of CM-25 obtained by the filtration of CM-25 after being immersed in D_2O at various temperatures for 24 h were collected, and then ¹H NMR analysis was conducted. The filtrates of CM-50 were also collected by the same procedures, and the ¹H NMR analysis was carried out for comparison. Figure 3.9 shows the ¹H NMR spectra of the collected filtrates of CM-25 and CM-50. The characteristic peaks from 5.50 to 8.50 ppm corresponding to SPAES90 can be observed in the ¹H NMR spectra of the filtrates of CM-25 collected at 50 °C or higher but are not observed in those of CM-50 showing a uniform surface SEM image. Since CM-Xs were soaked in 1 M H₂SO₄ at 50 °C during the ion-exchange process, the nonuniform surfaces with small pinholes observed by the surface SEM images of CM-25 and CM-33 should be associated with the leaching-out portion of uncross-linked SPAES90.

Ion-exchange capacity, water uptake, and swelling ratio

The ion-exchange capacity (IEC_w) of membranes is closely related to their water uptake and proton conductivity because the IEC_w value reflects the number of ion (H⁺) exchangeable groups such as sulfonic acid groups per unit mass of membrane [24]. The IEC_w value of CM-X determined by a titration method is listed in Table 3.2. The IEC_w value of CM-X increases markedly with increasing content of SPAES90 because the hydrophilic repeating unit of SPAES90 contains two sulfonate groups, while that of SPEEK88 has only one sulfonate group.

Figure 3.10 (a) shows the water uptake behavior of CM-X and Nafion 212 after being soaked in deionized water at a given temperature for 4 h. The water uptake values of CM-25 and CM-33 above 60 °C could not be obtained because they swelled excessively to form expanded gels. In contrast, the water uptake values of CM-50, CM-67, and CM-100 could be obtained above 60 °C and they decrease with increasing cross-linking density as reported previously [10, 37]. For example, the water uptake values of CM-50, CM-67, and CM-100 at 70 °C are 423.7, 320.1, and 72.5%, respectively. Figure 3.10 (b) and Figure 3.11 show the swelling ratio behavior of the membranes evaluated at 25 and 70 °C. Since the swelling ratio of the membrane is highly associated with the water absorption behavior, the ratio of CM-X was found to be close to the water uptake behavior; the smaller swelling ratio is obtained from CM-X with higher cross-linking density. This result clearly demonstrates that although the cross-linked membranes are only composed of highly sulfonated polymers, the dimensional stability of the membranes can be improved by effectively suppressing the excessive water absorption through control of the cross-linking density.

Oxidative stability and mechanical properties

The oxidative stability of the membrane was investigated using Fenton's reagent (4 ppm FeSO₄ in 3 wt % H₂O₂ aqueous solution) at 80 °C (Table 3.3). The oxidative stability estimated by the elapsed times when the membranes break into pieces (τ_1) and dissolve completely (τ_2) in the Fenton's reagent increases with increasing cross-linking density. For example, τ_1 and τ_2 of CM-25 are 30 and 45 min, respectively, while those of CM-100 are 80 and 100 min, respectively. It is well known that the

higher the cross-linking density, the higher the oxidative stability [38]. In addition, since the water absorption ability of CM-X decreases with increasing cross-linking density, the diffusion of reactive oxygen species (*e.g.*, HOO· and HO·) in the membrane can be effectively prevented by increasing the cross-linking density [39, 40].

The mechanical properties of CM-X including the tensile strength, Young's modulus, and elongation at break were measured using a universal testing machine at room temperature under 45% RH condition (Table 3.3 and Figure 3.12). The mechanical properties of CM-Xs were found to be affected by the composition of SPEEK88 and SPAES90. It is well known that the pure membranes composed of highly sulfonated polymers without further modification and/or cross-linking processing show poor physical stability [24, 41, 42]. Therefore, the mechanical properties of CM-25 having the largest content of SPAES90 among CM-Xs could not be measured because a dumbbell specimen could not be prepared due to the very poor mechanical strength. However, when the contents of SPEEK88 increase from 33 to 100 wt %, CM-Xs reveal the mechanical properties that are comparable to those of other hydrocarbon-based PEMs showing good fuel cell performance due to the increased contents of the mechanically robust cross-linked structure [43-47]. The tensile strength and elongation at break values of CM-Xs except for CM-25 are in the range of 28.0–114.9 MPa and 4.7–38.1%, respectively.

Proton conductivity

The proton conductivities of CM-Xs were measured at 80 °C under various RH conditions (Figure 3.13 and Table 3.2). The proton conductivity of the membrane increases with RH, as commonly observed in previous studies [23, 48]. In addition, the proton conductivity value of CM-Xs increases with the increase in SPAES90 content; the values are in the order of CM-25 > CM-33 > CM-50 > CM-67 > CM-6100. Such tendency can be ascribed to the increased contents of hydrophilic sulfonic acid groups forming larger and better connected ion-conducting channels in the membrane system [49-51]. In particular, the enhanced proton conductivity at low RH regions (<50% RH) by the incorporation of SPAES90 in the membrane system could be confirmed by comparing the proton conductivity difference between CM-Xs (X = 67, 50, 33, and 25) and CM-100. For example, the proton conductivity values of CM-50 at 40 and 90% RH are 4.94 and 205.59 mS cm⁻¹, respectively, while those of CM-100 are 1.52 and 103.73 mS cm⁻¹, respectively. The conductivity ratios of CM-50 and CM-100 at 40 and 90% RH are 3.25 (4.94:1.52) and 1.98 (205.59:103.73), respectively. The different morphological characteristics confirmed by the cross-sectional TEM images between CM-50 and CM-100 support the proton conductivity difference (Figure 3.14). Although both CM-50 and CM-100 exhibit well-distributed hydrophilic and hydrophobic domains, CM-50 containing SPAES90 shows more distinct hydrophilic/hydrophobic phase separation and larger ionic clusters than CM-100 without any SPAES90. These well-defined and larger ionic clusters can provide continuous and larger protonconducting pathways, resulting in better proton conductivity of CM-50, especially at low RH regions [15, 52]. Since SPEEK88 and SPAES90 having highly sulfonated structures are stably incorporated into the membrane system through our crosslinking technology, the proton conductivity values of CM-Xs are comparable to or larger than those of recently reported PEMs based on SHPs (Table 3.4). In addition, CM-25 having an IEC_w value of 2.88 meq g^{-1} shows larger proton conductivity than the commercially available PEM based on PFSA, Nafion 212, even at the low RH such as 50%; still, Nafion 212 has larger proton conductivity than CM-25 at 40% RH due to the well-developed hydrophilic domains and strong acidity [53, 54]. The other CM-Xs having larger IEC_w values than Nafion 212 (0.90 meq g^{-1}) such as CM-33, CM-50, CM-67, and CM-100 (2.75, 2.49, 2.30, and 1.80 meg g^{-1} , respectively) also show larger proton conductivity under high RH condition such as 90% than Nafion 212, although they revealed higher RH dependency than Nafion 212. For the investigation of the long-term stability of the membranes, the proton conductivity behavior of CM-50 and CM-100 was measured with humidity change by repeating the hydration and dehydration cycles, as shown in Figure 3.15.

Fuel cell performance

Considering the proton conductivity and physicochemical stability of CM-Xs, CM-50 was selected for the preliminary MEA performance test. Although the proton conductivity of CM-50 is lower than those of CM-33 and CM-25, the mechanical properties and oxidative stability of CM-50 are superior to theirs. Figure 3.16 shows the polarization and power density curves for the H₂/air single cell of MEA employing CM-50 at 80 °C and under 100% RH condition. For comparison, the MEA employing Nafion 212 was also prepared and measured under the same operating condition. The cell voltages of the MEA with CM-50 are lower than those with Nafion 212 in the low current density ranges $(0-0.6 \text{ A cm}^{-2})$ due to its larger interfacial resistance with electrodes. Since the binder materials used for the electrode layers are PFSA ionomers, the larger interfacial resistance between CM-50 composed of hydrocarbon polymers and the electrodes containing PFSA ionomers can be expected and thereby induces the rapid decrease in MEA performance at the charge-transfer resistance region (*i.e.*, low current density range) as reported by others [55, 56]. However, the MEA with CM-50 shows larger cell voltages from the current density ranges of 0.6 to 1.8 A cm⁻² due to the larger proton conductivity of CM-50, resulting in lowering the membrane resistance under the MEA operation. Furthermore, since Nafion 212 could be highly influenced by the mass transfer limitations in the high current density ranges above 0.8 A cm⁻², a drastic decrease in cell voltage values of Nafion 212 was observed as reported before [15, 46, 47]. Therefore, a larger maximum power density value of the MEA employing CM-50 (0.70 W cm⁻²) than that employing Nafion 212 (0.58 W cm⁻²) can be obtained from our preliminary MEA performance test. The cell performance of the MEA employing CM-50 was found to be better than and/or comparable to those employing SHPs reported before, as shown in Table 3.5. However, opencircuit voltage (OCV) of the MEA employing CM-50 is smaller than that of the MEA employing Nafion 212, as shown in the Y axis of Figure 3.16, indicating that a certain degree of fuel leakage might occur across CM-50 [58]. Although our cross-linking method could improve the physicochemical stability of highly sulfonated SPAES membranes for some degree, physical and dimensional stabilities of the CM-X are not good enough to achieve the larger OCV value. We believe that MEAs from CM-X would have much improved fuel cell performance once we can obtain the optimum condition for the preparation of the cross-linked membrane such as the DS value of the polymer, cross-linking density, and polymer structure.

3.3. Conclusions

Cross-linked membranes (CM-Xs) with different cross-linking densities could be easily prepared by *in situ* casting and heating the DMSO solution containing the mixture of sulfonated poly(ether ether ketone) (SPEEK88) and sulfonated poly(arylene ether sulfone) (SPAES90) in different ratios without any complicated chemical reaction steps and reagents. CM-Xs having outstanding proton conductivity and physicochemical stability could be produced through the solventinduced electrophilic aromatic substitution reaction using SPEEK88 and SPAES90 having high DS by controlling the composition and cross-linked density. Such SHPs with high DS having a linear structure have not been easily applied for PEM applications due to their poor physicochemical stability. Subsequently, the cell performance of the MEA employing CM-X with the optimized cross-linking density was found to be better than that employing the commercialized PFSA membrane, Nafion 212, at 80 °C and under 100% RH condition. We believe that such a simple and effective cross-linking strategy is applicable to the preparation of PEMs based on the SHPs with high DS for practical PEMFC applications. In addition, the CM-X system can be applicable to various energy materials because the membrane structure is easily tuned by changing the composition and ionexchange capacity of polymers to address various electrochemical devices.

3.4. Experimental

Materials

4,4'-Dihydroxybiphenyl (BP, 97.0%, Aldrich) and 4,4'-difluorodiphenyl sulfone (DFDPS, 99.0%, Aldrich) were purified by recrystallization from methanol and toluene, respectively. 3,3'-Disulfonate-4,4'-difluorodiphenyl sulfone (SDFDPS) was prepared by the procedure reported by Harrison *et al.* (80% of yield) [59]. Potassium carbonate (K₂CO₃, 99.0%, Aldrich) and calcium carbonate (CaCO₃, 99.0%, Aldrich) were dried under vacuum at 80 °C, prior to use. *N,N*-Dimethylacetamide (DMAc, 99.0%, Junsei), dimethyl sulfoxide (DMSO, 99.0%, Junsei), and toluene (99.5%, Junsei) were stored over molecular sieves under nitrogen. Isopropyl alcohol (IPA, 99.5%, Daejung), hydrogen peroxide (H₂O₂, 30.0%, Daejung), sulfuric acid (H₂SO₄, 95.0%, Daejung), and iron(II) sulfate heptahydrate (FeO₄S·7H₂O, 99.0%, Aldrich) were used as received. Poly(ether ether ketone) (PEEK, 450 PF, M_w = 39,200 g mol⁻¹) and Nafion 212 were purchased from Victrex and Aldrich, respectively. All other reagents and solvents were purchased from standard vendors and used as received.

Synthesis of sulfonated poly(ether ether ketone) and sulfonated poly(arylene ether sulfone)

Sulfonated poly(ether ether ketone) with a degree of sulfonation (DS) of 88 mol % (SPEEK88) was prepared by the sulfonation of PEEK using concentrated H₂SO₄ (Figure 3.17 (a)) [28]. PEEK (4.00 g) dissolved in 100 g of H₂SO₄ was stirred vigorously at 60 °C for 3 h. After cooling down to room temperature, the reaction mixture was precipitated in deionized water. The product was repeatedly washed with deionized water to completely remove the residual H₂SO₄ and then dried under vacuum at 80 °C for 24 h. The final product was obtained with 85% of yield.

Sulfonated poly(arylene ether sulfone) with a DS of 90 mol % (SPAES90) was synthesized from difluoro and dihydroxy monomers, as described in Figure 3.17 (b) [60]. The 500 mL three-neck round-bottom flask consisting of Dean–Stark apparatus, overhead stirrer, and nitrogen inlet and outlet was charged with 1.017 g (4.00 mmol) of DFDPS, 16.500 g (36.00 mmol) of SDFDPS, 7.450 g (40.00 mmol) of BP, 6.357 g (46.00 mmol) of K₂CO₃, and 4.604 g (46.00 mmol) of CaCO₃ in 161.36 mL of DMSO and 16.14 mL of toluene (DMSO/toluene = 10:1 v/v). The reaction mixture was refluxed at 150 °C for 10 h to allow azeotropic dehydration of the system; then, the temperature was raised to 190 °C to remove the toluene completely. The temperature was maintained for 48 h to obtain the viscous solution.
The resulting viscous solution was filtered to remove the salt and poured into IPA to precipitate the polymer. The precipitate was washed several times with IPA. After drying in a vacuum oven at 60 °C for 24 h, a yield of final polymer of 69% was obtained.

Preparation of the cross-linked membranes

Cross-linked membranes with various cross-linking densities formed by the mixtures of SPEEK88 and SPAES90 were named CM-X, where X denotes the weight percent (wt %) of SPEEK88 in the total amount of mixture (Figure 3.18). For example, CM-25 is composed of 25 wt % SPEEK88 and 75 wt % SPAES90. CM-Xs were prepared by the solution casting technique followed by subsequent thermal treatment: a total of 1.00 g of SPEEK88 and SPAES90 (the weight ratios of SPEEK88 and SPAES90 for CM-25, CM-33, CM-50, CM-67, and CM-100 are 1:3, 1:2, 1:1, 2:1, and 1:0, respectively) was dissolved in 7.33 g of DMSO to prepare a 12.0 wt % solution mixture. The solution was then spread onto a glass plate, thickness was controlled using an adjustable doctor blade, and the thermal treatment of the solution was followed. The cast solution was heated from 60 to 120 °C at a heating rate of 10 °C h⁻¹ and maintained at this temperature for 3 h in a convection oven until most of the solvent (*i.e.*, DMSO) evaporated. Then, the cast solution with

a trace amount of DMSO was heated at 160 °C for 12 h to construct the cross-linked structure *via* the residual DMSO-assisted electrophilic aromatic substitution reaction [25, 26]. After slowly cooling to room temperature, the obtained membrane was soaked in deionized water and detached from the glass plate. The membrane was treated with 1 M H₂SO₄ at 50 °C for 24 h and rinsed with deionized water several times to remove the residual solvent and H₂SO₄. The resulting membrane was dried in a vacuum oven at 60 °C for 24 h before use. The thicknesses of all the membranes were in the range from 20 to 30 μ m. Figure 3.18 shows a schematic representation of the CM-X preparation and photo image of CM-50 including the cross-linked structure formed by SPEEK88 and SPAES90. In addition, it can be confirmed that thermal decomposition of sulfonate groups in polymers did not occur during the thermal treatment, as shown in Figure 3.19.

Characterization

¹H NMR spectra were obtained from an AVANCE 400 (Bruker, Germany) at 400 MHz frequency using deuterated dimethyl sulfoxide (DMSO-*d6*) and deuterium oxide (D₂O). Fourier transform infrared (FTIR) spectra were recorded within the frequency range of 650 to 4000 cm⁻¹ in the attenuated total reflectance (ATR) mode using a Nicolet 6700 (Thermo Scientific, USA). The spectra were recorded as an

average of 32 scans with a resolution of 4 cm⁻¹. The molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC, Waters, USA) consisting of a Waters 2414 refractive index detector, a Waters 1515 isocratic HPLC pump at 40 °C, and three columns (Styragel HR 2, Styragel HR 3, and Styragel HR 4). The flow rate of HPLC-grade DMAc with lithium bromide was 1.0 mL min⁻¹. Calibration was performed using polystyrene standards.

The solubility test was conducted by soaking the samples in DMAc at 80 °C for 24 h. The gel fraction test was performed through the solvent extraction method. The dried membranes with 19 mm diameter were weighed (W_1) and then submersed in DMAc at 80 °C for 24 h. The membranes were washed several times with deionized water and then dried under vacuum until a constant weight (W_2) was obtained. The gel fraction of the membranes was calculated by the following equation

Gel fraction [%] = $W_2/W_1 \times 100$

The morphological characterization of the samples was analyzed using a JSM-6700F (JEOL, Japan) equipped with a field emission scanning electron microscope. Prior to the investigation, all the samples were coated by platinum under vacuum. The ion-exchange capacity (IEC_w) of the membranes was calculated by the back titration method. The dried membranes in the proton form (H⁺) were soaked in 1.0 M NaCl solution at 80 °C for 24 h, and then the obtained solution was titrated with 0.01 M NaOH solution. The IEC_w value was calculated from the following equation IEC_w = $(C_{NaOH} \cdot \Delta V_{NaOH}/W_s) \times 1000$

where C_{NaOH} , ΔV_{NaOH} , and W_s denote the concentration of NaOH, the consumed volume of NaOH, and the weight of the dried membrane, respectively.

The water uptake and volume swelling ratio of the membranes were obtained by measuring their changes in weight and volume in the dry and wet states, respectively. The dry membranes were cut into $1.0 \text{ cm} \times 2.0 \text{ cm}$ samples, and their weights and volumes were then recorded. Thereafter, the membranes were immersed in deionized water at various temperatures for 4 h. After the membranes were taken out and wiped, their weight and volume were measured. The water uptake and volume swelling ratio of the membranes were calculated using the following equations

Water uptake (%) = $(W_w - W_d)/W_d \times 100$

Volume swelling ratio (%) = $(V_w - V_d)/V_d \times 100$

where W_w and W_d denote the weights of the wet and dry membranes, respectively, and V_w and V_d denote the volumes of the wet and dry membranes, respectively.

The hydration number (λ) indicating the number of absorbed water molecules

per sulfonic acid group was obtained from the following equation

 $\lambda = (\text{water uptake} \times 10) / (18 \times \text{IEC}_w)$

The oxidative stability of PEMs was investigated by Fenton's test by monitoring the decomposition behavior of the membranes in Fenton's reagent (4 ppm Fe²⁺ in 3 wt % H₂O₂ aqueous solution) at 80 °C with an interval time of 5 min. τ_1 and τ_2 indicating the times when the membranes were decomposed into pieces and completely dissolved, respectively, were recorded. The mechanical properties of the membranes were measured using a Lloyd LS1 (Lloyd, UK). ASTM standard D638 (Type V specimens) was used for the preparation of dumbbell specimens. The measurement was carried out at room temperature and under 45% RH condition with a crosshead and a gauge length speed of 5 mm and 15 mm min⁻¹, respectively. For each measurement, at least 10 samples were tested and their average values were calculated.

The proton conductivity of the membranes was investigated by a four-probe method using an IM6ex impedance analyzer (ZAHNER-elektrik GmbH & Co. KG, Germany) at 80 °C with different relative humidity (RH) conditions from 40 to 90%. The conductivity values were determined by measuring the resistance acquired in a perturbation amplitude of 10 mV over the frequency range from 1 Hz to 1 MHz in the potentiostat mode. Before the measurement, all the membranes were equilibrated for 1 h in each RH condition using a humidity and temperature controllable chamber (Espec, SH-241). The proton conductivity (σ) was calculated using the following equation

Proton conductivity (σ) (mS cm⁻¹) = d/RS

where d, R, and S are the distance between the reference and sensing electrodes, the ohmic resistance, and the cross-sectional area (thickness × width) of the sample, respectively.

The transmission electron microscopy (TEM) images were obtained using a Talos F200S (FEI, USA) with 200 kV accelerating voltage. The samples were stained in 1.0 M lead acetate solution by ion exchange of the sulfonic acid groups. The stained samples were embedded in epoxy resin, cut into 80 nm-thick sections, and then placed on copper grids.

Fuel cell performance test

Membrane electrode assembly (MEA) was fabricated by the catalyst-coated gas diffusion layer (CCG) method, using the commercial gas diffusion layers coated with Pt/C and a Nafion binder (50 wt % Pt/C, FuelCellPower Inc.). After spraying an additional thin layer of Nafion, the gas diffusion layer and the membrane were

hot-pressed at 130 °C with a pressure of 10 kgf cm⁻². The geometric active area of the MEA was 5 cm², and Pt loadings were 0.4 mg cm⁻² in both the anode and cathode. The prepared MEA was inserted between two carved graphite channels with a serpentine-type flow path. The single cell was assembled with identical torque (80 kgf cm) and then connected to a fuel cell test station (Scitech Korea, Republic of Korea). Before measuring the single cell performance of the prepared MEA, the single cell was activated under hydrogen/air test condition. Fully humidified hydrogen and air without back pressure were supplied into the anode and the cathode at flow rates of 200 and 900 mL min⁻¹, respectively. For activation, 0.6 V was constantly applied to the MEA for 12 h prior to the cell performance evaluation. The polarization curve was obtained by the voltage sweep method with a step change of 50 mV per 25 s at 80 °C and 100% RH.

3.5. References

- [1] Y. Ye, L. Zhang, Q. Peng, G.-E. Wang, Y. Shen, Z. Li, L. Wang, X. Ma, Q.-H.Chen, Z. Zhang, J. Am. Chem. Soc., 137 (2015) 913-918.
- [2] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, Chem. Rev., 104 (2004) 4587-4612.
- [3] M. Marrony, R. Barrera, S. Quenet, S. Ginocchio, L. Montelatici, A. Aslanides,J. Power Sources, 182 (2008) 469-475.
- [4] K. Kim, P. Heo, J. Han, J. Kim, J.-C. Lee, J. Power Sources, 401 (2018) 20-28.
- [5] C. Heitner-Wirguin, J. Membr. Sci., 120 (1996) 1-33.
- [6] K. Kreuer, J. Membr. Sci., 185 (2001) 29-39.
- [7] K. Dutta, S. Das, P. P. Kundu, J. Membr. Sci., 473 (2015) 94-101.
- [8] W. H. Lee, K. H. Lee, D. W. Shin, D. S. Hwang, N. R. Kang, D. H. Cho, J. H. Kim, Y. M. Lee, J. Power Sources, 282 (2015) 211-222.
- [9] T. Higashihara, K. Matsumoto, M. Ueda, Polymer, 50 (2009) 5341-5357.
- [10] J. Han, K. Kim, J. Kim, S. Kim, S.-W. Choi, H. Lee, J.-j. Kim, T.-H. Kim, Y.-

E. Sung, J.-C. Lee, J. Membr. Sci., 579 (2019) 70-78.

[11] M. Gil, X. Ji, X. Li, H. Na, J. E. Hampsey, Y. Lu, J. Membr. Sci., 234 (2004)75-81.

[12] D. Li, Q. Guo, W. Zhai, J. Tong, X. Tan, Procedia Engineering, 36 (2012) 34-40.

[13] A. Reyna-Valencia, S. Kaliaguine, M. Bousmina, J. Appl. Polym. Sci., 98 (2005) 2380-2393.

[14] M. Di Vona, E. Sgreccia, M. Tamilvanan, M. Khadhraoui, C. Chassigneux, P. Knauth, J. Membr. Sci., 354 (2010) 134-141.

[15] N. R. Kang, S. Y. Lee, D. W. Shin, D. S. Hwang, K. H. Lee, D. H. Cho, J. H. Kim, Y. M. Lee, J. Power Sources, 307 (2016) 834-843.

[16] H. Hou, M. L. Di Vona, P. Knauth, J. Membr. Sci., 423 (2012) 113-127.

[17] C. Subramanian, M. Giotto, R. Weiss, M. T. Shaw, Macromolecules, 45 (2012)3104-3111.

[18] M. Hu, T. Li, S. Neelakandan, L. Wang, Y. Chen, J. Membr. Sci., 593 (2020)117435.

[19] L. Wang, Z. Liu, Y. Liu, L. Wang, J. Membr. Sci., 583 (2019) 110-117.

[20] M. Hu, B. Zhang, J. Chen, M. Xu, D. Liu, L. Wang, Int. J. Energy Res., 43(2019) 8753-8764.

[21] W. Mabrouk, L. Ogier, S. Vidal, C. Sollogoub, F. Matoussi, J. Fauvarque, J. Membr. Sci., 452 (2014) 263-270.

[22] S. Gu, R. Cai, Y. Yan, Chem. Commun., 47 (2011) 2856-2858.

[23] T. Ko, K. Kim, B.-K. Jung, S.-H. Cha, S.-K. Kim, J.-C. Lee, Macromolecules, 48 (2015) 1104-1114.

[24] K. Kim, P. Heo, T. Ko, K.-h. Kim, S.-K. Kim, C. Pak, J.-C. Lee, J. Power Sources, 293 (2015) 539-547.

[25] M. L. Di Vona, E. Sgreccia, S. Licoccia, G. Alberti, L. Tortet, P. Knauth, J. Phys. Chem B, 113 (2009) 7505-7512.

[26] B. Maranesi, H. Hou, R. Polini, E. Sgreccia, G. Alberti, R. Narducci, P. Knauth,M. Di Vona, Fuel Cells, 13 (2013) 107-117.

[27] S. J. Zaidi, S. D. Mikhailenko, G. Robertson, M. Guiver, S. Kaliaguine, J. Membr. Sci., 173 (2000) 17-34.

[28] J. Han, K. Kim, S. Kim, H. Lee, J. Kim, T. Ko, J. Bae, W. J. Choi, Y.-E. Sung,J.-C. Lee, J. Power Sources, 2019, 448, 227427.

[29] M. L. Di Vona, A. D'Epifanio, D. Marani, M. Trombetta, E. Traversa, S.

Licoccia, J. Membr. Sci., 279 (2006) 186-191.

[30] Y. Xue, R. Fu, C. Wu, J. Y. Lee and T. Xu, J. Membr. Sci., 350 (2010) 148-153.

[31] L. Chikh, V. Delhorbe, O. Fichet, J. Membr. Sci., 368 (2011) 1-17.

[32] X. Liu, Y. Zhang, S. Deng, C. Li, J. Dong, J. Wang, Z. Yang, D. Wang, H. Cheng, ACS Appl. Energy Mater., 1 (2018) 5463-5473.

[33] D. Liu, J. Peng, Z. Li, B. Liu, L. Wang, J. Power Sources, 378 (2018) 451-459.

[34] I. Bae, K.-H. Oh, M. Yun, M. K. Kang, H. H. Song, H. Kim, J. Membr. Sci., 549 (2018) 567-574.

[35] Y. Huang, L. Chuang, A. M. Kannan, C. Lin, J. Power Sources, 186 (2009) 22-28.

[36] C. Cuissinat, P. Navard, Macromol. Symp., 244 (2006) 1-18.

[37] B. Lin, F. Xu, F. Chu, Y. Ren, J. Ding, F. Yan, J. Mater. Chem. A, 7 (2019)13275-13283.

[38] J. Jang, D.-H. Kim, M.-K. Ahn, C.-M. Min, S.-B. Lee, J. Byun, C. Pak, J.-S. Lee, J. Membr. Sci., 595 (2020) 117508.

[39] R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, Chem. Rev., 107 (2007) 3904-3951.

[40] K. Kim, B.-K. Jung, T. Ko, T.-H. Kim, J.-C. Lee, J. Membr. Sci., 554 (2018)232-243.

[41] K. Kim, J. Bae, M.-Y. Lim, P. Heo, S.-W. Choi, H.-H. Kwon, J.-C. Lee, J. Membr. Sci., 525 (2017) 125-134.

[42] A. K. Mishra, N. H. Kim, D. Jung, J. H. Lee, J. Membr. Sci., 458 (2014), 128-135.

[43] Y. Lu, Y. Liu, N. Li, Z. Hu, S. Chen, J. Membr. Sci., 601 (2020) 117908.

[44] K. Kim, S.-K. Kim, J. O. Park, S.-W. Choi, K.-H. Kim, T. Ko, C. Pak, J.-C.Lee, J. Membr. Sci., 537 (2017) 11-21.

[45] L. Wang, Y. Wu, M. Fang, J. Chen, X. Liu, B. Yin, L. Wang, J. Membr. Sci.,602 (2020) 117981.

[46] K. H. Lee, J. Y. Chu, A. R. Kim, D. J. Yoo, ACS Appl. Mater. Interfaces, 10 (2018) 20835-20844.

[47] K. Kim, P. Heo, W. Hwang, J.-H. Baik, Y.-E. Sung, J.-C. Lee, ACS Appl. Mater. Interfaces, 10 (2018) 21788-21793.

[48] J. Miyake, M. Watanabe, K. Miyatake, ACS Appl. Mater. Interfaces, 5 (2013)5903-5907.

[49] S. Zhou, J. Kim, D. Kim, J. Membr. Sci., 348 (2010) 319-325.

[50] Y.-C. Yen, Y.-S. Ye, C.-C. Cheng, C.-H. Lu, L.-D. Tsai, J.-M. Huang, F.-C. Chang, Polymer, 51 (2010) 84-91.

[51] X. Li, C. Zhao, H. Lu, Z. Wang, H. Na, Polymer, 46 (2005) 5820-5827.

[52] H. Lee, J. Han, K. Kim, J. Kim, E. Kim, H. Shin, J.-C. Lee, J. Ind. Eng. Chem., 74 (2019) 223-232.

[53] H.-S. Lee, O. Lane, J. E. McGrath, J. Power Sources, 195 (2010) 1772-1778.

[54] A. Iulianelli, A. Basile, Int. J. Hydrogen Energy, 37 (2012) 15241-15255.

[55] C. H. Lee, S. Y. Lee, Y. M. Lee, S. Y. Lee, J. W. Rhim, O. Lane, J. E. McGrath, ACS Appl. Mater. Interfaces, 1 (2009) 1113-1121.

[56] K. Scott, W. Taama, P. Argyropoulos, J. Membr. Sci., 171 (2000) 119-130.

[57] K.S. Yoon, J.Y. Lee, T.-H. Kim, D.M. Yu, S.-K. Hong, Y.T. Hong, Eur. Polym.J., 66 (2015) 1-11.

[58] K. Teranishi, K. Kawata, S. Tsushima, S. Hirai, Electrochem. Solid-State Lett.,9 (2006) A475.

[59] W. L. Harrison, F. Wang, J. B. Mecham, V. A. Bhanu, M. Hill, Y. S. Kim, J. E. McGrath, J. Polym. Sci., Part A: Polym. Chem., 41 (2003) 2264-2276.

[60] K. Kim, P. Heo, T. Ko, J.-C. Lee, Electrochem. Commun., 48 (2014) 44-48.

Samples	Polymers used for membrane fabrication	Sulfonate groups in polymer (K ⁺ or H ⁺ form)	Thermal treatment temperature (°C)	Results of the solubility test ^a
0	SPAES90	K^+	160	(-) ^b
1	SPAES70°	\mathbf{K}^+	160	++
2	SPAES70	$\mathrm{H}^{+\mathrm{d}}$	120	++
3	SPAES70	H^+	140	±
4	SPAES70	H^+	160	_
5	SPEEK88	$\mathrm{K}^{+\mathrm{e}}$	160	++
6	SPEEK88	H^+	120	++
7	SPEEK88	H^+	140	±
8	SPEEK88	H^+	160	_

Table 3.1 Solubility test of samples using DMAc at 80 °C for 24 h.

^a ++, soluble; \pm , partially soluble; –, insoluble after being immersed in DMAc at 80 °C for 24 h.

^b Could not be prepared.

^c SPAES with DS of 70 mol% (SPAES70) was used instead of SPAES90 because SPAES90 membrane was soluble in deionized water during the preparation.

^d Obtained using 1.0 M H₂SO₄ solution.

^e Obtained using 0.1 M K₂CO₃ solution.

	IEC _w ^a	λ^{b}	Proton conductivity (σ) (mS cm ⁻¹) ^c					
Samples	(meq		40%	50%	60%	70%	80%	90%
	g ⁻¹)		RH	RH	RH	RH	RH	RH
CM-100	1.80	7.02	1.52	4.84	14.30	24.56	38.98	103.73
CM-67	2.30	17.40	2.71	8.95	21.08	35.82	66.88	126.50
CM-50	2.49	17.86	4.94	12.59	25.70	44.22	84.63	205.59
CM-33	2.75	20.24	10.17	24.65	43.73	74.02	126.77	259.87
CM-25	2.88	23.19	13.47	29.83	53.02	93.72	156.86	314.64
Nafion 212	0.90	-	19.80	26.50	37.55	50.48	68.80	94.20

Table 3.2 IEC_w, hydration number, and proton conductivities of membranes.

^a Measured by a back-titration method at 80 °C. ^b Calculated at 40 °C.

[°] Measured at 80 °C.

	Fenton's test		Mechanical properties			
Samples	$ au_1^a$ (min)	$ au_2^b$ (min)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	
CM-100	80	100	114.9 ± 7.7	6322 ± 832	38.1 ± 5.7	
CM-67	60	70	95.1 ± 6.2	5757 ± 878	27.0 ± 9.9	
CM-50	55	65	54.1 ± 2.0	3273 ± 522	26.7 ± 1.8	
CM-33	50	60	28.0 ± 6.5	2582 ± 257	4.7 ± 1.4	
CM-25	30	45	(-) ^c	(-) ^c	(-) ^c	

Table 3.3 Oxidative stability and mechanical properties of CM-Xs.

^a Elapsed time for membrane to start to break into pieces in Fenton's reagent at 80 °C.

^b Elapsed time for membrane to dissolve completely in Fenton's reagent at 80 °C. ^c Could not be measured due to the poor mechanical stability.

Table 3.4 Proton conductivity of various cross-linked membranes at mid temperatures (70-80 °C) under different RH conditions.

Deference	Mamhrana	Proton conductivity
Reference	Memoralie	$[mS cm^{-1}]$
		12.6 (50% RH)
This work	CM-50	44.2 (70% RH)
	Reference Membrane Proton Inis work CM-50 44.2 This work CM-50 44.2 205.0 29.8 This work CM-25 93.7 This work CM-25 93.7 Membr. Sci. 579 C-SPAES_7 43.0 2019) 70–78 C-SPAES_7 43.0 Membr. Sci. 549 CL-SPAEK/silica 2 018) 567–574 CL-SPAEK/silica 2 wer Sources 340 C-SPAEKS/K-SiO ₂ -8 132.0 017) 126-138 S-Am-2.0/C 135.0 019) 1104-1113 S-Am-2.0/C 135.0 019) 1104-1113 C-PEEK-sPOSS-3 160.0 18) 3624-3632 C-PEEK-sPOSS-3 160.0 State Ionics 316 CSPEN-CN-70 87.7	
		29.8 (50% RH)
This work	CM-25	93.7 (70% RH)
		314.64 (90% RH)
I Mambr Sai 570		11.9 (50% RH)
$\begin{array}{c} J. Memor. Sci. 579 \\ (2010) 70 78 \end{array}$	C-SPAES_7	43.0 (70% RH)
(2019) 70-78	C-SPAES_/ 43.0 (70% RH) 190.6 (99% RH 8-9 (at 70 °C and 50° RH) 220-230	
		8-9
		(at 70 °C and 50%
J. Membr. Sci. 549	CL SDAEK/silion	RH)
(2018) 567–574	CL-SFAEN/SIIICa	220-230
		(at 70 °C and 99%
		RH)
J. Power Sources 340	C-SPAEKS/K-SiO ₂ -8	132 (100% RH)
(2017) 120-150 Renewable Energy 138		
(2010) 1104-1113	S-Am-2.0/C	135.0 (100% RH)
Polym Chem 9		
(2018) 3624-3632	C-PEEK-sPOSS-3	160.0 (100% RH)
Solid State Ionics 316		
(2018) 110-117	CSPEN-CN-70	87.7 (100% RH)
RSC adv. 6 (2016)		
41428-41438	Cr-C/P-10	76.0 (100% RH)
Dolym Cham 7	CSPI90-6FATFVP10	210.0 (100% RH)
rolym. Cnem. / (2016) 1729 1725	CSPI85-6FATFVP15	171.0 (100% RH)
(2010) 4/28-4/33	CSPI80-6FATFVP20	153.0 (100% RH)

Solid State Ionics 323	C/COOH 10/NCC 10	142 0 (100% PH)
(2018) 5-15	C/COOII-10/NCC-10	142.0 (10070 KII)

Membrane	Membrane type	Thickness (µm) F	Fuels	Conditions (°C/ % RH/ Pressure)	Pt loading (mg cm ⁻²)		Peak power-	Ref.
					Anode	Cathode	density (mW cm ⁻²)	
CM-50	Cross-linked	25	H ₂ /Air	80/ 100/ ambient	0.4	0.4	700	This work
Nafion 212	-	50	H ₂ /Air	80/ 100/ ambient	0.4	0.4	580	This work
PEM-Si3	Composite	12-15	H_2/O_2	80/ 100/ ambient	0.38	0.38	738	[1]
sPEEK/POSS- SA (1.5 wt%)	Composite	30	H_2/O_2	80/ 100/ ambient	0.25	0.25	650	[2]
SPAEK (X9.1Y8.8)	Block copolymer	44	H_2/O_2	60/ 100/ ambient	0.3	0.3	323.9	[3]
sPPm- <i>b</i> -PAES- 16.6	Block copolymer	40	H ₂ /Air	80/ 100/ ambient	0.4	0.4	800	[4]
SPES 3	Block copolymer	50-60	H_2/O_2	80/ 100/ ambient	0.5	0.5	400	[5]
SQF-3	Terpolymer	15	H ₂ /Air	80/ 100/ ambient	0.5	0.5	650	[6]
SPP-QP	Random	30	H_2/O_2	80/ 100/ ambient	0.5	0.5	990	[7]
SPEEK	Random	-	H ₂ /Air	70/ 80/ ambient	0.5	0.5	636	[8]
SPEEK/SRGO- 1.0	Composite	-	H ₂ /Air	70/ 80/ ambient	0.5	0.5	705	[8]
SPAEK/PW- mGO 1 wt%	Composite	40-50	H_2/O_2	80/ 100/ ambient	1.0	1.0	486	[9]

Table 3.5 Fuel cell performance of MEAs operating from 60 to 100 °C.



Figure 3.1 ¹H-NMR spectra of (a) SPEEK88 and (b) SPAES90.



Figure 3.2 Schematics of possible mechanism of (a) $-SO_2^+$ formation from $-SO_3H$ by DMSO, (b) electrophilic aromatic substitution reaction between $-SO_2^+$ in SPEEK88 and electron rich positions of SPEEK88 or SPAES90, and (c) cross-linking reaction *via* aromatic sulfonic anhydride.



Figure 3.3 Schematics of ion exchange reaction of SPAES90, $-SO_2^+$ formation from $-SO_3H$ by DMSO, and electrophilic aromatic substitution reaction between $-SO_2^+$ in SPAES90 and electron rich positions of SPEEK88 or SPAES90.



Figure 3.4 (a) Before and (b) after solubility test of membranes using DMAc at 80 $^{\circ}$ C for 24 h.



Figure 3.5 FT-IR spectra of SPEEK88, SPAES90, CM-33, and rCM-33.



Figure 3.6 FT-IR spectra of (a) CM-100 (black line) and SPEEK88 membrane (blue line) and (b) difference spectrum between CM-100 and SPEEK88 membrane [(black line) – (blue line)]. SPEEK88 membrane (blue line) composed of linear structure was prepared using a casting solvent of DMAc instead of DMSO.



Figure 3.7 Contents of SPEEK88 used for the CM-Xs preparation and gel fraction of CM-Xs.



Figure 3.8 Surface (left) and cross-sectional (right) SEM images of CM-Xs: (a) CM-100, (b) CM-67, (c) CM-50, (d) CM-33, and (e) CM-25. The scale bars of surface and cross-sectional SEM images are 1 and 10 μ m, respectively. Photo images of each membrane are included.



Figure 3.9 ¹H-NMR spectra of SPAES90 and filtrates of CM-25 and CM-50 collected at various temperatures.



Figure 3.10 (a) Water uptake and (b) volume swelling ratio of membranes at various temperatures.



Figure 3.11 Area-based dimensional change of CM-X after being immersed in deionized water at 25 and 70 °C for 4 h: (a) CM-100, (b) CM-67, (c) CM-50, (d) CM-33, and (e) CM-25. Area-base dimensional change of CM-33 and CM-25 at 70 °C could not be measured due to the excessive swelling.



Figure 3.12 Stress-strain curves of CM-Xs.



Figure 3.13 Proton conductivity of the membranes.



Figure 3.14 Cross-section TEM images of (a) CM-100 and (b) CM-50.



Figure 3.15 Comparison of proton conductivity change between CM-50 and CM-100 with humidity cycling (*i.e.*, under repeated hydration (=80 °C, 98% RH for 1 h) and dehydration (=80 °C, 20% RH for 1 h)).

The proton conductivity of CM-50 and CM-100 was measured with humidity change by repeating the hydration (*i.e.*, under 80 °C, 98% RH for 1 h) and dehydration (*i.e.*, under 80 °C, 20% RH for 1 h) cycles to investigate the long-term stability of the membranes as shown in Figure S8. As expected, CM-100 having higher cross-linking density than CM-50 was found to have the better long-term stability showing less decrease in proton conductivity than CM-50 due to the better mechanical properties and dimensional and oxidative stabilities. This result indicates that the long-term stability can be controlled by the cross-linking density

and/or composition of SPEEK and SPAES in our CM-X system. However, it is noted that CM-50 showed larger conductivity values compared to CM-100 during the entire humidity cycling test. In the future work, we expect to improve the longterm stability of CM-X by controlling DS value, composition, and structure of polymers.



Figure 3.16 Cell performance of MEAs employing CM-50 and Nafion 212 at 80 °C and 100% RH condition.


Figure 3.17 Schematics of (a) sulfonated poly(ether ether ketone) (SPEEK88) and (b) sulfonated poly(arylene ether sulfone) (SPAES90).



Figure 3.18 (a) Schematic of CM-X preparation and (b) photo image of CM-50 including the cross-linked network structure formed by SPEEK88 and SPAES90. The weight ratios of SPEEK88 and SPAES90 used for the CM-X preparation are described.



Figure 3.19 (a) TGA thermogram of CM-50 and (b) isothermal TGA of CM-50 performed at 160 °C for 12 h.

Isothermal thermogravimetric analysis (TGA) was carried out to investigate whether thermal decomposition of sulfonate groups in polymers occurs during the cross-linked membrane preparation because the cast solution was thermally treated at high temperature (160 °C) for 12 h although it was reported that sulfonic acid groups are normally decomposed at 250 °C.¹⁴ Isothermal TGA of CM-50 was performed using Q-5000IR (TA instruments, USA) at 160 °C for 12 h and thermal decomposition of CM-50 from 120 to 700 °C was also characterized at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere for the comparison. All the samples were pre-heated at 120 °C for 15 min to evaporate the absorbed moisture and residual solvent. CM-50 shows a two-step thermal degradation behavior composed of decomposition of the sulfonic acid groups at about 250 °C and that of main chains

of polymers at about 500 °C, while the weight loss of CM-50 during the isothermal TGA performed at 160 °C for 12 h is very small as shown in Figure S11.¹⁴ From this result, it can be confirmed that thermal decomposition of sulfonate groups did not occur during the thermal treatment process.

초 록

본 연구에서는 나노복합막 및 가교막 제조를 위한 술폰화된 방향족 탄화수소계 고분자들의 합성, 그리고 이를 양성자 교환 막 연료전지 (PEMFC) 로 응용한 연구에 대하여 기술하였다. 먼저 PEMFC 로의 활용을 위한 술폰산 폴리(아릴렌 에테르 술폰) (SPAES) 복합막은 그 래핀 옥사이드 (GO) 와 술폰산 폴리(아릴렌 싸이오이써 술폰)이 도입 된 GO (SATS-GO) 를 복합재로 활용하여 제조하였다. SATS-GO 는 온화한 반응 조건 (50 ℃ 그리고 5 시간) 하에서 SATS 를 GO 표면에 도입시켜 제조하였다. SPAES 에 GO 와 SATS-GO 를 혼합 하여 복합막을 제조하였을 경우, 치수 안정성, 화학적 안정성, 기계적 강도가 증가하였다. 특히 SATS-GO 를 포함하고 있는 복합막은 프리 스틴 SPAES 막과 GO 를 포함하는 복합막 보다 높은 수소이온전도도 를 나타냈는데, 이는 GO 표면에 도입된 매우 술폰화된 고분자 (SATS) 가 수분 흡수율을 증가시키고 수소이온전도에 필요한 에너지 장벽을 낮추었기 때문이다. 또한 SATS-GO 의 술폰산기는 복합재와 주쇄고분자 사이의 상용성을 증가시킬 수 있는데, 이는 술폰산기와

133

SPAES 사이의 강한 수소 결합 때문이다.

둘째로, 가교 기술은 연료전지에 활용되는 양성자 교환 막 (PEM) 의 물리화학 안정성을 증가시키기 위한 효율적인 전략들 중 하나로 인 식된다. 그러나 양성자 전도성 가교막 제조를 위해 다양한 시약과 여러 단계를 거쳐야 하는 복잡한 과정은 가교 기술의 적용 확대를 저해하는 요인으로 인식된다. 본 연구에서는, 복잡한 화학 반응 및 촉매 또는 첚 가제를 활용하지 않는 고성능의 가교 된 PEM 개발을 위한 간단하고 효과적인 가교 기술을 기술하였다. 일련의 가교막들은 한 단계로 이루 어진 SPEEK 와 SPAES 를 포함하는 다이메틸 설폭사이드 (DMSO) 용액의 주조와 가열을 통해 제조되었으며, 이때 DMSO 는 용매와 촉 매로 동시에 활용되었다. 가교밀도를 조절함으로써, 가교막의 물리화학 안정성과 기계적 물성의 튜닝이 가능하였으며, 제조된 가교막은 우수한 전도도를 나타냈다. 완전히 가습된 수소/산소 연료 및 80 ℃ 온도 조 건에서 최적화된 가교 밀도를 갖는 가교막으로 제조된 막 전극 접합체 의 최대전력밀도는 0.70 W cm⁻² 로, 이는 상용화된 나피온212막으로 제조된 막 전극 접합체의 최대전력밀도 (0.58 W cm⁻²) 보다 더 높은 수치였다.

주요어: 술폰산 폴리(아릴렌 에테르 술폰), 술폰산 폴리(에테르 에테르 케톤), 그래핀 옥사이드, 복합막, 가교, 양성자 교환막, 연료전지

학번: 2017-28196

성명: 이현희