



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)



## Effect of the spirobiindane group in sulfonated poly(arylene ether sulfone) copolymer as electrode binder for polymer electrolyte membrane fuel cells

Ji Eon Chae<sup>a,b</sup>, Bo Hyun Kim<sup>a,c</sup>, Jee Hyun Noh<sup>a</sup>, Jaewoo Jung<sup>a</sup>, Jin-Young Kim<sup>a</sup>,  
Jong Hyun Jang<sup>a</sup>, Sung Jong Yoo<sup>a</sup>, Hyoung-Juhn Kim<sup>a,b</sup>, So Young Lee<sup>a,\*</sup>

<sup>a</sup> Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul 136-791, Republic of Korea

<sup>b</sup> University of Science Technology (UST), 217, Gajeong-ro, Yuseong-gu, Daejeon 305-350, Republic of Korea

<sup>c</sup> Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 20 September 2016

Received in revised form 11 November 2016

Accepted 30 November 2016

Available online xxx

#### Keywords:

PEMFC

Hydrocarbon polymer

Electrode binder

High gas permeability

Spirobiindane group

### ABSTRACT

Electrode properties determine the membrane-electrode assembly (MEA) performance of fuel cells and are influenced by the materials and processing. A high-performance electrode requires good adhesion between the membrane and catalyst, excellent gas permeability, and good ion conduction. Here, sulfonated poly(arylene ether sulfone) (SPAES) containing a bulky spirobiindane (Spiro) group is proposed as a new hydrocarbon electrode binder for MEAs. The effect of the Spiro group on MEA performance was compared to that of the common biphenylsulfone. The structural differences between the two binders affected the mass transport region of the current-voltage polarization (related to gas permeation). The spiro-polyethersulfone (PES) had 115 times higher O<sub>2</sub> permeability (30 Barrer) than that of PES. From <sup>1</sup>H NMR spectra, the degree of sulfonation (DS) of each SPAES was confirmed, where the proton conductivity of Spiro 30, Spiro 20, and BPS 30 were 28.2, 10.1, and 26.9 mS cm<sup>-1</sup>, respectively. In addition, the DS of the electrode binder contributed to the Ohmic region of the i–V curve. The Ohmic resistance of these hydrocarbon binders was similar to that of commercial Nafion binder (0.13–0.15 Ω cm<sup>2</sup>). However, the charge transfer resistance of our binders was higher than that of Nafion due to insufficient gas permeability and low proton conductivity.

© 2016 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

### Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are electrochemical devices that are a promising energy source as they release few pollutants and have high energy conversion efficiency [1]. The membrane-electrode assembly (MEA) is a core component of a PEMFC, where the electrochemical reactions take place at the three-phase boundary of the catalyst, electrode binder, and proton exchange membrane (PEM). The electrochemical performance of the MEA is greatly affected by the connectivity between catalyst particles and electrode binders, and low interfacial properties between the PEM and catalyst layers. As the most widely used PEM

and electrode binder, perfluorosulfonic acid ionomer (PFSI) such as Nafion<sup>®</sup> (DuPont) has advantages such as high proton conductivity, excellent chemical stability, outstanding gas permeability owing to a bulky main chain containing fluorocarbon [2], and good adhesion between the PEM and catalyst layers. However, the PFSI has several drawbacks, including a high cost of manufacturing and a limited operating temperature of 80 °C [3].

Many research groups have been motivated to solve these challenges [4] and develop alternative hydrocarbon-based PEMs, such as polysulfones [3,5,6], poly(ether ether ketone) [7,8], polybenzimidazole [9,10], and polyimide [11,12]. Despite these extensive studies, a severe delamination problem occurs between MEAs based on hydrocarbon PEM and Nafion-based catalyst layers owing to incompatibility between the electrode binder and membrane material. Hence, in parallel to the development of hydrocarbon PEMs, the development of electrode binder with good

\* Corresponding author.

E-mail address: [sylee5406@kist.re.kr](mailto:sylee5406@kist.re.kr) (S.Y. Lee).

<http://dx.doi.org/10.1016/j.jiec.2016.11.047>

1226-086X/© 2016 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

proton transport properties, sufficient fuel gas permeability to the electrode, and optimized interfacial compatibility with the PEM is required.

To date, few studies regarding new hydrocarbon electrode binders have been reported, for example, sulfonated poly(ether ether ketone) [13,14], poly(arylene ether sulfone) [15,16] and polyimide [13,17,18]. These studies mainly focused on improving long-term stability by enhancing the adhesion between the PEM and electrode binder by using the same polymer material.

In this study, we have developed new type of hydrocarbon electrode binder based on sulfonated poly(arylene ether sulfone), which was designed to optimize gas permeability and MEA performance. The effect of the spirobiindane structure of the new hydrocarbon binder on MEA performance was investigated and compared with that of biphenylsulfone (BPS), a standard binder material.

## Experimental

### Materials

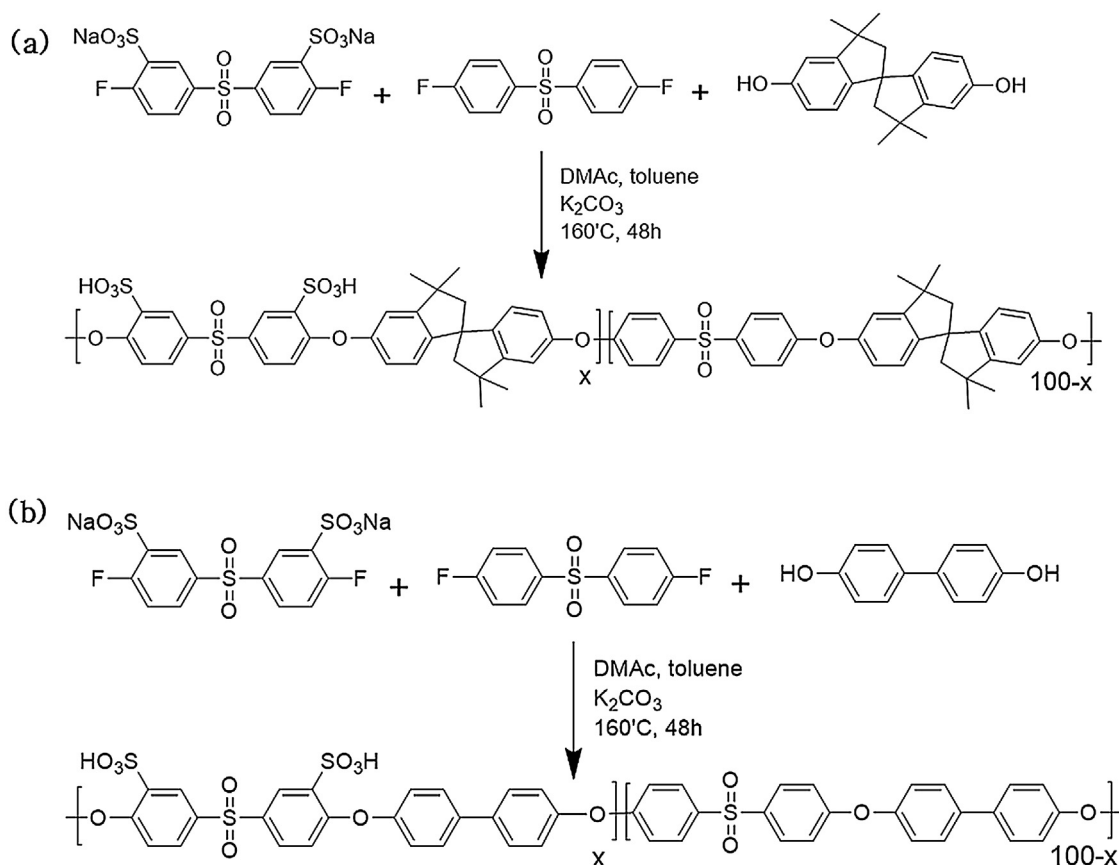
Bisphenol A (BPA), 4,4'-difluorodiphenylsulfone (DFDPS), 4,4'-dihydroxybiphenyl (BP), potassium carbonate ( $K_2CO_3$ ), methanesulfonic acid (MSA), anhydrous dimethylacetamide (DMAc), and toluene were obtained from Aldrich Chemical Co. Sulfuric acid was obtained from the Daejung Chemical Co. The DFDPS and BP were prepared by recrystallization using ethanol. 3, 3'-disulfonated DFDPS (SDFDPS) was synthesized as described in a previous study [19].

### Synthesis of monomer: spirobiindane-OH

BPA (20 g, 87.5 mmol) was added to MSA (35 ml) in a round bottom flask. The solution was stirred at 25 °C for 4 days. After this reaction, the solution was precipitated in deionized water in an ice bath at 10 °C. Finally, the product was obtained by recrystallization in ethanol. This spirobiindane-OH monomer was characterized by  $^1H$  NMR (300 MHz, dimethylsulfoxide-d<sub>6</sub>).  $\delta$  = 1.25–1.31 (m, 12H), 2.08–2.28 (m, 4H), 6.10 (s, 2H), 6.57–6.61 (m, 2H), 6.98–7.01 (m, 2H), and 8.99 (s, 2H) ppm.

### Synthesis of (SPAES)s (Spiro x and BPS x)

The synthesis conditions were calculated to achieve a degree of sulfonation of 30%. SDFDPS (1.3750 g, 3 mmol), DFDPS (1.7798 g, 7 mmol), and spirobiindane-OH (3.0842 g, 10 mmol) were placed in a 250 ml round bottom flask equipped with a mechanical stirrer, gas inlet, thermometer, condenser, and Dean-Stark apparatus. Anhydrous DMAc (12 ml) and toluene (6 ml) as a solvent and azeotropic reagent were injected into the flask and  $K_2CO_3$  (1.6752 g, 12 mmol) was added as a catalyst. The solution was stirred and heated up to 160 °C under reflux conditions to remove the water and toluene. After finishing the azeotrope, the reaction was maintained for 48 h. When the reaction was complete, the solution had a high viscosity and was precipitated in a 2-propanol/deionized water mixture (7:3 v/v) and washed several times. Then the precipitated copolymer was filtered and dried in a vacuum oven at 120 °C overnight. For the preparation of the sulfonated copolymers, the copolymers were soaked and stirred in 1 M



**Scheme 1.** Synthesis of sulfonated-poly(arylene ether sulfone)s (SPAES)s. (a) Structure including spirobiindane where x (the degree of sulfonation) is 20 or 30. (b) The common biphenylsulfone structure (BPS); x = 30.

Download English Version:

<https://daneshyari.com/en/article/6668893>

Download Persian Version:

<https://daneshyari.com/article/6668893>

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