

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhe

Synthesis and properties of bonding layer containing flexible and fluorinated moieties for hydrocarbon-based membrane electrode assemblies

Soo-Whan Nam ^{a,b}, Duk Man Yu ^{a,**}, Tae-Ho Kim ^{a,***}, Jang Yong Lee ^a, Sang Yong Nam ^b, Young Taik Hong ^{a,*}

^a Center for Membranes, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon, 305-600, Republic of Korea

^b Department of Materials Engineering, Gyeongsang National University, Jinju, Gyeongnam 660-701, Republic of Korea

ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form

22 April 2016

Accepted 25 April 2016

Available online 24 May 2016

Keywords:

Polymer electrolyte membrane

Bonding layer

Membrane electrode assembly

Sulfonated poly(arylene ether sulfone)

Decal transfer method

ABSTRACT

For membrane electrode assemblies (MEAs) consisting of hydrocarbon proton exchange membranes (PEMs) and Nafion-coated catalysts, the interfacial incompatibility between the membrane and electrodes has been a constant issue because it can seriously deteriorate the performance and long term stability of the MEAs. In this study, new bonding materials based on sulfonated aromatic copolymers with flexible and partially fluorinated structures (SPE/F) were prepared and tested as a proton conductive bonding layer on the surface of the hydrocarbon PEMs to increase the adhesive force to the catalyst layer. The SPE/F copolymers were synthesized by polycondensation of sulfonated and non-sulfonated dihalide monomers with two dihydroxy monomers, 4,4'-dihydroxy diphenyl ether (DHDPE) and hexafluoro bisphenol A (HFB). The molar feed ratio of DHDPE to HFB was varied (10:0, 7:3, and 4:6) in order to evaluate the effect of the polymer structure on the physical, electrochemical, and adhesive properties. With an increase in the HFB ratio, the proton conductivity and dimensional change of the resulting polymers decreased due to the enhanced chain rigidity and lower ion exchange capacity. The maximum adhesive strength of the bonding layer was obtained using a DHDPE:HFB ratio of 7:3 (SPE/F-7/3). Finally, the MEA utilizing SPE/F-7/3 as the bonding layer exhibited higher performance in the initial unit cell test, as well as a reduced increase in resistance after the durability cycling test compared with pristine MEA without the bonding layer.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +82 428607292; fax: +82 428607237.

** Corresponding author. Tel.: +82 428607198; fax: +82 428607237.

*** Corresponding author. Tel.: +82 428607379; fax: +82 428607237.

E-mail addresses: dmyu@kRICT.re.kr (D.M. Yu), thkim@kRICT.re.kr (T.-H. Kim), ythong@kRICT.re.kr (Y.T. Hong).
<http://dx.doi.org/10.1016/j.ijhydene.2016.04.174>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have received substantial attention as an alternative energy system because they can be used in various fields, such as automotive, stationary, and portable applications [1–3]. The proton exchange membrane (PEM) is a core component in PEMFCs because it functions not only as a proton conductor but also as a separator between the fuel and the oxidant. Nafion, a state-of-the-art polymer electrolyte material, is the most widely used PEM in PEMFC applications owing to its outstanding mechanical and chemical stability, along with its high proton conductivity. However, it still has critical drawbacks, such as high cost, high fuel permeability, and restricted operating temperatures below 100 °C, which prevent its practical application in PEMFCs [4–6].

Over the last decade, extensive research effort has been directed toward developing alternative membranes, i.e. hydrocarbon-based sulfonated polymers, to overcome the limitations of Nafion membranes. For example, sulfonated poly(ether ether ketone)s [7–10], sulfonated poly(arylene ether sulfone)s (SPAESs) [11–14], sulfonated polyimides (SPIs) [15–17], and sulfonated polyphenylenes [18,19] have been prepared and investigated as potential candidates for PEMs. In particular, SPAES membranes have received great attention due to their low production cost, excellent mechanical strength, high proton conductivity, excellent solubility, and membrane-forming property. Furthermore, they possess a wide operating temperature range because of their excellent thermal stability.

In spite of these beneficial features as PEMs, hydrocarbon-based sulfonated polymers have been considered unsuitable as binder materials for the catalyst layer, mainly due to their extremely low gas permeability [20–22]. Although there have been many attempts to displace the Nafion binder with a hydrocarbon-based substitute, most of them were unsuccessful owing to their much lower catalytic performance compared with that of Nafion binder-based electrodes [22]. In our previous study, we proposed a sulfonated poly(arylene ether sulfone) containing fluorenyl side groups as a new binder material, with the expectation that the bulky side groups would improve the oxygen permeability by increasing the *d*-spacing between the polymer chains [23]. Although the MEA utilizing this modified hydrocarbon-based binder was superior in performance and durability compared with the MEA utilizing a binder without bulky side groups, the performance was still much lower than that using the Nafion binder. Thus, use of the Nafion solution as the catalyst binder is still unavoidable, even for MEA fabrication using hydrocarbon-based PEMs [24,25].

Unfortunately, however, the combination of hydrocarbon PEMs and Nafion-coated catalysts for the MEA fabrication usually resulted in serious interfacial incompatibility between the membrane and the electrodes. For good contact between the membranes and electrodes in MEA, the use of binders that are similar in chemical nature to the membrane is strongly suggested. However, the Nafion binder with a perfluorinated structure in the electrode has very poor chemical affinity with hydrocarbon-based PEMs, which usually are composed of rigid chains with an entirely aromatic structure. As a result,

when using the decal transfer method (regarded as the most convenient process for mass-production of MEAs), the complete transfer of Nafion-binder-based catalyst layers to the surface of hydrocarbon-based PEM is very difficult to achieve, thus reducing the catalyst loading of the MEAs. Moreover, the interface instability of MEA causes the delamination of electrodes from the membrane during the running of the cell, which seriously deteriorates the performance and long-term stability [26–30].

To overcome these problems, McGrath et al. studied a SPAES random copolymer containing a partially fluorinated unit to improve the chemical affinity with the electrodes [31–33]. Park et al. fabricated MEAs with good interfacial adhesion by introducing a crosslinkable layer onto the surfaces of a SPI membrane [34]. The crosslinkable layer was coated by dipping the SPI membrane into poly(ethylene glycol) dimethacrylate solutions, and then was crosslinked together with the Nafion binder-based electrodes. They also reported the preparation of a crosslinkable layer using 1,1'-carbonyl diimidazole and hexamethylene diamine for sulfonated poly(ether ether ketone) membranes to improve the long-term stability in the hydration–dehydration cyclic test [35]. Recently, we developed a bonding layer composed of SPAES and polyvinylidene fluoride (PVdF) blends to improve the interfacial adhesion between the hydrocarbon-based membrane and electrodes [36]. The bonding layer was applied on the surface of a hydrocarbon-based PEM using a spraying technique to obtain an extremely thin layer (~700 nm) and thus minimize the increase in the MEA resistance. The membrane with the bonding layer containing 5 wt% PVdF exhibited the highest adhesion and cell performance as a result of the decrease in the interfacial resistance of the MEA.

In the present study, sulfonated aromatic copolymers with flexible and partially fluorinated structures (SPE/F) were prepared and utilized as a bonding layer to increase the adhesive force between the hydrocarbon-based PEMs and Nafion-binder-based catalyst layers. 4,4'-Dihydroxy diphenyl ether (DHDPE) and hexafluoro bisphenol A (HFB) were used as the monomers for preparation of the SPE/F copolymers. The former was chosen in order to enhance the adhesive property by increasing the concentration of flexible ether linkages in the backbone, and the latter was expected to improve the chemical compatibility with the Nafion binder in the electrode by providing fluorinated moieties on the membrane surfaces. The molar feed ratio of DHDPE to HFB was varied (10:0, 7:3, and 4:6) in order to evaluate the effect of the polymer structure on the physical, electrochemical, and adhesive properties. A spraying method was utilized to coat very thin SPE/F bonding layers on both sides of the hydrocarbon-based PEM. Finally, we fabricated the MEAs by a decal transfer method, and then measured the performance and durability of a unit cell using electrochemical analysis.

Experimental

Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was provided from Richem and recrystallized from ethanol. Disodium 3,3'-

Download English Version:

<https://daneshyari.com/en/article/1276813>

Download Persian Version:

<https://daneshyari.com/article/1276813>

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