



An electrode-supported fabrication of thin polybenzimidazole membrane-based polymer electrolyte membrane fuel cell

Seongmin Yuk ^{a,1}, Dong-Hyun Lee ^{a,1}, Sungyu Choi ^a, Gisu Doo ^a, Dong Wook Lee ^a, Hee-Tak Kim ^{a,b,*}

^a Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon, 34141, Republic of Korea

^b Advanced Battery Center, KAIST Institute for the NanoCentury, Korea Advanced Institute of Science and Technology (KAIST), 291, Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea



ARTICLE INFO

Article history:

Received 27 November 2017

Received in revised form

7 March 2018

Accepted 9 March 2018

Available online 11 March 2018

Keywords:

High temperature polymer electrolyte membrane fuel cell

Polybenzimidazole membrane

Membrane electrode assembly

Anode supported structure

Power performance

ABSTRACT

H₃PO₄-doped polybenzimidazole (PBI) membranes have been employed for high temperature polymer electrolyte membrane fuel cell (HT-PEMFC). Although a thinner PBI membrane is beneficial in enhancing power performance, the use of thin PBI membrane has been hindered by its poor mechanical property and consequent difficulty in membrane handling during membrane electrode assembly (MEA) fabrication. Here, novel fabrication route to realize a thin PBI membrane (~35 μm)-based HT-MEA is presented. The key feature of the process is to fabricate thin blend membrane of PBI and poly(ethylene glycol) (PEG) and laminate the blend membrane to anode gas diffusion electrode (GDE) followed by H₃PO₄ doping. The introduction of PEG to PBI film enables the tight bonding of the membrane to the GDE at a mild lamination temperature and mitigates the membrane expansion with the doping, preserving the tight interfacial bonding. Due to the lowered membrane thickness, the corresponding MEA exhibits a high power density of 264 mW cm⁻² at 0.6 V. Therefore, the new fabrication strategy based on the blend of PBI/PEG is highly effective in improving both process and power performance of HT-MEA.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

HT-PEMFC which operates in the temperature range of 150–180 °C without humidity have consistently attracted interest because of their advantages in comparison with low temperature PEMFCs which include high tolerance to fuel impurities, no need of humidifier, simpler cooling system and high temperature waste heat [1]. These features allow simpler and more efficient system design for co-generation of heat and power [1,2]. For providing proton transport at such high temperatures, MEA, the essential part of HT-PEMFC, exploits phosphoric acid (PA)-doped PBI membranes or their derivatives as a proton conducting membrane [3]. H₃PO₄ distributed in PBI matrix provides a proton conduction and PBI polymers impart a mechanical stability of the doped membrane.

For the fabrication of acid-doped PBI membrane, two methods have been suggested: 1) direct casting of the mixture of PBI and acid [4] and 2) after-doping of a preformed PBI membrane in a concentrated H₃PO₄ solution [5]. The doped membrane is then integrated with cathode and anode GDE [5–7].

The acid doping is an indispensable process, however, it softens PBI membrane, causing membrane tearing or folding in MEA fabrication. In fact, the difficulty in membrane handling is one of the factors restricting the use of a thinner PBI membrane for large scale MEA manufacturing. To avoid the failure during handling, a thick membrane (typically 100 μm) has been practically adopted [8], although the use of thick membrane is mainly responsible for the large ohmic polarization and poor power performance of HT-MEA. The mechanical property of the doped PBI membrane can be improved by lowering H₃PO₄ doping level, however, it inevitably accompanies a decrease of proton conductivity [9]. To overcome the trade-off between proton conductivity and mechanical strength, there have been some attempts including polymer blends [10–17], polymer composites [9,18–29], high molecular weight polymer [30], crosslinked copolymers [31–37], chemical treatment [38–45]

* Corresponding author. Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon, 34141, Republic of Korea.

E-mail address: heetak.kim@kaist.ac.kr (H.-T. Kim).

¹ These authors contribute equally.

and hybrid with porous support [46–49].

We believe that the aforementioned membrane handling issue can be also mitigated by a novel GDE-supported MEA fabrication. When the PBI membrane is processed with being supported on GDE, the stresses generated on the membrane during MEA fabrication can be reduced, and consequently, manufacturing failure be lessened. Such electrode-supported MEA has been employed for the fabrication of solid oxide fuel cells with a thin electrolyte; for cathode- and anode-supported SOFC design [50], electrolyte layer, thickness (10–20 μm) of which is much smaller than electrode thickness (100 μm), is formed on either cathode or anode, and is treated with being integrated with the supporting electrode during the subsequent MEA fabrication processes. However, the electrode-supported design has not been applied for PBI membrane-based HT-MEA yet. It is due to the technical hurdles lying in how to integrate PBI membrane and GDE and to preserve a tight interface between PBI membrane and GDE in whole fabrication processes. Namely, due to the high T_g of PBI (427 $^{\circ}\text{C}$), PBI membranes do not adhere to GDE at conventional fabrication temperatures. Furthermore, a volume expansion of PBI membrane during the acid doping could cause delamination of the membrane/GDE interface.

In this work, we present the novel electrode-supported fabrication of HT-MEA and demonstrate a 35 μm -thick PBI membrane-based HT-MEA. The key feature of this approach is the use of PEG as a plasticizer of PBI membrane. The function of PEG incorporated in PBI membrane is twofold. First, it lowers the T_g of PBI membrane and thus allows thermal lamination on anode GDE at a mild temperature of 130 $^{\circ}\text{C}$. Second, it minimizes the expansion of the PBI membrane during the acid doping, which prevents the delamination of the plasticized PBI membrane from GDE during the acid doping process, preserving a tight membrane/GDE interface in whole MEA fabrication steps. The PEG is dissolved out from the blend membrane during the acid doping process. Since the free volume generated by the removal of the PEG accommodates H_3PO_4 , the volume expansion by the acid doping can be minimized. The corresponding MEA with a 35 μm -thick, doped PBI membrane exhibits a high power density of 264 mW cm^{-2} at 0.6 V, which is much higher than that of the MEA with 100 μm PBI membrane fabricated by conventional method. Therefore, the new fabrication strategy based on the blend of PBI/PEG is highly effective in improving both production yield and power performance of HT-MEA.

2. Experimental

2.1. Preparation of GDE

Cathode catalyst layer is composed of PtCo alloy supported on carbon (Tanaka Kikinzoku Kogyo, 36V52E) and polyvinylidene fluoride (PVdF, Aldrich). The PtCo/C and PVdF were dispersed in NMP at the weight ratio of PtCo/C/ PVdF = 1/0.025. The resulting slurry was coated on diffusion layer with a microporous carbon layer (35BC, SGL) to fabricate cathode GDE. The Pt loading level for the cathode GDE was controlled to 1.6 mg-Pt cm^{-2} . For the anode catalyst layer, PBI was used as a binder instead of PVdF. Pt/C catalyst (46.6 wt% Pt), PBI solution (9 wt% PBI in DMAc), and vapor grown carbon fiber (VGCF) were added to DMAc solvent, followed by sonication for 2 h. The addition of VGCF was intended to improve the mechanical integrity of the catalyst layer. The weight ratio of catalyst, PBI, and VGCF was 1/0.243/0.08. The resulting slurry was coated on a diffusion layer (39BC, SGL) using knife coating method and the cast was dried at 60 $^{\circ}\text{C}$ overnight. The Pt loading for the anode GDE was controlled to be 0.39 mg-Pt cm^{-2} .

2.2. PBI/PEG blend membrane

For a tight interfacial bonding between the membrane and the anode GDE, a low molecular weight PEG (Mw: 400) was introduced to PBI membrane at a weight ratio of PBI/PEG = 1/1. A pre-determined amount of PEG was added to the 9 wt% PBI solution in DMAc, and stirred for 24 h. The resulting PBI/PEG solution was cast on a clean glass plate using a doctor-knife and the cast was dried at 60 $^{\circ}\text{C}$ overnight followed by the annealing at 110 $^{\circ}\text{C}$ for 10 min. The tensile strength of the PBI/PEG blend membrane was measured using universal test machine (Lloyd instruments, LR 5K) and compared with that of pristine PBI membrane. The thermal properties of the PBI/PEG membranes were investigated by using differential scanning calorimeter (DSC). In order to check whether the PEG remains in the membrane after the H_3PO_4 doping, Fourier transform infrared (FT-IR) spectra of the membrane before and after the doping were compared. To measure H_3PO_4 doping level and degree of volume expansion for the PBI/PEG membranes adhered to a supporter, the PBI/PEG membranes with various PBI/PEG ratios were prepared on a 25 μm -thick polyimide film; during the acid doping, the PBI/PEG blend membranes were tightly attached on the film. The H_3PO_4 doping level is usually measured by titration or weight change of membrane after acid doping [51–56]. Since the weight gains after the doping were quite large, the PA doping level of the membrane was determined gravimetrically by using the following equation.

$$\text{PA doping level (\%)} = \frac{W_a - w_{\text{PBI}} \times W_b}{w_{\text{PBI}} \times W_b} \times 100$$

where W_a and W_b are the weight of the membrane before and after doping, respectively, and w_{PBI} is the weight fraction of PBI of the pristine PBI/PEG blend membrane before doping.

2.3. MEA fabrication

A sub-gasket made of Kapton[®], which protects the membrane from electrode burr and provides a dimensional stability of the membrane required for cell assembly, was inserted in between the PBI/PEG membrane and the anode GDE. The assembly was then laminated at 130 $^{\circ}\text{C}$ and 30 atm for 10 min and further annealed at 150 $^{\circ}\text{C}$ for 10 min, resulting in a tight adhesion of the PBI/PEG membrane and the anode GDE. After that, the assembly was immersed in to H_3PO_4 solution (85 wt% H_3PO_4 in water) bath and stored at 60 $^{\circ}\text{C}$ for 12 h. The excess H_3PO_4 on surface of the membrane/anode assembly was carefully removed from the membrane. Under vacuum, the doped assembly was dried at 120 $^{\circ}\text{C}$ to remove any residual solvents and water. On the other hand, a pre-determined amount of H_3PO_4 solution was dropped and spread on the cathode GDE to impart proton conductivity to the cathode. The H_3PO_4 -impregnated cathode GDE and the H_3PO_4 -impregnated membrane/anode assembly were combined at a pressure of 10 atm.

2.4. Single cell measurement

A single cell, of which active area is 3 \times 3 cm^2 , was assembled using the HT-MEA, a pair of gasket, and a pair of graphite blocks with a single serpentine flow field. The single cells were connected to a test station equipped with an electronic load (Won A-Tech, Korea). The cells were typically operated at 150 $^{\circ}\text{C}$ and at total gas pressure of 100 kPa for both cathode and anode. Excess amounts of hydrogen (500 sccm) and air (1500 sccm) were injected to the

Download English Version:

<https://daneshyari.com/en/article/6603477>

Download Persian Version:

<https://daneshyari.com/article/6603477>

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