



Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

High-performance membrane-electrode assembly with an optimal polytetrafluoroethylene content for high-temperature polymer electrolyte membrane fuel cells



Gisu Jeong^{a, b, 1}, MinJoong Kim^{c, 1}, Junyoung Han^d, Hyoung-Juhn Kim^b, Yong-Gun Shul^a, EunAe Cho^{c, *}

^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

^b Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

^c Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

^d Section of Proton Conductors, Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark

HIGHLIGHTS

- PTFE has good potential for use as a binder material for MEA of HT-PEMFCs.
- Electrochemical characteristics and pore structure change with the PTFE content.
- PTFE in the electrode controls catalyst/electrolyte interface and pore volume.
- MEA containing 20 wt% PTFE exhibits the best cell performance of 0.5 A cm⁻² at 0.6 V.
- The MEA also exhibits excellent durability of the decay rate of 13 μV h⁻¹ for 500 h.

ARTICLE INFO

Article history:

Received 12 February 2016

Received in revised form

9 May 2016

Accepted 10 May 2016

Keywords:

High-temperature polymer electrolyte membrane fuel cell

Phosphoric acid

Membrane electrode assembly

Polytetrafluoroethylene

Pore structure

ABSTRACT

Although high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) have a high carbon monoxide tolerance and allow for efficient water management, their practical applications are limited due to their lower performance than conventional low-temperature PEMFCs. Herein, we present a high-performance membrane-electrode assembly (MEA) with an optimal polytetrafluoroethylene (PTFE) content for HT-PEMFCs. Low or excess PTFE content in the electrode leads to an inefficient electrolyte distribution or severe catalyst agglomeration, respectively, which hinder the formation of triple phase boundaries in the electrodes and result in low performance. MEAs with PTFE content of 20 wt% have an optimal pore structure for the efficient formation of electrolyte/catalyst interfaces and gas channels, which leads to high cell performance of approximately 0.5 A cm⁻² at 0.6 V.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are among the most attractive energy devices for use in stationary and automotive applications due to their high energy conversion efficiency, high power density and low air pollutant emissions. PEMFCs

generally operate at temperatures of below 80 °C under conditions of high humidity. This is primarily because the Nafion membranes that are used in these devices have sufficient proton conductivity only when they are in a hydrated state [1]. However, low temperature and high humidity operating conditions for PEMFCs lead to several issues, including a low tolerance to carbon monoxide (CO) poisoning of the platinum (Pt) catalyst [2] and water flooding in the stack [3–5]. Thus, PEMFCs require a complex fuel processor for CO removal and water management systems, resulting in a lack of system reliability and increased system costs.

* Corresponding author.

E-mail address: eacho@kaist.ac.kr (E. Cho).

¹ Equally contributed (co-1st author).

High-temperature operation (150–200 °C) yield a high CO tolerance [6,7], simple water management requirements [7] and efficient waste heat usage with combined cooling and heat. Accordingly, high-temperature PEMFC (HT-PEMFC) operation above 150 °C have been considered to solve the problems that are associated with low-temperature PEMFCs (LT-PEMFC) [8–10]. Nafion is not a suitable material for high-temperature operation. Thus, phosphoric acid-doped polybenzimidazole (PBI) membranes have been adopted as an electrolyte membrane due to their high thermal stability, high proton conductivity and low gas permeability at high temperatures [8,9]. However, the cell performance of HT-PEMFCs is still much lower than that of LT-PEMFCs and needs to be increased for practical applications; at a cell voltage of 0.6 V, current density has been reported to be $\sim 1.2 \text{ A cm}^{-2}$ for LT-PEMFCs [11] and $\sim 0.4 \text{ A cm}^{-2}$ for HT-PEMFCs [12,13].

The cell performance of a PEMFC strongly depends on the structure and fabrication process of the membrane-electrode assembly (MEA) because the electrochemical reactions and transport of reactants occur within the MEA [14–17]. In the case of LT-PEMFCs, impregnating a certain amount of Nafion ionomer, which acts as both a proton conductor and a binder, into the electrode is an effective way to enhance cell performance [18–21]. An optimal amount of Nafion in the electrode can maximize the amount of the triple phase boundaries (TPBs) where the Pt, reactant gases and a proton conducting phase are in contact. This MEA fabrication strategy enables high-performance LT-PEMFCs.

Phosphoric acid is used as the proton-conducting electrolyte in HT-PEMFCs. Because phosphoric acid is a liquid at operating temperatures, it can be distributed more evenly throughout the MEA than Nafion ionomers. A large amount of phosphoric acid in the MEA leads to a high catalyst/electrolyte interface area. However, phosphoric acid has very low oxygen solubility [22] and thus impedes the efficient transport of reactant gases to the Pt catalyst. Optimizing the phosphoric acid distribution can maximize the TPBs in the electrode. Many studies have attempted to accomplish this goal by examining appropriate polymeric binders, as was done for LT-PEMFCs [23–31]. As a result, PBI [23–27], polytetrafluoroethylene (PTFE) [27–30], and polyvinylidene fluoride (PVDF) [31] have been commonly assessed as candidate binder materials. Of these polymers, hydrophobic PTFE has good potential to be applied for efficient phosphoric acid distribution. PTFE-bonded MEAs with a proper level of hydrophobicity may allow for both a large phosphoric acid/catalyst interface area and large volume of reactant gas channels. However, the cell performance of PTFE-bonded MEAs has not improved significantly compared with MEAs bonded with other binder materials, and the MEA structure has not yet been optimized.

In this study, we focused on creating a high-performance HT-PEMFC MEA using a PBI membrane with high doping level of phosphoric acid and PTFE as an electrolyte and a binder material, respectively. Our *in situ* fabricated *p*-PBI membrane has a high phosphoric acid doping level of approximately 29 mol per PBI unit, which enhances the proton conductivity and cell performance [32]. To further increase the cell performance, we controlled the PTFE content in the electrode. Distribution of phosphoric acid in the electrode is affected by PTFE content owing to its hydrophobicity. Pore structure is also affected by PTFE content since PTFE makes catalyst particles agglomerate. By investigating the correlation between these structural variations and the electrochemical properties, we were able to generate high-performance MEAs for HT-PEMFCs with optimized binder content.

2. Experimental methods

2.1. MEA preparation

In situ p-PBI membranes were fabricated by the direct casting method described by Lee et al. [32]. 3,3-Diaminobenzidine, isophthalic acid (or terephthalic acid), and polyphosphoric acid were mixed in a three-neck reactor in an argon atmosphere at 220 °C for 18–24 h. The hot reaction solution was cast as a membrane with a doctor blade. The cast membrane was then cooled to room temperature. During the cooling process, the polyphosphoric acid was hydrolyzed to phosphoric acid by the moisture in the atmosphere.

The catalyst inks were prepared by mixing a carbon-supported Pt catalyst (Tanaka Kikinoku Kogyo, 45.9 wt% Pt) with a PTFE dispersion in water (Sigma Aldrich, 60 wt%), isopropyl alcohol, and deionized water. The amount of PTFE in the catalyst layer varied from 10 to 45 wt% (10, 20, 30 and 45 wt%). The mixed catalyst ink was sufficiently homogenized at approximately 13,000 rpm for 60 min to create a uniform dispersion and was then sprayed onto the gas diffusion media (SGL, Sigracet 10 BC). The catalyst-coated gas diffusion media, which is called the electrode, was dried at 60 °C in an atmospheric oven for 1 h and then heat-treated at 350 °C for 5 min in an N₂ gas environment. The MEAs were assembled by placing the fabricated electrodes on both sides of the *p*-PBI membrane without hot-pressing. The resulting active area of the MEAs was 7.84 cm², and the Pt loading of each electrode was 1.1 mg cm⁻².

2.2. Electrochemical and structural characterizations

Individual cells were assembled with the prepared MEA, graphite plates with serpentine flow-fields, and aluminum end plates. The assembled single cells were operated at 160 °C at atmospheric pressure using dry H₂ and air. The flow rates of H₂ and air were 114 cm³ min⁻¹ and 362 cm³ min⁻¹, respectively. Each cell was operated at 200 mA cm⁻² for 24 h before its electrochemical properties were measured. The current density – voltage (*i*-V) curves were measured to compare the performance of the cells. Electrochemical impedance spectroscopy (EIS) was conducted from 10 kHz to 10 mHz at 0.85 V with a 5 mV amplitude. Additionally, the pore size distribution of the electrodes were measured with a mercury porosimeter (Autopore IV 9500).

3. Results and discussion

Fig. 1(a) shows the *i*-V curves for the MEAs with various PTFE content. All of the *i*-V curves were measured after operating at 0.2 A cm⁻² for 24 h. This 24-h break-in period activated the MEAs until they reached a stable voltage. As shown in Fig. 1(a), the single cell with the 20 wt% PTFE MEA exhibited the best cell performance. With increasing PTFE content in the electrode from 10 to 20 wt%, the cell voltage at 0.2 A cm⁻² increased from 0.662 to 0.678 V; further increases in the PTFE content to 30 and 45 wt% led to decreases in the cell voltage to 0.661 and 0.638 V, respectively. To confirm the statistical relevance of the cell-performance according to PTFE content, we prepared three MEAs per each PTFE content (10, 20, 30 and 45 wt%) and then measured the voltage at 0.2 A cm⁻². As shown in Fig. 1(b), the MEA containing 20 wt% PTFE has the highest mean value of voltage at 0.2 A cm⁻². This change in cell performance was observed over the entire current density range. The change in current density at 0.6 V according to the PTFE content exhibited the same trend as the changes in cell voltage at 0.2 A cm⁻². The MEA that contained 20 wt% PTFE had a high cell performance of 0.5 A cm⁻² at 0.6 V. These results imply that the cell performance of an HT-PEMFC depends strongly on the PTFE content

Download English Version:

<https://daneshyari.com/en/article/7728039>

Download Persian Version:

<https://daneshyari.com/article/7728039>

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