Journal of Power Sources 283 (2015) 115–124

Contents lists available at ScienceDirect

Journal of Power Sources

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

Gas diffusion layers coated with a microporous layer containing hydrophilic carbon nanotubes for performance enhancement of polymer electrolyte fuel cells under both low and high humidity conditions

Tatsumi Kitahara [a, b, *], Hironori Nakajima [a, b], Kosuke Okamura [a]

[a] Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[b] International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

HIGHLIGHTS

- A GDL coated with the MPL containing hydrophilic CNTs is developed.
- Hydrophilic CNTs are effective at conserving the membrane humidity.
- Hydrophilic CNTs are effective at expelling excess water from the catalyst layer.
- The MPL with hydrophilic CNTs enhances the PEFC performance under both low and high humidity conditions.

ARTICLE INFO

Article history:
Received 3 December 2014
Received in revised form
19 January 2015
Accepted 21 February 2015
Available online 23 February 2015

Keywords:
Polymer electrolyte fuel cell
Gas diffusion layer
Microporous layer
Carbon nanotube
Hydrophilicity
Water management

ABSTRACT

Gas diffusion layers (GDLs) coated with a hydrophobic microporous layer (MPL) composed of carbon black and polytetrafluoroethylene (PTFE) have been commonly used to improve the water management characteristics of polymer electrolyte fuel cells (PEFCs). However, the hydrophobic MPL coated GDL designed to prevent dehydration of the membrane under low humidity conditions is generally inferior at reducing flooding under high humidity conditions. It is therefore important to develop a robust MPL coated GDL that can enhance the PEFC performance regardless of the humidity conditions. In the present study, a GDL coated with an MPL containing hydrophilic carbon nanotubes (CNTs) was developed. The less hydrophobic pores incorporating CNTs are effective at conserving the membrane humidity under low humidity conditions. The MPL with CNTs is also effective at expelling excess water from the catalyst layer while maintaining oxygen flow pathways from the GDL substrate, allowing the mean flow pore diameter to be decreased to 2 μm without reducing the ability of the MPL to prevent flooding under high humidity conditions. An MPL coated GDL with a CNT content of 4 mass% exhibits significantly higher performance under both low and high humidity conditions than a hydrophobic MPL coated GDL.

1. Introduction

Enhancement of the performance of polymer electrolyte fuel cells (PEFCs) requires an appropriate balance between the conservation of membrane humidity and the discharge of excess water produced in the cell. The design parameters associated with the gas diffusion layer (GDL) in a PEFC, such as its pore size, thickness and hydrophobic and hydrophilic properties, influence the water management characteristics during PEFC operation. Several investigations have demonstrated that a hydrophobic microporous layer (MPL) composed of carbon black and polytetrafluoroethylene (PTFE) coated on a GDL substrate can effectively improve the water management characteristics and thereby enhance the PEFC performance [1–7]. The appropriate MPL coated GDL will prevent dehydration of the membrane electrode assembly (MEA) under low humidity conditions and reduce flooding under high humidity conditions. However, the appropriate design parameters for the MPL coated GDL are different under low and high humidity

* Corresponding author. Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
E-mail address: kitahara@mech.kyushu-u.ac.jp (T. Kitahara).

http://dx.doi.org/10.1016/j.jpowsour.2015.02.115
0378-7753/

conditions [8]. An MPL coated GDL designed to prevent dehydration of the MEA under low humidity conditions is generally inferior at reducing flooding under high humidity conditions. It is highly desirable for a PEFC to be able to operate under a wide range of conditions, varying from low (or no) to high humidity. It is therefore important to develop a robust MPL coated GDL capable of enhancing PEFC performance regardless of the humidity conditions.

Although hydrophobic MPL coated GDLs have been commonly used in conventional PEFCs, some studies have recently reported that hydrophilic MPL coated GDLs [9–11] are effective at improving the water management characteristics of PEFCs, thereby enhancing the PEFC performance. The authors have also reported that a hydrophilic and hydrophobic double MPL coated GDLs was more effective at enhancing the PEFC performance under low humidity conditions than a hydrophobic MPL coated GDL [12]. This design involves the application of a thin hydrophilic layer on top of a hydrophobic MPL. The hydrophilic layer works to conserve the water content of the MEA, while the hydrophobic MPL between the hydrophilic layer and the carbon paper substrate prevents removal of water from the hydrophilic layer. This results in a significant enhancement of the ability to prevent dehydration of the MEA. The double MPL coated GDL is also effective at expelling excess water from the catalyst layer and thereby reducing flooding [13]. This enhances the performance under high humidity conditions as compared to that obtained when using a hydrophobic MPL coated GDL. The authors have subsequently developed a triple MPL coated GDL, in which the PTFE content in the hydrophobic MPL in contact with the hydrophilic layer is 30 mass%, and that in the MPL in contact with the substrate is 10 mass%, and found this approach to be an effective means of expelling excess water from the catalyst layer [14]. This results in further enhancement of the PEFC performance under high humidity conditions as compared to that obtained when employing the double MPL coated GDL. However, when fabricating either the double or triple MPL coated GDLs, the MPL slurries must be applied as coatings on the substrate several times using a bar coating machine, which is a drawback of this design since it renders the MPL coating process very complicated.

In the present study, a new GDL coated with an MPL containing hydrophilic carbon nanotubes (CNTs) is employed, such that the MPL coating process can be completed after only one application. Some studies have previously reported that MPLs containing CNTs effectively reduce the electrical resistance of GDL and, at the same time, increase mass transport, which enhances the PEFC performance under high humidity conditions [15–18]. In most of these studies, however, hydrophobic CNTs were used in the MPL, and thus the effect of hydrophilic CNTs applied to the MPL on the PEFC performance has not been clarified. Moreover, there are very few reports that have demonstrated that an MPL containing CNTs is effective at enhancing the performance under both low and high humidity conditions. Therefore, the present work examined the effects of using an appropriate MPL coated GDL containing hydrophilic CNTs, with the aim of achieving further enhancement of the PEFC performance regardless of the humidity conditions.

2. Experimental

2.1. Tested GDLs

The GDL used at the anode was commercial carbon paper without an MPL (SGL SIGRACET® 24BA) loaded with 5 mass% PTFE to impart hydrophobicity [3]. The SGL24BA GDL was 240 μm thick, with an areal weight of 54 g m^{-2} and 84% porosity. Table 1 summarizes the CNT, carbon black and PTFE contents in the MPL coated GDLs used at the cathode. The hydrophobic MPL (without CNTs) coated GDL consisted of a carbon paper substrate (SGL24BA) coated with an MPL composed of 80 mass% carbon black and 20 mass% PTFE. The MPL coated GDLs containing CNTs were made from a carbon paper substrate (SGL24BA) coated with MPLs composed of CNTs, carbon black and 20 mass% PTFE. The CNT content was varied between 2 and 8 mass%, and the sum of the CNT and carbon black contents was held constant at 80 mass% while maintaining the PTFE content at 20 mass%. The CNTs were 10–15 nm in diameter and had a length of 1–5 μm. The CNT surfaces had been modified by an oxidation treatment and, as a result, the contact angle of a CNT sheet was 30°, as shown in Fig. 1, demonstrating that the CNT surfaces exhibited relatively high hydrophilicity.

Table 1
CNT, carbon black and PTFE contents in MPL coated GDLs.

MPL coated GDL	CNT (mass%)	Carbon black (mass%)	PTFE (mass%)
MPL without CNTs	0	80	20
MPL with CNTs (2%)	2	78	20
MPL with CNTs (4%)	4	76	20
MPL with CNTs (8%)	8	72	20

2.2. Pore diameter, air permeability, water breakthrough pressure and contact angle measurements

Fig. 2 shows a schematic diagram of the test apparatus used to evaluate the air permeability values of the MPL coated GDLs [8]. A 13 mm-diameter GDL was placed between two cylindrical plates. The compressive force was controlled using a clamp screw and was measured using a load cell. The compression pressure was set at 1 MPa, which was similar to that measured in a typical PEFC. Air flow rates in the through-plane direction of the GDL were measured using a mass flow meter. The air permeance, q_a, was defined as the flow rate divided by the supplied air pressure and the permeable cross-sectional area at a diameter of 5 mm. The supplied air pressure was set at 1.23 kPa, this being the same pressure applied in the Gurley method [19].

The maximum pore and mean flow pore diameters of the GDLs were determined using a through-plane permeability technique according to the ASTM standard test method for pore size characteristics [20]. In this process, a low surface tension ($\gamma = 0.0157$ N m^{-1}) liquid [21] was used to wet the GDL and thus to fill its pores. The dry flow curve that represented the relationship between the flow rate and the supplied air pressure was obtained with a completely dry GDL. The wet flow curve was obtained with a wetted GDL, in which a wetting liquid filled the pores of the GDL. The half-dry flow curve corresponded to one half the measured dry flow curve at a given air pressure.

By applying an air pressure across the wetted GDL, the liquid

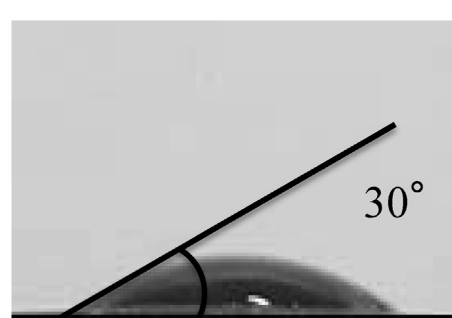

Fig. 1. Contact angle for a CNT sheet.