Journal of Power Sources 184 (2008) 165–171

Contents lists available at ScienceDirect

Journal of Power Sources

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

Highly efficient single-layer gas diffusion layers for the proton exchange membrane fuel cell

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ARTICLE INFO

Article history:
Received 25 March 2008
Received in revised form 25 May 2008
Accepted 26 May 2008
Available online 12 June 2008

Keywords:
Proton exchange membrane fuel cell
Single-layer gas diffusion layer
Carbon black
Poly(tetrafluoroethylene)
Vapor grown carbon nanofiber

ABSTRACT

In the present study, a series of highly efficient single-layer gas diffusion layers (SL-GDLs) was successfully prepared by the addition of a vapor grown carbon nanofiber (VGCF) in the carbon black/poly(tetrafluoroethylene) composite-based SL-GDL through a simple and inexpensive process. The scanning electron micrographs of the as-prepared VGCF-containing SL-GDLs (SL-GDL-CFs) showed that the GDLs had a microporous layer (MPL)-like structure, while the wire-like VGCFs were well dispersed and crossed among the carbon black particles in the SL-GDL matrix. Utilization of the SL-GDL-CFs for MEA fabrication was also done by direct coating with the catalyst layer. Due to the presence of VGCFs, the properties of the SL-GDL-CFs, including electronic resistivity, mechanical characteristic, gas permeability, and water repellency, varied with the VGCF content, with the overall effect beneficial to the performance of the proton exchange membrane fuel cell (PEMFC). The best performances obtained from the PEMFC with VGCFs at 15 wt.% was approximately 63% higher than those without VGCFs, and about 85% as efficient as ELAT GDL, a commercial dual-layer GDL, for both the H_2/O_2 and H_2/air systems.

1. Introduction

A promising alternative power plant for transportation, the proton exchange membrane fuel cell (PEMFC) boasts of high-energy efficiency, low emission, and low noise. This cell efficiency is determined by one of its core components: the membrane electrode assembly (MEA). Many factors, such as the amount of the catalyst [1–4], the type of proton exchange membrane [2,3,5], and the characteristics of the gas diffusion layer (GDL) [6–12], have been found to affect MEA efficiency. Among these factors, the GDL is a critical component for achieving high efficiency on the performance of PEMFC, with an ideal GDL requiring an optimal combination of the following: an effective path for the transport of gas reactants to the catalyst layers, a low electronic resistivity for the transmission of electrons, proper hydrophobicity for the prevention of water flooding, and a flexible surface for better contact with neighboring components. Recently, the effect of GDL's electronic resistivity on cell performance has been scrutinized through experimental investigations [9] and modeling studies [13,14]. The former revealed that while all other characteristics remained constant, the current density of the PEMFC increased with GDL's decreasing electronic resistivity [9]. As for modeling studies, these indicated that the lateral electronic resistivity of GDL, affected by the electronic conductivity, GDL thickness, and gas channel width, played a critical role in determining the current distribution and cell performance [13,14]. These results thereby confirmed the importance of reducing GDL's electronic resistivity for cell performance.

Our previous study prepared a novel single-layer gas diffusion layer (SL-GDL) based on the PTFE/carbon black composite [15]. Unlike the traditional multilayer GDL, the process for the preparation of the SL-GDL was simpler and less expensive. In addition, the as-prepared SL-GDL exhibited good mechanical property, high oxygen and air permeability, as well as sufficient water repellency, and it could be used without extra wet-proofing treatment and microporous layer (MPL) coating for MEA fabrication. Noteworthy too is that in both the H_2/O_2 and H_2/air systems, PEMFCs cell efficiencies fabricated with SL-GDL, including the current and power densities, were about half of that of ELAT GDL, which is a commercial dual-layer GDL with wet-proofing treatment and MPL on a non-woven web. Other factors might also affect PEMFCs performance; nevertheless, the discrepancies were mainly ascribed to SL-GDL's higher electronic resistivity caused by the disconnections between the carbon black particles, which are in turn due to the presence of the non-conductive PTFE. Therefore, diminution of electronic resistivity is one of the methods to further improve SL-GDL's efficiency on cell performance.

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doi:10.1016/j.jpowsour.2008.05.086

On the other hand, it is known that the vapor grown carbon nanofiber (VGCF), a graphitized carbon fiber with high aspect ratio, has high electronic conductivity, excellent mechanical properties, and a tendency to form a special network-like morphology [16–18]. It is for that reason that this study prepared a series of VGCF-containing SL-GDLs (SL-GDL-CFs) similar to the simple and inexpensive method used in SL-GDL [15]. The effects of VGCF on SL-GDL-CF properties were likewise studied and compared to those of SL-GDL and ELAT GDL. Moreover, the cell performance of the PEMFCs fabricated with as-prepared SL-GDL-CFs through direct coating with the catalyst layer and without extra wet-proofing treatment and MPL coating as applied on a conventional gas diffusion medium was also studied.

2. Experimental details

2.1. Preparation of VGCF-containing single-layer gas diffusion layers (SL-GDL-CFs)

The SL-GDL-CF samples were composed of carbon black (Vulcan XC-72, Cabot Co.), colloidal PTFE dispersion (D1-E, Daikin industries Ltd.), and vapor grown carbon nanofiber (VGCF; T-004, Yonyu Applied Technology Material Co., Ltd., Taiwan). The average size of the VGCF was approximately 30–100 nm in diameter and 1–10 μm in length. Preparation of the SL-GDL-CFs followed the same method used for SL-GDL preparation [15]. First, the VGCFs were dispersed in an appropriate amount of ethyl alcohol by an ultrasonic processor (VCX 750, Sonics & Materials, Inc.) with a frequency of 20 kHz. Sequential addition of the remaining ingredients to the dispersion was subsequently done; this was well mixed by a mechanical stirrer. The mixture was later calendered at room temperature and heat compressed under a pressure of approximately 75 kg cm^{-2}. Afterwards, the mixture was heated at 130 °C for 2 h to remove the residual solvent and then cooled to room temperature, resulting in the SL-GDL-CFs. These as-prepared SL-GDL-CF samples were homogeneous black sheets of about 0.38 ± 0.02 mm in thickness. The abbreviations and the corresponding compositions of the SL-GDL-CFs are summarized in Table 1. For comparison, ELAT LT 1200-N, which is a wet-proofed, MPL-coated, and non-woven webbed dual-layer GDL, was obtained from E-TEK Div. of De Nora N.A., Inc.; this was used as received.

2.2. Characterization and measurements

The morphology of the SL-GDL-CFs was characterized by a field-emission scanning electron microscope (FESEM, JEOL JSM-6330F). The electronic resistivity was measured by a four-point probe method using the combined system of a current supplier (AUTOLAB PGST30, Eco Chemie) and a voltmeter (Keithley 196). The measured current density and voltage were then converted to the corresponding electronic resistivity (Ω cm) [19]. Meanwhile, the mechanical properties of the as-prepared GDLs were determined using a tensile tester (Q-test) equipped with a 500 N load cell and a computer interfaced for data collection. All samples were prepared according to ASTM D638.

Concerning the GDLs' internal contact angles to water, these were determined via a combination of the Washburn method and Owens–Wendt calculation as previously reported [20]. The GDL sample was held by a metal clamp which was attached to a microbalance (AND, GR-120), while a beaker containing the test liquid was placed on a platform and was raised by a screw-type motor until the microbalance detected the GDL sample's contact to the liquid surface. The mass of liquid absorbed by the sample was recorded as a function of time through the computer interfaced with the microbalance. Consequently, the GDLs' internal contact angles to water and surface tensions were calculated according to the equations, as was described [20]. Five extra pure grade test liquids (*n*-hexane, acetone, methanol, toluene and benzyl alcohol; all acquired from ACROS Organic Company) were further applied for the measurements. All the results were determined with standard deviations based on the measurements of three samples for each GDL.

The GDL samples' gas permeability was performed by a gas permeability analyzer, which was designed as previously reported [5]. In the experiment, the inlet gas was humidified at 90 °C through a stainless steel water bottle, with the test temperature and flow rate of the inlet-humidified gas kept constant. The gas permeability coefficient (P, with unit of cm^3 (STP) cm/s cm^2 cm-Hg, also known as gas permeability) refers to the amount of gas, by volume, which penetrates a unit thickness and an area of specimen per unit time, under a constant temperature and unit pressure difference when the permeation is stable [21].

2.3. Fabrication of MEA and cell performance test

The as-prepared SL-GDL-CFs and the wet-proofed and MPL-coated ELAT GDL were separately coated with the catalyst layer to prepare the MEAs for use in the cell test. In preparation of the catalyst layer, 20 wt.% of Pt/C (HiSpec 3000, Johnson Matthey) was dispersed into 5 wt.% of Nafion solution (DE-2020, DuPont), keeping the weight ratio of Pt/C to the solid content of Nafion in the solution at 2 in order to form the slurry. The Pt/C slurry was then coated on the GDL sample by the spraying method. The amounts of Pt used were 0.3 mg cm^{-2} for the anode and 0.6 mg cm^{-2} for the cathode. The electrolyte membrane used was a Nafion membrane purchased from DuPont Company (NRE 212); this was pretreated according to a well-known membrane cleaning procedure prior to use [22], and was sandwiched between the two catalyst-coated GDLs at 140 °C under 70–75 kg cm^{-2} for 2 min. This resulted in a MEA of 25 cm^2 for a single cell test.

The corresponding single cell fixture was composed of the aforementioned MEA and a pair of graphite plates with a serpentine flow channel of 1 mm width and 1 mm depth. To circumvent the GDL from getting into the channels, the MEA (0.76 ± 0.04 mm in thickness) was placed between a pair of PTFE gaskets (TFE-15-25SP, Electrochem, Inc.), each of which has a thickness of 0.4 mm. Next, it was clamped between two stainless end plates, with eight bolts tightened to a uniform torque of 2.94 N m in order to ensure the GDLs' close contact with the graphite plates without getting into the channels.

During the test operation, the single cell fixture was connected to an in-house fuel cell test station. The fuel of the anode was hydrogen, and that of the cathode was either oxygen or air. Before cell testing, the leak test was performed with nitrogen gas to ensure that the single cell was gastight. Later, this single cell was operated at a constant voltage to activate the MEA until a stable current density was obtained [23]. The cell testing was carried out in both

Table 1
Abbreviations and corresponding compositions of the GDL samples

Sample	Carbon black (wt.%)	Colloidal PTFE dispersion (wt.%)[a]	VGCFs (wt.%)[b]
TFCB-3[c]	70	30	0
SL-GDL-CF0	80	20	0
SL-GDL-CF5	80	20	5
SL-GDL-CF10	80	20	10
SL-GDL-CF15	80	20	15

[a] Based on the weight of the solid content in the dispersion.
[b] Based on the percentage of carbon black.
[c] Sample prepared in Ref. [15].