

Short communication

Novel single-layer gas diffusion layer based on PTFE/carbon black composite for proton exchange membrane fuel cell

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Abstract

A series of poly(tetrafluoroethylene)/carbon black composite-based single-layer gas diffusion layers (PTFE/CB-GDLs) for proton exchange membrane fuel cell (PEMFC) was successfully prepared from carbon black and un-sintered PTFE, which included powder resin and colloidal dispersion, by a simple inexpensive method. The scanning electron micrographs of PTFE/CB-GDLs indicated that the PTFE resins were homogeneously dispersed in the carbon black matrix and showed a microporous layer (MPL)-like structure. The as-prepared PTFE/CB-GDLs exhibited good mechanical property, high gas permeability, and sufficient water repellency. The best current density obtained from the PEMFC with the single-layer PTFE/CB-GDL was 1.27 and 0.42 A cm⁻² for H₂/O₂ and H₂/air system, respectively.

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1. Introduction

The roles of gas diffusion layer (GDL) acting in a proton exchange membrane fuel cell (PEMFC) or a direct methanol fuel cell (DMFC) are not only as catalyst support but also as a transmitting path for electrons to flow between catalyst layers and bipolar plates. Moreover, the GDL also functions as the channel for transporting fuel to the catalyst layer and the path to remove the water produced from the catalyst layer of the cathode.

The GDLs used for fuel cell are usually constructed from conductive macro-porous substrates, such as woven carbon fiber cloth or non-woven carbon paper and known as gas diffusion medium (GDM). However, the macro-pores in GDM easily cause water flooding, resulting in hindering gas diffusion and reducing the catalyst's efficiency. Therefore, the overall performance of the fuel cell is decreased. In order to overcome the problem, a wet-proof treatment and microporous layer (MPL) are generally applied in sequence to form a multi-layer GDL. Depending on the type of fluoropolymeric resins, such as

poly(tetrafluoroethylene) (PTFE) or fluorinated ethylene propylene (FEP) dispersion, it has been reported that for better cell performance, the optimal fluoropolymeric resins loading should be about 10–30 wt.% in the GDL [1–5]. Nevertheless, due to the deposition of fluoropolymeric resins, the electronic resistivity of GDL is increased, and the pores are blocked, hindering water transportation [5].

On the contrary, the conductive substrates, either carbon fiber cloth or carbon paper, are all expensive materials. Furthermore, the traditional wet-proof treatment is a time-consuming process, which usually includes repeated dipping and heating steps [3,4]. Therefore, an effective and practical GDL for fabrication of the membrane electrode assembly (MEA) in PEMFC or DMFC requires not only sufficient conductivity, gas permeability, water repellency, and firm contacting with the bipolar plates, but also low cost and a simple process in preparation.

For the past decades, most researchers focused their studies on investigating the effects of PTFE loading [1–5], and the morphology [6–8], water transport [3,9–12], and characteristics [5,7,8,13–15] of the diffusion layer and the catalyst layer [16–20] based on the commercially available carbon fiber cloth or carbon paper GDLs. Only a few studies reported about the preparation of GDL using materials other than carbon paper or carbon cloth as the GDM. Recently, Hayashi et al. disclosed

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a low-cost process to produce a diffusion membrane from graphite, carbon black, sintered PTFE (preferably powder form) and un-sintered PTFE (preferably dispersion form) together with liquid lubricant and reported that the as-prepared diffusion membranes had sufficient water repellency, uniform properties throughout the layer, and suitable mass producibility. Their examples showed that the volume resistivity varied with the composition of graphite, carbon black, sintered PTFE, and un-sintered PTFE, implying that the corresponding performance of PEMFC with those GDL would be varied accordingly [21].

In this study, a series of PTFE/carbon black composite-based single-layer gas diffusion layers (PTFE/CB-GDLs) was prepared from carbon black and un-sintered PTFE, which included powder resin and colloidal dispersion, by a simple inexpensive method. The method comprised of mechanical mixing, rolling room temperature, and low-pressure compression. The effects of powder resin and the colloidal dispersion ratio (P/D) on the properties of PTFE/CB-GDLs were studied and compared with that of a commercial GDL with wet-proof treatment and MPL on non-woven web. In addition, the cell performance of the PEMFC fabricated with an as-prepared PTFE/CB-GDL without wet-proof treatment and MPL coating was also studied.

2. Experimental method

2.1. Preparation of PTFE/CB composite gas diffusion layers (PTFE/CB-GDLs)

The PTFE/CB-GDLs are composed of carbon black (Vulcan XC-72, Cabot Co.) and un-sintered PTFE, which included powder resin (L173J, ASAHI GLASS Co., Ltd.) and colloidal dispersion (D1-E, DAIKIN industries Ltd.). After mixing the ingredients well with a homemade shaker with frequency of 300 times min^{-1} [22], the mixture was calendered at room temperature and compressed at 75–85 °C under a low pressure between 70 and 80 kg cm^{-2} . Then the PTFE/CB-GDLs were obtained by heating the mixture at 130 °C for 2 h, and then cooling to room temperature. It was found that all the as-prepared PTFE/CB-GDLs were homogeneous black sheets and had a thickness of about 0.38 ± 0.02 mm. The abbreviations and corresponding compositions of the PTFE/CB-GDLs are summarized in Table 1. For comparison, a commercially available GDL with wet-proof treatment and microporous layer on non-woven web, ELAT GDL, was obtained from E-TEK (E-TEK Div. of De Nora N.A., Inc.) and was used as received.

Table 1
Abbreviations and corresponding compositions of the PTFE/CB-GDL samples

Sample	Carbon black (wt.%)	Powder resin (wt.%)	Colloidal dispersion (wt.%) ^a	P/D
TFCB-1	70	20	10	2.0
TFCB-2	70	10	20	0.5
TFCB-3	70	0	30	0

^a Based on the weight of the solid content in the dispersion.

2.2. Characterization and measurements

The morphology of PTFE/CB-GDLs was characterized by a filed-emission scanning electron microscope (FESEM, HITACHI S-4100). The electronic resistivity measurements of PTFE/CB-GDLs were performed by a four-point probe method using the combined system of a current supplier (AUTOLAB PGST30, Eco Chemie) and a voltmeter (KEITHLEY 196). The current density and voltage measured were further converted to the corresponding electronic resistivity ($\Omega \text{ cm}$) [23]. The mechanical properties of the as-prepared GDLs were determined using a tensile tester (Q-test) equipped with a 500 N load cell and interfaced with a computer for data collection. For the measurements, all the samples were prepared according to ASTM D638.

The internal contact angles to water of the GDLs were determined via a combination of the Washburn method and Owens-Wendt calculation as reported [24]. The GDL sample was held by a metal clamp which was attached to a microbalance (AND, GR-120). The test liquid in a beaker was placed on a platform and was raised by a screw-type motor until the microbalance detected the contact of GDL sample 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. After that, the internal contact angles to water and surface tensions of the GDLs were calculated in sequence according to the equations as described [24]. Five extra pure grade test liquids, *n*-hexane, acetone, methanol, toluene and benzyl alcohol, acquired from ACROS Organic Company was applied for the measurements. All the results were determined with standard deviations which were based on the measurements of three samples for each GDL.

The gas permeability of the GDL samples were performed by a gas permeability analyzer designed as reported [25]. The inlet gas was humidified through the stainless steel water bottle at 90 °C to simulate the situation of cell operation under the temperature. The pressure of the inlet humidified gas was kept at 1 kg cm^{-2} and the outlet pressure was measured, then the gas permeability (P) was calculated by the equations as described [26].

2.3. Fabrication of membrane electrolytes assembly (MEA) and cell performance test

For the cell test, two GDL samples were used. One was the commercially available wet-proof treated and MPL coated GDL, ELAT GDL, and the other was an as-prepared single-layer PTFE/CB-GDL, TFCB-2, used without extra wet-proof treatment and MPL coating. In the preparation of the catalyst layer, 20 wt.% of Pt/C (HiSpec 3000, Johnson Matthey) was dispersed into 5 wt.% of Nafion solution (DE-2020, Du Pont), i.e., the weight ratio of Pt/C to the solid content of Nafion in the solution was 2, to form the slurry. After that, the Pt/C slurry was coated on the GDL sample by the brushing 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 Du Pont Company (NRE 212). It

was pretreated according to a well-known membrane cleaning procedure prior to use [2], and was sandwiched between the two catalyst-coated GDLs at 140 °C under 70–75 kg cm⁻² for 2 min to obtain the MEA of 25 cm² for single cell test. The corresponding single cell fixture was composed of the aforesaid MEA and a pair of graphite bipolar plates with a serpentine flow channel of 1 mm width and 1 mm depth. In order to avoid the GDL getting into the channels, a gasket of 0.4 mm was placed between the GDL and the bipolar plates. 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 oxygen or air. Before the cell testing, the leak test was performed with nitrogen gas to ensure that the single cell was gastight. After that, the single cell was operated at the constant voltage to activate the MEA until a stable current density was obtained [27]. The cell testing was carried out in both H₂/O₂ and H₂/air systems. For the H₂/O₂ system, the flow rate of anode and cathode was 350 and 510 mL min⁻¹, respectively, while for the H₂/air system, the flow rate of anode and cathode was 350 and 710 mL min⁻¹, respectively. The operating temperatures of the anode humidification, the cathode humidification, and the cell test were 80, 65, and 65 °C, respectively, and the test was operated under an atmospheric pressure. The cell efficiency was obtained by controlling the cell voltage and recording the corresponding stabilized current.

3. Results and discussion

3.1. Morphology of PTFE/CB-GDLs

The SEM micrographs in Fig. 1 show the top-view of the PTFE/CB-GDLs and the commercial GDL. In Fig. 1(a–c) the light-colored regions, gray-colored regions and dark regions are assigned to the PTFE resins, the carbon black particles, and the pores, respectively. As can be seen, no cracks are observed on all the PTFE/CB-GDLs' surfaces. The carbon black matrices are in a microporous structure and the PTFE resins are homogeneously dispersed and covered on the carbon black particles. Besides, the surface morphologies are quite similar to that of ELAT GDL (Fig. 1(d)). This reveals that the as-prepared GDLs would be suitable for the catalyst coating in preparation of MEA as the MPL of ELAT GDL. This also implies that as the conventional MPL placed between the catalyst layer and the GDM, the surface of the as-prepared GDL may provide wicking of liquid water, minimize electric contact resistance with the adjacent catalyst layer, and furthermore, prevent the catalyst layer ink from leaking into the GDL, thereby increasing the catalyst utilization and reducing the tendency of electrode flooding [4]. Meanwhile, the SEM micrographs in Fig. 2 show the cross-sections of PTFE/CB-GDLs. The PTFE fibers bound on the carbon black particles and interconnected in the matrix are clearly observed and increase with increasing the colloidal PTFE dispersion (i.e., decreasing *P/D* value). This indicates that the fibers were mainly formed from the colloidal PTFE dispersion during the heat treatment and rolling process, which is similar to the findings on the MPL of conventional GDLs [28–30].

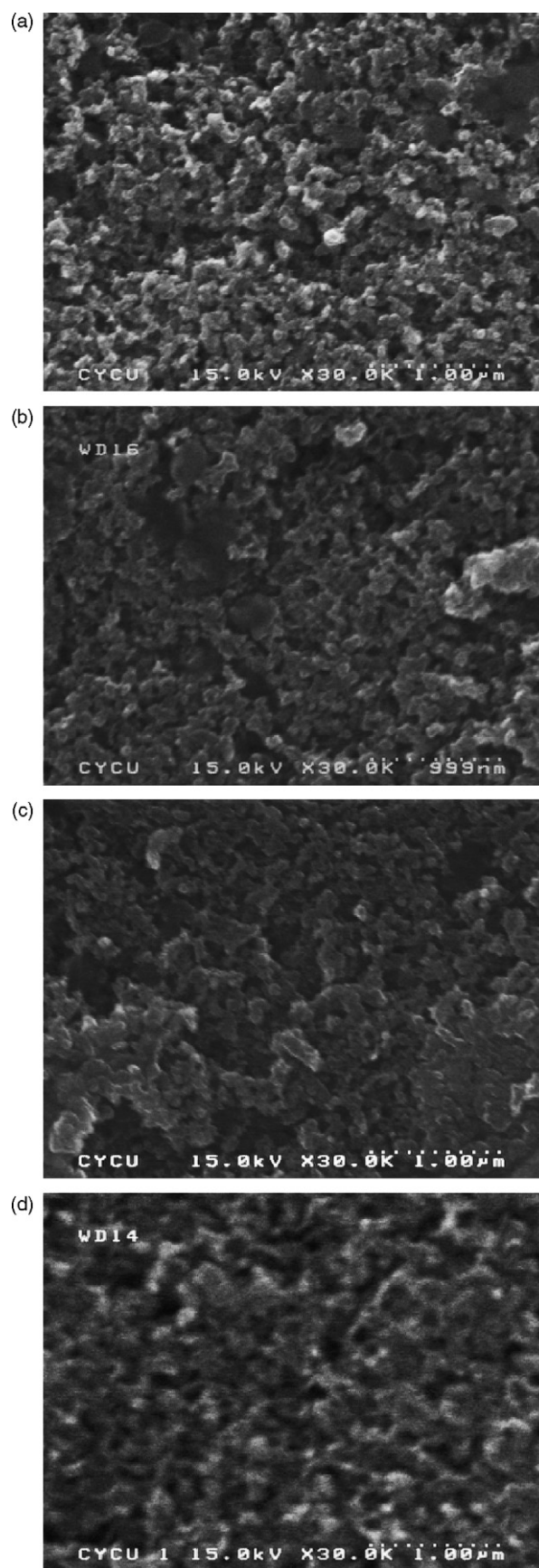


Fig. 1. SEM micrographs of the top-view of: (a) TFCB-1, (b) TFCB-2, (c) TFCB-3, and (d) ELAT GDL.

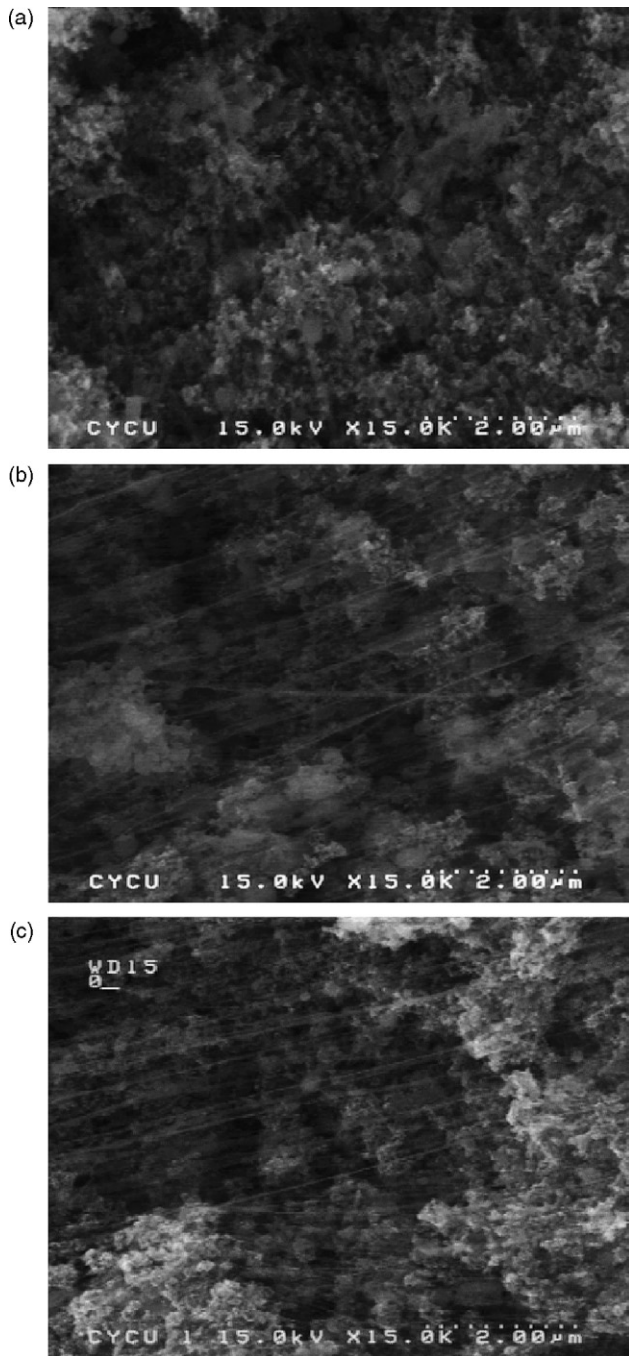


Fig. 2. SEM micrographs of the cross-section of: (a) TFCB-1, (b) TFCB-2, and (c) TFCB-3.

3.2. Electrical and physical properties of PTFE/CB-GDLs

The electrical and physical properties of PTFE/CB-GDLs with different P/D and ELAT GDL are presented in Table 2. As is indicated, the electronic resistivity of the as-prepared GDL decreases with increasing P/D , and the best value obtained ($0.442 \Omega \text{ cm}$) is from TFCB-1. Conceivably, due to the presence of nonconductive PTFE resins in the carbon matrix, causing the ohmic resistance and creating a resistance to the electrical current flow, the value is higher than that of ELAT GDL measured in the same way. Nevertheless, it is about 1.48-fold lower than the best value reported in Ref. [21]. This may be ascribed to the difference in the composition and the matrix structure of the composites.

On the other hand, Table 2 shows that the yield stresses and the yield elongations of PTFE/CB-GDLs are in the range of 0.6–0.9 MPa and 17–79%, respectively, and both properties increase with a decrease in P/D . This is ascribed to the increase of PTFE fibers caused by the increase of the colloidal PTFE dispersion as shown in Fig. 2. As indicated in the table, the PTFE/CB-GDLs are more flexible than the ELAT GDL, but are strong enough for the MEA fabrication of PEMFC. It is believed that the flexibility would make the as-prepared PTFE/CB-GDLs beneficial in closely coming in contact with the neighboring components of MEA, the catalyst layers, and the bipolar plates, in the compression process.

The Washburn constants, internal contact angles to water ($\theta_{\text{H}_2\text{O}}$) and the surface tensions of the GDL samples are shown in Table 3. It shows that the $\theta_{\text{H}_2\text{O}}$ of PTFE/CB-GDLs increases with decreasing P/D value, i.e., TFCB-3 is the most water repellency among the as-prepared PTFE/CB-GDLs. Besides, TFCB-3 exhibits about 1.16-fold higher $\theta_{\text{H}_2\text{O}}$ value than ELAT GDL. This is attributed to the increase of the hydrophobic PTFE fibers interconnected throughout the matrix.

3.3. Gas permeability of PTFE/CB-GDLs

It is known that at a low current density the current is affected by reaction kinetics, while at a high current density the current is affected by gas diffusion [6]. Therefore, an investigation of the gas permeability of GDL is important for studying the mass transport of the fuel cell. In order to simulate the situation of the cell operation, the inlet gas was humidified at 90°C before the measurement. As indicated in Table 2, the PTFE/CB-GDLs show higher gas permeability than ELAT GDL for both humidified oxygen and humidified air. This implies that the gas transport in the as-prepared GDLs is higher than in the

Table 2
Electrical and physical properties of the GDL samples

Sample	Electronic resistivity ($\Omega \text{ cm}$)	Yield stress (MPa)	Yield elongation (%)	Oxygen permeability ($\times 10^2 \text{ cm}^3 \text{ (STP) cm/s cm}^{-2} \text{ cm Hg}$)	Air permeability ($\times 10^2 \text{ cm}^3 \text{ (STP) cm/s cm}^{-2} \text{ cm Hg}$)
TFCB-1	0.442	0.6	17	2.7	2.7
TFCB-2	0.468	0.7	43	8.5	2.9
TFCB-3	0.540	0.9	79	2.4	1.7
ELAT GDL	0.020	1.0	0.9	0.9	0.5

Table 3

Washburn constant, internal contact angles to water and the surface tensions of GDL samples with dispersive and polar components

Sample	Washburn constant ($\times 10^6 \text{ cm}^5$)	$\theta_{\text{H}_2\text{O}}$ ($^\circ$)	$\gamma_{\text{SV}}^{\text{d}}$ (mN m^{-1}) ^a	$\gamma_{\text{SV}}^{\text{p}}$ (mN m^{-1}) ^b	γ_{SV} (mN m^{-1}) ^c
TFCB-1	1.67 ± 0.04	55 ± 6	4 ± 1	44 ± 2	48 ± 4
TFCB-2	1.76 ± 0.01	63 ± 6	5 ± 0	38 ± 5	43 ± 6
TFCB-3	1.70 ± 0.02	92 ± 7	8 ± 5	11 ± 8	19 ± 2
ELAT GDL	1.58 ± 0.02	79 ± 2	4 ± 2	23 ± 6	27 ± 4

^a Dispersive component of surface tension of solid–vapor interface.^b Polar component of surface tension of solid–vapor interface.^c Surface tension of solid–vapor interface.

commercial GDL. This is ascribed to the presence of the interconnected pore volume formed by the three-dimensional arrangement of the carbon black matrix structure, which provided interconnected gas transportation channels, and the presence of the dispersed hydrophobic PTFE resins, which reduced the gas adsorption on the carbon black matrix. However, no direct relationship between the gas permeability data and P/D is found, implying that other factors, such as the detail geometric shape of the conductive material and the porosity of the layer, also affect the gas permeability.

3.4. Cell performance of PEMFC test

According to the aforesaid results, considering the combination of the electronic resistivity, mechanical properties, gas permeability and water repellency, the PTFE/CB-GDL with $P/D=0.5$, TFCB-2, was selected to fabricate the MEA without extra wet-proof treatment and MPL coating to study its performance in PEMFC. As shown in Fig. 3(a and b), although the electronic resistivity of TFCB-2 is higher than that of the commercial GDL, the open circuit potential (OCP) obtained in the H_2/O_2 system and the H_2/air system is 0.96 and 0.92 V, respectively, which are as high as the values reported for the traditional wet-proof GDLs used in PEMFC [4–9,13,17,25]. This is attributed to that TFCB-2 is a single-layer GDL, reducing the fuel delivery path between the catalyst layer and the GDL. Besides, a decrease of I – V performance for TFCB-2 is observed clearly in the high current density regime, especially in the H_2/air system. Since TFCB-2 has high gas permeability as indicated in Table 2, lack of fuels would not be the cause of the decrease. The decrease may be attributed to the water flooding occurred in the cathode, which reduced the catalyst efficiency. The current density is 0.96 and 0.39 A cm^{-2} , and the power density is 0.37 and 0.15 W cm^{-2} at 0.4 V for the H_2/O_2 system and the H_2/air system, respectively. These values are about half of the values obtained from the PEMFC with ELAT GDL, i.e., TFCB-2 is about half as efficient as ELAT GDL on the PEMFC performance.

In all, instead of the expensive carbon paper and carbon cloth used in the conventional multi-layer GDL as the GDM material, the conductive material used in this study was the inexpensive carbon black. In addition, since the PTFE resin was softened and made to disperse well in the GDL during the heat treatment, and the pores on the GDL surface were microporous as evidenced by the SEM micrographs shown in Fig. 1, the multi-steps of the

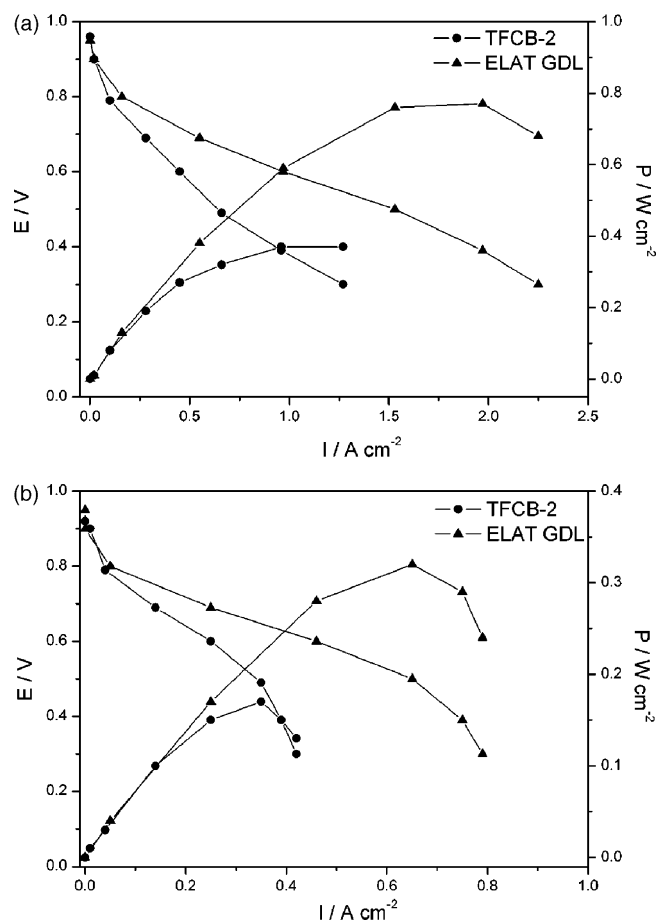


Fig. 3. Polarization curves of PEMFC with TFCB-2 and ELAT GDL in: (a) H_2/O_2 and (b) H_2/air system.

extra wet-proof treatment, coating process of MPL, and high-temperature sintering, usually applied on the conventional GDL, were omitted in preparing the MEA. Consequently, the process for the preparation of the PTFE/CB-based GDL in this work is a simple and inexpensive method, and the as-prepared GDL was used as a single-layer GDL for fabrication of the PEMFC.

4. Conclusions

In the present investigation, a series of PTFE/carbon black composite-based novel single-layer gas diffusion layers (PTFE/CB-GDLs) with different powder PTFE resins and colloidal PTFE dispersion ratios (P/D) was successfully prepared

by a simple and inexpensive method. The SEM micrographs indicated that the PTFE resins were homogeneously dispersed in the carbon black matrix and showed a microporous layer-like structure. The related properties such as electronic resistivity, mechanical strength and internal contact angle to water were varied with the P/D value. In addition, the PTFE/CB-GDLs exhibited higher gas permeability than ELAT GDL for both the humidified oxygen and the humidified air. The performance efficiency of the as-prepared GDL, TFCB-2, is about half of that of ELAT GDL in both of the H_2/O_2 and H_2 /air systems. Nevertheless, these as-prepared inexpensive PTFE/carbon black composites are still potential for use as single-layer GDLs in PEMFC. An improvement in the performance by enhancing the electronic conductivity and the related properties are in progress.

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