Journal of Power Sources 184 (2008) 38–43

Contents lists available at ScienceDirect

Journal of Power Sources

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

Carbon film coating on gas diffusion layer for proton exchange membrane fuel cells

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ARTICLE INFO

Article history:
Received 15 April 2008
Received in revised form 3 June 2008
Accepted 4 June 2008
Available online 22 June 2008

Keywords:
Carbon paper
Carbon film
Gas diffusion layer
Micro-porous layer
Proton exchange membrane fuel cell

ABSTRACT

This study discusses a novel process to increase the performance of proton exchange membrane fuel cells (PEMFC). In order to improve the electrical conductivity and reduce the surface indentation of the carbon fibers, we modified the carbon fibers with pitch-based carbon materials (mesophase pitch and coal tar pitch). Compared with the gas diffusion backing (GDB), GDB-A240 and GDB-MP have 32% and 33% higher current densities at 0.5 V, respectively. Self-made carbon paper with the addition of a micro-porous layer (MPL) (GDL-A240 and GDL-MP) show improved performance compared with GDB-A240 and GDB-MP. The current densities of GDL-A240 and GDL-MP at 0.5 V increased by 37% and 31% compared with GDL, respectively. This study combines these two effects (carbon film and MPL coating) to promote high current density in a PEMFC.

1. Introduction

Recently, much research has focused on proton exchange membrane fuel cells (PEMFC). However, many technological difficulties must be overcome before commercialization is possible. The gas diffusion layer (GDL) is a critical part of any PEMFC [1]. The GDL supports gaseous fuel transfer to the catalyst layer (CL) in a fuel cell. It should be electrically conductive to obtain current from the redox reactions at the CL. During fuel cell operation, water is produced by the redox process. At high current densities, the increased rate of water production can lead to liquid water formation and flooding of the GDL. In order to increase its ability to expel water, the GDL is normally treated with a hydrophobic agent or a micro-porous layer (MPL) [2–8]. Hydrophobic agents are usually treated with polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP). The MPL is generally mixed with carbon black powder and hydrophobic agent.

Park et al. [6] reported that 10 wt% FEP loading generates a hydrophobic surface to facilitate liquid water removal. High FEP content in excess of 10 wt% can only block GDL surface pores, thus causing significant mass transportation limitations to oxygen transportation and water removal through the GDL surface. Qi and Kaufman [9] found that a PTFE/carbon sub-layer added between the carbon paper and CL markedly enhanced the ability of PEMFC to manage water. Park et al. [10] prepared a MPL with different carbon loadings on the carbonfiber substrates; their porous structures were characterized using mercury porosimetry. U.S. Patent No. 6,733,915 [11] discloses that a piece of porous carbon substrate can be used as the substrate, which is immersed into a fluorinated polymer solution for a hydrophobic treatment. Subsequently, the immersed carbon substrate can be coated with a mixture of a fluorinated polymer and carbon particles and then dried at high temperature to obtain a modified carbon substrate. U.S. Patent No. 7,063,913 [12] discloses that a porous carbon substrate can be pretreated with a hydrophobic polymer, which is dried to obtain a hydrophobic carbon substrate. Then, the hydrophobic carbon substrate can be coated with a mixture of a fluorocarbon polymer and carbon particle mixture. The substrate is finally subjected to a heat treatment.

The performance of a PEMFC is controlled by fuel gas diffusion and the ionic conductivity of the GDL [13]. The effects of performance in a PEMFC are typically focused on water management, electron conductivity, the MPL, and operating conditions. However, the carbon paper and carbon cloth are both made of carbon fibers. Carbon fibers can be made by different manufacturing processes (intrudes precursor, temperature, and surface modified processes) and have slightly different properties. PAN and pitch are two types of carbon fiber precursor. In this study, we coated a pitch-based

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doi:10.1016/j.jpowsour.2008.06.040

carbon film on the self-made carbon paper. According to carbon material science, pitch-based carbon has higher electrical conductivity than PAN-based carbon [14]. A carbon film coating on self-made carbon paper is smooth and continuous over the carbon fiber surface; moreover, it also improves the through-plane resistance. In this study, in order to increase the electrical conductivity and reduce the surface indentation of the carbon fibers, we modified the carbon fiber with carbon-based materials (mesophase pitch and coal tar pitch). This study reports on a novel modified method to improve the properties of raw GDL and subsequently to improve performance of the PEMFC.

2. Experiment

2.1. The manufacture and modify of GDL

A GDL can be divided into its gas diffusion backing (GDB) and its MPL. The GDB mainly consists of carbon fiber paper or carbon fiber cloth. In this study, GDBs were manufactured from carbon fiber, and produced according to Taiwan patent I261639 [15] and U.S. application publication no. 2006/0214320 A1 [16]. MPL has a crucial role in achieving high performance for PEMFC. MPL consists of Vulcan XC-72 (Cabot Corp.) and FEP121A (Dupont Co., Ltd.), both of which are applied to the GDB surface.

In this study, we prepared GDB from oxidized fiber felt (Kuo Tung Felt Co., Ltd.) and phenolic resin (Chang Chun Plastics Co., Ltd.). The oxidized fiber felt was first precarbonized at 1000 °C to produce carbon fiber felt. The phenolic resin was mixed with methanol so as to constitute 10% of the solution. The carbon fiber felt was impregnated with the phenolic resin mixture, placed in an oven, and baked at 70 °C for 15 min. Hot pressing at a temperature of 170 °C and pressure of 10 kg cm^{-2} was performed to alter the composite material to the form of carbon paper. This self-made carbon paper was carbonized at 1400 °C (in N_2) to form the GDB.

Coal-tar pitch A240 (Ashland Oil Company) and mesophase pitch (China Steel Chemical Corp.) were used as carbon precursor to form a carbon film on GDB surface. Two coating solutions were prepared by dissolving A240 and mesophase pitch in aqueous toluene solution at a proportion of 0.1 g ml^{-1}, respectively. The coated GDBs were dried at 70 °C and carbonized at 1400 °C (in N_2). The two kind of coated GDBs were called GDB-A240 and GDB-MP, corresponding to the type of coating solution that we used.

For the coating MPL samples, Vulcan XC-72 (Cabot Corp.) was mixed with 10% FEP solution (diluted from 10 ml Dupont FEP121A solution and 90 ml deionized water) and then stirred for 5 min at room temperature. After the GDB heat treatment at 1400 °C, it was sprayed with this mixed solution to form a one-side precursor for the MPL. The sprayed GDB was baked at 70 °C for 15 min to dry, baked at 240 °C for 30 min, and sintered at 350 °C for 30 min. The coating MPL sample was called GDL. By the carbon film coating method, we used the modified GDB-A240 and GDB-MP to form a MPL on two set of sample surface. These coated MPL samples were named GDL-A240 and GDL-MP. The list of samples processed is shown in Table 1.

Table 1
List of sample processed under different conditions

Sample code	Processing conditions
GDB	Self-made carbon paper
GDL	Self-made carbon paper coated micro-porous layer (1.0 mg cm^{-2})
GDB-A240	Self-made carbon paper coated coal tat pitch A240 solution (0.1 g ml^{-1})
GDB-MP	Self-made carbon paper coated mesophase pitch solution (0.1 g ml^{-1})
GDL-A240	Self-made carbon paper coated coal tat pitch A240 solution (0.1 g ml^{-1}) and heat treatment at 1400 °C. Then coated micro-porous layer (1.0 mg cm^{-2})
GDL-MP	Self-made carbon paper coated mesophase pitch solution (0.1 g ml^{-1}) and heat treatment at 1400 °C. Then coated micro-porous layer (1.0 mg cm^{-2})

2.2. Characterization of GDL

Measurement of Gurley porosity was performed in a Gurley-type porosimeter (ASTM D726-58), with the specimen fixed on the instrument cylinder and fastened among sealing plates. Gas porosity characteristics for the various samples were evaluated directly with a Gurley apparatus (model 4110), whose cylinder with a 6.45 cm^2 opening was positioned at several locations on the cut GDL surface. Gurley porosity values were acquired as an average of several time (second) determinations for 300 cm^3 and weight of 142 g of displaced air. Different treatments of these GDLs were tested with a Digidrop apparatus (GBX model D-S Instruments), using the triple point calculation method. An HPLC-quality water drop was placed on the disk surface at a static contact angle (θ) of $0 < \theta < 90^\circ$ and $\theta > 90^\circ$, called hydrophilic and hydrophobic, respectively. Drop shape and contact angle magnitude were controlled by three interaction forces of interfacial tension for each participating phase (gas, liquid, and solid). However, there are some limitations which can limit the reproducibility of contact angle measurements. When the contact angle >160°, the drop of liquid will not drop on the sample surface, due to surface tension of the liquid. In general, if the droplet cannot adhere to the sample surface, that shows that the surface is hydrophobic and the contact angle >160°. Surface resistance was measured for a series of GDLs. The GDL test area was 25 cm^2. At least thirty samples were measured and the average value was calculated. Elemental analysis was performed using an Elemental Vario EL III. The through-plane resistance was measured by five point (10 mm in diameter) and various forces. Measurements were made a minimum of five points on a GDL and the average value was calculated for five pieces of GDL. The true densities of carbon paper were tested with an Accupyc 1330 Pycnometer. The sample was put in the instrument cell and subjected to helium gas. Measurements were made 90 times, with the last 10 cycles calculated for an average value. The surface morphology of the GDL was investigated visually via a multi-mode scanning probe microscope (SPM, Digital Instrument NS4/D3100CL/Multi-Mode) and a high-resolution scanning electron microscope (HRSEM) (HITACHI S-4800, Japan).

2.3. Electrochemical characterization of GDL in a PEMFC

Single-cell voltage and current density were measured simultaneously, using an FCED® PD50 (Asia Pacific Fuel Cell Technologies, Ltd., Taiwan). A five-layer MEA was fabricated using three-layer

Table 2
The properties of various self-made carbon paper

Sample code	Contact angle (θ)	In-plane resistance (mΩ cm^{-2})	Gurley porosity (cm^3 cm^{-2} s^{-1})
GDB	120.8	21.0	71
GDL	>160	25.5	59
GDB-A240	124.5	23.6	63
GDB-MP	126.1	24.6	61
GDL-A240	>160	27.5	54
GDL-MP	>160	28.1	53

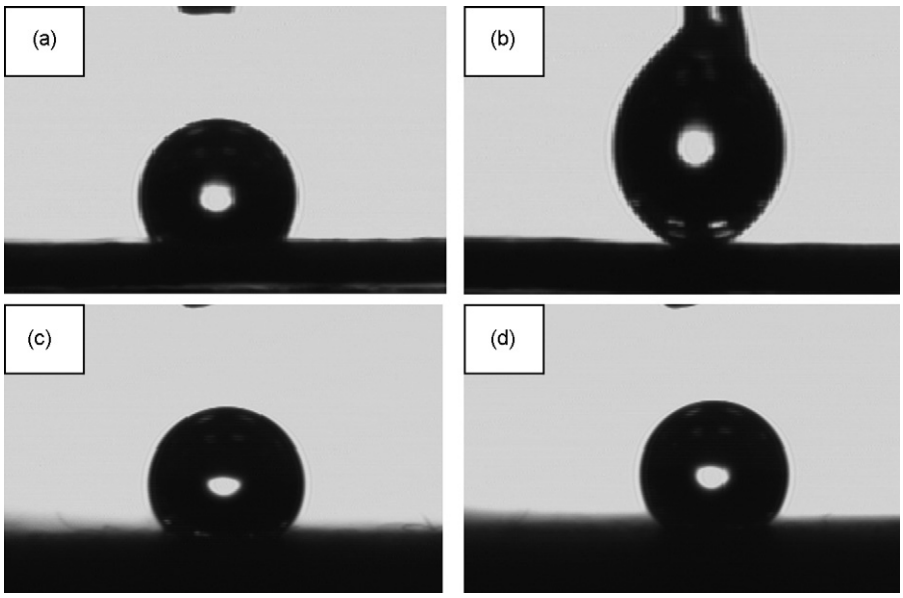

Fig. 1. The contact angle images of various self-made carbon paper. (a) GDB; (b) GDL; (c) GDB-A240; (d) GDB-MP.

MEA and two GDLs. The three-layer MEA was obtained from Gore (PRIMEA® Series 5621 MESGA, 35 μm thick with 45 Pt Alloy/60 Pt.). The activated area in each cell was 25 cm^2, and the bipolar plates consisted of serpentine-type grooved graphite plates made of highly compact graphite. Polarization (voltage versus current density) of a single PEMFC was obtained under specific operating conditions: cell temperature, 40 °C; pure H_2 was supplied fuel gas for the anode (0.5 SLPM); pure O_2 (0.5 SLPM) was supplied for the cathode; both gases had a relative humidity (RH) of 95%.

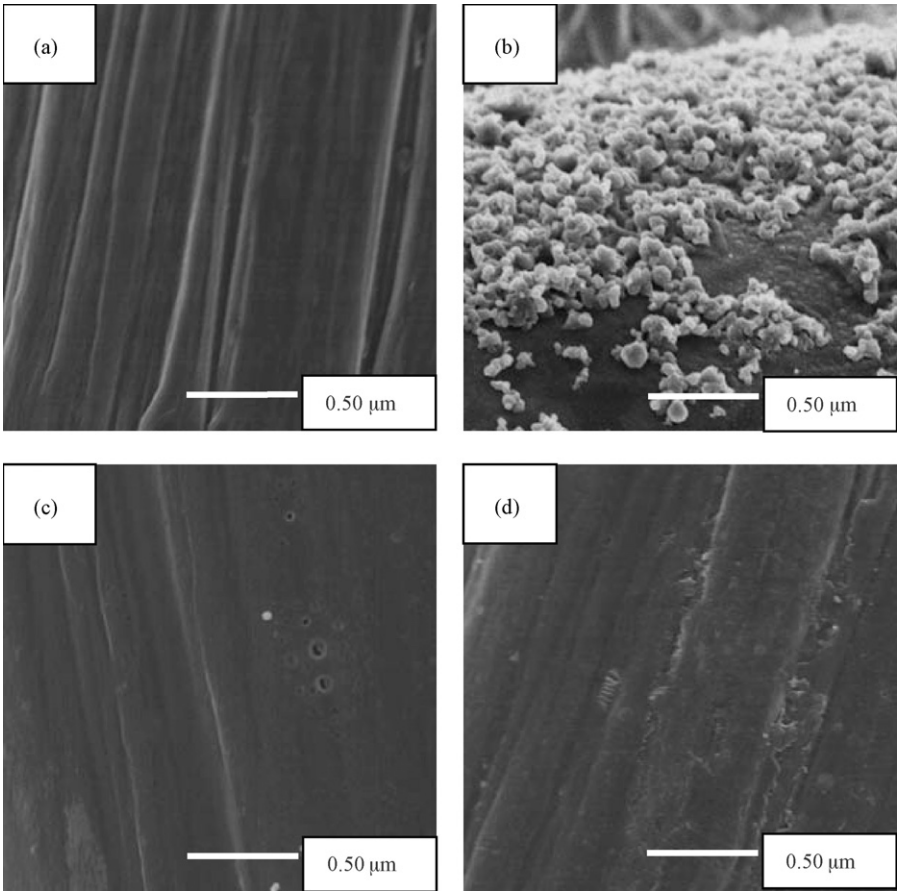

Fig. 2. Surface micrographs of various self-made carbon paper (high-resolution scanning electron microscopy, (HRSEM)). (a) GDB; (b) GDL; (c) GDB-A240; (d) GDB-MP.

3. Results and discussion

3.1. Characterization analysis of GDL

The contact angle, in-plane resistance, and porosity values of our self-made carbon paper under different treatments are shown in Table 2. This structure improves transmission of electrons and augments vertical fibers conductivity. The micro structures probably increased the width and length of micro crystallites at treatment temperatures of 1300–2500 °C. The electrical resistance and functional group of carbon fibers as a function of heat treatment temperature decreased as treatment temperature increased [17,18]. The results show that GDB heat treatment at 1400 °C acquires a hydrophobic property (>90°). In addition, the contact angles of GDB-A240 and GDB-MP were 124.5° and 126.1°, similar to GDB (120.8°). The coal tar pitch A240 and mesophase pitch were coated on the GDB, respectively. Fig. 1 shows the water drop contact angles of the self-made carbon paper as a function of deposition. As a result of the hydrophobic agent mixed into the MPL slurry, the thin MPL, coated on the GDB surface, has the possibility to improve water removal. GDL, GDL-A240, and GDL-MP all show a high hydrophobic surface and a larger contact angle (>160°) than GDB, GDB-A240, and GDB-MP.

The in-plane resistance of GDB is significantly lower than GDL due to the self-made carbon paper MPL process. The MPL includes an insulating solution (FEP) and carbon powder (XC-72). The insulating solution causes the GDL surface to have high resistance. The in-plane resistance of GDL increases with increasing concentrations of the insulating hydrophobic agent. In addition, the microstructure of GDB can be described as quite rough, and consists of cylindrical carbon fibers (Fig. 2(a)). The surface morphologies of GDB-A240 and GDB-MP were smooth. The GDL was rough, and blanketed the surface of the carbon fibers (Fig. 2). The microstructural changes probably caused increased smoothness and continuity of surface crystallites in the carbon fibers. In Fig. 2(b), the deposition exhibits a spherical shape with accumulation on the carbon fiber surface. It contains carbon black powder and hydrophobic agent.

The mixed XC-72 and FEP121A solution formed a precursor of the MPL. The true densities of GDB, GDL, GDB-A240, and GDB-MP were shown as 1.351, 1.598, 1.576, and 1.511 g cm^{-3}, respectively. The true density of GDL was greater than GDB as a result of the Vulcan XC-72, which had a true density of 1.965 g cm^{-3}. The densities of GDB-A240 and GDB-MP were greater than that of GDB due to the coating of carbon film which capped the open pores in the fibers and increased the true density. The surface shape of the coated sample shows a smooth and continuous appearance (Fig. 3). SPM provided the above findings. By SPM measurement, the surface roughness averages (Ra) of GDB, GDB-A240, GDB-MP were 79, 47, and 52 nm, respectively. The result means that the coated carbon film blanketed the grooves on the carbon fiber surface and caused a smooth surface on GDB-A240 and GDB-MP.

The Gurley porosities of GDB, GDL, GDB-A240, and GDB-MP are shown in Table 2. The porosities of the coated samples (GDL, GDB-A240, and GDB-MP) were greater than that of GDB. This phenomenon is caused by the porous surface of the blanketed MPL which blocked the path of gas. The MPL loading compacted the structure and reduced the surface pores. Furthermore, the coating solutions of coal tar pitch A240 and mesophase pitch smoothed the carbon fiber surface and cross-linked parts of the carbon fibers in self-made carbon paper.

Fig. 4 presents a comparison of the carbon paper compression and through-plane electrical resistance curves for the self-made carbon paper. The through-plane resistance of GDB, GDL, GDB-A240, and GDB-MP were reduced during the pressure process. Increased pressure caused the electrical transportation path to interlock and increased the carbon fiber density. This was the key factor in changing the through-plane resistance. Moreover, Vulcan XC-72 is a carbon material with low electrical resistance (<20 Ω cm) and FEP121A solution is an insulating material. The superabundant FEP121A solution infiltrated the GDB, causing the through-plane resistance of GDL to be higher than that of GDB.

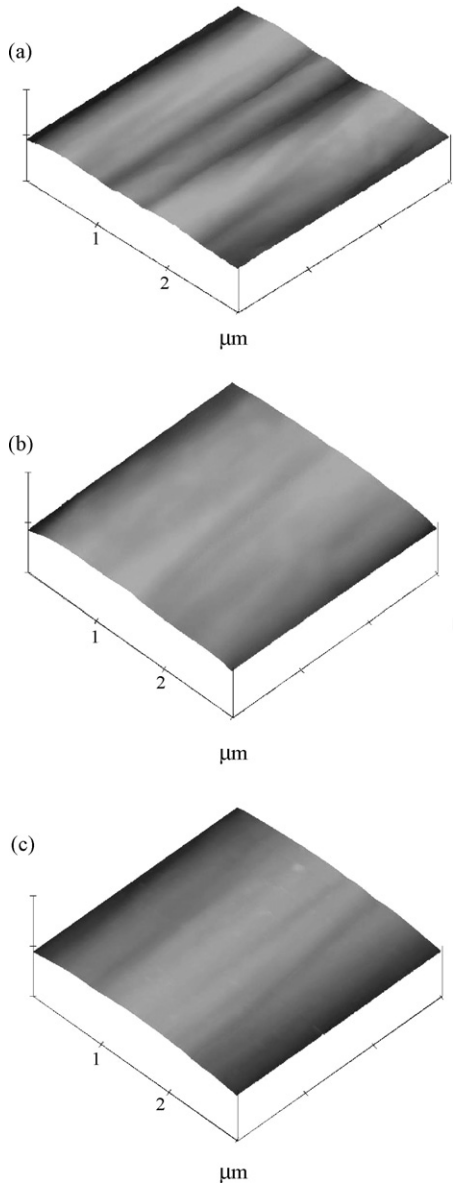

Fig. 3. Surface micrographs of various self-made carbon paper (scanning probe microscope, (SPM)). (a) GDB; (b) GDB-A240; (c) GDB-MP.

3.2. Electrochemical performance of a PEMFC

The above results can be confirmed by the polarization curves for a PEMFC using different self-made carbon papers (Fig. 5). The fuel cell temperature was operated at 40 °C, 95% RH of anode/cathode at 40 °C, and 0 psig back-pressure. Electrochemical performance tests were performed (to obtain polarization curves) using various self-made carbon papers to elucidate the effects of these alterations on performance. Polarization of the membrane electrode assembly (MEA) at 0.5 V with GDB and GDL achieved current densities of 702 and 882 mA cm^{-2}, respectively. The per-

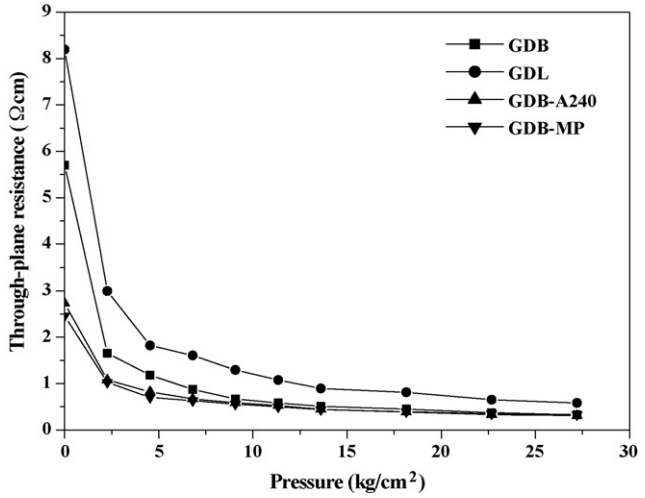

Fig. 4. Through-plane resistances of various self-made carbon paper under different pressures. (■) GDB; (●) GDL; (▲) GDB-A240; (▼) GDB-MP.

formance of GDL increased by 26% compared with that of GDB. The MEA made from GDB-A240 had a current density of 929 mA cm^{-2} at 0.5 V, whereas the MEA from GDB-MP recorded a current density of 934 mA cm^{-2} at 0.5 V.

Recent studies [2–3,10] have demonstrated that a thin MPL enhances the performance efficiency of PEMFC by improving the gas permeability and electrical conductivity while simultaneously maintaining the ability for water management. This study has proved that the GDL performance is superior to GDB performance. The outcome is caused by GDL having better hydrophobic and MPL characteristics than GDB. This was already known to fuel cell technology researchers. As the hydrophobic treatment prevents the water flooding, over a long measurement time, the current densities do not seriously decrease. Some studies [19–22] have considered the effects of the electrical resistance of GDL, and have proved that under certain conditions, the electrical resistance of GDL is sufficient to alter the characteristics of current density distributions under gas channels and solid areas. The performances of GDB-A240 and GDB-MP at 0.5 V increased by 32% and 33% compared with GDB, respectively. However, the self-made carbon paper coating carbon film has excellent performance in some respects, but it does not have good hydrophobic property.

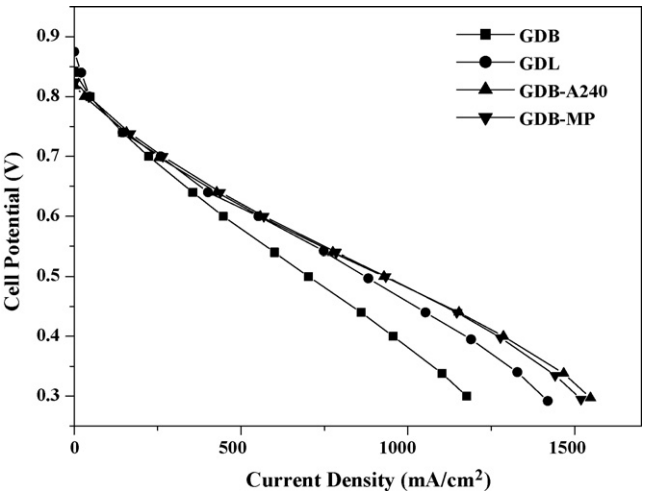

Fig. 5. Polarization curves of the PEMFC using various self-made carbon paper. (■) GDB; (●) GDL; (▲) GDB-A240; (▼) GDB-MP.

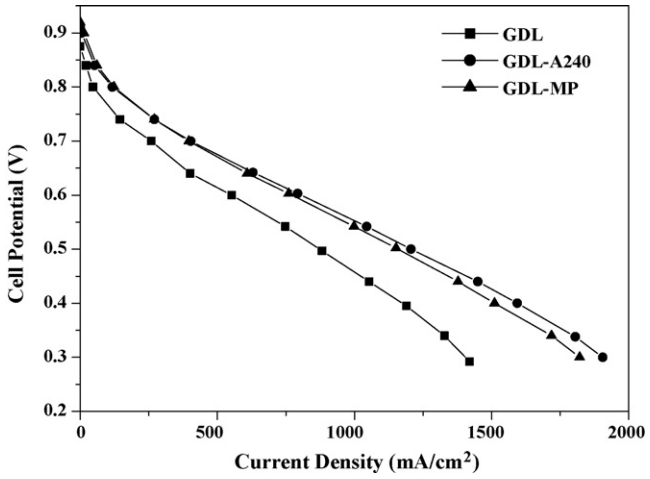

Fig. 6. Polarization curves of the PEMFC using various self-made carbon paper. (■) GDL; (●) GDL-A240; (▲) GDL-MP.

To prevent water flooding as above, the GDB-A240 and GDB-MP were coated on the surface of MPL (1.0 mg cm^{-2}) and transferred to GDL-A240 and GDL-MP. Fig. 6 shows the effects of GDL, GDL-A240 and GDL-MP on the polarization behavior of MEA under operating conditions of 40 °C cell temperature, 95% RH of anode/cathode at 40 °C, and 0 psig back-pressure. The current densities of GDL-A240 and GDL-MP at 0.5 V increased by 37% and 31% compared with GDL, respectively. In this case, the carbon film coating increased the performance and MPL coating improved this effect. The MPL coating provided an optimal gas transportation path and hydrophobic properties in the PEMFC; the carbon film coating provided a smooth carbon fiber surface and excellent electrical conductivity in self-made carbon paper. The combination of these two effects promote high current density in a PEMFC. As a result, the PEM fuel cell using GDL-A240 and GDL-MP exhibited great performance.

4. Conclusion

In this study, the current density and power density have been enhanced, especially under low operating voltages. This is an excellent way to improve performance in a PEMFC. Polarizations at 0.5 V of the MEA with GDB, GDB-A240, GDB-MP, GDL, GDL-A240, and GDL-MP were 702, 929, 934, 882, 1206, and 1151 mA cm^{-2}, respectively. The performances of GDL-A240 and GDL-MP at 0.5 V were 72% and 64% higher than GDB, respectively. The MPL and carbon film coating improved the self-made carbon paper with respect to PEMFC performance. The combination of these two effects promote high current density in a PEMFC.

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