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

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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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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