Materials Chemistry and Physics 114 (2009) 151–155

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Characterization of Teflon-like carbon cloth prepared by plasma surface modification for use as gas diffusion backing in membrane electrode assembly

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ARTICLE INFO

Article history:
Received 15 June 2008
Received in revised form 27 August 2008
Accepted 29 August 2008

Keywords:
Plasma surface modification
Gas diffusion backing
Hydrophobic property
Proton exchange membrane fuel cell

ABSTRACT

The hydrophobic property of carbon cloth was largely improved by plasma treatment and the Teflon-like property was effectively applied to fabricate a gas diffusion backing (GDB) for use in membrane electrode assembly (MEA). The surface morphology, hydrophilic/hydrophobic property and electron conductivity of the as-prepared GDB was fully characterized. The water contact angle and SEM microstructure image of the CF_4, CHF_3 plasma-treated GDB were both indicated as ~130°, and very few gas diffusion pores either sealed or blocked by excessive hydrophobic material residual. The measured resistivity values of CF_4 plasma, CHF_3 plasma, SF_6 plasma and commercial carbon were 0.45, 0.5, 0.47 and 0.49, respectively, which indicates that the electrical resistivity of carbon cloth with CF_4 plasma treatment was slightly lower than others. In cell performance test, the CF_4 plasma-treated modules could also produce better property than those MEAs prepared with CHF_3 plasma-treated GDB, SF_6 plasma-treated GDB and commercially available GDB, leading to the highest fuel cell performance with an optimal power output of 350 mW cm^{-2}.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising mainstream green power source for mobile and stationary applications. The porous gas diffusion layer (GDL), which can affect the diffusion of reactants and water as well as the conductivity, plays a crucial role among all components inside the PEMFC. The GDL consists of two parts, i.e., macro-porous gas diffusion backing (GDB) and micro-porous layer (MPL) [1]. Carbon cloth [1–3] and carbon paper [4,5] are the most common used macro-porous GDB in GDL to serve as current collector and physical support structure for the catalyst layer (CL). The function of GDB can be summarized as follows: (1) to provide a proper pore structure and hydrophobicity to allow for a better gas transport and water removal from the electroosmotic drag through the electrolyte membrane [6,7], (2) to condense water vapor from the humidified reactant feed [8–10], (3) to direct involve in the reduction reaction at the cathode [8] and (4) to minimize electric contact resistance with the adjacent CL. An ideal GDB should therefore be highly conductive, highly porous and wet-proofed [11,12]. It can then provide an efficient pathway for the gas reactants to be fed homogeneously and the produced liquid water to be removed rapidly without blocking the reactant gases [9,12]. An effective wet-proofing procedure manipulates the hydrophobic property of the porous GDB and subsequently affects the overall power output performance of the PEMFC.

Typically, the wet-proofed GDBs are prepared by coating with hydrophobic materials (e.g., polytetrafluoroethylene (PTFE)) [13–15] or fluorinated ethylene propylene (FEP) [13,16,17] onto a raw GDB (e.g., carbon paper or carbon cloth) [12,18]. This treatment can lead to a large contact angle between liquid water and the coated GDB and so the porous channels inside the wet-proofed GDB are less blocked or flooded by the produced liquid water [18]. However, the surface characterization of the GDB depends not only on the loading of hydrophobic materials but also on the techniques utilized to coat the hydrophobic materials onto the GDB [15,19]. For example, Jaszewski et al. reported that the anti-adhesive property was very different for PTFE-like film prepared either by plasma polymerized or ion sputtered methods [20]. Ioroi et al. investigated the influence of PTFE loading on GDB and found a better performance with smaller PTFE loading. Nevertheless, a very poor fuel cell performance was observed for GDB without PTFE loading [21].

It is believed that the surface morphology and distribution of the hydrophobic coating materials on carbon paper or carbon cloth can largely affect the MEA performance [16]. The surface morphology and distribution problem arises from the fact that excessive liquid

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doi:10.1016/j.matchemphys.2008.08.092

hydrophobic materials may migrate (via capillary action) towards the carbon paper or carbon cloth surfaces and subsequently blocks or seals the surface pores during the drying processes of the wet-proof procedures. Once the percentage of the sealed surface pores in the GDB gets higher, neither the removal of liquid water nor the feed of reactant gas can function well, and can thus considerably reduce the power output of fuel cell. Overall, the development of a new GDB wet-proof procedure that provides pore sealing free (SF) or blocking free GDB (i.e., homogeneous hydrophobic coating) has become a challenging issue in MEAs.

In this work, the radio frequency (RF) plasma treatment method widely applied in polymer surface property modification [22,23] was adapted to improve the hydrophobic property of GDB. The chance of leaving excessive hydrophobic material residuals to block or seal the gas diffusion pores is expected to be very low by this surface plasma treatment. The as-formed surface morphologies and microstructure of the wet-proofed GDB can then enhance the MEA power output without additional usage of expensive hydrophobic materials (e.g., PTFE or FEP).

2. Experimental

2.1. Plasma-treated Teflon-like materials for GDB

In recent years, there has been an increased interest in plasma deposition technology. Plasma is energetically the fourth state of matter, apart from the solid, liquid, and gas state. When a RF power is applied to a gas, it is excited into glow discharge condition through oscillation and collision. The elastic collision frequency (υ) of gas under this condition is normally between 10^9 and 10^{11} collisions s^{-1}, which is much higher than of the applied RF [24] and the electron species in the excited gas experience much more collisions during each applied field cycle [25]. Due to the glow discharge, the excited and globally neutral plasma phase contains highly reactive species, such as electrons, ions and excited molecules, originated from the mother gas. The RF power is continuously supplied so that the excited gas remains in the plasma phase for further operations. Physical characteristics and chemical compositions of the plasma are generally determined by gas species and system parameters as reported earlier [23].

The preparation procedure of the hydrophobic GDB is described as follows. First, a square carbon cloth with an area of 5 cm^2 (BEAM ASSOCIATE, Taiwan) was cleaned by a reactive ion etcher system (Trion Phantom III) under the following working conditions: 10 sccm O_2 mass flow, 50 W RF power, 5×10^{-3} Torr working pressure, and 10 min reaction time. After cleaning the carbon cloth, CF_4, SF_6, and CHF_3 plasmas were used to treat the carbon surface in the present study. The Teflon-like materials were finally deposited in a high vacuum chamber under the following working conditions: 5×10^{-3} Torr base pressure, 25 sccm mass flow rate, 100 W RF power, and 40 min reaction time, in the reactive ion etcher system (Trion Phantom III).

2.2. Membrane electrode assembly fabrication

The MEAs were fabricated by first immersing a Nafion 112 (Du Pont) polymer electrolyte membrane (PEM) in 5% H_2O_2 at 80 °C for 1 h to eliminate the membrane surface impurities. The PEMs were then sunk into 0.5 M H_2SO_4 solution at 80 °C for another 1 h. The PEMs were frequently washed with 80 °C deionized water before use [3]. A 10 wt% Pt/C catalyst ink, containing chloroplatinic acid (as the metal precursor, Seedchem), carbon (XC-72) and 5 wt% Nafion solution, was prepared by the impregnation method [26]. The catalyst ink was then coated onto one side of the as-prepared PEMs [3], and dried at 80 °C, 1×10^{-2} Torr vacuum atmosphere for 1 h. The opposite side of the membrane was treated similarly after the first side of the PEM was dried. The pre-treated PEM was sandwiched between two layers of Pt/C catalyst ink to serve as anode and cathode. The anode/PEM/cathode modules was designated as pre-MEAs. Note that the Pt loading was kept at a constant value of 0.4 mg cm^{-2} in the catalyst ink. Finally, under a vacuum atmosphere of 0.6 Torr, the GDLs and pre-MEAs were first pressed by 10 kgf cm^{-2} at 50 °C for 10 s, followed by 500 kgf cm^{-2} at 140 °C for 90 s.

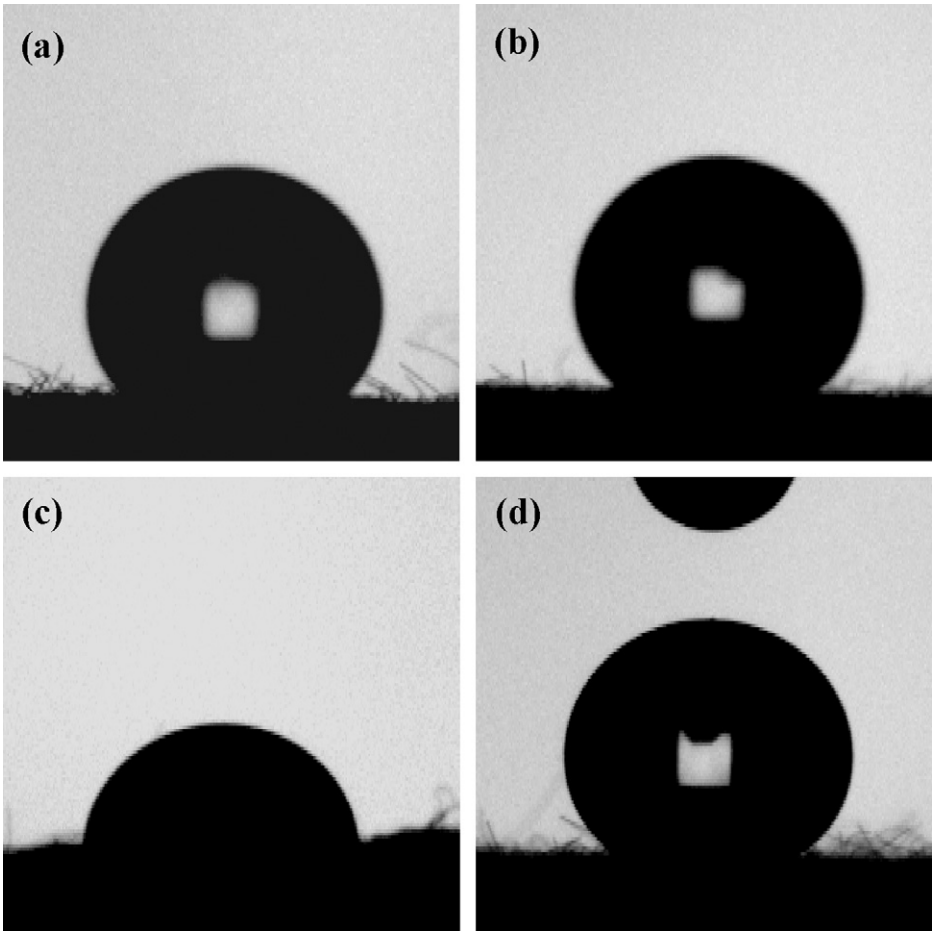

Fig. 1. Images of (a) CF_4 plasma treated, (b) CHF_3 plasma treated, (c) SF_6 plasma treated and (d) commercial carbon cloth.