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CF_4 plasma treatment for preparing gas diffusion layers in membrane electrode assemblies

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Abstract

The hydrophobic properties of carbon fibers improved by a CF_4 plasma treatment were used to fabricate gas diffusion layers (GDLs) for use in proton exchange membrane fuel cells. The water contact angle of the CF_4 plasma treated GDL was measured as $132.8 \pm 0.2^\circ$ at 45 °C and very few surface gas diffusion pores were either sealed or blocked by the excessive hydrophobic material residuals. Polarization measurements verified that the CF_4 plasma treated modules can indeed enhance fuel cell performance, compared to the membrane electrode assemblies (MEAs) with a non-wet-proofed GDL, 10 wt% PTFE dip-coated GDL, and commercially available GDL (10 wt% PTFE).

Keywords: Plasma surface modification; Wet-proofed gas diffusion layer; Hydrophobic property; Water management

1. Introduction

Water management in the gas diffusion layer (GDL) plays a crucial role in the research and development of proton exchange membrane fuel cells (PEMFC). In a typical PEMFC system, water transport arises from: (1) the electroosmotic drag through the electrolyte membrane [1,2], (2) the direct production from the cathodic reduction reaction [3] and (3) the condensation of water vapor from the humidified reactant feeds [3–5]. Ideally, a GDL should provide an efficient pathway for the gas reactants to be fed homogeneously and at the same time act as an effective conduit for the produced liquid water to be removed rapidly without blocking the reactant gases [4,6]. With water transport which occurs either nearby or inside the GDL, a good GDL should be therefore not only be highly conductive but also porous and wet-proofed [6,7]. An effective wet-proofing procedure determines the hydrophobic property of the porous GDL, and subsequently affects the overall power output performance of the PEMFC.

Wet-proofed GDLs are usually prepared by coating with hydrophobic materials (e.g., polytetrafluoroethylene (PTFE) [8–10] or fluorinated ethylene propylene (FEP) [11]) onto a raw GDL (such as carbon paper or carbon cloth) [6,12]. This treatment can lead to a large contact angle between liquid water and the coated GDL. The porous channels inside the wet-proofed GDL are thus less blocked or flooded by the produced liquid water [12]. However, the wet-proofing quality of the GDLs is generally determined not only by the loading of hydrophobic materials [8–11] but also by the techniques utilized to coat the wet-proofed materials onto the GDLs [10,13]. For example, power output differences were compared in the work of Lee et al. among the rolling, spraying and screen printing methods for fabricating wet-proofed GDL [13]. Paganin et al. [9] and Giorgi et al. [10] investigated the influence of PTFE loading on the GDL and found that the polarization performances of the membrane electrode assembly (MEA) tend to decline with the increase in the PTFE contents.

Although the non-intuitive decrease of the potential–current polarization is generally attributed to the GDL porosity variation as the loading of the hydrophobic material increases [9–11], Lim and Wang [11] also pointed out the surface morphology and distribution of the hydrophobic coating materials on the carbon paper or carbon cloth should not be neglected. This surface morphology and distribution problem arises from the fact that excessive liquid in hydrophobic materials may migrate (via cap-

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illary action) towards the carbon paper or carbon cloth surfaces and consequently block or seal the surface pores during the drying process of the wet-proofing procedure. The power output of the MEA then reduces considerably once a high percentage of surface pores in a single GDL are sealed. Nowadays, a homogeneous hydrophobic coating has become a challenging issue.

The present work proposes a new CF_4 plasma treatment method to effectively improve the hydrophobic property of the GDL. The idea is adapted from the radio frequency (rf) plasma treatment widely applied in polymer surface property modifications (such as adhesion, etching, grafting, penetrability and wettability) [14,15]. The surface plasma treatment does not leave excessive hydrophobic material residuals to block or seal the gas diffusion pores. In order to demonstrate the importance and significance of a "seal-free GDL (SF-GDL)" for the power output of a PEMFC, the Pt loading utilized in the electrode catalyst layer (CL) in this study was intentionally lowered to a level conventionally called "ultra-low Pt loading", e.g., 0.04–0.05 mg cm^{-2} [16–18]. The plasma treatment can modify the surface morphologies and microstructure of the wet-proofed GDL to enhance the MEA or fuel cell power output without additional usage of expensive electrocatalytic elements. Overall, the achievement of SF-GDL and ultra-low Pt loading through the CF_4 plasma treatment are remarkable.

2. Experimental

2.1. GDL preparation

Before going to the details of the GDL preparation, the principle of the radio frequency plasma treatment used in this study is briefly introduced. When rf power is applied to a gas, it is excited into the glow discharge condition through molecular oscillations and collisions. The elastic collision frequency (υ) of the gas in this condition is usually between 10^9 and 10^{11} collisions s^{-1}, which is much higher than the applied rf [19] and the electron species in the excited gas experience much more collisions during each applied field cycle [20]. Due to the glow discharge, the excited and globally neutral plasma phase containing highly reactive species, such as ions, electrons and excited molecules, originates from the mother gas. The rf power is continuously supplied so that the excited gas remains in the plasma phase. The chemical compositions and physical characteristics of the plasma are generally determined by system parameters as reported earlier [15,21].

A schematic of plasma treatment of active carbon fibers (ACF) is shown in Fig. 1. The ACFs (square carbon cloth mats with an area of 5 cm^2) were obtained from BEAM ASSOCIATE (Taiwan) and were cleaned by a reactive ion etcher system (Trion Phantom III) under the working conditions of: 25 sccm O_2 mass flow, 150 W working power, 1×10^{-3} Torr working pressure, and a 2400 s reaction time. After cleaning the ACFs, they were treated by the CF_4 plasma method with a CF_4 mass flow rate of 25 sccm, a rf power of 150 W, a working pressure of 1×10^{-3} Torr, and a reaction time of 2400 s in the reactive ion etcher system (Trion Phantom III). The CF_4 plasma treated carbon cloth mats then serve as the first set of GDL in this work. The second set of GDL used in this work was made by dip-coating method. The ACF mats were dip-coated in 10 wt% PTFE solutions, a procedure manually performed in an open beaker with a dipping time of approximately 12 s. The dip-coated carbon cloth mats were then dried in a vacuum oven at room temperature for 1 day.

2.2. Membrane electrode assembly preparation

The MEAs fabrication procedure is as follows. A Nafion® 112 (Du Pont) polymer electrolyte membrane (PEM) was first

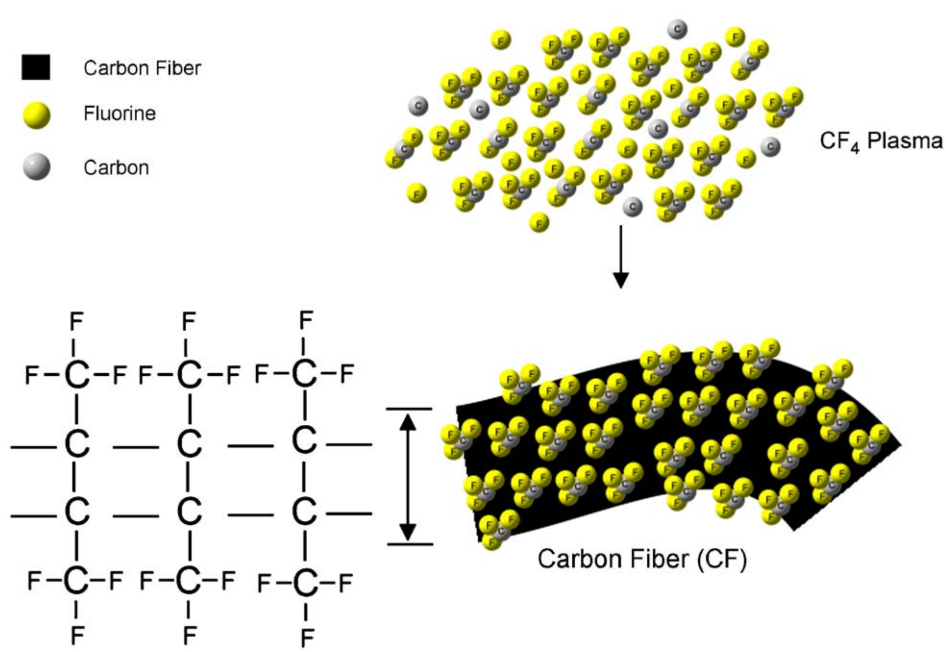

Fig. 1. Schematic diagram of the CF_4 plasma treatment on the ACFs.