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Full Length Article

Assessment of graphene as an alternative microporous layer material for proton exchange membrane fuel cells

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ABSTRACT

Microporous layer (MPL) is a key component in the management of water (and to a lesser degree, heat) for enhanced performance, reliability and durability of proton exchange membrane (PEM) fuel cells at high current densities for a wide range of commercial applications. In this study, as an alternative to conventional nanomaterials, such as Ketjenblack, graphene, a monolayer of carbon atoms arranged in a two-dimensional lattice, is considered to be an ideal MPL material due to its unique characteristics, including excellent electrical and thermal conductivity. A graphene-based MPL has been prepared and investigated for its effective water management and performance enhancement for PEM fuel cells through morphological, structural, physical and electrochemical characterization and performance testing for single large cells. Comparison studies are also conducted with the MPL made of conventional material, Ketjenblack. It is shown that the graphene-based MPL demonstrates comparable performance to the one made of Ketjenblack under high-humidity operation, while exhibiting excellent performance superiorities (up to a peak power density improvement of approximately 55%) under low- and intermediate-humidity operation. Overall, the graphene-based MPL has significant potential to meet performance demand under a wide range of operating conditions.

1. Introduction

Although reached the early stage of commercial deployment, proton exchange membrane (PEM) fuel cell technology is still under intensive development for higher-current density operation to achieve better performance, durability, reliability and cost reduction for wider applications [1–4]. Membrane-electrode assembly (MEA), the core component within the PEM fuel cell where electrochemical reactions occur to produce electric energy, requires a substantial improvement for better water and heat management for higher current density operation, and the conventional use of a microporous layer (MPL), composed of a carbon powder and a polymeric binder and placed on both the anode and cathode gas diffusion layers (GDLs) of the MEA, can function reasonably [5–9], requiring drastic improvement to meet the needs of various practical applications.

Extensive studies have been directed towards the improvement and optimization of MPL materials, design and fabrication processes [10–16]. Due to their favorable properties, such as low cost, wide availability, high corrosion resistance, acceptable thermal and electrical conductivity and environmental acceptability, various types of carbon-based nanomaterials – ranging from Vulcan XC-72R [17], Ketjenblack® EC-300 J [18], Ketjenblack® EC-600JD [19], to Black Pearls® 2000 [10] and Hicon Black® [20] – have been investigated as MPL materials. Because different carbon-based nanomaterials possess their own unique characteristics, their potential as MPL materials need to be confirmed [21]. It is known that the PEM fuel cells with the MPLs made of these carbon-based nanomaterials exhibit promising performance under a very limited range of operating condition (see, [10,22] for example), which is not fully satisfactory for large-scale commercialization, and more specifically, for the goal of achieving long-term operation under low-humidity conditions [23].

As an alternative to the conventional nanomaterials, graphene, “a monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice” [24,25], would be an appealing material owing to its unique characteristics, such as favorable electrical and thermal conductivity [23,26]. Graphene flakes are also prone to stack horizontally to form a smooth layer [24]. Thus, placement of such a compact and smooth layer between the catalyst layer and GDL could promote catalyst utilization, minimize interfacial resistance, and facilitate heat transport. However, thus far, there have been few studies centered upon introducing

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graphene into MPL structures. For instance, Leeuwner et al. [27] have reported various benefits of situating a free-standing commercial graphene foam between the catalyst layer and GDL for small-scale PEM fuel cells (with an electrode geometric area of 5 cm^2). These benefits include reduced contact resistance, improved mechanical integrity between the GDL and catalyst layer, and performance enhancements, notably at the low- and intermediate-current densities. Nevertheless, the free-standing commercial graphene foam employed in their work is not purposefully designed and manufactured for its use as an MPL. In addition, unlike purposefully designed MPLs, the graphene foam employed as an MPL does not involve a hydrophobic agent, which restricts its ability to remove accumulated water, specifically under high-humidity conditions. Recently, Najafabadi et al. [23] have manufactured ultrathin electrochemically exfoliated graphene sheets for use in small-scale PEM fuel cells. Similar to those reported by Leeuwner et al. [27], their results confirm the performance-enhancing effects of the graphene-based MPLs, specifically at low- and intermediate- current densities and low-humidity conditions. Overall, previous research on graphene-based MPLs seems to be encouraging, particularly when the operational flexibility targets established by the United States Department of Energy (DOE) for 2020 are considered [23]. These studies have provided a good basis for further work by revealing the potential use of graphene as an MPL material for PEM fuel cells. Nevertheless, it is suggested that further investigation of the morphological, structural, physical and electrochemical characteristics of graphene-based MPLs as well as their performances in scaled-up cells is needed to gain a better understanding [23].

Therefore, the objective of the present study is to investigate graphene as an alternative MPL material for scaled-up PEM fuel cells through morphological, physical, structural and electrochemical characterization and single cell performance testing. To this end, a graphene-based MPL has been spray-deposited onto the single-layer GDL, and the resulting double-layer has been extensively characterized to shed light on its morphological, structural (e.g., porosity, pore-size distribution, pore surface area and pore volume) and physical (e.g., air permeability, wettability and electrical resistivity) characteristics. The potential effect of situating a compact and smooth graphene-based MPL layer between the catalyst layer and GDL on catalyst activity is also investigated through in-situ cyclic voltammetry (CV). Performance characteristics of the PEM fuel cell with the graphene-based MPL are examined in a scaled-up PEM fuel cell (with an electrode geometric area of 45 cm^2) under various operating conditions. For comparison purposes, all these characterizations are also carried out for a double-layer GDL with an MPL made of Ketjenblack. Hereinafter, for brevity, the MPLs made of graphene and Ketjenblack powders are referred to as the graphene MPL and KB MPL, respectively.

2. Experimental

2.1. Materials

The following materials are used in the preparation of the MEAs: AvCarb EP40 carbon paper is employed as the cathode single-layer GDL, Avcarb GDS3250 as the anode double-layer GDL, carbon-supported platinum (Pt/C, 68 wt%, Tanaka Kikinzoku Koygo (TKK)) as both the anode and cathode catalysts, 25 wt% perfluorosulfonic acid, Nafion® 211 membrane as received, 2-propanol (IPA, 99.9%, Sigma-Aldrich®) and deionized (DI) water produced via a water purification system. For MPL preparation, the materials used include graphene powder (Grade DU25, NanoXplore, BET surface area: 305 $m^2 g^{-1}$), Ketjenblack® EC-600JD (Akzo Nobel, BET surface area: 1255 $m^2 g^{-1}$), 60 wt% polytetrafluoroethylene (PTFE, Sigma-Aldrich®) and deionized (DI) water. For pore characterization, octane (> 99%, anhydrous, Sigma-Aldrich®) is employed as a working fluid because of its small wetting angle to ensure all the pores would be wetted without external forcing.

2.2. Microporous layer (MPL)

The graphene and KB MPLs are fabricated by following a three-step procedure that involves consecutive pretreatment steps. The first step is the preparation of MPL ink, through which graphene powder, 2-propanol, deionized (DI) water and hydrophobic agent (PTFE) are mechanically mixed and continuously stirred in an ultrasonic bath (Fischer Scientific™ Model 5800) for 2 h at room temperature. Thereafter, the resulting slurry is spray-deposited onto one side of the single-layer GDL at 80 °C, followed by heat treatment at 240 °C for 1 h to evaporate any remaining solvent. Finally, the fully dried double-layer GDL is sintered at 350 °C for 40 min to homogeneously distribute PTFE throughout the MPL. A similar three-step procedure is also repeated for the fabrication of the KB MPL. The carbon powder (either graphene or Ketjenblack® EC-600JD powders) and PTFE loadings are held constant at 2.0 mg cm^{-2} and 20 wt%, respectively, as suggested in [10,28].

2.3. Membrane electrode assembly (MEA)

The catalyst ink is prepared by ultrasonically blending Pt-C (68 wt %, TKK) with 25 wt% perfluorosulfonic acid, deionized (DI) water and 2-propanol for 1 h at room temperature. The resulting ink is directly sprayed onto each surface of Nafion® 211 until a total Pt loading of 0.5 mg cm^{-2} (a cathode loading of 0.4 mg cm^{-2} and anode loading of 0.1 mg cm^{-2}) is achieved. Commercially available anode double-layer GDL (Avcarb GDS3250 GDL) is placed on the anode side, while the test of interest double-layer GDL fabricated according to the procedure reported in the previous subsection is placed on the cathode side.

2.4. Physical characterization of carbon powders

Brunauer-Emmett-Teller (BET) surface areas and pore-size distributions of graphene and Ketjenblack® EC-600JD powders are determined through nitrogen physisorption analyses at −196 °C via a Quantachrome Autosorb-1 analyser. Prior to analyses, degassing procedure is carried out at 130 °C to remove any remaining moisture.

2.5. Characterization of double-layer GDLs

2.5.1. Morphological and microstructural characterization

The morphological characteristics of the double-layer GDLs and a single-layer GDL (before MPL was deposited on) are examined by a scanning electron microscopy (SEM) (Zeiss GeminiSEM 500). SEM images are intentionally captured from both the top and cross-sectional views of the samples to gain information about their surface and through-plane structures. All the images are recorded without any gold coating.

To assess the pore characteristics of the double-layer GDLs, a series of measurements are performed by adopting a procedure similar to that reported in [29] via an automated standard porosimeter (Porotech Standard Porosimeter 3.1). To perform the analyses, the sample of interest is first dried at 180 °C for 1 h under a vacuum environment along with two standard samples. Thereafter, the samples are weighed and immersed in a working fluid (i.e., octane) under a vacuum environment, followed by sandwiching the tested sample between the standard ones. The stacked samples are loaded onto the porosimeter, weighed and recorded at time intervals of 3 min to determine the amount of liquid saturation, due to evaporation of the working fluid. Then, the capillary pressure curve of the tested sample is determined by using the known capillary pressure curves of the standard samples, with the assumption that the test and two standard samples are in capillary equilibrium.

2.5.2. Physical characterization

The through-plane air permeabilities of the double-layer GDLs are determined by an in-house experimental apparatus, which is capable of