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Effect of microporous layer composed of carbon nanotube and acetylene black on polymer electrolyte membrane fuel cell performance

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ABSTRACT

The cathode microporous layer (MPL) is fabricated by composite carbon materials composed of multi-wall carbon nanotubes (CNT) and acetylene black (AB) and its effect on polymer electrolyte membrane fuel cell (PEMFC) is examined. The mixing ratio of CNT and AB are adjusted in the experiments and the cell performance is characterized by the methods of polarization curve, electrochemical impedance spectroscopy, and cyclic voltammetry. The results are compared with the cases of MPL made by pure AB and CNT. It is found that the employment of CNT as MPL material indeed may significantly improve fuel cell performance. The case of pure CNT exhibits better cell performance than that of pure AB. Especially, once AB and CNT are mixed to form composite carbon black and fabricate MPL, the cell performance can be enhanced further. The optimal mixing ratio of AB and CNT and the corresponding optimal loading are determined. Moreover, the optimal PTFE content for such a MPL is also evaluated. The results show that the cathode MPL with mixing ratio of 1: 4 of AB and CNT in mass-based gives the highest performance in all the experimental cases. The optimal loading and PTFE content are 1.5 mg cm^{-2} and 20 wt%, respectively. The present work reveals that the application of CNT as MPL composition is an efficient way to improve PEMFC performance.

Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has received much attention in the past decades as a novel power source for diverse applications. However, its performance still needs improvement especially in water management problem in order to meet the fast response to power requirement in the system [1]. The water vapor produced by oxygen reduction reaction (ORR) at the cathode catalyst layer (CL) may condense into liquid water and accumulate within the CL and the adjacent gas diffusion layer (GDL). This phenomenon may impede reactants transport through GDL and CL, and reduce catalytic sites for electrochemical reaction. Hence, the condensed liquid water should be removed through GDL to gas flow channel to prevent degradation in cell performance. Accordingly, the GDL properties are quite critical in water

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management and become a challenge to achieve maximum cell performance.

The GDL is sandwiched between the CL and the gas flow channel. In general, the GDL is a dual-layer structure which consists of a macroporous substrate made by carbon paper or carbon cloth and a thin carbon layer coated on its surface. The thin carbon layer is named microporous layer (MPL) which generally contains carbon black powder and hydrophobic agent like polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP) for the management of two-phase water flow. Hence, the MPL properties affect the catalyst utilization rate in the adjacent CL and the overall cell performance profoundly. Numerous studies have been published in the literature to investigate the effects of GDL and MPL on PEMFC performance. The details could be found in the review articles [1,2].

Recently, many studies have tried to employ carbon nanotubes (CNTs) as the material of GDL [3] or MPL [4–10]. A novel type of GDL prepared by growing carbon nanotubes directly on the fiber surface of carbon cloth was proposed in the work [4]. Stampino et al. [5] fabricated a multi-wall CNTs-based MPL in which carbon black in the formulation of MPL was partially substituted by CNT. They assembled a single cell with the CNT-based MPL and found that its electrochemical performance was better than that obtained with a conventional MPL made by Vulcan XC-72R carbon black without any addition of CNT. Gharibi et al. [6] also studied the effects of the addition of multiple-wall CNTs in a MPL containing Vulcan XC-72R on the oxygen reduction reaction (ORR). Their results showed the optimal MPL composition at various Pt loadings in the CL. The effect of cathode MPL composed of carbon powder (Vulcan XC-72) or CNTs on the direct ethanol fuel cell was considered in the work of Li et al. [7]. Their results show that the cathode potential can be improved significantly by the employment of CNTs as MPL material. Schweiss et al. [8] modified the MPL by doping multiwall CNTs using a wet-chemical approach. They found that the electronic resistance of GDL was reduced significantly and accordingly the PEMFC performance was improved by using such CNT-doped GDLs. The effect of CNT loading and type in MPL had been studied in the work of Purwanto et al. [9]. At the same CNT content of 50 wt% in MPL, they found that the case of single-wall CNT gives higher cell performance than that of multi-wall CNT. Comparison of three types of carbon (Vulcan XC-72R, long vapor-grown CNTs, and short vapor-grown CNTs) as MPL materials was performed in the study of Jung et al. [10].

Traditionally, MPL is made either by acetylene black (AB) or Vulcan XC-72R. It has been found that the employment of AB exhibits better cell performance than the case of Vulcan XC-72R [11,12]. Hence, in the present study we use multi-wall CNT and AB to make composite carbon black and apply it to the fabrication of cathode MPL. Its influence on PEMFC performance is explored in details. The objective is to determine the optimal mixing ratio of CNT and AB as cathode MPL material. The effect of PTFE content on the cell performance is also evaluated to determine the optimal composition. The results benefit the understanding for the application of CNT as MPL material and the improvement of PEMFC performance.

MEA preparation and performance characterization

To make the gas diffusion media, the commercial SGL® 10BA carbon paper with 5 wt% PTFE content was used as the substrate for cathode GDL. The paper was washed with acetone before MPL coating to remove possible surface contaminants. For MPL coating, carbon slurry was first prepared from a mixture of multiwall CNT and AB with a pre-assigned weight percentage of PTFE using ethylene glycol as solvent. The multiwall CNT was provided by Golden Innovation Business Co., Ltd with series number S-MCNT-2012. The dimensions of CNT and AB are listed in Table 1. The mixture was sonicated in an ultrasonic cleaner and then agitated by a dispersing instrument for 1 h in each process to ensure sufficient mixing of CNTs, AB, and PTFE. Next, the slurry was coated uniformly on the surface of the carbon paper by a blade coating machine to form the MPL. Subsequently, the MPL-coated carbon paper was dried in a convection oven at 90 °C. Finally, it was dried further at 240 °C for 30 min and then sintered in a high-temperature oven at 350 °C for 40 min to complete the MPL coating. All the experiments used the SGL® 10BC carbon paper as the gas diffusion media in the anode side. The MEA was assembled by a catalyst-coated polymer electrolyte membrane (CCM, Nan-Ya®, bMEA5) with anodic and cathodic gas diffusion media on opposite sides of the CCM. The active reaction area of the MEA is 2 cm × 2 cm. A single cell comprising the MEA, graphite flow field plates, current collectors, and end plates was connected to a fuel cell test station to measure the cell performance. Pure hydrogen and air were used as the fuel and the oxidant and both reactant gases were humidified by bubbling through distilled water tanks held at an assigned temperature of 70 °C. The temperature of the cell was also held at 70 °C in all experiments by electrical pipe heaters. During the performance characterization process, the flow rates of hydrogen and air were first held at minimum values of 200 sccm and 500 sccm, respectively, and then they were adjusted automatically by the stoichiometric values of 2.0 for both hydrogen and air, respectively. The method of electrochemical impedance spectroscopy (EIS) was used to identify the contributions of cell resistance. The measurements were performed by a frequency response analyzer (FRA) module added on to the potentiostat (Autolab PGSTAT 302N). The impedance spectra were recorded by sweeping frequencies over the range of 10 mHz–10 kHz with the amplitude of the AC current held at 5% of that of the DC current. The obtained spectra were further analyzed by an equivalent circuit to explore the variations of ohmic resistance, charge transfer resistance, and gas transfer resistance. In situ cyclic voltammetry (CV) measurements were also conducted in order to

Table 1 – The dimensions of CNT and AB used in the experiments.

Type of carbon	Diameter (nm)	Length (μm)	Specific surface area ($m^2\ g^{-1}$)
CNT	10–20	1–2	>160
AB	42	_	62