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Design of Polymer-Coated Multi-Walled Carbon Nanotube/Carbon Black-based Fuel Cell Catalysts with High Durability and Performance Under Non-humidified Condition

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ABSTRACT

To realize a high catalyst utilization, better fuel cell performance and durability as well as low production cost, an efficient design strategy of the catalyst layer that can improve both the oxygen accessibility and structure stability is highly required. Here, we describe the preparation of fuel cell electrocatalysts with an efficient fuel cell performance and better stability based on hybrids of multi-walled carbon nanotubes (MWNTs) and carbon black (CB) which were wrapped by a proton conducting polymer, poly[2,2′-(2,6-pyridine)-5,5′-bibenzimidazole], before deposition of the platinum (Pt) metal catalyst. The catalyst mass activity after feeding only 10%-MWNTs to CB increased by 1.5 and 2 times than those of the MWNTs-based- and CB-based catalysts, respectively. The results also demonstrated that 90 wt% of the MWNTs in the catalyst layer allows it to be replaced by CB without any significant change in its durability and performance under 120 °C and non-humidified condition.

1. Introduction

Fuel cells, in particular polymer electrolyte membrane fuel cells (PEMFCs), are receiving increasing attention for transportation, portable electronic devices and power supplies due to their high energy density, high efficiency and green emissions [1–9]. It has been widely recognized that cost, performance and durability are the main roadblocks that prevent PEMFCs from reaching their wide spread applications [10].

The PEMFC electrocatalysts strongly affect the final production cost of the FC units [11]. In addition, they mainly determines the lifetime of the PEMFC unit [12]. These electrocatalysts are usually based on metal-supported carbon materials. Platinum (Pt) as a precious metal has been widely used as a catalyst for both the anode and the cathode of the membrane electrode assemblies (MEAs) due to its high durability and catalytic activity compared to the other metals or metal oxide catalysts [13–19]. The mass activity of Pt strongly depends on the carbon supports [20], and several kinds of carbon materials have been introduced as catalyst supports in order to increase the Pt electrochemical surface areas. Carbon black (CB) has been the most widely used carbon support in the PEMFCs because it is commercially available, has a high surface area, high electrical conductivity and low cost compared to the other carbon support materials. However, it undergoes a fast corrosion process in terms of durability during the FC operation process, especially under high temperature operating conditions [21]. Therefore, the use of CB accelerates the degradation process of the corresponding MEA, leading to a short life time of the FC. Hence, searching for a new technique that improves the durability of the FC catalyst-support, while reducing its cost, has become an essential and urgent target for the global commercialization of the FCs.

The graphitization of CB to change its morphology or to modify its nanostructures through the enhancement of its crystal degree was one of the techniques of improving the durability of CB, while graphitization usually results in lowering the interaction between the CB and Pt nanoparticles (NPs), leading to aggregation of the Pt-NPs and the loss of the active surface area [22,23]. Recently, Gharibi et al. reported that feeding MWNTs into a micro-porous catalyst layer containing CB enhanced the oxygen reduction reaction (ORR) [24]. Kim et al. sputtered Pt on the MWNTs-CB hybrid supports and got the highest electrochemical surface area (ECSA, 20.6 m^2/g_{Pt})

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with the weight ratio of 50:50 [25]. Chua et al. also directly sputtered Pt on CNT grown on carbon paper and found an enhancement in power density compared to CB-based gas diffusion electrode (GDE) [26]. Meanwhile, Ramaprobhu et al. and Yan et al. loaded the Pt-NPs on the hybrids of acid-oxidized MWNTs and CB and reported the optimized weight ratio (50:50) according to the FC performance [27,28]. However, in these studies, the durability of the electrocatalysts was not clear. Moreover, the lack of triple phase boundary (TPB) resulted in the low Pt utilization, and the oxidization of the MWNTs lowered the long-term durability of the electrocatalyst. Thus, the development of an electrocatalyst using the pristine MWNTs-CB as the carbon support having a high Pt utilization efficiency and long-term durability is strongly required. Especially, such performance is important in the design and development of high-temperature PEMFC having advantages of higher carbon monoxide (CO) tolerance, faster electrochemical kinetics, and easier water management [29,30].

Recently, we reported a homogeneous deposition technique of Pt nanoparticles onto the surfaces of the pristine-MWNTs, in which the MWNTs were first wrapped with a proton conducting polymer, poly[2,2′-(2,6-pyridine)-5,5′-bibenzimidazole] (PyPBI), before immobilization of the Pt-NPs. The PyPBI-wrapped MWNT composite worked as a binding site for the Pt-NPs. The obtained electrocatalyst exhibited a high Pt utilization efficiency, a high fuel cell performance and a remarkable durability as well as the fabrication of TPB due to the presented unique technique of Pt immobilization and the remarkable mechanical and electrical properties of the MWNTs that make the feeding of the reactant and the transfer of the electrons from/to the active sites in the catalyst layer more facile [31–34]. Thus, we applied the polymer wrapping method to the pristine MWNTs-CB hybrid supporting materials to improve the Pt utilization and long-term durability in the non-humidified high-temperature PEMFC.

Herein, in this study, we prepared FC electrocatalysts with hybrid support materials by varying the blending ratios of the CB and MWNTs that were wrapped by PyPBI. The electrochemical surface area (ECSA) durability and oxygen reduction reaction (ORR) as well as the high temperature fuel cell performance of the obtained electrocatalysts under non-humidified conditions were investigated in detail. We here describe the first report on the use of MWNTs-CB hybrid supporting materials in non-humidified high temperature PEMFC studies.

2. Experimental

2.1. Materials

LiBr was supplied by Nacalai Tesque, Ltd. 2-Propanol, *N,N*-dimethylacetamide (DMAc), ethylene glycol (EG), hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), and 85% phosphoric acid (PA) were purchased from Wako Pure Chemical, Ltd. The MWNTs with ~20-nm diameter were kindly provided by the Nikkiso Corp. CB (Vulcan XC-72R) was purchased from the Cabot Chemical Co. CB/Pt was purchased from Tanaka Kikinzoku Kogyo K. K., in which 37.9 wt% of Pt-NPs was supported on Vulcan® XC-72. All the chemicals were used as received without any purification. PyPBI and poly[2,2′-(2,6-phenyl)-5,5′-bibenzimidazole] (PBI) were synthesized according to previously reported methods [35,36].

2.2. Synthesis of the electrocatalysts

In a flask, x mg of the MWNTs and y mg of CB (x+y=10 mg) were placed in DMAc (20 mL) and dispersed by sonication (Yamato 5510, Branson) for 1 h to obtain a CB-MWNT mixture, to which PyPBI dissolved in 10 mL of DMAc was mixed and sonicated for 2 h. The formed composite was filtered, and then dried overnight under vacuum at 80 °C. The deposition of the Pt-NPs was carried out by the reduction of $H_2PtCl_6{\cdot}6H_2O$ in an EG aqueous solution at 140 °C. First, 10 mg of the PyPBI/MWNTs/CB composite was dispersed in a 30 mL EG aqueous solution to which aqueous EG (20 mL) containing 24 mg of $H_2PtCl_6{\cdot}6H_2O$ was added, then refluxed at 140 °C for 6 h under a N_2 atmosphere. The obtained composite was collected by filtration, and then dried overnight at 60 °C. The composites with various ratios of the MWNTs and CB were denoted as PyPBI/$_x$MWNT-$_y$CB/Pt, where the $_x$ and $_y$ values are the feeding ratios of the MWNTs and CB, respectively.

2.3. Material characterization

The X-ray photoelectron spectra (XPS) were measured using an AXIS-ULTRA^{DLD} (Shimadzu). Thermal gravimetric analysis (TGA) measurements were conducted with an EXSTAR 6000 (Seiko, Inc.) at the heating rate of 5 °C/min under 100 mL/min flowing air. The transmittance electron micrographs (TEM) were obtained using a JEM-2010 (JEOL) electron microscope at the acceleration voltage of 120 kV. A copper grid with a carbon support (Okenshoji) was used for the TEM observations. X-ray diffraction (XRD) measurements were carried out by using a Rigaku SmartLab diffractometer (Cu, Kα, λ=1.5406 Å, 40 kV, and 30 mA), the diffraction patterns were collected from 20° to 90° at a scan rate of 1°/min and with a step of 0.01°.

2.4. Electrochemical and durability measurements

The electrochemical measurements were performed on a rotating ring disk electrode connected to a rotating ring disk instrument, RRDE-3 (Bioanalytical Systems, Inc.) with a conventional three-electrode configuration in a vessel at room temperature. A glassy carbon electrode (GCE) with a geometric surface area of 0.196 cm^2 was used as the working electrode. A Pt wire and an Ag/AgCl were used as the counter and reference electrodes, respectively. The potential of the electrode was controlled by an ALS-Model DY2323 (BAS) potentiostat. Typically, the catalyst suspension was prepared as follows. The composite (1.0 mg) was ultrasonically dispersed in an 80% aqueous EG solution (2.0 mL), and a portion of the dispersion was then cast on a GCE to provide a catalyst layer (the loading amount of Pt was controlled at 14 μg/cm^2). Finally, the cast film on the electrode was air-dried. The cyclic voltammetry (CV) measurements of the electrocatalysts at the scan rate of 50 mV/s were carried in an N_2-saturated 0.1 M $HClO_4$ solution in order to determine the electrochemical surface areas (ECSAs). The measurements were repeated twice to determine the average of the ECSA values. The oxygen reaction reduction (ORR) was tested in an O_2-saturated 0.1 M $HClO_4$ solution at room temperature at the scan rate of 10 mV/s. Durability test was carried out by continued CV cycling from −0.17 to 0.93 V *vs.* Ag/AgCl. The ECSA values were calculated after every 200CV cycles, and the results were used to obtain the normalized ECSA values.

2.5. Fuel cell test

Typical fabrication procedure of a gas diffusion electrode (GDE) is as follows. The composite was dispersed in a 50 mL 2-propanol aqueous solution by sonication for 1 h. The obtained solution was filtered using a gas diffusion layer (GDL) as the filter paper. The Pt loading amount on the GDL was controlled at 0.45 mg/cm^2. The obtained GDE was dried overnight under vacuum at room temperature to remove any residual solvent.

In a 50-mL glass bottle, 100 mg of LiBr was dissolved in 10 mL of DMAc, to which 200 mg of PBI polymer was added. The bottle was