



Homogeneous coating of ionomer on electrocatalyst assisted by polybenzimidazole as an adhesive layer and its effect on fuel cell performance



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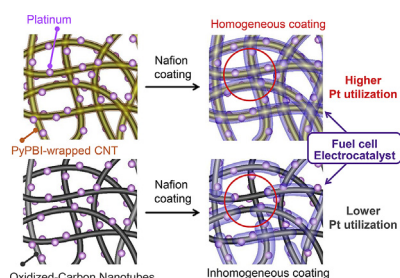
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HIGHLIGHTS

- Polybenzimidazole on carbon nanotubes assists an adhesion of a Nafion ionomer.
- A homogeneous Nafion network structure in the fuel cell catalyst layer is formed.
- Pt-efficiency and power density of the Nafion-coated electrocatalyst are enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

The fabrication of homogeneous ionomer distribution in fuel cell catalyst layers is necessary and important to improve the platinum utilization as well as the power density. Here, we focus on the effect of poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) wrapped on multi-walled carbon nanotubes (MWNTs) for anchoring Nafion ionomer to the electrocatalyst, in which PyPBI functions as the binding sites for platinum nanoparticles (Pt-NPs) used as a catalyst. Based on the result using a control composite without having PyPBI, a strong interaction of the Nafion onto the PyPBI layer is recognized. Importantly, we find that the membrane-electrode assembly (MEA) shows a much higher maximum power density than that of the MEA without PyPBI. A homogeneous coating of Nafion on the electrocatalyst using the PyPBI forms a long-range network of the ionomer, leading to an improved Pt-NP utilization efficiency as well as an enhanced power density of the MEA.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are attractive and promising energy generation sources for sustainable low-carbon society due to their cleanness as well as the high energy density [1–3]. Typically, perfluorinated polymers having a sulfonic acid group,

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such as Nafion, have widely been used as the electrolyte due to their high proton conductivity as well as easy availability [4–6]. Carbon black (CB) has traditionally been used as the electron-conductive supporting material for the platinum nanoparticles (Pt-NPs) used as the catalyst. Recently, a power generation device based on the PEFCs mainly for a stationary battery for residential and automotive vehicles offered commercially. However, the enhancement of the durability and the improvement of the efficiency of the catalysts are still main issues in the PEFCs for further global commercialization. Especially, a serious oxidation corrosion of CBs ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, 0.207 V vs. RHE) [7–9] has been known to trigger the detachment of the Pt-NPs from the carbon support and/or the agglomeration of the Pt-NPs, resulting in deterioration of the performance of the PEFCs [8,10–12]. Thus, improvement of the durability of the carbon support is a strong demand in the development of the next generation PEFCs. Among the various alternate carbon support materials being proposed to date [8,13,14], multi-walled carbon nanotubes (MWNTs) have been considered as one of the promising substitute due to their highly graphitized structure and high electron conductivity [3,15,16]. For use of the MWNTs, the introduction of binding sites of the Pt-NPs on the pristine MWNTs is necessary because the Pt-NP loading on the pristine MWNTs, is very difficult, thus harsh oxidation of the pristine MWNTs has been applied to introduce –COOH or –OH groups for anchoring Pt-NPs [17–20]. However, such an oxidation of the pristine MWNTs may lower the durability. In our previous reports, we reported a novel methodology to introduce the binding sites for Pt-NPs without oxidizing the surfaces of the MWNTs, in which poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI; Fig. 1) was used to wrap the MWNTs and provide binding sites for the Pt-NPs to prepare an applicable catalyst of the PEFCs [21–26]. In previous system, we used phosphoric acid (PA) or poly(vinylphosphonic acid) (PVPA) as the electrolyte in the electrocatalyst (so called ionomer) since the PA and PVPA have been doped for polybenzimidazole (PBI) to facilitate the proton conductivity in the membrane [26–30]. Also the coating of the metal/metal oxide particles is a new technology used in the fabrication of the catalysts [31,32]. However, these electrolytes showed a high proton conductivity only in the high operation temperature ($>100^\circ\text{C}$), thus they are not applicable to the current PEFC system.

In this study, we employed Nafion as an ionomer for the Pt-NP-deposited PyPBI-wrapped MWNTs for the current PEFC system to take advantage of the high durability of non-oxidized MWNTs against corrosion. Similar to PA and PVPA, Nafion is expected to interact and immobilize on the PyPBI through the acid–base reaction between the acidic sulfonic group and basic imidazole group, leading to the formation of a proton conduction path on the surfaces of the MWNTs [33,34]. Thus, homogeneous coating of PyPBI onto the surface of the MWNTs is expected to form a homogeneous Nafion-coating to create a long-range proton conduction network in the electrocatalyst layer. To study this issue, we prepared an electrocatalyst without using PyPBI as the control, in which oxidized-MWNTs (ox-MWNT) were used to deposit Pt-NPs [35–37]. Fabrication of a continuous Nafion network is still challenge for the formation of a state-of-the-art CB-based electrocatalyst to improve the power density [38,39]. Therefore, the present study will offer the useful knowledge not only in the design

strategy for the MWNT-based electrocatalyst used in the next generation but also for the CB-based electrocatalyst in the current PEFC systems.

2. Experimental section

2.1. Materials

Hydrogen hexachloroplatinat hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), 2-propanol, *N,N*-dimethylacetamide (DMAc) and ethylene glycol (EG) were purchased from Wako Pure Chemical, Ltd. The MWNTs with a ~20 nm diameter were kindly afforded by Nikkiso. Corp. The Nafion solution (5 wt%) and Nafion[®] 117 membrane were purchased from Sigma–Aldrich. The Pt-NP-deposited CB (CB/Pt) catalyst was purchased from Tanaka Kikinokogyo K. K., in which 37.9 wt% of Pt-NPs was supported on Vulcan[®] XC-72. The PyPBI was synthesized according to a previous report [40]. All the chemicals were used as received without any purification.

2.2. Preparation of ox-MWNT/Pt and MWNT/PyPBI/Pt

The MWNTs (10 mg) were dispersed in DMAc (20 mL) using a bath-type sonicator (Branson 5510) for 1 h to which PyPBI (5 mg) dissolved in DMAc (10 mL) was added, and then sonicated for 1 h. The formed composite (MWNT/PyPBI) was filtrated and washed with DMAc, then dried overnight under vacuum at 80°C .

To oxidize the MWNTs by ozone irradiation, the pristine MWNTs (100 mg) were placed in a chamber of an ozone generator (Cute-MP, Femto Science) under UV irradiation in the presence of O_2 (99.9%, flow rate, 10 mL min^{-1}). To oxidize the MWNTs by acid, the pristine MWNTs (100 mg) were sonicated in a 40 mL mixture of H_2SO_4 and HNO_3 (v/v = 3:1) at 60°C for 10 h. The obtained powder (ox-MWNT) was collected by filtration and washed by Mill-Q water. The composite was 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 a 60% EG aqueous solution at 140°C . Firstly, 10 mg of the MWNT/PyPBI (or ozone-oxidized MWNT or ox-MWNT) composite was dispersed in a 60% EG aqueous solution (30 mL) to which $H_2PtCl_6 \cdot 6H_2O$ (24 mg) dissolved in a 60% EG aqueous solution (20 mL) was added, then refluxed at 140°C for 6 h under N_2 atmosphere. The obtained composite was collected by filtration, and then dried overnight at 60°C .

2.3. Material characterization

The X-ray photoelectron spectroscopic (XPS) measurements were carried out using an AXIS-ULTRA^{DL} (Shimadzu) instrument. The thermogravimetric analysis (TGA) measurements were conducted by an EXSTAR 6000 (Seiko Inc.) at the heating rate of 5°C min^{-1} under 100 mL min^{-1} of flowing air. The transmission electron microscope (TEM) micrographs were obtained using a JEM-2010 (JEOL, acceleration voltage of 120 kV) electron microscope. A copper grid with a carbon support (Okenshoji) was used for the TEM observations.

2.4. Electrochemical measurements

The electrochemical measurements were performed on a rotating ring disk electrode equipped with a RRDE-3 (Bioanalytical Systems, Inc.) based on a conventional three-electrode configuration in a vessel at room temperature. A glassy carbon electrode (GCE) with a geometric surface area of 0.1257 cm^2 (electrode diameter = 4 mm) 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 a

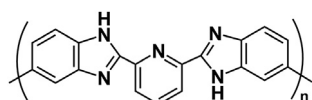


Fig. 1. Chemical structure of PyPBI.

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