Homogeneous Coating of Ionomer on Electrocatalyst Assisted by Polybenzimidazole as an Adhesive Layer and its Effect on Fuel Cell Performance

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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.

Keywords: Carbon nanotubes; Fuel cell; Ionomer; Membrane electrode assembly; Nafion; Polybenzimidazole.

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, 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 ($\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$, 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 oxidization 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 °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

Materials: Hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), 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 Kikinzoku Kogyo 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.

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 O₂ (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 H₂SO₄ and HNO₃ (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 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (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.

Material characterization: The X-ray photoelectron spectroscopic (XPS) measurements were carried out using an AXIS-ULTRA^{DLD} (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.

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 cm² (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 potentiostat (ALS-Model DY2323, BAS). To prepare a catalyst suspension, the composites (0.5 mg) were ultrasonically dispersed in an 80% aqueous EG solution (2.0 mL). A portion of the dispersion was then cast on a GCE, and air-dried to provide a uniform catalyst layer (the loading amount of Pt was controlled to be $14 \mu\text{g cm}^{-2}$). Cyclic voltammetry (CV) measurements of the electrocatalysts were carried in an N_2 -saturated 0.1 M HClO_4 at the scan rate of 50 mV s^{-1} in order to determine the electrochemical surface area (ECSA) of the catalysts.

The carbon corrosion was tested using the protocol proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ) (measured in an N_2 -saturated 0.1 M HClO_4 at room temperature without rotation), where the hold the potential was set at 1.0 V vs. RHE for 30 s and increased the potential to 1.5 V vs. RHE at the scan speed of 0.5 V s^{-1} , then the potential was decreased to 1.0 V vs. RHE. After every 1,000 cycles, CV was measured to determine the ECSA values [41].

Fuel cell testing: To prepare gas diffusion electrode (GDE), the electrocatalyst was dispersed in an 80 % of 2-propanol aqueous solution (50 mL) by sonication for 1 h to which 5 wt% of a Nafion solution (1.0 mL) was added and sonicated for 30 min. The obtained mixture was then filtered using a gas diffusion layer (GDL, SIGRACET®

GDL25BC, SGL Group) as a filter paper. The Pt loading amount on the GDL was controlled to be 0.45 mg cm^{-2} . The obtained GDE was dried overnight under vacuum at room temperature to remove any residual solvent. Membrane Electrode Assembly (MEA) was prepared by laminating two GDEs onto both sides of a Nafion® 117 membrane. The active area of the MEA was 1.0 cm^2 . The performance of the assembled MEAs was evaluated at $80 \text{ }^{\circ}\text{C}$ under 100% relative humidity (RH) using a computer-controlled fuel cell test system (Model 890e, Scribner Associate, Inc.). The I-V and the power density curves were obtained under the atmospheric pressure by flowing humidified hydrogen (flow rate; 100 mL min^{-1}) and humidified air (flow rate; 200 mL min^{-1}) at the anode and the cathode, respectively.

3. Results and Discussion

Electrocatalyst having Pt-NPs on the PyPBI-wrapped MWNTs (MWNT/PyPBI/Pt) was fabricated based on previous reports and as shown in Fig. 2a, the TEM image of the MWNT/PyPBI/Pt showed a homogeneous dispersion of the Pt-NPs with a narrow diameter distribution ($3.8 \pm 0.4 \text{ nm}$, also see Supporting Information, Fig. S1a), which is similar to our previous reports [22-26, 42]. This time, the control electrocatalyst having Pt-NPs directly loaded on the surface of the MWNTs was fabricated to explore the role of PyPBI wrapping, in which the oxidized MWNTs was used due to the absence of

loading ability of the pristine MWNTs. In the Raman spectra of the oxidized MWNTs and pristine MWNTs, two peaks appeared at ~ 1310 and 1580 cm^{-1} representing the defect (D) and graphite (G) bands of the carbon nanotubes. The higher G/D ratio suggests the highly graphite structure of the carbon materials. It was revealed the lower G/D ratio for the acid-oxidized MWNTs (*ox*-MWNTs, $G/D=1.2$) than that of the ozone-oxidized MWNTs (Fig. 2b, $G/D=1.4$), while the pristine MWNTs showed the G/D ratio of 3.4, indicating the higher degree of oxidation for the *ox*-MWNTs (Fig. 2b).

As shown in Fig. 2c, the Pt-NPs on the *ox*-MWNTs were deposited homogeneously compared to that of the Pt-NPs on the ozone-oxidized MWNTs (Fig. 2d; for lower magnification, see Supporting Information, Fig. S2). These results suggested that the severe oxidation is necessary for the homogenous loading of the Pt-NPs on the oxidized MWNTs. For further experiments, the Pt-NPs on the *ox*-MWNT/Pt having diameters of $4.7 \pm 1.0\text{ nm}$ was used (for the histogram, see Supporting Information, Fig. S1b).

To explore the interaction between the composites and ionomer, Nafion solution in 2-propanol was mixed with the composites and the resulting solutions were filtered and washed with methanol several times to remove any unbound Nafion. Fig. 3a and 3b show the XPS spectra of the composites after the vigorous washing (red line) together with the original composite (black line). For the MWNT/PyPBI/Pt (Fig. 3a), the peaks

due to the N_{1s} at ~400 eV derived from the imidazole in the PyPBI [22] and Pt_{4f} at around 72-75 eV were observed. Importantly, new peaks at ~689 and 168 eV due to the F_{1s} and S_{2p} , respectively [43], were observed after the washing, suggesting successful coating of Nafion on the MWNT/PyPBI/Pt to provide an ionomer-coated electrocatalyst (MWNT/PyPBI/Pt-*i*). On the other hand, both the F_{1s} and S_{2p} peaks were not detected from the *ox*-MWNT/Pt after washing (Fig. 3b; for narrow scans, see Supporting Information, Fig. S3), indicating that the Nafion ionomer was washed away from the electrocatalyst. The observed clear contrast indicated that the Nafion was immobilized on the MWNT/PyPBI/Pt surfaces based on the strong interaction through the acid-base reaction as schematically shown in Fig. 3c similar to the PVPA on the MWNT/PyPBI/Pt reported previously [27, 28], while the interaction between the *ox*-MWNT and Nafion was not sufficiently strong to immobilize on the *ox*-MWNT as presented schematically in Fig. 3d. Indeed, the MWNT/PyPBI/Pt-*i* provided a homogeneous dispersion in methanol after coating with Nafion (Fig. 3e), while aggregation was observed in the dispersion of the MWNT/PyPBI/Pt due to the hydrophobic property of the PyPBI (Fig. 3f).

The Nafion content in the MWNT/PyPBI/Pt-*i* was determined by the TGA, in which we observed a two-step weight reduction attributing the decomposition of Nafion (~300

°C) and MWNT/PyPBI (~500 °C), respectively (Fig. 3g) [24]. Based on the TGA data, the Pt contents of the MWNT/PyPBI/Pt and MWNT/PyPBI/Pt-*i* were determined to be 47.3 wt% and 45.7 wt%, respectively. Based on the decrease in the Pt content for the sample after the Nafion coating, the amount of Nafion on the MWNT/PyPBI/Pt-*i* was calculated to be 3.2 wt%. According to our previous report [24], the weight ratio between the PyPBI and MWNTs was 8/92, thus, the weight ratio of the PyPBI and Nafion ionomer was evaluated to be 4/3 in the MWNT/PyPBI/Pt-*i*. On the other hand, the *ox*-MWNT/Pt showed the nearly identical TGA curve even after the Nafion coating (Fig. 3h), indicating the absence of the Nafion after washing as observed in the XPS (Fig. 3b).

One of the advantages for the use of the non-oxidized MWNTs in place of the *ox*-MWNTs is the improvement of the durability of the fuel cell electrocatalyst. The durability of electrocatalysts was measured in 0.1 M HClO₄ solution by the protocol proposed by Fuel Cell Commercialization Conference of Japan (FCCJ), in which the potential was cycled from 1.0 to 1.5 V *vs.* RHE to accelerate the oxidation of the carbon support (see Supporting Information, Fig. S4) [41]. Upon cycling, the cyclic voltammograms (CVs) were measured after every 1,000 cycles to evaluate the electrochemical surface area (ECSA) of the Pt-NPs based on the peak due to adsorption

of hydrogen in the range of 0.1 ~ 0.4 V *vs.* RHE based on the following equation (1),

$$\text{ECSA} = Q_H / 210 \times (\text{Pt loading on electrode}) \quad (1)$$

where Q_H is the charge exchanged during the electroadsorption of hydrogen on Pt [44-47].

It was found that before and after the durability tests, the areas of the hydrogen adsorption peaks of the MWNT/PyPBI/Pt (range: 0.1 ~ 0.4 V *vs.* RHE) were almost identical (Fig. 4a), while the peak area of the *ox*-MWNT/Pt obviously decreased (Fig. 4b) after the durability tests probably due to the detachment and/or agglomeration of the Pt-NP upon the cycles [8, 48]. As in Fig. 4d, the evaluated initial ECSA value of the MWNT/PyPBI/Pt ($44.7 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$) decreased only around 10% after 10,000 potential cycles, while that of the *ox*-MWNT/Pt (initial ECSA value: $40.7 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$) showed a 23%-loss after the same number of cycling.

TEM observation has revealed that, after the durability test, the diameters of the Pt-NPs on the MWNT/PyPBI/Pt only slight increase to $4.3 \pm 0.7 \text{ nm}$ (Fig. 4e), whereas the diameter of the Pt-NPs on the *ox*-MWNT/Pt was largely grown to $5.6 \pm 2.4 \text{ nm}$ (Fig.

4f) (for the histograms, see Supporting Information, Fig. S5). This result clearly indicated the Pt-NPs on the pristine MWNTs are much stable compared to those on the *ox*-MWNT/Pt. It is also important to note that the Pt-NPs on the CB (CB/Pt) having initial ECSA of $60.6 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ (Fig. 4c) exhibited a much larger ECSA decrease ($\sim 47\%$, Fig. 4d). The relatively large hydroquinone-quinone (HQ/Q) redox peak observed at 0.55 V vs. RHE after durability testing (Fig. 4c) also suggested the lower oxidation resistance of the CB than those of pristine MWNTs and *ox*-MWNT [49]. Comparison studies between the *ox*-MWNT versus CB for the electrochemical durability have been carried out by many researchers in order to develop a carbon supporting material with higher durability, and the present data agreed well with them [50, 51]. Thereby, such result manifests that our approach to use the pristine-MWNTs by polymer-wrapping offers the better carbon supporting materials studies so far for the fuel cell electrocatalysts.

In order to utilize the composite as an electrocatalyst for membrane electrode assembly (MEA), the composites were casted on a carbon paper to fabricate a gas diffusion electrode (GDE) by vacuum filtration method using the dispersion of the MWNT/PyPBI/Pt and *ox*-MWNT/Pt containing Nafion (Fig. 5). In the preparation of GDE, the washing process was eliminated to avoid the removal of Nafion from the

composites during the filtration since the *ox*-MWNT/Pt has weak interaction to Nafion as we discussed above. Two sheets of GDEs were laminated on the both sides of the Nafion film to prepare the two types of MEAs, ie. *ox*-MEA and PyPBI-MEA prepared using MWNT/PyPBI/Pt and *ox*-MWNT/Pt, respectively. Prior to the fuel cell testing, the Nafion contents in the GDEs were measured using the XPS (Fig. S6). As shown in Table S1, the quantitative analyses of the F_{1s} and Pt_{4f} peaks revealed that the ratios between the F and Pt for both the GDEs were comparable, indicating that the ionomer contents for the two GDEs were similar since both GDEs possess the same amount of Pt ($0.45 \text{ mg}_{Pt} \text{ cm}^{-2}$).

Fig. 6a shows the polarization curves of the MEAs measured at 80 °C under 100% relative humidity (RH), in which we recognized that the PyPBI-MEA (red line) exhibited much higher current density than that of the *ox*-MEA (black line) and the maximum power density of the PyPBI-MEA reached as high as 430 mW cm^{-2} , although the two MEAs have the same amount of the Nafion, that of the *ox*-MEA was only 226 mW cm^{-2} (for the power density curves, see Supporting Information, Fig. S7). It is assumed that the difference in the performance is due to the difference in distribution of the ionomer in the electrocatalysts in the GDEs. Since the Nafion strongly interacted with the MWNT/PyPBI/Pt due to the PyPBI coating, we suppose the Nafion distribution

was more homogeneous compared to the Nafion distribution on the *ox*-MWNT/Pt, thereby the proton was delivered more efficiently in the PyPBI-MEA rather than in the *ox*-MEA. To prove this hypothesis, the *in-situ* CV measurements were performed for both MEAs to estimate the ratio of the Pt-NPs involved in the electrochemical reaction, and we found that the PyPBI-MEA showed ECSA as high as $40.3 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ which was similar with that in the half-cell, while the *ox*-MEA only showed $17.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ (Fig. 6b). Since the both electrocatalysts have almost comparable ECSA values in the half-cell measurements as discussed (Fig. 4a and 4b), the result clearly indicated that the larger amount of Pt-NPs in the PyPBI-MEA were incorporated in the proton conduction network compared to that of the *ox*-MEA. All the obtained results supported that the presence of the PyPBI on the MWNTs assisted the homogeneous coating of the ionomer, resulting in the formation of well-developed proton conduction paths (Fig. 6c), while the weak interaction between the Nafion and *ox*-MWNT/Pt resulted in the inhomogeneous coating (Fig. 6d).

Quite interestingly, we found that the MEA prepared using the MWNT/PyPBI/Pt-*i* by vigorous washing of the GDE provided a maximum power density of 300 mW cm^{-2} and ECSA of $23.5 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$, which were even higher than those of the *ox*-MEA (226 mW cm^{-2} and $17.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$, respectively). Notably, the Nafion content in the MEA using the

MWNT/PyPBI/Pt-*i* was only 3.2 wt% (Fig. 3g) which is ~7 times lower than that of the PyPBI-MEA that containing 21.5 wt% of Nafion as showed by the TGA analysis (see Supporting Information, Fig. S8). Such an effective utilization of Nafion can be also explained by the homogeneous coating of Nafion assisted by the PyPBI as discussed in Fig. 3c. The results emphasized importance and role of the PyPBI for the formation of ionomer networks along with the MWNT networks, leading to the improvement of the utilization efficiency of Pt-NP.

Formation of the effective proton conduction path in the electrocatalysts have been a key issue in the design of the PEFCs with a high activity as stated in introduction, thereby the present study provides a useful strategy for the development of the PEFCs with high performance.

4. Conclusion

We studied the effect of interaction of Nafion ionomer on the electrocatalyst for the activity of the fuel cell. In the MWNT/PyPBI/Pt, Nafion binds on the surfaces strongly due to the acid-base reaction between the PyPBI and Nafion to form an ionomer-coated MWNT/PyPBI/Pt (MWNT/PyPBI/Pt-*i*), whereas on the *ox*-MWNT/Pt, no such coating was recognized due to the absence of the interaction. Fuel cell testing of membrane-electrode assembly (MEA) under 80 °C with 100%RH exhibited that the

MEA having MWNT/PyPBI/Pt (PyPBI-MEA) showed—almost two-times higher maximum power density (430 mW cm^{-2}) than that of the MEA prepared from *ox*-MWNT/Pt (*ox*-MEA, 226 mW cm^{-2}). *In-situ* CV measurements of the two MEAs revealed that the PyPBI-MEA possessed a much higher ECSA value ($40.3 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$) than that of the *ox*-MEA ($17.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$) and the value was almost comparable to the ECSA in the half-cell ($44.7 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$), indicating that the most of the surfaces of the Pt-NPs was efficiently used in the MEA. Surprisingly, MEA prepared by the MWNT/PyPBI/Pt-*i* having a Nafion content of 3.2 wt% exhibited a higher maximum power density (300 mW cm^{-2}) than that of the *ox*-MEA. All the results supported that the homogeneous coating of Nafion on the MWNTs assisted by the PyPBI realized the formation of a long-range proton conduction path, resulting the improvement of the utilization efficiency of the Pt-NPs. The present work provides a novel methodology to form a long-range ionomer network in the fuel cell catalyst layer for improving the utilization efficiency of the Pt-NP. The finding is very important for lowering Pt amount in PEFC.

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Fig. 1. Chemical structure of PyPBI.

Fig. 2. TEM image of MWNT/PyPBI/Pt (a). Raman spectroscopy of pristine (black line), ozone-oxidized (blue line) and acid-oxidized (red line) MWNTs (b). The spectra were normalized to the G-band peaks. TEM images of Pt on acid-oxidized MWNTs (c) and ozone-oxidized MWNTs (d).

Fig. 3. XPS survey scans of MWNT/PyPBI/Pt (a) and ox-MWNT/Pt (b) before (black line) and after (red line) Nafion coating. Indium was used as the substrate. Schematic illustrations of Nafion coating for MWNT/PyPBI/Pt (c) and ox-MWNT/Pt (d). Photos of the aqueous dispersions of MWNT/PyPBI/Pt-i (e) and MWNT/PyPBI/Pt (f). TGA curves of MWNT/PyPBI/Pt (g) and ox-MWNT/Pt (h) before (black line) and after

Nafion coating (red line) measured under air flow (100 mL min^{-1}) at a heating rate of $5 \text{ }^{\circ}\text{C min}^{-1}$.

Fig. 4. CV curves were recorded in 0.1 M HClO_4 with a scan rate of 50 mV s^{-1} for MWNT/PyPBI/Pt (a), *ox*-MWNT/Pt (b) and CB/Pt (c) before (solid line) and after (dotted line) durability test. (d) Plots of normalized ECSAs of MWNT/PyPBI/Pt (red line), *ox*-MWNT/Pt (black line) and CB/Pt (green line) as a function of the numbers of potential cycles from 1.0 to 1.5 V vs. RHE. TEM images of MWNT/PyPBI/Pt (e) and *ox*-MWNT/Pt (f) after durability test.

Fig. 5. Schematic illumination of the preparation for *ox*-MEA and PyPBI-MEA.

Fig. 6. (a) Polarization curves of *ox*-MEA (black line), PyPBI-MEA (red line) and MEA having MWNT/PyPBI/Pt-*i* (light blue line) under 80 °C with humidified H₂ (100 mL min⁻¹) and air (200 mL min⁻¹) for anode and cathode, respectively. The maximum power densities of the MEAs were indicated. (b) *In-situ* CV curves of *ox*-MEA (black line), PyPBI-MEA (red line) and MEA having MWNT/PyPBI/Pt-*i* (light blue line). ECSAs of MEAs were indicated. Schematic illustration of PyPBI-MEA (c) and *ox*-MEA (d), showing homogeneous and inhomogeneous coatings of Nafion (purple), respectively.

Graphical Abstract