Electrocatalyst composed of Platinum Nanoparticles Deposited on Doubly Polymer-coated Carbon Nanotubes shows a High CO-tolerance in Methanol Oxidation Reaction

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Abstract

High CO-tolerance and durability of anodic fuel cell electrocatalysts is one of the important factors for commercialization of direct methanol fuel cells (DMFCs). In this study, we describe the preparation of an electrocatalyst composed of poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) and poly(vinylphosphonic acid) (PVPA) coated multi-walled carbon nanotubes (MWNTs) on which ~3 nm Pt nanoparticles (Pt-NPs) are deposited. The fabricated electrocatalyst shows 1.5-times higher CO tolerance compared to the commercial CB/Pt, which would be due to the wrapping of the CNTs with PVPA by the aid of PyPBI. Meanwhile, the electrocatalyst almost maintains its initial electrochemical surface area (ECSA) and mass activity during the methanol oxidation reaction (MOR) after 10,000 potential cycling in the range of 1~1.5 V *vs.* RHE. In contrast, the commercial CB/Pt shows almost a 50% loss in its ECSA and mass activity. These results indicate that the durability of the newly fabricated electrocatalyst is quite high and the obtained high CO-tolerance and durability are important for the design of an electrocatalyst for DMFC applications.

Keywords: Carbon nanotubes; Electrocatalyst; CO tolerance; Direct methanol fuel cells; Polymer-coated carbon nanotubes.

Introduction

The global energy crisis has forced us to develop sustainable energy sources and polymer electrolyte fuel cells (PEFCs) that have attracted much attention due to their higher energy conversion efficiency, environmental friendliness and lower operating temperature. [1-3] Based on the different phase in the fuel, PEFCs are classified as hydrogen PEFCs and direct liquid fuel cells, which feed hydrogen and liquid fuels to the anode, respectively. Liquid fuels, such as borohydride [4-9] and methanol, received considerable attention because of easy storage and transportation compared to hydrogen. In Direct methanol fuel cells (DMFCs), the methanol oxidation reaction (MOR) offers an almost comparable cell voltage (1.19 V) to that of the hydrogen oxidation reaction (HOR, 1.23 V). [10, 11] The DMFCs can be used as portable energy sources for electronic products due to their easy storage and high energy density (5.04 KWh L⁻¹) [12-14], while the DMFCs face three serious anodic problems; namely, i) CO poisoning of the electrocatalysts that is induced by the incomplete MOR [15-17] ii) low durability in the electrocatalysts due to the use of carbon black as the platinum (Pt) support in the commercial CB/Pt [18], and iii) a sluggish MOR [19].

Many researchers have tried to separately solve three problems. Alloying Pt with some transition metals (Ru, [20-22] Au, [23, 24] Sn, [16, 25]) was found to enhance the

CO tolerance of the electrocatalysts due to their lower potential for forming the M-OH species, which react with the Pt-CO to remove CO from the Pt surfaces, while the transition metals are easily dissolved in the acidic medium, which is the practical environment in the real DMFC operation due to the use of Nafion membranes. Changing the Pt support to carbon nanotubes (CNTs), [7, 26, 27] graphene [28-30] or metal oxides [20, 31, 32] has proved to provide a higher durability. Also, we reported that the CO tolerance and durability of the electrocatalyst are simultaneously enhanced after coating with poly(vinylphosphonic acid) (PVPA) assisted by the poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) due to the acid-base interaction between the -OH groups of PVPA and -NH groups on PyPBI. [18, 33, 34] The enhanced CO tolerance and durability is considered to be that the phosphorus on the PVPA weakened the binding energy between the Pt and CO species and the Pt-NPs sandwich structures, respectively. Nevertheless, the mass activity of the coated electrocatalyst decreased by 35% due to the coverage of the Pt-NPs by the PVPA, which negatively affected the methanol adsorption on the Pt surfaces. [33] Thus, coating the Pt-NPs with PVPA did not enhance the sluggish MOR.

Fig. 1. Schematic illustration for the preparation of the MWNT/PyPBI/PVPA/Pt electrocatalyst.

In this study, we synthesized a Pt electrocatalyst that was deposited on doubly-polymer-coated multi-walled carbon nanotubes (MWNTs) as shown in Fig. 1, in which the MWNTs are coated with PyPBI and then with PVPA. Briefly, the MWNTs were dispersed in a solvent by the aid of PyPBI due to the π - π interaction between the MWNTs and the PyPBI [35, 36], then coated with the PVPA based on the acid-base interaction. Finally, the Pt-NPs were deposited onto the surfaces of the doubly polymer-coated MWNTs. Importantly, the Pt-NPs are not covered by any polymer in this structure and the PVPA in the electrocatalyst is expected to enhance the CO tolerance of the electrocatalyst. The CO tolerance during the MOR of the synthesized electrocatalyst was compared with that of the commercial CB/Pt and the previously reported MWNT/PyPBI/Pt/PVPA. [37]

Experimental section

Materials and reagents

2-Propanol, hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), ethylene glycol (EG), *N,N*-dimethylacetamide (DMAc) and PVPA (30 wt%) were purchased from Wako Pure Chemical Co., Ltd. The MWNTs with $\sim 20\text{ nm}$ diameter were provided by the Nikkiso Corp. The Pt-NPs-deposited CB (CB/Pt) catalyst was purchased from Tanaka Kikinzoku Kogyo K. K., in which the Pt loading on the CB was 37.5 wt%. A Nafion solution (5 wt%), perchloric acid (HClO_4 , 70%) and methanol were purchased from Sigma-Aldrich, EMD Millipore Chemical Co., Ltd., and Kanto Chemical Co., Inc., respectively. Poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) was synthesized according to a previous report.[38] The Milli-Q water ($18.2\text{ M}\Omega\text{ cm}$) was used to prepare the solutions during all the experiments and all the chemicals were used as received without any further purification.

Synthesis of MWNT/PyPBI/PVPA/Pt

Briefly, the MWNTs (10 mg) were dispersed in DMAc (20 mL) to which 10 mg of the PyPBI dissolved in 10 mL of DMAc was added at room temperature, then sonicated for 1 h to obtain a solution of the composite, MWNT/PyPBI, which was then collected by filtration followed by rinsing with DMAc. The obtained black powder was dried under

vacuum overnight at 60 °C to completely remove the solvent. MWNT/PyPBI(10 mg) was dispersed in an EG aqueous solution ($v/v=3:2$) to which 1 mL of the PVPA (30 wt%) was added and stirred for 10 min. The mixture was filtered and dried under vacuum overnight at 60 °C. Finally, the Pt loading was carried out by the reduction of the $H_2PtCl_6 \cdot 6H_2O$ in an EG aqueous solution ($v/v=3:2$) at 140 °C for 30 min under an N_2 atmosphere. The obtained product was filtered, washed, then dried overnight under vacuum at 60 °C to obtain the MWNT/PyPBI/PVPA/Pt.

Materials Characterization

The X-ray photoelectron spectroscopy (XPS) was carried out using an AXIS-ULTRA^{DLD} (Shimadzu) instrument. The pressure in the XPS analysis chamber was maintained at 10^{-9} Pa. For the calibration process, the binding energy (BE) of the core level C_{1s} peak was fixed at 284.5 eV. Thermogravimetric analysis (TGA) measurements were conducted using a TGA analyzer (EXSTAR 6000, Seiko, Inc.) at the heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$ and 100 mLmin^{-1} air-flow. The TEM images were obtained using a JEM-2010 (JEOL, acceleration voltage of 120 kV) electron microscope. A copper grid with a carbon support (Okenchoji Co., Ltd.) was used for the TEM observations.

Electrochemical surface area measurement

The electrochemical measurements were performed using a rotating ring disk electrode attached to an RRDE-3 (Bioanalytical Systems, Inc.) with a three-electrode configuration in a vessel at room temperature. A glassy carbon electrode (GCE) with a diameter of 4 mm was used as the working electrode. A Pt wire and Ag/AgCl(3M KCl) were used as the counter and reference electrodes, respectively. The potential of the electrode was controlled by an ALS-Model DY2323 (BAS) potentiostat. The electrocatalyst solution was typically prepared as follows. The catalyst (1.0 mg) was ultrasonically dispersed in a 2-propanol aqueous solution (2.0 mL, $v/v=4:1$) to form a homogeneous suspension, which was cast on a GCE (the loading amount of Pt was controlled at $14 \mu\text{g cm}^{-2}$), then air-dried under vacuum for 2 h. The cyclic voltammetry (CV) measurements of the electrocatalyst at the scan rate of 50 mVs^{-1} were carried in an N_2 -saturated 0.1 M HClO_4 solution after a 13 CV-cycle pretreatment at the scan rate of 5 mVs^{-1} in order to activate the electrocatalyst and to obtain a stable CV, then the electrochemical surface area (ECSA) value was determined from the average value from three measurements. All the potentials were referenced to the reference hydrogen electrode (RHE).

Durability test

The carbon corrosion was tested based on the protocol of the Fuel Cell Commercialization Conference of Japan (FCCJ)[39] (measured in N₂-saturated 0.1M HClO₄ at room temperature), in which the potential was held at 1.0V vs. RHE for 30s, then increased to 1.5V vs. RHE at the scan speed of 0.5Vs⁻¹ followed by a potential-return to 1.0V vs. RHE. This procedure was cycled, and after each 1,000 cycles, the ECSA measurement was carried out three times to calculate the average value (see Supporting information, Fig. S1).

Methanol oxidation reaction (MOR)

The MOR was measured before and after the durability test using an N₂-saturated 0.1M HClO₄ and 1M methanol solution at the scan rate of 50 mVs⁻¹ at room temperature. The electrode was the same as used for the ECSA measurement. The Pt loading on the electrode was controlled at 14 μgcm⁻². Before the MOR measurement, 50 cycles were carried out to activate the electrocatalyst in order to obtain a stable curve.

CO-stripping

CO stripping voltammetry was performed by feeding the working electrode with N₂ for 1h and the activation of the electrocatalyst was carried out by 13CV cycles, then purged with CO gas (10%, balanced with Ar) for 1h at the flow rate of 100 mLmin⁻¹, while holding the working electrode potential at 0.2 V vs. RHE. After the adsorption, the CO

was removed from the electrolyte, then changed to N₂ bubbling for 50 min to completely remove the dissolved CO in the electrolyte. The CO stripping voltammogram was measured at the scan rate of 50 mVs⁻¹.

Results and Discussion

Fundamental Characterisation of MWNT/PyPBI/PVPA/Pt

Fig. 2. (a) TGA curve of the MWNT/PyPBI/PVPA/Pt measured under flowing air (100 mLmin⁻¹) at the heating rate of 10 °Cmin⁻¹. (b) TEM image of the MWNT/PyPBI/PVPA/Pt before the durability test. Histogram of particle size distributions (100 particles) of the MWNT/PyPBI/PVPA/Pt is shown as the inset.

Fig. 3. XPS narrow scans of the regions of C_{1s} (a), N_{1s} (b) and P_{2p} (c) of MWNT/PyPBI/PVPA/Pt (red line) and CB/Pt (black line). XPS narrow scan of the Pt_{4f} region of MWNT/PyPBI/PVPA/Pt (d) and CB/Pt (e), in which the deconvolution curves are shown.

After the synthesis of the electrocatalyst, some fundamental characterizations were carried out to evaluate the composite as shown in Fig.2 and Fig.3. From Fig.2a, the residual weight was 47wt% suggesting that almost all the Pt ions were efficiently loaded on the MWNT assisted by the PyPBI due to the Pt-N bonding.[40] The weight loss starting at around 200 °C is due to the decomposition of the PVPA since the decomposition temperatures of PyPBI and MWNTs are ~500 °C and 700 °C, respectively. [35, 36] Thus, the PVPA amount in the composite was evaluated to be 3.5wt%. Based on the weight ratio between the PyPBI and MWNTs (7:93),[35] the detailed amount of each material was 3.5wt%, 3.5wt%, 46wt% and 47wt% for PyPBI, PVPA, MWNTs and Pt, respectively. From Fig.2b, the typical TEM image shows that the Pt-NPs (diameter = 3.2 ± 0.5 nm) are homogeneously deposited on the MWNTs (for a low magnification TEM image, see Supporting Information, Fig.S2), in which the diameter of the Pt-NP was somehow smaller than that deposited on the CB (3.9 ± 0.6 nm, see Supporting information, Fig. S3a). The particle size of the synthesized electrocatalyst evaluated from the XRD was 2.7 nm as shown in Fig. S4. The particles size calculated from the XRD is normally smaller than that from the TEM since the XRD detects the crystallized Pt. It is important to show evidence of the existence of the PVPA in the composite (for the survey scan, see Supporting Information, Fig. S5). In

the XPS spectra (Fig.3b), the typical N_{1s} peak is observed at 400 eV, which is derived from the PyPBI[4], and the apparent peak that appeared at 132eV (Fig. 3c) was assigned to the P_{2p} peak which is derived from the PVPA,[41] suggesting a successful coating by the PVPA. As shown in Fig.3(d, e), the ratio of Pt(0):Pt(II):Pt(IV) was 65.3:15.2:19.5, which was similar to that of the CB/Pt (57.3:17.1:25.6).

Evaluation of electrochemical surface area and durability

Fig. 4. CV curves were recorded in 0.1M HClO₄ at the scan rate of 50mVs⁻¹ for CB/Pt (a) and MWNT/PyPBI/PVPA/Pt (b) before (solid line) and after (dotted line)

the durability test. (c) Normalized ECSAs of CB/Pt (black line), and MWNT/PyPBI/PVPA/Pt (red line) as a function of the number of potential cycles in the range of 1.0 ~ 1.5V vs. RHE.

Fig. 5. TEM image of MWNT/PyPBI/PVPA/Pt after the durability test. Histogram of particle size distributions (100 particles) of MWNT/PyPBI/PVPA/Pt is shown as the inset.

The electrochemical surface area (ECSA) is an important factor to evaluate the anodic electrocatalyst, which was evaluated from the peak area due to the 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 electro-adsorption of hydrogen on the Pt.[42, 43]

As shown in Fig. 4b, the ECSA of MWNT/PyPBI/PVPA/Pt was $50.2 \text{ m}^2 \text{ g}^{-1}$, which was lower than that of CB/Pt ($60.6 \text{ m}^2 \text{ g}^{-1}$, Fig. 4a), while it was higher than that ($44.7 \text{ m}^2 \text{ g}^{-1}$) of MWNT/PyPBI/Pt[44] due to the smaller Pt-NP size. The long-term durability of the electrocatalyst was evaluated based on the carbon corrosion test, which was carried out according to the protocol from the Fuel Cell Commercialization of Japan (see Supporting Information, Fig. S1). The potential was cycled from 1.0 to 1.5 V *vs.* RHE to accelerate the carbon corrosion causing the detachment and coalescence of the Pt-NPs. From Fig. 4a, the pronounced hydroquinone-quinone (HQ/Q) redox peak was observed at 0.55 V *vs.* RHE after the durability testing of the commercial CB/Pt since the CB has a very low resistance toward carbon corrosion, while MWNT/PyPBI/PVPA/Pt showed a stable CV curve even after the durability testing, indicating a higher durability.[45] The ECSA was calculated after every 1,000 potential cycles and the results are plotted in Fig. 4c, having the commercial CB/Pt showed a 46% loss, which is in a sharp contrast to that of MWNT/PyPBI/PVPA/Pt, in which almost no change in the ECSA value. Also, the diameter of the Pt-NPs in MWNT/PyPBI/PVPA/Pt ($3.7 \pm 0.5 \text{ nm}$, Fig. 5) is almost the same as the initial size, while the Pt-NPs on CB/Pt have been reported to increase to $5.0 \pm 1.0 \text{ nm}$ (Fig. S3b), indicating the Pt-NPs were more stable in the synthesized electrocatalyst due to the strong Pt-N bonding.

Estimation of activity and CO tolerance

Fig. 6. Methanol oxidation reaction (MOR) curves measured in an N₂-saturated 0.1M HClO₄ and 1Mmethanol solution of CB/Pt (a) andMWNT/PyPBI/PVPA/Pt (b) before (solid line) and after (dotted line) the durability test. (c) Magnification of the MOR profiles of CB/Pt (black line) and MWNT/PyPBI/PVPA/Pt (red line) in the range of 0.27 ~ 0.6 V vs. RHE. (d) Bar displays the mass activities of CB/Pt and MWNT/PyPBI/PVPA/Pt before (black) and after (grey) the durability test.

Fig. 7.First cycles of the CO stripping voltammograms of CB/Pt (black line) and MWNT/PyPBI/PVPA/Pt (red line) at the scan rate of 50 mVs⁻¹ at 25 °C.

Table 1.Comparisons of CO tolerance for CB/Pt and MWNT/PyPBI/PVPA/Pt before and after the durability test.

Electrocatalyst	I_f/I_b (before durability)	I_f/I_b (after durability)
CB/Pt	0.87	0.83
MWNT/PyPBI//PVPA/Pt	1.30	1.26

During the real fuel cell applications, the methanol is oxidized on the anodic side, while incomplete methanol oxidation generates carbon monoxide(CO),which adsorbs onto the Pt surface, poisons the Pt-NPs,thus leading to the deterioration of the fuel cell performance. Thus, the CO anti-poisoning is of importance for the anodic

electrocatalyst for the DMFC. The MOR is carried out in a half-cell to evaluate the performance of the electrocatalyst as well as the CO anti-poisoning. The MOR curve is shown in Fig. 6. As indicated in the figure, two peaks that represent the anodic peak (I_f) and reverse anodic peak (I_b) were observed. The I_f peak is the oxidation of the methanol to CO_2 , CO and HCOOH [46, 47]. The I_b peak is the oxidation of the CO and HCOOH . The CO anti-poisoning can be estimated from the ratio of I_f/I_b because the abundant by-product is CO. The higher I_f/I_b ratio indicates less generation of the by-product, which denotes a higher CO anti-poisoning. [22, 48] The MOR was measured before and after the durability test, and the I_f/I_b ratios of CB/Pt and MWNT/PyPBI/PVPA/Pt are shown in Table 1. The CO-tolerance of MWNT/PyPBI/PVPA/Pt was 1.5 times higher than that of the commercial CB/Pt before and after the durability test. The stable I_f/I_b ratio of MWNT/PyPBI/PVPA/Pt suggested that the PVPA was stable during the potential cycling. Also, the CO stripping voltammetry is an important method to directly prove the CO-tolerance, in which the CO was oxidized by the electrocatalyst. As shown in Fig. 7, the sharp peak that appeared at 0.9 V vs. RHE was due to the oxidation of the absorbed CO species. The peak of the MWNT/PyPBI/PVPA/Pt showed a negative shift compared to that of the commercial CB/Pt, indicating that the CO species were more easily removed from the Pt-NP surfaces. Thus, the I_f/I_b ratios from

the MOR and CO stripping suggested that the synthesized MWNT/PyPBI/PVPA/Pt shows a higher CO tolerance than the commercial CB/Pt.

The sluggish MOR is also an obstacle for commercialization of the DMFC. As shown in Fig. 6c, the MOR curve of MWNT/PyPBI/PVPA/Pt showed a higher current at the initial potential compared to CB/Pt, suggesting that MWNT/PyPBI/PVPA/Pt is more active during the MOR. The mass activity of the MOR was evaluated from the current of the I_f peak. Before the durability test, MWNT/PyPBI/PVPA/Pt showed a comparable mass activity to CB/Pt, while the value of MWNT/PyPBI/PVPA/Pt was two times higher than that of MWNT/PyPBI/Pt/PVPA, in which the PVPA-coating was carried out after the Pt deposition, as previously reported by us.[37] The results indicate that the PVPA-coating on the Pt-NPs is not favorable for such a high activity. Importantly, the CO-tolerances of the two electrocatalysts were comparable, which would be due to an efficient amount of PVPA on the electrocatalyst since the PVPA is vital for the enhancement of CO tolerance during the MOR because the phosphorus moiety weakens the binding energy between the Pt and CO species. Thus, the Pt deposition onto the outer surfaces of the catalyst has an advantage for the MOR since the sluggish MOR was enhanced and the CO-tolerance remained. The mass activity of the

commercial CB/Pt lost about 50% after the durability test. The stable MOR of MWNT/PyPBI/PVPA/Pt was attributed to the higher durability.

Conclusions

In conclusion, we synthesized MWNT/PyPBI/PVPA/Pt by Pt-deposition onto the surfaces of the MWNT/PyPBI/PVPA, whose structure is different from MWNT/PyPBI/Pt/PVPA, in which the PVPA-coating was carried out on MWNT/PyPBI/Pt. It was revealed that the MWNT/PyPBI/PVPA/Pt showed almost no loss in the ECSA during the potential cycling in the range of 1.0 ~ 1.5 V vs. RHE, while the commercial CB/Pt showed a 46% loss in the ECSA. Meanwhile, the CO-tolerance of the MWNT/PyPBI/PVPA/Pt evaluated from the MOR and CO stripping voltammetry indicated that the electrocatalyst has a higher tolerance towards the CO species than that of the CB/Pt. In addition, the MWNT/PyPBI/PVPA/Pt is more active during the MOR compared to the CB/Pt and MWNT/PyPBI/Pt/PVPA. Preparation of such a highly durable, CO-tolerant electrocatalyst is important as an anode material for actual use in the DMFC.

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Graphical Abstract