**Synthesis of multiwall carbon nanotube-supported platinum catalysts by solution
plasma processing for oxygen reduction in polymer electrolyte fuel cells**

Naoki Matsuda¹, Tatsurou Nakashima¹, Takumi Kato² and Hidenobu Shiroishi^{2*}

¹ Measurement Solution Research Center, National Institute of Advanced Industrial
Science and Technology (AIST), 807-1, Shukumachi, Tosu, Saga 841-0052, Japan

² Department of Chemical Science and Engineering, Tokyo National College of
Technology, 1220-2 Kunugida, Hachioji, Tokyo 193-0997

Abstract

Two preparation methods with solution plasma (SP) processing were carried out to
produce Pt nanoparticles (PtNPs) on multi-wall carbon nanotubes (MWCNTs). One is
the method that PtNPs were attached on MWCNTs using a SP irradiation after PtNPs
were solely produced by a SP irradiation. The other is that the formation of PtNPs on
MWCNTs was performed using a SP irradiation after a Pt precursor was adsorbed on
MWCNTs. PtNPs were well anchored and uniformly dispersed on the MWCNTs prepared
by using the latter method. The average sizes of PtNPs estimated by transmittance
electron microscopy (TEM) images were about 5 to 9 nm with the former method and
about 2 to 3 nm with the latter method, respectively. It was revealed that the bulk of PtNPs

* *Corresponding author.* Tel&Fax: +81-42-668-5867, E-mail: h-shiroishi@tokyo-
ct.ac.jp

produced by a solution plasma irradiation is in metal state analyzed on the basis of X-ray diffraction (XRD) measurements. An accelerated durability test was performed using a saw-tooth potential wave. Apparent degradation rates of Pt/MWCNTs prepared by the methods toward oxygen reduction activity were smaller than that of 20 % Pt-XC72R.

Keywords: Solution plasma, Oxygen reduction, Pt catalysts, Durability

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been attracting much attention as one of the next generation power sources. PEFCs have a huge advantage for reducing the environmental impact because hydrogen and oxygen were used for power generation. In recent years, it was reported that carbon nanotubes (CNTs) were useful as catalyst support materials because of their high oxidation resistance.

The synthesis of carbon nanotube-supported Pt nanoparticles (NPs) has required the pretreatment of carbon materials with chemical reagents or reactions, and this causes complex reaction process and increase in waste materials. Thus, simple and environment-friendly processes should be developed for reducing cost and decreasing environmental burden.

Plasma processing technology has been utilized in many fields for semiconductor fabrication, material synthesis, surface treatment and so on [1-4]. With applying high pulse voltage to a set of electrodes in solution phase, a plasma emission in a solution

which is known as solution plasma (SP), is observed in bubbles generated between discharge electrodes [5]. In recent years, SP techniques have been studied mainly for surface treatment and metal nano-particles (NPs) synthesis [5-16]. Imasaka et al. successfully prepared water-soluble CNTs using a pulsed streamer discharge in water without any electrolyte [8]. Nomura et al. and Yonezaya et al. reported the synthesis of metal NPs using plasma in solution [6, 7, 12]. Saito et al. synthesized many kinds of metal NPs by SP processing [9-11, 13-14]. Matsuda et al. prepared AuNP suspension using hydrogen peroxide (H_2O_2) aqueous solution without any surfactant [15-16]. However, there are no reports for the attachment of metal NPs simultaneously formed by SP irradiation on a carbon support and for the performance of the catalysts toward oxygen reduction reaction.

In this paper, multi wall carbon nanotube (MWCNT)-supported Pt NPs (Pt/CNT) were synthesized by a SP technique under four different conditions to provide a better guideline for catalyst preparation, and an electrochemical oxygen reduction reaction with the catalysts was investigated by a rotating ring-disk electrode method.

2. Experimental

2.1 Materials

Pt (2 mm ϕ , 99.99 % Tanaka Kikinzoku Kogyo K.K., Japan) and tungsten (1 mm ϕ , 99.99 %, Nippon Tungsten Co. Ltd., Japan) were used as SP discharged electrodes.

Hexachloroplatinic(IV) acid ($\text{H}_2[\text{PtCl}_6]$, Kanto Chemicals, Japan), MWCNTs (20-30 nm, Wako Pure Chemical Industries, Ltd., Japan), H_2SO_4 (97 %, Kishida Chemicals Co. Ltd., Japan), Pt/XC72 (E-tek, USA) and H_2O_2 (Kanto Chemicals Co. Ltd., Japan) were used as received. Milli-Q pure water (18.2 M Ω) was used for the preparation of all solutions.

2.2 Solution Plasma Set-up

A beaker of 200 mL volume was utilized as a SP reaction chamber. A high voltage bipolar pulsed power supply (MPS-06K-01C, KURITA Seisakusho Co. Ltd., Japan) was utilized as a power source. A set of tungsten- or Pt- wire electrodes with 1 mm gap were inserted into the solution in the cell to make the SP of ark-discharge as shown in Fig. 1(a). The applied bipolar voltage, pulse width and frequency were 1.4 kV, 2.5 μsec , and 25 kHz as shown in Fig. 1 (b), respectively.

2.3 Preparation of Pt/CNT

Two kinds of synthesis methods were performed in this paper. One method is that PtNPs prepared by a SP irradiation in advance were attached onto MWCNTs by a second SP irradiation with MWCNTs (Pt/CNT-A and Pt/CNT-D), which is named “Two-step SP method”. The other is that the formation and immobilization of PtNPs on MWCNTs were simultaneously performed by a SP irradiation (Pt/CNT-B and Pt/CNT-C), which is named “Pt precursor adsorption method”. The details were described below. After the synthesis, all the catalysts were washed by decantation with water, and dried under vacuum.

Pt/CNT-A: PtNP aqueous suspension was prepared in a 50 mL of 5 mM H_2PtCl_6 aqueous solution by SP irradiation for 10 min. 220 mg of MWCNTs pre-treated in 7.0 wt% H_2O_2 aqueous solution for 5 min. was mixed with the PtNP aqueous suspension, and the PtNPs were immobilized on MWCNTs by SP irradiation for 20 min.

Pt/CNT-B: A 2.5 mL of 250 mM NaOH aqueous solution was added to a 50 mL of 2.5 mM H_2PtCl_6 aqueous solution and allowed to remain at room temperature for 2 h to replace Cl^- ligands by OH^- . After the solution was mixed with 220 mg of MWCNTs with ultrasonication for 30 min, a Pt precursors ($[\text{PtCl}_{6-x}(\text{OH})_x]^{2-}$) were adsorbed on MWCNTs with reflux for 2 h. The SP irradiation was performed in the suspension for 15 min to reduce Pt precursors to PtNPs and to immobilize the PtNPs on MWCNTs.

Pt/CNT-C: Pt/CNT-C was prepared in a similar manner to the preparation of Pt/CNT-B except for the ligand replacement time (22 h) and adsorption time (4 h).

Pt/CNT-D: A PtNP suspension containing Pt ions was prepared in a 10.5 wt% H_2O_2 aqueous solution by a SP irradiation, and a 0.2 mL of 25 mM NaOH aqueous solution was added to the suspension, and allowed to remain at room temperature for 24 h to replace a few ligands of Pt ions by OH^- . The suspension was refluxed for 2 h to facilitate the adsorption of Pt ions and colloids after sonication for 30 min, and a SP irradiation was performed in the suspension for 15 min to attach the PtNPs onto MWCNTs.

2.3 Characterization of Catalysts

X-ray diffraction powder patterns of Pt/CNTs were collected using a Bruker AXS D8

Advance system. Transmission electron microscopy (TEM) analysis of Pt/CNTs carried out using a JEOL JEM-ARM200F microscope operating at 300 kV. The thermal stability and Pt loadings of Pt/CNT catalysts were estimated by thermogravimetry in an air flow of 100 mL min⁻¹ at a heating rate of 5 K min⁻¹ with a EXSTAR6000 TG/DTA 6300 (SII Nano Technology Inc.).

2.4 Electrochemical Measurement

A 4.0 mg of Pt/CNTs was suspended in 2 mL of 0.1 wt% Nafion-EtOH by ultrasonication. A 10 µL of the suspension was cast onto a glassy-carbon disk (6 mm ϕ , 0.283 cm²) – Pt ring electrode (Nikko Keisoku) and dried for 1 h under N₂ atmosphere. The reproducibility was $\pm$ 2.6 % (RSD) based on the cyclic voltammogram (CV) measurements, which was smaller than that in the literature [17].

Electrochemical measurements were performed with a conventional three electrode system equipped with the modified disk electrode, a gold wire counter electrode and a reversible hydrogen reference electrode (RHE). Electrochemical measurements and data acquisition were conducted with a multipotentiostat (Toho technical research model PS-08) and a function generator (Toho technical research model FG-02) by a homemade apparatus and measurement program [18]. The collection efficiency of the ring disk electrode was determined to be $N = 0.40$ with the [Fe(CN)₆]^{3-/4-} couple. The efficiency of the O₂ reduction to H₂O, %H₂O, was calculated from the equation [19]:

$$\%H_2O = 100 \times (i_D - i_R / N) / (i_D + i_R / N) \quad (1)$$

where i_D and i_R are disk and ring currents, respectively. All electrochemical measurements were carried out at room temperature (25 ± 2 °C) and under ordinary pressure.

After 30 min of O₂ bubbling, a RRDE measurement was performed at 600 rpm. Next, a blank measurement was conducted in N₂ atmosphere, followed by a CV measurement at 50 mV s⁻¹. Finally, an accelerated durability test (ADT) was done with a sawtooth waveform shown in Fig. 2 for 1 h. Mitsushima et al. demonstrated that Pt is dissolved at relatively high rate during negative going scan [20], and Shiroma and co-workers reported that the degradation of carbon supports was accelerated by the rectangular waveform with larger potential range [21], thus waveforms was combined so as to give damages both to Pt particles and carbon support. A set of above measurement was performed 9 times per a catalyst.

3. Result and Discussion

Fig. 3 shows TEM images of the Pt/CNTs prepared by SP processings, and particles sizes obtained by TEM images were summarized in Table 1. Most PtNPs were not fixed on MWCNT in Pt/CNT-A which was made by the two-step SP method, whereas most of Pt particles were uniformly fixed on MWCNTs by the Pt precursor adsorption methods (Pt/CNT-B and Pt/CNT-C), and the average sizes of the Pt particles were 2.0 nm (Pt/CNT-B) and 3.7 nm (Pt/CNT-C), respectively, which were smaller than that prepared by the two-step method. Although PtNPs could be immobilized on MWCNTs even by the two-step method in which Pt ions produced by a first SP irradiation were adsorbed on

1 MWCNTs (Pt/CNT-D), the Pt precursor adsorption method was preferable to the two-
2 step methods since the size of Pt particles in Pt/CNT-D was inhomogeneous compared to
3 that in Pt/CNT-B and Pt/CNT-C.

4 Fig. 4 shows XRD patterns of the catalysts. The patterns were assigned as face-
5 centered cubic (fcc) crystal structures, and the patterns derived from Pt oxide species were
6 not observed in the catalysts, indicating that the bulk of PtNPs was in metal state. The
7 average particle sizes were summarized in Table 1 using Scherrer equation from the (1 1
8 1) reflection in the Pt fcc lattice. The particle sizes obtained from the XRD measurement
9 did not necessarily correspond to those from TEM measurement, suggesting that the large
10 PtNPs exist in the catalysts. This is because the ratio of the particle sizes cannot be
11 reflected by XRD measurements, since the peak intensities of smaller particles in XRD
12 patterns are so much weak compared to those of large particles.

13 The amounts of Pt in the catalysts were also summarized in Table 1. The amount of
14 Pt loadings in Pt/CNT-C was almost the same as that in Pt/CNT-B. However, the
15 electrochemically active surface area (ECSA) of Pt/CNT-C, discussed further below, was
16 much larger than that of Pt/CNT-B, suggesting that the elongation of the times for the
17 ligand replacement and adsorption is preferable to prepare active PtNPs.

18 Fig. 5 shows thermogravimetric curves of the catalysts in air atmosphere. Starting
19 temperature of MWCNT oxidation increased with the average sizes of PtNPs except
20 Pt/CNT-A. On the basis of Arrhenius analysis, the activation energies and frequency
21 factors for the oxidation of MWCNTs in the catalysts are summarized in Table 1. It is

proved that the activation energy and frequency factor decrease with increasing particle size of PtNPs in the catalysts. It is well known that the oxidation of carbon supports was catalyzed by Pt in air atmosphere [22]. The frequency factors should be affected by the size and dispersivity of PtNPs fixed on MWCNTs because the contact area between PtNPs and MWCNTs increases with decreasing size of PtNPs and/or increasing dispersivity on MWCNTs. However the frequency factors obtained by the thermogravimetric measurements were mostly affected by the size of PtNPs, because the PtNPs immobilized on MWCNTs should have high mobility as well as non-immobilized PtNPs at higher temperatures where MWCNTs combust.

The CVs of the modified electrodes normalized by geometric electrode area were shown in Fig. 6. A pair of redox peaks around 0.65 V derived from quinone/hydroquinone species in Pt/CNT-B and Pt/CNT-C increased compared to that in untreated MWCNTs, whereas the peaks in Pt/CNT-A and Pt/CNT-D were almost the same as that in untreated MWCNTs. Since most of PtNPs were fixed on MWCNTs in Pt/CNT-B and Pt/CNT-C, the quinone/hydroquinone species might be produced during the reduction process of Pt precursors adsorbed on MWCNTs by the SP irradiation. The cathodic peak at around 0.65 V in the catalysts increased compared to that in untreated MWCNTs. This is due to the overlap of reduction peaks of both the quinone/hydroquinone species and Pt oxide species. It was reported that the reduction peak potential of Pt oxide in PtNP modified electrode shifted to the cathodic direction with a decrease in particle sizes owing to the strong adsorption of oxygen species [23].

Table 2 shows the ECSA per unit weight of the catalysts prepared by SP processings and 20 % Pt/XC72(E-tek) obtained by hydrogen adsorption/desorption region (0.05 V and 0.4 V) in CVs. An ECSA of Pt/CNT-C was the largest in the catalysts, and a pair of redox peaks derived from quinone/hydroquinone species in Pt/CNT-C was larger than that in untreated MWCNTs indicating that the surface of MWCNTs was oxidized during the catalyst preparation process, whereas the ECSA and a pair of redox peaks associated with quinone/hydroquinone species of Pt/CNT-B were smaller than those of Pt/CNT-C regardless of the similar PtNPs sizes. This suggests that longer time for the ligand displacement and the adsorption of Pt precursors is preferable during the catalyst preparation process to synthesize electroactive catalysts. The ECSAs per unit weight of Pt/CNT-A and Pt/CNT-D were 50 – 60 % as much as that of Pt/CNT-C probably due to the large particle sizes and the existence of many non-electroactive PtNPs which were not immobilized on MWCNTs.

Fig. 7(b) shows the polarization curves for oxygen reduction obtained by RRDE measurements. Onset potentials where 1 mA of cathodic current flows were more positive in the order of Pt/CNT-C(0.991 V) > Pt/CNT-A(0.990 V) > Pt/CNT-B(0.981 V) > Pt/CNT-D(0.979 V).

Fig. 7(a) shows the relationship between 4-electron reduction efficiency and applied potential. The 4-electron reduction efficiency of Pt/CNT-A was the highest in the catalysts. It is known that oxygen reduction progresses on Pt surface via either side-on adsorption of O₂ with two nearest neighbor Pt atoms to form H₂O or end-on adsorption of O₂ with a

Pt atom to form H₂O₂. The ratio of atoms located at kinks and steps to the total atoms in Pt particles increases with decreasing size of Pt particles to increase end-on adsorption of O₂ [24]. The particle sizes of Pt/CNT-A were so large that 4-electron reduction efficiency of Pt/CNT-A was relatively high. However, 4-electron reduction efficiency of Pt-CNT-D was low regardless of large particle size estimated by XRD which disagreed with that by TEM observation. The ratio of the particle sizes cannot be measured by XRD, thus, most of Pt particles in Pt/CNT-D are close to the average size estimated by TEM measurement.

Fig. 8 shows the dependence of oxygen reduction current at 0.95 V on ADT time. The oxygen reduction current of Pt/CNT-B reached at maximum after 1 h of ADT, probably due to the elimination of impurities, thus the lifetime analysis for Pt/CNT-B was performed from 1 h of ADT. Assuming that the catalyst consists of degradation and non-degradation regions, and that oxygen reduction current in the degradation region decreases exponentially, total oxygen reduction current (i [A]) is represented as

$$i = i_0 \exp\left(-\frac{t}{\tau}\right) + i_c \quad (14)$$

where i_0 [A] is oxygen reduction current derived from the degradation region before an ADT, t [h] is an ADT time, τ [h] is an apparent lifetime which means that oxygen reduction current decreases $1/\exp(1)$ as much as that before an ADT test, and i_c [A] is oxygen reduction current derived from the non-degradation region.

Table 3 shows the summary of the lifetime analysis. Apparent lifetimes of the catalysts were longer than that of a commercial catalyst (20 % Pt/XC-72R, E-Tek). Particularly, the lifetime of Pt/CNT-B was the largest in the catalysts. The lifetimes of the

1 catalysts made by the two-step SP method were relatively short compared to that of the
2 catalysts made by the Pt precursor adsorption method. This is because the most of PtNPs
3 in Pt/CNT-A and Pt/CNT-D were not attached on MWCNTs. Since the catalyst surface in
4 Pt/CNT-C was relatively oxidized to form quinone/hydroquinone analogues, the lifetime
5 of Pt/CNT-C was shorter than that of Pt/CNT-B. The rates of non-degradation region in
6 the catalysts made by SP methods were larger than that in the commercial catalyst, which
7 is due to the high tolerance of oxidation.

9 **Conclusion**

10 Pt/MWCNTs were synthesized by the two-step method and the Pt precursor
11 adsorption method. Using the latter method, almost all Pt particles were uniformly
12 immobilized on MWCNTs, and the average size of Pt particles was about 3 nm, which
13 was smaller than that by the two-step method. XRD measurements revealed that the bulk
14 of PtNPs produced by a solution plasma irradiation was in metal state. The lifetimes of
15 the catalysts made by the latter method were longer than that of the catalysts made by the
16 former methods.

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Table 1 Particle sizes of Pt estimated by Scherrer equation, Pt loadings obtained by TG measurement and summary of Arrhenius analysis.

	XRD	TEM	TG		
	Particle size [*] / nm	Particle size [*] / nm	Pt loadings [*] / wt%	$\log_{10}A^{\dagger}$	$\Delta E^{\dagger}$ / kJmol ⁻¹
Pt/CNT-A	9.3 ± 0.23	9.1 ± 1.9	21 ± 1.8	7.84 ± 0.024	171.4 ± 0.38
Pt/CNT-B	6.5 ± 0.18	2.0 ± 0.56	14 ± 1.8	16.90 ± 0.073	276 ± 1.0
Pt/CNT-C	5.9 ± 0.10	3.7 ± 1.1	12 ± 1.8	11.58 ± 0.039	209.0 ± 0.56
Pt/CNT-D	19.3 ± 1.0	4.8 ± 0.89	17 ± 1.8	2.67 ± 0.029	95.5 ± 0.44

Errors were expressed by standard deviations (*) and standard errors (†).

Table 2 ECSA of Pt/CNTs.

	ECSA / $\text{cm}^2 \text{mg}_{\text{Pt}}^{-1}$
Pt/CNT-A	129 $\pm$ 3.3
Pt/CNT-B	79 $\pm$ 2.1
Pt/CNT-C	221 $\pm$ 5.7
Pt/CNT-D	154 $\pm$ 4.0
20% HP Pt on Vulcan XC-72R	528 $\pm$ 13.7

Table 3 Result of a lifetime analysis.

	i_0 [mA]	i_c [mA]	$i_c / (i_0 + i_c)$	τ [h]	$10^{-2} \tau_s$ [h]	R^2
Pt/CNT-A	0.92 $\pm$ 0.068	0.63 $\pm$ 0.026	0.41 $\pm$ 0.025	0.9 $\pm$ 0.17	1.1 $\pm$ 0.22	0.96
Pt/CNT-B	0.22 $\pm$ 0.014	0.22 $\pm$ 0.016	0.49 $\pm$ 0.043	4.3 $\pm$ 0.67	3.4 $\pm$ 0.53	0.99
Pt/CNT-C	0.54 $\pm$ 0.034	0.36 $\pm$ 0.014	0.40 $\pm$ 0.022	1.1 $\pm$ 0.16	2.3 $\pm$ 0.36	0.97
Pt/CNT-D	0.93 $\pm$ 0.046	0.04 $\pm$ 0.017	0.32 $\pm$ 0.127	0.79 $\pm$ 0.010	1.22 $\pm$ 0.04	0.98
20% HP Pt on Vulcan XC-72R	2.81 $\pm$ 0.10	0.87 $\pm$ 0.039	0.24 $\pm$ 0.013	0.75 $\pm$ 0.039	4.0 $\pm$ 0.23	0.99

Errors were expressed by standard errors.

Figure Captions

Figure 1 (a) Photograph of solution plasma irradiation and reaction cell, and (b) bipolar voltage pattern.

Figure 2 Sawtooth wave used in accelerated durability tests.

Figure 3 TEM images of catalysts.

Figure 4 X-ray diffraction patterns of catalysts and schematic patterns based on ICDD cards. —, Pt(00-004-0802); —, PtO₂(00-023-1306); —, PtO(00-042-0866).

Figure 5 TG curves of Pt/CNTs.

Figure 6 Cyclic voltammograms of GC|0.1 μ m Nafion [Pt/CNTs] in 0.05 M H₂SO₄ under 1 atm N₂ at 298 K. Scan rate is 50 mVs⁻¹.

Figure 7 (a)Dependence of the efficiency of the O₂ reduction to H₂O (%H₂O) and (b)polarization curves for oxygen reduction on applied potential with GC|0.1 μ m Nafion[Pt/CNTs] in 0.05 M H₂SO₄ under 1 atm O₂ at 298 K during positive going scan at 600 rpm. Scan rate is 5 mVs⁻¹.

Figure 8 Dependence of ORR current density at 0.95 V on ADT time in 0.05 M H₂SO₄ under 1 atm O₂ at 298 K.

(a)

(b)

Figure 1

Figure 2

(a) Pt/CNT-A

(b) Pt/CNT-B

(c) Pt/CNT-C

(d) Pt/CNT-D

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8