

# Uniformity of carbon supported Pt nanoparticles produced by arc plasma deposition

Yoshiaki Agawa<sup>a\*</sup>, Hiroyuki Tanaka<sup>a</sup>, Shigemitsu Torisu<sup>a</sup> and Satoshi Tominaka<sup>b</sup>

<sup>a</sup>Arc Plasma Deposition System Business Promotion Division, ADVANCE RIKO, Inc., 4388 Ikonobe-cho, Tsuzuki, Yokohama 224-0053, Japan

<sup>b</sup>Mesoscale Materials Chemistry Group, International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

\*+81-45-934-4671 yoshiaki\_agawa@advance-riko.com

## Abstract

We propose a new approach for the preparation of Pt/C catalysts by arc plasma deposition (APD), in which Pt nanoparticles are deposited on carbon in a vacuum; this method has been applied in a number of fields other than fuel cell catalysts. The solid cathode material is transformed into completely ionized plasma that leaves the cathode with a velocity of  $1-2 \times 10^4$  m/s. This velocity corresponds to an ion kinetic energy of 20 eV (light ions such as carbon) to 300 eV (heavy ions such as platinum). Thus, the cathode material is eroded and forms an energetic plasma jet.

**Keywords:** arc plasma deposition method<sup>1</sup>, nanoparticles<sup>2</sup>, deposition parameters<sup>3</sup>.

## 1. Introduction

Polymer electrolyte membrane fuel cells typically use a Pt/C catalyst, consisting of a dense coating of Pt nanoparticles (NPs) on carbon black particles. Wet processes such as the impregnation and colloid methods are generally used to produce a support catalyst with a high Pt dispersion. However, several processes such as dispersion, absorption, and segregation, filtration, cleaning, drying and heating are required, which increases the production costs in the impregnation method. Meanwhile, Pt/C catalysts can be also produced by dry methods, which have an advantage in that there are no liquid waste disposal processes required. Nanoparticles are synthesizing on a support material by adjusting the amount of deposition during the APD process.<sup>1,2</sup> Nanoparticles synthesized by APD have uniform diameters, and its applications<sup>3,4</sup> have been reported elsewhere.<sup>5</sup>

## 2. Experimental

Figure 1 shows a schematic representation of the APD vapor deposition unit (ADVANCE-RIKO, Inc. APD-1P) and the container that holds the support material sample, both of which are within the APD chamber.<sup>6</sup> Carbon black powder (Ketjen Black, EC600D) was used for the support material. 20 mL of the carbon black powder was placed in the sample container. The Pt/C catalyst was synthesized by rotating the container to stir the carbon black powder while it was being irradiated by Pt plasma formed by the APD unit mounted on the upper side, so that Pt NPs were deposited on the carbon black powder to form the Pt/C catalyst. The parameters used for depositing Pt NPs onto the carbon black were a condenser capacity of 1080  $\mu$ F and a discharge voltage of 150 V. The chamber pressure during deposition was roughly  $6.5 \times 10^{-3}$  Pa.

## 3. Results and discussion

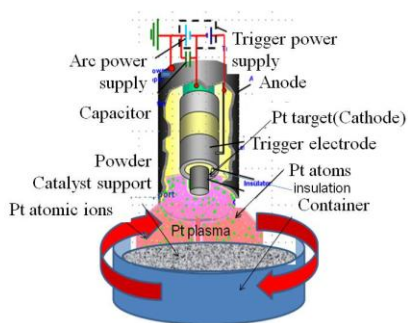
When carbon powder is irradiated with a platinum-based plasma, the  $\text{Pt}^+$  ions collide with the carbon and become atoms, which then migrate and interact with other Pt atoms to form nanoparticles (NPs) with dimensions of 2 to 3 nm on the carbon surface. Figure 2 shows a scanning electron microscopy (SEM) image of Pt NPs on Ketjen black. Although the surface of the Ketjen black is extremely rough, the NPs are seen to be uniformly distributed. We compared the electrochemical properties of Pt/C catalysts prepared by APD with those of the commercially available catalyst TEC10E50E. Although the electrochemical surface area (ECSA) was almost the same, the specific activity for Pt/C (APD) was about 2 times higher than that for TEC10E50E, which led to an approximately 2 times higher mass activity (This result is shown in table1). However, one remaining problem with Pt/C (APD) is that NPs are not deposited in some regions. Figure 3 shows an SEM image of Ketjen black containing regions where no Pt NPs are present. At first, the modification of the stirring vessel has been done in order to agitate carbon powders uniformly. The image of new stirring vessel is shown in Fig 4. To evaluate stirring condition quantitatively, the number of rotation of the stirring vessel and rotation rate of the brush, which is to crash the powders in the vessel should be

adjusted. Additionally, it was changed a carbon power form from Ketjen Black to VULCAN. And deposition condition to prepare Pt/C catalyst was changed as below-mentioned,

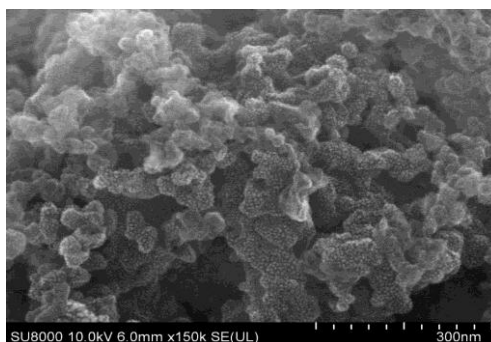
1) Discharge voltage: 100V, 2) Capacitor: 1080  $\mu$ F. Figure 6 shows a TEM image of Pt supported VULCAN which Pt NPs with dimension of 1nm are deposited uniformly.

#### 4. Conclusions

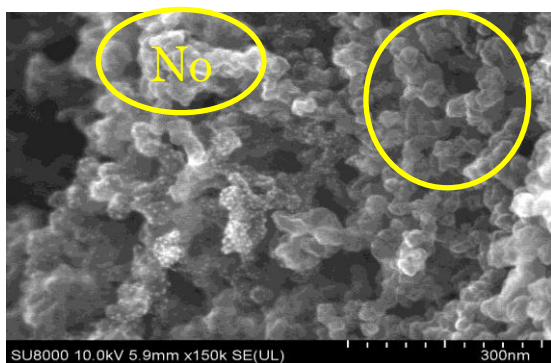
We made improvements to the stirring vessel, and optimized deposition parameters such as the plasma pulse interval and the powder surface conditions. We also improved the uniformity of the Pt NPs on the carbon powder.



**Figure 1** Schematic layout of the APD device and deposition container within the APD chamber.



**Figure 2** SEM image of Pt NPs uniformly deposited on Ketjen black.



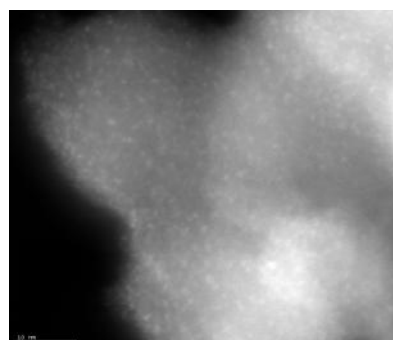
**Figure 3** SEM image of Pt NPs non-uniformly deposited on Ketjen black

	Specific activity @0.9 V ( $\mu$ A/cm <sup>2</sup> )	@0.8 V ( $\mu$ A/cm <sup>2</sup> )	Mass activity @0.9 V (A/g-Pt)	@0.8 V (A/g-Pt)	ECSA (m <sup>2</sup> /g-Pt)	Pt load ( $\mu$ g/cm <sup>2</sup> )
Flat Pt	6.6	164	NA	NA	NA	NA
TEC10E50E	4.8	101	2.9	60	60.0	8.7
CAPD Pt/C	10.5	188	5.6	101	53.3	0.96

**Table 1** Electrochemical properties of Pt/C (APD) and TEC10E50E



**Figure 4.** New stirring vessel of APD



**Figure 5.** TEM image of Pt supported VULCAN

#### References

1. Y.Yamamoto, Y.Agawa, Y.Hara, S.Amano, A. Chayahara, Y. Horino, and A. Fujii, *International Conference on Ion Implantation technology proceedings*, 1148 (1998).
2. Y. Agawa, K. Sakae, S. Saito, K. Yamaguchi, M. Matsuura, Y. Suzuki, Y. Hara, H. Nakano, N. Tsukahara, and H. Murakami, *ULVAC Technical Journal (English)*, **65E**, 1 (2006).
3. S. Hinokuma, K. Murakami, K. Uemura, M. Matsuda, K. Inoue, N. Tsukahara, and M. Machida, *Top. Catal.*, **52**, 2018 (2009).
4. S. Hinokuma, Y. Katsuhara, E. Ando, K. Ikeue, and M. Machida, *Catal. Today*, **201**, 92 (2013).
5. Y. Agawa, S. Endou, M. Matsuura, and Y. Ishii, *Adv. mater. res.*, **123**, 1067 (2010).
6. Y. Agawa, M. Kunimatsu, T. Ito, Y. Kuwahara and Hiromi Yamashita, *ECS Electrochemistry Letters*, 4 (10) F57-F60 (2015)