Chemical Engineering Journal 143 (2008) 225–229

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Dispersion of Pt/Ru catalyst onto arc-soot and its performance evaluation as DMFC electrode

S. Oke[a,*], K. Higashi[a], K. Shinohara[a], Y. Izumi[a], H. Takikawa[a], T. Sakakibara[b], S. Itoh[c], T. Yamaura[c], G. Xu[d], K. Miura[e], K. Yoshikawa[e], T. Sakakibara[f], S. Sugawara[f], T. Okawa[g], N. Aoyagi[g]

[a] Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi 441-8580, Japan
[b] Gifu National College of Technology, 2236-2 Kamimakuwa, Motosu 501-0495, Japan
[c] Futaba Corporation, 1080 Yabutsuka, Chosei-mura, Chosei-gun 299-4395, Japan
[d] Shonan Plastic Mfg. Co., Ltd., 31-27 Daikan-cho, Hiratsuka 254-0807, Japan
[e] Tokai Carbon Co., Ltd., 394 Subashiri, Oyama-cho, Sunto-gun 410-1431, Japan
[f] ENAX Inc., 2-11-19 Otowa, Bunkyo-ku, Tokyo 112-0013, Japan
[g] Daiken Chemical Co., Ltd., 1-3-3 Techno Port, Mikuni-cho, Sakai 913-0038, Japan

ARTICLE INFO

Article history:
Received 25 December 2007
Received in revised form 1 April 2008
Accepted 10 April 2008

Keywords:
Direct methanol fuel cell
Pt/Ru catalyst
New twin-torch-arc apparatus
Arc-soot nano-carbon
Electrocatalytic activity
Index of dispersion

ABSTRACT

The arc-soot (AS) nano-carbon was synthesized by using arc discharge apparatuses which were the conventional arc apparatus and the new twin-torch-arc apparatus. AS synthesized with the conventional arc apparatus contained cocoon-like carbon nano-horn (CNH), dahlia-like CNH, and graphite ball. On the other hand, AS which was synthesized using the new twin-torch-arc apparatus contained mainly cocoon-like CNH and dahlia-like CNH, and contained a little graphite ball. The quality of dispersion was characterized and evaluated by the index of dispersion which was based on a diameter and a number density of catalyst particles. The electrocatalytic activity of the Pt/Ru catalysts was evaluated by the methanol-impregnated paper burning method. If the index of dispersion of the AS was high, then the AS burned violently. In the dispersion process, the optimum dispersion temperature obtained was 150 °C. Some MEAs of DMFC cell consisted of each Pt/Ru–AS catalyst which had different characteristics. It was observed that the power density increased with the index of dispersion. It was suggested that the power density of DMFC increased by 500% with a 350% increase in the index of dispersion. Pt/Ru–AS catalyst used AS, which was synthesized using the new twin-torch-arc apparatus, was better than Pt/Ru–AS catalysts using AS which were synthesized with the conventional arc apparatus to apply for the catalyst of DMFC.

1. Introduction

Direct methanol fuel cells (DMFCs) are very promising power sources for portable applications and high efficiency due to simple handling and processing of fuel. Various DMFCs have been developed and improved [1–3]. However, their sufficient performance has not yet been obtained. Typically, DMFC electrocatalysts are based on precious metals, and their high cost still remains one of the drawbacks to the widespread use of these energy conversion systems. Carbon-supported Pt/Ru is the catalyst of choice for the DMFC anode, and much research is focused on the development of high catalytic activity electrodes for methanol oxidation by pursuing new synthetic routes as well as by developing new catalyst supports [4–10]. Electrocatalysts for fuel cell electrodes are mostly composed of Pt-based metal nano-particles, which are usually dispersed on porous carbon supports. For the fuel cell applications, carbon supports should have several characteristics, which include high surface area for finely dispersing catalytic metal particles, high electrical conductivity for providing electrical pathways, mesoporosity for facile diffusion of reactants and by-products, and water handling capability for removing water generated at the cathode. Various nano-carbons, including carbon nanofiber [11,12], carbon nanotube [13,14], macroporous carbon [15,16], graphitic carbon nanocoil [17,18], and ordered mesoporous carbon [19–23], have been utilized as catalyst supports for fuel cells. The electrocatalysts employing such nano-carbon supports exhibited promising catalytic activities for methanol oxidation and oxygen reduction reactions, which were attributed to the unique structural characteristics inherent in the nano-carbons, including high conductive framework structure by graphitization, periodic pore structure in mesoporous or macroporous regime, and high specific surface area.

---

* Corresponding author at: Toyohashi University of Technology, Electrical and Electronic Engineering, 1-1 Hibarigaoka, Tempaku, Toyohashi 441-8580, Aichi, Japan. Tel.: +81 532 44 6728; fax: +81 532 44 6757.
E-mail address: oke@eee.tut.ac.jp (S. Oke).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.04.010

Carbon nano-horn (CNH), which is a kind of the nano-carbon, attracts attention as an electrode material of DMFC [24]. It was found able to be synthesized as an arc-soot (AS) nano-carbon by the arc discharge method under specific condition [25,26]. Characteristics of AS such as the shape, the diameter, the structure, and the composition had been observed using TEM and Raman spectroscopy [27]. In addition, it was indicated that the non-dahlia-like AS supported the finer Pt/Ru particles with high dispersion [28]. The dahlia-like AS, however, has low electrical conductivity and this adversely affects cell performance. Hence, we used the device that can continuously synthesize AS to synthesize a structured AS.

In the present paper, AS was synthesized by using arc discharge apparatuses, Pt/Ru was supported on AS under various conditions, and the catalysts were prepared and evaluated.

2. Experimental

The AS was prepared by arc discharge plasma with graphite rod electrode in nitrogen (N_2) ambient. The experimental apparatuses for arc discharge are depicted in Fig. 1. Fig. 1(a) is a conventional arc apparatus which has opposite electrodes in a closed camber. The chamber contains a pair of graphite rods surrounded by a water-cooled inner jacket. A dc arc discharge was generated between the electrodes. Materials evaporated from the graphite anode were deposited on the cathode as well as on the jacket and chamber walls. Synthesis conditions were as follows. Ambient N_2 gas pressure, 80 kPa or 100 kPa; cathode diameter, 10.5 mm; anode diameter, 6.4 mm; anode current density, 6.2 A/mm^2; electrode gap, less than 1 mm; discharge time, 1–1.5 min; arc voltage, 20 V. Fig. 1(b) is a new twin-torch-arc apparatus with two arc torch electrodes located with an angle of 80° in order to prevent materials from depositing on the cathode. An ac arc discharge was generated between the electrodes. Both electrodes of the arc torches were continuously supplied, for long-term operation. In the apparatus, a constant amount of gas flows in from the torches and is evacuated by the pump. Pressure in the chamber was constantly controlled by a conductance valve, balancing the gas supply and exhaust. Synthesized materials were deposited on chamber walls, a cold trap chilled by liquid nitrogen, and a paper filter. Synthesis conditions were as follows: ambient N_2 gas pressure, 80 kPa; cathode diameter, 10 mm; anode diameter, 6 mm; anode current density, 7.1 A/mm^2; electrode gap, less than 1 mm; discharge time, 1–1.5 min; arc voltage, 20 V; gas flow rate, 20 L/min.

AS was modified to add a functional group as hydroxy group (—OH) and carboxy group (—COOH) in 15 wt% H_2O_2 solution at 120 °C for 2 h, and was filtered and washed with de-ionized water and then dried at 250 °C for 2 h. Metallic catalyst particles were supported on AS by the colloidic process [29]. The modified AS was activated to disperse catalyst at 250 °C for 2 h in air. 300 mg of the activated AS was homogenized with 40 ml ethylene glycol (EG) solution that pH of the solution was adjusted to above 13 by KOH at 80 °C for 30 min. Ru·EG solution and Pt·EG solution were dissolved into AS·EG·nOH over a period of 30 min. Ru·EG solution was made by dissolving 280 mg of the $RuCl_3{\cdot}nH_2O$ in EG, and the Pt·EG solution by dissolving 580 mg of the $Na_2PtCl_6{\cdot}6H_2O$ in EG. The solution was heated at a dispersion temperature, which was a parameter of the performance of dispersion in our research for 2 h. A flow of argon was passed through the reaction system to eliminate oxygen and to remove organic by-products. After filtration, washing by de-ionized water, and vacuum drying at 120 °C for 2 h, Pt/Ru was dispersed onto AS. We also prepared other catalyst using ketjen black (KB) for comparing the performances of DMFC electrode with our Pt/Ru–AS catalyst.

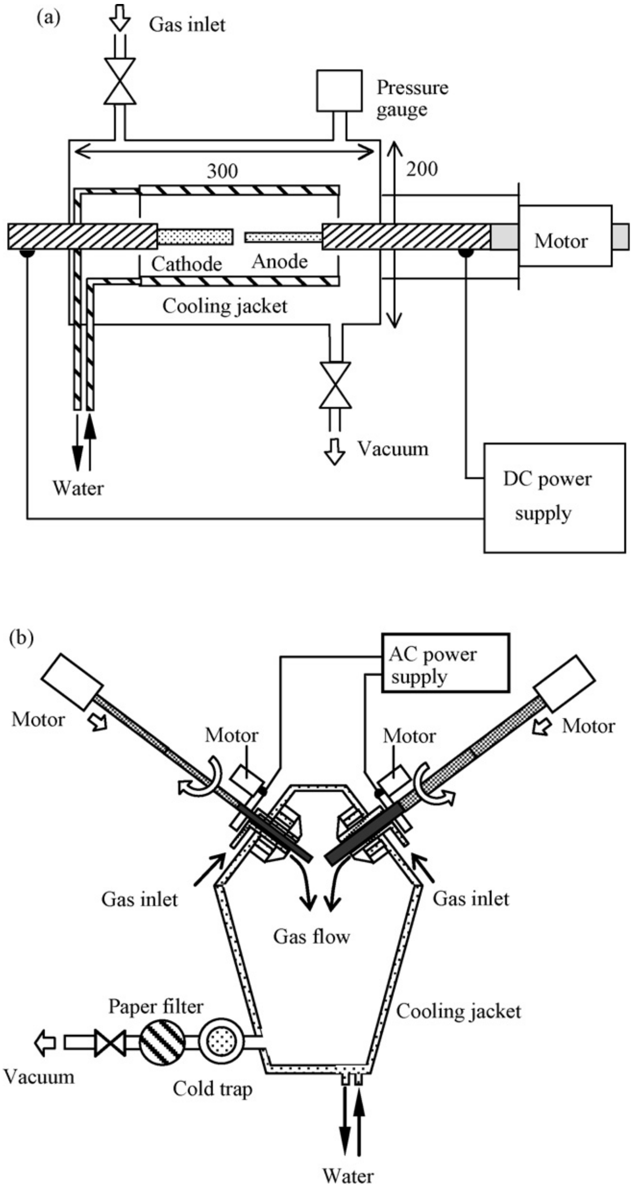

Fig. 1. Experimental apparatus for arc discharge. (a) Conventional arc apparatus and (b) new twin-torch-arc apparatus.

The synthesized AS was observed using a transmission electron microscope (TEM; JOEL, JEM-2010), and characterized by Raman spectroscopy (JASCO, NRS-1000). An average diameter and a number density of Pt and Ru particles which supported on AS were observed using the TEM. Activity of Pt/Ru–AS catalyst was evaluated by observation of the burning in air immediately after being dropped on the methanol-impregnated paper (methanol-impregnated paper burning method). In this method, Pt/Ru–AS catalyst was placed on a paper impregnated with methanol (98%), and the paper was observed to burn. If activity of the catalyst is high, then the paper is burned violently.

Some MEAs of DMFC cell consisted of each Pt/Ru–AS catalyst which had different characteristics. In the single cell, 20 wt% Pt/Ru–AS catalyst and 20 wt% Pt–AS catalyst were used as the anodic and the cathodic catalysts, respectively. Nafion 115 membrane was used as the proton exchange membrane. The slurries of the anodic and cathodic catalysts were spread onto untreated carbon papers (SGL carbon, GDL31AA). Before hot pressing, a 5 wt%

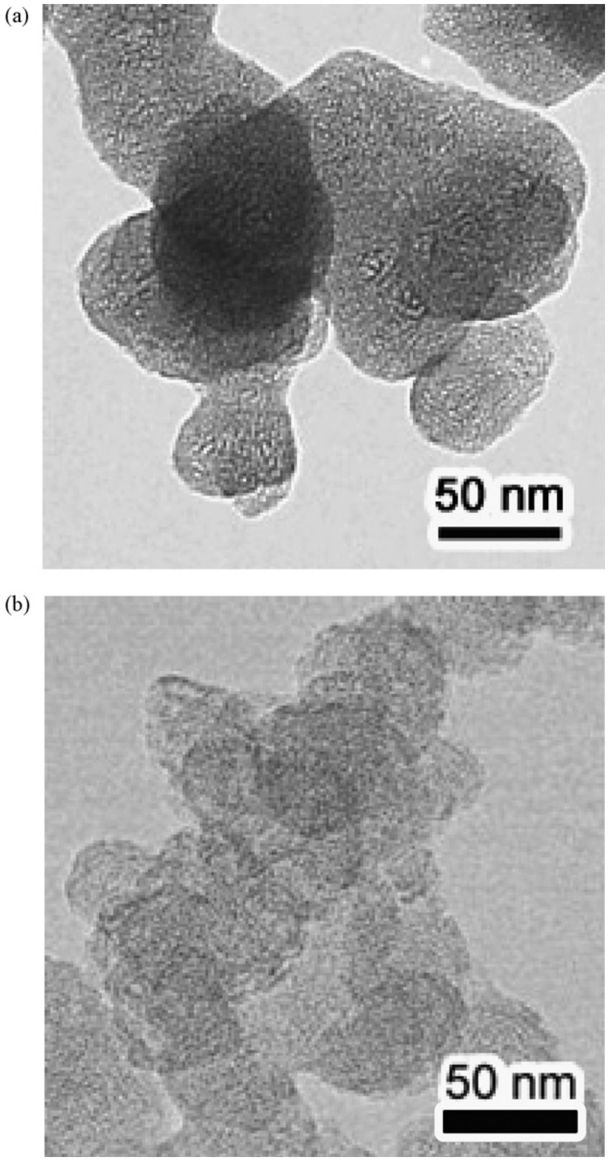

Fig. 2. AS synthesized using (a) conventional arc apparatus and (b) new twin-torch-arc apparatus.

Nafion solution was sprayed onto the catalyst side of the electrode. The MEA was prepared by pressing the anodic and cathodic electrodes onto two sides of a Nafion 115 membrane. The apparent surface area of the electrode was 16 cm^2. Finally, the single cell was installed. The performance of the single cell was measured with an FC impedance meter (KIKUSUI, KFM2030).

3. Results and discussion

AS synthesized using the conventional arc apparatus (N_2 gas pressure, 80 kPa) is shown in Fig. 2(a). Cocoon-like CNH, dahlia-like CNH, and graphite ball were contained in the AS. The AS synthesized using the new twin-torch-arc apparatus is shown in Fig. 2(b). The cocoon-like CNH and dahlia-like CNH were contained, not the graphite ball. Therefore, the new twin-torch-arc apparatus can selectively synthesize the shape of AS. Fig. 3 shows the Raman spectrum obtained from each AS synthesized using the conventional arc apparatus (N_2 gas pressure, 80 kPa) and new twin-torch-arc apparatus. In each AS, much more amorphous carbon was contained than graphite, since the D-peak was stronger than the G-peak.

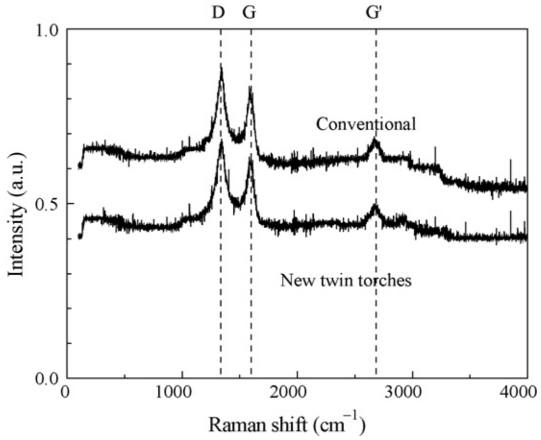

Fig. 3. Raman spectrum obtained from each AS synthesized using conventional arc apparatus (N_2 gas pressure, 80 kPa) and new twin-torch-arc apparatus.

Fig. 4 is the TEM image of the Pt and Ru particles on the AS and KB where the dispersion temperature was 150 °C. The AS was synthesized using the conventional arc apparatus (N_2 gas pressure, 80 kPa). Fig. 4(a) shows that the Pt and Ru particles in the Pt/Ru–AS catalyst are highly dispersed. The average diameter of Pt and Ru particles and the number density of Pt and Ru on AS synthesized using the conventional arc apparatus (N_2 gas pressure, 80 kPa) at several dispersion temperatures from 120 °C to 180 °C were observed from several visual fields. If the dispersion temperatures were 120 °C, 150 °C, and 180 °C, then the average diameters of the Pt and Ru particles were 3.2 nm, 2.0 nm, and 2.7 nm, respectively, and the

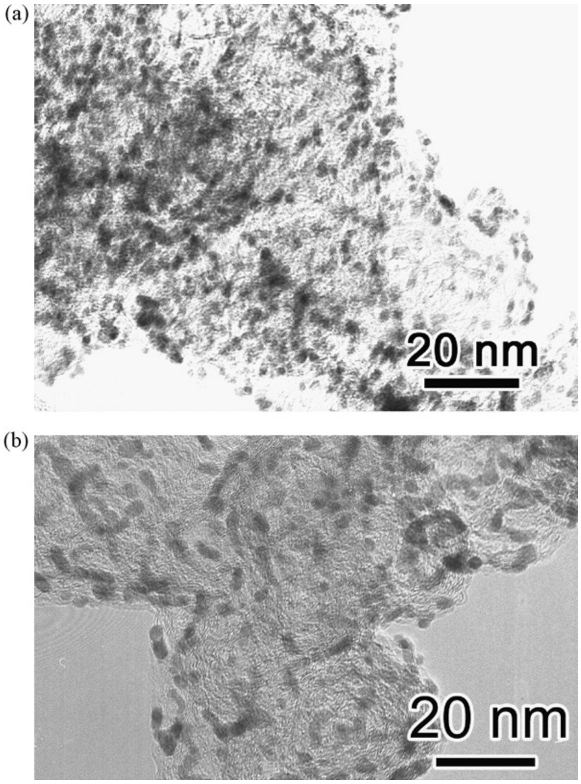

Fig. 4. TEM image of (a) Pt/Ru–AS catalyst and (b) Pt/Ru–KB catalyst when dispersion temperature was 150 °C.

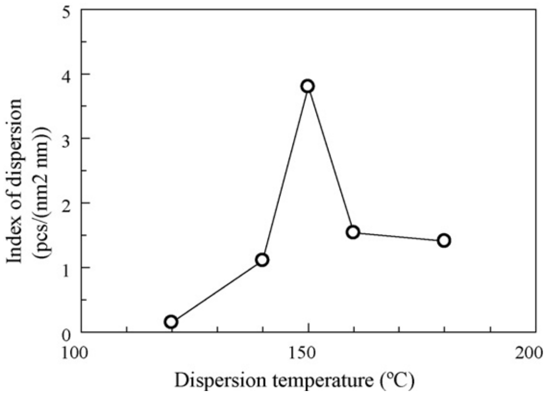

Fig. 5. Dependence of index of dispersion on dispersion temperature.

number densities of the Pt and Ru particles were 0.48 pcs/100 nm^2, 7.6 pcs/100 nm^2, and 2.7 pcs/100 nm^2, respectively. The TEM image of Pt and Ru particles in the Pt/Ru–KB catalyst is shown in Fig. 4(b). The average diameter and the number density of the Pt and Ru particles were 2.1 nm and 3.1 pcs/100 nm^2, respectively.

High dispersion is required in which many small metallic particles are widely dispersed so that the Pt/Ru–AS catalyst may exhibit high activity. In the present study, the index of dispersion D (pcs/(100 nm^2 nm)), which is presented to evaluate the catalyst activity, is calculated as follows:

$$D = \frac{n}{d} \tag{1}$$

where d is the average diameter of Pt and Ru particles (nm) and n is the number density of Pt and Ru particles on AS (pcs/100 nm^2). Fig. 5 shows the dependence of the index of dispersion on the dispersion temperature. The largest index of dispersion (3.8 pcs/(100 nm^2 nm)) was obtained when the dispersion temperature was 150 °C. It is suggested that the optimum dispersion temperature of the Pt/Ru–AS catalyst is 150 °C. The result of the activity evaluation of Pt/Ru–AS catalyst by the methanol-impregnated paper burning method is shown in Table 1. The table shows that if the index of dispersion was high, then the paper was burned violently. In case of Pt/Ru–KB catalyst, the index of dispersion was 1.48, thus the paper was burned. Therefore, the activity of Pt/Ru–AS catalyst can be evaluated using the methanol-impregnated paper burning method.

Table 1
Characteristics of catalyst particle dispersion of Pt/Ru–AS

Dispersion temperature (°C)	Index of dispersion (pcs/(100 nm^2 nm))	Methanol-impregnated paper burning method
120	0.15	Not burned
140	1.11	Burned
150	3.80	Burned violently
160	1.54	Burned
180	1.41	Not burned

Table 2
Synthesis and dispersion conditions of Pt/Ru–AS catalyst and KB used to make MEA

Sample	Synthesis apparatus	Ambient pressure (kPa)	Containing particles
a	Conventional	100	CHN and graphite ball
b	Conventional	80	CNH and graphite ball
c	Conventional	80	CNH
d	Conventional	80	Graphite ball
e	Twin-torch-arc	80	CNH and graphite ball
f	–	–	KB

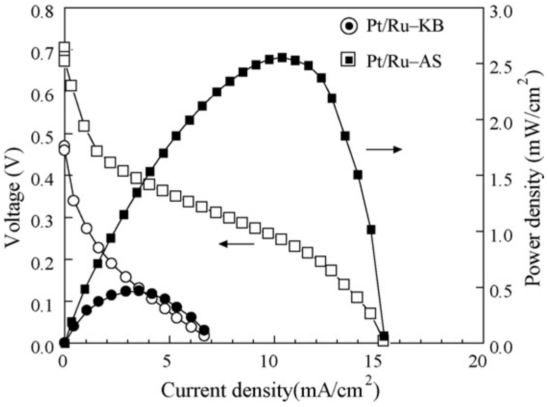

Fig. 6. Polarization curves and single-cell performances for various MEAs equipped with (a) Pt/Ru–AS catalyst and (b) Pt/Ru–KB catalyst.

Some MEAs of DMFC cell consisted of the Pt/Ru–AS catalyst which had different characteristics. AS and KB which used to consist of MEA are shown in Table 2. They had been synthesized using different apparatuses and ambient N$_2$ pressures, supported metallic catalyst particles at 150 °C. To observe the difference in the characteristics of each kind of nano-carbons, AS which was synthesized using the conventional arc apparatus was classified into two kinds of nano-carbon, CNH and graphite ball.

The polarization curves and performance of MEAs equipped with the Pt/Ru–AS catalyst and the Pt/Ru–KB catalyst are shown in Fig. 6. The open circuit voltages of MEA using Pt/Ru–AS catalyst (0.7 V) are higher than that of MEA using Pt/Ru–KB catalyst (0.47 V). The reason is that Pt/Ru–AS has higher catalytic activity compared with Pt/Ru–KB. The maximum power density values obtained are 2.6 mW/cm^2 and 0.47 mW/cm^2, respectively. It can be seen that the good performance is exhibited by the Pt/Ru–AS in the catalyst layer.

Fig. 7 shows the relationship between the power density and the index of dispersion of the single DMFC with the Pt/Ru–AS catalyst. It was observed that the power density of DMFC increased by 500% with a 350% increase in the index of dispersion. Sample e using AS was synthesized with the new twin-torch-arc apparatus, and was better than samples a–d using AS synthesized using the conventional arc apparatus for the catalyst of DMFC.

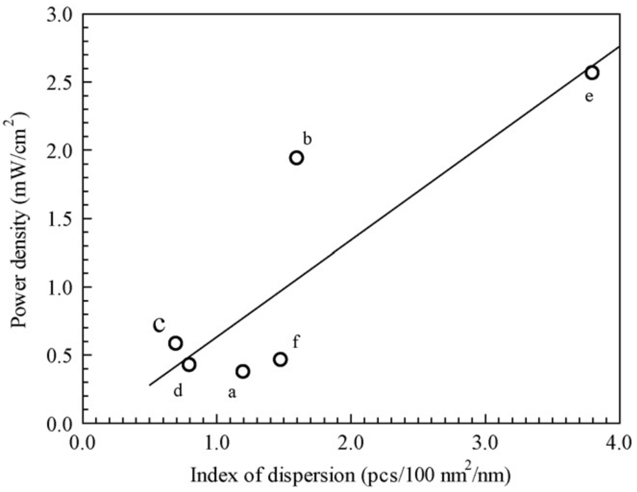

Fig. 7. Relationship between power density and index of dispersion of single DMFC with Pt/Ru–AS catalyst.

4. Conclusions

AS containing CNH and graphite ball was synthesized using arc discharge apparatuses. AS, which was synthesized using the conventional arc apparatus, contained cocoon-like CNH, dahlia-like CNH, and graphite ball. AS, which was synthesized using the new twin-torch-arc apparatus, contained mainly cocoon-like CNH, dahlia-like CNH, and a little graphite ball. Pt and Ru catalysts were supported on each AS. The index of dispersion and the methanol-impregnated paper burning method were proposed to evaluate the activity of the Pt/Ru–AS catalyst. If the index of dispersion of the AS was high, then the AS was burned violently. In the dispersion process, the optimum dispersion temperature obtained was 150 °C. Some MEAs of DMFC cell consisted of each Pt/Ru–AS catalyst which had different characteristics. It was observed that the power density increased with the index of dispersion. It was suggested that the power density of DMFC increased by 500% with a 350% increase in the index of dispersion. Pt/Ru–AS catalyst used AS, which was synthesized using the new twin-torch-arc apparatus, was better than Pt/Ru–AS catalysts used AS synthesized using the conventional arc apparatus and Pt/Ru–KB catalyst for the DMFC.

Acknowledgements

This work has been partly supported by the Excellent Research Project of the Research Center for Future Technology and the Research Center for Future Vehicle from Toyohashi University of Technology, the 21st Century COE Program “Intelligent Human Sensing” from the Ministry of Education, Culture, Sports, Science and Technology, the JSPS Core University Program, and the Global COE Program “Frontiers of Intelligent Sensing,” from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.
[2] C.K. Witham, W. Chun, T.I. Valdez, S.R. Narayanan, Electrochem. Solid State Lett. 3 (2000) 497.
[3] C.Y. Chen, P. Yang, J. Power Sources 123 (2002) 37.
[4] E. Antolini, Mater. Chem. Phys. 78 (2003) 563.
[5] G. Lister, G. McLean, J. Power Sources 130 (2004) 61.
[6] M. Huchida, Y. Fukuoka, Y. Sugawara, N. Eda, A. Ohta, J. Electrochem. Soc. 143 (1996) 2245.
[7] V. Raghuveer, A. Manthiram, Electrochem. Solid State Lett. 7 (2004) A336.
[8] G.G. Park, T.H. Yang, Y.G. Yoon, W.Y. Lee, C.S. Kim, Int. J. Hydrogen Energy 28 (2003) 645.
[9] M. Mastragostino, A. Missiroli, F. Soavi, J. Electrochem. Soc. 151 (2004) A1919.
[10] V. Rao, P.A. Simonov, E.R. Savinova, G.V. Plaksin, S.V. Cherepanova, G.N. Kryukova, U. Stimming, J. Power Sources 145 (2005) 178.
[11] C.A. Bessel, K. Laubernds, N.M. Rodriguez, R.T.K. Baker, J. Phys. Chem. B 105 (2001) 1115.
[12] E.S. Steigerwalt, G.A. Deluga, C.M. Lukehart, J. Phys. Chem. B 106 (2002) 760.
[13] W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zhou, G. Sun, Q. Xin, J. Phys. Chem. B 107 (2003) 6292.
[14] Y. Lin, X. Cui, C. Yen, C.M. Wai, J. Phys. Chem. B 109 (2005) 14410.
[15] J.S. Yu, S. Kang, S.B. Yoon, G. Chai, J. Am. Chem. Soc. 124 (2002) 9382.
[16] G.S. Chai, S.B. Yoon, J.S. Yu, J.H. Choi, Y.E. Sung, J. Phys. Chem. B 108 (2004) 7074.
[17] T. Hyeon, S. Han, Y.E. Sung, K.W. Park, Y.W. Kim, Angew. Chem. Int. Ed. 42 (2003) 4352.
[18] K.W. Park, Y.E. Sung, S. Han, Y. Yun, T. Hyeon, J. Phys. Chem. B 108 (2004) 939.
[19] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, Nature 412 (2001) 169.
[20] J. Ding, K.Y. Chan, J. Ren, F.S. Xiao, Electrochem. Acta 50 (2005) 3131.
[21] F. Su, J. Zeng, X. Bao, Y. Yu, J.Y. Lee, X.S. Zhao, Chem. Mater. 17 (2005) 3960.
[22] J.H. Nam, Y.Y. Jang, Y.U. Kwon, J.D. Nam, Electrochem. Commun. 6 (2004) 737.
[23] C. Pak, D.J. Yoo, S.A. Lee, J.M. Kim, H. Chang, J. Samsung, Innovative Technol. 1 (2005) 239.
[24] T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kudo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka, S. Iijima, Physica B 323 (2002) 124.
[25] M. Ikeda, H. Takikawa, T. Tahara, Y. Fujimura, M. Kato, K. Tanaka, S. Itoh, T. Sakakibara, Jpn. J. Appl. Phys. 41 (2002) L852.
[26] H. Niwa, K. Higashi, K. Shinohara, H. Takikawa, T. Sakakibara, K. Yoshikawa, K. Miura, S. Itoh, T. Yamaura, J. High Temp. Soc. Jpn. 1 (2006) 57.
[27] G. Xu, H. Niwa, T. Imaizumi, H. Takikawa, T. Sakakibara, K. Yoshikawa, A. Kondo, S. Itoh, New Diamond Frontier Carbon Technol. 2 (2005) 73.
[28] K. Higashi, H. Niwa, H. Takikawa, T. Sakakibara, S. Itoh, T. Yamaura, G. Xu, K. Miura, K. Yoshikawa, J. IAPS 13 (2005) 99.
[29] W. Li, C. Liang, W. Zhou, J. Qiu, H. Li, G. Sun, Q. Xin, Carbon 42 (2004) 436.