

Electron-beam reduction method for preparing electrocatalytic particles for membrane electrode assemblies (MEA)

Yi-Hao Pai^a, Hsin-Fu Huang^a, Yu-Chen Chang^b, Chih-Cheng Chou^c, Fuh-Sheng Shieu^{a,*}

^a Department of Materials Engineering, National Chung Hsing University, Taichung 40227, Taiwan

^b Environment Group, CTCI Corporation, Taipei 10683, Taiwan

^c Department of Chemical Engineering, National Chung Hsing University, Taichung 40227, Taiwan

Received 26 October 2005; received in revised form 14 December 2005; accepted 15 December 2005

Available online 3 February 2006

Abstract

A new method, the electron-beam (e-beam) reduction method, is presented for fuel cell electrocatalytic particle preparation. The method utilizes the idea of reducing ions of the catalyst species right on the carbon cloth fibers and the multi walled carbon nano tubes (MWNTs) via direct electron-beam bombardment. The morphology of the electron-beam reduced catalyst particles is presented to show that the catalyst particles were dispersed in an equal and homogeneous manner within the MWNTs/carbon cloth electrode carriers, and imply that the electroactive surface area of the e-beam reduced catalysts should assume a larger value than those from currently reported methods. With the Pt (catalyst) loadings being controlled, data obtained from electrochemical and polarization tests show that the electrodes and membrane electrode assemblies (MEA) prepared from the e-beam reduction have larger active surface areas and better working performances than those prepared from the sputtering method; the quantitative results show good consistency with the qualitative morphology images.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Electron-beam reduction; Microwave plasma chemical vapor deposition (MPCVD) system; Proton exchange membrane fuel cells (PEMFC); Membrane electrode assembly (MEA); Multi walled carbon nano tubes (MWNTs)

1. Introduction

Over the past few decades, proton exchange membrane fuel cells (PEMFC) have become a major research interest and could become a mainstream power source due to their quietness, low pollution, and high working efficiencies. Among all components inside PEMFC systems, catalyst particles deposited on the porous electrodes are of the most importance because they provide the electroactive sites for the oxidation and reduction reactions, which convert chemical energy directly into electricity, to proceed efficiently, and are therefore often regarded as the “real working electrochemical electrodes” [1]. In other words, the efficiencies and overall working performances of PEMFC systems are mostly determined by the properties and characteristics of catalyst particles, and the method of particle preparation and distribution [2].

From the literature, these nano-scaled catalyst particles are generally prepared from either physical or chemical methods. For example, ball milling [3], laser ablation [4], and physical vapor deposition (PVD, or sputtering) [5] are the commonly reported physical methods for catalyst fabrication. On the other hand, the redox [6], hydrothermal [7], and sol–gel [8] techniques are the representative chemical based methods. While the resulting electrode and fuel cell performances are not reported extensively, most of these preparation techniques not only require strict processing controls and tedious operation procedures, but also limit or confine the space where the catalyst particles are distributed in the electrodes, i.e., the available electrode space or surface area is not fully utilized.

Specifically, take the physical vapor deposition, or sputtering, method, for example. The method is now generally applied in Pt particle preparation for Pt/MWNTs/carbon cloth electrodes, and has the advantage of generating fine-sized Pt particles (~2 nm [2]) that are theoretically considered to provide a considerable reactive surface area [9]. However, besides the strict operational environment demands, the method merely deposits the

* Corresponding author. Tel.: +886 4 2285 4563; fax: +886 4 2285 7017.

E-mail addresses: fsshieu@dragon.nchu.edu.tw, d9366102@mail.nchu.edu.tw (F.-S. Shieu).

Pt particles onto the electrode surface region within a range of depth characterized by several nano meters, that is, the Pt catalyst particles cannot penetrate into the full depth of the electrodes via this method, a fact that renders most of the electrode space deserted of catalyst particles, and a fact that seriously harms the fuel cell efficiency.

In order to resolve this undesirable feature and take the most advantage of the available electrode space, we propose a new method, the electron-beam reduction method (e-beam method), for catalyst particle deposition. The method employs the idea of reducing ions via direct electron-beam bombardment [10] and aims at preparing catalyst particles with a better penetration depth and distribution. In the next section, we clarify the concept and demonstrate the operational procedure of the electron-beam reduction method. The electrode preparation and experimental setup are then described so that the electrodes and cells made from sputtering and e-beam procedures can be compared with respect to their activities and efficiencies. The results are then compared and discussed.

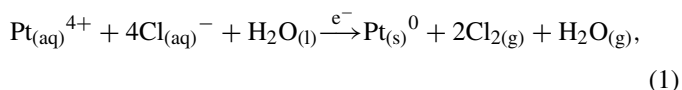
2. Experimental

2.1. The electron-beam reduction method

In this method, ions or ionic solutions of the catalyst species are directly bombarded by high energy electron-beams emitted from transmission electron microscopes (TEM), scanning electron microscopes (SEM), or electron-beam writers. Due to the results of the electron impact, the catalyst ions undergo reduction processes, which subsequently generate nano-scaled catalyst particles. In other words, we have transformed the TEM or SEM into a device that fabricates catalyst particles for fuel cell electrodes.

The basic procedure of the method involved an ionic solution, such as PtCl_4 , with a concentration of 0.1 wt.%; the solution was then wetted onto the TEM specimen copper grid and dried in the air. We placed the air-dried copper grid on the specimen holder and inserted the whole module into the TEM column. With an accelerating voltage of 80 kV and a 2×10^{-6} Torr vacuum, the Pt^{4+} ions were struck by 80 keV electrons (e^-) and reduced to Pt^0 nanoparticles on the copper grid. Meanwhile, the $\text{Cl}_{2(\text{aq})}^-$ and $\text{H}_2\text{O}_{(\text{l})}$ were transformed into $\text{Cl}_{2(\text{g})}$ and $\text{H}_2\text{O}_{(\text{g})}$ and were immediately removed by the TEM vacuum pump. The above

reaction is described by the following equation:



and the metal reduction rate was 1.644×10^8 ions s^{-1} in vacuum [11]; the procedure of the e-beam method is summarized in Fig. 1.

Since the catalyst ions were carried within a liquid phase before the bombardment, the catalyst particles were transported much further into the porous structured substrates via combined actions of liquid convection and permeation. Thus, the nanoparticles reduced from these solutions were well-dispersed with desirable distributions and penetration depths in the porous supports or substrates, e.g., fuel cell electrodes, after a more homogeneous liquid solution spreading and the e-beam process. For further applications, tests of the e-beam method were also performed on other materials; the e-beam reduction method was also suitable for producing nano metal particles from other ionic solutions, such as FeCl_2 and AgNO_3 .

2.2. Electrode preparation

Two sets of electrodes were prepared, tested, and compared in the present study. One was with the electrodes prepared from the e-beam reduction method; the other was prepared from sputtering, or physical vapor deposition methods. Details of the electrode preparation are described as follows.

Shown in Fig. 2 is the preparation flow chart for the e-beam reduced electrodes. Firstly, a 25 cm^2 area of carbon cloth was processed to have a clean surface; the cloth was then immersed in a 0.1 wt.% Fe ionic solution and subsequently dried in the atmosphere. We next attached the dried carbon cloth to the specimen holder and inserted the holder into the SEM column. With an accelerating voltage of 15 kV and a 9.56×10^{-5} Torr vacuum, Fe ions on the carbon cloth surface were reduced into Fe^0 catalyst particles through the e-beam process. Multi walled carbon nano tubes (MWNTs) were grown on the Fe catalyst sites by microwave plasma chemical vapor deposition (MPCVD) [2] with a methane to hydrogen ratio of 1:4, the microwave power was 300 W, the working pressure was 5×10^{-4} Torr, and the working temperature was 590°C . After completing the MWNTs/carbon cloth carrier, a 0.1 wt.% Pt ionic solution was

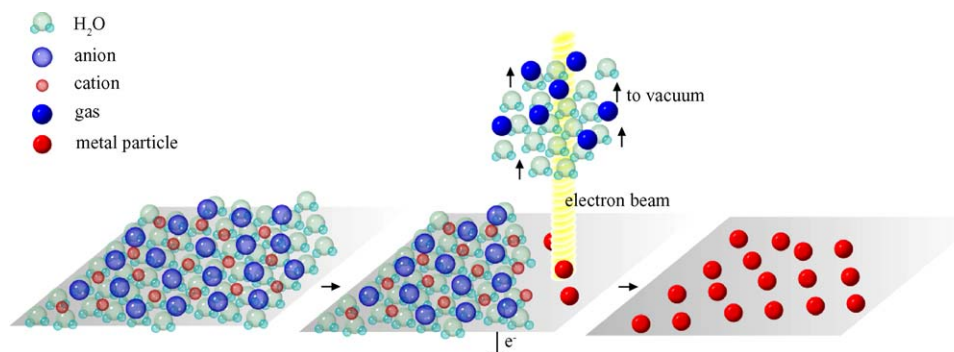


Fig. 1. Conceptual description of the electron-beam reduction method for metal nanoparticle fabrication.

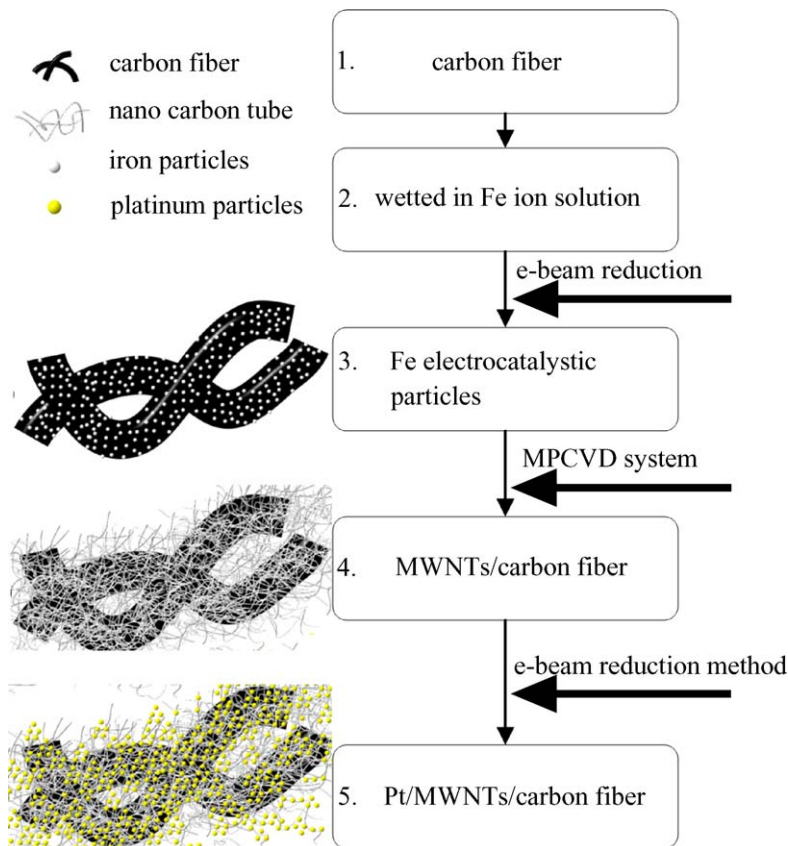


Fig. 2. Flow chart of the electrode preparation via the electron-beam reduction method.

sprayed onto the surface of the MWNTs/carbon cloth carrier and was then dried in the atmosphere. Again, we utilized the e-beam reduction method (15 kV and a 9.56×10^{-5} Torr vacuum) to obtain the reduced Pt particles. The Pt loading was 0.44 mg cm^{-2} in this procedure.

As for the electrodes prepared by the sputtering method, the procedures were the same as those described above except for the last step: the Pt catalyst was deposited onto the MWNTs/carbon cloth via sputtering (PVD, ULVAC VPS-020 Quick Coater) [2] (sputtering current was 20 mA, sputtering time 45 s, in an Argon atmosphere). The Pt loading for the sputtering prepared electrodes was 0.46 mg cm^{-2} . Test and experimental results of the two sets of electrodes are given and compared in Section 3; and the differences in the required processing conditions, e.g., the catalyst particle generation speed, the particle distribution, etc.,

between the sputtering and e-beam methods are compared in Table 1.

2.3. Experimental setup

Experiments were designed and performed to investigate three aspects: (i) the morphology and the crystalline phase of the e-beam prepared catalyst particles, (ii) the electrochemical analysis of the e-beam and sputtering prepared electrodes, and (iii) the single cell polarization curves of two sets of cells built from the e-beam and sputtered electrodes, respectively.

Morphology analysis and the preparation of the electrocatalytic particles were, respectively, done by the JEOL 6700F SEM and Zeiss 902 A TEM. The crystalline phase analysis was performed by comparison of the selected area diffraction (Zeiss 902

Table 1
Comparison of the e-beam reduction and sputtering methods

	Method	
	e-Beam reduction	Sputtering
Environment	Vacuum	Vacuum
Method of particle generation	High-energy electron-beam bombardment	Target bombarded by noble gas plasma to cause material deposition
Particle generation rate	Very fast	Fast
Region of particle distribution	From the surface to the inner layers of the MWNTs	Within a surface region of several nano meters
Material loss during fabrication	Approximately zero material during process	Considerable material loss in the chamber during process

A TEM, SAD) patterns of the e-beam produced catalyst particles to those of standard compounds reported in the JCPDS Data File.

Electroactivities and electrochemical properties of the Pt/MWNTs/carbon cloth electrodes prepared from e-beam and sputtering methods were tested and analyzed by cyclic voltammetry (CV) through a CHI614B Electrochemical Analyzer. In our CV tests, the Pt/MWNTs/carbon cloth electrodes were measured in a 1 M H₂SO₄ solution with a 10 mV s⁻¹ scanning rate, while a Pt wire served as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode.

Before any of the tests or measurements concerning the cell polarization curves were performed, the electrodes were attached onto a polymer electrolyte membrane (PEM) to form a membrane electrode assembly (MEA), and then installed, together with the whole MEA, into a single cell. The PEMs used in our experiments were Nafion[®] 117 (Du Pont Chemical), and were immersed in a 5% H₂O₂ solution at 80 °C for 1 h so that the organic impurities on the membrane surface were removed. We next immersed the PEMs into a 0.5 M H₂SO₄ solution at 80 °C for 1 h, and finally washed the PEMs with boiled (~80 °C) deionized (D.I.) water several times. The cleaned PEMs were then assembled with the Pt/MWNTs/carbon cloth fiber electrodes by a vacuum hot pressed system at 6×10^{-1} Torr with the hot pressing conditions being 5 kg cm⁻², 60 °C for 30 s, and subsequently 22 kg cm⁻², 130 °C, for 60 s. After installing the hot pressed MEAs into the single cells, polarization curves were measured and plotted by the Fuel Cell System from Beam Associate Co. Ltd., Taiwan. Reactant, hydrogen and oxygen, streams were saturated with pure water at 27 °C, and were fed into the single cell at 27 °C with a 15 psi back pressure and flow rates of 100 sccm. The temperature of the single cell was kept at 45 °C throughout the tests.

3. Results and discussion

3.1. Characterization of the electrocatalytic particles

Shown in Fig. 3(a) is the bright field image of the e-beam reduced, Fe electrocatalytic particle morphology on the TEM specimen copper grid; the original ionic solution was a 0.1 wt.% FeCl₂ solution. From the measurement results, the Fe electrocatalytic particles had an average particle diameter of 25 nm, while the (1 0 1) reflection of the Fe phase corresponded to a *d* spacing of 2.027 Å. In Fig. 3(b), the Fe electrocatalytic particles were e-beam reduced on the carbon cloth fibers, which is the process before developing the multi walled carbon nano tubes upon the electrocatalytic sites. From the field emission SEM (FE-SEM) morphology shown in this figure, it appears that the Fe electrocatalytic particles were equally distributed on the carbon cloth fibers, and that the average particle diameter of the Fe particles fell in a range from 12 to 15 nm. Together with Fig. 3(c), Fig. 3(b and c) presents the actual morphology of the material being processed that corresponds to the third and fourth steps in the electrode preparation flow chart of Fig. 2.

Fig. 4(a) shows the bright field morphology of the Pt electrocatalytic particles e-beam reduced from a 0.1 wt.% PtCl₄

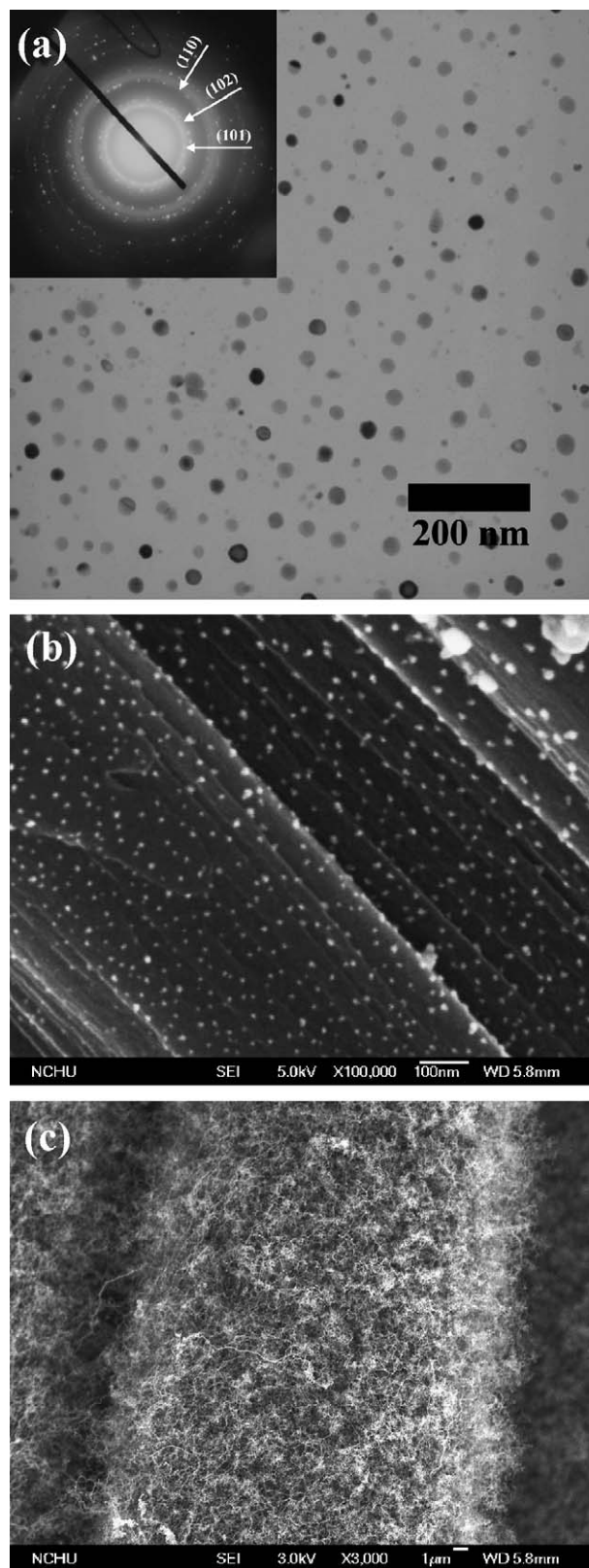


Fig. 3. SEM micrographs of: (a) bright field images and SAD patterns of metal nanoparticles prepared from 0.1 wt.% FeCl₂, (b) Fe nanoparticles on carbon cloth fiber surface, and (c) MWNTs branching out the carbon cloth fibers on the Fe active sites.

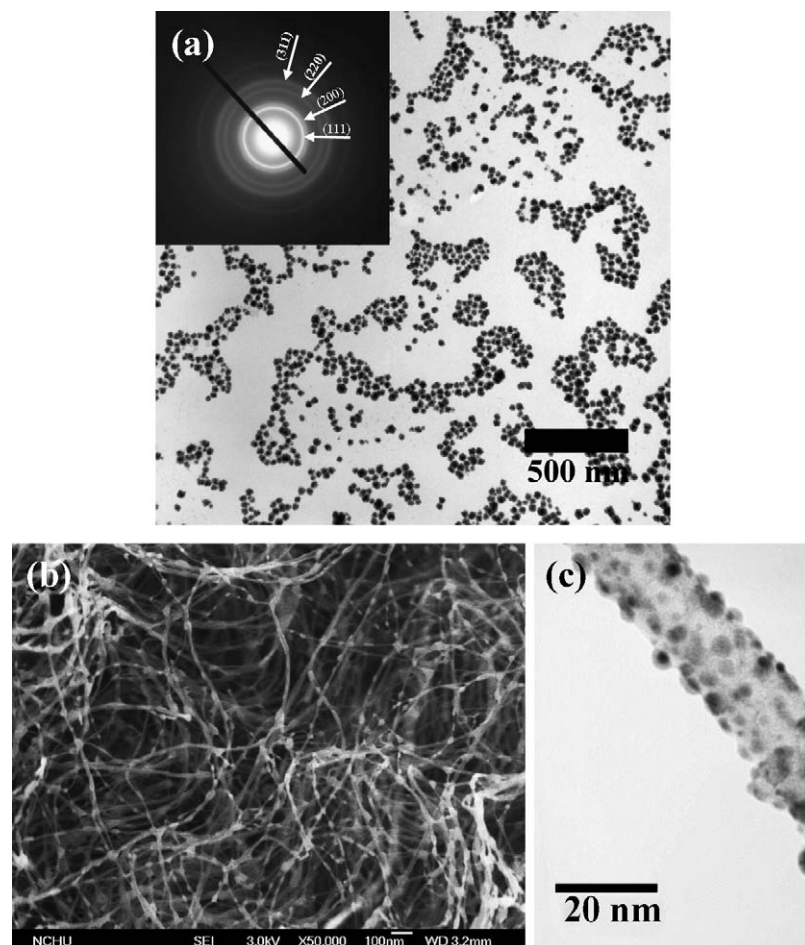


Fig. 4. (a) Bright field images and SAD patterns of metal nanoparticles prepared from 0.1 wt.% PtCl_4 solutions upon electron-beam bombardment. (b) SEM micrographs of Pt ions reduced into Pt nanoparticles on the MWNTs. (c) Bright field images of the morphology of Pt/NWNTs.

solution onto the TEM copper grid. The measured average particle diameter is 23 nm and the (1 1 1) reflection of the Pt phase corresponded to a d spacing of 2.265 Å. The FE-SEM morphology of the e-beam reduced Pt particles on the MWNTs is shown in Fig. 4(b), the actual image that corresponds to the fifth or the last step in the flow chart of Fig. 2. From Fig. 4(b), it is easily observed that the Pt electrocatalytic particles were homogeneously or well-dispersed on the entangled MWNTs, namely from the surface to the outer layer, and to the inner layer. Based on the scale bar of Fig. 4(c), the average particle diameter of the Pt particles was estimated to be 4 nm.

In sum, the results described above show qualitatively that the electrocatalytic particles were well-dispersed on the carbon cloth fibers and MWNTs. The distribution of the particles shown above is favorable since much more of the electrode space was occupied by the electrocatalytic particles.

3.2. Electroactivity of Pt/MWNTs/carbon cloth electrodes

In order to obtain information concerning the electrode activities, electrochemical measurements were performed and cyclic voltammograms were made for the Pt/MWNTs/carbon cloth electrodes prepared from both e-beam reduction and sputtering methods. The results are shown in Fig. 5, with the thin

solid curve representing the electrode from sputtering and the thick solid curve representing that from e-beam reduction. Fig. 5 shows that the electrode with e-beam reduced Pt particles had a higher specific current in the hydrogen region (-0.3 to 0.2 V)

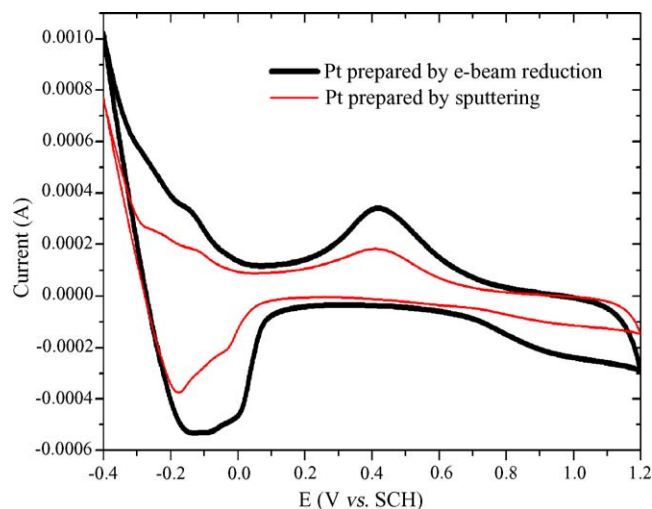


Fig. 5. Cyclic voltammograms (at 10 mV s^{-1} , in $1 \text{ M H}_2\text{SO}_4$ aqueous solution) of the electrodes prepared from the e-beam reduction and the sputtering methods.

than that of the electrode with sputtered Pt particles. The active surface area for the catalysts in the electrodes was calculated by integrating the H-adsorption and H-desorption curves on the CV plots [12]; however, first estimations of the active surface area S_{Pt} for the two sets of electrodes were made by calculating the charge transferred for H-adsorption Q_H (the shaded area in Fig. 2 of Ref. [13]), i.e.,

$$S_{Pt} = \frac{Q_H}{Q_H^0}, \quad (2)$$

where Q_H represents the measured value of charge per unit area (cm^2) of Pt with monolayer hydrogen adsorption and Q_H^0 represents the value $210 \mu\text{C cm}^{-2}$ [12,13]. The calculated active surface areas for the e-beam electrode and the sputtering electrode were 45.72 and 21.67 cm^2 , respectively.

The above results provide quantitative evidence that the e-beam reduced Pt catalytic particles had a larger electroactive surface than that of the sputtered Pt catalysts, and imply that while the Pt loadings for both cases were kept nearly the same, the e-beam reduced Pt particles had a better distribution than the sputtered particles in the whole electrode space [13] as already seen qualitatively in Fig. 4.

3.3. Membrane electrode assembly performance in single cell tests

The environment and conditions in our single cell tests for the MEAs followed those given in Ref. [14]; however, in our work, reactant streams were saturated with pure water at 27°C and fed into the single cell at 27°C , which are conditions more close to room temperature. The $V-I$ curves obtained from the polarization tests are shown in Fig. 6, where the circle dotted curve represents MEAs prepared from sputtering, and the triangle dotted curve represents MEAs from Beam Associate Co. Ltd., and the square dotted curve represents MEAs prepared from e-beam reduction; all had Pt loadings of approximately 0.4 mg cm^{-2} .

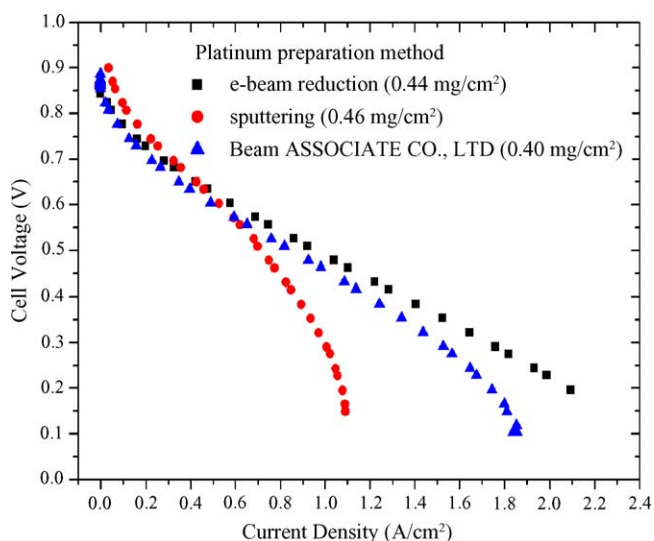


Fig. 6. The cell voltage vs. current density curves of Pt–MWNTs/carbon fiber MEAs with different platinum preparation methods.

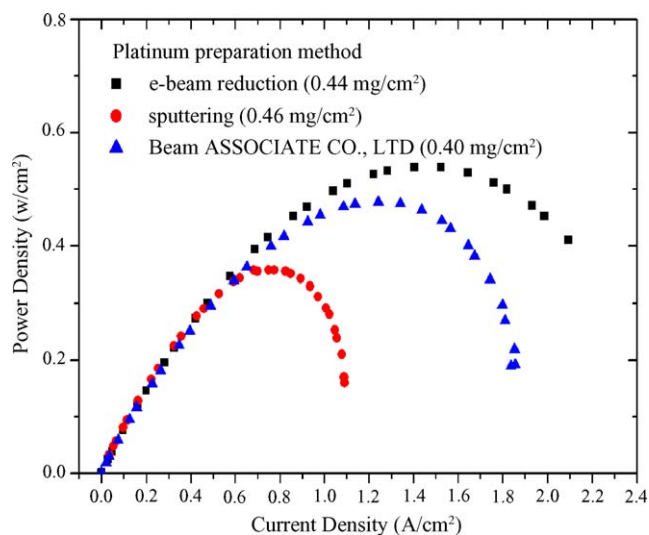


Fig. 7. The power density vs. current density curves of Pt–MWNTs/carbon fiber MEAs with different platinum preparation methods.

In the three cases listed above, the open circuit voltages (OCV) were around 0.88 V , and the reversible potentials of the fuel cell electrochemical reactions were 1.23 V under standard conditions. However, the actual voltage in the three cases is expected to be lower than the theoretical value due to irreversible losses [15].

It is also found from Fig. 6 that the ohmic polarization of the e-beam MEAs was around the range of $0.3\text{--}2.0 \text{ A cm}^{-2}$, which is a bit larger than that of the Beam Associate Co. Ltd. MEAs, and yet larger than that, e.g., $0.2\text{--}0.9 \text{ A cm}^{-2}$, of the sputtering prepared MEAs. In accordance with Fig. 6, Fig. 7 shows the power density to current density ($P-I$) plot to reveal the corresponding power outputs of the three cases, i.e., circle dotted curve for sputtering, triangle dotted for Beam Associate Co. Ltd., and square dotted for e-beam reduction. The electrodes or MEAs prepared from the e-beam reduction method had an optimal power output value of 0.56 W cm^{-2} at a 1.5 A cm^{-2} current density. These values are observed to be higher than the values, i.e., power output: 0.36 W cm^{-2} and current density: 0.75 A cm^{-2} , of electrodes or MEAs prepared from sputtering.

4. Conclusion

We have successfully transformed transmission and scanning electron microscopes into devices for fuel cell electrocatalytic particle preparation, namely the electron-beam reduction method. The method utilizes the idea of reducing ions of catalyst species right on the carbon cloth fibers and the multi walled carbon nano tubes via direct electron-beam bombardment, and has merits of high particle production rates, broad application convenience, and simple operation-environment requirements. The morphology of the electron-beam reduced catalyst particles is presented to show that the catalyst particles were dispersed in an equal, homogeneous manner within the MWNTs/carbon cloth carriers and imply that the electroactive surface area of the e-beam reduced catalysts should assume a larger value than those of currently reported methods. With the Pt (catalyst) loadings being comparable, data obtained from electrochemical and

polarization tests show that the electrodes and membrane electrode assemblies prepared from the e-beam reduction have larger active surface areas and better working performances than those prepared from the sputtering method; the quantitative results show good consistency with the qualitative morphology images. Future work is pursued with considerations of the documentation of single cell performances under different operation pressure, temperature, and reactant stream humidity.

Acknowledgements

The work is financially supported by the National Science Council (NSC) through grants NSC-093-2218-E-005-040 and NSC-094-2218-E-005-007. The authors would also like to thank Prof. J.J. Lin for reviewing the manuscript and Mr. C.C. Chen for good comments on CV plots.

References

- [1] B. Sorensen, *Hydrogen and Fuel Cells: Emerging Technologies and Applications*, Elsevier Academic Press, London, 2005, pp. 191–196.
- [2] C.C. Chen, C.F. Chen, C.H. Hsu, I.H. Li, *Diamond Relat. Mater.* 14 (2005) 770.
- [3] M. Endo, Y.A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, M. Terrones, M.S. Dresselhaus, *Nano Lett.* 3 (2003) 723.
- [4] F. Mafune, J.Y. Kohno, Y. Takeda, T. Kondow, *J. Phys. Chem. B* 10 (2002) 7575.
- [5] L. Qu, L. Dai, *J. Am. Chem. Soc.* 127 (2005) 10806.
- [6] X.S. Wang, H. Wang, N. Coombs, M.A. Winnik, I. Manners, *J. Am. Chem. Soc.* 127 (2005) 8924.
- [7] C. Kim, M. Noh, M. Choi, J. Cho, B. Park, *Chem. Mater.* 17 (2005) 3297.
- [8] W. Yan, S.M. Mahurin, Z. Pan, S.H. Overbury, S. Dai, *J. Am. Chem. Soc.* 127 (2005) 10480.
- [9] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, second ed., John Wiley, New York, 2003, pp. 1–24.
- [10] J.J. Lin, C.C. Chu, C.C. Chou, F.S. Shieu, *Adv. Mater.* 17 (2005) 301.
- [11] D.B. Williams, C.B. Carter, *Transmission Electron Microscopy*, Plenum, New York, 1996, pp. 11–13.
- [12] Y. Xing, *J. Phys. Chem. B* 108 (2004) 19255.
- [13] M. Umeda, M. Kokubo, M. Mohamedi, I. Uchida, *Electrochim. Acta* 48 (2003) 1369.
- [14] W. Li, X. Wang, Z. Xhen, M. Waje, Y. Yan, *Langmuir* 21 (2005) 9386.
- [15] M. Gangeri, G. Centi, A. La Malfa, S. Perathoner, R. Vieira, C. Pham-Huu, M.J. Ledoux, *Catal. Today* 102–103 (2005) 50.