Filtered Cathodic Vacuum Arc Deposition of Porous and Nanostructured Carbon and Hybrid C–Mo Thin Films for Fuel Cell Membranes

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In our proton exchange membrane (PEM) fuel cells, the electrolyte is a catalyst platinum (Pt) coated nafion membrane. In order to increase the electrochemically active catalyst area to enhance the cell performance but without sacrificing the electrical conductivity of the membrane, carbon thin films were deposited onto the membrane by using the filtered cathodic vacuum arc deposition (FCVAD) technique. With varying the deposition conditions, it was possible to form porous carbon films and nanoisland and nanorod structure surface which increased the catalyst area when a higher He working gas pressure and a low number of pulses were used. Based on this result, hybrid C-Mo thin films were deposited for further enhancing the Pt catalytic effect. Under the varied deposition conditions, the surface morphology and C and Mo grain sizes of the hybrid thin films were measured and their relations with the catalytic performance were studied.

Keywords: Filtered cathodic vacuum arc deposition (FCVAD), Nanostructure, Carbon, Hybrid C-Mo, Thin film, Fuel cell.

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1. INTRODUCTION

The electrochemical reactions in the proton exchange membrane fuel cell (PEMFC) occur at the catalyst layers on the electrolyte such as nafion membrane. A commonly used catalyst is platinum, which is supported by a carbon layer. Normally the carbon layer should have good adhesion with platinum catalyst, good electrical conductivity, good hydrogen and oxygen gas diffusibility, the same requirements as currently popularly used the microporous layer (MPL) on the gas diffusion layer (GDL) which can actually be carbon paper. To improve performance and reduce cost of PEMFC, we are carrying out a systematic study to improve the components of PEMFC such as bipolar plate, hard ware, electrolyte membrane and catalyst layer. As a complex of supporting material such as carbon and catalyst such as platinum, there are plenty of rooms to improve the catalyst layer. In order to increase the electrochemically active catalyst area to enhance the cell performance but without sacrificing the electrical conductivity of the membrane, a number of methods have been developed to grow the carbon layer such as the chemical method, sputtering technique [1] and filtered cathodic vacuum arc deposition (FCVAD) technique [2]. The FCVAD has been recognized to possess special advantages such as abilities to provide enhanced adhesion, film density, and composition stoichiometry due to high kinetic energy of the ions and multi ion sources available [3]. Moreover, control of the base gas pressure in the FCVAD chamber allows control of the ion energy and consequent control the coating structure [4]. In this study, we applied our self-developed FCVAD facility [5] with varied conditions to deposit carbon (C) and carbon-molybdenum (C-Mo) films for enhancing fuel cell performance.

2. EXPERIMENT

The FCVAD setup is shown in Fig. 1. Details about the setup have been described elsewhere [6].

For carbon film deposition, the plasma source was a graphite cathode. When computer-controlled high-current pulses were supplied from an arc power supply, arc formed between the cathode and the anode to generate plasma of the cathode material. The pulse length was 160 µs. The arc voltage and current were 450 V and 470 A, respectively. The system resistance was controlled at 500 ohm. The ions in the plasma were guided by a 90° solenoid filter after passing a 1-cm gap between the source and the filter to the substrate which was placed on a sample stage at the exit of the filter. No bias was applied in the experiment. The pressure in the deposition chamber as the key parameter to study was varied from 5×10^{-2}, 5×10^{-1} and 5 to 50 Torr with helium gas. For deposition of hybrid C-Mo thin films, the cathode was first carbon and then changed to molybdenum. For each type of the cathode, the arc voltage was controlled at 300 V, the base pressure of He was 2×10^{-5} Torr, the system resistance was 500 ohm and the total number of the depositing pluses was 200. In both film depositions, the substrate materials were silicon wafer and nafion membrane. Each substrate sample was a square of $5 \, mm \times 5 \, mm$.

The deposited films were characterized using scanning electron microscopy (SEM) and atomic force microscope (AFM). The contact angles of the films were measured to check the wettability.
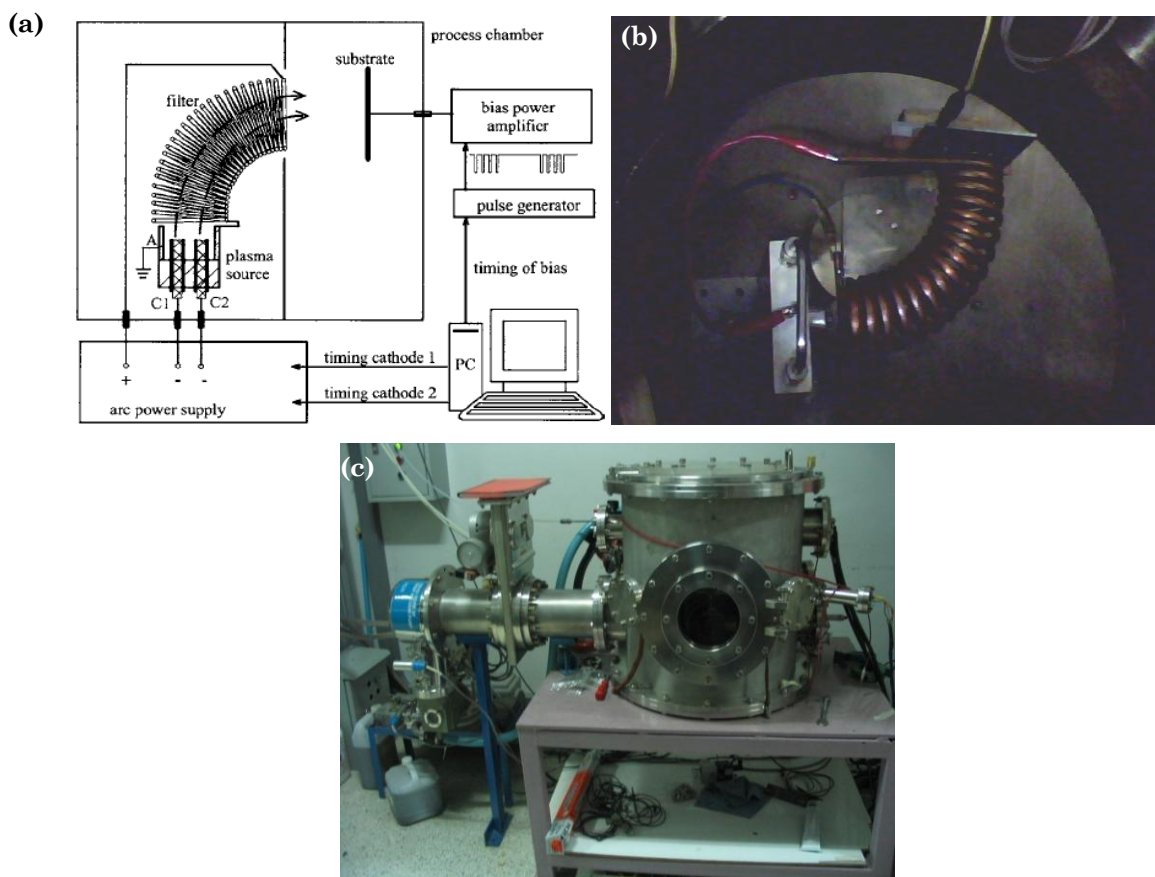
Fig. 1 – The filtered cathodic vacuum arc plasma system at Chiang Mai University. (a) Schematic diagram of the system. (b) Photo of the arc source (lower-left), filter and sample stage (upper-right) inside the chamber. (c) Photo of the whole system appearance. The chamber diameter is 60 cm

3. RESULTS AND DISCUSSION

For the FCVAD-formed carbon films on the nafion membrane, the SEM images in Fig. 2 show the effect of increasing the helium pressure on the film morphology and also the estimate of the carbon grain size at the pressure of 5×10^{-5}, 5×10^{-1}, 5, and 50 Torr. It is clearly seen that there is a tendency for C clusters to coalesce as the He partial pressure increases. However, at the 50-Torr He pressure, the film becomes porous. The initial increase in the cluster size with increasing the helium pressure may be due to the enhanced interaction between the carbon atoms in the presence of the helium atoms as the He pressure partly reduces the kinetic energy of the C ions and also prevents them from diffusing away. This enhances the interaction between the C ions leading to cluster formation. The He atoms also impinge upon the carbon clusters and release their excess energy. This helps the surface mobility of the small clusters, and with the addition of more carbon atoms, they coalesce to form bigger clusters. As the He pressure controlled to be 50 Torr, the C cluster size is seen starting from about 100 nm and the porosity seems as high as about one to one. Our energy dispersive x-ray spectroscopy (EDS) confirmed the films to be carbon dominant (result not shown).

In order to investigate the pulse number effect on the film structure, the number of the pulses was varied but using a low pressure of 2×10^{-5} Torr, without He inlet, to deposit C films on Si. Fig. 3 shows the AFM images of the film topography as a function of the total number of pulses. It was found that the low number of pulses was possibly able to produce nanorods or nanoislands on the carbon film. There have been many reports on producing carbon nanorods or nanofibers using various techniques including arc discharge [7], but not yet using FCVAD (for the authors' best knowledge). Our finding provides a hint to control the CVAD conditions, particularly the number of pulse, to produce nanostructured carbon film surface.

For the hybrid C-Mo thin films, figure 4 shows that carbon and molidinum particles can mix well together on the substrate. Section analysis found that the carbon particle size was about 39 nm and molybdenum particle size about 13 nm. Similar to the deposition of C films, the hybrid films also showed pulse-number dependent surface structure. As shown in figure 5, when the number of pulses was controlled appropriately low, abundant number of nanorods or nanoislands could be formed. It should be noted that the nanorods or nanoislands are singly elemental though the film is hybrid. This is understandable because the same elemental atoms are certainly intimate to their own species and thus easier to build nanostructure of their own species. The electrical properties of the FCVAD-formed hybrid C-Mo film have been studied [8] to provide hints for further depositing C-Pt hybrid films which would be the final goal of the study.
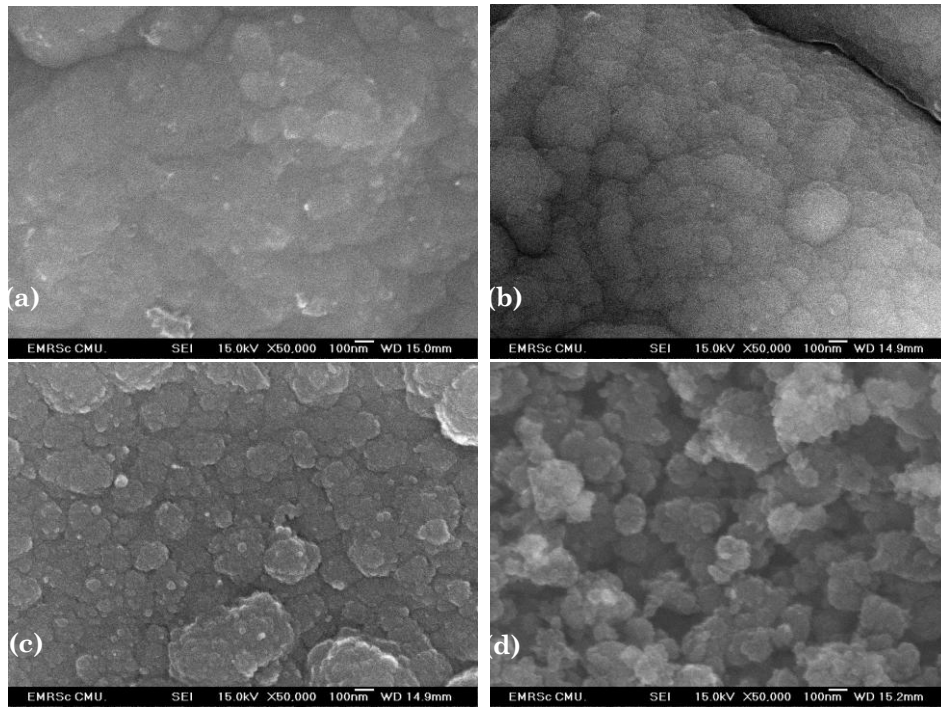
Fig. 2 – SEM images of the top view of the FCVAD-formed carbon films with the deposition conditions of 20-min deposition time and 450-V arc voltage. (a) $P = 5 \times 10^{-5}$ Torr, without He inlet. (b) $P = 5 \times 10^{-1}$ Torr, (c) $P = 5$ Torr and (d) $P = 50$ Torr, with He inlets
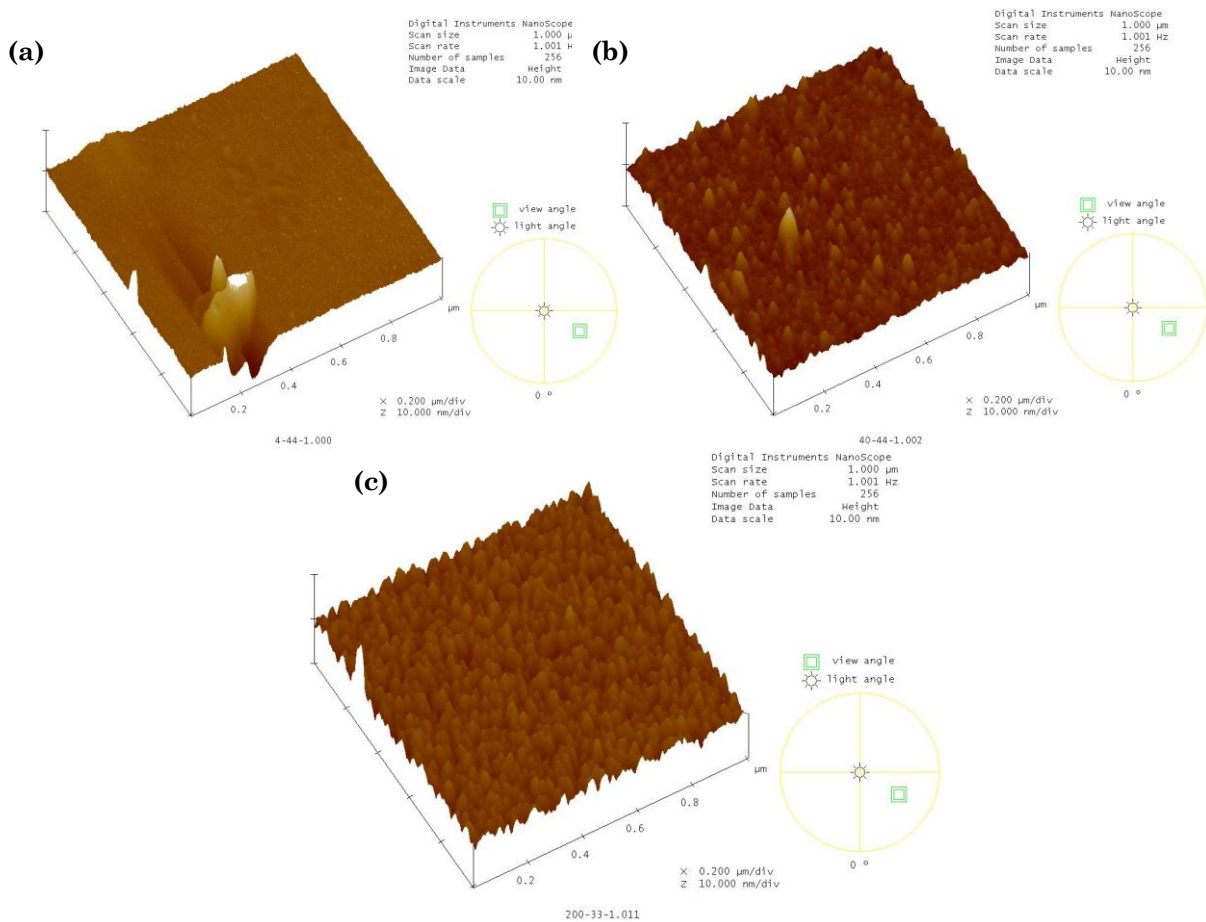
Fig. 3 – AFM images of the topography of FCVAD-formed carbon film as a function of the number of pulse. (a) 4 pulses, (b) 40 pulses, and (c) 200 pulses

Table 1 – Contact angle measurement result

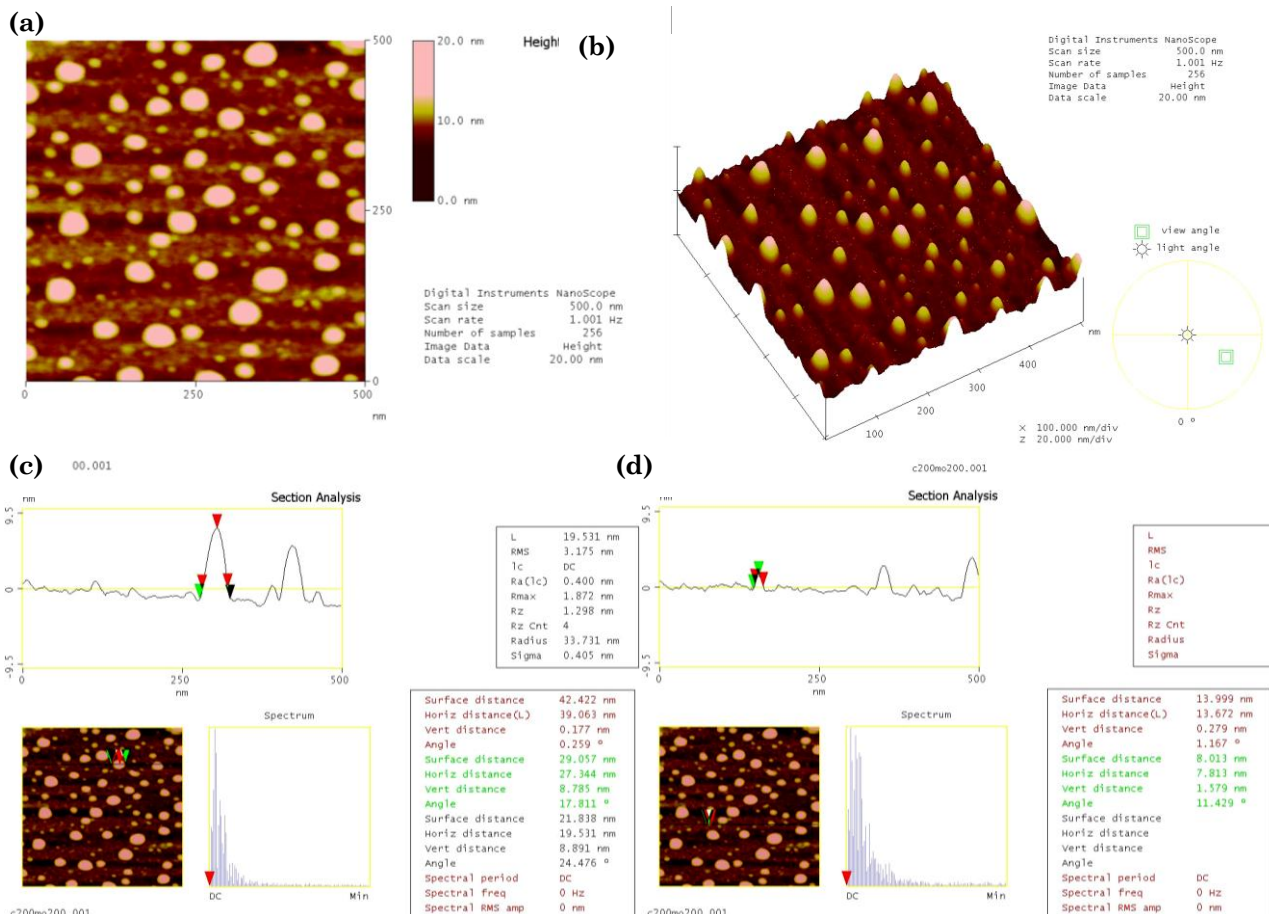| Pressure (Torr)	Contact angle (degree)
Nafion membrane blank	90.0
5×10^{-5}	66.4
5×10^{-1}	50.8
5	45.8
50	17.3

Fig. 4 – AFM images of C-Mo thin films (C = 200 pluses and Mo = 200 pluses, 300 arc volt). (a) Morphology scan size 500 nm, (b) Cross section scan size 500 nm, (c) Carbon size analysis and (d) Molidinum size analysis.
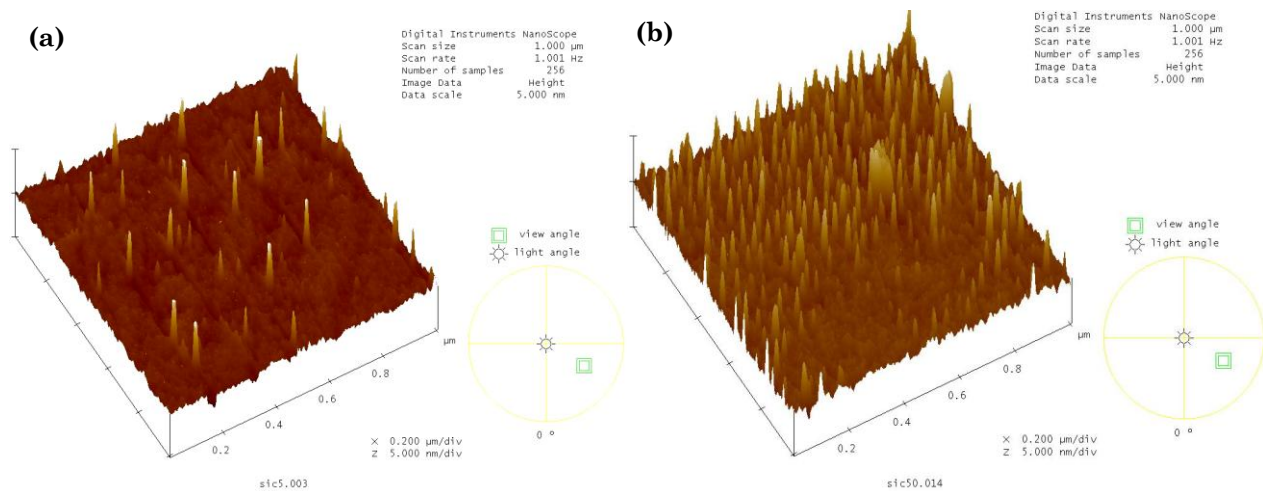

Fig. 5 – AFM images of hybrid C-Mo films CVAD deposited with (a) 5 pulses and (b) 50 pulses

4. CONCLUSION

The FCVAD conditions have critical effects on deposited carbon and hybrid C-Mo films. The He pressure plays a role in determining porosity of the C film, the higher pressure the more the porous. The number of pulses affects the surface structure of the films. Generally, an appropriately controlled low number of pulses can produce nanorods or nanoislands of C and C-Mo films. Either high porosity or nanostructure of the film can greatly increase the interaction area between the catalyst and the hydrogen and hence benefit enhancing the fuel cell performance.

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