



Short communication

Platinum-sputtered electrode based on blend of carbon nanotubes and carbon black for polymer electrolyte fuel cell

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ABSTRACT

A novel Pt-sputtered electrode based on a blend layer of carbon black (CB) and carbon nanotubes (CNTs) is developed for polymer electrolyte fuel cells. The Pt is sputtered on the surface of the blend to form a catalyst layer. The CNTs generate a pore in the blend layer, and the CB provides a high surface roughness for the blend layer. At a CNT content of 50 wt.%, the maximum value ($20.6 \text{ m}^2 \text{ g}^{-1}$) for the electrochemical area of the Pt is obtained, which indicates that the surface area of the blend layer exposed for Pt deposition is the largest. The power density of a membrane-electrode assembly (MEA) employing the Pt-sputtered electrodes shows a linear increase with electrochemical area. The mass activity of the optimized Pt-sputtered electrode with a Pt loading of 0.05 mg cm^{-2} is 8.1 times that of an electrode with a Pt loading of 0.5 mg cm^{-2} prepared using a conventional screen-printing technique. Excellent mass transfer is obtained with the Pt-sputtered electrode.

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1. Introduction

For nearly a decade, many workers have examined the sputter deposition technique as a means to reduce the costs of membrane electrode assemblies (MEAs) by achieving ultra-low levels of catalyst loading [1–11]. Fuel-cell catalysts such as Pt and PtRu have been sputtered on the surfaces of membranes [1,2] or those of carbon layers [3–9]. A unique feature of the direct sputtering technique is that the catalyst deposit is highly localized directly at the membrane|electrode interface. This results in extremely high catalyst utilization, which to a certain extent compensates for the ultra-low loading level. Nevertheless, the maximum power density attainable is still far lower than that obtained from a conventional electrode because the total surface area of the deposited catalyst in the interfacial reaction zone is smaller. An increase in catalyst loading does not lead to an extension of the reaction zone due to limited catalyst penetration through the substrate [3]. According to Caillard et al. [6], the penetration depth of Pt deposited on a commercial carbon layer based on carbon black is a few hundred nanometers. Recently, sputtering of Pt on CNTs directly grown on a carbon cloth diffusion layer has been reported [10]; compared with pristine carbon cloth, the CNT-grown carbon cloth exhibited an enlarged Pt surface, which indicated that the extension of the surface area of the carbon substrate was effective for attaining a large Pt surface. Wan

et al. [11] prepared a catalyst-layer structure composed of multi two-dimensional active layers by alternatively depositing a Pt layer by means of sputter deposition on a Nafion-carbon layer to increase the active area of the Pt deposit.

In order to expand the two-dimensional thin film structure of the sputter Pt catalyst layer to a three-dimensional reaction zone, a carbon substrate with high surface roughness and high porosity is suggested. The conventional carbon layer based on spherical carbon black (CB) [3–9] forms a dense but rough surface, and two-dimensional Pt deposit is formed only on the top surface of the carbon layer, as illustrated schematically in Fig. 1(a). By contrast, a carbon layer based on carbon nanotubes (CNTs) with a filamentous structure would exhibit a porous morphology and provide increased Pt penetration (see Fig. 1(b)). The main proposal of this study is that a large surface area of the Pt deposit is achieved by blending a spherical CB and a filamentous CNT. If CB partially fills the pores generated by the CNTs, the surface roughness could be enhanced while still maintaining an appropriate porosity for increased Pt penetration through the carbon substrate (see Fig. 1(c)). A three-dimensional catalyst layer with increased surface roughness and increased penetration depth could result in an increased Pt surface.

In this work, the morphology of the carbon substrate was changed by varying the blend ratio of Vulcan XC-72 and multi-wall carbon nanotubes. Vulcan XC-72, a kind of carbon black, is currently the most widely used carbon material for the preparation of supported catalysts. This is because it contains a smaller number of micropores and a large surface area sufficient to accom-

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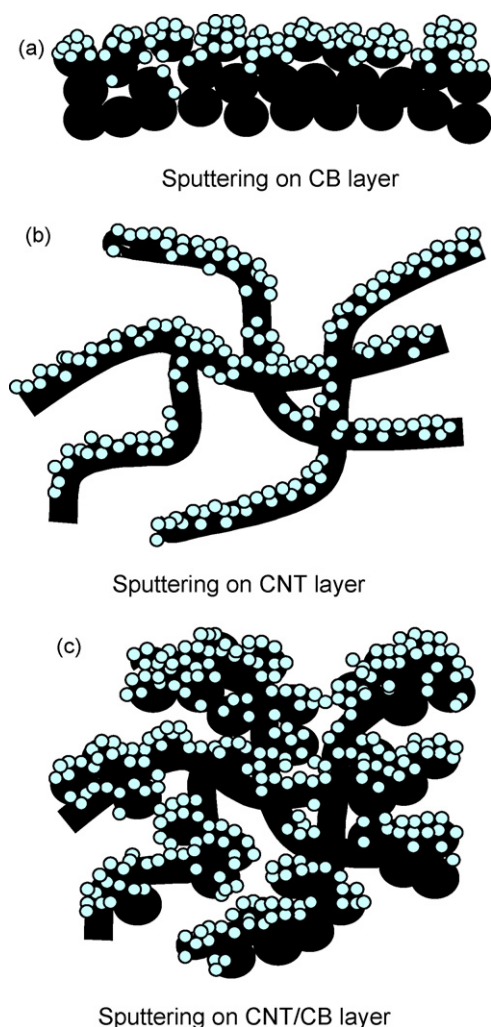


Fig. 1. Schematic illustration of Pt-sputtered electrodes based on: (a) carbon black; (b) carbon nanotubes; (c) a blend of carbon black and carbon nanotubes.

moderate a high loading of the metal phase [12]. The diameter and surface area of Vulcan XC-72 are several tens of nanometers and approximately $250 \text{ m}^2 \text{ g}^{-1}$, respectively. The multiwall carbon nanotubes employed in this work have an outer diameter of 40–60 nm, an inner diameter of 10–30 nm, and a length of $20 \mu\text{m}$. Platinum is sputtered on the blended carbon layers with a Pt loading of 0.05 mg cm^{-2} . The electrochemical area of the Pt deposit and the power performance of the corresponding MEAs are measured. A trial is performed to investigate the correlation between the electrochemical area and the power performance. In addition, a Pt-sputtered electrode based on the optimized binary carbon blend is compared with that based on a 0.5 mg cm^{-2} Pt/C catalyst layer prepared via a conventional screen-printing method.

2. Experimental

2.1. Preparation of CNT/CB layer

Multiwall carbon nanotubes (Power Hollow CNT50, NanoKarbon) and carbon black (Vulcan X-72, Carbot) were used as received. The mixture of CNTs and CB (1 g) was added to isopropyl alcohol (20 g) and homogenized by sonication at 60°C for 5 h, followed by the addition of an appropriate amount of Nafion solution (5 wt.%, DuPont). The weight ratio of Nafion to carbon was maintained at 0.33, irrespective of the blend ratio of CNTs and CB. The ink

was sprayed on a diffusion layer (31BC, SGL) and dried at 80°C for 3 h. The carbon loading was controlled at 0.2 mg cm^{-2} . The carbon-layer-coated diffusion layer was immersed in 20 wt.% HNO_3 aqueous solution for 1 h under sonication to remove any metallic impurities included in the CNTs that could harm fuel-cell performance. Morphological characterization of the carbon layer was performed by means of scanning electron microscopy (SEM) with a JEOL JSM-6700F microscope.

2.2. Preparation and electrochemical characterization of Pt-sputtered electrodes

The Pt was deposited on the carbon substrate at room temperature by using a RF-magnetron sputtering system. Before the carbon substrate was inserted into the sputter chamber, it was gently flushed with pure nitrogen. The distance between the target and the substrate was 5.0 cm. The sputtering deposition system consists of a stainless-steel chamber, which was evacuated down to $5 \times 10^{-5} \text{ Pa}$ with a turbomolecular pump backed up by a rotary pump. Before the deposition, the Pt target (purity 99.95%) was sputtered cleaned in pure Ar. The deposition rate was controlled at $0.005 \text{ mg min}^{-1}$ for a flat substrate irrespective of the carbon substrate.

Cycling voltammetry (CV) was carried out to determine the electrochemical area (ECA) of the catalyst. The active platinum surface was obtained by measuring the charges required for hydrogen desorption from the platinum surface after subtraction of the electrochemical double-layer current density. Details of the procedure for the measurement can be found elsewhere [2]. For each composition, three samples were evaluated.

In order to quantify the gap in power performance between the Pt-sputtered electrode based on the CNT/CB blend layer and that based on conventional coating technology, an electrode employing a commercial supported catalyst (Pt/XC-72, 20 wt.% Pt) and a commercial diffusion layer (31BC, SGL) was prepared by screen-printing. The Pt and Nafion loadings were 0.5 and 1.4 mg cm^{-2} , respectively. The value for the Nafion loading was selected from an empirical equation which determined the optimum Nafion loading suggested by Antolini et al. [13].

2.3. MEA preparation and performance measurements

Two sheets of the Pt-sputtered electrode, each of size 5 cm^2 were placed on either sides of a Nafion 112 membrane. The stack was pressed at 130°C at 70 MPa for 10 min to provide interfacial bonding between the membrane and the electrode.

Polarization curves were recorded at 60°C using a MEA test station (WonATech). The MEAs were sandwiched between anode and cathode monopolar plates with triple serpentine flow channels. Fully humidified air and hydrogen were injected into the cathode and anode compartments, respectively. The stoichiometry of the feed was 3.0 for the cathode and 1.2 for the anode. For each electrode, three MEAs were evaluated.

3. Results and discussion

Scanning electron microscopy (SEM) images of the surfaces of the CNT/CB layers are shown in Fig. 2(a–e). As expected, the CB layer shows relatively dense and rough morphology (Fig. 2(a)). The CNT layer (Fig. 2(e)) has a highly porous morphology due to the sparse packing of the CNTs, and the CNT buried into the inside of the carbon layer can be seen from the top through the pores, which suggest that Pt could be deposited even on the inside of the CNT layer. With the addition of CNTs to the CB layer, porosity appears to increase. After Pt sputtering on the carbon layers with a loading of 0.05 mg cm^{-2} , the layers turned from black to dark grey. The SEM image of the

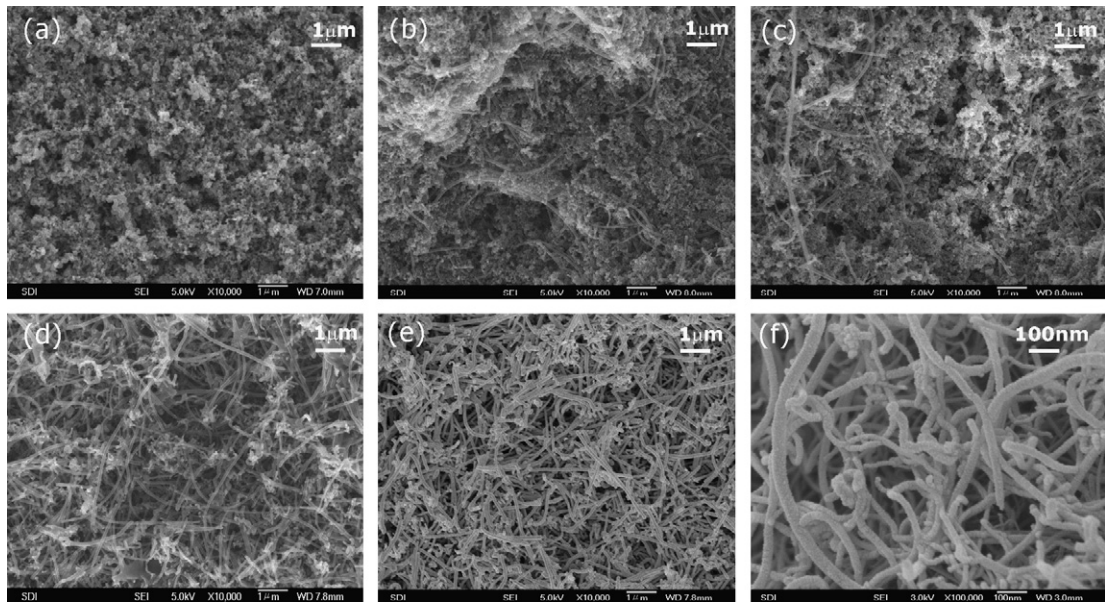


Fig. 2. Scanning electron micrographs of the surface of carbon layers (CNT content: (a) 0 wt.%, (b) 16.7 wt.%, (c) 33.3 wt.%, (d) 50 wt.%, and (e) 100 wt.%) and of (f) Pt-sputtered carbon layer (CNT content of 100 wt.%).

Pt-sputtered CNT layer is shown in Fig. 2(f). Apparently, the morphology of the Pt-sputtered CNT layer does not differ from that of the pristine CNT layer. This is understandable given the thickness of the Pt deposit. The Pt loading of 0.05 mg cm^{-2} corresponds to Pt film thickness of 23.3 nm for a completely flat substrate. Considering the roughness of the carbon layers, the Pt film thickness would be much lower than 23.3 nm.

The change in ECA (determined by the hydrogen desorption technique) with CNT content is presented in Fig. 3. The ECA of the CNT layer ($16.1 \text{ m}^2 \text{ g}^{-1}$) is 1.8 times that of the CB layer ($9.1 \text{ m}^2 \text{ g}^{-1}$), which demonstrates the importance of a three-dimensional pore structure for enlarging the Pt surface. A synergy is found between the blend of CNTs and CB; the maximum value for the ECA ($20.6 \text{ m}^2 \text{ g}^{-1}$) is observed at an intermediate composition (CNT content of 50 wt.%). It is much higher than the previously reported values for a commercial diffusion layer ($2.8\text{--}7.5 \text{ m}^2 \text{ g}^{-1}$) [3]. At a content of 50 wt.%, as can be seen in Fig. 2(d), the CNTs form a porous frame and CB increases the surface roughness by structuring agglomerates that do not block the pores generated by the CNTs.

It is evident that the three-dimensional pore structure with an increased roughness can enhance the surface area of the Pt deposit. Assuming that the Pt deposit is uniform in thickness, the thickness can be simply calculated by dividing the ECA by the Pt loading. It is 5.1, 2.3, and 2.9 nm for CNT contents of 0, 50 and 100 wt.%, respectively.

Fig. 4 shows the power densities measured at 0.6 and 0.4 V for MEAs employing the Pt-sputtered electrodes as a function of ECA. The power density increases linearly with ECA at both 0.6 and 0.4 V. This confirms that ECA is the decisive factor for the power performance of the Pt-sputtered electrodes. At the low cell voltage of 0.4 V, where the mass-transport overpotential generally dominates the reaction, ECA governs the power performance, i.e., the mass-transport limitation is insignificant for the electrodes.

As mentioned above, the drawback of the Pt-sputtered electrode is the lower power performance compared with a conventional electrode based on a carbon-supported electrocatalyst prepared by slurry-coating such as the screen-printing method. A comparison of the $I\text{--}V$ polarization for the optimized sputtered electrode

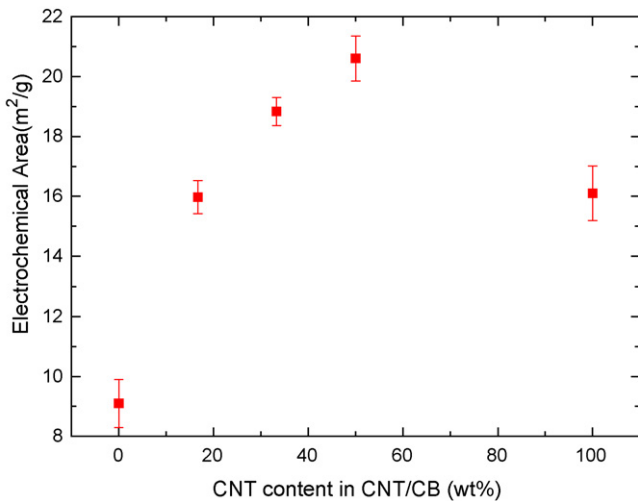


Fig. 3. Plot of ECA as function of CNT content for Pt-sputtered electrodes.

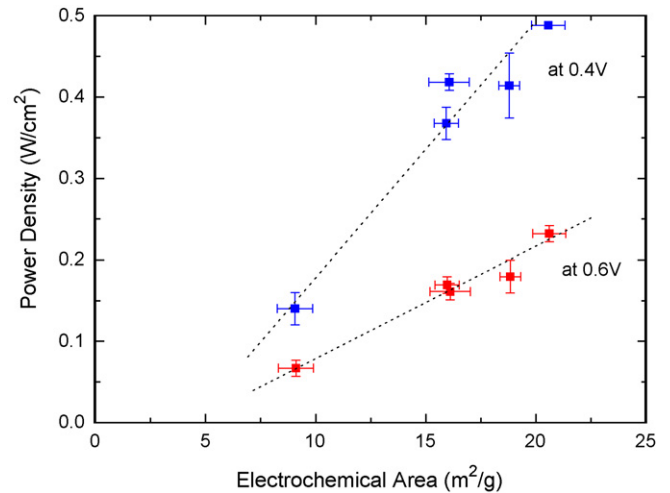


Fig. 4. Plot of power densities at 0.6 and 0.4 V as function of ECA of Pt-sputtered electrode.

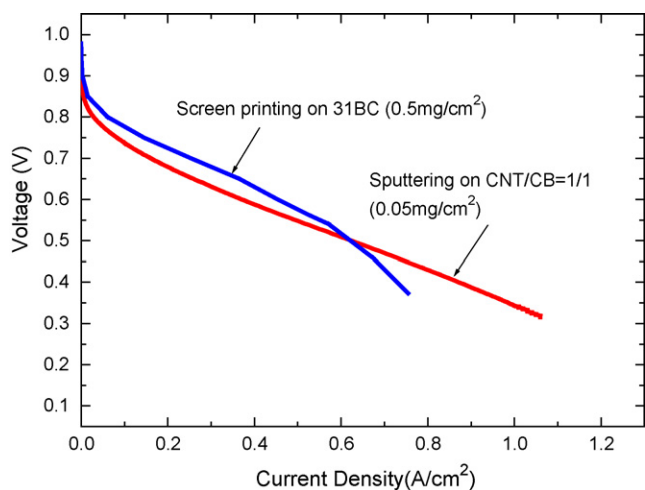


Fig. 5. Comparison of I - V polarization of Pt-sputtered electrode (CNT content of 50 wt.%) with Pt loading of 0.05 mg cm^{-2} and screen-printed electrode with Pt loading of 0.5 mg cm^{-2} .

(CNT content of 50 wt.%) and the screen-printed electrode is given in Fig. 5. The screen-printed electrode has a higher power density than the sputtered electrode. At 0.6 V, the power density of the sputtered electrode is 82% of that of the screen-printed electrode. Given that the screen-printed electrode has a ten times higher Pt loading than that of the sputtered electrode, a much higher Pt utilization is assured. A specific power density of $2.22 \text{ kW g}_{\text{Pt}}^{-1}$ is obtained at 0.6 V for the sputtered electrode. This is in contrast to the screen-printed electrode for which the specific power density at 0.6 V is $0.27 \text{ kW g}_{\text{Pt}}^{-1}$.

In the low-voltage regime ($<0.5 \text{ V}$), the sputtered electrode shows higher power density than the screen-printed electrode. For the sputtered electrode, the voltage drop due to mass-transport limitations is not as significant as for the screen-printed electrode. A thinner catalyst layer is believed to be associated with less mass-transport loss. From this result, it is expected that the sputtered electrode would be useful for an air-breathing fuel cell for which excellent mass transport is required.

On the basis of the above results, it can be concluded that morphological control of the carbon layer is an effective means to increase the surface area of the Pt deposit for a Pt-sputtered electrode. The Pt-sputtered electrode exhibits excellent mass-transport characteristics and high mass activity. Further increase in the electrochemical area using an advanced three-dimensional structure of the carbon layer remains a challenge.

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