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# Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes

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## ABSTRACT

The use of multiwalled carbon nanotubes as a platinum support for proton exchange membrane fuel cells has been investigated as a way to reduce the cost of fuel cells through an increased utilization of platinum. Carbon nanotubes were selectively grown directly on the carbon paper by chemical vapor deposition with electrodeposited cobalt catalyzing the growth of the carbon nanotubes. The as-prepared carbon nanotubes were employed as the support for the subsequent platinum catalyst, which is electrodeposited on the carbon nanotubes. Physicochemical and electrochemical characterizations were conducted to identify the morphologies of the cobalt, the carbon nanotubes, and the electrodeposited platinum on the carbon nanotubes. The feasibility of a fuel cell using the carbon nanotube-based electrodes was demonstrated.

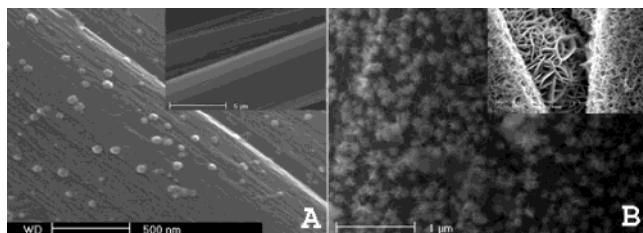
As a potential candidate for an environmentally benign and a highly efficient electric power generation technology, proton exchange membrane fuel cells (PEMFC) are now attracting enormous interest for various applications such as low/zero-emission vehicles, distributed home power generators, and power sources for small portable electronics.<sup>1–4</sup> One of the challenges in the commercialization of PEMFCs is the high cost of noble metals used as catalyst (e.g., Pt). Decreasing the amount of Pt used in a PEMFC via the increase of the utilization efficiency of Pt has been one of the major concerns during the past decade.<sup>5</sup> To effectively utilize the Pt catalyst, the Pt must have simultaneous access to the gas, the electron-conducting medium, and the proton-conducting medium. In the catalyst layer of a Pt-based conventional fuel cell prepared by the ink-process, the simultaneous access of the Pt particle by the electron-conducting medium and the proton-conducting medium is achieved via a skillful blending of Pt-supporting carbon particles and Nafion. The carbon particles conduct electrons and the Nafion conduct protons. However, even with the most advanced conventional electrodes, there is still a significant portion of Pt that is isolated from the external circuit and/or the PEM, resulting in a low Pt utilization. For example, Pt utilization in current commercially offered prototype fuel cells remains very low (20–30%), although higher utilization has been achieved in laboratory devices. Efforts directed at improving the utilization efficiency of the

Pt catalyst have focused on finding the optimum material configurations while minimizing the Pt loading and satisfying the requirements of gas access, proton access, and electronic continuity. In the conventional ink-process, a common problem has been that the necessary addition of Nafion for proton transport tends to isolate carbon particles in the catalyst layer, leading to poor electron transport.

Due to their unique structural, mechanical, and electrical properties, carbon nanotubes have been recently proposed to replace traditional carbon powders in PEMFCs and have been demonstrated by making membrane electrode assemblies (MEA) using a carbon nanotube powder through a conventional ink process.<sup>6–8</sup> However, these results did not show many advantages over carbon black (Vulcan XC-72) because the Pt utilization within the PEMFC catalyst layer remained unaddressed. Growing carbon nanotube arrays directly on the carbon paper and then subsequently electrodepositing the Pt selectively on the carbon nanotubes promises to improve the Pt utilization by securing the electronic route from Pt to the supporting electrode in a PEMFC. The use of carbon nanotubes and the resulting guaranteed electronic pathway eliminate the previously mentioned problem with conventional PEMFC strategies where the Nafion would isolate the carbon particles from the electrode support. Eliminating the isolation of the carbon particles from the electrode support would thereby improve the utilization rate of Pt.

Generally, there are two categories of carbon nanotubes: single-walled nanotubes (SWNTs) and multiwalled nanotubes

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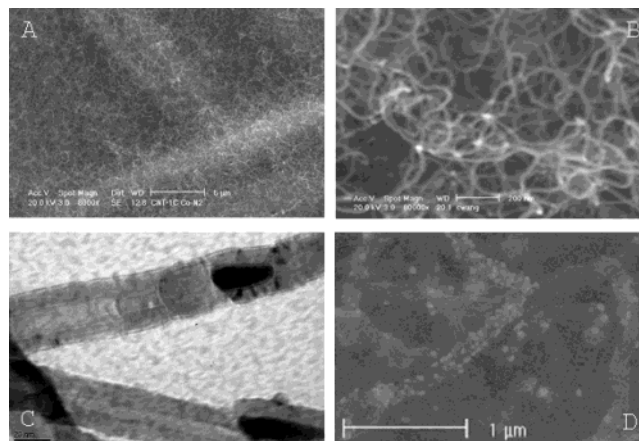


**Figure 1.** SEM micrographs of carbon paper after electrodeposition of Co: (A) with 0.26 mg/cm<sup>2</sup> Co (inset is bare carbon paper) and (B) with 4 mg/cm<sup>2</sup> Co (inset is 20 mg/cm<sup>2</sup> Co).

(MWNTs). A SWNT is a single graphene sheet rolled into a cylinder. A MWNT consists of several coaxially arranged graphene sheets rolled into a cylinder. According to theoretical predictions, SWNTs can be either metallic or semiconducting depending on the tube diameter and helicity.<sup>9</sup> The band gap is proportional to the reciprocal diameter,  $1/d$ .<sup>10</sup> For MWNTs, scanning tunneling spectroscopy (STS) measurements indicate that the conduction is mainly due to the outer shell,<sup>11</sup> which are usually much larger than SWNTs. Therefore, MWNTs should have a relatively high electrical conductivity. In this paper, we will focus on MWNTs as a support for the Pt catalyst in PEMFCs because of their relatively high electrical conductivity and because current growth methods for MWNTs are simpler than those for SWNTs.

Earlier attempts to deposit MWNTs on carbon paper were conducted by S. Désilets and his group,<sup>12,13</sup> who dipped carbon paper in a solution containing silica and group VIII metal salts and used this silica gel on carbon paper to catalyze the growth of the MWNTs on the carbon paper by an ohmic heating process. Although MWNTs are firmly attached on the carbon paper, electrical contact between the MWNTs and the carbon paper could be hindered by the existence of silica. Our group is currently working on fuel cells that use MWNTs as a Pt catalyst support by directly growing MWNTs on carbon paper through a chemical vapor deposition (CVD) process using electrodeposited Co as the catalyst for MWNT growth and subsequently depositing Pt catalyst selectively on these MWNTs. This nonink process ensures that all of the electrodeposited Pt catalyst particles are electronically accessible to the external circuit of a PEMFC.

The Co catalyst for MWNT growth is electrodeposited on one side of the carbon paper by a three-electrode dc method in a 5 wt. % CoSO<sub>4</sub> and 2 wt. % H<sub>3</sub>BO<sub>3</sub> solution at 20 °C.<sup>14</sup> The deposition potential used was −1.2 V vs SCE (saturated calomel electrode, Aldrich) and the loading was controlled by the total charge applied. Figure 1 shows the SEM (Philips XL30-FEG) images of the carbon paper with and without electrodeposited Co. The carbon paper is made of fibers having a diameter between 5 and 10 µm and the surface of the carbon fiber is clean before deposition (inset in Figure 1A). The contact angles for carbon paper by double-distilled water are around 104.5°, as determined from the hydrophobic test (VCA-Optima). This hydrophobic property enables the selective deposition of Co on the side of the carbon paper facing the electrolyte solution, which also makes it possible for selective growth of MWNTs on

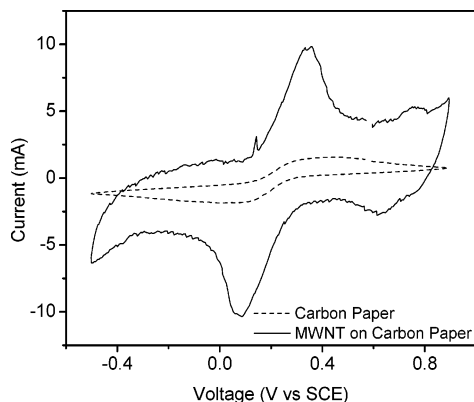


**Figure 2.** SEM and TEM micrographs of MWNTs grown by 0.26 mg/cm<sup>2</sup> Co loading on carbon paper: (A) SEM with low magnification showing high coverage of MWNTs on carbon paper; (B) SEM with higher magnification showing the diameter of the MWNTs and presence of Co catalyst particles; (C) TEM of MWNTs; (D) SEM of Pt particles electrodeposited on MWNTs.

one side of carbon paper. This is also necessary for fuel cell applications because further selective deposition of Pt catalyst becomes feasible. After applying 2 coulombs charge on 2.55 cm<sup>2</sup> circular carbon paper for depositing cobalt, which equals 0.26 mg/cm<sup>2</sup> of Co loading assuming 100% yield of the electrodeposition, nanocrystalline Co could be found on the surface of carbon fibers (Figure 1A). The particle size is in the range of 20 to 50 nm. With the increase of Co loading, the particle size increases. We observed dendrimetric nanocrystalline Co (Figure 1B) when the loading was 4 mg/cm<sup>2</sup>. Further increases in loading, for example to 20 mg/cm<sup>2</sup> as shown in the inset of Figure 1B, made it possible to cover and connect the carbon fibers on the whole surface of carbon paper by a porous Co structure.

An important aspect of the MWNTs is the high surface area for subsequent Pt deposition. Considering the fact that small catalyst particles are beneficial for the growth of MWNTs with small diameters (therefore high surface area), a loading of 0.26 mg/cm<sup>2</sup> Co on carbon paper was employed in all of the subsequent experiments. For the MWNT growth, CVD was employed due to its suitable growth temperature and ease to scale-up.<sup>15</sup> The MWNTs were grown with a procedure described elsewhere<sup>16</sup> with slight modifications. Carbon paper with Co electrodeposited on one side of the paper was placed in a furnace at ambient pressure and heated to 550 °C in 3 h under a 150 sccm N<sub>2</sub> flow and 7.5 sccm H<sub>2</sub> flow. These conditions were maintained for 30 min. The temperature was then raised to 700 °C over a 30 min time interval. Upon reaching 700 °C, acetylene was introduced at 7.5 sccm for 1 h to facilitate MWNT growth. Finally, the acetylene and H<sub>2</sub> flow was cut off and the furnace cooled to room temperature under 150 sccm N<sub>2</sub>.

Figure 2 presents the SEM and TEM pictures of the resulting MWNTs after CVD growth using a 0.26 mg/cm<sup>2</sup> Co loading. As shown in Figure 2A, a thin layer of MWNTs covers the carbon paper. The as-prepared MWNTs are wavy with lengths in the micrometer range and diameters in the range of 20 to 40 nm (Figure 2B). Some bright particles on



**Figure 3.** Cyclic voltammetry in a  $\text{K}_3\text{Fe}(\text{CN})_6$  solution (5 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  + 0.5 M  $\text{K}_2\text{SO}_4$ ) of: (1) 3.46  $\text{cm}^2$  of carbon paper alone; (2) MWNTs grown by 0.26  $\text{mg}/\text{cm}^2$  Co loading covering the same 3.46  $\text{cm}^2$  carbon paper. Scan rate: 50  $\text{mV}/\text{s}$ .

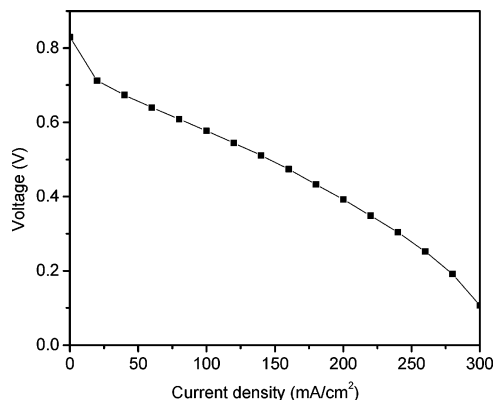
MWNTs can also be observed from Figure 2B, which were identified as Co under electron diffraction X-ray spectroscopy (EDX). The TEM (Philips CM300) image in Figure 2C shows two MWNTs with outer shell diameters of 30 and 40 nm along with some metal particles present in the inner cavity of the MWNTs. The inner diameters of the MWNTs are about 10 nm.

To obtain a high yield of MWNTs on carbon paper to serve as the Pt catalyst support for fuel cell applications, a higher Co loading and repetition of both Co electrodeposition and subsequent CVD carbon nanotube growth was attempted. However, a higher loading of Co on the substrate caused an increase of Co particle size, and the diameter distribution of MWNTs becomes broader, such as 20–130 nm. Also, repetitions of electrodeposition and CVD carbon nanotube growth resulted in amorphous carbon generation.

Following the CVD growth of the MWNTs, Pt was electrodeposited on the MWNTs by a three-electrode dc method in 5 mM  $\text{H}_2\text{PtCl}_6$  and 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution.<sup>17</sup> The deposition potential used was 0 V vs SCE and the loading of Pt was controlled by the total charge applied. Figure 2D shows the SEM image of the Pt electrodeposited on the MWNTs with 0.2  $\text{mg}/\text{cm}^2$  Pt loading. The average diameter of these particles is about 25 nm. The successful deposition of Pt indicates a good electrical contact between the MWNTs and the substrate.

The surface area of the MWNT-carbon paper composite electrode is determined to be in the range between 80 and 140  $\text{m}^2/\text{g}$  from nitrogen adsorption by the Brunauer–Emmett–Teller method (Micromeritics ASAP 2010), while that of carbon paper alone is less than 2  $\text{m}^2/\text{g}$ . This is consistent with what we have obtained from cyclic voltammetry (CV) measurements in potassium ferricyanide (III) solution (Figure 3) where the redox current is much higher for the MWNT-carbon paper composite, further indicating that MWNTs are electrically connected to the carbon paper substrate.

One of the major concerns for the application of MWNTs in PEMFCs is to ensure the strong adhesion of these MWNTs to the carbon paper so that it will remain on the surface of carbon paper during the subsequent procedures for Pt



**Figure 4.** Polarization curve of a MEA prepared by electrodeposition of Pt on MWNTs grown by 0.26  $\text{mg}/\text{cm}^2$  Co loading. Pt loading on both electrodes: 0.2  $\text{mg}/\text{cm}^2$ . Membrane: Nafion 115. Operating conditions: cell temperature, 70  $^\circ\text{C}$ ; humidifier temperature, 80  $^\circ\text{C}$ ; pressure, 2 atm.

deposition and MEA preparation. To test this, we submerged the MWNT-carbon paper composite electrode into 50 mL of double-distilled water and ultrasonicated. After an hour of sonication, there were no discernible black particles in the solution, suggesting a strong adhesion between MWNT and carbon paper.

An MEA was prepared using two MWNT-carbon paper composite electrodes by first immersing the two electrodes into 5 wt% commercial Nafion solution for 30 min and subsequent hot pressing (135  $^\circ\text{C}$ , 140 atm, 3 min) these two electrodes with a Nafion 115 membrane between the two electrodes. The MWNTs were grown using a 0.26  $\text{mg}/\text{cm}^2$  Co loading. The performance (Figure 4) of this MEA was tested using a fuel cell test station (ElectroChem. Inc.). Although the performance of the CNT based fuel cell is still lower than that of the conventional PEMFC with comparable Pt loading, the feasibility of our design involving electrodeposition of catalyst for MWNT growth directly on the carbon paper and subsequent electrodeposition of Pt on the MWNTs is demonstrated. It is recognized that the Pt particle size by electrodeposition is rather large at present time (25 nm versus 2–3 nm of commercial Pt/C catalyst), and this is believed to be the major reason for the low performance of our current MEA. It is expected that once the Pt particle size is reduced (e.g., 2.5 nm) and the yield of the MWNTs is increased and their diameter is reduced, the carbon nanotube-based fuel cell will show superior performance. Work on the optimization of the MWNT loading and nanotube dimensions, as well as on the decrease of Pt particle size, is under way in order to ultimately achieve a high performance PEMFC.

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