

Pt–Ru Supported on Double-Walled Carbon Nanotubes as High-Performance Anode Catalysts for Direct Methanol Fuel Cells

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Pt–Ru supported on carbon nanotubes (CNTs) (single-walled nanotubes, double-walled nanotubes (DWNTs), and multi-walled nanotubes) catalysts are prepared by an ethylene glycol reduction method. Pt–Ru nanoparticles with a diameter of 2–3 nm and narrow particle size distributions are uniformly deposited onto the CNTs. A simple and fast filtration method followed by a hot-press film transfer is employed to prepare the anode catalyst layer on a Nafion membrane. The Pt–Ru/DWNTs catalyst shows the highest specific activity for methanol oxidation reaction in rotating disk electrode experiments and the highest performance as an anode catalyst in direct methanol fuel cell (DMFC) single cell tests. The DMFC single cell with Pt–Ru/DWNTs (50 wt %, 0.34 mg Pt–Ru/cm²) produces a 68% enhancement of power density, and at the same time, an 83% reduction of Pt–Ru electrode loading when compared to Pt–Ru/C (40 wt %, 2.0 mg Pt–Ru/cm²).

Introduction

Polymer electrolyte based low temperature fuel cells, with their two best known variants, direct hydrogen proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), have been considered promising for powering automobiles, homes, and portable electronics. Their successful commercialization is, however, very much dependent on the activity and durability of their electrocatalysts. At present, all pre-commercial low-temperature fuel cells use supported Pt and Pt alloys as their electrocatalysts. The critical properties to consider when choosing an electrocatalyst support include its electrical conductivity, surface area, macromorphology, microstructure, corrosion resistance, and cost. Carbon black (CB), such as Vulcan XC-72, has been the most widely used electrocatalyst support because of its reasonable balance among electronic conductivity, surface area, and cost.^{1–3} Recently, many nanostructured carbon materials with graphitic structure, such as nanotubes (CNTs),^{4–11} nanofibers (CNFs),^{12,13} nano-coils,¹⁴ nanoarrays,¹⁵ and nanoporous hollow spheres,¹⁶ have been studied. Among them, CNTs are of particular interest due to their unique electronic and micro- and macrostructural characteristics.^{17–19} CNTs have also been shown to be more corrosion resistant than CB under simulated fuel cell operation conditions.²⁰

Among the two variants of low-temperature fuel cells, DMFCs have been attracting great attention for powering small devices, such as laptop computers, cell phones, and personal digital assistants, because of their high energy density, ease of handling liquid fuel, and low operating temperature.^{21–25} However, the slow electrokinetics of the anode reaction—methanol oxidation reaction (MOR)—is still a key problem to

the commercialization of DMFCs.²² Normally, expensive noble metal alloys, typically Pt–Ru, with a high electrode metal loading (e.g., >2.0 mg/cm²) are employed in order to offer a reasonable fuel cell performance (e.g., 80 mW/cm² at cell temperature of 90 °C and O₂ pressure of 2 atm).²⁴ It has long been desired to develop a high-performance anode catalyst so that the electrode metal loading and thus the cost of DMFCs can be reduced.

Some early investigations have found that, by simply replacing CB with CNTs in the conventional ink-paste electrode fabrication method, superior DMFC performance can be obtained. For example, a DMFC single cell with a cup-stacked CNT-supported Pt–Ru anode catalyst showed nearly 2 times the maximum power density at 90 °C of a DMFC with a CB-(Vulcan XC-72)-supported Pt–Ru anode catalyst, and it was suggested that CNTs can provide better charge and mass transfer.²⁶ Very recently, we developed a filtration method for preparing the catalyst layer that is much simpler and faster than the ink-paste method. This filtration method is similar to the so-called decal method in that the catalyst layer is transferred to the proton conductive membrane by hot pressing,²⁷ but it is also significantly different by being faster (e.g., seconds vs minutes) than spraying. It can also lead to a partially oriented catalyzed MWNT film. Higher PEMFC performance was achieved by the filtration method mainly due to improved Pt utilization and its superhydrophobicity.²⁸ Our results show that the electrode fabrication method is another important factor for obtaining a high fuel cell performance.

Despite the large number of studies carried out on CNTs as electrocatalytic supports for low-temperature fuel cells, all of the previous studies employed either single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). And, there has been no study that compares the performance of these two important types of CNTs. Furthermore, there has been no study on double-walled carbon nanotubes (DWNTs) as fuel cell catalyst supports. Here, we provide for the first time

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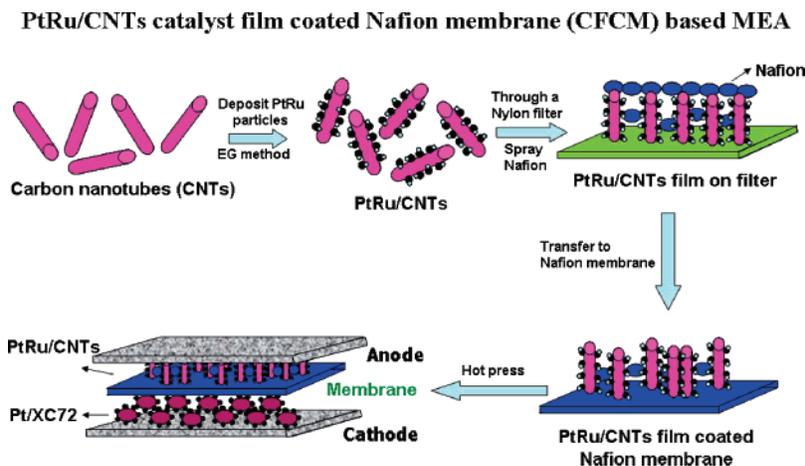


Figure 1. Schematic illustration of Pt–Ru/CNTs-film-based MEA for DMFC.

a systematic study of the three types of CNTs. Our motivation for studying these three types of CNTs, in particular the DWNTs, is as follows: SWNTs can have a large surface area (e.g., 500–1000 m²/g) due to their small diameter (e.g., 1 nm), which is a favorable property as catalysts support. However, they normally contain a significant amount (e.g., ²/₃) of semiconducting tubes, which are poor electron conductors and thus are expected to be a poor electrocatalytic support. We have argued previously that MWNTs are highly conducting but they have limited surface area (e.g., 100–200 m²/g) due to their large diameter (e.g., >40 nm).^{8,9,29} It was recently shown that most DWNTs are conducting tubes and that they can have high surface areas (e.g., 500–1000 m²/g).³⁰ Thus a natural and logical choice for an electrocatalyst support is DWNTs. In this study, we investigate the three different types of CNTs as anode catalytic supports for DMFCs, and show clearly that DWNTs produce remarkably higher DMFC performance than SWNTs, MWNTs, or CB.

Experimental Section

MWNTs were purchased from the MER Corp., which were produced by chemical vapor deposition (CVD). The MWNTs have a diameter of 80–120 nm and surface area of approximately 100 m²/g. The DWNTs were purchased from NANOCYL S.A. and also produced by CVD. The diameters of the DWNTs range from 1.5 to 2 nm (bundled at 4–10 nm), and their surface area is about 500 m²/g. The highly purified SWNTs were self-prepared by an arc-discharge method, and the bundled diameter is 4–10 nm, and their surface area is also about 500 m²/g. All the CNTs in the experiments were surface oxidized by a 4.0 N H₂SO₄–HNO₃ mixture for 6 h under refluxing condition.

Pt–Ru/CNTs catalysts were prepared by an ethylene glycol (EG) reduction method.⁵ The preparation method is briefly described below using MWNTs as a typical example. The surface-oxidized MWNTs (200 mg) were suspended in an EG solution and treated in an ultrasonic bath. Then an EG solution of hexachloroplatinic acid and ruthenium chloride was added dropwise under mechanically stirred conditions for 4 h. A solution of 1.0 M NaOH in EG was added to adjust the pH of the synthesis solution to above 13, and then the mixture was heated at 140 °C for 3 h to reduce the Pt–Ru completely. The entire EG solution has a DI water content of 5 vol %. A condenser was used in order to keep the water content constant in the synthesis system and the whole preparation process was

conducted under flowing argon. After filtration (Whatman, Grade 1), washing, and drying in vacuum at 80 °C for 8 h, the Pt–Ru/MWNTs catalyst was obtained. The filtrated solvent was clear with slight yellowish tone. The weight calculation showed the Pt–Ru conversion was nearly 100% during the deposition process, and thermogravimetric analysis of the finished catalysts shows the PtRu/DWNTs sample has about 49.7 Pt–Ru wt % loading, which is very close to the targeted 50 wt % catalyst loading. We prepared 30 wt % Pt–Ru/CNT catalyst for MWNTs, DWNTs, and SWNTs, and a 50 wt % Pt–Ru/DWNTs catalyst. The 40 wt % Pt–Ru/C catalyst was kindly provided by E-TEK and used as a control sample.

Pt–Ru/CNTs powders were characterized by X-ray diffraction (XRD) using Cu K α radiation with a Ni filter. The tube current was 40 mA with a tube voltage of 40 kV. The 2θ regions between 20 and 85° were explored at a scan rate of 5°/min. Transmission electron microscopy (TEM) was carried out on a PHILIPS CM300 operating at 300 kV. Scanning electron microscopy (SEM) was conducted on a PHILIPS XL30-FEG with an operating voltage of 10 or 15 kV.

The MOR activity of the Pt–Ru/CNTs catalyst was conducted in a rotating disk electrode (RDE) setup using an Ag/AgCl reference electrode, and a platinum wire counterelectrode. The RDE working electrode was prepared as follows. A mixture containing 7.6 mg of Pt–Ru/CNTs catalyst and 2.0 mL of ethanol was ultrasonically blended in a glass vessel for half an hour to obtain a homogeneous ink. Ink (20 μ L) was spread with a micropipet on the surface of a glassy carbon electrode (Pine Instrument, 5 mm in diameter) and dried for 10 min. Then 10 μ L Nafion solution (0.05 wt %) was dropped onto the surface of the thin catalytic layer. The cyclic voltammetry (CV) tests were obtained after nitrogen bubbling for 10 min. The electrolyte was 0.5 M H₂SO₄ solution for the PtRu electrochemical surface area test and 0.5 M CH₃OH + 0.5 M H₂SO₄ solution for methanol oxidation activity test. The scan range was from –0.3 to 0.8 V, and the scan rate was 50 mV/s.

For a DMFC membrane electrode assembly (MEA), both the anode and the cathode consist of a backing layer, a gas diffusion layer, and a catalyst layer. Teflonized (30 wt % Teflon in the cathode and 10 wt % in the anode) carbon papers (Toray Corp.) were employed as backing layers in these electrodes. Then an ethanol suspension with 20 wt % Teflon and 80 wt % Vulcan XC-72 was agitated in an ultrasonic water bath and spread on the cathode backing layer to prepare the cathode gas diffusion

layers. The anode diffusion layer was similarly prepared, but 20 wt % Nafion was used in place of 20 wt % Teflon.

For the anode catalyst layer fabrication, we used a modified filtration method to make a compact Pt–Ru/CNTs film. The schematic illustration of the fabrication process is described in Figure 1. A Pt–Ru/CNTs suspension in ethanol with known solid loading was drawn through a 0.2- μm -pore hydrophilic Nylon filter paper. To incorporate Nafion into the catalyst layer, the suspension was divided into 5 equal portions and the filtration was carried out 5 times. After each filtration, a 20 wt % Nafion solution was sprayed on the surface of the filtrated Pt–Ru/CNTs solid (1.0 mg Nafion / cm^2). Then the final deposited layer on the filter paper was transferred onto Nafion membrane directly by hot pressing the CNT coated side of the filter onto the ionic membrane to produce a catalyst film coated Nafion membrane (CFCM). For the Pt–Ru/C anode, we used the conventional spraying method as we are interested in demonstrating the benefits of the Pt–Ru/CNTs and the filtration method over the current technology benchmark.

The cathode catalyst layer includes two layers. The first layer is 1.0 mg Pt/ cm^2 (80 wt % Pt/C, E-TEK) mixed with 20 wt % Teflon, and the second layer is 1.0 mg Pt/ cm^2 (80 wt % Pt/C, E-TEK) mixed with 15 wt % Nafion. A thin layer of 5 wt % Nafion solution was finally spread onto the surface of cathode (1.0 mg Nafion/ cm^2).

The MEAs with an active electrode area of 5 cm^2 were obtained by hot pressing a cathode, a Pt–Ru/CNTs film coated Nafion 115 membrane and an anode diffusion layer with a pressure of 140 atm, at 135 $^\circ\text{C}$ for 1.5 min. For comparison, two conventional anode catalyst layers were prepared by spraying. The catalyst area loadings were 2.0 mg Pt–Ru/ cm^2 and 0.5 mg Pt–Ru/ cm^2 (40 wt % Pt–Ru/C, E-TEK). The catalyst layer also contained 15 wt % Nafion. The comparison MEAs were fabricated by hot pressing the anode, Nafion 115, and cathode according to the same hot-press conditions as described above.

The MEAs were tested in a homemade automatic DMFC cell test instrument with a Scribner electronic load. The operation conditions are described as follows: The oxygen operating pressure was 0.2 MPa and the flow rate was 200 mL/min, and the methanol concentration was 1.0 M and flow rate was 2.0 mL/min. The temperatures of the cell and cathode humidifier were 90 and 75 $^\circ\text{C}$, respectively.

Results and Discussion

The XRD patterns for the Pt–Ru/CNTs samples are shown in Figure 2. The diffraction peak at 23–27 $^\circ$ observed is attributed to the hexagonal graphite structure (002), which can reflect the graphite degree of a carbon material. Among all of the samples, MWNTs have the highest diffraction peak (002), indicating that MWNTs have the highest graphite degree and likely the best electrical conductivity. SWNTs, DWNTs, and CB appear to have similar graphite degree. The analysis of other diffraction peaks shows that all catalysts, Pt–Ru/CNTs and Pt–Ru/C, have a Pt face-centered cubic (fcc) crystal structure and Pt and Ru did not form alloys. No Ru peak was detected, suggesting that Ru exists in an amorphous form. From the isolated Pt (220) peak, the mean particle size was about 2.0 nm, calculated with the Scherrer formula for all the Pt–Ru/CNTs and Pt–Ru/C samples. This suggests that, by using the EG reduction method, very small Pt–Ru nanoparticles can be produced. The particle size does not depend on the support type because the Pt–Ru colloidal nanoparticles were produced before they were deposited onto the support.

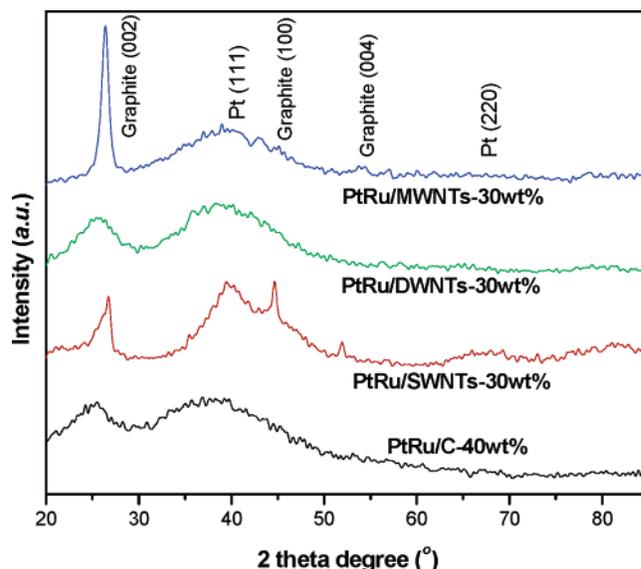


Figure 2. Powder XRD patterns of Pt–Ru/CNTs catalyst.

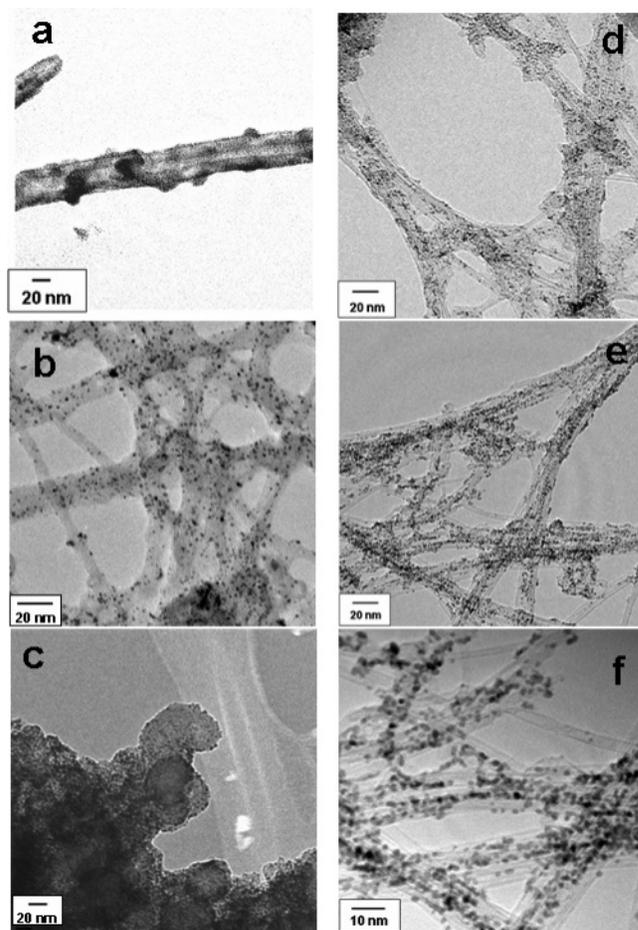


Figure 3. TEM micrograph of (a) Pt–Ru/MWNTs 30 wt %, (b) Pt–Ru/SWNTs 30 wt %, (c) Pt–Ru/C 40 wt %, (d) Pt–Ru/DWNTs 30 wt %, (e) Pt–Ru/DWNTs 50 wt % with lower magnification, and (f) higher magnification of Pt–Ru/DWNTs 50 wt %.

Typical TEM images of the Pt–Ru/MWNTs, Pt–Ru/SWNTs, Pt–Ru/C, and Pt–Ru/DWNTs catalysts are shown in Figure 3. Overall, small and uniform Pt–Ru nanoparticles with diameter from 2 to 3 nm are dispersed onto CNTs, even at high metal loading (i.e., 50 wt % Pt–Ru/DWNTs). This is consistent with the XRD results. Minor aggregation of nanoparticles on

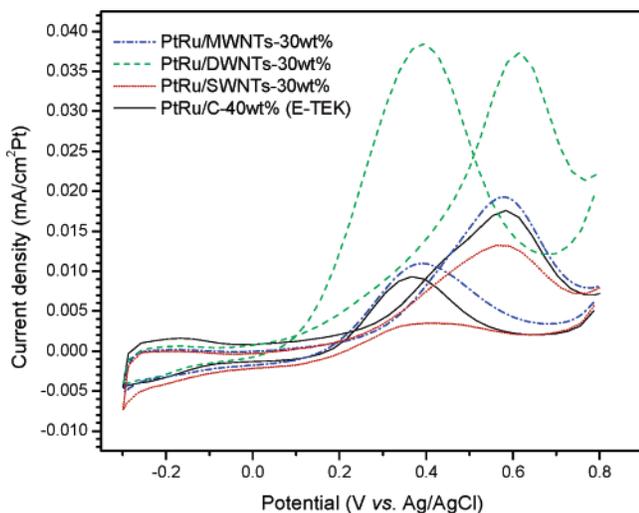


Figure 4. MOR activity of Pt–Ru/SWNTs, Pt–Ru/DWNTs, Pt–Ru/MWNTs in 0.5 M CH₃OH + 0.5 M H₂SO₄ at room temperature. Scan rate: 50 mV/s.

MWNTs is observed, and this is attributed to the lower surface area of the MWNTs (~ 100 m²/g) (Figure 3a). By contrast, aggregations of nanoparticles were not observed on SWNTs, CB, or DWNTs (parts b–f of Figure 3), most likely because SWNTs and DWNTs have high surface areas (~ 500 m²/g).

The Pt–Ru/CNTs and Pt–Ru/C catalysts were tested for their MOR activity in a half cell configuration using an RDE setup (Figure 4). RDE tests can provide the specific activity of the Pt–Ru catalyst in a well-controlled environment without mass transportation effects. Although the starting oxidation potential for these Pt–Ru catalysts were the same at about 0.1 V, the oxidation peak for Pt–Ru/DWNTs is about 0.037 mA/cm² Pt, which is much higher than the other samples (i.e., 0.019 mA/cm² Pt for Pt–Ru/MWNTs, 0.017 mA/cm² Pt for Pt–Ru/C, and 0.012 mA/cm² Pt for Pt–Ru/SWNTs). In other words, the

Pt–Ru/DWNTs catalyst can generate higher currents and thus have a higher specific activity than Pt–Ru/MWNTs, Pt–Ru/CB, or Pt–Ru/SWNTs catalysts. The half-cell results suggest that Pt–Ru/DWNTs catalysts would be the best anode catalyst for a methanol fuel cell.

Before the fabrication of MEAs, the anode catalyst film coated membranes were prepared. The cross-sectional SEM images and the corresponding EDaX elemental analysis of the Pt–Ru/DWNTs and Pt–Ru/DWNTs catalyst film coated Nafion membranes are shown in Figure 5. It was noted that the MWNTs of the Pt–Ru/MWNTs layers do not seem to have preferred orientation as previously observed for a Pt/MWNT cathode layer for PEMFC.²⁸ It is believed that the orientation was a result of the hydrophobicity of the MWNTs and the hydrophilicity of the filter paper. Thus the unfavorable interaction forces the MWNTs to “stand up.” In the present study, Nafion was sprayed during the filtration process and is probably responsible for the random orientation of the CNTs, because Nafion makes the CNT film more hydrophilic. At a PtRu metal loading of 0.5 mg/cm², the Pt–Ru/MWNTs catalyst layer is about 7–8 μ m and the thickness for Pt–Ru/DWNTs catalyst layer about 15–20 μ m.

EDaX/SEM shows that Pt and Ru from the catalyst, C from support, and F and S from the Nafion are all present. The presence of F and S suggests that Nafion was mixed well within Pt–Ru/CNTs catalyst layer, and this is believed to be essential to facilitate the mass transport of the fuel, methanol. For elemental analysis, five spots of the catalyst layer were examined from each sample, and the calculated Pt:Ru atomic ratio is approximately 1:1.

The *I*–*V* curves of single DMFCs with different anode catalyst supports and metal electrode loadings are shown in Figure 6. The open circuit voltage (OCV) for the Pt–Ru/DWNTs catalyst (30 wt %, 0.50 mg/cm²) is 0.627 V, which is 50 mV higher than that of Pt–Ru/C (30 wt %, 0.50 mg/cm²). Even when the electrode loading for the Pt–Ru/C was increased to 2.0 mg/cm², the OCV was still about 0.620 V. The OCVs of Pt–Ru/MWNTs and Pt–Ru/SWNTs-based cells are 0.610 and

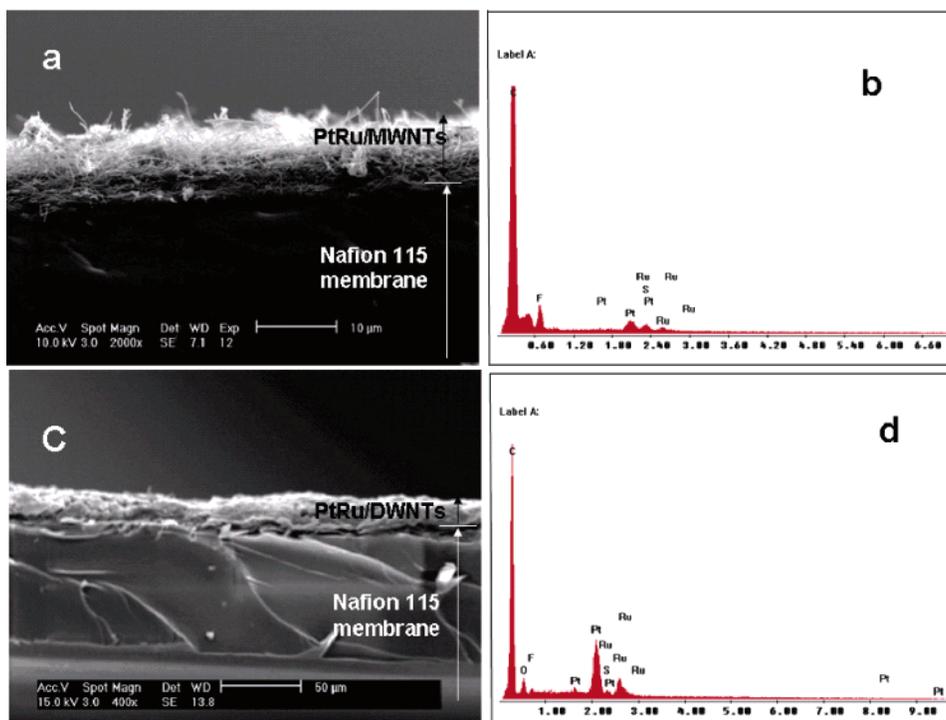


Figure 5. SEM micrographs and EDaX analysis of Pt–Ru/CNTs catalyst (0.5 mg Pt–Ru/cm²) coated on Nafion 115 membrane (a) and (b) for Pt–Ru/MWNTs (30 wt % Pt–Ru), (c) and (d) for Pt–Ru/DWNTs (50 wt % Pt–Ru).

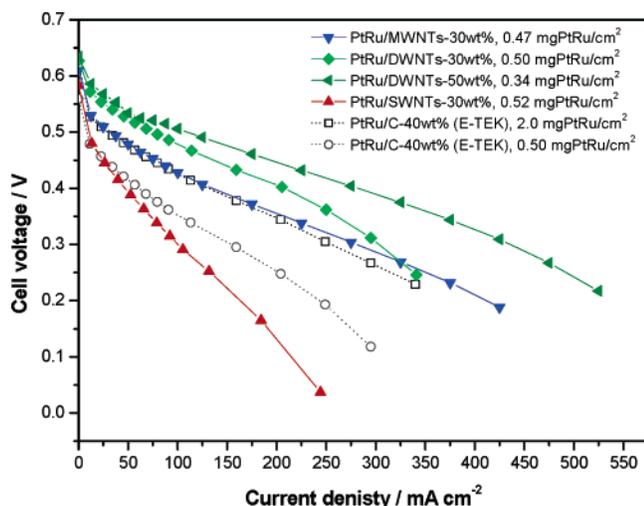


Figure 6. I – V curves of DMFC with low noble metal loading (ca. 0.5 mg Pt–Ru/cm²) anode catalyst. Cathode, 2.0 Pt mg/cm² (80 wt % Pt/C, E-TEK); membrane, Nafion 115; cell, 90 °C; O₂, 75 °C, 0.2 MPa, 200 mL/min; methanol, 1.0 mol/L, 2.0 mL/min.

0.583 V, respectively. The value of OCV can reflect the activity of the anode catalyst because the same cathode was used. The highest OCV shown by the Pt–Ru/DWNTs catalyst suggests that it has the highest MOR activity, which is consistent with the RDE results.

In the activation-controlled region (i.e., at 0.55 V) the current density for the Pt–Ru/DWNT catalyst of 0.5 mg/cm² is 26 mA/cm², which is much higher than that of the Pt–Ru/C catalyst with the same electrode loading (0.5 mg/cm², 1.5 mA/cm²) and still much higher even when the electrode metal loading is four times as high (2.0 mg/cm², 8.5 mA/cm²).

The remarkably high MOR activity of Pt–Ru/DWNTs is not fully understood. Some of the possible favorable factors are its high electrical conductivity, high surface area, and small diameter. The small diameter of the DWNTs may have led to a unique interaction between Pt and the DWNTs that facilitates charge transfer from Pt to the tubes, and thus increasing the specific activity of Pt. The bundle morphology of the DWNTs may also help the uniform dispersion and retention of Nafion, further improving Pt mass activity.

From the overall I – V curves, Pt–Ru/DWNT catalysts (0.5 mg/cm²) outperform Pt–Ru/MWNT catalysts at low current density regions, but lose their advantage at the high current density regions. This is probably attributed to the fact that the Pt–Ru/DWNT layer is thicker than the Pt–Ru/MWNT layer (15–20 vs 7–8 μm). In addition, it is also found that the Pt–Ru/SWNT catalyst shows the lowest DMFC performance among all DMFC single cells, which is most likely because the SWNTs are usually a mixture of electrically conducting and semiconducting tubes.

To further improve the overall performance, a Pt–Ru/DWNTs catalyst with high metal loading (50 wt %) was prepared and used in an MEA with a low electrode metal loading of 0.34 mg/cm². Its DMFC I – V curve is also shown in Figure 6. This MEA showed a superior DMFC performance at the whole current density range and had the highest power density of 131 mW/cm². This is attributed to its higher specific MOR activity, and thinner catalyst layer. It is exciting to note that the DWNT-supported Pt–Ru anode catalyst could offer a 68% enhancement of the DMFC's highest performance when compared with carbon black supported anode catalyst with a 5.9 times more Pt–Ru noble metal.

Conclusions

The EG reduction method used in this study is an effective method for preparing Pt–Ru nanoparticles with small and uniform particle size on SWNTs, DWNTs, MWNTs, and CB. The Pt–Ru/DWNTs catalyst exhibits an exceptional MOR activity in RDEs and excellent MEA performance. The filtration method is a simple and fast method for generating a thin catalyst layer which is well adhered to the membrane. The results shown here call into question the superiority of the results observed on SWNTs, which in our study consistently showed poor performance.

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