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# Carbon supported Pt–Ni nanoparticles as catalysts in direct methanol fuel cells

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Two types of carbon supported Pt–Ni nanoparticles were fabricated as catalysts for the cathode part of a direct methanol fuel cell, and were characterized by X-ray diffraction, transmission electron microscopy and cyclic voltammetry analyses. TEM and XRD analyses pointed to a good dispersion of the catalysts with carbon black and carbon nanotubes (CNTs) having sizes of ca. 2–6 nm, which is very important for supporting catalysts of the methanol fuel cell. CV analysis showed that the catalytic activity of a Pt–Ni/CNTs catalyst is more efficient than that of other catalysts. We also noticed that it is more appropriate to use a glassy carbon electrode rather than carbon paper as the working electrode for the methanol electrooxidation of Pt Ni/CNTs catalysts.

Key words: *carbon nanotubes; carbon black; direct methanol fuel cell*

## 1. Introduction

Fuel cells are efficient, silent and clean energy conversion systems producing electricity via electrochemical reactions. Direct methanol fuel cells (DMFC) are expected to be the first fuel cells to provide a power source for portable electronic devices, such as mobile phones, laptop computers and advanced mobile electronic devices [1]. A successful commercialization of DMFC is very much dependent, however, on the activity of their electrocatalysts. Nowadays, all pre-commercial, low-temperature fuel cells use supported Pt and Pt alloys as electrocatalysts. Critical properties to consider when choosing an electrocatalyst support include its electrical conductivity, surface area, microstructure, macromorphology, corrosion resistance and cost. carbon nanotubes (CNTs) have been shown to be more corrosion-resistant under operational conditions than carbon black (CB) in a simulated fuel cell [2–6]. Ever since their discovery in 1991 [7], CNTs have shown a highly electrochemically accessible surface area and offered a remarkable electronic conductivity in comparison with the vulcan carbon black.

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In the present study, we pretreated CNTs, CB and prepared electrocatalysts, then characterized these supporting Pt–Ni electocatalysts in order to find out better catalysts for DMFC, and finally we observed the performance of two types of working electrodes for Pt–Ni/CNTs.

## 2. Experimental

CNTs of diameters ranging from 10 nm to 20 nm were treated separately with 30% HCI and $HNO_3$ step by step at 120 °C with 300 rpm on a hot plate. Then they were washed twice and dried in an oven at 120 °C. CB was refluxed with 30% $HNO_3$ at 60 °C at 80 rpm. It was also finally filtrated, washed twice and dried in an oven at 120 °C. 20 wt. % of Pt–Ni nanoparticles were loaded separately onto CNTs and CB by the impregnation method. These catalysts were refluxed at room temperature and stirred for 12 h. The solutions were then evaporated by heating, rotating and drying at 100 °C. The impregnated samples were finally reduced with hydrogen at 350 °C. Before the hydrogen gas reduction, nitrogen was purged for 35 min to prevent re-oxidation. For TEM investigations, catalysts were ultrasonicated in ethyl alcohol for 30 min and then deposited on Cu grids.

X-ray diffraction measurements of catalysts were accomplished using a $CuK_\alpha$ source. Scans were recorded at 5 $deg \cdot min^{-1}$ for $2\theta$ in the range of 30–90°. Electrochemical measurements were performed with a computer-controlled voltammetric analyzer EGG 273 potentiostat/galvanostat.

A three electrode cell composed of an Ag/AgCl reference electrode, Pt wire as a counter electrode and a glassy carbon electrode (GCE) was used as the working electrode. The working electrode was polished with 0.5 mg alumina powder on a polishing cloth prior to each electrochemical measurement. Then, it was thoroughly rinsed with methanol and rinsed twice in distilled water, and then gently dried with tissue paper. The Nafion-impregnated Pt–Ni catalysts ink were prepared by mixing carbon material with 5% of Nafion (Aldrich Inc.) solution and electrocatalysts was applied on it. 1 M $CH_3OH$ in 1 M $H_2SO_4$ solution was used as the electrolyte. To record another current –potential curve for Pt–Ni/CNTs, another three electrode cell was used, made of an Ag/AgCl reference electrode, Pt wire as a counter electrode and the sample pasted on carbon paper, used as working electrode. The working electrode was made of a paste of 5% Nafion and a catalyst sample (4 mg per square inch with catalysts). Voltammograms were recorded after fifty activation cycles for each measurement.

## 3. Results and discussion

Figure 1 presents a schematic diagram of fabrication of Pt–Ni nanoparticles with CNTs and CB. From Figure 2, one may conclude that the methanol oxidation on the two catalysts commenced in the potential range 0.7–0.9 V. The peak corresponding to full oxidation was found at 0.81V for Pt–Ni/CNTs catalysts; the peak is much higher and wider than the corresponding one for Pt–Ni/CB. This fact is very important for improving DMFC catalysts, and is probably due to a higher electrical conductivity of multiwall CNTs.

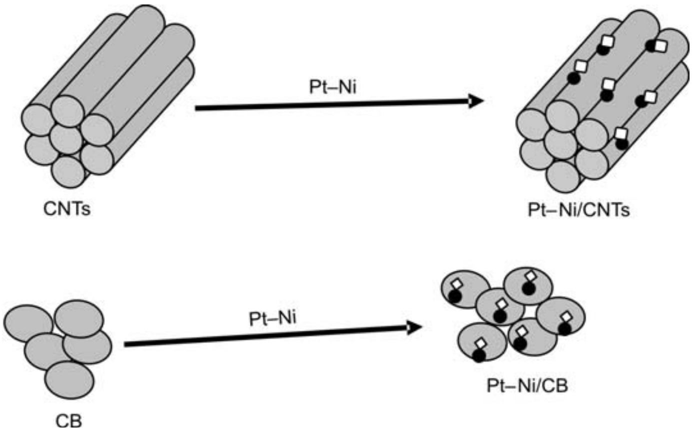

Fig. 1. Schematic diagram of fabrication of Pt–Ni/CNTs and Pt–Ni/CB catalysts

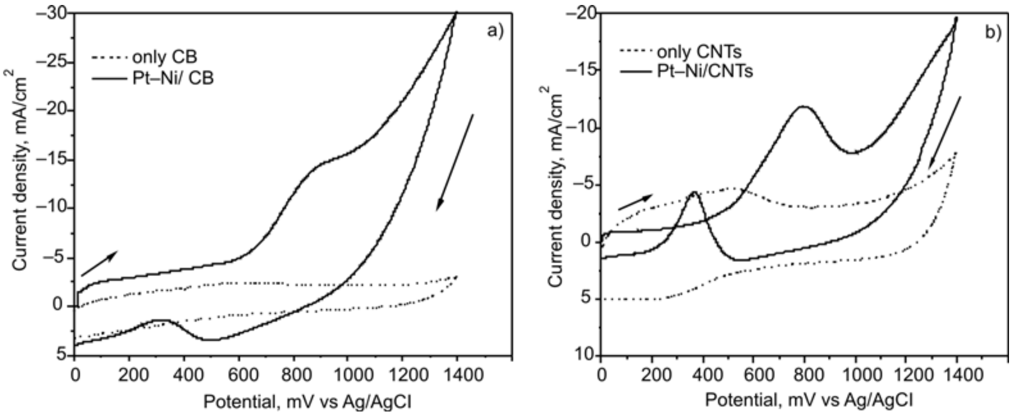

Fig. 2. Cyclic voltammetry of the catalysts: a) Pt–Ni/CB, b) Pt–Ni/CNTs

In fact, CNTs with Pt–Ni nanoparticles attached showed much more electroactivity. The change of the potential toward more positive values proved that the catalysts have high electrocatalytical activity. The peaks in the current were also protected from the methanol crossover voltages. The peak current densities associated with methanol oxidation at the forward scan were –12.0 and –12.7 mA/cm$^2$ for Pt–Ni/CNTs and Pt–Ni/CB, respectively. Moreover, CNTs are promising materials for improving the catalytic activity supporting fuel cell electrode reactions. Previous studies have also shown that Pt (or Pt alloys) supported on CNTs exhibits a better performance for the electrooxidation of methanol and oxygen reduction than that on vulcan XC-72 [8–11].

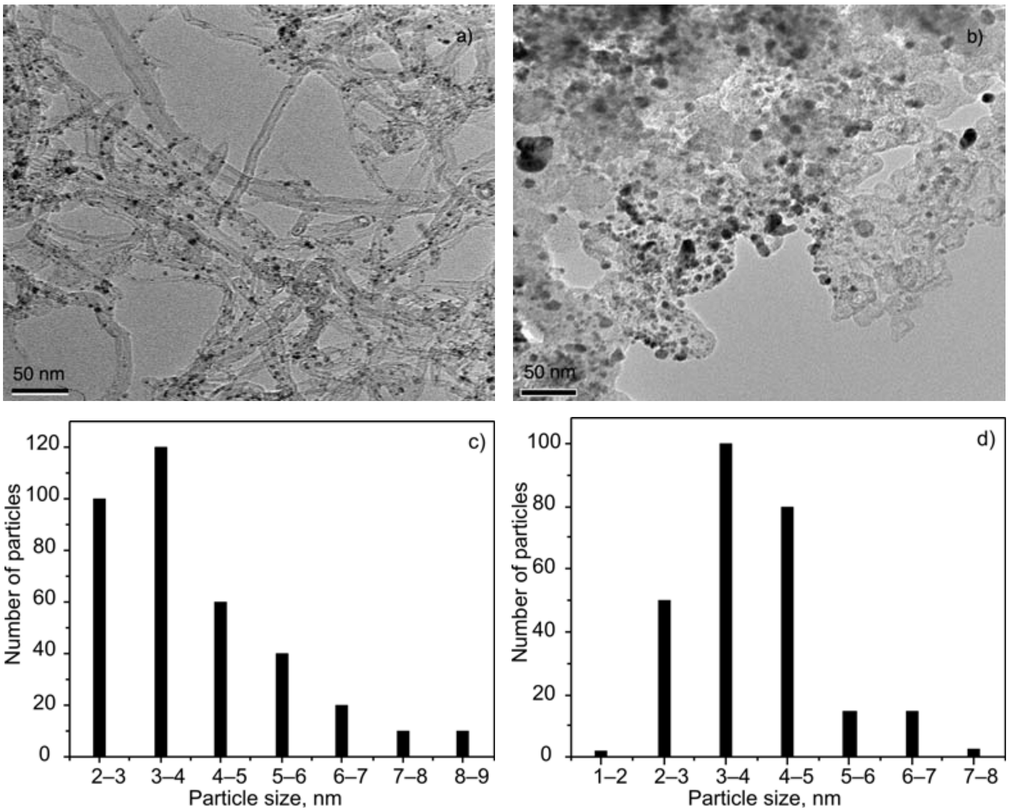

Fig. 3. TEM images of CNTs and CB supported catalysts: a) Pt–Ni/CNTs, b) Pt–Ni/CB taken at 50 nm wavelength and particle sizes shown in (c) for Pt–Ni/CNTs and (d) for Pt–Ni/CB

Figure 3 presents the TEM images of two types of catalysts. TEM was used to confirm the dispersion of the nanoparticles in the support, and the histograms for particle size distribution of each catalyst were obtained. The average sizes of each sample were respectively 2.12 nm (Pt–Ni/CNTs) and 3.26 nm (Pt–Ni/CB). The dependence of electroactivity on the particle size of the catalytically active component is well known. It is known that metal–support interactions can significantly affect supported catalysts. On the TEM image, Pt–Ni/CNTs catalysts indicated that the small black particles are better dispersed on the carbon support than that of Pt–Ni/CB catalysts. TEM images also confirmed that metal catalysts were uniformly and finely deposited on to CNTs.

In Figure 4, the TEM images are shown of the two catalysts taken at 20 nm wavelength. From these photographs, we can see that the CNTs surface acted as a stabilizer for the nanoparticles, to inhibit agglomeration. A high stability of Pt–Ni/CNT is probably due to a specific interaction between Pt–Ni and the support.

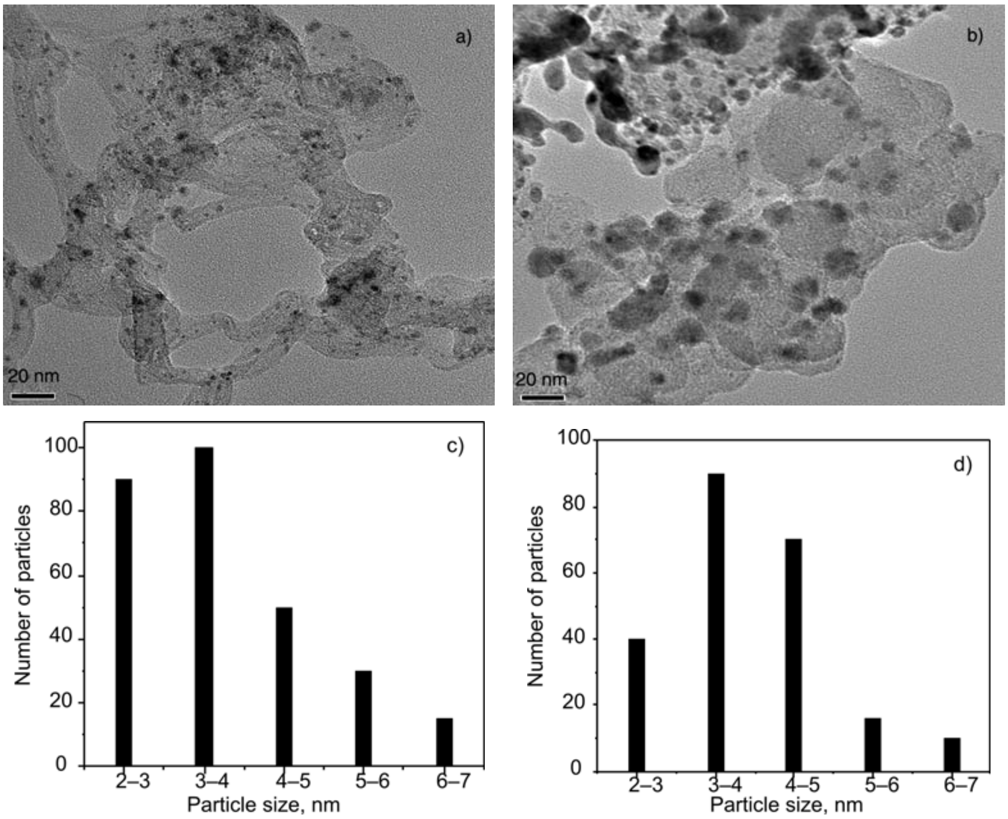

Fig. 4. TEM images of CNTs and CB supported catalysts: a) Pt–Ni/CNTs, b) Pt–Ni/CB at 20 nm wavelength and particle sizes shown in (c) for Pt–Ni/CNTs and (d) for Pt–Ni/CB

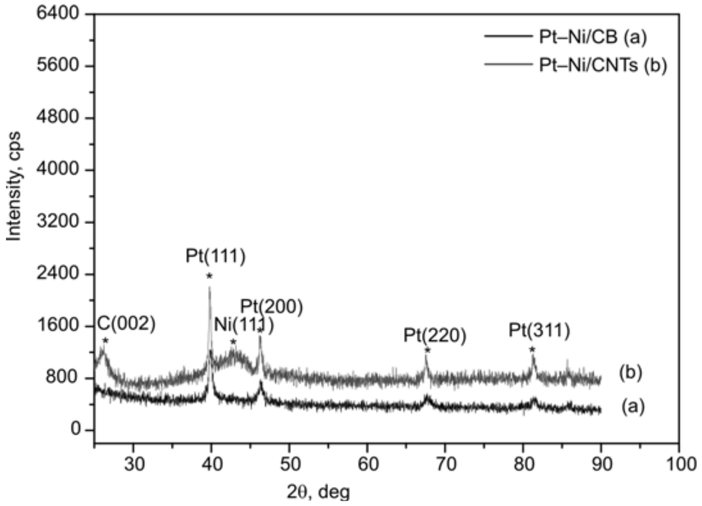

Fig. 5. XRD pattern of CNTs and CB supported Pt–Ni catalysts

The XRD patterns of Pt–Ni/CNTs and Pt–Ni/CB catalysts are shown in Fig. 5. In the case of Pt–Ni/CNTs and Pt–Ni/CB catalysts, Pt peaks are identifiable in the (111), (200), (220), (311) planes, and Ni peaks in the Ni (111) plane for specific $2\theta$ values. The width of all peaks in Pt–Ni/CNTs is quite sharp and well localised, which is necessary for supporting catalysts of DMFC. It can be seen that the Pt–Ni/CNTs catalysts have the most intense diffraction peak in the (111) plane, among the supporting catalysts. This may indicate that the crystallization of the (111) plane has improved the Pt–Ni/CNTs catalyst activity.

The Pt–Ni/CNTs catalysts displayed the diffraction peaks characteristic of the *fcc* structure of Pt. The broader diffraction peaks for the two catalysts also led to smaller average particle size as calculates from Scherrer's equation:

$$L = \frac{0.9\lambda_{k\alpha 1}}{B_{2\theta}\cos\theta_B}$$

Here, $L$ is the average particle size, $\lambda_{k\alpha 1}$ is the X-ray wavelength (1.54056 Å for $\mathrm{CuK}_{\alpha 1}$ radiation), $B_{2\theta}$ is the half-peak width for Pt (111), and $\theta_B$ is the maximum angle of the (111) peak. The calculated values of the average Pt particle sizes are 6.7±0.6 nm and 6.7 ±0.6 nm for CNTs and CB, respectively. The negligible differences between the particle sizes obtained by XRD with TEM are probably due to the fact that Scherrer's equation is only approximate. Another important detail is that the average particle sizes obtained from TEM are generally smaller than those for crystallites of XRD, but in most cases TEM results confirm the average values obtained from XRD when the standard deviation is considered. It has to be taken into account that only a fraction of particles were measured by TEM. TEM and XRD analyses consistently showed that the Pt–Ni/CNTs catalyst has a smaller particle size and more uniform distribution than Pt–Ni/CB.

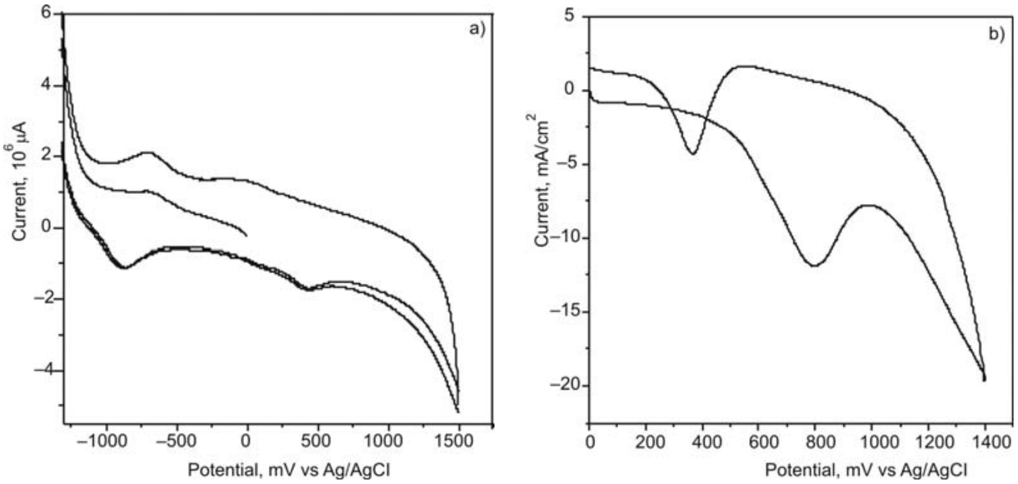

Fig. 6. Cyclic voltammogram of Pt–Ni/CNTs catalysts with:
a) carbon paper, b) GCE as a working electrode

Figure 6a shows the voltammogram of Pt–Ni/CNTs with carbon paper used as a working electrode. The oxidation-reduction peaks are observed in the potential region of –0.12 V to 0.4 V, demonstrating an electrochemically active surface area of the catalysts. However, upon comparison of the glassy carbon electrode (GCE) with the carbon paper electrode (Fig. 6b), it can be confirmed that the methanol oxidation peak for the Pt–Ni/CNTs catalysts appears in a more suitable potential range in the case of GCE: the peak appears at higher positive voltages thus allowing a higher methanol tolerance. For the Pt–Ni/CNTs, a very large cathodic current was detected between 0.7~0.9 V thus indicating a high electro-catalytic activity of the Pt–Ni/CNTs with GCE.

Figure 6b confirms that the peak is protected and very far from methanol crossover voltage because the methanol crossover drop voltage is from 0.2 to 0.3 V [8]. However, in the case of 20 wt. % Pt–Ni/CNTs (with GCE), the thickness of the catalyst layer is reduced and methanol can penetrate more easily into the electrode, even if the current is high. Probably due to that the current-potential curve for Pt–Ni/CNTs catalysts with GCE, better methanol electrooxidation occurs through electro-catalytic activity.

## 4. Conclusions

The performances of the two types of electrocatalysts were distinct with impregnation method for DMFC under similar conditions. The experimental results of methanol electrooxidation showed that the catalysts prepared on CNTs as supporting catalysts for cathodes produce better performance and have stronger resistance compared with those prepared on CB. However Pt–Ni/CNTs catalysts also have good particle sizes, according to morphological tests. Pt–Ni/CNTs will be efficient catalysts due to their particle size, adhesion, uniformity and electro-activeness for DMFC.

On the other hand, GCE for Pt–Ni/CNTs catalysts showed better electrochemical activity for methanol oxidation, compared with carbon paper as the working electrode. Thus the method is useful for direct methanol fuel cell applications and can be used as a general method for the preparation of other carbon supporting catalysts for methanol fuel cells.

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