

# Nitrogen containing carbon nanotubes as supports for Pt – Alternate anodes for fuel cell applications

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## Abstract

Aligned nitrogen containing carbon nanotubes have been synthesized using Anodisc alumina membrane as template. Highly dispersed platinum nanoparticles have been supported on the nitrogen containing carbon nanotubes. Nitrogen containing carbon nanotubes as platinum catalyst supports were characterized by electron microscopic technique and electrochemical analysis. The EDX patterns show the presence of Pt and the micrograph of TEM shows that the Pt particles are uniformly distributed on the surface of the nitrogen containing carbon nanotube with an average particle size of 3 nm. Cyclic voltammetry studies revealed a higher catalytic activity of the nitrogen containing carbon nanotube supported Pt catalysts.

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## 1. Introduction

Since the last decade, fuel cells have been receiving an increased attention due to the depletion of fossil fuels and rising environmental pollution. Fuel cells have been demonstrated as interesting and very promising alternatives to solve the problem of clean electric power generation with high efficiency. Among the different types of fuel cells, direct methanol fuel cells (DMFCs) are excellent power sources for portable applications owing to its high energy density, ease of handling liquid fuel, low operating temperatures (60–100 °C) and quick start up [1,2]. Furthermore, methanol fuel cell seems to be highly promising for large-scale commercialization in contrast to hydrogen-fed cells, especially in transportation [3]. The limitation of methanol fuel cell system is due to low catalytic activity of the electrodes, especially the anodes and at present, there is no practical alternative to

Pt based catalysts. High noble metal loadings on the electrode [4,5] and the use of perfluorosulfonic acid membranes significantly contribute to the cost of the devices. An efficient way to decrease the loadings of precious platinum metal catalysts and higher utilization of Pt particles is by better dispersion of the desired metal on the suitable support [6]. In general, small particle size and high dispersion of platinum on the support will result in high electrocatalytic activity. Carbon materials possess suitable properties for the design of electrodes in electrochemical devices. Carbon is an ideal material for supporting nano-sized metallic particles in the electrode for fuel cell applications. No other material except carbon material has the essential properties of electronic conductivity, corrosion resistance, surface properties, and the low cost required for the commercialization of fuel cells. In general, the conventional supports namely carbon black is used for the dispersion of Pt particles [7].

The appearance of novel carbon support materials, such as graphite nanofibers (GNFs) [8,9], carbon nanotubes (CNTs) [10–17], carbon nanohorns [18], and carbon nanocoils [19–22], provides new opportunities of

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carbon supports for fuel cell applications. Bessel et al. [8] and Steigerwalt et al. [9] used GNFs as supports for Pt and Pt–Ru alloy electrocatalysts and observed better activity for methanol oxidation. The high electronic conductivity of GNFs and the specific crystallographic orientation of the metal particles resulting from well-ordered GNF support were believed to be the important factors for the observed enhanced electrocatalytic activity. The morphology and the nature of the functional groups of the support influence the activity of fuel cell electrocatalysts [23–26]. Carbon with sulphur or nitrogen based functionality [25], can influence the activity of the catalyst.

The present report focuses on the efforts undertaken to develop unconventional supports based platinum catalysts for methanol oxidation. Nitrogen containing carbon nanotubes were used to disperse the platinum particles effectively without sintering and to increase the catalytic activity for methanol oxidation. The tubular morphology and the nitrogen functionality of the support have influence on the dispersion as well as the stability of the electrode. In this communication the preparation of highly dispersed platinum supported on nitrogen containing carbon nanotubes, the evaluation of the activity for the methanol oxidation of these electrodes and comparison with the activity of conventional electrodes are reported.

## 2. Experimental

### 2.1. Materials

All the chemicals used were of analytical grade. Polyvinyl pyrrolidone (Sisco Research Laboratories, India), dichloromethane and concentrated HF (both from Merck) were used. Hexachloroplatinic acid was obtained from Aldrich. 20 wt% Pt/Vulcan carbons were procured from E-TEK. Methanol and sulphuric acid were obtained from Fischer chemicals. The alumina template membranes (Anodisc 47) with 200 nm diameter pores were obtained from Whatman Corp. Nafion 5 wt% solution was obtained from Dupont and was used as received.

### 2.2. Synthesis of nitrogen containing carbon nanotubes

Pyrolysis of nitrogen containing polymers is a facile method for the preparation of carbon nanotube materials containing nitrogen substitution in the carbon framework. Nitrogen containing carbon nanotubes were synthesized by impregnating polyvinylpyrrolidone (PVP) inside the alumina membrane template and subsequent carbonization of the polymer [27]. Polyvinylpyrrolidone (PVP – 5 g) was dissolved in dichloromethane (20 ml) and impregnated directly in the pores of the

alumina template by wetting method [28]. After complete solvent evaporation, the membrane was placed in a quartz tube (30 cm length, 3.0 cm diameter), kept in a tubular furnace and carbonized at 1173 K under Ar gas flow. After 3 h of carbonization, the quartz tube was cooled to room temperature. The resulting template with carbon–nitrogen composite was immersed in 48% HF at room temperature for 24 h to remove the alumina template and the nitrogen containing CNTs were obtained as an insoluble fraction. The nanotubes were then washed with distilled water to remove the residual HF and dried at 393 K.

### 2.3. Loading of Pt catalyst inside nanotube

Platinum nanoclusters were loaded inside the N-CNT as follows; the C/alumina composite obtained (before the dissolution of template membrane) was immersed in 73 mM  $\text{H}_2\text{PtCl}_6$  (aq) for 12 h. After immersion, the membrane was dried in air and the ions were reduced to the corresponding metal(s) by a 3 h exposure to flowing  $\text{H}_2$  gas at 823 K. The underlying alumina was then dissolved by immersing the composite in 48% HF for 24 h. This procedure resulted in the formation of Pt nanocluster loaded N-CNT and the complete removal of fluorine and aluminum was confirmed by EDX analysis.

### 2.4. Preparation of working electrode

Glassy carbon (GC) (Bas electrode,  $0.07 \text{ cm}^2$ ) was polished to a mirror finish with 0.05 m alumina suspensions before each experiment and served as an underlying substrate of the working electrode. In order to prepare the composite electrode, the nanotubes were dispersed ultrasonically in water at a concentration of  $1 \text{ mg ml}^{-1}$  and 20  $\mu\text{l}$  aliquot was transferred on to a polished glassy carbon substrate. After the evaporation of water, the resulting thin catalyst film was covered with 5 wt% Nafion solution. Then the electrode was dried at 353 K and used as the working electrode.

### 2.5. Characterization methods

The chemical composition of the nanotubes was determined by elemental analysis using Hereaus CHN analyzer after the removal of alumina template. The scanning electron micrographs were obtained using JEOL JSM-840 model, working at 15 keV. The nanotubes were sonicated in acetone for 20 min and then were dropped on the cleaned Si substrates. The AFM imaging was performed in air using the Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in contact mode. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were placed on the copper grid and the

images were obtained using Phillips 420 model, operating at 120 keV.

### 2.6. Electrochemical measurements

All electrochemical studies were carried out using a BAS 100 electrochemical analyzer. A conventional three-electrode cell consisting of the GC ( $0.07\text{ cm}^2$ ) working electrode, Pt plate ( $5\text{ cm}^2$ ) as counter electrode and Ag/AgCl reference electrode were used for the cyclic voltammetry (CV) studies. The CV experiments were performed using  $1\text{ M H}_2\text{SO}_4$  solution in the absence and presence of  $1\text{ M CH}_3\text{OH}$  at a scan rate of  $50\text{ mV s}^{-1}$ . All the solutions were prepared by using ultra pure water (Millipore,  $18\text{ M}\Omega$ ). The electrolytes were degassed with nitrogen gas before the electrochemical measurements.

### 3. Results and discussion

Elemental analysis was conducted to examine whether nitrogen has really entered the carbon nanotube framework. It has been found that the samples prepared contained about 87.2% carbon and 6.6% nitrogen (w/w). The SEM images of the nitrogen containing carbon nanotubes support are shown in Fig. 1(a)–(c). Top view of the vertically aligned nitrogen containing carbon

nanotubes is shown in Fig. 1(a). Fig. 1(b) shows lateral view of the nitrogen containing carbon nanotubes with low magnification and Fig. 1(c) shows lateral view of the nitrogen containing carbon nanotubes with high magnification. The hollow structure and well alignment of the nitrogen containing carbon nanotubes have been identified by SEM.

AFM images of the nitrogen containing carbon nanotubes deposited on a silicon substrate are shown in Fig. 2. The AFM tip was carefully scanned across the tube surface in a direction perpendicular to the tube axis. From the AFM images, it is inferred that a part of the long nanotube is appearing to be cylindrical in shape and is found to be terminated by a symmetric hemispherical cap. Because of the finite size of the AFM tip, convolution between the blunt AFM tip and the tube body will be giving rise to an apparently greater lateral dimension than the actual diameter of the tube [29].

The TEM images are shown in Fig. 3(a)–(c). The open end of the tubes observed by TEM shows that the nanotubes are hollow and the outer diameter of the nanotube closely match with the pore diameter of template used, with a diameter of  $200\text{ nm}$  and a length of approx.  $40\text{--}50\text{ }\mu\text{m}$ . It is evident from the micrographs that there is no amorphous material present in the nanotube. Fig. 3(c) shows the TEM image of Pt nanoparticles filled carbon nanotubes. TEM pictures reveal that the Pt

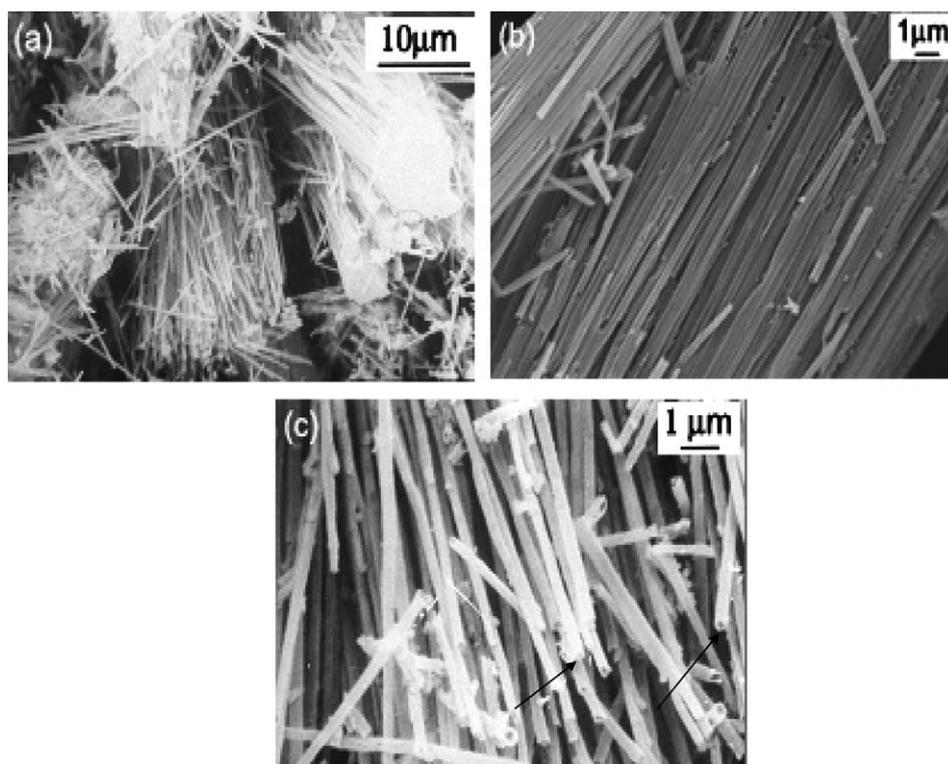


Fig. 1. SEM images of the nitrogen containing carbon nanotubes: (a) the top view of the nanotubes; (b) side view of the vertically aligned nanotubes and (c) high magnification lateral view of the nanotubes.

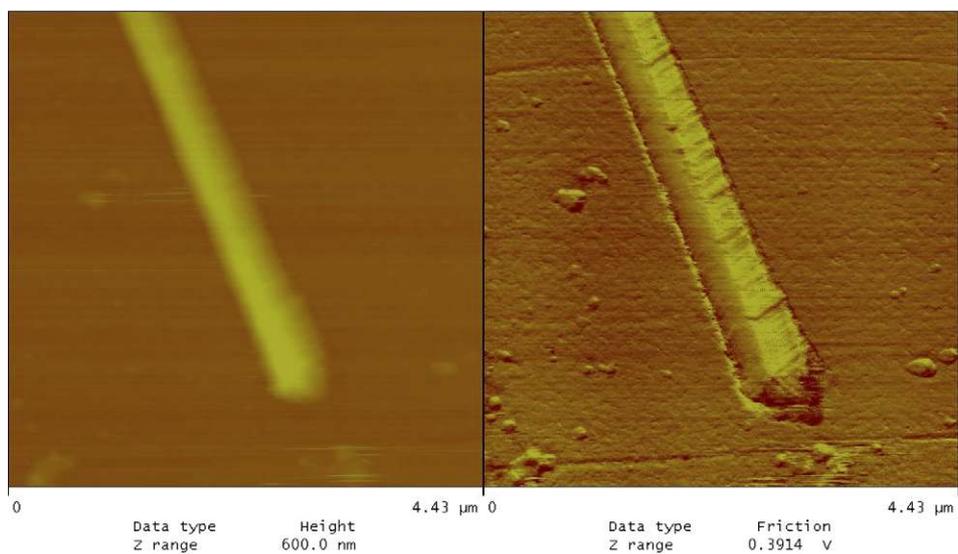


Fig. 2. AFM image of the nitrogen containing carbon nanotubes.

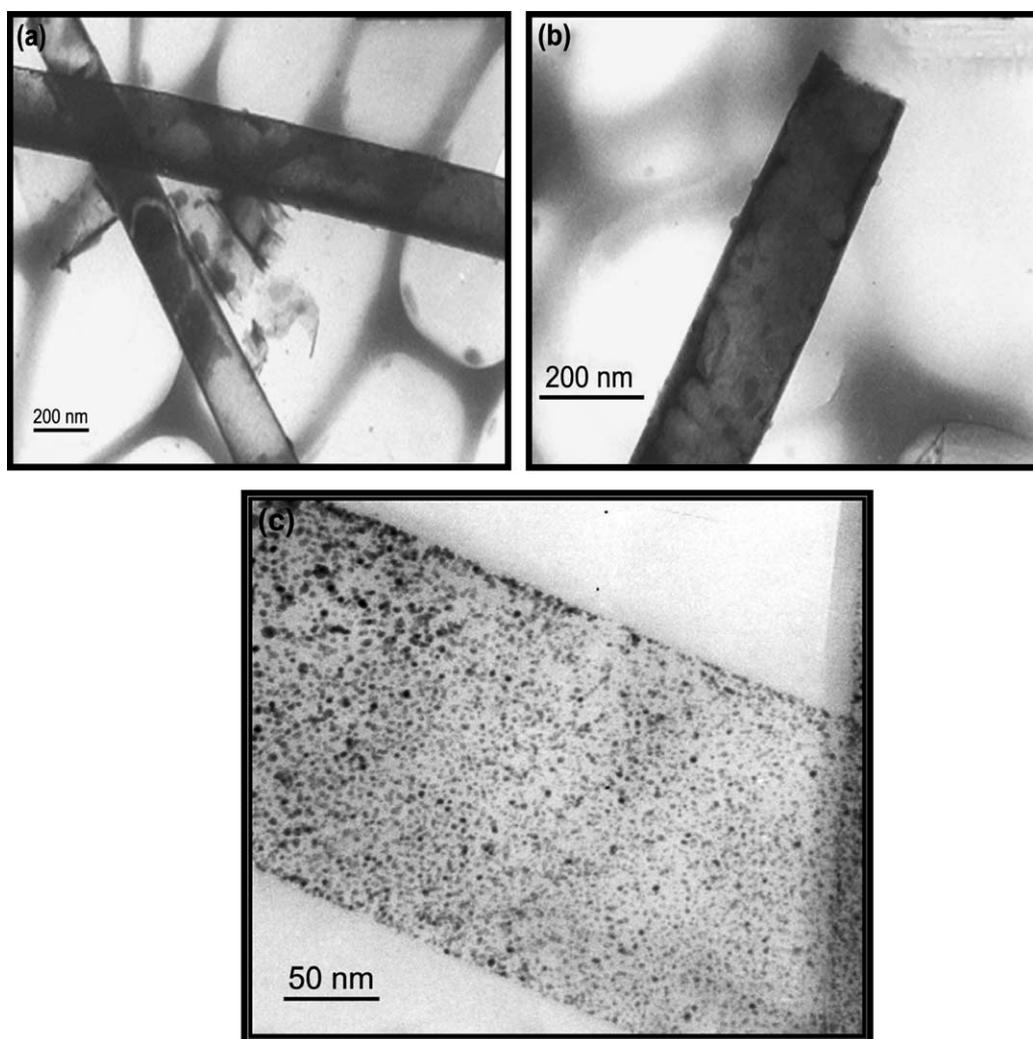


Fig. 3. TEM images of the nitrogen containing carbon nanotubes: (a) at lower magnification; (b) at higher magnification image of the individual nanotube (an arrow indicating the open end of the tube) and (c) Pt filled nitrogen containing carbon nanotubes.

particles have been homogeneously dispersed on the nanotubes and particle sizes were found to be around 3 nm. The optimal Pt particle size for reactions in the  $H_2/O_2$  fuel cell is 3 nm [30]. The importance of the Pt particle size on the activity for methanol oxidation is due to the structure sensitive nature of the reaction and the fact that particles with different sizes will have different dominant crystal planes and hence the different intercrystallite distances, which might influence methanol adsorption. The commercial Pt/C has a very high specific surface area but contributed mostly by micropores less than 1 nm and are therefore more difficult to be fully accessible. It has been reported that the mean value of particle size for 20% Pt/Vulcan (E-TEK) catalyst was 2.6 nm [31]. The EDX pattern of the as synthesized catalyst shows the presence of Pt particles in the carbon nanotubes and also the complete removal of fluorine and aluminum has also been confirmed in Fig. 4. It has been reported that the electronic and physical structures of a Pt particle deposited on carbon differ from those of the bulk Pt. The electronic change in Pt/C is considered as a result of functional groups of the carbon support that might influence the electronic structure of Pt particulate [32–36]. The nitrogen functional group on the carbon nanotubes surface intensifies the electron withdrawing effect against Pt and the decreased electron density of platinum facilitate oxidation of methanol.

Fig. 5(a)–(c) shows the cyclic voltammogram of methanol oxidation. Fig. 5(c) shows the cyclic voltammogram of Pt/N-CNT electrode in 1 M  $H_2SO_4$ /1 M  $CH_3OH$  run at a scan rate of  $50 \text{ mV s}^{-1}$ . The electrocatalytic activity of methanol oxidation at the Pt/N-CNT electrodes was evaluated and compared with that of the conventional electrodes. During the anodic scan,

the current increases quickly due to dehydrogenation of methanol followed by the oxidation of absorbed methanol residues and reaches a maximum in the potential range between 0.8 and 1.0 V vs. Ag/AgCl. In the cathodic scan, the re-oxidation of methanol is clearly observed due to the reduction of oxide of platinum. Electrocatalytic activity of methanol oxidation has been found to be strongly influenced by the metal dispersion. Pure Pt electrode shows an activity of  $0.167 \text{ mA cm}^{-2}$ . The Pt/N-CNT shows a higher activity of  $13.3 \text{ mA cm}^{-2}$  where as conventional 20% Pt/Vulcan (E-TEK) electrode shows less activity of  $1.3 \text{ mA cm}^{-2}$  compared to nitrogen containing carbon nanotube supported electrode. The nitrogen containing carbon nanotube supported electrodes shows a ten fold increase in the catalytic activity compared to the E-TEK electrode. The Pt/N-CNT electrode showed higher electrocatalytic activity for methanol oxidation than commercial Pt/Vulcan (E-TEK) electrode. The anodic current density of Pt/N-CNT electrode is found to be higher than that of Pt/Vulcan (E-TEK) electrode, which indicates that the catalyst prepared with nitrogen containing carbon nanotubes as the support has excellent catalytic activity on methanol electrooxidation.

The onset potential and the forward-scan peak current density for the different electrodes are given in Table 1. The onset potential of methanol oxidation at nitrogen containing carbon nanotube supported catalysts occurs at 0.22 V, which is relatively more negative to that of the other catalysts. This may be attributed to the high dispersion of platinum catalysts and the nitrogen functional groups on its surface. The higher electrocatalytic activity of the nitrogen containing carbon nanotube supported electrode is due to higher dispersion and a good interaction between the support and the Pt particles. The Vulcan

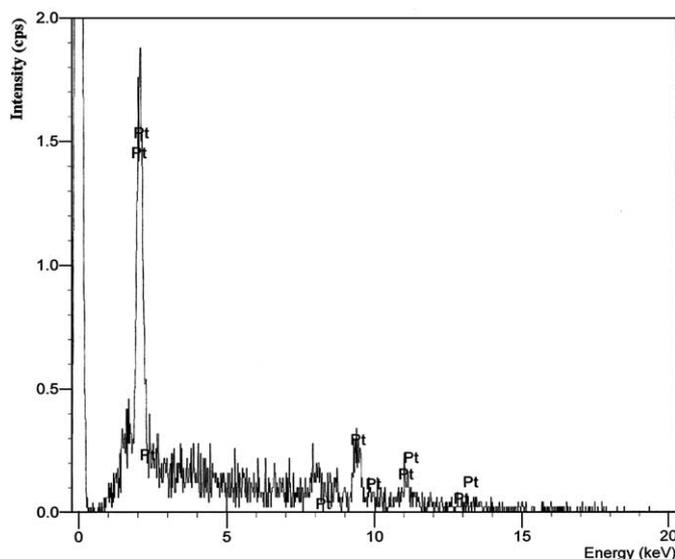


Fig. 4. EDX pattern of Pt/N-CNT electrode.

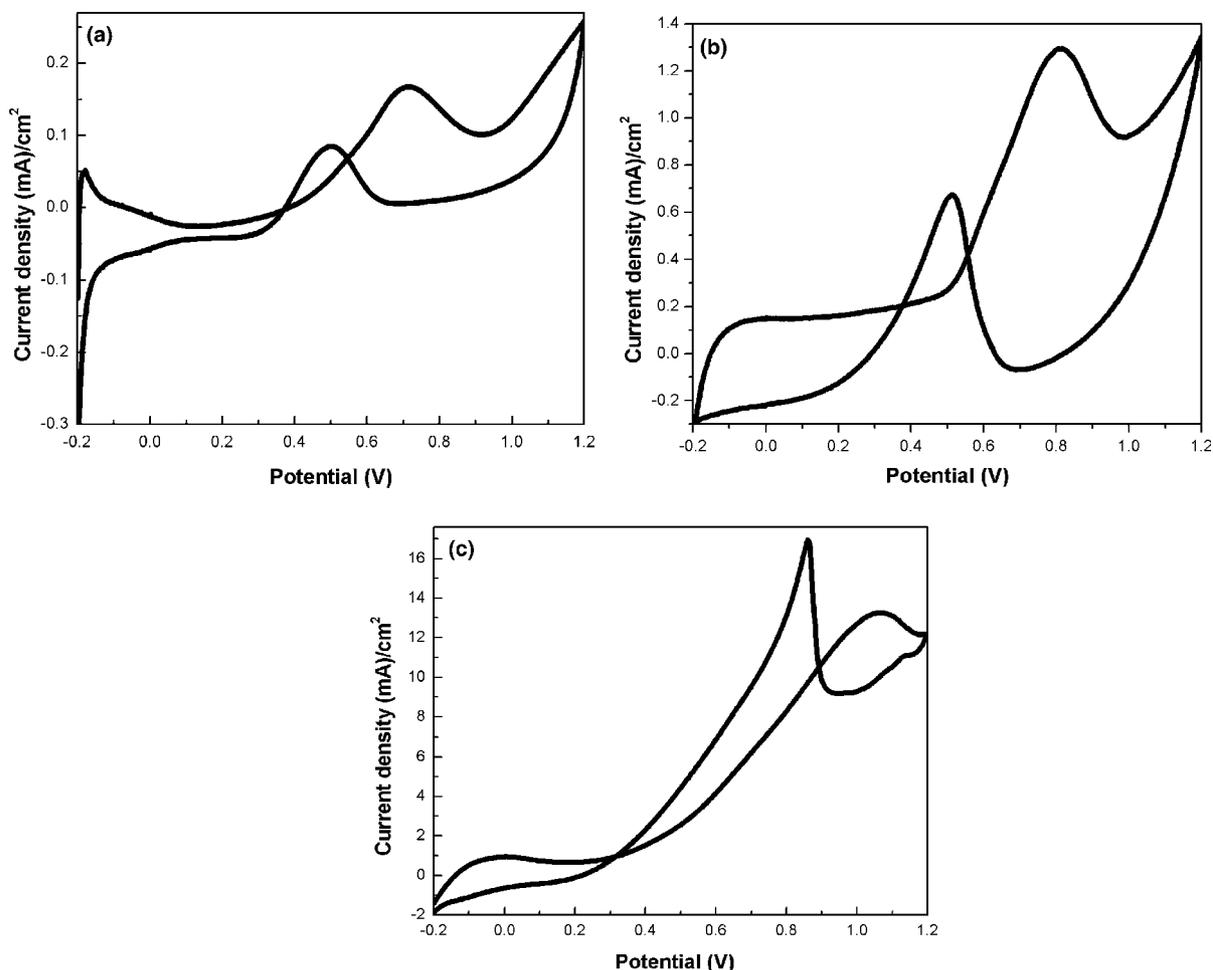


Fig. 5. Cyclic voltammograms of (a) pure Pt; (b) Pt/Vulcan (E-TEK) and (c) Pt/N-CNT in 1 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$  run at  $50 \text{ mV s}^{-1}$ .

Table 1

Electrochemical parameters for methanol oxidation on the various electrodes

Electrocatalyst	Methanol oxidation onset potential (V) vs. Ag/AgCl	Forward peak current density ( $\text{mA cm}^{-2}$ )
Bulk Pt	0.4	0.167
20% Pt/C (E-TEK)	0.45	1.3
Pt/N-CNT	0.22	13.3

carbon support has randomly distributed pores of varying sizes which may make fuel and product diffusion difficult whereas the tubular three-dimensional morphology of the nitrogen containing carbon nanotubes makes the fuel diffusion easier. The Vulcan carbon contains high levels of sulfur (ca. 5000 ppm or greater), which could potentially poison the fuel-cell electrocatalysts [37]. Nitrogen containing carbon nanotubes used in this study contains heterocyclic nitrogen so that it preferentially attaches the Pt particles. The selective attachment of Au nanoparticles on nitrogen doped carbon nanotubes has

also been reported [38]. All these results indicate that the nitrogen functionality on CNT influences the catalytic activity of the catalyst. The enhanced electrocatalytic effect of the nitrogen containing carbon nanotube supported electrodes could also be partly due to the following factors which require further investigation: (1) higher dispersion on the nitrogen containing carbon nanotube support increases the availability of an enhanced electrochemically active surface area, (2) appearance of the specific active sites at the metal-support boundary and, (3) strong metal-support interaction.

Long-term stability is important for practical applications. Fig. 6 shows the current density–time plots of various electrodes in 1 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{CH}_3\text{OH}$  at 0.6 V. The performance of Pt electrodes was found to be poor compared to the E-TEK and Pt/N-CNT electrode. The nitrogen containing carbon nanotube electrodes are the most stable for direct methanol oxidation. The increasing order of stability of various electrodes is; Pt < Pt/Vulcan (E-TEK) < Pt/N-CNT. We are currently investigating whether nitrogen has a catalytic role that contrib-

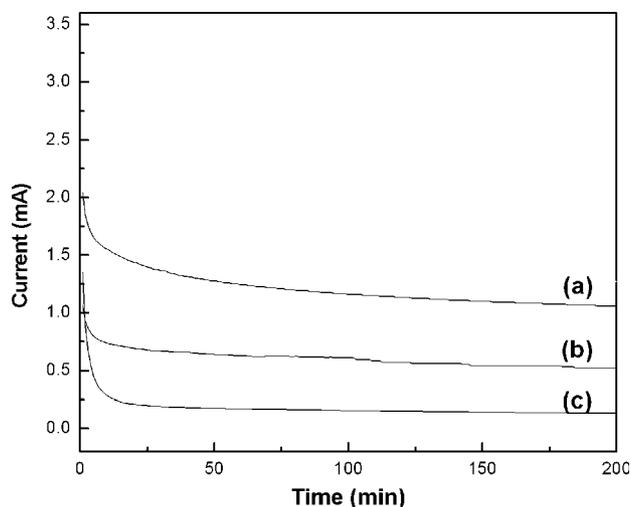


Fig. 6. Current density vs. time curves at (a) Pt/N-CNT; (b) Pt/Vulcan (E-TEK) and (c) Pt measured in 1 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$ . The potential was stepped from the rest potential to 0.6 V vs. Ag/AgCl.

utes to the observed enhancement in the methanol oxidation. Recent experiments conducted in our laboratory on Pt supported N-doped and undoped CNTs reveal the importance of nitrogen functionalities on methanol oxidation activity [39].

In summary, it is reported platinum catalysts are highly dispersed on the surface of well-aligned nitrogen containing carbon nanotube. The tubular morphology and the nitrogen functionality favour dispersion of the Pt particles. The electrocatalytic properties of Pt particles supported on the three-dimensional nitrogen containing carbon nanotube electrode shows higher catalytic activity for methanol oxidation than the commercial E-TEK electrode, which implies that the well-aligned nitrogen containing carbon nanotube arrays have good potential application as a catalyst support in direct methanol fuel cells.

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