Architecture of carbon support for Pt anodes in direct methanol fuel cells[☆]

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ABSTRACT

Instead of the conventional carbon supports for Pt, the use of supports like carbon nanotubes and carbon nanotubes containing nitrogen has been shown to give rise better activity and stability for methanol oxidation. The anchoring sites (namely the hetero atoms) disperse the Pt crystallites and also contribute to alteration of the onset potential for methanol oxidation.

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1. Introduction

Generally for fuel cell electrode applications, platinum supported on high surface area carbon is employed. The choice of the supports is connected with the possibility of dispersing the stable metal crystallites with favourable electronic and metal support interactions. The ratio of Pt to C is one of the variables which has been given consideration in these studies. In most of the studies this ratio is optimized around 0.2–0.4 mg/cm^2 or 20–40 wt.% of Pt loading [1,2]. Wang et al. [3] have reported the use of thin films of binary (Vulcan XC–72 and Black Pearl 2000) carbon supports with a loading of 0.2 mg/cm^2. This system exhibited increased utilization of surface Pt species in the combustion of the fuel. A variety of other textural carbons like carbon nanotubes (CNT) [4], nanofibres, nanohorns [5], nanocoils nanobeads and mesoporous carbons have also been employed as supports for Pt for applications as fuel cell electrodes. The objective of this study is to exploit the possible functional groups in these architectures of carbon materials to anchor stable platinum crystallites and also to generate preferentially active Pt sites on the surface of the support. For example Yoo et al. [6] have shown that the electric power derived from a fuel cell using 12 wt.% Pt on CNT as anode is higher than what was obtained from a cell employing 29 wt.% Pt on carbon black. Even though it is now known that the new forms of carbon, especially carbon nanotubes including Single walled (SWNT) [7–13] and Multiwallled (MWNT) [14–17] are promising supports for Pt for anode application in Direct Methanol Fuel Cell (DMFC), it is not yet clear why the CNT support is more suitable for Pt particles toward methanol oxidation. In addition, functionalized (especially nitrogen and sulphur containing) carbon nanotubes have been examined as supports due to the possibility of anchoring Pt crystallites and thus reducing the agglomeration of Pt crystallites and it has been shown that sulphur containing carbon nanotubes are better supports compared to the unfunctionalized carbon nanotues [18]. It is commonly believed that functionalization with hetero atoms can increase the conductivity of the material by raising the Fermi level towards the conduction band and the presence of hetero atoms generates catalytic sites which are responsible for the observed increased activity for methanol oxidation. The purpose of this presentation is therefore to examine how the utilization of Pt is increased when supported on hetero atom substituted CNT thereby reducing the amount of Pt loading as well as to examine the reasons for the increased stability of these electrode systems.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade. Polyvinyl pyrrolidone (PVP) (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

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nanotubes were synthesized by impregnating polyvinylpyrrolidone (PVP) inside the alumina membrane template and subsequent carbonization of the polymer. Polyvinylpyrrolidone (PVP – 5 g) was dissolved in dichloromethane (20 ml) and impregnated directly in the pores of the alumina template by wetting method. 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 H_2PtCl_6 (aq) (the loading of Pt is around 20%) 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 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. A typical flow chart for the synthesis of hetero atom containing CNT as well as subsequent loading of the active phase is shown in Scheme 1.

Similar procedure was adopted to prepare other electrodes namely poly(paraphenylene) (PPP), poly(vinylpyrolidone) (PVP), poly pyrrole (PPY) and poly(N-vinylimidazole) (PVI).
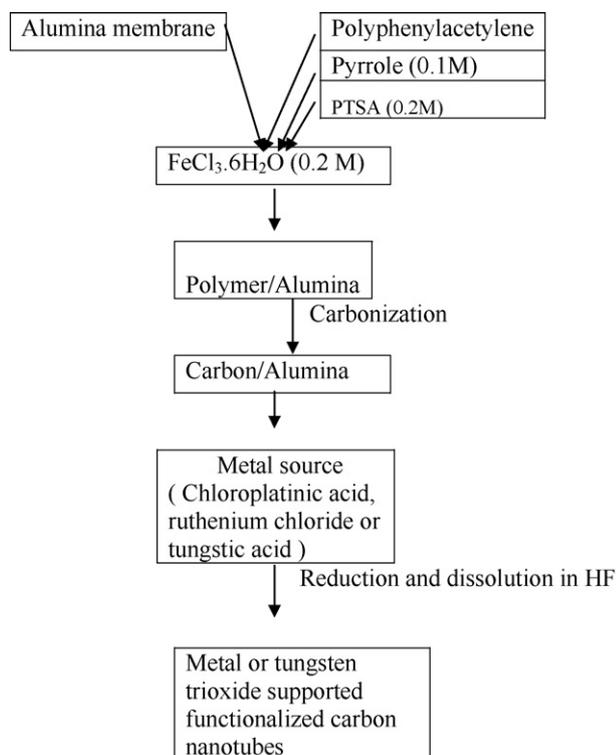
Scheme 1. A typical reaction scheme for preparing metal supported on functionalized carbon nanotubes.

2.4. Preparation of working electrode

Glassy carbon (GC) (Bas electrode, 0.07 cm²) 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 mg/ml and 20 μl 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 cm²) working electrode, Pt plate (5 cm²) as counter electrode and Ag/AgCl reference electrode were used for the cyclic voltammetry (CV) studies. The CV experiments were performed using 1 M H_2SO_4 solution in the absence and presence of 1 M CH_3OH at a scan rate of 50 mV/s. All the solutions were prepared by using ultra pure water (Millipore, 18 MΩ). The electrolytes were degassed with nitrogen gas before the electrochemical measurements.

3. Results and discussion

In order to make sure that the Pt dispersion on the carbon nanotubes are well dispersed, the electron micrographs have been recorded. Typical micrographs of metal supported carbon nanotubes obtained are shown in Fig. 1.

The results obtained for the activity in methanol oxidation using varying amounts of nitrogen in the CNT are given in Table 1. The activity data were extracted from the respective cyclic voltammograms.

The N-CNT electrodes show higher activity for methanol oxidation compared to bare C/Pt and CNT/Pt electrodes as seen from the data given in Table 1. It is seen from the data shown in Table 1 that there is an optimum content of nitrogen around 10% which gives highest activity electrode. This is a reflection of the nitrogen functionalization on the carbon nanotubes. The dispersed Pt obtained by stabilization of colloidal metal particles on N-CNT support with around 10% display high activity for the oxidation of methanol. It is therefore deduced that nitrogen functionalization influences not only the dispersion of Pt but also its inherent activity. In addition particle aggregation is not observed indicating that the surface morphology of the support also affects the dispersion of the Pt particles.

The data for comparison of activity for different CNT electrodes are given in Table 2.
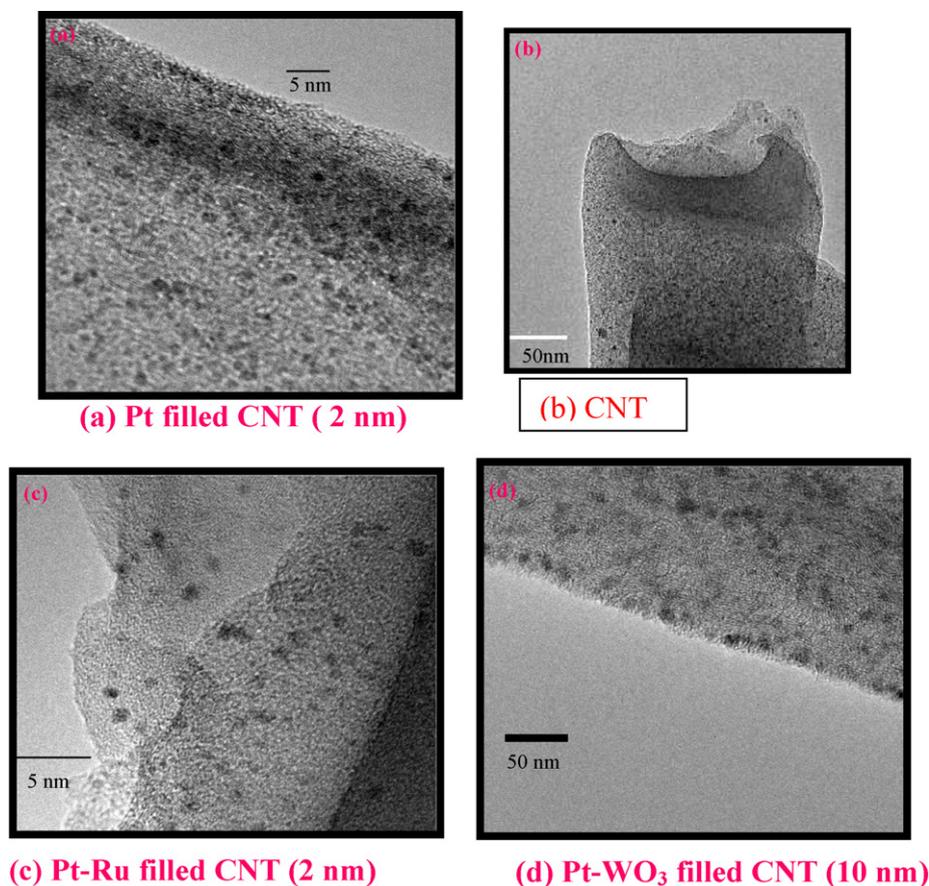
(a) Pt filled CNT (2 nm)

(b) CNT

(c) Pt-Ru filled CNT (2 nm)

(d) Pt-WO$_3$ filled CNT (10 nm)

Fig. 1. Micrographs of (a) Pt/CNT (b) CNT (c) Pt–Ru /CNT and (d) Pt–WO$_3$/CNT.

The points that emerge from the results of these studies are:

(i) The electrodes prepared using carbon nanotubes exhibit better activity for methanol oxidation compared to the commercial catalysts.

(ii) The nitrogen functionalization of the carbon nanotubes favours better dispersion of Pt and also better stability for the electrode. Typical stability plot for a chosen system is given in Fig. 2. However there is an optimum amount of nitrogen content necessary for increased activity for methanol oxida-tion. This optimum amount is around 10% as indicated above which shows that isolated nitrogen sites favour better dispersion of Pt and also controls the metal crystallite sizes.

(iii) The onset potential depends on the nature of the electrode as well as the support. This is a reflection on the reduction of over potentials and also removal of the adsorbed impurities on the electrode.

Wu et al. [19] have deduced from their impedance measure-ments that the mesoporous SWNTs are apparently more suitable

Table 1
Data of the measured activity for methanol oxidation on Pt loaded nitrogen containing carbon nanotubes

Designation of the electrode	Nitrogen content (%)	Activity (mA/cm^2)
Pt	–	0.08
GC/ETek 20%Pt/C Nafion	–	1.3
GC/CNT$_{PPP}$–Pt–Nafion	0.0	12.4
GC/CNT$_{PVP}$–Pt–Nafion	6.6	16.2
GC/CNT$_{PPY}$–Pt–Naion	10.5	21.4
GC/CNT$_{PVI}$–Pt–Nafion	16.7	18.6

Table 2
The activity for the electrochemical oxidation of methanol on different electrodes

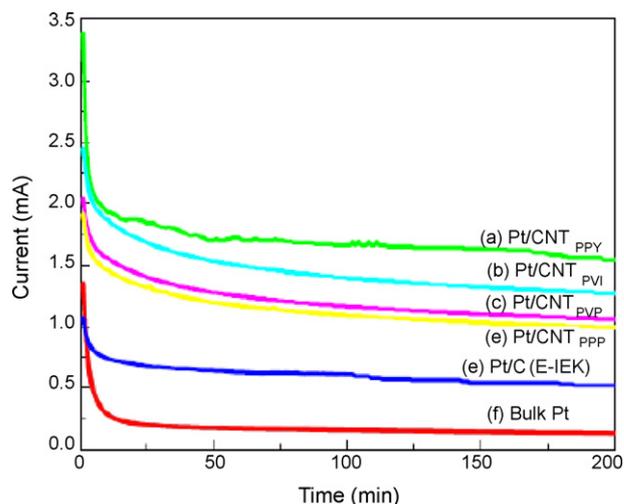| Electrode designation	Epa (V) vs Ag/AgCl	Activity (mA/cm^2)
GC/CNT/WO$_3$–Pt–Nafion	0.70	98
GC/CNT–Pt–Nafion	0.67	14
GC/ETek–20%Pt–Nafion	0.70	1.3
GC/ETek–20%Pt–Ru–Nafion	0.50	12

Fig. 2. Chronoamperogram curves for (a) Pt/N-CNT$_{PPY}$; (b) Pt/N-CNT$_{PVI}$; (c)Pt/N-CNT$_{PVP}$; (d)Pt/CNT$_{PPP}$; (e) 20 wt.% Pt/C(E-TEK); and (f) bulk Pt measured in 1 M H$_2$SO$_4$ + 1 M CH$_3$OH.

to act as a support material for electro-catalyst due to large amount of functional groups, accessibility of high surface area for electrochemical reactions and low charge transfer resistance at the interface. They have also observed that Pt is well dispersed on the CNT with a diameter of 5–10 nm. Their data on electrochemical active area probably account for the observed increase in mass activity which is nearly twice that observed on Pt/XC 72 (commercial catalyst). Kim et al. [20] have studied Pt–Ru catalyst supported on acetylene Black (66 m^2/g), MWNT (179 m^2/g), Vulcan XC 72 (250 m^2/g), Ketjen Black (845 m^2/g) and Black Pearl 2000 (2221 m^2/g). They have also observed difference in activities for methanol oxidation in single cell mode. However their results could not establish the advantages of other carbon supports as compared to that of XC-72. Yoo et al. [6] raise the question why does CNT show good performance as a support material. According to them, the chemical differences between CNT and carbon black induce flat disposition for Pt on the surface of CNT. This configuration of the Pt crystallite leads to a decrease in the adsorption energy of hydrogen as deduced from TPD measurements. Their contention is that the decrease in the adsorption energy can be due to lowering of the d band center induced by the reduction of the Pt lattice constant. However the alteration of the d band centre need not be only due to the variation in the lattice constant but also arises from the charge transfer from the anchoring sites of Pt.

Even though the changes in the electronic properties may be responsible for the electrochemical reaction, it does not however account for the dispersion and stability of the Pt crystallites. The architecture of the carbon nanotubes can give rise to specific sites (edge sites) where the Pt crystallites are anchored and these sites may be more active than the conventional sites obtainable in carbon black. Essentially carbon black may be presenting equi-potential sites and hence almost all Pt sites will be equally moderately active while tubular morphology of carbon nanotubes can provide specific active sites for anchoring Pt crystallites and hence the activity of the resulting system can be different from what is obtainable in conventional carbon black support. Secondly when the hetero atoms are substituted in the carbon nanotubes, it provides additional anchoring sites for Pt crystallites and these crystallites may be stable by virtue of their anchoring and restricts migration and agglomeration.

The change in the onset potential of the oxidation reaction is a common observation in these experiments. This alteration can be due to any of the following factors:

(i) Since the sites are specific, the adsorption of the substrate will be different from the conventional sites and hence the onset potential can change. This can be in both directions depending on what type of metallic sites is formed on the surface and how the substrate molecule is activated on the surface site.

(ii) The electronic property of the crystallite may be altered depending on the nature of anchoring and this can result in a change in redox behaviour of the crystallite. This has been viewed as though the alteration of the Fermi level of the metallic crystallites stem from charge transfer from the support or due to metal support interaction. Essentially, the electronic effect in metal support interaction is usually viewed from the possibility of the charge transfer from the support or the active metallic species depending on the relative positions of the HOMO states in these systems.

(iii) The changes in the wave functions of the metallic crystallite though may also account for the changes in nature of adsorption, can also alter the over potentials for the process and thus can result in the changes on the on set potential of the process.

4. Conclusion

The present study has demonstrated that nitrogen containing carbon nanotubes are better supports for the oxidation of methanol since they could sustain better dispersion of Pt crystallites and also prevent the agglomeration of the Pt particles. It is also necessary that the magnitude and direction of the changes in the onset potential have to be precisely and properly accounted for to understand the process of electron transfer at the electrode/electrolyte interface. These changes in the onset potential reflecting changes in over potential arise due to metal support interaction with the hetero atoms in the support.

Acknowledgement

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