# Electrocatalytic Properties of Carbon Nanofiber Web– Supported Nanocrystalline Pt Catalyst as Applied to Direct Methanol Fuel Cell

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Carbon nanofibers (CNFs) web supported platinium nanoparticles were prepared by an electrochemical deposition method at sweep times of 5, 10, 20 and 40. Structure, composition and surface morphology of Pt incorporated CNF were analyzed by using X-ray diffraction (XRD), Energy dispersive x-ray spectroscopy (EDX), Field emission scanning electron microscopy (FE-SEM) and High resolution transmission electron microscopy (HR-TEM) techniques. Structural analysis by XRD showed face centered cubic crystal structure of Pt. Particle size and loading level (wt%) of Pt were found to increase from 10.7 to 18.6 nm and 3.3 to 7.0 6%, respectively with the increase of sweep times. SEM images showed that the Pt nano particles were agglomerated and effectively adhered on CNF with increase of sweep times. Nanocrystalline Pt and its FCC structure were also confirmed by using HR-TEM. Electrocatalytic activity of the nano Pt/CNF composite was demonstrated by linear voltammetry, cyclic voltammetry and impedance spectra. The results showed increment in catalytic activity with the increase of sweep time.

Keywords: Nanocrystalline Pt catalysts, CNF; catalytic activity; cathodic electrodeposition

# **1. INTRODUCTION**

The direct methanol fuel cell (DMFC) is considered as a promising power source for the nextgeneration portable electronic devices, owing to its high energy density, green emission, convenient refueling of liquid fuel and ambient operation conditions[1-3]. Unlike the other types of fuel cell, the DMFC needs no fuel processor to reform hydrocarbon fuels. It makes DMFC advantageous for application to the small and portable devices. For the conversion of chemical energy into electricity, DMFCs require the development of better catalysts to improve the cell performance. Considerable interest has been devoted in recent years [1-7] to develop suitable electrode materials for methanol oxidation for the possible application in DMFC. In general, Pt or its alloy based nanocluster impregnated carbon supports are the best electrocatalysts for anodic and cathodic reaction of fuel cells. Pt, the standard catalyst for the oxidation of small organic molecules including methanol, is rather active for the dehydrogenation step. One of the major problems for the efficient conversion of methanol fuel to electric current in a DMFC is the slow methanol oxidation kinetics on the anode catalyst. This is mostly due to self-poisoning of the surface by reaction intermediates such as CO, which are formed during stepwise dehydrogenation of methanol [8-10]. Therefore, methanol oxidation on Pt is possible only at potentials where adsorbed CO and other poisoning intermediates are effectively oxidized, leading to a significant over potential and loss in efficiency. This problem necessitates the search for Pt based catalysts.

Due to the scarcity and high costs of the noble metals used as catalysts, it is necessary to extend and enhance their catalytic performance by depositing them homogeneously on different supports in order to obtain an extensive and highly active surface [11, 12]. For example, surfaces covered with Pt nanoparticles have proved to be valuable catalysts for hydrogenation reactions showing also higher reactivity for C–H bonds activation in CH<sub>4</sub> when compared to other noble metals (e.g. Rh, Ru and Ir) for a given cluster size [10]. Thus, Pt has become an important component of automotive catalytic converters that reduce the emission of toxic pollutants such as CO, NO<sub>x</sub> and other hydrocarbons [13]. Development of more active and durable anode catalyst becomes one of the major issues towards the realization of DMFC. In order to improve the catalyst performance, many studies have been done on the electro-oxidation of methanol [14-17]. To date, nanocrystalline Pt remain as the most active catalysts for the reaction [18-19] due to its large surface area in the nanometric regime that favors electrocatalytic behavior.

Electrocatalysts adopting nanostructured carbon supports exhibited promising catalytic activities toward the oxygen reduction and methanol oxidation reactions, which were attributed to the unique structural features of the nano carbons, such as highly conductive framework structures, periodic pore structures in the meso porous or macro porous regime and high surface to volume ratio. Since attempts to improve the activity of an anode catalyst without Pt group elements has not been highly successful, the development of the nanocrystalline Pt-catalyst supported on various carbons are interesting. Different types of carbon materials have been used to prepare new carbon-supported catalysts for low-temperature fuel cells, such as graphitic nanofibers [20], carbon nanotubes (CNTs) [21-26], carbon nanofibers [27,28] and carbon nanocoils [29] in order to have high catalyst dispersion and synergic effects. The Pt-based catalyst supported on carbon nano fibers is the general anode catalyst for DMFC [30]. It is well known that the particle size and the distribution of Pt-based catalysts are key factors that determine their oxygen reduction reaction activity and cell performance for DMFCs. The electrochemical activity of CNF supported Pt catalysts depends on the size and dispersion uniformity. Synthesis of highly dispersed Pt catalysts with uniform size and morphology still remains a challenge for high performance catalysts. The CNF supports provide a mechanical support and an electronic continuity as well as a uniform dispersion of the Pt catalysts. They were found to be excellent catalyst supports, which significantly increase the performance of methanol oxidation in DMFC. Carbon supported Pt like noble metal nanoparticles are key fundamental materials used as the electrode catalysts in DMFCs. The ideal carbon support should possess good electron conduction, favorable macro/meso-pore structure for reactant-product mass transportation, high surface area and strong interaction with metal nanoparticles to allow a high dispersion of the latter.

Therefore, in this study, nanocrystalline Pt, a noble metal, was supported on carbon nanofibers. To improve the activity of the CNF supported nanocrystalline Pt catalyst and study its performance, Pt was incorporated onto CNF web using cathodic eletrochemical deposition technique under different sweep times. The influence of size, concentration and distribution of Pt nanoparticles on electrocatalytic activity was investigated by means of linear voltammetry, cyclic voltammatry and impedance spectroscopy.

## 2. EXPERIMENTAL PART

A beaker-type electrochemical half-cell equipped with the working electrode, a platinum Pt foil  $(2 \times 2 \text{ cm})$  counter electrode and an Ag/AgCl (3M KCl, 0.196V versus SCE, Metrohm) reference electrode was used for all electrochemical measurements. All potentials throughout this paper are referred to the reference Ag/AgCl electrode scale.

# 2.1. Preparation of CNF web-supported Pt nanoparticles

CNF-supported Pt catalysts were prepared by electrochemical potential sweep methods. Carbon nanofiber web, which was supplied by Amotec Co.(Korea) have a diameter of 100-125 nm and a length of 5-50 micro meters, resulting in a large aspect ratio. The CNF webs were mounted onto glassy carbon substrate with the help of 0.1% Naflon solution. A 10 mM hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) was dissolved in 0.5M HCl aqueous solution. A potential was swept from -0.7 to -0.2 V (versus Ag/AgCl) with a scan rate of 20 mV/s at four various sweep times such as 5, 10, 20 and 40 for the deposition of Pt nanocrystalline particles over CNF webs. After the deposition, Pt supported CNF webs were separated from glassy carbon substrate and then used for further characterizations.

## 2.2. Characterization of CNF-supported Pt nanoparticles

These CNF supported Pt nanoparticles were characterized by various techniques in order to analyze microstructure, composition and morphology of Pt particles over CNF web with the increase of sweep time. Powdered X-ray diffraction technique (XRD-Rigaku, D/MAX 2500H) was recorded using a Cu*Ka* source radiation. The diffractometer was operated in the step scan mode with a step of 0.02 and in the  $2\Theta$  range of  $10^{\circ}$ – $90^{\circ}$ . Pt content was estimated by using energy dispersive x-ray spectroscopy. FE-SEM (JEOL, JSM-6300) and HR-TEM data were used to determine the active site distribution, particle size and morphology of the nano Pt catalysts. To prepare the TEM sample, a small amount of catalyst was ultrasonically dispersed in ethanol. A drop of such suspension was dropped onto a 200 mesh Cu grid with holey carbon film and then dried in air completely.

## 2.3. Electrochemical measurements of CNF web supported Pt nanoparticles

Linear sweep voltammetry for the sample prepared above was studied by changing the potential linearly from 0.4 to 1.1 V in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.5M CH<sub>3</sub>OH with a scan rate of 20 mVs<sup>-1</sup>. Impedance analysis for Pt catalysts were studied in the frequency range of 1 MHz to 0.01 Hz in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.5M CH<sub>3</sub>OH. Cyclic voltammograms of all the Pt-CNF catalysts were obtained in 0.5M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mVs<sup>-1</sup>.



**Figure 1.** X-ray diffraction patterns of (b) bare CNF and nanocrystalline Pt incorporated CNF at a sweep time of (b) 5, (c) 10, (d) 20 and (e) 40.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Structure and composition

The structure and composition of metal nanoparticles on carbon nanofiber supports are very important because they have a great effect on its catalytic activity. X-ray diffraction patterns of bare CNF web and Pt nanoparticles coated CNF webs under different sweep times are shown in Fig.1. The results clearly showed amorphous behavior for the bare CNF with a broad peak at 23° corresponds to the (002) planes of graphitized CNF. Upon Pt incorporation, the crystallinity was found to be increased. In the case of small sweep time of 5, two minute peaks were observed at 39.75° and 46.27° along (111) and (200) crystallographic directions. This shows the growth of Pt particles over CNF web. Upon increase of sweep time from 5 to 10, the intensity of these peaks was found to increase. In addition to these two peaks, three peaks were also observed at 67.64°, 81.47° and 85.8° along (220), (311) and (222), respectively. Subsequent increment in sweep time leads to the increase in intensity of these peaks. All the four peaks were similar to the results obtained by Yanhui Xu et al [31] for Pt

particles grown on MWCNTs that crystallize in face centered cubic (FCC) structure. The intensity of diffraction peaks corresponding to Pt was noticed to increase with successive sweep times such as 5, 10, 20 and 40. It clearly showed the augmentation of Pt content with sweep time. Lattice parameter values along (111) and (200) crystallographic directions were calculated as 3.9Å by using the relation [32],  $a = d(h^2 + k^2 + l^2)^{1/2}$ , where 'a' is lattice parameter, d interplanar spacing and h, k and 1 are miller indices. This value is similar to the already reported value. The average size of Pt particles was calculated by using a Scherrer equation [32],  $d = (0.94 \times \lambda)/(\beta \times \cos \theta)$ , where,  $\beta$  is *FWHM* ×( $\pi/180$ ), d particle size,  $\lambda$  wavelength of the X-ray used and FWHM is the full width at half maximum of the diffraction peak. The calculated values of particle size are given in Table 1. The average size of Pt increased from 10.2 to 18.66 nm gradually by changing the sweep times of electrochemical deposition from 5 to 40. The increment in grain size of Pt clearly suggests the aggregation of Pt nanoparticle with increase of sweep times. From this result, it is concluded that the particle size can be changed by controlling the condition of electrochemical deposition.

**Table 1.** Average Pt particle size (D) calculated from XRD and Pt loading (wt%) obtained from EDS spectra as a function of sweep times

Sample	Particle size (nm)	Pt loading* (wt%)
Pt 5	10.22	15.56
Pt 10	12.21	28.41
Pt 20	14.86	43.99
Pt 40	18.66	63.36



\*Pt loading: Weight percentage of Pt alloy to CNF

Figure 2. EDS spectra of Pt incorporated CNF at a sweep time of (a) 5 and (b) 40

Composition analysis was done by using EDS for CNF supported Pt particles deposited under sweep times of 5, 10, 20 and 40. Figs.2(a,b) shows the EDS spectra of CNF supported Pt particles deposited under the sweep time of 5 and 40. The obtained spectra clearly showed the presence of carbon and Platinum. A strong signal of Pt was observed for larger sweep time. On the other hand, a small signal of Pt was noticed for the sweep time of 5. The obtained values of loading level of Pt are given in Table 1 and it shows an increase of Pt loading from 15.56 to 63.36 (wt%) with an increase of sweep time from 5 to 40.



**Figure 3.** SEM images of (a) uncovered and Pt incorporated CNF prepared by potential sweep method as a function of sweep times of (b) 5, (c) 20 and (d) 40.

## 3.2. Morphological analysis

Morphology of the bare CNF and Pt incorporated CNF at different sweep times such as 5, 10, 20 and 40 were investistigated by using SEM analysis in the magnification of x2 K and the images are shown in Fig 3(a-e). SEM image of bare CNF showed horizontally aligned nanofibers. For the short sweep time of 5, Pt nano particles were found to adhere on nanofibers in anisotropic manner. For the

sweep time of 10, the particle size was found to increased and distributed isotropically. Subsequent increase in sweep time enhanced Pt deposition over CNF and covers the entire CNF web for the sweep time of 40. The images clearly showed that the particles adhered onto CNF very well with improvement in Pt incorporation and agglomeration.



**Figure 4.** HRTEM images of CNF supported Pt catalyst prepared by potential sweep method at a sweep time of 40.

For the particle size measurements of Pt particles, TEM and electron diffraction studies were carried out for CNF-Pt catalyst deposited at the higher sweep time of 40. Fig. 4a. shows the TEM image of Pt nanoparticles deposited on CNF web prepared by electrochemical deposition. It clearly showed particles in the range of 10-15 nm were successfully deposited and well-dispersed on CNF surface. The appearance and population of particles are plenty due to the high Pt loading. Transmission electron diffraction pattern is shown in Fig. 4b. The crystal lattice fringes of Pt is revealed as the lattice planes of (111), (200), (220), (311) and (222) with the lattice spacing about 0.251, 0.216, 0.152, 0.129 and 0.123 nm. The lattice spacing (d<sub>hkl</sub>) were calculated for Pt nano particles using TEM analysis and are nearly equal to the reported values in JCPDS data [33]. Therefore, the prepared Pt nanoparticle catalysts have been again proved to be of face centered cubic structure with the major planes of (111), (200), (220), (311) and (222) which is in accordance with the XRD pattern shown in Fig. 1.

## 3.3. Electrochemical measurements

The electro catalytic activity of nano Pt supported CNF by linear sweep voltammograms was measured by varying the potential from 0.4 to 1.1 V and the obtained results are shown in Fig 5. The tendency of current density showed increasing manner with sweep times. The observed values of peak potentials and current density are given in Table 2. It is clear that the anodic peaks of methanol

oxidation clearly seen for Pt incorporated CNF showing the influence of nano Pt catalyst particles. On the other hand, in the case of bare CNF, a depressed and wide peak was noticed. The current density of anodic peaks of Pt incorporated CNF was found to increase from 0.08 to 1.8 mA/cm<sup>2</sup> by increasing sweep times from 5 to 40. This indicates that the electrocatalytic activity increased with sweep times due to the improvement in Pt incorporation and electrical conduction between nano Pt and CNF network.



**Figure 5.** Linear sweep voltammograms of methonal electrooxidation on Pt-CNF electrode prepared by potential sweep method as a function of sweep times of (a) 5, (b) 10, (c) 20, and (d) 40. Measurements were performed in  $0.5M H_2SO_4 + 0.5M CH_3OH$  with a scan rate of  $10mVs^{-1}$ .

Table 2. Peak parameters obtained from linear cyclic voltammograms at different sweep times

Sample	Peak potential (mV)	Peak current density (mA/cm2)
Pt5	0.600	0.13
Pt10	0.607	1.08
Pt20	0.655	1.19
Pt40	0.666	1.71

Fig. 6(a). shows impedance plots of CNF supported Pt nano catalysts deposited at different sweep times in  $0.5M H_2SO_4 + 0.5M CH_3OH$ . These plots were obtained by changing the frequency from 1 MHz to 0.1 Hz. The plots show a depressed semi-circle part in the low frequency region and a linear line part in the high frequency region. The bulk resistance is obtained by taking into account the real part of impedence at x-axis intercept and they are described in Fig. 6b as a function of sweep times. With an increase in sweep time from 5 to 40, the resistance was decreased from 9.8 to 4.14 ohm

cm<sup>2</sup>. The change in resistance with sweep times showed a similar trend with the increment in current density of anodic peak as observed in linear voltammograms. It suggests that the resistance is largely decreased by the improved electrical conduction between Pt particles and CNFs supports due to the enhanced Pt incorporation and adhesion onto the surface of CNFs.



Figure 6(a). Impedance plots of Pt catalysts prepared by potential sweep method as a function of sweep times of (a) 5, (b) 10, (c) 20 and (d) 40.



Figure 6(b). Bulk resistance of Pt catalysts prepared by potential sweep method as a function of sweep times.



**Figure 7.** Cyclic voltammograms of (a) uncovered CNF web and Pt incorporated CNF web at a sweep time of (b) 5 (b) 10 (c) 20 and (d) 40. Measurements were performed in  $0.5M H_2SO_4$  (without methanol) at a scan rate of 50 mV/s.

To analyze the electro catalyst effect of catalyst particles deposited under different sweep times, cyclic voltammogram of CNF supported Pt nanoparticles were performed in 1.0M sulphuric acid solution (in the absence of methanol). It was scanned between -3 V to 5 V and run at 50 mVs<sup>-1</sup> as shown in Fig 7. Upon comparing the obtained plots, it is clear that the Pt incorporated CNF has better electrocatalytic response than the bare CNF. In addition, the catalytic activity was found to increase with increase of sweep time. It is noted that for low sweep times of 5, 10 and 20, the  $H_2$ absorption/desorption peaks are mild. In the case of large sweep time of 40, three obvious peaks that correspond to hydrogen absorption/desorption were observed. This suggests that the redox couple undergoes three sequential electronic transfers for the sweep time of 40. On the other hand, in the case of lower sweep times, both the reduced or oxidized species shall be unstable and that results in the mild absorption/desorption peaks. These observations clearly showed that the Pt nanoparticles deposited under a sweep time of 40 has electro catalytic activity much effective than that deposited under lower sweep times. This indicated that the catalytic activity is dependent on particle size and concentration. It means that the agglomeration of Pt nanoparticles into nanoclusters with increment of sweep time did not decline the catalytic activity of CNF-Pt nano catalyst. It clearly indicates that the nanocrystalline Pt and loading under the sweep time of 40 had favored catalytic activity of Pt-CNF. This means that the distribution of Pt nano particles and large surface to volume ratio has enhanced the electrocatalytic activity. It is also believed that the further increment in sweep time and hence the consequence agglomeration of nanoparticles shall diminish the catalytic activity of Pt nanoparticles caused by the decrease in surface to volume ratio.

# 4. CONCLUSIONS

In summary, we have reported here a successful way to deposit nanocrystaline Pt particles on CNF surface with high dispersion and effective adhesion by using cathodic electro chemical deposition method at sweep times of 5, 10, 20 and 40. Nanocrystalline Pt and its face centered cubic crystal structure were confirmed by using XRD and HRTEM analysis. The average size and loading level of Pt particles were found to increase gradually with increase of potential sweep times. The electroactivity of Pt catalyst electrode showed a highest performance at a sweep time of 40. This showed that the distribution, adhesion and electrical conduction of Pt on CNF web were improved with increase of sweep time. From these results, it was concluded that the agglomeration of nanoparticles into nanoclusters did not decline the electro catalytic behavior of Pt supported CNF web. Further investigations are under research, which aims to improve the electrocatalytic activity by means of using Pt binary based alloys as catalyst on CNF network.

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