Synthesis and Electrochemical Characterization of Uniformly-Dispersed High Loading Pt Nanoparticles on Sonochemically-Treated Carbon Nanotubes

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A sonochemical process was developed to treat carbon nanotubes in nitric and sulfuric acids to create surface functional groups for metal nanoparticle deposition. Carbon nanotubes treated in the sonochemical process are shown to lead to the deposition of uniformly dispersed high loading Pt nanoparticles, which have not been achieved with carbon nanotubes treated in reflux processes. Pt nanoparticles of a size less than 5 nm and loading up to 30 wt % with little aggregation were synthesized on the sonochemically treated carbon nanotubes. Cyclic voltammetry measurements in 1.0 M H_2SO_4 showed that the Pt nanoparticles on carbon nanotubes are more than 100% active in the electrochemical adsorption and desorption of hydrogen than the Pt nanoparticles supported on carbon black. This enhancement of electrochemical activity is attributed to the unique structures of carbon nanotubes and the interactions between the Pt nanoparticles and the carbon nanotube support. The ability to synthesize high loading Pt on carbon nanotubes using the sonochemical technique makes it possible to prepare high loading catalysts for the cathode of polymer electrolyte membrane (PEM) fuel cells.

Introduction

Since their discovery, carbon nanotubes have attracted much attention due to their extraordinary electrical, mechanical, and structural properties.[1] In recent years there has been increasing interest in carbon nanotubes as heterogeneous catalyst support. Studies have shown that metal nanoparticles supported on carbon nanotubes may provide much improved catalytic activity.[2] Planeix et al.[3] have shown that Ru nanoparticles deposited on multiwalled carbon nanotubes (MWNTs) have more than 100% increase in product selectivity in the hydrogenation of cinnamaldehyde as compared to the Ru nanoparticles supported on active carbon;[4] Li et al.[5] have shown that Pt nanoparticles supported on carbon nanotubes produced a much higher maximum power density (ca. 47%) than those supported on carbon black in direct methanol fuel cells.

To prepare high-quality supported metal catalysts, one must be able to deposit dispersed metal particles, preferably with sizes in the nanometer range, on carbon nanotubes. Deposition of Ru nanoparticles on MWNTs has been achieved with a physical adsorption technique,[3] in which Ru salt precursor was impregnated in carbon nanotubes and then was reduced to metallic Ru nanoparticles. This technique can produce fairly uniform nanoparticles with a mean size of 3.5 nm and a metal loading of 0.2 wt %. Direct chemical reduction of Au, Pt, and Ag salts was investigated by refluxing metal precursors with MWNTs in nitric acid.[6] The resulting metal nanoparticles have a mean size in the range 1−10 nm and metal loadings less than 10 wt %. An improved technique was later developed and involves refluxing carbon nanotubes in nitric and sulfuric acids to create surface functional groups, such as carboxylic (−COOH), carbonyl (−CO), and hydroxylic (−COH). The treated carbon nanotubes were then used for nanoparticle deposition by reducing metal precursors in ethylene glycol solutions.[7−9] Several workers have reported deposition of Pt, Ru, and alloy

PtRu nanoparticles based on this improved technique,[5,10,11] and nanoparticles of 1−10 nm with metal loading generally less than 10 wt % have been obtained.

Despite the previous studies, highly dispersed high loading metal nanoparticles on carbon nanotubes have not been achieved or reported. Although the physical adsorption technique can produce relatively uniform Ru nanoparticles, the metal loading is low. The direct chemical reduction technique can increase metal loadings by almost 50-folds, but the nanoparticles are not uniform. The improved technique using refluxed carbon nanotubes also failed to produce highly dispersed nanoparticles.[5,6,9,11] Furthermore, efforts to make high Pt loading did not obtain satisfactory results because when high nanoparticle loading (67.3 wt %) was achieved, the Pt nanoparticles were seen to exist in large aggregates rather than uniformly dispersed on carbon nanotubes.[11]

In this paper, we report a sonochemical process that was developed to treat carbon nanotubes in nitric and sulfuric acids to create surface functional groups for metal nanoparticle deposition. It is shown that the sonochemically treated carbon nanotubes can lead to the deposition of uniformly dispersed high loading Pt nanoparticles. The Pt nanoparticles on carbon nanotubes are shown to have much higher catalyst activity than the Pt nanoparticles supported on carbon black. The ability to synthesize high loading Pt nanoparticles on carbon nanotubes makes it possible to prepare catalyst for the cathode of PEM fuel cells, which often needs much higher Pt loading than the anode.[12]

Experimental Methods

Sonochemical Treatment of Multiwalled Carbon Nanotubes. In a typical experiment, the surface treatment process is as follows. MWNTs (10.0 mg, 95% purity from NanoLab) were weighed and placed in a 25 mL Pyrex glass flask; 9.4 mL of HNO_3 (69%), 8.0 mL of H_2SO_4 (96.2%), and 0.6 mL of deionized H_2O were added to the flask. This makes an acidic
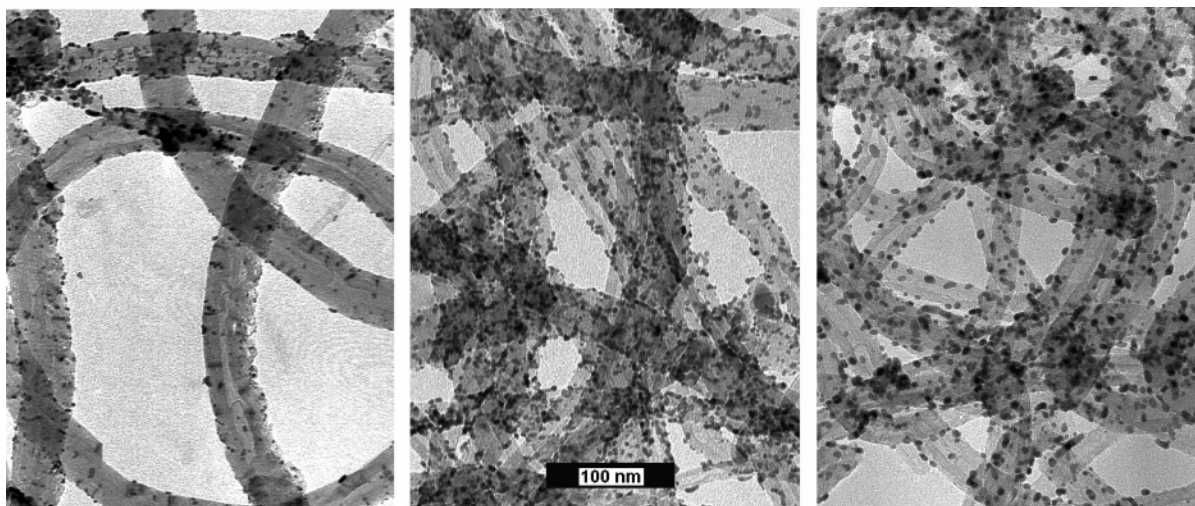
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Figure 1. TEM images of Pt nanoparticles deposited on the sonochemically treated carbon nanotubes with Pt loading of 10, 20, and 30 wt %, respectively, from left to right. The scale bar in the middle image is applied to all images.

solution of 8.0 M HNO_3 and 8.0 M H_2SO_4 with a total volume of about 18.0 mL. The solution, with the as-purchased carbon nanotubes in it, was first stirred using a vortex mixer (Vortex Gene 2, Scientific Industries) for about 1 min, and then was put in a laboratory ultrasonic bath (Fisher Scientific, 130 W and 40 kHz) for 5 min to allow dispersion of the carbon nanotubes. This mixing and dispersion process was repeated twice to break big carbon nanotube aggregates. The flask was then put in the ultrasonic bath, and the bath temperature was raised to 60 °C and remained the same throughout the treatment experiment. The treatment process lasted for 2 h. After the surface treatment, the carbon nanotubes were separated from the acids in a centrifuge (Thermal Dec, CL 2.0) at 4500 rpm and washed with 15.0 mL of deionized water five times. The sonochemically treated carbon nanotubes were then ready for use in the deposition of Pt nanoparticles.

Deposition of Pt Nanoparticles on Multiwalled Carbon Nanotubes. Deposition of Pt nanoparticles on MWNTs was achieved by reducing the Pt salt precursor, K_2PtCl_4, in an ethylene glycol−water solution.[5,8] In a typical experiment, the sonochemically treated carbon nanotubes were put in a 25 mL flask. A 15.0 mL aliquot of ethylene glycol−water solution (2:1 volume ratio) was added to the flask. The metal precursor is a 0.01 M aqueous solution, and depending on the desirable nanoparticle loading, an appropriate amount of the precursor was added to the flask using a pipet. The flask was then put on a hot plate with magnetic stirring. The reduction reactions were performed under reflux conditions (ca. 125 °C) for 2 h. The carbon nanotubes with Pt nanoparticles on them were then separated from the ethylene glycol solution in the centrifuge and washed with deionized water five times. Two hours was long enough to reduce all Pt precursors on the carbon nanotubes, as inductively coupled plasma−mass spectroscopy results showed a negligible amount Pt left in solutions after the reduction reaction. Thus, a catalyst, i.e., Pt nanoparticles supported on MWNTs, with a desirable metal loading is obtained and is ready for physical property and electrochemical characterization.

Catalyst Characterization. Characterization of the obtained catalysts was achieved using a transmission electron microscope (TEM) (EM 430, Philips) operating at 300 kV. The TEM grid preparation is as follows. A small amount of the catalyst was dispersed in ethanol, and a drop of the dispersion was taken using a pipet and put on a TEM grid. The TEM grid was a 400-mesh carbon-coated copper grid (Electron Microcopy

Sciences). The drop on the grid was allowed to dry under open atmosphere. The catalyst was then examined with the TEM and images of the Pt nanoparticles supported on MWNTs were taken. The size of the Pt nanoparticles was measured from the TEM images using image analysis software (Scion). A total of 450 to 500 nanoparticles was counted to ensure statistically representative of the nanoparticle size.

To prepare samples for X-ray diffraction (XRD) (Scintag 2000), a certain amount (∼5 mg) of the catalysts was dried in a vacuum furnace at 70 °C. The dried catalyst powder was pressed onto one side of double-sided Scotch tape on a piece of glass slide. Scanning of the catalyst samples was performed at 0.015°/s to ensure obtaining fine crystalline structures of the Pt nanoparticles.

Electrochemical Measurements. Cyclic voltammetry was used to study the electrochemical properties of the catalysts. A thin film electrode technique was used to make the measurements. This technique was previously developed to characterize high surface area electrocatalysts.[13] Specifically, glassy carbon disks (3 mm in diameter) were used as the substrate, on which 20 μL of a paste of the catalyst was applied. The paste is a water−ethanol (3:2 volume ratio) solution in which a known amount of the catalyst is dispersed. After the paste dried in a vacuum furnace, a drop of 5 wt % Nafion in water solution (Alfa Aethar) was spread on the catalyst and allowed to dry. A recast ionomer thin film covering the catalyst was thus obtained.

The prepared thin film electrode was mounted in a rotating disk electrode cell and immersed in 1.0 M H_2SO_4 solution for electrochemical measurements. The solution was deaerated with ultrahigh purity nitrogen (Airgas). The potentialstat used in this work is an Electrochemical Workstation (BAS100, Bioanalytical Sciences). A Ag/AgCl electrode was used as the reference electrode, and a Pt wire was used as the counter electrode. Measurements were performed at a scan rate of 20 mV/s at room temperature. The electrode rotating speed was 1000 rpm.

Results and Discussion

Characterization of Pt Nanoparticles on Multiwalled Carbon Nanotubes. Figure 1 shows typical TEM images of the Pt nanoparticles supported on sonochemically treated MWNTs with three metal loadings, i.e., 10, 20, and 30 wt %. It can be seen from the images that aggregation of the Pt nanoparticles is minimal. The Pt nanoparticles are highly dispersed on the carbon nanotubes and their dispersion is much
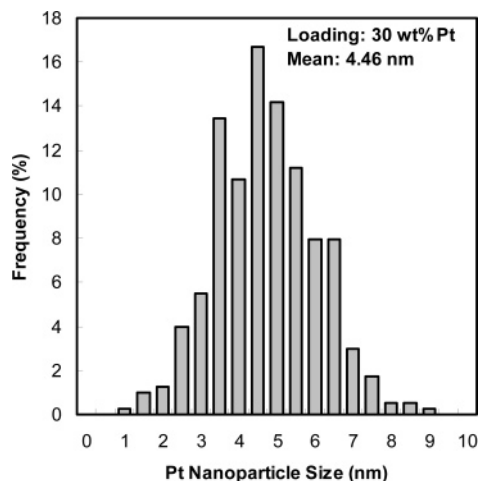
High Loading Pt Nanoparticles on Carbon Nanotubes

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Figure 2. Size distribution of Pt nanoparticles on carbon nanotubes with 30 wt % Pt loading.
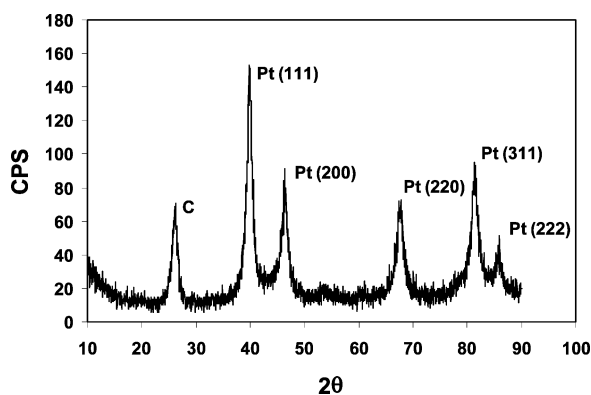

Figure 3. X-ray diffraction pattern of the 20 wt % Pt nanoparticles on MWNTs showing characteristic crystalline faces of Pt. The peak of C was identified as graphite from the carbon nanotubes.

better than those obtained previously by other workers. The nanoparticle sizes can be clearly seen to increase from the 10 wt % catalyst to the 30 wt % catalyst. The Pt nanoparticle sizes obtained from image analysis have a relatively narrow size distribution, as shown in a typical histogram in Figure 2 for the 30 wt % catalyst. The mean nanoparticle sizes (diameter) were found to be 2.78 ± 0.86, 3.57 ± 0.78, and 4.46 ± 1.33 nm for the 10, 20, and 30 wt % catalysts, respectively.

The increase of nanoparticle size with loading is attributed to the fact that the number densities of surface functional sites on the carbon nanotubes produced from the sonochemical process are the same. Consequently, saturation of the surface sites available for Pt deposition is reached, and particles can only grow bigger.

The X-ray diffraction (XRD) pattern for the 20 wt % Pt catalyst is shown in Figure 3; similar patterns were obtained for the other two catalysts. The XRD showed that Pt nanoparticles are crystalline, as indicated by the characteristic peaks in Figure 3. The peak at ca. $2\theta = 26°$ is the graphite, attributed here to the graphitic structure of carbon nanotubes.

The deposition of uniformly dispersed nanoparticles on sonochemically treated carbon nanotubes is believed to be the result of uniform surface functional sites on all nanotubes that can be created in the sonochemical process. The nonuniform nanoparticle deposition on refluxed carbon nanotubes may be attributed to the fact that carbon nanotubes cannot be oxidized or can only be partially oxidized in the reflux process. Although ultrasonication was generally used in those previous studies to
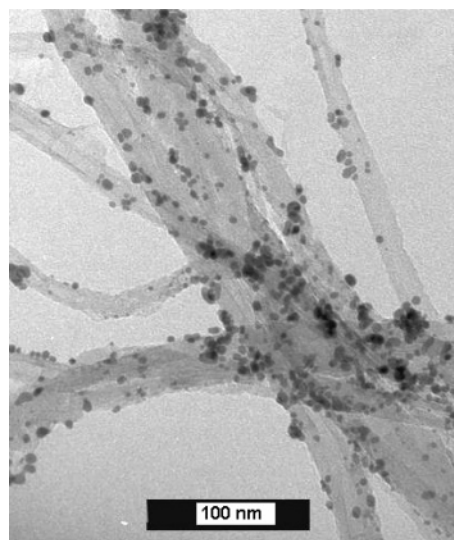
disperse carbon nanotubes before refluxing, carbon nanotubes can form aggregates again as soon as they were removed from the ultrasonic bath due to their highly hydrophobic surfaces. Consequently, the acids cannot get into the inside of the aggregates during the refluxing process, and carbon nanotubes inside the aggregates were left unmodified.

To compare the sonochemically treated carbon nanotubes with those treated in the reflux process, deposition of Pt nanoparticles was also conducted on refluxed MWNTs. The as-purchased MWNTs were treated in a reflux process[5] at 140 °C for 2 h, with the same acidic concentrations as in the sonochemical process. The nanoparticle deposition conditions were the same as those used to deposit the nanoparticles on the sonochemically treated carbon nanotubes. Figure 4 shows the Pt nanoparticles deposited on the refluxed carbon nanotubes. Compared to Figure 1 (with 20 wt % Pt), Figure 4 apparently shows that the Pt nanoparticles are not well dispersed and have bigger sizes (5.74 nm). Pt nanoparticles on refluxed carbon nanotubes tend to exist in aggregates due to less available surface functional groups as anchor sites. This observation is consistent with previous studies.[11]

It is noticed that in a previous study carbon nanotubes were ultrasonically treated in nitric acid for 1 h before further being refluxed in nitric acid for 48 h, but the resulting nanoparticles were not uniformly dispersed on carbon nanotubes.[11] That study used nitric acid only and its concentration (volume ratio 1:1) was much more diluted. It is therefore not comparable to what was obtained in this study.

Ultrasonication has been used previously to shorten carbon nanotubes,[14] and a recent study also used it to treat nitrogen-doped carbon nanotubes for ionic adsorption of Au nanoparticles.[15] Ultrasound can produce extremely high local temperatures ($\sim$5000 K) due to the implosive collapse of liquid bubbles.[16] They may expedite the surface oxidation process of carbon nanotubes. The surface treatment process in the sonochemical process only takes 2 h, whereas the reflux treatment process often needs 4 to 48 h. We believe that the sonochemical process provides a much faster and better way to functionalize carbon nanotubes for metal nanoparticle deposition.

Electrochemical Activity of Pt Nanoparticles on MWNTs. Figure 5 shows the electrochemical measurement results of the three catalysts with metal loadings of 10, 20, and 30 wt %. The cyclic voltammetry (CV) plot is presented with the ordinate in milliamperes per milligram of Pt. It can be seen that the 10 wt
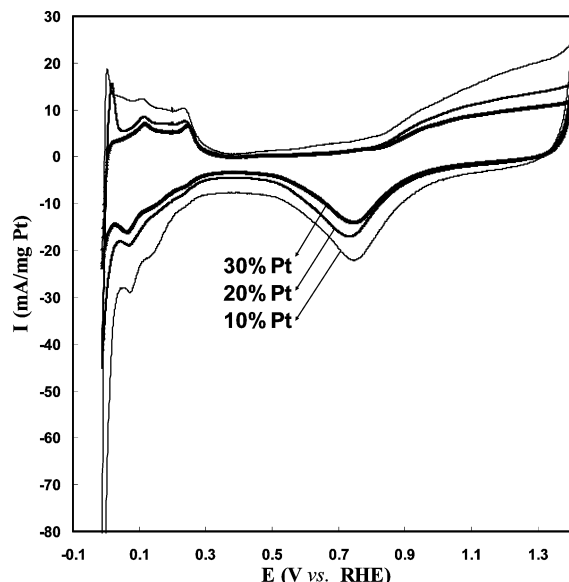

Figure 4. 20 wt % Pt nanoparticles on refluxed carbon nanotubes.

Figure 5. Cyclic voltammograms of the three catalysts of Pt nanoparticles supported on MWNTs. Measurements were performed using a rotating disk electrode in 1.0 M H₂SO₄ with scan rate of 20 mV/s and rotating speed at 1000 rpm.

% catalyst produced the highest specific current in the hydrogen region (~0.05−0.4 V). This result is believed to be due to the highest dispersion of the 10 wt % catalyst, of which the Pt nanoparticle size is seen to be the smallest.

To obtain the electrochemical activity of the catalysts, we have calculated the active surface areas of the catalysts, which involves calculation of the charge transfer for the hydrogen adsorption and desorption of the catalysts from the cyclic voltammograms (Figure 5). The specific charge transfer due to hydrogen adsorption and desorption can be obtained from[12]

$$Q_H = \frac{1}{2}(Q_T - Q_{DL})$$

where Q_T is the total specific charge transfer in the hydrogen adsorption/desorption potential region and Q_{DL} is the specific capacitive charge in the double layers of both Pt and carbon support. Q_T can be obtained by integration of the CV curves in the relevant potential region:[17]

$$Q_T = \frac{1}{v}\int_{0.05}^{0.4}(I_d - I_a)\,dE$$

where v is the scan rate, I_d and I_a are the specific current of desorption and adsorption, respectively, and E is the potential. Q_{DL} can be similarly obtained by integrating the double layer charging region.

Assuming the charge per real cm² of Pt with monolayer adsorption of hydrogen is $Q_H^0 = 210\ \mu C/cm$,[2,18] then the active specific surface areas can be obtained from

$$S_{act} = \frac{Q_H}{Q_H^0}$$

The geometrical specific surface areas of Pt nanoparticles can be calculated from

$$S_{geom} = \frac{6}{\rho d}$$

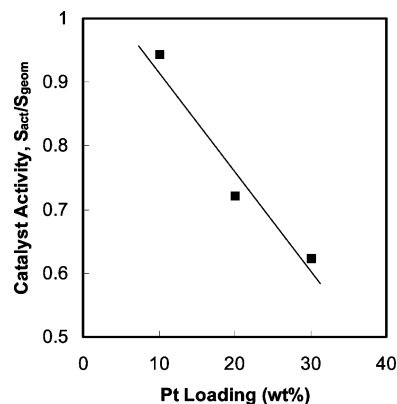where ρ is the density of Pt (21.09 g/cm³) and d is the mean

Figure 6. Catalyst activity vs of Pt loading. The lowest loading catalyst has the highest activity (~0.96). Catalyst activity decreases with the increase of Pt loading for the catalysts.
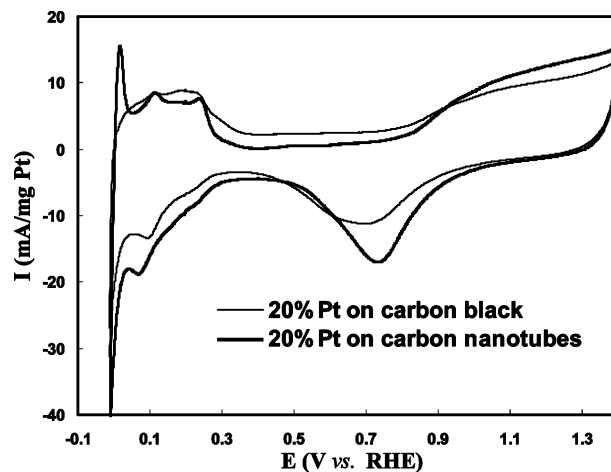

Figure 7. Cyclic voltammograms of the 20 wt % catalyst and the commercial catalyst with 20 wt % Pt on carbon black. Measurements were performed using a rotating disk electrode in 1.0 M H₂SO₄ with scan rate of 20 mV/s and rotating speed at 1000 rpm.

diameter of the Pt nanoparticles in the catalyst. A comparison of S_{act} with S_{geom} can tell how many surface atoms are electrochemically active, i.e., contributing to the electrochemical reactions. Thus, the ratio, S_{act}/S_{geom}, is considered here as a measure of the activity of a catalyst. The higher the ratio is, the higher activity the catalyst has. For a catalyst with activity of 1.0, it means that every surface atom on the Pt nanoparticles is electrochemically active. Figure 6 is a plot of the catalyst activity vs the Pt loading. It can be seen that the 10 wt % catalyst has the highest activity. As the Pt loading increases, the catalyst activity quickly decreases. It should be noted that although the Pt loading was used to present the results, the nanoparticle sizes in the three catalysts are different and may play a more important role in affecting the catalyst activity. In other words, for two catalysts with the same Pt loading but with different nanoparticle sizes, their activity can be different. Further work is needed to clarify particle size effects on the catalyst activity.[19]

To compare the catalysts with commercial PEM fuel cell catalysts, the cyclic voltammogram of a commercial catalyst under identical experimental conditions was obtained. The commercial catalyst is the 20 wt % Pt (2.5 nm in diameter) on Vulcan XC72 carbon blacks (De Nora North America (E-TEK)). The cyclic voltammogram of the commercial catalyst is displayed in Figure 7, together with that of the 20 wt % Pt on carbon nanotubes, redrawn here for comparison. Calculation of the specific active surface areas shows that our catalyst is 48%

higher than the commercial catalyst. In terms of catalyst activity defined above, our catalyst is 102% better than the commercial catalyst.

From the CV curves, it is seen that the double layer charging region for the commercial catalyst is larger than that of our catalyst. This may be partially attributed to the fact that the capacitive charges produced on the carbon support are different for carbon nanotubes and carbon black. Carbon nanotubes have a graphitic structure, whereas carbon black has a turbostratic and amorphous surface structure.[20] Therefore, carbon nanotubes conduct electrons better than carbon black. Consequently, the capacitance on carbon nanotubes is smaller than that on carbon black. This may also explain a previous observation that Pt supported on carbon nanotubes has a much lower electrode overpotential.[5]

The activity enhancement of carbon nanotube supported Pt nanoparticles may also come from metal−support interactions. Hills et al. have previously studied PtRu nanoparticles supported on carbon black and fullerenes.[21] They found that carbon black resulted in structural disorders in the nanoparticles in which the nearest coordination number was smaller, whereas nanoparticles deposited on fullerenes have a more ordered crystalline structure. It was suggested that the different nanoparticle properties observed are the result of nanoparticle interactions with the two carbon supports. Carbon nanofibers also were studied as a catalyst support before,[22] and it was found that the Pt or PtRu nanoparticles supported on them exhibit much enhanced electrochemical activity, which was attributed to their "platelet", "ribbon", or "herringbone" surface structures.

Carbon nanotubes have totally different surface structures from the other forms of carbon. They are roll-ups of graphene sheets, but the curved surface changes the π-bonding in the graphene sheets resulting in different electronic structures.[23] Although the mechanisms leading to the catalyst activity enhancement are still not well understood for the Pt nanoparticles supported on carbon nanotubes, it is believed that the metal−support interactions may very well contribute to it.

Conclusions

The quality of catalysts often depends on their preparation techniques. The basic requirement for supported metal catalysts is that the metal is highly dispersed on the support. This is often hard to achieve when preparing high loading catalysts because higher loading often increases the tendency of aggregation. This paper presents a sonochemical technique for the treatment of carbon nanotubes that allows deposition of highly dispersed high loading Pt nanoparticles on them. Compared to previous techniques for the treatment of carbon nanotubes, the sonochemical technique is able to functionalize most of the carbon nanotubes by preventing them from forming aggregates during the treatment process. It also seems to produce more surface functional groups on the carbon nanotubes, as is seen to allow deposition of much higher loading of Pt nanoparticles with little aggregation. With this technique, catalysts of Pt nanoparticles on carbon nanotubes with Pt loading up to 30 wt % have been prepared. The Pt nanoparticle sizes are less than 5 nm with a relatively narrow size distribution. Cyclic voltammetry showed that the catalysts have different specific activity; the specific activity decreases as the Pt loading increases. This was partially attributed to the fact that the lowest Pt loading (10 wt %) catalyst

has the smallest nanoparticle size. In the comparative study, it was shown that the 20 wt % catalyst has a 102% increase in electrochemical activity over the commercial PEM fuel cell catalyst (E-TEK) of the same loading of Pt nanoparticles supported on carbon black. The enhancement in electrochemical activity of our catalyst was attributed to the fact that carbon nanotubes result in smaller capacitive charges in the double layers than carbon black, as well as to the fact that metal−support interactions may lead to more active sites for the Pt nanoparticles supported on carbon nanotubes.

The catalysts prepared in this study, i.e., Pt nanoparticles supported on carbon nanotubes, seem to promise better catalysts for PEM fuel cells. The sonochemical technique for the surface functionalization of carbon nanotubes makes it possible to prepare high loading catalysts for the cathode of PEM fuel cells.

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