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Application of Green Chemistry Techniques to Prepare Electrocatalysts for Direct Methanol Fuel Cells[†]

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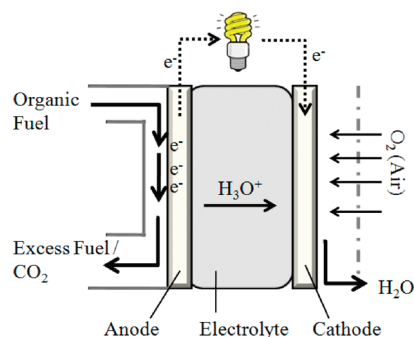
A series of green techniques for synthesizing carbon nanotube-supported platinum nanoparticles and their high electrocatalytic activity toward methanol fuel cell applications are reported. The techniques utilize either the supercritical fluid carbon dioxide or water as a medium for depositing platinum nanoparticles on surfaces of multiwalled or single-walled carbon nanotubes. The catalytic properties of the carbon nanotubes-supported Pt nanoparticle catalysts prepared by four different techniques are compared for anodic oxidation of methanol and cathodic reduction of oxygen using cyclic voltammetry. One technique using galvanic exchange of Pt^{2+} in water with zerovalent iron present on the surfaces of as-grown single-walled carbon nanotubes produces a Pt catalyst that shows an unusually high catalytic activity for reduction of oxygen but a negligible activity for oxidation of methanol. This fuel-selective catalyst may have a unique application as a cathode catalyst in methanol fuel cells to alleviate the problems caused by crossover of methanol through the polymer electrolyte membrane.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been investigated extensively because of the declining fossil fuel reserves and increasing environmental problems caused by fossil fuel consumption.¹ Use of a dilute organic solvent as anode fuel can provide a fuel cell with properties such as lightweight, quick recharge, low operating temperature, and high energy output, which are highly desirable for portable electronic devices.² In direct organic fuel cells, short-chain hydrocarbons such as methanol and formic acid are oxidized by an anode catalyst to produce electrons, protons, and carbon dioxide. Electrons are passed through an external circuit, whereas protons are transferred through a fluorinated, sulfonated polymer electrolyte such as Nafion to the cathode, at which reduction of oxygen takes place (Scheme 1). Use of organic fuels is advantageous over conventional hydrogen for its low cost, and ease of storage and distribution.

One of the major drawbacks of a direct organic fuel cell is the use of a scarce precious metal (namely, Pt) as the primary catalyst. A number of publications have suggested suitable and low-cost alternative catalysts.^{3–13} None, however, appears to have the performance of Pt in both anodic and cathodic processes. Consequently, Pt appears to have the best catalytic activity toward methanol and formic acid oxidations as well as oxygen reduction. The catalytic activity of Pt often becomes sluggish with time due to strong absorption of reaction intermediates such as CO in the anode and formation of oxide layers on the catalyst surface in the cathode.¹⁴ Rising interest is focused on applications of nanoparticles in fuel cells that would increase the active surface area of Pt while reducing the amount applied.¹⁵ In this application, the nanoparticles have to be dispersed evenly on an inert, high surface area and conductive carbon support to ensure the low electrical resistance. Carbon

SCHEME 1: Direct Organic Fuel Cell



nanotubes (CNTs), multiwalled or single-walled, appear to satisfy these requirements and, thus, are considered attractive supports for dispersing catalytic nanoparticles for fuel cell applications.^{16,17}

Many reported methods for preparing CNT-supported Pt catalysts (Pt/CNTs) involve reduction of Pt(II) salt through means such as microemulsion, chemical vapor deposition, and electrochemical deposition.^{15,18,19} Zheng and co-workers have reported a method of preparing the Pt/CNT for methanol oxidation using ethylene glycol as a reducing agent in dimethyl formamide solvent.²⁰ The authors illustrated the effectiveness of the nanometer-sized catalysts in fuel cell systems by showing good activity toward methanol oxidation. In the microemulsion method, the Pt particle size is well-controlled by the molar ratio of water to surfactant, known as the *W* value.^{21–23} However, the surfactant residues often stay on the catalyst surface, which could decrease the active surface area of the Pt.^{24–26}

This paper describes several green chemical techniques to prepare Pt/CNTs to reduce the cost and environmental impact of the synthesis, one of which is the use of the supercritical fluid carbon dioxide (sc-CO_2) as a solvent. One advantage of using the sc-CO_2 is that the solvent strength can easily be adjusted through the control of temperature and pressure, making it easier to control dissolution of active ingredients. The use of

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the solvent is also considered to be within green chemistry practices because it is recyclable, nontoxic, and inexpensive.²⁷ Furthermore, surfactant residues and dissolved reagents are effectively removed by the sc-CO₂ as the system is depressurized.²⁸ For direct Pt deposition in the sc-CO₂, a CO₂-soluble precursor Pt^{II}(acetylacetonate)₂ or Pt(acac)₂ is subjected to reduction by H₂ in a moderately heated, high-pressure reactor with CNTs.²⁹ Previous studies have shown that the direct supercritical fluid deposition method is capable of depositing Pt nanoparticles onto the CNT surfaces, and the catalyst shows a good activity.^{29–32} This method, however, lacks a mechanism for controlling the particle size of Pt. Hence, we have altered the microemulsion method to be carried out in a sc-CO₂ medium. The new method eliminates the use of organic solvent and reduces the amount of chemical wastes.³³ Since the sc-CO₂ can effectively remove the surfactant from catalyst surfaces, activity of the catalyst is dramatically increased.

We have taken other approaches to prepare fuel cell catalysts that do not require pretreatment of CNTs. Most of the reported methods of preparing Pt/CNTs require surface treatment of the substrate to obtain suitable interactions with the reaction mixture during catalyst synthesis.^{34–37} Strong acids are used for that purpose; however, this pretreatment method often leads to structural damage and loss of electron conductivity. We have investigated spontaneous reduction of Pt(II) in water using methanol and using galvanic exchange with zerovalent Fe particles originally present on the nanotubes for synthesizing single-walled carbon nanotube-supported Pt nanocatalysts (Pt/SWNTs). The advantages of these synthetic approaches are the economical and environmental sustainability because reactions are carried out in an aqueous solution at room temperature in addition to high utilization of Pt. Especially, the synthesis of Pt catalysis via galvanic exchange with zerovalent Fe enables almost perfect dispersion of Pt on the carbon nanotube support and shows interesting fuel selectivity toward oxygen reduction. Nanometer-sized Fe particles are present on the surfaces of the as-grown SWNTs that are synthesized in the HiPco process catalyzed by the zerovalent iron.^{38,39} This galvanic exchange approach is unique because the SWNT support does not require pretreatment and the entire reaction takes place in an aqueous solution.

Experimental Section

Chemicals and Materials for Synthesis of Electrocatalysts.

Multiwalled carbon nanotubes (MWNT, Nanostructured & Amorphous Materials, Inc.; Houston, TX) were treated and functionalized according to a previous study.⁴⁰ CO₂-soluble metal precursors Pt(acac)₂ and ruthenium(III) acetylacetonate, Ru(acac)₃, were purchased from Strem Chemicals, Inc. (Newburyport, MA) and used as received. High-purity nitrogen (99.97%) and oxygen (99.9%) were obtained from Oxarc (Spokane, WA). Methanol used in this work was obtained from J. T. Baker (HPLC grade). Unpurified and as-grown SWNT was purchased from Carbon Nanotechnology Inc. (Lot no. R0560, Houston, TX) and was used as received. Pt salt (K₂PtCl₄) was obtained from Alfa Aesar (46.7% Pt, Ward Hill, MA). Deionized water used in this experiment was the house-distilled water that was filtered through a graphite cartridge purchased from Barnstead International (D8922, Dubuque, IA). Sulfuric acid and nitric acid were purchased from EMD (ACS grade, Darmstadt, Germany). Sulfuric acid was calibrated against tris(hydroxymethyl)aminomethane (Aldrich, St. Louis, MO) before being used as an electrolyte. The XC-72R carbon-black-supported Pt catalysts (Pt/CB with 20 wt % Pt) were purchased

from ETEK (Somerset, NJ). A 5% Nafion 117 solution was obtained from Fluka (Milwaukee, WI). Ethyl alcohol (200 proof), which was used to dilute the Nafion 117 solution, was of ACS/USP grade from Pharmco (Brockfield, CT). A 3.0-mm-diameter glassy carbon working electrode and a Ag/AgCl (3 M NaCl) reference were obtained from Bioanalytical Systems Inc. (BASi, West Lafayette, IN). A glassy carbon rotating disk electrode (5.0 mm diameter) was obtained from Pine Instrument Company (Grove City, PA). The counter electrode used in this study was a graphite rod purchased from Alfa Aesar (99%, Ward Hill, MA).

Catalyst Synthesis by the Direct Supercritical CO₂ Deposition. The experimental setup for the direct sc-CO₂ deposition was described in our previous reports.^{17,29–32,41} Typically, equal masses (~20 mg) of carbon nanotubes and Pt(acac)₂ were used in the synthesis. In addition, Ru(acac)₃ was added so that the mole ratio of Pt and Ru became 1:1.²⁹ The metal precursors and the pretreated MWNTs were placed in a high-pressure reaction cell and 100 atm of CO₂. The precursors were dissolved in sc-CO₂ at 200 °C for 1 h. Polarity of the CO₂ was adjusted using methanol so that solubility for dissolution of precursors could be enhanced. Then a mixture of hydrogen (10 atm) and CO₂ (240 atm) was introduced into the cell. The reduction process took place for 30 min before the cell was depressurized and cooled down to room temperature. The Pt/MWNT remaining inside the cell was collected. The synthesized catalyst was washed several times by dispersing in methanol under ultrasonication.

Catalyst Synthesis by the Water-in-Supercritical CO₂ Microemulsion. Pt deposition by the water-in-sc-CO₂ microemulsion method was conducted as follows:^{33,42} A 98 μL portion of 0.1 M Na₂PtCl₄ solution and 15 mM sodium bis(2-ethylhexyl)sulfosuccinate (AOT, 99%, Aldrich) at $W = [\text{H}_2\text{O}]/[\text{AOT}] = 10$, 3 mL of hexane [8.5% (v/v) of hexane/CO₂], and 3–5 mg of the pretreated MWNTs were added to a glass beaker. A magnetic stirrer was used to agitate the water-in-hexane microemulsion for 20 min. After that, the microemulsion was loaded into a high-pressure reaction cell, and CO₂ was introduced into the reactor at 170 bar and at room temperature for 1 h. A mixture of 12 bar H₂ and 180 bar CO₂ was then introduced into the reactor for the hydrogen reduction of Pt(II) to Pt(0). The final pressure of the system was adjusted to 200 bar by adding CO₂. The reactor solution was stirred at that pressure for 1 h before the pressure of the system was slowly reduced. The final product was washed several times by dispersing in methanol under ultrasonication/centrifugation.

Catalyst Synthesis by Spontaneous Reduction of Pt by Methanol. Synthesis of Pt/SWNT using the spontaneous reduction method is as follows:⁴³ Unpurified SWNTs were weighed to 4–7 mg using an analytical balance (0.01 mg limit) and then 0.3 mL of methanol was added. Methanol was added to prevent scattering of the SWNTs as well as to be used as a reducing agent. The concentration of Pt(II) ion (as K₂PtCl₄) was adjusted so that the weight ratio of Pt(II) ion to SWNTs could become 0.2:1. A 6 mL aliquot of the aqueous solution with an appropriate Pt(II) ion concentration was placed into the SWNTs/methanol mixture. The vial was then shaken vigorously by hand for 30 s to give an initial dispersion before it was stirred mechanically for 30 min. The Pt/SWNTs were then separated and rinsed using deionized water to remove any unreacted reagents. The synthesized Pt/SWNTs were dried in a low-temperature oven overnight before electrochemical analysis.

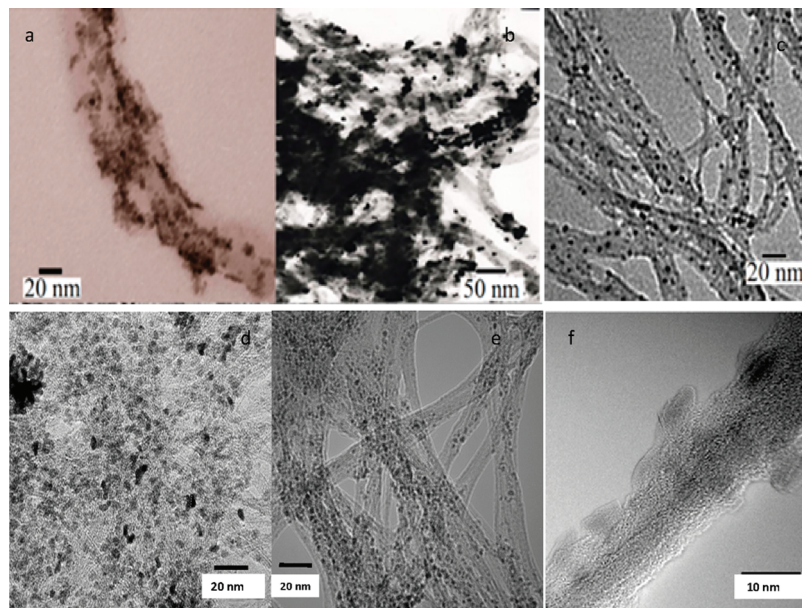


Figure 1. TEM images of (a) PtRu/MWNT catalyst via direct sc-CO₂ deposition, (b) Pt/MWNT catalyst via direct sc-CO₂ deposition, (c) Pt/MWNT catalyst via water-in-sc-CO₂ microemulsion, (d) Pt/SWNT catalyst via spontaneous reduction by methanol, (e) Pt-Fe/SWNT catalyst via galvanic exchange reaction, and (f) a magnified image showing the surface of the Pt-Fe/SWNT catalyst prepared by galvanic exchange reaction.

Catalyst Synthesis by Galvanic Exchange Reaction with Fe⁰. The detailed synthetic procedure may be referred to in our previous publication.⁴⁴ The catalyst synthesis by galvanic exchange reaction follows very closely the spontaneous reduction method, except that methanol was not applied. Instead, the 6 mL aliquot of aqueous solution with adjusted concentration of Pt(II) was added directly to the weighed SWNTs. Newly synthesized catalyst was washed with deionized water at least three times, followed by oven drying at 75 °C.

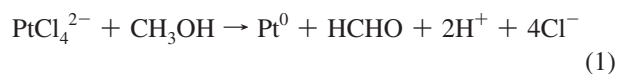
Because SWNTs scatter easily by static dislocation, it is difficult to make accurate measurements of the weight. The following procedure is suggested in order to reduce the scattering. First, a bulk sample of the SWNTs was transferred to a smaller glass container. Then, a metal spatula and the outside walls of the glass container and a small glass vial were rinsed with methanol. Finally, after the methanol had dried out, the SWNTs were dragged out slowly using the metal spatula and fell into the vial that was located right beneath the container on a balance. Avoiding any methanol contact with the inside of the glass vial as it reduces Pt(II) must be ensured. Note that because of the possible toxicities of carbon nanotubes, a dust-mask should be worn at all times.

Electrode Modification and Electrochemical Analysis. A working electrode was modified according to the following steps: A glassy carbon working electrode was polished with an aqueous slurry of 1 μm alumina (Pace Tech., Tucson, AZ) on a polishing cloth (Mark V Lab, East Granby, CT). The electrode was then briefly sonicated to remove the alumina residues from the surface. Diluted Nafion 117 was prepared by combining the commercial 5% solution with a 50/50 (v/v) mixture of water/ethanol. Electrocatalysts were mixed with the diluted Nafion solution to make a 2 mg/mL catalyst/Nafion mixture. To ensure that electrocatalysts were evenly suspended, the mixture was sonicated for 30 min prior to the electrode modification. A small amount of the catalyst mixture was then deposited using a micropipet onto the surface of the working electrode, followed by 2 h of drying at ambient temperature and pressure.

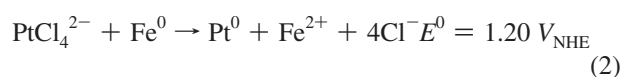
Results and Discussion

Physical Characterizations. Figure 1 illustrates TEM (transmission electron microscopy) images of the catalysts prepared using the green chemical approaches described in this paper. The direct sc-CO₂ deposition successfully prepared and deposited metal nanoparticles onto the MWNT support (Figure 1a and b). Pt/MWNT prepared using water-in-sc-CO₂ shows much better particle dispersion as compared to the direct deposition method (Figure 1c). A characteristic TEM image of the Pt catalyst prepared by methanol reduction using untreated SWNTs is shown in Figure 1d. The Pt catalyst prepared by galvanic exchange with Fe particles on untreated SWNTs is shown in Figure 1e and f.

Preparation of the Pt/SWNT catalyst using spontaneous reduction of Pt(II) by methanol works very quickly and efficiently. An energy dispersive X-ray spectrum (EDS) of the catalyst is given in the Supporting Information (Figure S1). Though the detailed mechanism is not known at this point, we suspect that the reduction process takes place as shown below.⁴⁵



Deposition of Pt using a galvanic exchange reaction utilizes the Fe impurity present in untreated, as-grown SWNTs. According to our prior experiments, the Fe impurities are in contact with water regardless of the report that the Fe particles are coated with carbon.^{37,46} The difference in redox potential of the two metals, as shown below, provides a thermodynamic drive for deposition of Pt onto the Fe surface.



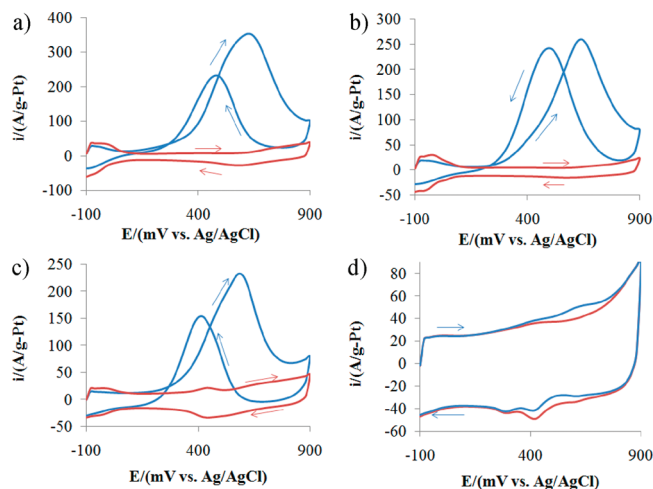
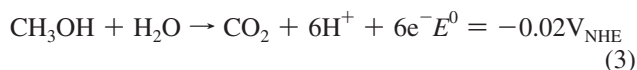


Figure 2. CVs of methanol oxidation on (a) PtRu/MWNT prepared using direct sc-CO₂ deposition, (b) Pt/MWNT prepared using water-in-sc-CO₂ microemulsion, (c) Pt/SWNT prepared in spontaneous reduction with methanol, and (d) Pt-Fe/SWNT prepared in galvanic exchange reaction. CVs were collected in N₂ purged 0.1 M methanol with 1.0 M H₂SO₄ electrolyte. Scan rate, 50 mV/s. The current is normalized to the same amount of Pt (ampere/g-Pt).

EDS of randomly selected particles on a small area of the catalyst (Supporting Information, Figure S2) indicates coexistence of Fe and Pt.

Activity of the Catalysts in Methanol Oxidation. Activity of the newly prepared catalysts toward anodic oxidation was tested in 0.1 M methanol solution with 1.0 M sulfuric acid electrolyte using cyclic voltammetry (CV). A typical CV result of an active fuel cell catalyst for methanol oxidation shows an oxidative peak on both cathodic and anodic directed scans. This is because methanol oxidation can take place at any point of the applied potential window of the CV due to its reaction potential (eq 3).



We will not discuss in detail the reason for the appearance of an oxidative peak in this paper because it deserves another full article by itself. Nonetheless, the characteristic CVs were obtained from all the catalysts except for the one prepared using the galvanic exchange reaction (Figure 2). The fuel-selective activity of Pt-Fe bimetallic catalyst has been reported previously.^{47,48}

The activity of metal alloy catalysts for anodic reaction is generally characterized by a prominent bifunctional effect. A secondary metal catalyst in a bifunctional mechanism is able to assist Pt to oxidatively remove poisoning species from the surface. This is because the secondary metal catalyst is capable of generating active oxygen species, OH_{ads}, through dissociative absorption of water.⁴⁹ This metal hydroxide can be used in the oxidative removal of CO from the Pt surface. It is well-known that Ru is the best secondary catalyst for the bifunctional effect in methanol oxidation and therefore is primarily used in the direct methanol fuel cells. Our PtRu/MWNT catalyst synthesized using the direct deposition method exhibited the highest activity toward methanol oxidation among the catalysts tested in this study. This is an expected result because PtRu is a superior anodic catalyst, in comparison to the Pt monometallic catalyst. To our surprise, we have observed a high catalytic

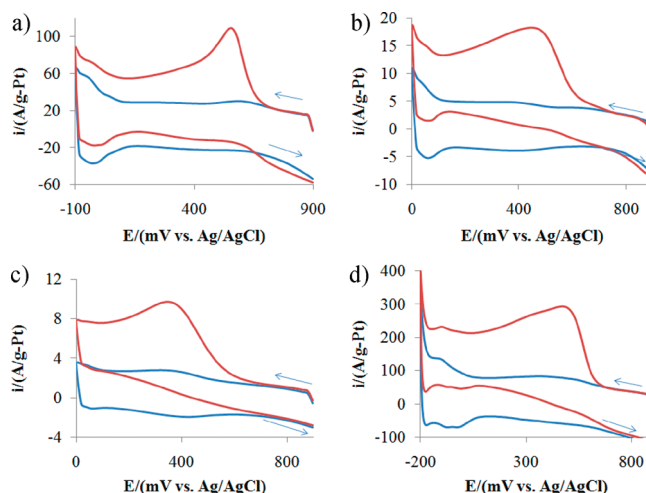


Figure 3. CVs of O₂ reduction on (a) Pt/SWNT prepared by the spontaneous reduction by methanol, (b) Pt/MWNT prepared by water-in-sc-CO₂ microemulsion, (c) Pt/MWNT prepared on the direct sc-CO₂ deposition, and (d) Pt/SWNT prepared by the galvanic exchange reaction. Background CVs (blue) were collected in N₂-purged 1.0 M H₂SO₄ electrolyte. The same solution was purged with O₂ prior to the collection of O₂ reduction CVs. Scan rate was 50 mV/s.

activity of the Pt/MWNT catalyst prepared by the water-in-sc-CO₂ microemulsion toward methanol oxidation. The conventional water-in-oil microemulsion method, which we investigated previously, exhibited excellent particle size control and dispersion on the MWNT support. However, the negative effect of the surfactant residues on the surface was evident in the catalytic activity.³³ The result in this study suggests that the surfactant was removed more effectively by the sc-CO₂. Future development of the supercritical fluid method may lead us to a nanoparticle catalysts synthesis technique with minimal liquid waste generation, especially if the surfactant could be collected through a depressurizing process and recycled.

The Pt/SWNT catalyst synthesized using spontaneous reduction by methanol also exhibited good activity toward anodic oxidation. The anodic peak current of this catalyst was only ~30 A/g-Pt lower than that of the Pt/MWNT prepared using the CO₂-microemulsion method. The formation of clusters such as the one observed in the left corner of Figure 1d may have caused the loss of utilization of the catalyst surface. Nevertheless, the synthetic process is fast and provides almost complete reduction of applied Pt(II) ions; thus, scaling up of this process is significantly easier than any of the previously reported methods.

The Pt-Fe/SWNT catalyst synthesized by the galvanic exchange reaction is not active toward methanol oxidation (Figure 2d). It is possible that this result is due to the fact that the catalyst does not have enough Pt to be effective toward the anodic process. The weight percent of Pt being deposited on the SWNTs by the galvanic exchange reaction was 5.4%, which is significantly smaller than the other three samples tested in this study. However, this catalyst shows an unusually high activity in cathodic reduction of oxygen that may have special applications in methanol fuel cell technology.

Activity of the Catalysts in Oxygen Reduction. The CNT-supported Pt nanoparticle catalysts were also tested in oxygen reduction reaction, and characteristic CVs are shown in Figure 3. The Pt/SWNT catalyst prepared using the methanol spontaneous reduction method exhibits excellent activity toward the cathodic reduction process (Figure 3a), and its activity is superior to that prepared by the sc-CO₂ microemulsion method (Figure

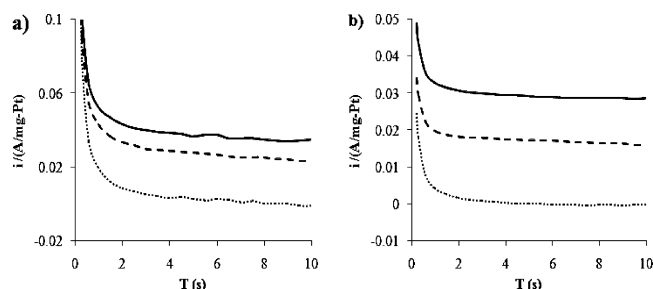


Figure 4. Chronoamperometry for oxygen reduction reaction in 1.0 M H_2SO_4 with (—) and without (---) 0.1 M methanol on (a) the Pt–Fe/SWNT and (b) Pt/CB. The electrode was rotated at 1000 rpm. Dotted line indicates background current response that was collected in electrolyte-only solution.

3b). The Pt/MWNT catalyst prepared using the direct sc-CO_2 deposition method has the lowest activity, as indicated by the peak current expressed in amperes per gram of Pt in Figure 3c. The electroactive surface area measured for the catalyst, using a hydrogen chemisorption method described by Shimizu et al.,³³ was the smallest ($6.04 \text{ m}^2/\text{g-Pt}$) of all catalysts tested in this article. This may be because nanoparticles tend to aggregate more easily at the elevated temperature of the direct deposition method. A surprising result is that the Pt–Fe/SWNT catalyst prepared using the galvanic exchange reaction exhibited the best performance toward oxygen reduction among the four catalysts tested. This is attributable to the largest electroactive surface area of Pt exhibited by the catalyst ($150 \text{ m}^2/\text{g-Pt}$). The electroactive surface areas of the other two catalysts, the Pt/MWNT prepared using the CO_2 -microemulsion and the Pt/SWNT prepared using methanol reduction method, are 31.1 and $45.3 \text{ m}^2/\text{g-Pt}$, respectively. Hence, the trend in the electroactive surface areas agrees with the activities of the catalysts.

One of the considerations in development of fuel cell catalysts is that the cathodic catalyst should have specificity for oxygen reduction in the presence of the anodic fuel; for example, methanol.⁵⁰ This is because the fuel crossover—that is, the migration of methanol across the polymer electrolyte membrane into the cathodic compartment—remains a pervasive problem in the direct methanol fuel cell.^{51–53} Interference of anodic fuels in the cathodic reduction of oxygen includes a short circuit and loss of overall performance. Unique to the Pt–Fe/SWNT catalyst is the tolerance toward the presence of methanol. Previous reports have indicated that Pt–Fe bimetallic electrocatalyst for oxygen reduction showed enhanced methanol tolerance.^{47,48} The Pt–Fe/SWNT catalyst produced in this work has demonstrated a strong preference for oxygen reduction in the presence of 0.1 M methanol. This is also evident in the chronoamperometry studies ($E_{\text{step}} = 600 \text{ mV}$ vs Ag/AgCl) presented in Figure 4a. In the presence of methanol, the average current loss of the Pt–Fe/SWNT was observed at $16.4\% (\pm 3.7)$ after 10 s, whereas that of the commercial Pt/CB was found to be $37.3\% (\pm 8.6)$ for the same time period. Fuel selectivity of Pt–Fe/SWNT may very well be attributable to the effect of the Pt particle size, as mentioned by Bergamaski et al.⁵⁴ Production of the Pt–Fe/SWNT in this work may aid in the development of a membraneless methanol fuel cell. This sort of cell may have performance advantages over the PEMFC as well as a reduction in cost.

Conclusions

This study has tested four different green chemistry techniques for preparation of CNT-supported Pt nanoparticle catalysts for

methanol fuel cell applications. The direct sc-CO_2 deposition method often results in agglomeration of Pt particles. The water-in- sc-CO_2 microemulsion improves catalytic activity by producing more uniform Pt nanoparticles and by removing the surfactant residue effectively from the catalyst. Well-controlled particle size and distribution makes this synthetic method suitable for a fuel cell catalyst. The synthetic method that is most probable for scaling up is the spontaneous reduction of Pt(II) by methanol. This method converts almost 100% of the applied Pt(II) ions to nanoparticles, and the synthesized catalyst is highly active for both anodic and cathodic processes. Moreover, reproducible Pt deposition can be achieved on the untreated, as-grown SWNT support using the methanol reduction method eliminating the costly and environmentally harsh pretreatment. The most unique synthetic method for preparation of the SWNT-supported Pt catalyst is the galvanic exchange reaction. This method makes use of the difference in redox potentials of the two metals in an aqueous medium to deposit Pt onto Fe^0 that is present in the as-grown SWNTs. The deposited Pt probably forms a shell around the Fe core. Unlike the other catalysts tested in this study, the Pt–Fe/SWNT exhibits a negligible activity toward methanol oxidation. On the other hand, it shows superior activity toward oxygen reduction, suggesting its methanol tolerance. This was analyzed using chronoamperometry and demonstrates $16.4\% (\pm 3.7)$ current loss after 10 s, whereas the commercial Pt/CB catalyst has experienced $37.3\% (\pm 8.6)$ loss. Therefore, it can be suggested that the Pt–Fe/SWNT prepared by the galvanic exchange method is a fuel-selective catalyst.

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Supporting Information Available: Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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