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Rapid and One-Step Synthesis of Single-Walled Carbon Nanotube-Supported Platinum (Pt/SWNT) Using As-Grown SWNTs through Reduction by Methanol

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Synthesis of single-walled carbon nanotube-supported platinum (Pt/SWNT) electrocatalyst using a rapid, one-step reduction of an aqueous $PtCl_4^{2-}$ solution by methanol is reported. Pt nanoparticles are deposited onto SWNTs within 30 min of vigorous stirring with a small amount of methanol. Efficiency of this synthetic method is as high as 98%, and the mass of the Pt nanoparticles deposited on SWNTs is directly proportional to the initial concentration of the metal ion. Cyclic voltammetric analysis indicates excellent catalytic activity of the Pt/SWNT catalyst for methanol oxidation, with a peak current that is 2.5 times larger than a commercial Pt carbon black catalyst. The Pt/SWNT catalyst also exhibits significantly better activity with respect to oxygen reduction in comparison to the commercial Pt catalyst.

Introduction

Direct methanol fuel cells (DMFCs) have garnered much interest related to the challenges to reduce dependence on fossil fuels and greenhouse gas pollution.[1] In recent years, the fabrication of nanosized Pt electrocatalysts has significantly increased catalytic activity because of the enhanced surface area/mass ratio.[2–4] Support for the metal catalyst has also evolved over the past few years. The discovery of single-walled carbon nanotubes (SWNTs) has gained great attention as a new conductive material in scientific communities.[5,6] This is because of their remarkable abilities to enhance catalytic activities, particularly with respect to fuel cell applications.[7–9] In comparison to the conventional carbon black support, carbon nanotubes provide larger active surface area and higher chemical resistivity and mechanical strength.[3,10–13] Furthermore, its hair-like structure allows for entanglements among the nanotubes, resulting in increasing electron conductivity over carbon black.[10] SWNTs have attracted more interest in fuel cell applications because they demonstrate more conductivity than multiwalled carbon nanotubes (MWNTs).[14,15] Furthermore, Girishkumar et al. have reported that the SWNT supported Pt electrocatalyst (Pt/SWNT) exhibited 4-fold enhancement in the power density of a DMFC operated at room temperature when compared to the commercially available catalysts.[14]

There are many methods for the preparation of a carbon-nanotube-supported Pt catalyst. Most involve the reduction of Pt^{II} salts through means such as microemulsion,[3] chemical vapor deposition,[16] and electrochemical deposition.[17] Most recently, Zheng et al.[18] have reported a preparation method of a MWNT-supported Pt electrocatalyst for methanol oxidation using ethylene glycol as a reducing agent in dimethyl formamide. Transmission electron microscopy (TEM) images indicated well-dispersed Pt nanoparticles on MWNTs as well as good electrocatalytic activity of the catalyst, as measured by cyclic voltammetry (CV).[18] Although carbon-nanotube-supported Pt electrocatalysts have shown their effectiveness in fuel cell systems, many of the reported methods of catalyst preparation may only be applicable in a laboratory scale because of the high cost of the synthesis. Furthermore, those methods often require a harsh pretreatment of the carbon nanotube substrates prior to a metal deposition. For example, a widely used method of pretreatment is by refluxing the substrates in strong acids, such as nitric and sulfuric acid. This treatment also produces surface-bound carboxylic acid groups, which provide sites for a metal deposition.[19] However, the acid treatment method does not appear suitable for SWNTs because it leads to structural damage and loss of electron conductivity.

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In our laboratory, we have focused on green chemical approaches, according to the 12 principles provided by the Environmental Protection Agency.[20] Our goal is to develop a green synthetic method for preparation of Pt/SWNT catalysts, also keeping in mind applicability to industrial scales. In a recent paper, we have examined the deposition of Pt onto MWNTs using water-in-supercritical CO_2 microemulsion and H_2 as a reducing agent.[21] In this study, we examined a method for the deposition of Pt onto SWNTs without the need for harsh pretreatments that lead to damaging nanotubes. The experimental design was inspired by the recent report of using ethanol as a reducing agent in the liquid−solid-solution synthesis of noble metal nanoparticles.[22] The use of alcohol has three advantages over syntheses that use H_2 as a reducing agent: (i) Alcohol is liquid at room temperature, and thus, experimental setup can be greatly eased. (ii) SWNTs readily disperse in alcohol; as a result, application of the co-solvent can be omitted. (iii) Excess reagent can be easily evaporated off from Pt/SWNTs.

The synthetic method reported in this paper is rapid, simple, and inexpensive and generates only a small amount of chemical waste. Synthesis of Pt/SWNTs with various weight percentages of Pt is discussed along with some of the initial results from electrocatalytic activities toward the oxidation of methanol and reduction of oxygen.

Experimental Section

Reagents. Unpurified SWNTs were purchased from Carbon Nanotechnologies Incorporated (CNI, Houston, TX) and used as received. Deionized water used in this work was further purified by filtration through a Barnstead International (Dubuque, IA) D8922 ion-exchange column. Methanol was purchased from J.T. Baker (HPLC grade). Platinum salt (K_2PtCl_4) was supplied by Alfa Aesar (46.7% Pt, Ward Hill, MA). Nafion 117 solution (5 wt %, m/m), purchased from Fluka, was diluted using ACS/USP-grade ethanol solution, which was from Pharmco (Brookfield, CT), and deionized water. High-purity nitrogen (99.97%) and oxygen (99.9%) were obtained from Oxarc (Spokane, WA). Sulfuric acid was purchased from EMD (ACS grade, Damstadt, Germany) and calibrated against tris-(hydroxymethyl)aminomethane (Aldrich) before use. The 20 wt % Pt on XC-72R carbon black (Pt/CB) was purchased from E-TEK (Somerset, NJ).

Synthesis of Pt/SWNT. As-received SWNTs were weighed using an analytical balance (0.01 mg limit). Note that a researcher must be aware of the possible danger of inhalation of SWNTs, and a dust mask should be worn at all time. A small amount of methanol was added before the sample container was removed from the balance to prevent SWNT scattering. The concentration of Pt^{II} (as K_2PtCl_4) used for the synthesis was determined, so that the weight ratio of Pt^{II} to SWNTs could be set at 0.1:1, 0.2:1, and 0.4:1. A 6 mL aliquot of the aqueous solution with the appropriate Pt^{II} concentration was pipetted into the vial, which contains as-received SWNTs and methanol. This mixture was shaken vigorously by hand for 30 s to provide initial dispersion before it was stirred at maximum speed (600 rpm) for 30 min. Pt/SWNTs were separated and rinsed using centrifuge and deionized water to remove any unreacted reagents. The catalyst was then dried in a low-temperature oven overnight before electrochemical analyses. For the reporting purpose, the Pt/SWNT electrocatalysts synthesized in this work are labeled as shown in Table 1, depending upon the initial conditions of synthesis.

Characterization. Metal composition of the electrocatalysts was obtained by energy-dispersive X-ray spectroscopy (EDS) using an

Table 1. Experimental Conditions for Pt/SWNT Synthesis and Weight Percentages of Pt Present in the Samples[a]

	Pt^{II}/SWNT[b] weight ratio	Pt (wt %)	Pt^{II} use (%)	particle diameter (nm)[c]
Pt/SWNT-1	0.1:1	5.6[d] (0.4)	61.5	3.5
Pt/SWNT-2	0.2:1	14.1[d] (1.9)	84.4	6.1
Pt/SWNT-3	0.4:1	28.2[d] (1.7)	98.6	6.5
Pt/CB[e]		20		6.9

[a] Each reaction mixture contained 0.3 mL of methanol, 5−6 mg of SWNT, and an appropriate amount of Pt^{II} solution, so that weight ratio of Pt^{II}/SWNT became as indicated in this table. The total volume of the reaction mixture was 6.3 mL, and the reaction time was 30 min with vigorous stirring. The values in parentheses are the standard deviation. [b] Pt^{II} added as K_2PtCl_4. [c] The average particle diameter of Pt was calculated using full width at half-height of an XRD peak for the Pt (220) plane and Scherre's equation.[31] [d] Pt (wt %) was obtained by EDS analysis using Pt/CB as an internal standard. [e] Pt/CB is the commercial catalyst purchased from E-TEK. In the catalyst, Pt nanoparticles are deposited onto the surface-enhanced carbon black, XC-72R.

AMRAY 1830 at 20.0 keV with a sampling time of 60 s. A small amount of the electrocatalyst was placed onto an aluminum support using methanol to prevent scattering. The EDS peak of aluminum did not overlap with any element of interest in this study. Transmission electron microscopy (TEM) images of Pt/SWNTs were taken by a JEOL JEM 2010-1200EXII 1830 at the operating voltage of 200 keV. Pt/SWNTs were deposited onto the copper grid and air-dried before an image was taken. The X-ray diffraction (XRD) spectroscopy patterns of the electrocatalysts were obtained using a Siemens diffraktometer D5000 1830. The region of the diffraction angle, 2θ, between 10° and 90° was analyzed at a step size of 0.02° s^{-1}.

Electrode Preparation. Catalyst ink was prepared by mixing Pt/SWNTs with diluted Nafion solution. The ink was placed under ultrasonic agitation for 30 min to ensure the dispersion of Pt/SWNTs in the solution. Then, a 6 μL aliquot of the mixture was deposited onto a clean glassy carbon working electrode using a micropipette. The catalyst film was then dried at least 2 h at room temperature before used in analyses.

Electrochemical Analysis. Electrochemical analyses, CV, and linear sweep voltammetry (LSV), were carried out in a conventional three-electrode cell using a Bioanalytical System, Inc. (BASi) CV-50w potentiostat (version 2.31, West Lafayette, IN). The 3.0 mm diameter glassy carbon working electrode and Ag/AgCl (3 M NaCl, 209 mV versus NHE) reference electrode were obtained from BASi. The counter electrode used in this study was a graphite rod (Alfa Aesar, 99%, Ward Hill, MA). A glassy carbon rotating disk electrode (5.0 mm in diameter) used for LSV was obtained from the Pine Instrument Company (Grove City, PA). Working electrodes were polished on the polishing cloth (Mark V Laboratory, East Granby, CT) with an aqueous slurry of 1 μm alumina (Pace Technology, Tuscon, AZ). Ultrasonication was used to remove alumina residue from the surface of the working electrode. The electroactive surface area of Pt was calculated from the current associated with the hydrogen desorption.[23−26]

Results and Discussion

Characterization of As-Received SWNT. The HiPco process of SWNT fabrication is based on the gas-phase dispro-

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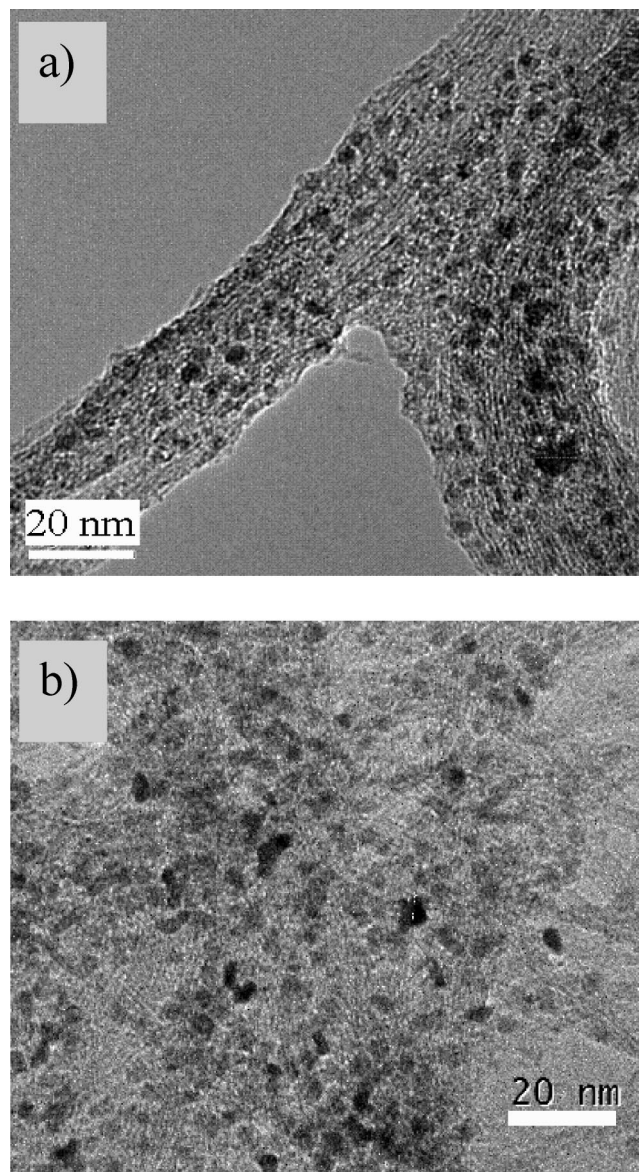
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Figure 1. Low-magnification high-resolution transmission electron microscopy (HRTEM) images of (a) as-received SWNT and (b) Pt/SWNT-2 with 14.1 wt % Pt.

portionation reaction: $CO + CO = C + CO_2$.[27,28] This reaction is catalyzed by the zero-valent iron from the precursor $Fe(CO)_5$. The iron impurity is finally present as nanometer-sized particles on the surfaces of the synthesized SWNTs. A TEM image of the as-received SWNTs in Figure 1a shows the presence of numerous spherical particles on the SWNT surfaces. Interestingly, despite the clear image of Fe particles taken by TEM, the XRD diffraction pattern showed no peak representing Fe (results not shown). We assume that the lack of diffraction peak for Fe on the SWNT is because the particle is too small in size and/or heavily coated by amorphous carbon, which may alter XRD. Carbon coatings on Fe occur as a result of incomplete formation of the carbon nanotube.[29] Atomic absorption studies revealed that the as-received SWNT contained 30 wt % Fe (29

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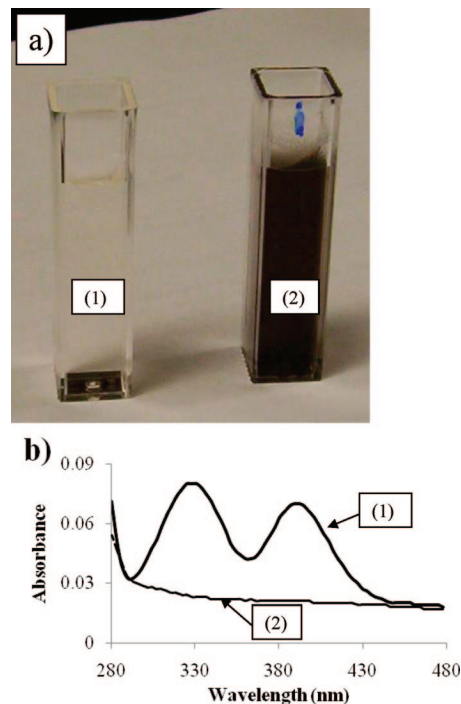
Figure 2. (a) Picture of cuvettes that contained 1.1 mM K_2PtCl_4: (1) Before 0.3 mL of methanol is added and (2) 30 min after the addition of methanol. (b) UV−vis spectrum of the above samples.

wt % Fe was reported by the vendor). Also noteworthy is that as-received SWNTs exhibit magnetic properties when tested with a hand-held magnet. While removal of the iron impurity is possible in various ways,[29−33] it was not necessary for this work.

Synthesis of Pt/SWNT. Figure 2 exhibits the conversion of aqueous $PtCl_4{}^{2−}$ to platinum black within 30 min after the addition of methanol. This process is thought to be carried out by the following reaction:[34]

$$PtCl_4{}^{2-} + CH_3OH \rightarrow Pt^0 + HCHO + 2H^+ + 4Cl^- \quad (1)$$

Newly synthesized Pt/SWNTs were analyzed using EDS to obtain the weight percent of Pt using the commercial sample as an internal standard (Table 1). It was found that the weight percent of Pt deposited onto SWNTs was directly proportional to the initial weight ratio of Pt^{II}/SWNT in the methanolic solution. This result suggests that the amount of Pt deposited on SWNTs could be controlled by simply varying the amount of Pt salt added to the synthesis.

TEM could not provide conclusive information regarding the particle size of Pt because of the pre-existing Fe nanoparticles on the SWNT surface (Figure 1b). Nonetheless, we attempted to estimate the sizes of Pt nanoparticles using interactive imaging software of Matrax Inspector. For Pt/SWNT-1, Pt/SWNT-2, and Pt/SWNT-3, the estimated diameters were 2.6 ± 0.4, 3.2 ± 0.5, and 3.0 ± 0.5 nm, respectively. These values are not so different from the average size of the Fe nanoparticles (4.0 ± 0.5 nm) originally present on the surfaces of the as-grown SWNTs.

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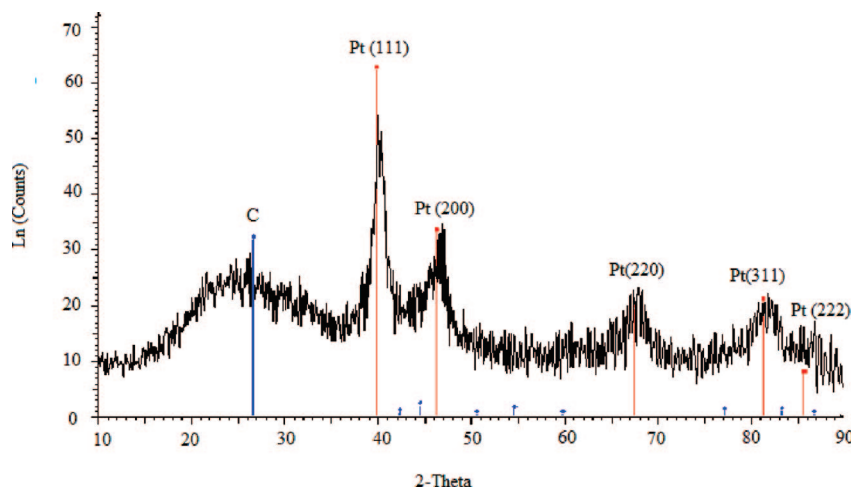
Figure 3. Characteristic XRD spectra collected using Pt/SWNT-2 with 14.1 wt % Pt. Reflection angles of Pt are 39.9°, 46.5°, 67.8°, 81.5°, and 86.1°. The broad peak at around 25° corresponds to carbon (graphite) of SWNT.

Selection of Pt nanoparticles over Fe is subjective because it appears slightly darker in the TEM image (Figure 1) and lacks consistency and reliability.

The X-ray diffraction pattern of Pt/SWNTs (Figure 3) shows the peaks corresponding to various Pt crystal surfaces. The diffraction peaks observed at 39.9°, 46.5°, 67.8°, and 81.5° correspond to the Pt planes of (111), (200), (220), and (311), respectively. This result was consistent with reports of other carbon-supported Pt electrocatalysts.[10,35,36] A less resolved diffraction peak observed at 86.1° could be coincided with Pt (222).[36] The XRD diffraction pattern of the Pt−Fe alloy formed by the co-deposition method[37] showed a positive shift for all platinum peaks. In this study, however, there is no such evidence for the formation of the Fe−Pt alloy.[37] Therefore, the Pt particle size can be estimated using Scherrer's equation (eq 2) and the diffraction peak at 67.8°.[2,37−39]

$$L = \frac{0.94\lambda_{\kappa\alpha1}}{B_{(2\theta)}\cos\theta} \qquad (2)$$

where L is the average particle diameter, $\lambda_{\kappa\alpha1}$ is the wavelength of X-ray radiation (0.154 18 nm), $B_{2\theta}$ is the full width at the half-height in radians of the diffraction peak, and θ is the diffraction angle of the peak ($2\theta = 67.8°$). Average sizes of Pt nanoparticles calculated from that equation are shown in Table 1. The particle sizes of our catalyst are comparable to that reported by Poizo et al.[2] (2.0−5.4 nm), Li et al.[37] (2.9−7.3 nm), and Tian et al.[39] (4.2 nm). Furthermore, increasing the particle size from Pt/SWNT-1 to Pt/SWNT-3 is attributed to the higher initial concentration of $PtCl_4^{2-}$ used in the latter case, as mentioned by Lafuente et al.[38]

The catalytic activity of Pt/SWNTs is often attributable to the electroactive surface area of Pt.[40] This surface area can be estimated by measuring the charge associated with the hydrogen desorption in a steady-state CV containing only the supporting

Table 2. Comparison of the Catalytic Activity of Each Catalyst toward Methanol Oxidation (in 1 M H_2SO_4 and 0.1 M CH_3OH under N_2 Saturated Conditions) and Oxygen Reduction (in 1 M H_2SO_4 Purged with O_2 for at Least 30 Min)[a]

catalysts	surface area (m²/g of Pt)	methanol oxidation		oxygen reduction	
		Ep (mV)[b]	Ip (A/g of Pt)	Ep (mV)[b]	Ip (A/g of Pt)
Pt/SWNT-1	34.1 (19.2)	560 (5.7)	80.8 (35.2)	463 (13.4)	66.8 (2.8)
Pt/SWNT-2	45.3 (12.3)	585 (0.4)	206.2 (4.4)	560 (4.7)	67.0 (3.4)
Pt/SWNT-3	23.6 (5.8)	591 (10.3)	93.2 (26.6)	581 (16.5)	22.8 (0.5)
Pt/CB[c]	26.0 (1.7)	562 (1.3)	82.6 (1.3)	480 (8.1)	28.9 (0.4)

[a] The electroactive surface area was calculated using eq 3.[23−26] Each measurement was replicated 4 times. [b] Potentials are reported versus the Ag/AgCl reference electrode. [c] Pt/CB is the commercial catalyst purchased from E-TEK. In the catalyst, Pt nanoparticles are deposited onto the surface-enhanced carbon black, XC-72R.

electrolyte. The following equation was used to calculate the electroactive surface area of Pt:[23−26]

$$S = \frac{A}{\nu 210 \, \mu C/cm^2} \qquad (3)$$

In the above equation, S, A, and ν indicate the electroactive surface area in cm², the area in ampere−volt associated with the hydrogen desorption, and the potential scan rate (V/s), respectively. The average charge associated with a monolayer of hydrogen is assumed to be 210 $\mu C/cm^2$.[26] From this analysis, the electroactive surface areas of Pt/SWNT-1 (5.6 wt % Pt) and Pt/SWNT-2 (14.1 wt % Pt; see Table 1) were found to be nearly equal (Table 2). The commercial catalyst exhibited a smaller active surface area than a previously reported work.[2] The reason is not known at this time; however, our experiments were carried out consistently for all of the catalysts tested in this work. Therefore, a relative comparison of our catalyst to other reported catalysts can still be made. Electroactive surface areas of Pt/SWNT-1 and Pt/SWNT-2 were significantly larger than either Pt/SWNT-3 (28.2 wt % Pt) or the commercial catalyst (Table 2). A similar observation was made by Zheng et al. and suggested that increasing the initial concentration of Pt^{II} ion did not result in a wider dispersion of the metal particles on the nanotubes but rather formed larger clusters.[18]

Catalytic Activity of Pt/SWNT in Anodic Oxidation of Methanol. The Pt/SWNT catalysts were examined for the anodic oxidation of methanol in 1 M H_2SO_4 at room temperature and ambient pressure. Figure 4 shows a CV for the oxidation of 0.1 M methanol by Pt/SWNT-2 (Figure 4a) and by the

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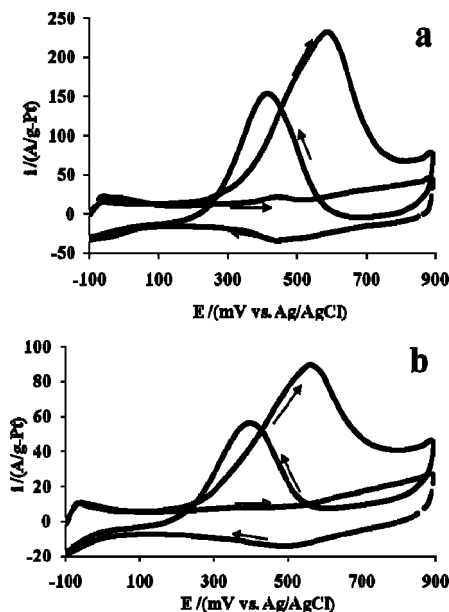
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Figure 4. CV responses of (a) Pt/SWNT-2 with 14.1 wt % Pt and (b) the commercial catalyst for methanol oxidation. Reaction mixture contained 0.1 M CH_3OH with 1 M H_2SO_4 as an electrolyte. The solution was deoxygenated with N_2 gas for at least 30 min prior to analysis. Background scans ($\cdots$) contained only the electrolyte. The potential was swept at 50 mV/s in the direction as shown by the arrows.

commercial catalyst (Figure 4b). Currents in the figure were normalized with respect to the mass of Pt on the working electrode. Key parameters, the forward peak potential and current, are summarized in Table 2. In previously reported works, Pt catalysts synthesized using supercritical CO_2,[8] electrochemical deposition methods,[41] and microwave-assisted polyolysis[40] have exhibited the peak potential at 0.7 $V_{Ag/AgCl}$, 0.68 V_{SCE}, and 0.69 V_{SCE}, respectively. In comparison to those values, the forward peak potentials of our Pt/SWNTs are much lower (between 560 and 591 $mV_{Ag/AgCl}$). Therefore, our method generated a more active Pt catalyst than the other synthetic methods. As shown in Table 2, the peak current for methanol oxidation on Pt/SWNT-2 was 2.5 times larger than that of the commercial catalyst. This peak current was also the highest among the Pt/SWNTs synthesized in this report (Table 2), attributable to its electroactive surface area.

Catalytic Activity of Pt/SWNT in the Electro-reduction of Oxygen. Pt/SWNTs were also examined for the cathodic reduction of oxygen in 1 M H_2SO_4 at room temperature and pressure. Figure 5 shows the representative CVs of Pt/SWNT-2 and the commercial Pt/CB catalyst. A comparison of the peak currents revealed that Pt/SWNT-2 indicated 2.3 times relative enhancement from 28.9 A/g of Pt observed with the commercial catalyst. Similar current enhancements were noted for Pt/SWNT-1 (5.6 wt % Pt) over Pt/CB. Also significant was that the peak potential for oxygen reduction on Pt/SWNT-2 was 80 mV more positive (560 $mV_{Ag/AgCl}$) than the commercial catalyst (480 $mV_{Ag/AgCl}$). This indicates that a DMFC based on the Pt/SWNT-2 cathode catalyst would generate 80 mV more voltage over the reference commercial system. Furthermore, the peak potential of Pt/SWNT-2 is over 100 mV more positive than the previously reported values,[21] indicative of a better catalytic activity for the Pt/SWNT catalyst. LSV was also employed in this study, and the results are shown in Figure 6. The general trend of the catalyst

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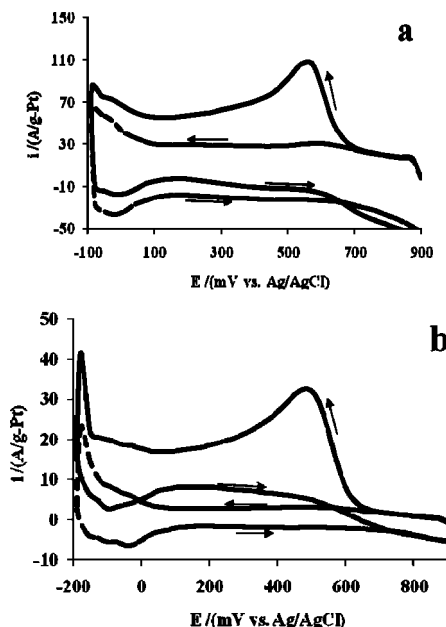
Figure 5. CV responses of (a) Pt/SWNT-2 with 14.1 wt % Pt and (b) a commercial catalyst for oxygen reduction. Each CV was conducted in oxygen-saturated 1 M H_2SO_4. Dotted lines indicate background scans that were collected in the electrolyte solution deoxygenated with N_2 gas for at least 30 min prior to analysis. The potential was swept at 50 mV/s in the direction as shown by the arrows.
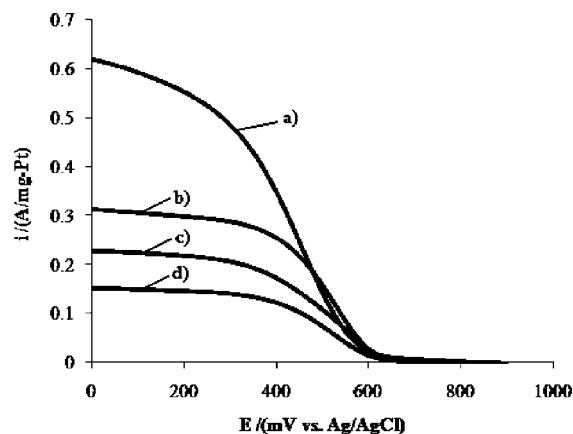
Figure 6. LSV of (a) Pt/SWNT-1, (b) Pt/SWNT-2, (c) Pt/CB, and (d) Pt/SWNT for the oxygen reduction reaction. LSV was conducted in 1 M H_2SO_4 under O_2-purged conditions at 10 mV/s, while the electrode was rotated at 1000 rpm.

activity correlates to the CV result shown in Figure 5, which indicates that Pt/SWNT-1 and Pt/SWNT-2 have higher activity toward oxygen reduction reaction than the commercial Pt/CB. An interesting observation is that a much higher current response is obtained from Pt/SWNT-1 than from Pt/SWNT-2, suggesting that the former has a better Pt dispersion than the latter. This is probably because Pt/SWNT-1 contains a smaller average particle size than Pt/SWNT-2, while the electroactive surface area is within one standard deviation.

Conclusion

A simple, rapid, and economical method for the preparation of Pt/SWNTs is demonstrated. Furthermore, it does not require purification or functionalization of SWNTs, indicating a strong possibility for scale up. The newly synthesized Pt/

SWNTs are more active toward DMFC electrochemical processes than a commercial catalyst. This efficient preparation of Pt nanoparticles is achieved through spontaneous reduction by methanol, and as much as 98.6% of the original Pt concentration can be reduced during the synthesis. The synthetic method shows a linear correlation between the weight percent of Pt deposited onto SWNTs and the original concentration. This result suggests that the amount of Pt deposited can be easily controlled as needed for commercial applications. Electrochemical characterization of Pt/SWNTs exhibits high catalytic activities toward anodic oxidation of methanol and cathodic reduction of oxygen of DMFC, as indicated by our CV experiments. Thus, application of this catalyst in a DMFC is expected to increase the cell performance. Research along this direction is currently in progress in our laboratory.

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