

Remarkable support effect of SWNTs in Pt catalyst for methanol electrooxidation

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Abstract

Carbon nanotubes have been proposed as advanced metal catalyst support for electrocatalysis. In this work, different carbon support materials including single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) and XC-72 carbon black, were compared in terms of their electrochemical properties using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The SWNTs is found to exhibit the highest accessible surface area in electrochemical reactions and the lowest charge transfer resistance at the SWNTs/electrolytes. These carbon materials are then loaded with varying amount of Pt by the electrodeposition technique to prepare carbon supported Pt catalysts. Electrochemical measurements of methanol oxidation reveal that the SWNTs supported Pt catalyst exhibits the highest mass activity (mA/mg-Pt). In comparison with Pt-XC-72 and Pt-MWNTs, the remarkably enhanced electrocatalytic activity of the Pt-SWNTs maybe attributed to a higher dispersion and utilization of the Pt particles, which are directly related to the electrochemical characteristics of SWNTs. The high concentration of oxygen-containing functional groups, high accessible surface area, low charge transfer resistance at the carbon/electrolyte interfaces can be important for the Pt dispersing and strong metal-support interaction in the Pt-SWNTs catalyst.

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1. Introduction

Electrocatalytic oxidation of methanol is of great importance in the electrochemistry of direct methanol fuel cell (DMFC) aimed to applications ranging from transportation to portable devices [1,2]. Multifunctionality, such as surface reactivity, electronic conductivity, ionic conductivity, separation of electron–hole pairs and mass transport of molecules, is obligatory to the

electrocatalyst in enhancing the chemical conversion [3]. To achieve high catalytic activity and reduce the metal loading, Pt- and Pt-based catalyst particles should display nanometric dimension and be uniformly distributed on porous carbon support surface with appropriate interparticle distances via chemical or electrochemical reduction of the catalyst precursors.

Carbon materials have been generally used to support nanosized metallic particles toward the electrooxidation of methanol or hydrogen at the anode as well as the electroreduction of oxygen at the cathode in proton membrane fuel cells. At present, one of the primary carbon supports is Vulcan XC-72. Although its high surface area (ca. 250 m²/g) generally enhances the catalyst

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dispersion, the presence of micropores (<2 nm diameter) in the XC-72 carbon can induce a poor Pt utilization, as Pt particles in the micropores are inaccessible to the methanol molecules [4]. Furthermore, the XC-72 carbon generally has sulfur groups and may cause aggregation of the Pt particle [5].

Recently, as new forms of carbon, carbon nanotubes (CNTs) including single-walled (SWNTs) [6–12] and multi-walled (MWNTs) [13–16] appeared to be promising supporting materials in electrocatalysis. Some results indicated that the CNTs support induced higher catalytic activity than the conventional Vulcan XC-72 carbon support, however, the reason why the CNTs support is more suitable for the Pt particles toward methanol oxidation is still unclear. A primary goal of this work is to make a comparison among the different carbon support materials (XC-72 carbon, MWNTs and SWNTs) in terms of their electrochemical characteristics to understand the inherent properties and advantages of SWNTs as a support of Pt catalyst for methanol electrooxidation. The carbon support materials are characterized using cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) in H_2SO_4 solutions. The carbon materials are then loaded with varying amounts of Pt by the electrodeposition technique, an effective and convenient method to deposit Pt particles [17,18] and further characterized using XPS and TEM techniques. It is discovered that Pt deposited on SWNTs exhibits, in comparison with the Pt on MWNTs and XC-72 carbon, remarkably enhanced catalytic activity in the electrooxidation of methanol. The results indicate that the SWNTs can be exploited as an advanced support material for metal catalyst in fuel cell and heterogeneous catalysis.

2. Experimental details

2.1. Pretreatment of the carbon support materials

The employed MWNTs (i.d., 3–10 nm; o.d., 6–20 nm; length-to-diameter ratio 100–1000) were prepared by chemical vapor deposition (CVD) method using Fe/ Al_2O_3 as catalyst and propylene as carbon source [19]. SWNTs with diameters of 1.25 ± 0.2 nm and length in between 1 and 10 μm were also produced via CVD method, which was described in ref [20]. A general method to modify surface of the nanotubes for the deposition of nanometric Pt particles is the oxidation treatment with oxidative mineral acids. In the present study, the MWNTs and SWNTs samples were pretreated by refluxing in $\text{HNO}_3 + \text{H}_2\text{SO}_4$ (1:3) solution for 1 h, followed by extensive washing with deionized water. For a comparison, carbon black powders (Vulcan XC-72, Cabot International) were also used without any further pretreatment.

2.2. Electrochemical characterizations of the carbon materials

Paste electrodes of XC-72, MWNTs and SWNTs were prepared by mixing each of the carbon materials with 5% Nafion isopropanol solution, respectively. The paste were applied to a glassy carbon rotating disc electrode (GC-RDE) and air-dried for 30 min at 60 °C. The loading of carbon material was controlled to 1.0 mg/cm^2 in all the measurements.

An EG&G model 273 potentiostat/galvanostat and 1025 Frequency Response Detector were used for all electrochemical measurements in a conventional three-electrode cell, using a SCE as reference electrode and a large-area Pt sheet as the counter electrode at room temperature (23 ± 2 °C). Each of the GC-RDE loaded with the individual carbon materials was characterized as a working electrode in 0.5 M H_2SO_4 by CV and EIS. The sweep rate in CV measurement is 20 mV/s. The EIS measurements were performed under open circuit potential with an excitation signal of 5 mV at frequency ranges of 100 kHz to 0.1 Hz.

2.3. Electrocatalytic activity measurements

Electrodeposition of Pt was conducted in 0.5 M H_2SO_4 solution containing 3 mM H_2PtCl_6 at constant potential (0.05 V) and the GC-RDE loaded with the carbon materials are used as the working electrodes. The carbon materials loaded Pt were denoted as Pt-XC-72, Pt-MWNTs and Pt-SWNTs, respectively. The amount of loaded Pt was evaluated from the charge consumed during the electrodeposition, assuming that Pt^{4+} to Pt^0 reduction is 100% efficiency [21]. The Pt particles deposited on different carbon materials were characterized by XPS using an ESCA 210 and MICROLAB 310D spectrometer. The morphology of the electrodeposited Pt on nanotubes was measured using a JEM-100S transmission electron microscope (TEM).

Electrocatalytic oxidation of methanol on the Pt-XC-72, Pt-MWNTs and Pt-SWNTs was carried out in 0.5 M $\text{CH}_3\text{OH} + 0.5$ M H_2SO_4 solutions by a CV technique at 20 mV/s between 0 and 1.25 V. To evaluate the stability of methanol oxidation on the different carbon materials supported Pt particles, current–time curves were also performed at given potential 0.45 V.

3. Results and discussion

3.1. Electrochemical characterizations of the carbon materials

Fig. 1 compares the CVs of the Vulcan XC-72, MWNTs and SWNTs in 0.5 M H_2SO_4 solution between 0 and 1.25 V at a sweep rate of 20 mV/s. The upper

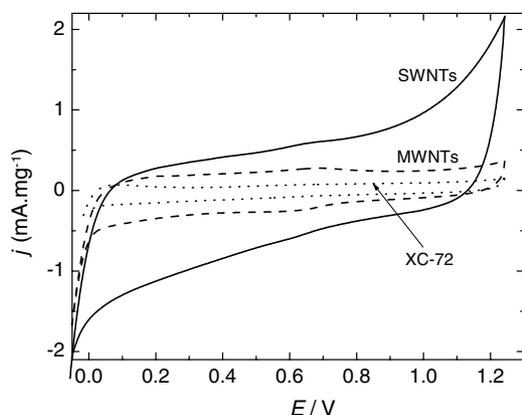


Fig. 1. Cyclic voltammograms recorded in 0.5 M H₂SO₄ with a scan rate of 20 mV/s.

branch of the voltammograms between 0.3 and 0.8 V is presumably due to Faradaic pseudocapacitances associated with oxygen-containing surface functionalities on the carbon support materials, which can not be eliminated by N₂ purging. The magnitude of the current depends on the concentration of the surface groups. The presence of surface functional groups can enhance hydrophilism and thereby facilitate the access of the electrolyte to the internal pore structure and increase the effective accessible surface area S_a (m²/g) of the carbon support materials. The S_a is the area of the working electrode that participates in the double-layer charging and related to the gravimetric double layer capacitance C (F/g) at a given scan rate ν [22]

$$C = I/\nu m,$$

where I is the current and m is the electrode mass. The S_a can be estimated as the specific value from the gravimetric capacitance C of the carbon support materials by the equation

$$S_a = C/C_{GC},$$

where C_{GC} is the double layer capacitance (F/m²) of glassy carbon electrode surface, for which the typical value of 0.2 F/m² was used. The S_a value for SWNTs (105.1 m²/g) is obviously much higher than those for MWNTs (52.5 m²/g) and XC-72 (14.3 m²/g).

From the above analyses, it is clear that the concentration of oxygen-containing functional groups and S_a of the SWNTs material are much higher than those of the XC-72 and MWNTs materials. The XC-72 sample, despite it shows the highest S_{BET} (ca. 250 m²/g), has a low S_a value, and only 6.4% of its surface is electrochemically available. This is probably because that the majority of the XC-72 carbon surface is associated with the micropores, which are difficult to access by solvated ions. Furthermore, the small pores of the XC-72 carbon may be partially blocked by the Nafion film uniformly spread at the carbon surface. Hence, a high accessible

surface area of the carbon support materials is very necessary for electrochemical reactions.

Besides S_a , electron resistance of the carbon support materials is also a key parameter for the development of DMFCs with low overpotentials. Furthermore, proton conductivity in the catalyst layer is of great importance at high rates of the methanol electrooxidation [23]. We measured the impedance spectra of the carbon support materials to investigate the conductivity and charge transport property of the carbon/electrolyte interfaces. The Nyquist plots for XC-72, MWNTs and SWNTs samples at open circuit potential are shown in Fig. 2(a)–(c), respectively. It can be seen that the impedance spectra of the three carbon samples displayed similar characteristics, i.e., a depressed semi-circle in the high frequency region and a straight line with a slope of nearly 45° in the low frequency region, which is typical for the impedance spectra of porous films coated on metals in the asymmetric metal/film/electrolyte configuration [24]. The depressed semi-circle in the high frequency region is ascribed to the Faradaic process of the charge exchange at the carbon/electrolyte interface. Due to the semi-infinite diffusion of ions at the carbon/electrolyte interfaces, a straight line at low frequencies can be expressed by using a Warburg diffusion element [24].

Thus an equivalent circuit shown in Fig. 3 can be depicted to explain the impedance behaviors of various carbon support materials in H₂SO₄ solution at open circuit potential. The corresponding solid lines in Fig. 2 are the fitted results according to the equivalent circuit, which were listed in Table 1. The good fittings imply that the equivalent circuit models can reasonably explain the electrochemical processes. By comparing fitted results of the carbon support materials, larger CPE and smaller n values were obtained for SWNTs, which means a higher level of available surface areas and well confirms the conclusion made from S_a values in the preceded CV measurements. The lowest W values of SWNTs also mean a facile diffusion of ions in the SWNTs pore system. In addition, the R_{ct} value in SWNTs is almost 11 times lower than that of XC-72, which reveals easier charge (ion and electron) transfer at the SWNTs/electrolyte. Moreover, to evaluate electron conductivity of various carbon supports, comparison of carbon support materials resistance R_f indicates a decrease from 1.13 Ω cm² for XC-72 to 0.66 Ω cm² for MWNTs and then to 0.47 Ω cm² for SWNTs, suggesting that the SWNTs also shows higher electron conductivity comparing to XC-72 and MWNTs. Therefore, the mesoporous SWNTs material is apparently more suitable to act as a support materials for electrocatalyst due to its large amount oxygen-containing functional groups, high accessible surface area for electrochemical reactions, and low charge transfer resistance at the interface of carbon/electrolytes.

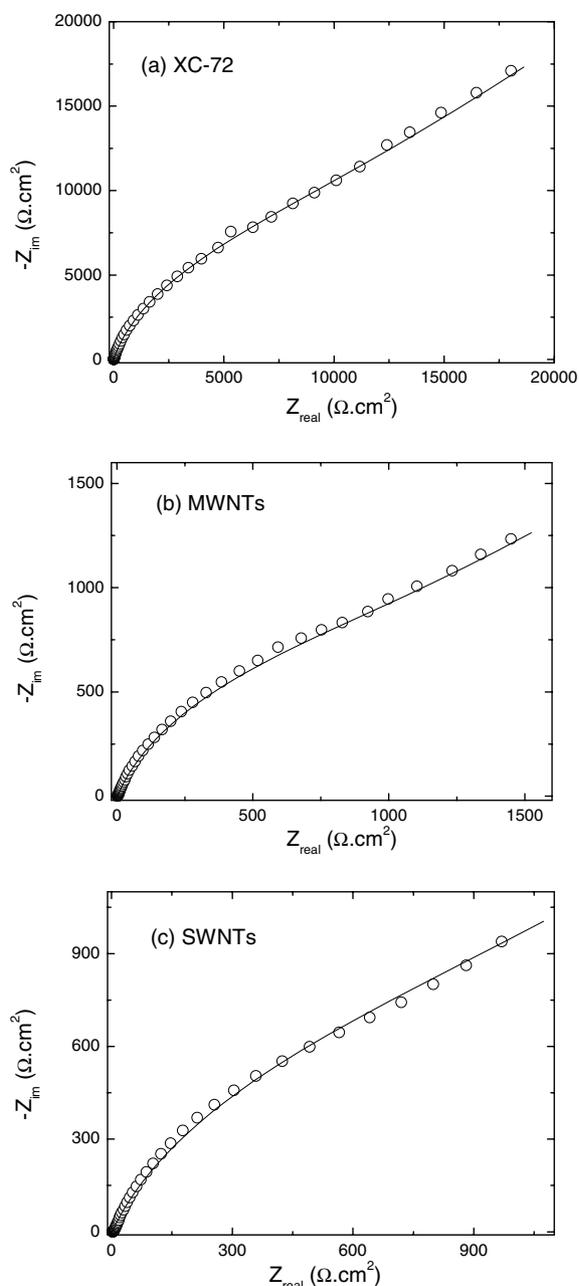


Fig. 2. Nyquist plots of XC-72 (a), MWNTs (b) and SWNTs (c) in 0.5 M H_2SO_4 at open circuit potential, the solid lines represent the fitted results.

3.2. XPS and TEM analysis of Pt catalyst supported on the carbon support materials

The carbon materials with deposited Pt particles were analyzed by XPS to determine the oxidative state of Pt as well as the interaction between metal particle and support. The XPS spectra of Pt 4f shown in Fig. 4 are found to be composed of three pairs of doublets. The most intensive doublet (at ca. 71.1 and 74.4 eV) is the signal of metallic Pt [25]. The detected slight shift to higher binding energies of the doublet peaks in Pt-SWNTs (71.8 and 75.3 eV) is probably indicative of stronger Pt-carbon support interaction or smaller Pt cluster-size effects. The second set of doublet (72.4 and 75.7 eV), whose BE are 1.4 eV higher than that of the metallic Pt, can be assigned to Pt(II) states as in PtO and Pt(OH)₂. The third doublet of Pt, which appeared at higher BEs (74.2 and 77.7 eV), is the weakest in intensity and would suggest the existence of a small amount of Pt(IV) species. Oxygen chemisorptions easily occur at the step and kink sites at the surface of Pt clusters. It is worthwhile to note that the relative amount of oxidized states of Pt in Pt-SWNTs (45%) is significantly higher than those in Pt-XC-72 (30%) sample and Pt-MWNTs (34%) samples. According to the bifunctional mechanism of methanol electrooxidation [26], the PtO and PtO₂ would enhance the electrocatalytic activity of Pt-SWNTs sample.

The samples of Pt-MWNTs and Pt-SWNTs were characterized using TEM and the results are shown in Fig. 5. It can be seen that Pt particles were well dispersed on the MWNTs (a,b) and SWNTs (c,d) with a diameter of 5–10 nm. In comparison with Pt-MWNTs, the Pt particles in Pt-SWNTs appear to have closer contact with network of entangled and branched bundles of SWNTs, and their shapes are more close to round or sphere-like, demonstrating more uniform Pt dispersion and stronger Pt-carbon interaction in the Pt-SWNTs sample. This may be due to the presence of higher concentration of functional groups (e.g., carboxylic groups) on the SWNTs surface, thus providing more anchoring sites for Pt deposition and interaction between Pt and the carbon material. In addition, the density of Pt particles

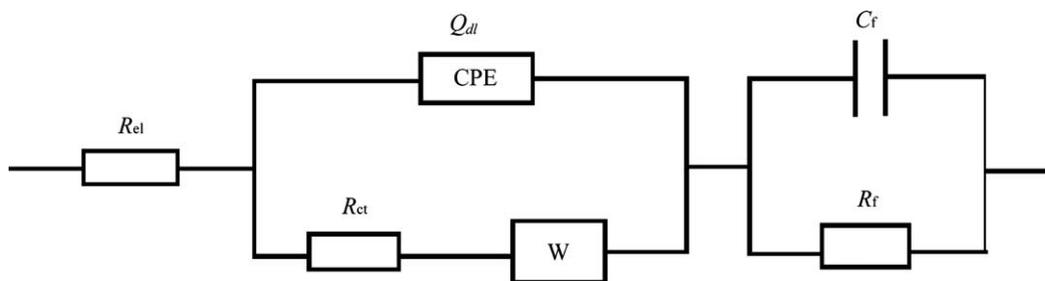
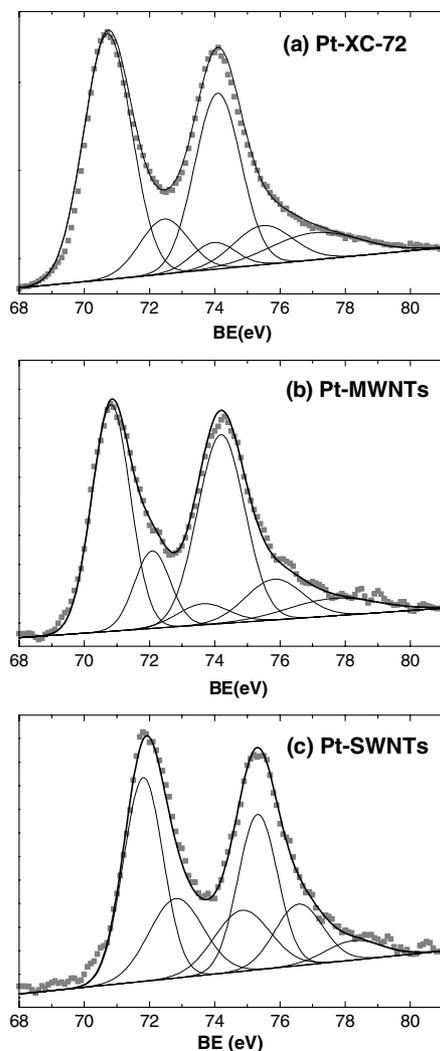


Fig. 3. Equivalent circuit for the carbon–Nafion paste electrodes in H_2SO_4 solution: R_{el} solution resistance; R_{ct} , charge transfer resistance; Q_{dl} constant phase element related to the double layer capacitance; W , Warburg impedance; R_f , C_f , carbon–Nafion paste film resistance and capacitance.

Table 1

Fitted parameters of the elements in equivalent circuits for the carbon–Nafion paste electrodes in 0.5 M H₂SO₄ solution at open circuit potential

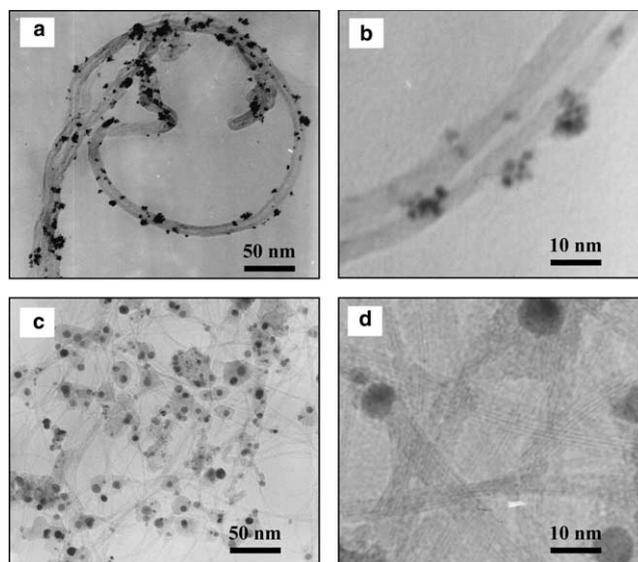
Carbon samples	CPE $\times 10^5$ ($\Omega^{-1} s^n \text{cm}^{-2}$)	n	R_{ct} (Ωcm^2)	$W \times 10^3$ ($\Omega^{-1} \text{cm}^{-2} s^{0.5}$)	$C_f \times 10^6$ (F cm^{-2})	R_f (Ωcm^2)
XC-72	113	0.85	12,590	0.16	4.8	0.479
MWNTs	146	0.81	1343	2.3	13	0.664
SWNTs	260	0.79	1074	3.1	37	1.135

Fig. 4. The Pt 4f core level XPS spectra of Pt particles supported on various carbon materials, at Pt loading of 100 $\mu\text{g}/\text{cm}^2$.

associated with the dense bundles of SWNTs was greater than that on the “incompact” ones of SWNTs. This is probably because the concentration of functional groups in the dense bundles is greater than that in the “incompact” bundles.

3.3. Methanol electrooxidation study

The CV of methanol oxidations on the different carbon supported Pt catalyst were measured at two different Pt loadings (10 and 100 $\mu\text{g}/\text{cm}^2$) and the results are

Fig. 5. TEM images of Pt-MWNTs (a,b) and Pt-SWNTs (c,d), at Pt loading of 100 $\mu\text{g}/\text{cm}^2$.

shown in Fig. 6. The calculated electrochemical active area (ECA) and mass activities (mA/mg-Pt) of methanol oxidation at a chosen potential (0.65 V) on the three carbon support materials are compared in Table 2. Irrespective of the Pt loading on the electrodes, the Pt supported on SWNTs shows much higher ECA and mass activity than those on XC-72 and on MWNTs, suggesting a higher utilization of the Pt particles.

Another important evaluation of catalytic performance for methanol oxidation is their stability at given working potentials. We measured the current–time curves at 0.45 V for the electrooxidation and the results are plotted in Fig. 7. Apparently, the Pt-SWNTs is advantageous over Pt-MWNTs and Pt-XC-72 by producing the highest current density, despite that all the three catalysts show a slightly current decay due to unavoidable formation of Pt oxides as well as adsorbed reaction intermediates during the methanol electrooxidation [27].

The better Pt dispersion and utilization in Pt-SWNTs catalyst can be accounted for by the higher accessible surface area and surface functionalities of the SWNTs materials. In addition, high conductivity (ion and electron) would also contribute to achieve the high current density of methanol oxidation on the Pt-SWNTs catalyst. The stronger interaction between Pt particles and

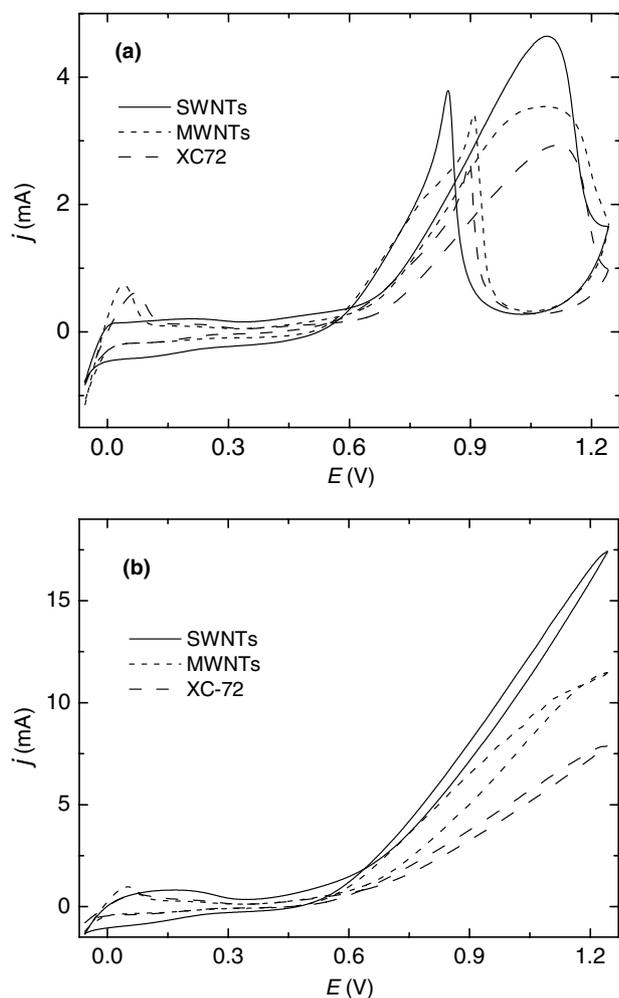


Fig. 6. CV curves of methanol electrooxidation on electrodeposited Pt particles on various carbon supports at Pt loading of (a) 10 and (b) 100 $\mu\text{g}/\text{cm}^2$ in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution with a scan rate of 20 mV/s.

the carbon of SWNTs as revealed by XPS of Pt 4f core level (Fig. 4) may be another possible reason to cause the enhanced electrocatalytic activity.

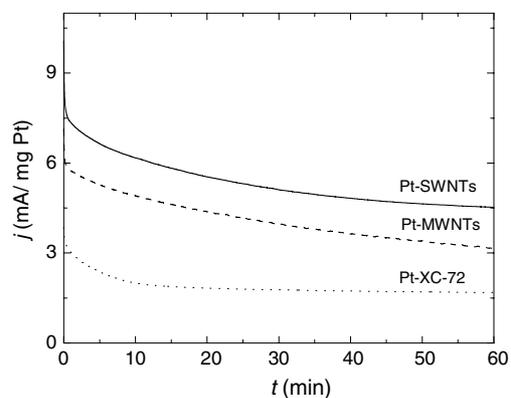


Fig. 7. Current–time curves for methanol oxidation at 0.45 V on the carbon supports deposited with Pt loading of 100 $\mu\text{g}/\text{cm}^2$.

4. Conclusions

This present work demonstrates that among the different carbon materials investigated (XC-72, MWNTs and SWNTs), the SWNTs is the most suitable support materials for Pt electrocatalyst due to its excellent electronic conductivity (graphitic crystallinity properties), high accessible surface area in electrochemical reactions and low charge transfer resistance at the carbon/electrolytes. Consequently, in comparison with the Pt-XC-72 and Pt-MWNTs catalysts, the Pt-SWNTs catalyst exhibits the highest mass activity (expressed in mA/mg-Pt) in the electrooxidation of methanol. The excellent electrocatalytic performance arises from the better dispersion and utilization of Pt particles as well as a stronger Pt-support interaction in the Pt-SWNTs catalyst. Further optimization of the Pt deposition and Pt nanoparticle formation on the SWNTs material can be expected to generate highly efficient electrocatalyst for advanced DMFC and other PEM fuel cells.

Table 2

ECA and mass activity of Pt electrodeposited on different carbon support materials for methanol electrooxidation

Samples	Pt loading ($\mu\text{g}/\text{cm}^2$)	Electrochemical active surface area of Pt (m^2/g) ^a	Mass activity, j (mA/mg-Pt) at 0.65 V vs. SCE
Pt-SWNTs	5	128	105
	10	90	100
	50	86	76
	100	71	50
Pt-MWNTs	5	110	60
	10	88	90
	50	76	60
	100	63	48
Pt-XC-72	5	84	50
	10	57	65
	50	47	50
	100	23	35

^a Determined from the hydrogen adsorption/desorption region of the CV curves in 0.5 M H_2SO_4 .

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