

Short communication

# Electrochemical durability investigation of single-walled and multi-walled carbon nanotubes under potentiostatic conditions

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## Abstract

The electrochemical corrosion behaviors of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) were investigated with potentiostatic oxidation at 1.2 V for 120 h. The surface oxygen contents of the two types of carbon nanotubes were analyzed by cyclic voltammograms (CV) and X-ray photoelectron spectroscopy (XPS). The increase in oxygen content on the SWNTs surface is higher than that on the MWNTs after 120 h oxidation. The results indicate that MWNTs exhibit higher electrochemical stability than SWNT, thus a good electrode material for PEMFC.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are expected to be promising for transportation application due to the high-power density, low-operating temperature, and fast response to power change. In recent years, the material durability has been one of the most important issues to be solved before the commercialization of the PEMFCs. The loss of electrochemically active surface area (EAS) of Pt catalyst due to catalyst material corrosion and Pt dissolution–agglomeration is considered one of the major reasons for the degradation in PEMFCs performance [1–4].

Carbon materials with high-surface areas are widely used as the support materials for Pt catalyst to increase the catalytic activity and Pt metal dispersion. However, besides the enhanced catalytic activity, the ideal support should also show good corrosion resistance because the carbon corrosion behavior will affect the performance and stability of the Pt catalyst [5,6]. If the support is oxidized to CO<sub>2</sub>/CO, Pt may be lost from the support. If

the support is partially oxidized to surface oxide, it may accelerate the increase of Pt particle size, because the presence of oxygen surface oxides may weaken the platinum-support interaction, leading to a lower resistance to surface migration of Pt particles [7]. Thus, the carbon material corrosion plays a negative effect on the stability of the Pt/C catalyst.

In recent years, carbon nanotubes have been proposed as the promising electrode materials for fuel cell due to their special electronic and mechanical properties. Compared with multi-walled carbon nanotubes (MWNTs), single-walled carbon nanotubes (SWNTs) have been received increasing attention as the electrode materials due to the higher surface areas. Some researchers [8] also demonstrated that the beneficial effect of SWNTs is more than an increased surface area of the supporting material. The potential use of SWNTs as catalyst supporting material deserves further investigation. As mentioned above, besides the high surface area, the supporting material should also exhibit high-corrosion resistance. Our previous work [9,10] indicated that Pt/MWNTs catalysts were more stable than Pt/Vulcan XC-72 catalysts under electrochemical operation conditions, which could be attributed to the specific interaction between Pt and the support and the higher resistance of MWNTs to electrochemical oxidation. Yan and co-workers [11] also found the similar result. To our best knowledge, however, no studies have

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been reported on the durability of SWNTs as electrode materials for PEMFCs.

In this work, the resistance to electrochemical oxidation of MWNTs and SWNTs was investigated under potentiostatic oxidation conditions. By comparing the electrochemical oxidation properties of the two types of carbon nanotubes, it is found that SWNTs exhibit poor electrochemical stability. The result indicates that SWNTs may not be used as the promising electrode materials with a view to the less resistance to electrochemical oxidation.

## 2. Experimental

SWNTs (purity of CNTs >90%, purity of SWNTs >50%, specific surface area >400 m<sup>2</sup> g<sup>-1</sup>) and MWNTs (purity >95%, specific surface area = 40–300 m<sup>2</sup> g<sup>-1</sup>), obtained from Shenzhen Nanotech Port Company, were used as received. The support electrode was prepared as follows [9]: SWNTs (or MWNTs) and PTFE emulsions (Du Pont) were mixed in isopropanol solution to form a dispersion of ink. The mixed ink was sprayed onto a PTFE hydrophobized carbon paper (Toray, containing 20 wt% PTFE) as the working electrode. The loading of spraying layer (for both SWNTs and MWNTs) was 3 mg cm<sup>-2</sup>, with 95 wt% carbon nanotubes and 5 wt% PTFE.

The corrosion investigation of CNTs was conducted in a three-electrode cell setup. A platinum foil and a reversible hydrogen electrode (RHE) were employed as the counter electrode and reference electrode, respectively. The above-prepared working electrode (1.0 cm × 1.0 cm) was held vertically in a chamber filled with 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, with the carbon support layer exposed to the electrolyte solution. For investigation of the carbon corrosion behavior, a constant potential of 1.2 V was applied at the working electrode with a HA-501 potentiostat/galvanostat (Hokuto Denko Ltd., Japan). The same cyclic voltammograms (CV) from 0.05 to 1.2 V was recorded at different oxidation time intervals to monitor the carbon corrosion. The current density was expressed by the geometric area of the electrode. After the corrosion test, the carbon nanotubes electrodes were washed with ultrapure water several times to remove the H<sub>2</sub>SO<sub>4</sub> solution for further physical characterization.

The surface oxygen-containing contents of carbon nanotubes were analyzed with X-ray photoelectron spectroscopy (XPS) (Physical Electronics model 5700 instrument). The samples were dried in vacuum at 60 °C immediately before XPS experiments.

## 3. Results and discussion

For the electrochemical surface oxidation experiments, the GDE samples were immersed in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at a constant potential of 1.2 V. The applied potential of 1.2 V was selected in the experiment because the cathode potential of the PEMFCs is close to 1.2 V under open circuit conditions where the carbon support is very prone to oxidation. The CVs curves recorded after 1.2 V potential holding for 0, 24 and 120 h are shown in Fig. 1. The CVs measured after oxidation show the increase of the capacitive current with the holding time. The

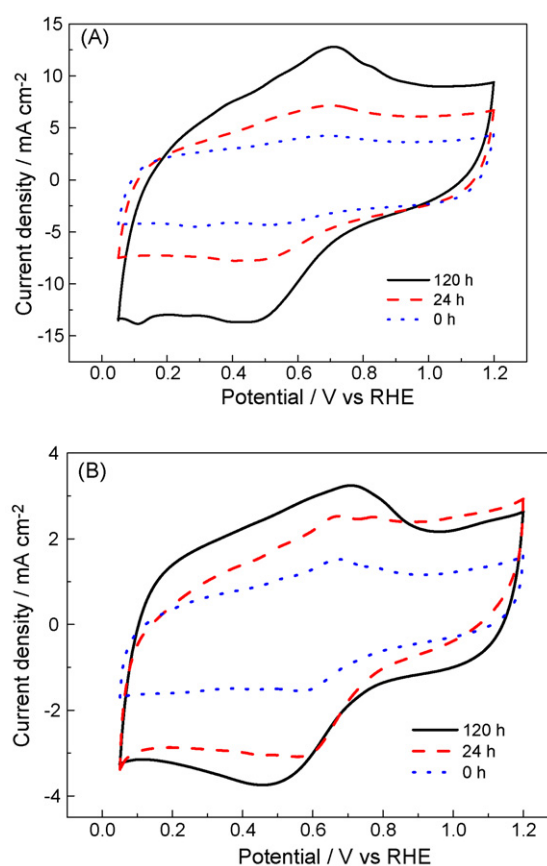


Fig. 1. Cyclic voltammograms recorded after SWNTs (A) and MWNTs (B) electrodes hold at 1.2 V for 0, 24 and 120 h in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, scan rate: 0.02 Vs<sup>-1</sup> and temperature: 20 ± 1 °C.

increase of the capacitive current indicates a higher oxidation degree of carbon with potential-holding time.

On the other hand, it can be seen that there is an obvious current peak at about 0.6 V in each CNT electrode. The faradic peak indicates the surface oxide formation due to the hydroquinone–quinone (HQ–Q) redox couple on the carbon nanotubes surface [12–14]. In order to demonstrate that the amount of HQ–Q redox couple increases throughout the oxidation experiment, the observed charge due to the above reaction can be calculated by subtracting the pseudo-capacitance charge from the total charge in the HQ–Q region [15]. The result is shown in Fig. 2. An increase in the amount of HQ–Q redox couple is observed with oxidation time indicating that surface oxide species are formed throughout the 120 h potential hold. Furthermore, the rate of surface oxidation is fast during the first 24 h and then is slow continuously.

The amount of HQ–Q redox couple produced on the SWNTs electrode (41.7 mC cm<sup>-2</sup>) is about 4.7 times that on the MWNTs electrode (8.8 mC cm<sup>-2</sup>). As is known, the  $i_{DL}$  is proportional to the effective accessible surface area ( $S_a$ ) of the electrode at a constant potential scan rate. The  $S_a$  is the surface area of the carbon nanotube electrode that contributes to the double-layer charging. From Fig. 1, it can be seen that the double-layer current density (around 0.9 V) on SWNTs (3.6 mA cm<sup>-2</sup>) is 3.0 times that on MWNTs (1.2 mA cm<sup>-2</sup>), which means that the  $S_a$

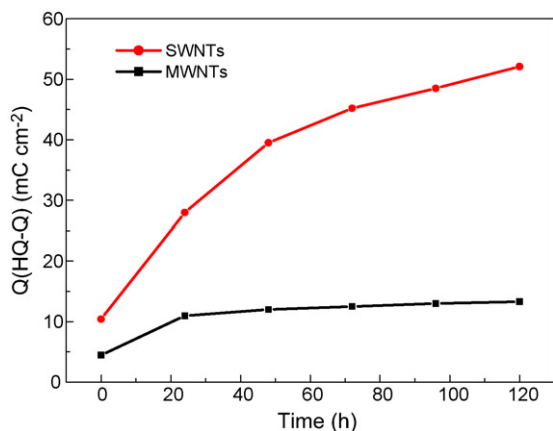


Fig. 2. The amount of the charge from HQ–Q redox as a function of hold time at 1.2 V as determined from CVs shown in Fig. 1.

of SWNTs is 3.0 times that of MWNTs. Thus, it can be concluded that the increased amount of HQ–Q on SWNTs is about 1.6 times that on MWNTs if the  $S_a$  is referred. These results suggest a higher oxidation degree on the SWNTs surface, i.e. SWNTs are less stable than MWNTs under the same corrosion conditions.

In order to characterize the electrochemical oxidation of the carbon material, the XPS analysis technique was used to determine the oxygen extent on the carbon nanotube during the corrosion test. Fig. 3 shows the survey XPS spectra of SWNTs (A) and MWNTs (B) before and after electrochemical oxidation at 1.2 V for 120 h in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution. It can be seen from the spectra that a significant increase in O 1s peak value appears in each oxidized CNTs electrode, which is attributed to the higher content of surface oxides on carbon nanotubes due to electrochemical oxidation. Furthermore, the increased extent of O 1s in the SWNTs electrode is higher than that of MWNTs. This result indicates that a higher oxidation degree appears on the surface of SWNTs. Also note that the F 1s appears on each carbon nanotubes electrode after oxidation treatment. F 1s spectra formation comes from PTFE during the electrode preparation process.

Due to the existence of F1s, it is hard to identify several oxide functional groups by deconvolution of the C 1s XPS peak. Herein what we are interested in the total increased amount of the surface oxygen content, which indicates the degree of surface oxidation. The larger the surface oxygen content, the higher the oxidation degree of carbon [16]. The surface oxygen content is determined from the O/C atomic ratio which can be obtained by integrating the area under the high-resolution XPS O 1s and C 1s spectra peaks, followed by correction with their sensitivity factors [17]. The result indicates that the O/C atomic ratio of SWNTs increases from 2.6 to 9.1% after oxidized treatment 120 h. By comparison, the O/C atomic ratio increases from 2.4 to 6.7% for MWNTs under same treatment conditions, which is less than that of SWNTs.

From the above analyses, it can be seen that SWNTs is less resistant to electrochemical oxidation than MWNTs. This can be explained as follows. It is well known that SWNTs possess higher BET surface areas and effective accessible surface

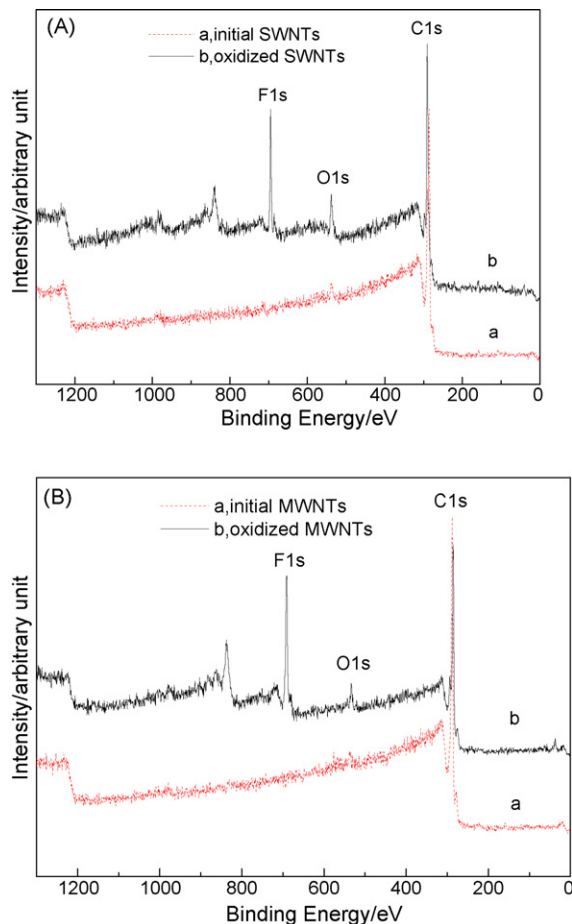


Fig. 3. Survey XPS spectra of SWNTs (A) and MWNTs (B) supports before and after electrochemical oxidation at 1.2 V for 120 h in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .

area ( $S_a$ ) than MWNTs. In our previous study [18], by the corrosion comparison of the two carbon black materials with similar characteristics and structures, a good correlation was observed between increasing carbon surface area and corrosion rate. The higher the surface area is, the more the support corrosion does. This may be one of the main reasons for the low corrosion resistance of SWNTs. On the other hand, according to the research of Ruoff and co-workers [19], smaller tube diameters should increase the oxidation rates, since the local strain energy will be raised along the entire length of the tube due to the decreased radius of curvature. Compared with the diameter of 10–20 nm for MWNTs in this study, the diameter of SWNTs is less than 2 nm. Thus, the higher local strain energy occurs on the SWNTs, which will also result in the higher corrosion rates of SWNTs.

#### 4. Conclusions

The two types of carbon nanotubes (MWNTs and SWNTs) were investigated by applying a fixed potential of 1.2 V. The increased amount of HQ–Q on SWNTs is about 1.6 times that on MWNTs if the effective accessible surface area is referred. The O/C atomic ratio of SWNTs increases from 2.6 to 9.1% after oxidized treatment 120 h. By comparison, the O/C atomic ratio

increases from 2.4 to 6.7% for MWNTs under same treatment conditions. These results suggest that SWNTs are less resistant to electrochemical oxidation than MWNTs. Thus, whether SWNTs can be used as the promising electrode materials or not for PEMFCs should be reconsidered in view of the durability issue.

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