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Short communication

Electrochemical durability of carbon nanotubes at 80 °C

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Abstract

Carbon nanotubes (CNTs) have been studied as an alternative catalyst support in polymer electrolyte membrane (PEM) fuel cells. Recent studies showed that CNTs appear to be more resistant to electrochemical corrosion than carbon black (CB). In a previous study, we have demonstrated the room temperature durability of multiwalled CNTs in both non-catalyzed and catalyzed electrochemical oxidations. This paper is to report results conducted at 80 °C—an operational temperature of PEM fuel cells. It was found that multiwalled CNTs are still more resistant than CB at the elevated temperature. However, the electrochemical oxidation rate is more rapid than that at the room temperature. As a result, a decrease in oxidation currents was observed with cyclic voltammetry, attributed to that the initial surface oxides were quickly converted to more stable oxides or carbon dioxide due to the high temperature. For CNTs, extended oxidation could not occur, in contrast to CB, because it requires attacking on the intact graphite planes which are corrosion resistant under the experimental conditions. It was found that the kinetics followed different power laws in time for different carbons.
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1. Introduction

Carbon nanotubes (CNTs) have been continuously pursued as an alternative catalyst support in proton exchange membrane (PEM) fuel cells [1–4]. In addition to their promotion effect on catalyst activity and enhancement for mass transfer in the electrodes, recent studies have demonstrated their better resistance to electrochemical corrosions than carbon black (CB) [5–7]. This latter attribute has turned out to be no less important than the former since it has been realized that electrode degradation due to CB corrosion is a significant issue in PEM fuel cells.

We have recently reported the electrochemical durability of CNTs at room temperature [5]. In contrast to CB that can be electrochemically oxidized in a wide range of potentials [8–10], CNTs were shown to be resistant to electrochemical oxidation in H$_2$SO$_4$ under both catalyzed and non-catalyzed conditions for prolonged time even at a potential as high as 1.2 V. The electrochemical oxidation of CNTs stabilized after an initial oxidation stage that was due to the defects on the CNTs; electrochemical oxidation of CB, however, was shown to undergo progressive oxidation [5,11,12].

The operational temperature of PEM fuel cells is normally at 70–90 °C [12–14]. The conclusions drawn from our previous study conducted at the room temperature may not be fully applied to the elevated temperatures in PEM fuel cells. Two recent papers by other workers [6,7] have reported experimental studies conducted at 60 °C. Shao et al. [6] reported a study performed in 0.5 M H$_2$SO$_4$ with a potential held at 1.2 V under non-catalyzed conditions. Their study showed that CNTs are more resistant to electrochemical oxidation than CB. Wang et al. [7] also studied oxidation of CNTs in 0.5 M H$_2$SO$_4$, but at a lower potential of 0.9 V. The latter workers also studied catalyzed oxidation of CNTs. However, since their experiments were performed without eliminating faradaic reactions from the Pt catalyst, it is difficult to determine the real electrochemical oxidation extent of the carbons.

In this paper, we report a further study conducted at an elevated temperature of 80 °C that is suitable for PEM fuel cell operations. Both noncatalyzed and Pt catalyzed electrochemical oxidations of multiwalled CNTs were studied in 1.0 M H$_2$SO$_4$.

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CB was also studied under the same conditions as a comparison to the CNTs. The carbons were electrochemically oxidized for up to 48 h at a potential of 1.2 V. It was again found that CNTs are electrochemically durable at the elevated temperature, and CB is not. In addition, the kinetics of the oxidations was studied, which was found to follow different power laws in time for different carbons.

2. Experimental

CB (Vulcan XC-72R) was obtained from Cabot Corporation (Tuscola, IL). Multiwalled CNTs, with ~95% in purity, 20 ± 5 nm in diameter and 5–20 μm in length, were purchased from Nanolab, Inc. (Newton, MA). The as-purchased CNTs were functionalized using a sonochemical process [15,16]. The CB was used as received. For the study of catalyzed oxidation, Pt nanoparticles were deposited on the sonochemically functionalized CNTs (i.e., Pt/CNT) [15]. A Pt/CNT catalyst with 20 wt.% Pt was used.

Electrochemical oxidation experiments were conducted in a three-electrode electrochemical cell using a glassy carbon electrode, with an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode was prepared using a thin-film technique [17]. An aqueous suspension of the carbons (CB, pure CNTs, functionalized CNTs, or 20 wt.% Pt/CNT) with a concentration of 1.0 mg mL^{-1} was prepared by ultrasonically dispersing 5 mg of the carbons in 5 mL deionized water. A 30 μL aliquot of the suspension was pipetted onto the glassy carbon substrate (3 mm in diameter). After evaporation of the water, 10 μL of a Nafion solution (5 wt.%, Alfa Aesar) was pipetted on the substrate surface, which acted as both a binder and an electrolyte.

In the electrochemical oxidation experiment, the working electrode was immersed in Ar purged 1.0 M H$_2$SO$_4$. A constant potential of 1.2 V was applied to the working electrode using a potentiostat (BAS 100B, Bioanalytical Sciences) and was held for 8, 16, and 48 h to electrochemically oxidize the carbons. A water bath circulator (Polystat, Cole-Parmer) was used to keep the experiments running at 80 °C. After the electrochemical oxidation, cyclic voltammetry (CV) was conducted on the carbons in 1.0 M H$_2$SO$_4$ solution to monitor the total surface oxides that are electrochemically active [5,11,18]. Briefly, the oxidized thin-film electrode was put in an electrochemical cell in a Faraday cage (C3 Cell, Bioanalytical Sciences) and CV was recorded from 0 to 1.0 V at a scanning rate of 20 mV s^{-1}. Ultrahigh pure Ar was the purge and protection gas. All potentials reported herein are relative to the standard reversible hydrogen electrode (RHE) potential.

To eliminate faradaic reactions due to the Pt nanoparticles in the Pt/CNT catalyst, an ion adsorption protection technique was used [5,18]. The technique involves using potassium iodide (KI) to inhibit the Pt surface. Potassium iodide aqueous solution at 0.4 mM was added to the electrolyte and the working electrode was conditioned in the electrolyte at 0.3 V for 1.0 h before recording CV. The iodine ions were found to be a good blocker for the Pt surface and can make the catalyst inactive during the CV measurements.
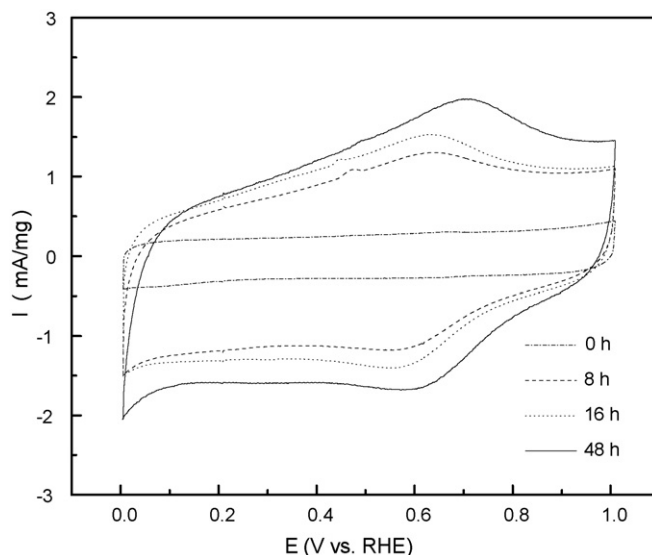

Fig. 1. Cyclic voltammograms of non-catalyzed electrochemical oxidation of CB at different durations.

3. Results and discussion

Fig. 1 shows the CV results of the electrochemical oxidation of CB at different durations. The current densities are mass-based [18–20]. The CV curve of the raw CB, i.e., the 0 h sample, is flat, which means there are negligible surface oxides. The observed currents were from the double-layer charging. The voltammograms show redox peaks that were from the surface oxides due to the hydroquinone/quinone couples. The amount of surface oxides on the carbons was quantitatively obtained by integrating the area below the anodic scan curve less the double layer charge region area. The results are listed in Table 1. Compared with the results obtained at the room temperature [5], CB still showed the same trend of progressive increase of surface oxides. However, for the same initial electrochemical oxidation period, the amount of surface oxides obtained at 80 °C is much higher than that obtained at the room temperature [5]. For 8 h, the electrochemical oxidation was measured at 9.9 C g^{-1} at 80 °C, compared to 7.4 C g^{-1} for the room temperature. This can be attributed to the acceleration of the electrochemical oxidation at high temperatures. When the electrochemical oxidation was conducted for 48 h, the oxidation was much lower than that obtained at the room temperature, with 19.3 C g^{-1} at 80 °C vs. 30.2 C g^{-1} at the room temperature. This observation was not initially expected. However, it may be explained if the mechanisms of oxidation are taken into account.
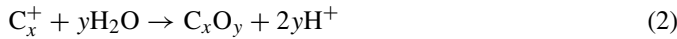
Table 1
Amount of surface oxides determined from integrating the anodic CV curves

Time (h)	Specific charge transfer (C g^{-1})			
	CB	Catalyzed CB	CNT	Catalyzed CNT
0	0.0	11.5 ± 0.7	20.5 ± 1.0	19.0 ± 1.0
8	9.9 ± 0.5	18.3 ± 0.6	27.2 ± 0.4	30.3 ± 0.1
16	14 ± 0.4	23.1 ± 0.4	28.9 ± 0.4	31.5 ± 0.5
48	19.3 ± 0.1	32.1 ± 1.0	27.6 ± 0.5	29.4 ± 0.3

Binder et al. [8] have described the electrochemical oxidation of carbons by the following steps. First, oxidation of carbon atoms occurs

$$C_x \rightarrow C_x^+ + e \tag{1}$$

This is followed by hydrolysis

$$C_x^+ + yH_2O \rightarrow C_xO_y + 2yH^+ \tag{2}$$

and then by disproportionation that leads to stable surface oxides and CO_2. Kinoshita et al. [18] also have pointed out that reaction of water molecules provides the oxygen to form surface oxides or CO_2 in electrochemical oxidations. At room temperature, the electrochemical oxidation of carbons is mild and the surface carbon atoms are oxidized to form surface oxides. However, an in-depth oxidation can occur in CB due to accelerated oxidation rate at the high temperature. As a result, CO_2 may be formed from the further oxidation that leads to the loss of mass and surface areas of the carbon. This reduction in surface areas would lead to a decrease in the surface oxides monitored by the CV. In addition, since the mass loss was not known and only the original mass was used in calculating the specific current densities, the results shown are only a representation of the lower limit in current densities. In a previous work [7], it is the geometric electrode area that was used for data representation, but that does not produce the real current densities either. Despite the difficulty in obtaining the actual current densities, it does not change the conclusion that CB has a progressive oxidation characteristic. It is just that the actual case is worse.

The CV results of the electrochemical oxidation of functionalized CNTs are shown in Fig. 2. Only a notable increase of the surface oxides occurred within 8 h of electrochemical oxidation and after that, prolonged electrochemical oxidation did not further increase the surface oxides, demonstrating that the amount of surface oxides was stabilized after 8 h. This obser-
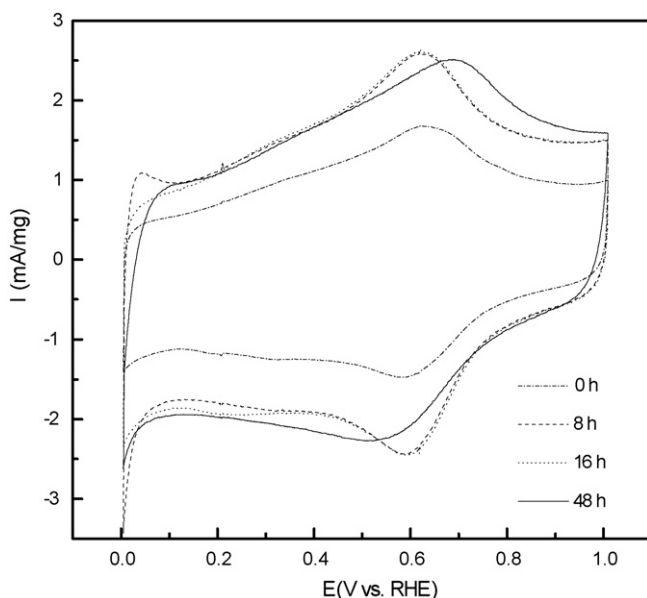
Table 2
Anodic peak current positions determined from cyclic voltammograms

Time (h)	E_p (V)			
	CB	Catalyzed CB	CNT	Catalyzed CNT
0	–	0.64	0.64	0.65
8	0.64	0.66	0.64	0.65
16	0.65	0.67	0.65	0.65
48	0.7	0.71	0.69	0.73

vation is consistent with the results reported previously for the room temperature case [5]. Because the sonochemical surface functionalization introduced surface defects on the CNTs [16], even the CNTs without electrochemical oxidation, i.e., the 0 h sample, showed the presence of redox peaks on them.

There are several types of surface oxides that can be generated on carbons, including phenol, carbonyl, carboxylic and lactone groups. For the sonochemically treated CNTs, the main surface oxides are >COH, >C=O and >COO– groups [16]. In our previous study [5], we reported a shift of the peak positions in the anodic scan that were found to move to higher potentials as the oxidation duration was increased. Because the peak current position is a result of collective contributions from all of the surface oxides participating in the redox reactions, the shift suggested a variation of surface groups that were produced during the electrochemical oxidation. This study also found shifts of peak current positions for all of the samples (see Table 2), with a similar trend to that observed at the room temperature [5]. However, the peak current positions at the elevated temperature were somewhat shifted to higher potentials, indicating that the different degree of surface oxidations occurred at the elevated temperature, leading to different types of surface oxides.

The CVs of catalyzed electrochemical oxidation of CNTs after iodine anion adsorption on the Pt surface are shown in Fig. 3. Clearly, the catalyzed oxidation occurred, and the amount of surface oxides increased significantly at the beginning; the catalyzed oxidation was also stabilized after 8 h, similar to the non-catalyzed oxidation case. Thus, CNTs again showed much higher electrochemical durability than CB at 80 °C in either non-catalyzed or catalyzed oxidations. The durability of CNTs can be attributed to the graphitic surface structures of CNTs [5]. For CNTs, the electrochemical oxidation was believed to be limited only to the top one or two graphene layers [21] where surface defects were created during the functionalization process [5]. Further oxidation can occur on the damaged graphene layers. However, in-depth oxidation must attack the intact basal planes beneath the surface carbons, which was difficult even at the elevated temperature. It is worth noting that the specific current densities presented for the CNTs should be close to the actual current densities because there was not much mass loss of the CNTs due to their resistance to electrochemical corrosion.

Transient changes of the surface oxides were studied with chronoamperometry. The chronoamperometric curves of CB, catalyzed CB, functionalized CNTs, and catalyzed CNTs during the first 8 h electrochemical oxidation are shown in Fig. 4. Both functionalized CNTs and catalyzed CNTs have less oxidation currents than CB under the same conditions. Catalyzed carbons

Fig. 2. Cyclic voltammograms of non-catalyzed electrochemical oxidation of multiwalled CNTs at different durations.
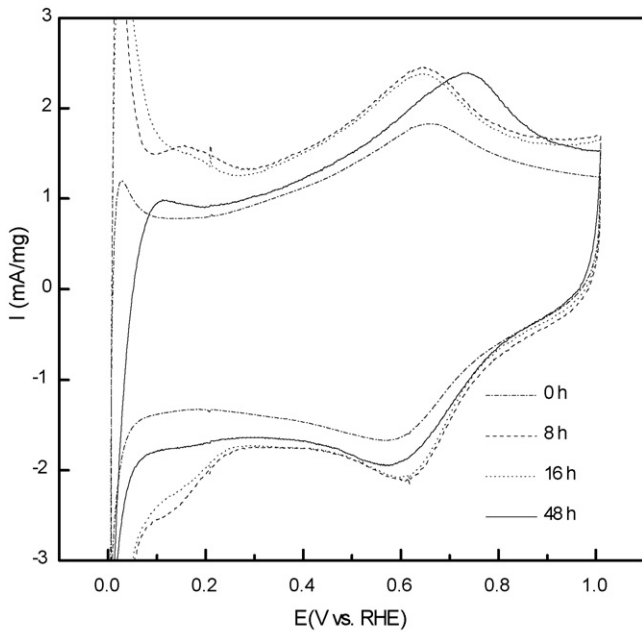
Fig. 3. Cyclic voltammograms of catalyzed electrochemical oxidation of CNTs at different durations.

showed higher current than non-catalyzed carbons, which can be attributed to the catalytic effect of the Pt nanoparticles on them.

Previous studies showed that the presence of both edge sites and surface oxides plays a role in the electrochemical corrosion rate of carbon [5,22], and the corrosion process of carbon can be proposed by two independent pathways [22,23]:
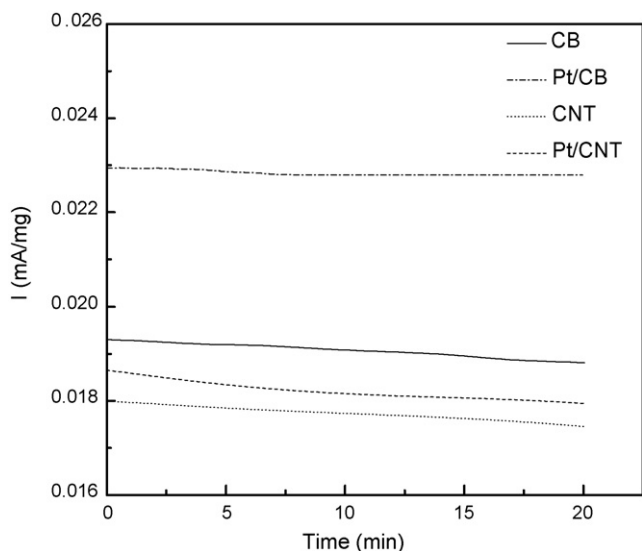
$$C \rightarrow CO_2 \tag{3}$$

$$C \rightarrow C_{oxide} \rightarrow CO_2 \tag{4}$$

Fig. 4. Chronoamperometric curves for the carbons after 8 h electrochemical oxidation, obtained at 1.2 V and 80 °C in Ar purged 1.0 M H_2SO_4.
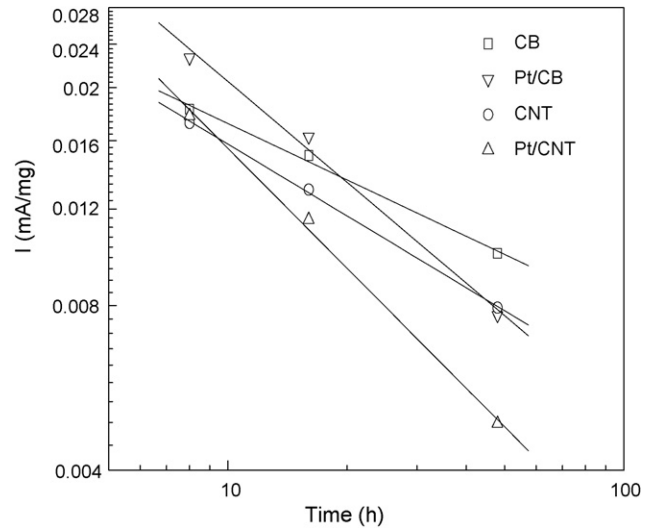

Fig. 5. Specific corrosion rates for the carbons at different electrochemical oxidation durations.

In the above two reactions, the formation of surface oxides in reaction (4) is much faster than the follow-on oxidation to CO_2. Thus, carbon surface oxides can accumulate on the carbon and the specific corrosion rate can be correlated to the surface concentration of oxygen. Because the surface concentration of oxygen changes with reaction time, the overall electrochemical corrosion rate can be expressed by the equation [22]:

$$It^n = k \tag{5}$$

where I is the specific corrosion rate (i.e., the specific current density), t the reaction time, and n and k the constants. The curves of I vs. t for CB, catalyzed CB, functionalize CNTs and catalyzed CNTs are shown in Fig. 5. From Fig. 5, it can be seen that the specific corrosion rates decrease with the increase of corrosion time. Giordano et al. [22] also reported declining corrosion rate of CB in H_3PO_4, which was attributed to the formation of surface oxides that may act to passivate the carbon surface. From the above discussion, in the case of H_2SO_4 the declined corrosion rates can be attributed to the loss of "oxidizable" surface areas or surface oxides.

The values of n can be obtained from the slopes of the linear plots in Fig. 5. They were found to be 0.34, 0.61, 0.44 and 0.73 for CB, catalyzed CB, functionalized CNTs and catalyzed CNTs, respectively. Lower values showed that the decline of corrosion rate is slower and it would take a longer time to achieve stability. For both catalyzed CB and CNT, the values of n are higher than those of the non-catalyzed due to the catalytic effect of Pt nanoparticles. Non-catalyzed CB has the lowest value of n which means the electrochemical oxidation occurred continuously. CNTs have higher values of n, and they therefore quickly stabilized in electrochemical oxidations. It is also noted that the corrosion current for catalyzed CNTs after 48 h electrochemical oxidation is lower than that of functionalized for non-catalyzed CNTs. This can be explained as follows. At the beginning of the electrochemical oxidation, there were plenty active surface oxides on both CNTs, which led to the very high corrosion currents at early stage (<8 h). After the initial electrochemical

oxidation, the active surface oxides are oxidized to more stable oxides such as CO_2 that have much less reactivity compared to the surface oxides initially present on the CNTs. Because of the catalytic effects of Pt, the rate to form more stable surface oxides on catalyzed CNTs would be much faster than that on non-catalyzed CNTs, leading to the higher corrosion currents on the catalytic CNTs initially. However, the surface oxidation on catalyzed CNTs achieved stabilization much earlier than that on functionalized CNTs as soon as the defect graphene layers were oxidized. Since in-depth oxidation cannot occur on CNTs, the decrease in currents was observed. This further evidenced that CNTs are electrochemically durable. Although catalyzed CB showed the same decrease in corrosion current, the corrosion current after 48 h electrochemical oxidation was much higher than that of catalyzed CNTs, indicating that electrochemical oxidation was still occurring on CB.

4. Conclusions

In summary, we report a study on the electrochemical oxidations of CNTs and CB at an elevated temperature (80 °C) suitable for PEM fuel cell operations. CB still displayed progressive electrochemical oxidation that was attributed to the amorphous carbons in CB and the swelling of CB in H_2SO_4 that led to in-depth oxidation. At the elevated temperature, oxidation inside the CB occurred after a prolonged period leading to mass and surface area losses. Electrochemical oxidations of CNTs were found to be stabilized after an initial period of time of 8 h, similar to that observed previously at room temperature. For non-catalyzed CNTs, the initial oxidation was attributed to the surface defects created in the sonochemical functionalization process. Catalyzed oxidation also stabilized after an initial period of time, but the oxidation rate was found to decelerate due to fast consumption of the defected surface layers at the beginning. The results obtained in this study again suggest that CNTs are technically a better catalyst support than CB.

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