

Short communication

Durability investigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell

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Received 6 July 2005; received in revised form 21 September 2005; accepted 26 September 2005

Available online 28 November 2005

Abstract

Electrochemical surface oxidation of carbon black Vulcan XC-72 and multiwalled carbon nanotube (MWNT) has been compared following potentiostatic treatments up to 168 h under condition simulating PEMFC cathode environment (60 °C, N₂ purged 0.5 M H₂SO₄, and a constant potential of 0.9 V). The subsequent electrochemical characterization at different treatment time intervals suggests that MWNT is electrochemically more stable than Vulcan XC-72 with less surface oxide formation and 30% lower corrosion current under the investigated condition. As a result of high corrosion resistance, MWNT shows lower loss of Pt surface area and oxygen reduction reaction activity when used as fuel cell catalyst support.

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Keywords: Carbon nanotube; Fuel cell; Catalyst; Support; Durability; Carbon black

1. Introduction

The durability of proton exchange membrane fuel cells (PEMFCs) has been recently recognized as one of the most important issues to be addressed before the commercialization of the PEMFCs [1–5]. It is believed that excessive degradation of stack voltage is the major failure mode for fuel cell systems. Among the reasons for the voltage degradation, Pt surface area loss due to carbon support corrosion and Pt dissolution/aggregation is considered one of the major contributors [2].

In the state of the art PEMFC, carbon black is normally used as catalyst support material for PEMFCs. Despite its widespread use, carbon black is known to undergo electrochemical oxidation to surface oxides, and eventually to CO₂ at the cathode of a fuel cell, where it is subject to high acidity, high potential, high humidity, and high temperature (~80 °C) [6]. Furthermore, during the start-up and shutdown of a fuel cell, local cathode potential can reach as high as 1.5 V, which significantly speeds

up the carbon corrosion. As carbon is corroded away, noble metal nanoparticles will be lost from the electrode or aggregated to larger particles. Oxidation of carbon support can also lead to changes in surface hydrophobicity that can cause gas transport difficulties. Early investigations of carbon corrosion in fuel cell environment were motivated by phosphoric acid fuel cell (PAFC) which runs at higher temperature than PEMFC [7,8]. Recently, Jarvi and co-workers [6] investigated electrochemical surface oxidation of Vulcan XC-72 at different potential and temperature ranges under PEMFC condition. The characterization by various techniques verifies surface oxide formation under simulated fuel cell environment. The same group also studied the influence of Pt on the corrosion of carbon support and found that Pt accelerated the corrosion rate of carbon black, in agreement with the results obtained under PAFC condition [9].

One strategy to reduce performance degradation due to carbon corrosion is to use alternative more stable carbon support. For example, it has been proposed that carbon material with more graphite component can be more stable. Recently, carbon nanotube has been proposed as promising support material for fuel cell catalyst due to its unique characteristics, including high aspect ratio, high electron conductivity, and enhanced mass transport capability [10,11]. In this paper, the corrosion current

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of carbon nanotube is examined under conditions simulating the cathode environment of PEMFC. By comparing the electrochemical properties of multiwalled carbon nanotube (MWNT) with Vulcan XC-72, it is found that the use of carbon nanotube can be promising in effectively reducing the carbon corrosion problem.

2. Experimental

The deposition of Pt on carbon black (Vulcan XC-72, Cabot) and MWNT (90%, MER Corp.) was realized by a reported ethylene glycol method [12]. The Pt loading is 30 wt%.

All the electrochemical measurements were conducted in a thermostated (60 °C) three-electrode electrochemical cell using a rotating disk electrode setup with an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode (rotating disk electrode) was prepared by applying the ink to the glassy carbon disk (Pine Instrument, 5 mm diameter) [13]. The ink was produced by ultrasonically dispersing 8.0 mg specimen (either Vulcan XC-72, MWNT, 30 wt% Pt/MWNT, or 30 wt% Pt/Vulcan XC-72) in 2 mL ethanol for 30 min. Before each experiment the glassy carbon disk was polished to a mirror finish with 0.05 μm alumina suspension, followed by ultrasonication in acetone and DI water. An aliquot of 20 μL catalyst suspension was then pipetted onto the disk. After drying the suspension at 80 °C, 10 μL of a 0.05 wt% Nafion[®] solution (diluted from 5 wt%, Ion Power Inc.) was pipetted on the electrode surface in order to attach the catalyst particles onto the glassy carbon substrate [14]. The loadings of carbon and Pt in terms of the disk area are 0.41 mg C cm⁻² and 0.12 mg Pt cm⁻², respectively.

For the surface oxidation experiments, working electrode was immersed in N₂ purged 0.5 M H₂SO₄. A constant potential (0.9 V) was applied with PAR VMP2 Potentiostat (Princeton Applied Research). The current response as a function of time was then recorded. All potentials herein are reported versus NHE at 25 °C. For Vulcan XC-72 and MWNT, throughout the oxidation process cyclic voltammetry (CV) was recorded at dif-

ferent time intervals (0, 24, 72, and 168 h) from 0.2 to 0.9 V at 10 mV s⁻¹ to monitor the surface oxidation. For Pt catalyzed Vulcan XC-72 or MWNT, besides conducting CV at from 0 to 1.2 V at 50 mV s⁻¹ to determine Pt active surface area, the activity for oxygen reduction reaction (ORR) was also examined by potentiodynamic current measurement from 0 to 1.1 V at sweeping rate of 10 mV s⁻¹ and rotating rate of 3000 rpm.

The Pt morphology before and after the oxidation treatments was examined by transmission electron microscopy (TEM, Philips CM300).

3. Results and discussion

Fig. 1a shows the forward scan of cyclic voltammogram for Vulcan XC-72 after oxidation treatment for different durations. The current density was calculated based on the geometric electrode area. The positive current offset shown in Fig. 1a is different from the current measured at a fixed potential in the range of 0.4–0.5 V, under which condition, the measured current is negligible. By scanning potential at 10 mV s⁻¹, the double layer charging of the support forms the baseline for the positive current offset. The peak current comes from the surface oxide formation due to the hydroquinone–quinone redox couple on the support surface. Note that the peak in the hydroquinone–quinone region becomes stronger with treatment time and that is also accompanied by a general increase in capacitive current. The increased peak current and capacitive current suggest a higher degree of surface carbon oxidation with time. Similar results have been reported by Jarvi and co-workers [6] who identified different oxidized groups including carboxyl, hydroxyl, and carbonyl generated on the carbon surface through X-ray photoelectron spectroscopy and thermal gravimetric analysis coupled to mass spectrometry.

In contrast, the peak current is barely visible in the case of MWNT and shows negligible change with time. The capacitive current does not change with time either. Both facts suggest that the surface of MWNT is more difficult to oxidize than Vulcan

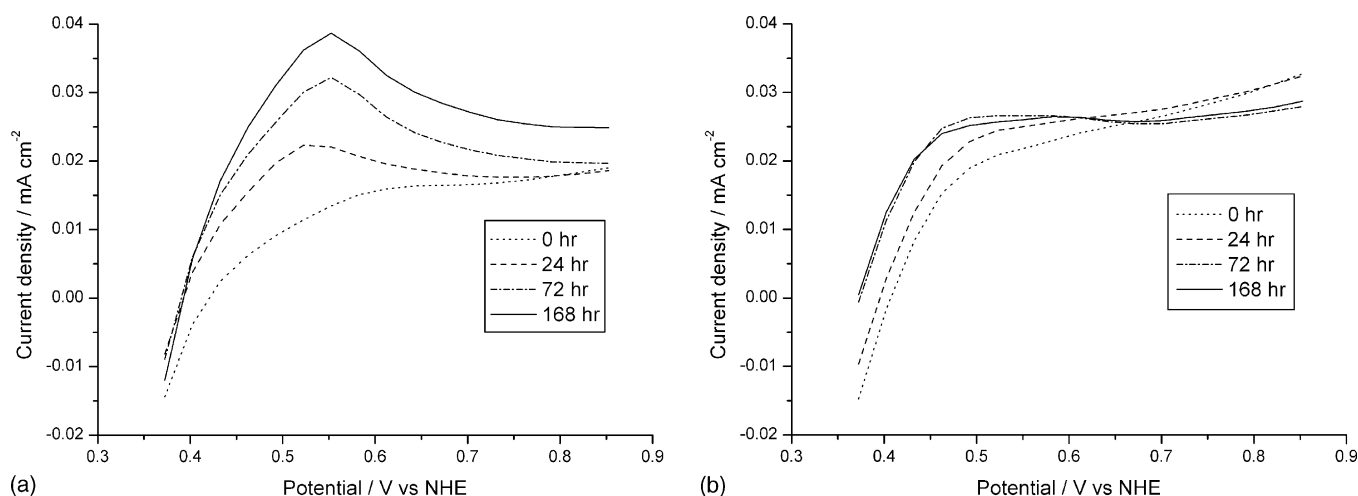


Fig. 1. Forward scan of the cyclic voltammograms of (a) Vulcan XC-72 and (b) MWNT at different time intervals during oxidation treatment in N₂ purged 0.5 M H₂SO₄, scan rate 10 mV s⁻¹.

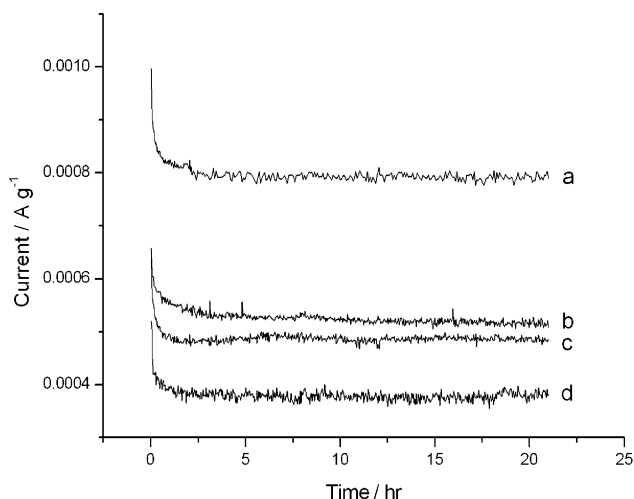


Fig. 2. Chronoamperometric curve for (a) 30 wt% Pt/Vulcan XC-72, (b) 30 wt% Pt/MWNT, (c) Vulcan XC-72, and (d) MWNT, measured at 0.9 V and 60 °C in N_2 purged 0.5 M H_2SO_4 .

XC-72 under the tested conditions. This means MWNT could potentially be more corrosion resistant and durable when used in a fuel cell.

The chronoamperometric curves of Vulcan XC-72 and MWNT and (Fig. 2c and d) show that the MWNT indeed shows 30% less corrosion current than Vulcan XC-72 under same conditions. Fig. 2 also shows the increased corrosion currents when these two materials are catalyzed with Pt nanoparticles (Fig. 2a versus Fig. 2c and Fig. 2b versus Fig. 2d). Such catalytic effect of Pt on carbon corrosion has been previously reported in PAFC and recently in PEMFC. However, the Pt catalytic effect is less significant for MWNT than Vulcan XC-72. The corrosion current is only enhanced by 40% for MWNT while 70% for Vulcan XC-72. This suggests that MWNT is more stable than Vulcan XC-72. At this corrosion rate, 9.0% of Vulcan XC-72 for the Pt/Vulcan XC-72 will be lost in approximately 1000 h, while only 5.7% for the case of Pt/MWNT. It should be mentioned that the MWNT used in this study has a claimed purity of 90%. It is likely the amorphous carbon in the MWNT have contributed to the corrosion observed. Also note that the current density reported in Fig. 2 is based on the geometric electrode area. If the corrosion current is normalized in terms of BET surface area of the support (Vulcan XC-72: $235 \text{ m}^2 \text{ g}^{-1}$ and MWNT: $100 \text{ m}^2 \text{ g}^{-1}$), the obtained corrosion current density is higher for the MWNT than for Vulcan XC-72. This may seem to suggest that the MWNT has higher corrosion rate than Vulcan XC-72. But normalization to BET surface area is problematic in that the measured BET surface area of Vulcan XC-72 contains significant contributions from micropores which may not be accessible to the electrolyte, while most of the MWNT surface area is accessible external surface area.

Most of the previous works on carbon corrosion were conducted under phosphoric fuel cell conditions [7,8], which are significantly different from this study (e.g., $\sim 160^\circ\text{C}$ versus 60°C) and thus not particularly relevant to the current study for a comparison. The most relevant work was carried out by Mathias et al. [2] who measured the carbon corrosion under conditions

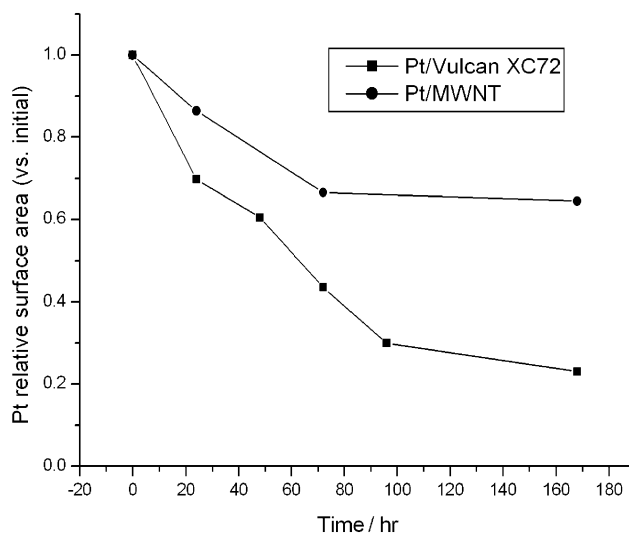


Fig. 3. Comparison of Pt active surface area loss for the case of Vulcan XC-72 and MWNT at different time intervals during oxidation treatment.

simulating PEMFC operation (95°C and 1.2 V). The corrosion rate obtained is almost five times higher than what measured in this study (0.0028 A g^{-1} versus 0.00052 A g^{-1}). Considering the differences in experiment temperature and potential, it is believed that the results obtained in this study are in a reasonable range.

To quantify the effect of oxidation treatment on Pt surface area, CV was conducted on Pt catalyzed Vulcan XC-72 and MWNT in N_2 purged 0.5 M H_2SO_4 at different time intervals during their treatment at 0.9 V and 60°C . The Pt surface area was then determined by integrating the hydrogen desorption peak of the cyclic voltammogram, after correcting for double layer charging current. The loss of Pt surface area with the time is plotted in Fig. 3. It can be seen that almost 80% of Pt surface area was lost for Vulcan XC-72 after 168 h oxidation treatment, while only 37% loss is observed for MWNT. Furthermore, most of the surface area loss for the case of MWNT occurs within 72 h, and after 72 h the rate for the Pt area loss is very small,

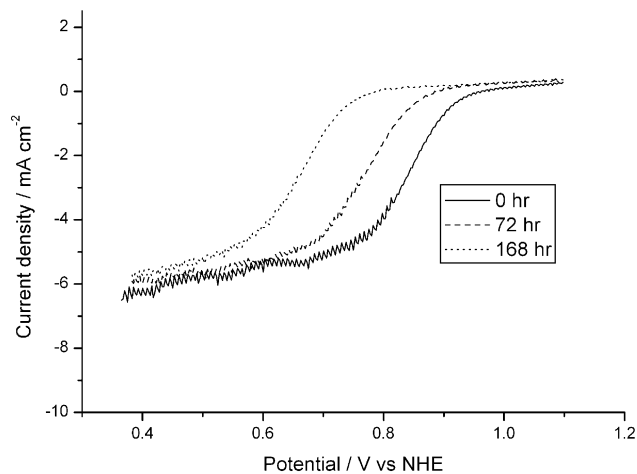


Fig. 4. Potentiodynamic currents of oxygen reduction reaction on Pt/Vulcan XC-72 as a function of oxidation treatment time. Operating condition: sweeping rate 10 mV s^{-1} , rotating rate 3000 rpm, 60°C in O_2 saturated 0.5 M H_2SO_4 .

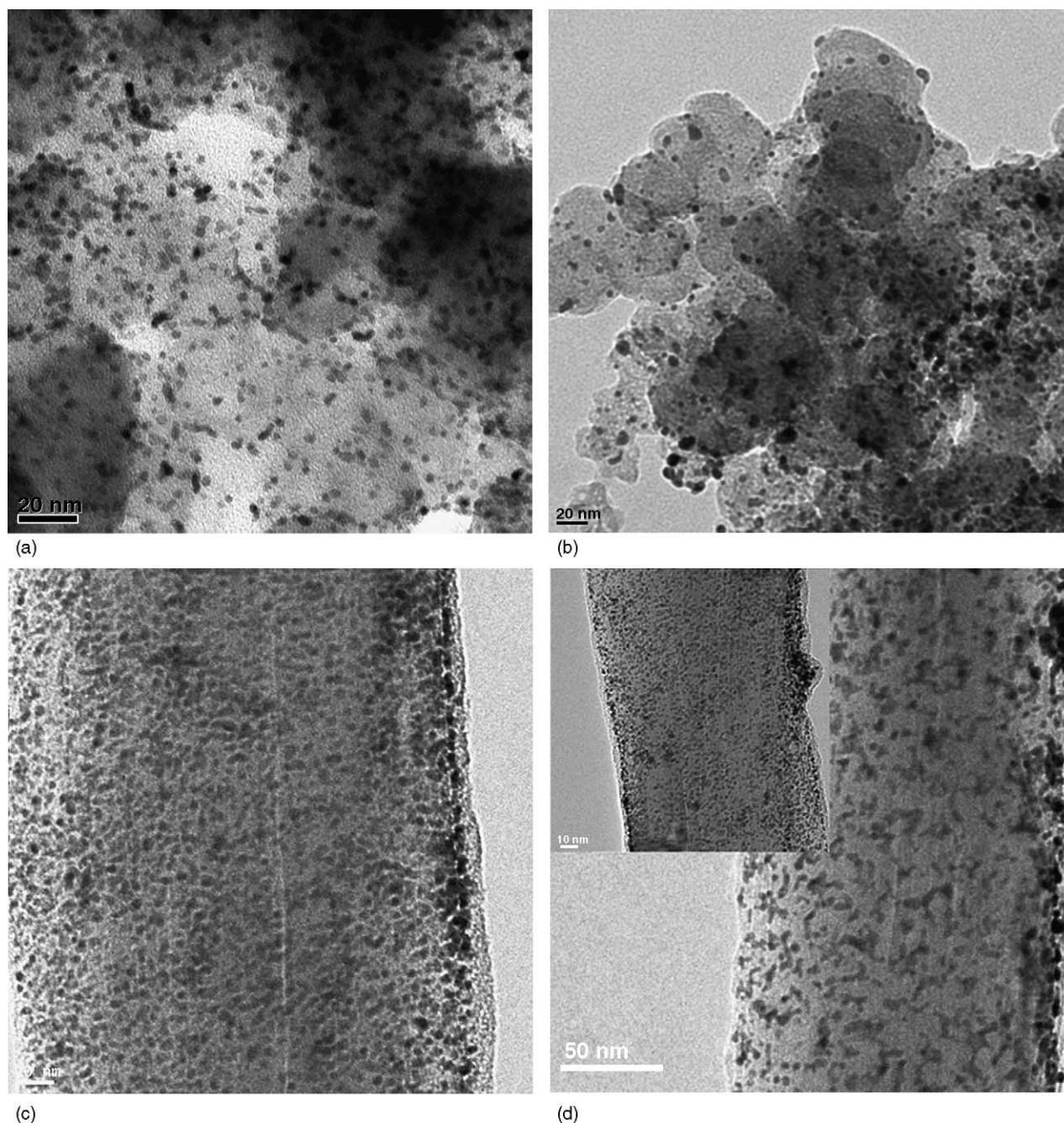


Fig. 5. TEM micrographs of (a) Pt/Vulcan XC-72 before durability test, (b) 30 wt% Pt/Vulcan XC-72 after durability test for 168 h, (c) Pt/MWNTs before durability test, and (d) 30 wt% Pt/MWNTs after durability test for 168 h. Inset of (d) shows a typical region.

indicating that MWNT could potentially provide much higher durability than Vulcan XC-72.

The initial Pt surface areas before the oxidation treatments were examined by CV, and the measured Pt surface areas are 50 and $55 \text{ m}^2 \text{ g}^{-1}$ Pt for Vulcan XC-72 and MWNT, respectively. Note that these values are in the reasonable range as reported by others. The slight surface area difference between the two catalysts may not necessarily be due to the Pt dispersion difference. In fact, if one examines carefully at the TEM images (Fig. 5), it can be seen that the Pt size on MWNT is slightly smaller than that on Vulcan XC-72. Thus, the possibility that larger initial Pt

particle size on the MWNT causes lower surface area loss can be excluded. It is most likely that the slight Pt surface area difference is caused by the different morphologies of the two supports. When the catalyst powders are dried on glassy carbon surface to form the electrode film, their packing are different due to their morphology difference, leading to the slight different surface accessibility of Pt.

The catalytic activities in terms of ORR were also examined at different time intervals by potentiodynamic current measurement in the same electrolyte saturated with O_2 . The potentiodynamic currents for ORR on Pt/Vulcan XC-72 measured at

time = 0, 72 and 168 h are presented in Fig. 4. Although the Pt surface area decreases as the treatment times increased (Fig. 3), there are no changes in the limiting currents. It is believed that at the high voltage bias used, the reaction kinetics is so fast that the process is still diffusion limited even after some significant reduction of Pt surface area. On the other hand, the half wave potential shows a continuous decrease as the treatment increases and thus used to quantify the activity difference. Half wave potential, defined as the potential at which the measured current reaches the half of the limiting current, was extracted from the potentiodynamic curve. As listed in Table 1, Pt supported on MWNT and Vulcan XC-72 has similar initial half wave potential. With time going on, both show a decrease in the activity, evidenced by the lowering of the half wave potential. However, MWNT exhibits a much slower decrease rate than Vulcan XC-72, particularly after 72 h treatment. This is in agreement with the trend observed for the Pt surface area change.

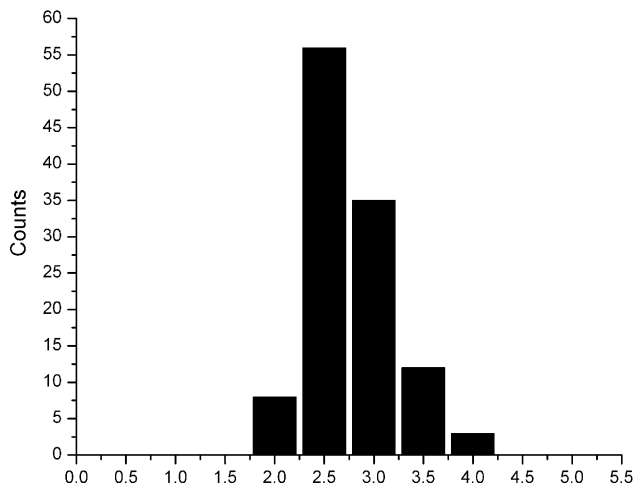
Basically there are two reasons for the Pt surface area loss, one is the Pt dissolution, and the other is Pt migration and

Table 1

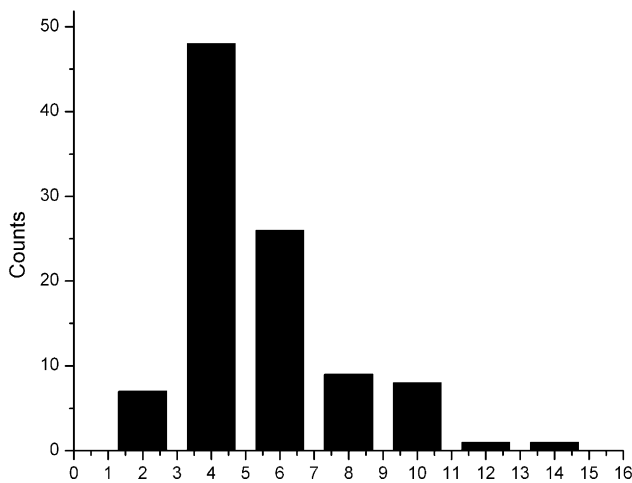
Comparison of half potential for ORR between Pt supported on Vulcan XC-72 and MWNT as a function of oxidation treatment time, rotating rate 3000 rpm

Time (h)	Vulcan XC-72 (V)	MWNT (V)
0	0.84	0.84
24	0.8	0.82
72	0.76	0.79
168	0.65	0.77

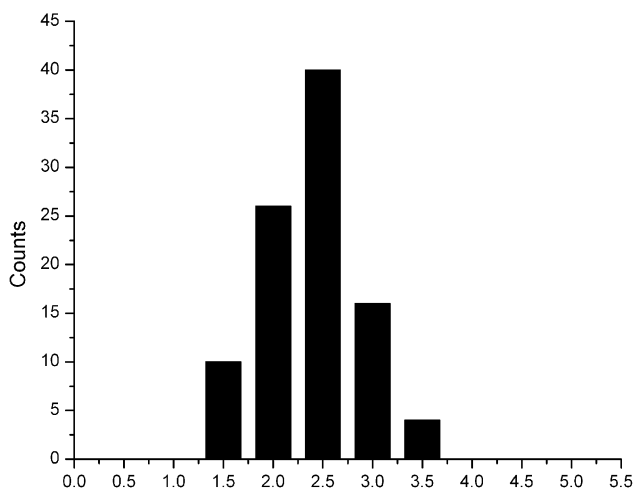
ripening/aggregation. Although a significant problem for PAFC because of its high operating temperature (140–190 °C), Pt dissolution is not a major contributor under the current investigated conditions (0.9 V and 60 °C). A simple calculation based on Pt solubility in the 0.5 M H₂SO₄ at the specified conditions [2,15] shows that, even under equilibrium condition, only 10% Pt can be dissolved. This suggests that most of the Pt surface area loss is due to the Pt migration and ripening/aggregation, which apparently can be greatly facilitated by carbon corrosion.



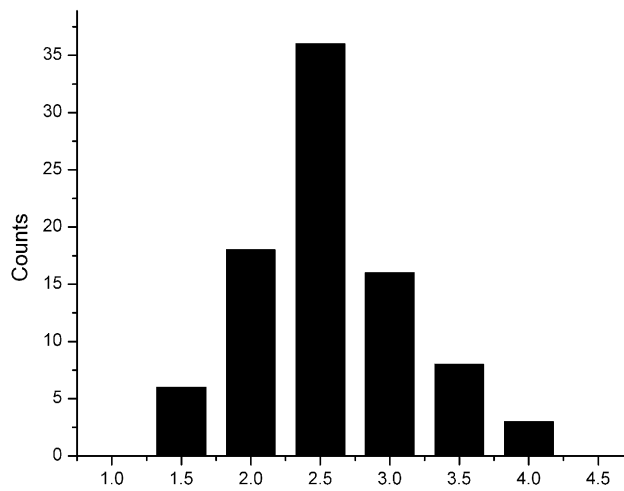
(a) Particle size / nm



(b) Particle size / nm



(c) Particle size / nm



(d) Particle size / nm

Fig. 6. Histogram of Pt particle size distribution on (a) Vulcan XC-72, before durability test, (b) Vulcan XC-72, after durability test for 168 h, (c) MWNT, before durability test, and (d) MWNT, after durability test for 168 h.

Finally, the morphology of the Pt before and after the oxidation treatment was examined by TEM (Fig. 5). The Pt/Vulcan XC-72 and Pt/MWNT have similar initial Pt particle size, and this is consistent with the fact that both catalysts were prepared by the colloidal method where the Pt nanoparticles were formed before the deposition onto the support material. Thus, the initial sizes of Pt on both supports are expected to be very similar.

Specifically, for the Pt/Vulcan XC-72 before oxidation treatment, the Pt nanoparticles show a narrow size distribution with an average size of 2.5 nm (Figs. 5a and 6a). After 168 h oxidation treatment, the particle size distribution becomes broader and the average size is around 5–6 nm (Figs. 5b and 6b).

In contrast, for MWNT, Pt particle size barely shows any increase in most regions (Figs. 5c and d and 6c and d). However, some aggregation of Pt nanoparticles is indeed observed in some isolated areas on the MWNT surface (Fig. 5d) as opposed to the uniform aggregation in the case of Vulcan XC-72. The difference in aggregation phenomena in the case of Vulcan XC-72 and MWNT is attributed to the higher corrosion resistance of the MWNT.

4. Conclusions

In summary, electrochemical characterizations show that MWNT has improved corrosion resistance over Vulcan XC-72. The catalytic effect of Pt on MWNT corrosion is less significant than that on Vulcan XC-72. Finally, the durability test demonstrates that MWNT as catalyst support exhibits less Pt surface area loss without sacrificing catalytic activity, suggesting that MWNT is a promising catalyst support for PEMFC application.

Acknowledgements

This work is supported by Pacific Fuel Cell Corp., UC-Discovery Grant, and DOD/DARPA/DMEA.

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