On-line mass spectrometry study of carbon corrosion in polymer electrolyte membrane fuel cells

Hyung-Suk Oh [a], Jong-Gil Oh [a], Seungjoo Haam [a], Kundu Arunabha [a], Bumwook Roh [b], Inchul Hwang [b], Hansung Kim [a,*]

[a] *Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-gu, 120-749 Seoul, Republic of Korea*
[b] *Hyundai Motor Company, Mabuk-Ri, Gyeonggi-Do, Republic of Korea*

ABSTRACT

The electrochemical corrosion of carbon catalyst supports in polymer electrolyte membrane (PEM) fuel cells is investigated by monitoring the generation of CO_2 using an on-line mass spectrometer at a constant potential of 1.4 V. Our results suggest that carbon supports with a high degree of graphitization are more corrosion-resistant, which results in a dramatic improvement of the catalyst durability. We also show that CO_2 measurements performed using on-line mass spectrometry represent a time-effective and reliable method for studying the electrochemical corrosion of carbon supports in PEM fuel cells.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The electrochemical corrosion of carbon in the catalyst layer of polymer electrolyte membrane (PEM) fuel cells is a topic of increasing interest because this process is considered to be one of the critical factors determining the lifetime of this type of fuel cells [1–3]. Almost all the existing electrocatalysts used in PEM fuel cells are carbon-supported Pt-based materials. From a thermodynamic point of view, carbons are prone to oxidation under the operating conditions of PEM fuel cells. The standard potential for the electrochemical oxidation of carbon as shown in Eq. (1) is only 0.207 V (vs. NHE) [4].

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E = 0.207\ V_{NHE} \tag{1}$$
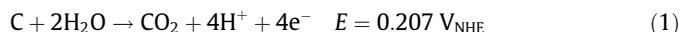
This implies that carbon corrosion is possible at potentials more positive than 0.207 V. Under normal PEM-fuel-cell operation conditions, the cathode potential is likely to be between 0.4 and 0.8 V. Although carbon corrosion is thermodynamically favored within this potential range, no severe carbon corrosion is observed because of the slow electrochemical kinetics. However, the corrosion rate can be increased, especially under abnormal operating conditions called "reverse current phenomena" [5,6]. It has been reported that an air/fuel boundary develops at the anode side during repeated start/stop procedures, which can increase the cathode

potential to a value that is two times higher than the open circuit voltage (OCV). Such a high potential would quickly corrode the carbon catalyst support, thus resulting in rapid fuel-cell-performance degradation.

Research in carbon corrosion can be classified into two categories. The first one is concerned with finding out how to prevent carbon corrosion, whereas the second one is interested in determining how to test carbon corrosion effectively to screen promising carbon supports. Various carbon materials were investigated, and it was found that those materials with a high degree of graphitization—for example, carbon nanotubes and carbon nanofibers—were more corrosion-resistant than carbon black [7–9]. To investigate carbon corrosion, cyclic voltammetry (CV) experiments are generally performed in an acidic electrolyte using a three-electrode system. After exposing the carbon materials to electrochemical-oxidation conditions, the amount of generated surface oxides is quantified by integrating the area below the curve corresponding to the anodic scan, after subtracting the double-layer charge [10]. The increased charge is then used as an indicator of the degree of carbon oxidation. However, CV results may sometimes be misleading. Surface oxides can be oxidized further to CO_2 due to the accelerated oxidation rate observed at elevated temperatures or in the presence of a catalyst [11]. The formation of CO_2 leads to a loss in carbon mass, which in turn causes a decrease in the oxidation current detected by CV [12]. Recently, the effect of Pt on the corrosion of carbon supports was studied by means of mass spectrometry carried out during the CV experiments [13]. However, a direct

---

correlation between carbon corrosion and degradation of the fuel cell performance has not been reported.

In the present work, mass spectrometry is applied to measure the amount of CO_2 produced under electrochemical oxidation conditions. Since the generation of CO_2 represents a direct evidence of carbon corrosion, it can be used to compare the corrosion resistance of different types of carbon supports. The influence of carbon corrosion on the performance loss of the fuel cells is explored by measuring the changes in the resistance and the active surface area of Pt.

2. Experimental

Two Pt/C samples (from Tanaka Kikinzoku Kogyo Co. Ltd., TKK) were used as cathode catalysts to compare their carbon-corrosion behavior, namely, a Pt/C material (with 50 wt.% Pt) containing a graphitized carbon support (G-Pt/C) and a Pt/C material (with 46 wt.% Pt) containing a non-graphitized support (N-Pt/C). The anode catalyst was 40 wt.% Pt/C (from Johnson Mathey); this material was used for all the membrane electrode assemblies (MEAs). The catalyst was ultrasonically mixed with 5 wt.% Nafion ionomer in isopropanol, and the mixed suspension was then spray-deposited onto a Nafion 112 membrane. The cell geometric area was 5 cm^2 and the Pt loading was 0.4 mg cm^{-2}. Previous to the corrosion experiments, the polarization curves, CVs, and impedances of the fresh MEAs were determined. The polarization curves were obtained at the cell temperature of 75 °C under 1 atm using O_2 and H_2. The carbon-corrosion experiments were conducted by applying a constant potential of 1.4 V against the anode for 30 min. The cathode was exposed to humidified N_2 at a constant flow rate of 30 ccm whereas humidified H_2 at a flow rate of 20 ccm was supplied to the anode. The cell and humidifier temperatures were fixed at 90 °C. The amount of CO_2 produced at the cathode was monitored as a function of time using mass spectrometry. After corrosion, the polarization curves, CVs, and impedances were measured again. X-ray diffraction experiments were performed to examine the crystallinity of the Pt/C catalysts.

3. Results and discussion

The XRD patterns of G-Pt/C and N-Pt/C are shown in Fig. 1. A diffraction peak is observed at $2\theta = 26°$ for G-Pt/C. This peak is attributed to the graphite structure of the carbon support. However, in the case of the N-Pt/C catalyst, the corresponding signal is not detected, which indicates that this carbon support is less graphitized. Fig. 2 shows a mass spectrogram recorded during CO_2 formation for the prepared MEA using G-Pt/C and N-Pt/C as the cathode catalysts. A constant potential of 1.4 V was applied for 30 min to oxi-
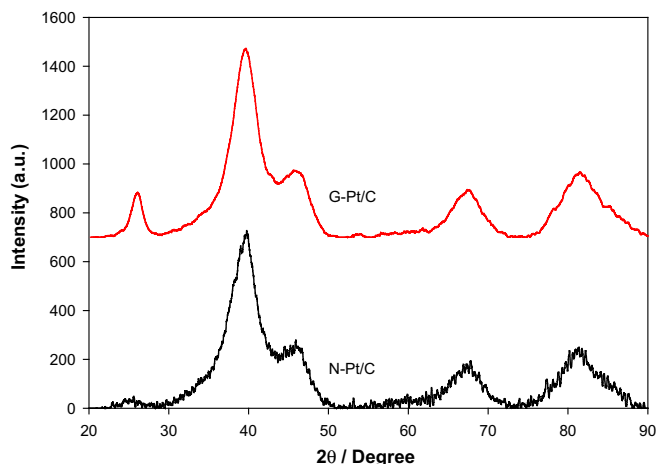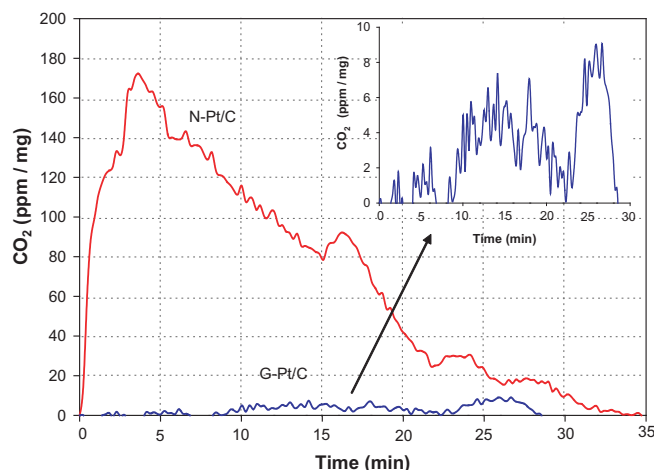

Fig. 2. Comparison of CO_2 mass-spectra profiles for MEAs with N-Pt/C and G-Pt/C at 1.4 V.

dize the carbon support because the cathode of fuel cell experiences more than 1.4 V in the abnormal operating conditions. In the case of the MEA containing the N-Pt/C catalyst, CO_2 is measured as soon as the potential is applied. The concentration of CO_2 initially increases up to 173 ppm mg^{-1} and then decreases as a function of time. On the other hand, the MEA containing G-Pt/C shows a considerably reduced CO_2 generation, below 10 ppm mg^{-1}. This result indicates that the graphitized carbon support is highly corrosion-resistive.

Fig. 3 shows the performance of PEM fuel cells before and after the corrosion test. After this test, the N-Pt/C-based MEA shows a performance decay of about 66% at 0.6 V, whereas the performance of the system containing the graphitized carbon support, G-Pt/C, remains essentially the same after the corrosion test. In order to examine the changes in the active surface area of Pt, we also carried out CV measurements of the MEAs using both types of catalysts before and after the corrosion test. The results are shown in Fig. 4. The specific surface area of the N-Pt/C catalyst decreases by 69% from 48.9 to 14.8 $m^2 g^{-1}$ after the corrosion test. It is believed that the CO_2 species formed during carbon corrosion decrease the amount of carbon available for Pt loading, which forces the Pt nanoparticles to migrate on the carbon surface, thus resulting in a decrease of the active surface area. This explanation is supported by the CV measurements performed on the MEA containing the graphitized carbon support (G-Pt/C). The result does not show any significant changes in the specific surface area of Pt after the corrosion test. If the dissolution of Pt and redeposition, which is called ostwald ripening were the main reason for the loss of active surface area, both MEAs would show a similar trend. Besides, the dissolving rate of Pt decreases as a result of the formation of a protective platinum-oxide film above 1.1 V. Therefore, it is concluded that the coalescence of Pt particles, which results from carbon-corrosion-driven migration, is the main contribution to the observed decrease of the active surface area in our electrochemical system.

Impedance analyses were carried out to determine the resistance changes associated with carbon corrosion and the results were shown in Fig. 5. The experiments were performed at 0.8 V in the frequency range of 0.1–1 kHz. The charge-transfer resistance was found to increase for N-Pt/C. It should be noted that the resistance measured at high frequency increases by 47% in the N-Pt/C-based system. However, the resistance for the G-Pt/C sample remains constant after the corrosion test. The hydrogen-permeation rate through the membrane measured using a mass spectrometer does not change after the corrosion test. Therefore, it is considered that carbon corrosion increases the electrode resistance by increasing
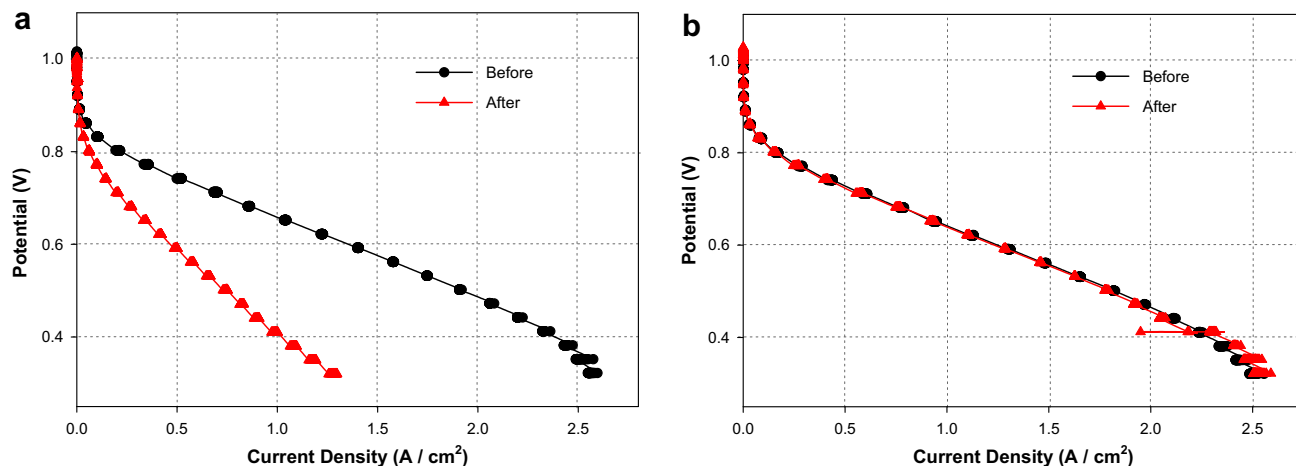

Fig. 1. XRD patterns of Pt/C powders containing different types of carbon supports.

Fig. 3. Comparison of the MEA performances before and after the corrosion test for (a) N-Pt/C- and (b) G-Pt/C-based systems.
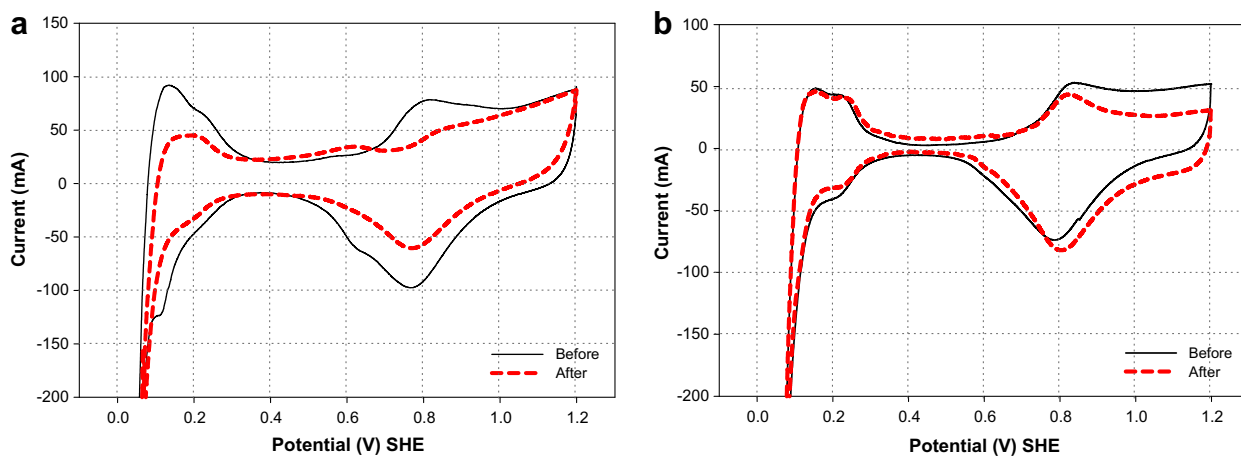

Fig. 4. Cyclic voltammograms of the MEAs before and after the corrosion test at scan rate of 50 mV s^{-1}: (a) N-Pt/C and (b) G-Pt/C.
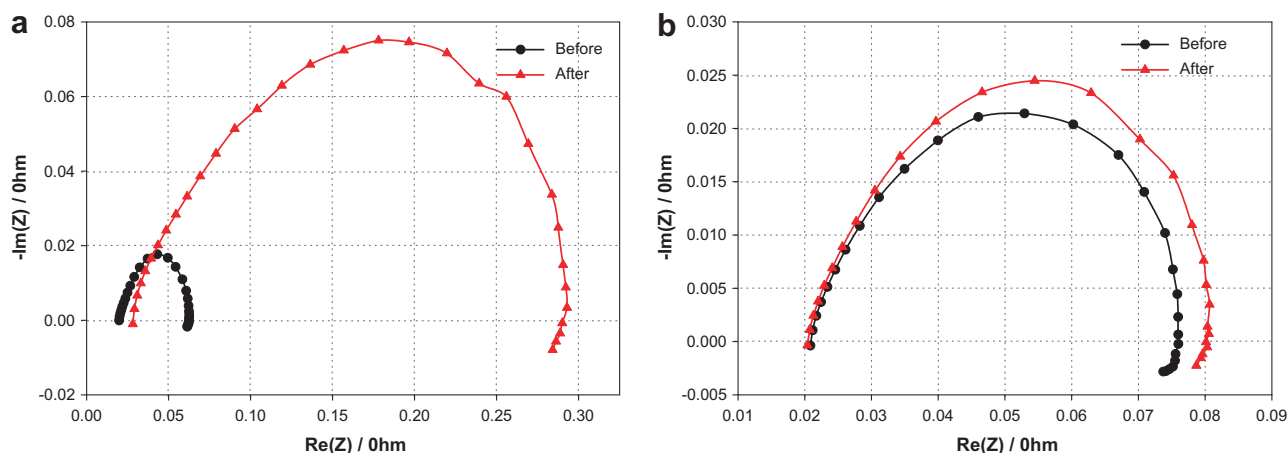

Fig. 5. Nyquist plots of MEAs based on different types of carbon supports at 0.8 V before and after the corrosion test: (a) N-Pt/C and (b) G-Pt/C.

the contact resistance in the electrode not by the damage of the membrane. These observations suggest that electrochemical carbon corrosion is a key factor determining the durability of PEM fuel cells, and that a graphitized carbon would be a better catalyst support for this type of fuel cells.

4. Conclusions

The electrochemical corrosion of different carbon supports is examined as a function of the degree of graphitization by measuring the CO_2 emission using an on-line mass spectrometer. The

G-Pt/C catalyst, which is based on highly graphitized carbon, shows a negligible CO_2 formation compared to the N-Pt/C catalyst, which consists of a non-graphitized carbon support. These results indicate that carbon supports exhibiting a high graphitization degree are more corrosion-resistant. Corrosion of the carbon supports is shown to significantly affect the performance of PEM fuel cells. This performance degradation leads to a decrease in the active surface area of Pt and an increase in both the contact resistance of the electrode and the charge-transfer resistance.

Acknowledgement

References

[1] M. Mathias, H. Gasteiger, R. Makharia, S. Kocha, T. fuller, J. Pisco, Abstract Paper, Am. Chem. Soc. 228 (2004) U653.
[2] X. cheng, L. Chen, C. Peng, Z.W. Chen, Y. Zhang, Q.B. Fan, J. Electrochem. Soc. 151 (2004) A48.
[3] J. Willsau, J. Heitbaum, J. Electroanal. Chem. 161 (1984) 93.
[4] Y. Shao, G. Yin, Y. Gao, J. Power Sources 171 (2007) 558.
[5] C.A. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry, T.D. Jarvi, Electrochem. Solid-State Lett. 8 (2005) A273.
[6] H. Tang, Z. Qi, M. Ramani, J.F. Elter, J. Power Sources 158 (2006) 1306.
[7] X. Wang, W. Li, Z. Chen, M. Waje, Y. Yan, J. Power Sources 158 (2006) 154.
[8] Y. Shao, G. Yin, Y. Gao, P. Shi, J. Electrochem. Soc. 153 (2006) A1093.
[9] Y. Shao, G. Yin, J. Zhang, Y. Gao, Electrochim. Acta 51 (2006) 5853.
[10] L. Li, Y. Xing, J. Electrochem. Soc. 153 (2006) A1823.
[11] D.A. Stevens, J.R. Dahn, Carbon 43 (2005) 179.
[12] L. Li, Y. Xing, J. Power Sources 178 (2008) 75.
[13] L.M. Roen, C.H. Paik, T.D. Jarvi, Electrohem. Solit-State Lett. 7 (2004) A19.