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Electrochemical Corrosion of Carbon Materials in an Aqueous Acid Solution

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Received July 31, 2006 ; Accepted October 4, 2006

In this fundamental study on corrosion of the carbon catalyst support in a PEMFC cathode, corrosion rates of electrodes made of carbon powder were investigated by measuring CO₂ generation. The corrosion rate was affected by not only the retention potential but also by the presence of dissolved oxygen in the electrolyte. The corrosion rate showed two stages; initial corrosion was observed for several hours, and was followed by steady-state corrosion. Even in this latter stage, change to a lower potential induced a peak in the corrosion rate that exceeded the previous steady value just after the potential was restored. Corrosion was also accelerated by platinum catalyst.

Key Words : Corrosion, Carbon, Catalyst Support, Proton Exchange Membrane Fuel Cell

1 Introduction

Recently, the corrosion of carbon materials used for the catalyst support has attracted attention as a cause of the degradation of PEMFCs.¹⁻³⁾ Such carbon materials have been considered to be stable up to 1.0 V vs. RHE in an acidic aqueous solution. Indeed, compared with the possibility of the corrosion of carbon material in phosphoric acid fuel cells (PAFCs),⁴⁻⁸⁾ that in PEMFCs seems to be less severe because of their lower operating temperature. However, corrosion of even a thin layer on the surface may cause catalyst particles to fall from the support, and lead to a loss of contact with the electrolyte, and a decrease in the hydrophobicity of the gas diffusion layer. The acceleration of carbon corrosion by platinum catalyst particles^{1,2,9)} should also be considered. Furthermore, a specific inhomogeneity of the atmosphere in a cell, such as a local incursion of oxygen into the anode, is considered to result in an anomalous high potential at the cathode that is sufficient to cause carbon corrosion.³⁾ Therefore, to predict or reduce carbon corrosion at the cathode catalyst, the fundamental nature of the electrochemical corrosion of the carbon material should be elucidated. Morphological changes in carbon surfaces during corrosion in aqueous acid solutions have been investigated microscopically,¹⁰⁻¹²⁾ and the results suggest that carbon corrodes even at potentials below 1.0 V. In this study, the corrosion of several carbon materials in an aqueous acid solution under the potential region of a PEMFC cathode was investigated quantitatively.

2 Experimental

Each electrode for the test was made by spreading an ink containing carbon powder, which is similar to that

used to fabricate the catalyst layer of PEMFCs, onto a gold mesh (2 cm × 2 cm × 0.2 mm, 0.1AU0.2-M15F, Katsurada). The ink consisted of carbon powder with or without Pt catalyst, Nafion[®] solution (5 wt%, Aldrich), and 2-propanol. As the carbon powder, natural graphite (15 μm, 13 m² g⁻¹, SNO-15, SEC), carbon black (254 m² g⁻¹, Vulcan XC-72R, Cabot), or carbon black with a Pt catalyst (5 wt% Pt on Vulcan XC-72R, E-TEK) was used. The amount of the carbon material in each electrode was *ca.* 0.1 g. The electrode was dried for 24 h in a vacuum.

A potentiostatic corrosion test was performed for each electrode using a 3-electrode cell at 80 °C for 48 h. An aqueous solution of sulfuric acid (100 cm³ of 1 mol dm⁻³) was used for the electrolyte. A Pt wire and Pt-black-plated Pt foil were used as a counter electrode and a reference electrode, respectively. Hydrogen bubbles were supplied to the surface of the reference electrode to construct a reversible hydrogen electrode (RHE). The spaces for the reference electrode and the counter electrode were separated from that for the working electrode by glass filters to avoid the mixing of atmospheres. Prior to and during the corrosion test, oxygen or nitrogen gas was bubbled into the electrolyte continuously at a rate of 20 cm³ min⁻¹ to control the atmosphere of the working electrode. The concentration of CO₂ in the exhaust gas was monitored by gas chromatography (G3810, Yanaco).

3 Results and Discussion

The time-dependence of the concentration of CO₂ in the exhaust gas from the electrode made of graphite powder kept at 1.0 V vs. RHE for 48 h in an O₂ or N₂ atmosphere is shown in Fig. 1. The concentration values

were divided by the weight of the carbon material to normalize the corrosion rate. In general, a comparatively high rate of corrosion was observed at the beginning of the test, followed by a decrease toward a constant value (including nil) after several hours. This means that some areas on the surface are relatively easy to oxidize. An edge plane of a graphite crystal is much more reactive than a basal plane, and is a bundle of surface functional groups, which is shown schematically.¹³⁾ Therefore, it is thought that the distribution of the kinds of surface functional groups was fixed depending on the potential after a steady state was reached, and the high corrosion rate observed initially was due to the oxidation of the surface functional groups. Since graphite is highly resistant to corrosion among carbon materials, it is likely that the steady-state corrosion of graphite under a mild condition, such as retention at 1.0 V, proceeds as the repeated recession and renewal of the edge planes only.

As illustrated in Fig. 1 for the oxygen data, the amount of CO₂ emission was divided into a stationary component and an initial component. The dependences of these two components on the potential and atmosphere are plotted in Fig. 2, in which the initial component is plotted as total amount and the stationary component as amount per unit time. Retention at a higher potential results in a large amount of corrosion. An oxygen atmosphere enhanced the corrosion rate. However, it is unlikely that oxygen gas affects the electrochemical corrosion of carbon directly, since the oxygen source in CO₂ generation is water:

If carbon reacts with oxygen molecules directly, this would be a chemical reaction and should not depend on the retention potential. The mechanism of the effect of the atmosphere on carbon corrosion is now under investigation. A possible explanation is that some intermediates react with oxygen. If graphite corrosion proceeds

Fig. 1 Time-dependence of CO₂ generation from graphite electrodes during a potential retention at 1.0 V vs. RHE in an acid electrolyte with O₂ or N₂ flow.

with renewal of the edge plane as mentioned above, bulk carbon should become some surface functional groups before oxidation to CO₂ as intermediates. Dependence on the atmosphere (N₂ or O₂ flow) has also been reported in the case of corrosion in phosphoric acid at 145 °C.⁸⁾ In this case, the amount of surface oxides after corrosion in an O₂ atmosphere was less than that in a N₂ atmosphere. The authors speculated that this was because the surface oxides were readily oxidized to CO₂ under an O₂ atmosphere.

As shown in Fig. 2, the corrosion rate at 1.0 V was much slower than that at 1.2 V, but not zero, under an oxygen atmosphere. Generally, the open circuit potentials of the cathode of PEMFCs reach to 1.0 V vs. RHE. Therefore, our results suggest that degradation of the cathode catalyst layer caused by leaving the cell in an open circuit condition is greater under an oxygen atmosphere.

The details of the initial corrosion were investigated by stepwise changes in the retention potential, as shown in Fig. 3. After steady corrosion was reached at 1.2 V, the potential was switched between 1.2 V and 0.1 V repetitively. When the potential was returned to 1.2 V, a transient peak that exceeded the previous steady value was observed. This means that surface regions relatively easy to oxidize were regenerated during retention at the lower potential. Surface functional groups both on the initial (as-received) materials and under a steady-state distribution at a lower potential include species that undergo “initial oxidation”. Practically, protecting the cathode of a PEMFC against a drop in potential during shutdown should reduce the amount of carbon corrosion.

To elucidate the effects of a Pt catalyst, the corrosion rates of electrodes made of carbon powder with and without Pt catalyst were compared, as shown in Fig. 4. To adjust the conditions to those in fuel cells, carbon black was used for the carbon material and potential

Fig. 2 The amount of initial corrosion and the steady-state corrosion rate at various potentials with O₂ or N₂ flow.

Fig. 3 Effects of potential steps on the CO_2 generation from a graphite electrode.

retention was performed under an O_2 atmosphere. The Pt catalyst clearly accelerated corrosion. The presence of the catalyst seemed to affect both the initial and steady corrosion. However, corrosion of the electrode with a catalyst was not strictly “steady” after the initial corrosion, but rather gradually decreased and finally reached the value without catalyst. In the case of highly oriented pyrolytic graphite (HOPG) corrosion, the lateral movement and aggregation of Pt particles on the surface accompanying carbon corrosion by H_2O_2 have been reported,¹⁴⁾ and the formation of blisters around Pt particles was observed after potential retention.⁹⁾ As in these phenomena, it is probable that some structural changes occurred around the particles with CO_2 generation, which resulted in a terminal condition, such as falling off or aggregation on relatively stable sites.

The mechanism of the effect of Pt catalyst on carbon corrosion is now under investigation. Since oxidative species such as H_2O_2 are not expected to be generated thermodynamically at 1.0 V, the acceleration shown in Fig. 4 is explained by corrosion of the portion in contact with platinum particles.

4 Conclusions

The corrosion rate was measured as a function of the retention potential and time. Depending on the conditions, corrosion was not zero even at 1.0 V, which indicates that degradation of the cathode catalyst support occurs by leaving the cell as an open circuit. On the other hand, a change in retention to a low potential seems to regenerate some surface species which are more easily oxidized when the potential is restored. This acceleration of corrosion may be mitigated by some technical devices. The presence of oxygen also accelerated corrosion. It is presumed that, overall, the chemical reactions of some intermediates with oxygen gas accelerate the electrochemical corrosion. A platinum catalyst also accelerated corrosion, as in previous reports. However, the effect of the catalyst gradually diminished

Fig. 4 Time-dependence of CO_2 generation from carbon black electrodes with and without Pt catalyst during a potential retention at 1.0 V with O_2 flow.

during potential retention, which suggests that the particles on the surface underwent some structural changes.

Acknowledgement

This work was financially supported by the New Energy and Industrial Technology Development Organization (NEDO) as a part of the Research and Development of Polymer Electrolyte Fuel Cell Technology Project directed by the Ministry of Economy, Trade and Industry (METI), Japan.

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