



Short communication

Thermal and electrochemical durability of carbonaceous composites used as a bipolar plate of proton exchange membrane fuel cell

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ARTICLE INFO

Article history:

Received 12 January 2010

Received in revised form 13 April 2010

Accepted 15 April 2010

Available online 21 April 2010

Keywords:

Proton exchange membrane fuel cells

Unitized regenerative fuel cells

Bipolar plate

Carbonaceous composites

Durability

ABSTRACT

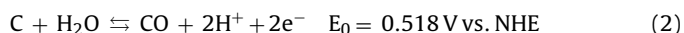
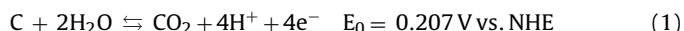
Thermal and electrochemical durability of carbonaceous composite plates, which are made from graphite powders and a resin for use as bipolar plates of PEMFC (proton exchange membrane fuel cell), were investigated. The thermal durability was investigated by TG (thermal gravimetry) coupled with DTA (differential thermal analysis) technique under air up to 600 °C. A weight loss was significant over 300 °C, but the hydrophobicity was decreased after heated at 80 °C for 192 h.

The electrochemical durability was investigated in 10 μmol dm⁻³ of hydrochloric acid solution under nitrogen or oxygen atmosphere by means of potential holding test from 0.8 to 1.5 V against RHE (reversible hydrogen electrode) at 80 °C. During the potential holding tests, CO₂ production due to the corrosion was quantified by a GC (gas-chromatography) and the production was detectable above 1.3 V irrespective with atmosphere; on the other hand, it was clarified from the contact angle measurements that the hydrophobicity was changed below 1.3 V. The results of this study showed that the carbonaceous composite plates were electrochemically degraded under PEMFC condition and were seriously degraded in URFC (unitized regenerative fuel cell) condition.

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1. Introduction

PEMFCs (proton exchange membrane fuel cells) are expected as power sources for stationary co-generation systems, FCVs (fuel cell vehicles) and FCHVs (fuel cell hybrid vehicles). In PEMFCs, carbon materials are commonly used for the electrode supports, the gas diffusion layer and the bipolar plates because of their characteristics such as low cost, good electric conductivity. Recently, the carbonaceous composite materials between several kinds of polymer such as epoxy [1], phenol resin [2], poly(styrene-co-acrylonitrile) [3,4], PMMA [5,6], polyamide-6 [7], polystyrene [8] and poly(vinyl acetate) [9] and conductive carbon materials (graphite powders and carbon fibers) are promised as the bipolar plates for meet the DOE (Department of Energy) targets [10]. On the other hand, theoretical standard potential of carbon is denoted below [11].



Hence, the carbonaceous bipolar plate is likely to be oxidized at the cathode and loss of carbon atoms as CO and CO₂ may occur. Unfortunately, there is no research report regarding durability of the carbonaceous bipolar plates since it has been strongly believed

that such carbonaceous materials are completely stable under the operation conditions of PEMFC.

In this study, we investigated the thermal and electrochemical durability of the carbonaceous composite plates made from graphite powders and a resin under simulated condition of the cathode of PEMFCs. For the electrochemical stability, not only CO₂ production due to the corrosion but also change in the surface property was carefully investigated by two kinds of the electrochemical durability tests. Moreover, the electrochemical durability up to 1.5 V was also investigated to clarify its durability under URFCs (unitized regenerative fuel cells) condition. The results of this study are informative to develop durable PEMFCs and URFCs.

2. Experimental

Commercially available carbonaceous composite plates without gas channels were employed as the test specimen (50 mm × 50 mm, thickness: 2 mm). The in-plane electrical conductivity is ca. 1.8 × 10² S cm⁻¹, which satisfy with the DOE target [10].

2.1. Thermal durability

The test specimen was carefully grounded in a mortar to investigate the thermal durability by TG (thermal gravimetry) coupled with DTA (differential thermal analysis) system (TG–DTA, Rigaku, TG8120). TG–DTA measurements were carried out under atmo-

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spheric air between 25 and 600 °C. Here, we used an aluminum dish to escape catalytic combustion of the samples.

The test specimen was placed in an electric furnace and was heated at 300 and 500 °C for 12 h under atmospheric air. Then, the surface morphology was observed by SEM (scanning electron microscope, Hitachi, H-800).

2.2. Electrochemical durability

The electrochemical durability was investigated by means of potential holding test. A glass-made cell used in this study was same composition as reported in elsewhere [12–14]. The electrolytic solution was 10 $\mu\text{mol dm}^{-3}$ of HClO_4 aqueous solution ($\text{pH} \approx 5$) to simulate PEMFC environment. The counter electrode was gold mesh placed in a separate compartment *via* a glass frit. Reference electrode was $\text{Ag}|\text{AgCl}$ electrode that was connected to the cell by a Luggin capillary, and potential was controlled in reversible hydrogen electrode (RHE) scale. One side surface of the test specimen was brought into contact with the electrolyte solution and the geometric surface area was restricted as ca. 8 cm^2 by an O-ring. Nitrogen gas (99.9998%, Japan Fine Products) or oxygen gas (99.999%, Japan Fine Products) was bubbling through the electrolyte solution sufficiently, and then both of an inlet and an outlet of gas were sealed off by rubber septum. The electrochemical durability tests were carried out by using a potentiostat (Hokuto Denko, HA-151A, and Bio-logic, VMP3) between 0.8 and 1.5 V in a heating chamber controlled at 80 °C. The potential was changed stepwise at 0.1 V positive every 24 h. After the one test period, defined amount of the gas was collected from the cell by a glass syringe and CO_2 was quantified by a gas-chromatography (GC, Agilent, 6890N) and the electrolyte solution was then changed fresh for the next period. This test procedure is called as “continuous test”. Another durability tests were also carried out between 0.6 and 1.0 V at 80 °C for 500 h by using the same electrochemical cell, which is called as “long-term test”.

Hydrophobic property of the test specimen was investigated by contact angle measurements against water droplet with a contact angle meter (Kyowa Interfacial Science, Model CA-DT, and Excimer Inc., SImage mini). We obtained the contact angle (θ) at various locations on the specimen and get the average value.

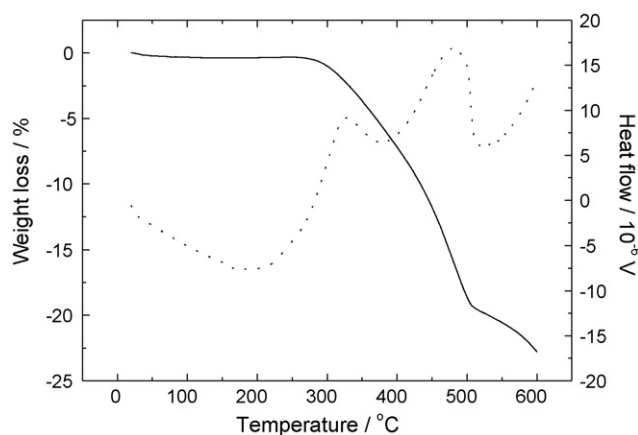


Fig. 1. TG–DTA curves of the test specimen.

3. Results and discussion

3.1. Thermal durability

Fig. 1 shows TG–DTA curves of the test specimen. A solid line and a dash line shows TG and DTA curve, respectively. In TG result, a small change in weight was observed below 80 °C, which was due to vaporization of absorbed water. On the other hand, large weight loss was observed stepwise from 300 to 500 °C accompanied with exothermic reactions.

In order to origin the large weight losses, the specimen was observed after heated at 300 and 500 °C for 12 h under atmospheric air and then surface morphology was observed by SEM. Fig. 2 shows the surface SEM images of the specimen of as-received and after heating at 300 °C. In Fig. 2(a), we could clearly observe two regions as indicated that one is a resin domain and the other is a graphite powder domain, respectively. On the other hand, a large part of whitish region was diminished after heating at 300 °C for 12 h as shown in Fig. 2(b), indicating that a large amount of the immanent resin would be thermally decomposed as gaseous products. The test specimen was reduced to powder after heated at 500 °C for 12 h; therefore we considered that the immanent resin was completely

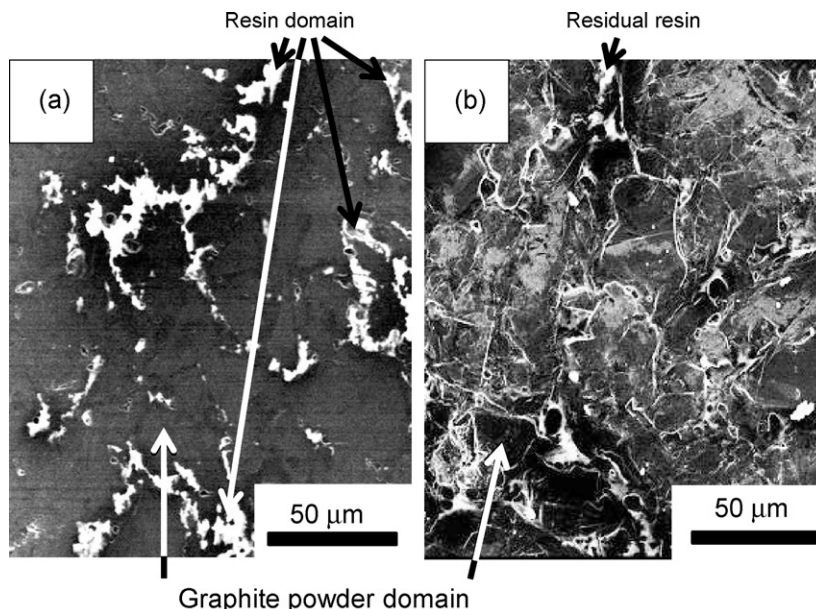


Fig. 2. SEM images of the test specimens (a) as-received and (b) heated at 300 °C for 24 h.

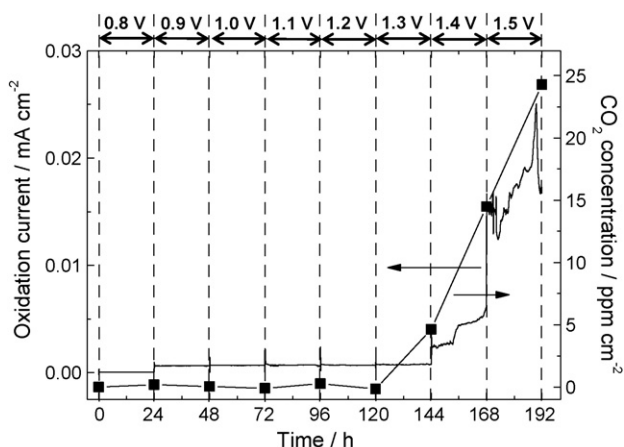


Fig. 3. Chronoamperogram and CO₂ production (■) of the test specimen during the continuous test under N₂ atmosphere at 80 °C.

decomposed over this temperature and carbon powder would also be oxidized.

Based on these results, the carbonaceous composite plate used here is seems to be stable at 80 °C as the normal operation temperature of PEMFC. Unfortunately, it was founded that the hydrophobicity was changed by heating at 80 °C for 192 h. This detail is mentioned in a later section.

3.2. Electrochemical durability

The oxidation current was observed during the durability tests. Fig. 3 summarized oxidation current and CO₂ production upon the test time under nitrogen atmosphere at 80 °C. The result obtained under oxygen atmosphere was shown in Fig. 4. An upper horizontal axis and a right vertical axis give the holding potential and CO₂ production per the geometric surface area of the test specimen, respectively. For both cases, oxidation current was slightly increased with an increase in the potential up to 1.2 V and was steeply increased above 1.3 V and simultaneously CO₂ production

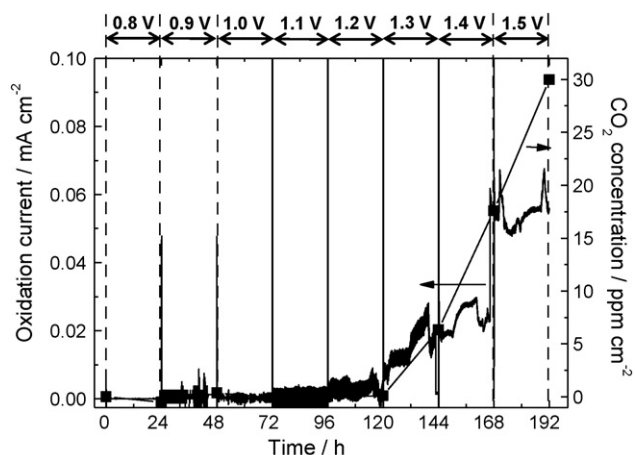


Fig. 4. Chronoamperogram and CO₂ production (■) of the test specimen during the continuous test under O₂ atmosphere at 80 °C.

was increased irrespective of the atmosphere. Thus, the carbonaceous composite plate was corroded to CO₂ above 1.3 V at 80 °C, though we could not know whether the immanent resin was also corroded or not. These are very reasonable since the theoretical potentials for electrochemical oxidation of carbon are rather noble than 1.3 V as denoted in Eqs. (1) and (2) [11]. From the comparison between Figs. 3 and 4, not only the production amount of CO₂ but also the oxidation current was seemed to be larger under oxygen atmosphere than these under nitrogen atmosphere; unfortunately this reason has not been clarified yet.

Fig. 5 shows photographs of the test specimen before and after the continuous test under nitrogen atmosphere. The bottom images are taken obliquely. As shown in the upper photo of (b), a part of the specimen that was exposed to the electrolyte solution was seemed to be grayish and θ_{av} was decreased at ca. 57° from ca. 95° before test. Surprisingly, θ_{av} for the outer part, which does not behave as a working electrode under the durability test, was also decreased to ca. 68°. This shows that hydrophobicity of the specimen was

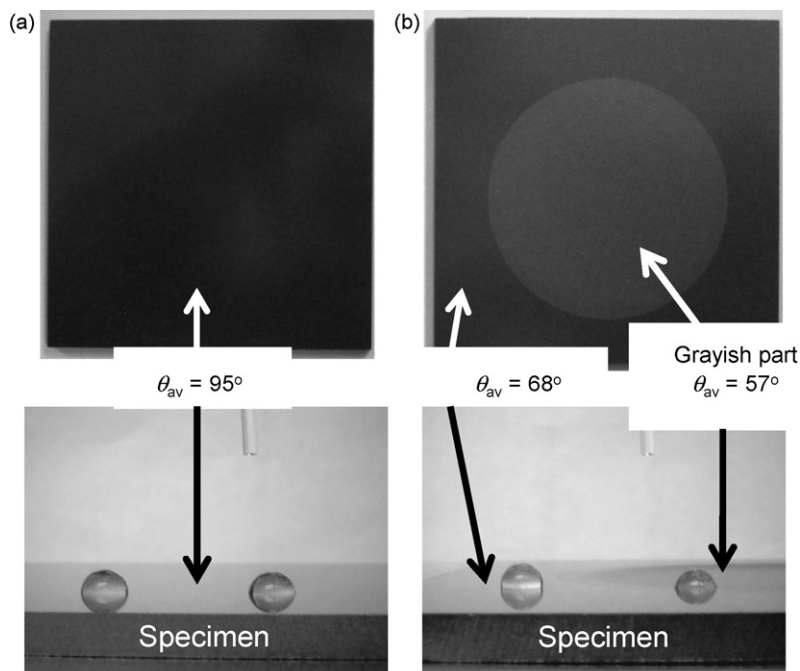


Fig. 5. Photographs of the test specimens (a) as-received and (b) after the continuous test under N₂ atmosphere. Bottom images are taken obliquely.



Fig. 6. SEM image of the test specimen after the continuous test under N_2 atmosphere.

changed by heating at $80^\circ C$ for 192 h in atmospheric air and that the carbonaceous bipolar plate is chemically degraded in the actual operating condition of PEMFCs. This is the first finding result and must be care to use a carbonaceous bipolar plate. The bipolar plate is actually exposed to highly humidified gases and to condensed water in the ideal operation condition of PEMFCs; unfortunately, at the present, it would make contact with somewhat acidic solution as used in this study: $\sim pH = 5$, due to the decomposition of the electrolyte membrane under open circuit condition, low (inadequate) humidified and low load operating conditions [15].

Contact angle is depended on the hydrophobicity (hydrophilicity) as well as the surface roughness. We then investigated the change in surface roughness by SEM and a probing surface roughness meter (Kosaka Laboratory Ltd., ET4000). A typical SEM image is shown in Fig. 6, which is very similar to Fig. 2(a). We could not find drastic change in the surface roughness even though by using the roughness meter. Therefore, a decrease in the contact angle would be related to chemical change of the surface during the durability test. There are several reports for electrochemical oxidation of the carbonaceous materials such as highly oriented pyrolytic graphite (HOPG) and some kinds of carbon blacks [13–16]. In these reports, several functional groups such as alcohol, carbonyl, carboxyl and lactones groups are produced by electrochemical oxidation and the surface changed hydrophilic [13,14]. Hence, it was considered that such functional groups would be produced on the test specimens during the durability tests and the surface made hydrophilic.

It is difficult to think that potential of the bipolar plate is reached over 1.3 V under the normal operation condition of PEMFC. We then investigated the θ below 1.3 V by “long-term tests”. Fig. 7 shows relation between θ and holding potential. Here, the surface roughness was neither significantly changed as far as SEM observation in all cases. θ_{av} was clearly decreased with increasing in the holding potential, which shows that hydrophobicity of the specimen was degraded under moderate oxidation condition where no CO_2 production. If hydrophobicity of the bipolar plates was decreased, “flooding” of the gas channels might be occurred and would be lead to deterioration of the cell performance.

When surface of the carbonaceous bipolar plates were oxidized to CO_2 under the cell operation, a decrease in the electric conduc-

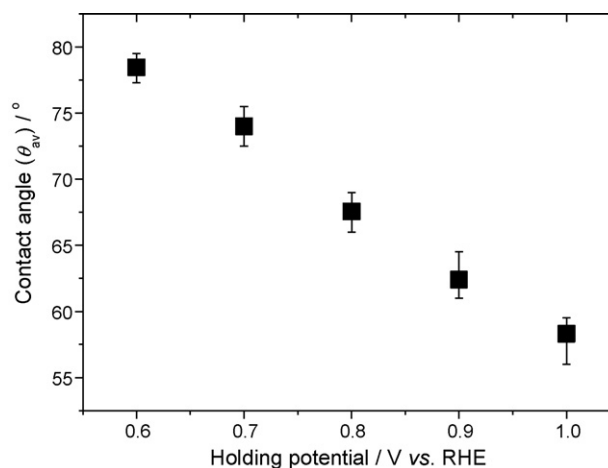


Fig. 7. Contact angles of the test specimens against holding potential after the long-term tests.

tivity as well as morphology change of the gas channel could also be occurred, leading to severe deterioration of the cell performance. However, it might be difficult to think about potential of the bipolar plate was over 1.3 V under normal operation of PEMFCs. Such high potential situation was likely at anode of the unitized regenerative fuel cells (URFCs) [17,18]. The results of this study show that carbonaceous composites were not preferable as bipolar plates for URFCs without any improvements for increasing the electrochemical durability.

4. Conclusion

Thermal and electrochemical durability of carbonaceous composite plates, which are made from graphite powders and a resin for use as bipolar plates of PEMFC, were investigated. The thermal durability was investigated by TG and DTA and a weight loss was significant over $300^\circ C$. It was also clarified that hydrophobicity of the specimen was degraded after heated at $80^\circ C$ for 192 h, which should be care for PEMFCs application.

The electrochemical durability was investigated by two types of potential holding tests from 0.8 to 1.5 V against RHE at $80^\circ C$. CO_2 production due to corrosion of the specimen was observed above 1.3 V; on the other hand, the hydrophobicity was degraded even between 0.6 and 1.3 V. The results of this study show that an increase in the electrochemical durability is necessary for use carbonaceous composites as PEMFCs and URFCs to achieve long-term reliability.

Acknowledgements

We gratefully acknowledge Mr. Toshihiro Urakawa of Fukuoka Industrial Technology Center for contact angle measurements. This work was supported by the research project C of the venture business laboratory of Oita University and also Comprehensive Support Programs for Creation of Regional Innovation Science and Technology Incubation Program in Advanced Regions FY2009 “Research for Promoting Technological Seeds” A from Independent Administrative Corporation Japan Science and Technology Agency (JST), Japan.

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