Lactone Formation on Carbonaceous Materials during Electrochemical Oxidation

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We focused on lactone formation during the electrochemical oxidation of highly oriented pyrolytic graphite (HOPG) as a model carbonaceous material for use in polymer electrolyte fuel cells in the potential range between 0.6 and 1.0 V against a normal hydrogen electrode. Lactone groups could be identified on the oxidized HOPG surface after holding at 1.0 V. Therefore, lactone groups are formed from the reaction between carbonyl groups and carboxylic groups as an intermediate in the electrochemical carbon oxidation reaction to CO_2 evolution.

Degradation of the electrode materials is one of the most important issues for commercialization of polymer electrolyte fuel cells (PEFCs). Among the causes of such degradation, oxidation of the carbon material is a major concern in the deterioration of carbon-supported Pt catalyst as well as “flooding” in the electrode layer.[1] Although there have been numerous studies on PEFCs, the stability and mechanism of the deterioration of the electrode materials in PEFCs have not yet been well clarified.[2,3] To develop durable electrode catalysts, it is important that we elucidate the mechanism of chemical deterioration.

The electrochemical carbon oxidation reaction can generally be described with eqs 1 and 2, although carbon is also electrochemically oxidized via the formation and oxidation of functional groups.[3–11]

$$C + H_2O \leftrightarrows CO(g) + 2H^+ + 2e^- \qquad E_0 = 0.52\,V \quad (1)$$

$$C + 2H_2O \leftrightarrows CO_2(g) + 4H^+ + 4e^- \qquad E_0 = 0.21\,V \quad (2)$$

Previously, we investigated the electrochemical oxidation of carbon by using HOPG as a model carbon material between 0.2 and 1.2 V vs. a normal hydrogen electrode (NHE) and reported that some functional groups were formed on the surface.[12,13] In the present study, we investigated the functional groups formed on HOPG during electrochemical oxidation to further clarify the details of the mechanism of electrochemical oxidation.

A block of HOPG (Advance Ceramics, STM-1 grade, mosaic spread 0.8 ± 0.2°, grain size 1 µm) that was carefully cleaved with adhesive tape was used as a working electrode. A three-electrode cell made of glass and a poly(tetrafluoroethylene) body was used for the electrochemical measurements.[2,12,13] Freshly cleaved HOPG was mounted at the bottom of the cell and its geometric surface area was fixed at $0.28\,cm^2$ by an O-ring. The counter electrode was carbon paper placed in a separate compartment via a glass frit. The reference electrode was a Ag/AgCl electrode with a Luggin capillary, and all potentials are given against NHE. Electrochemical oxidation was conducted in a $0.5\,mol\,dm^{-3}$ aqueous H_2SO_4 solution under a nitrogen atmosphere by applying potentials at 0.6, 0.7, 0.75, and 1.0 V for 15 h with a VMP3® potentiostat (Princeton Applied Research).

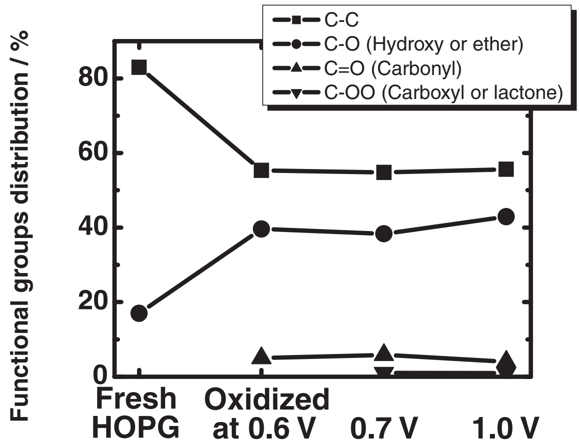
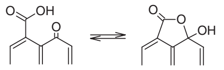


Figure 1. Calculated contents of carbon in aromatic bonding and functional groups on the HOPG surface before and after constant potential tests, based on the results of XPS.

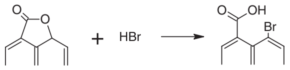
After these procedures, the HOPG electrode was washed with deionized water and dried in a vacuum chamber. The well-dried surface was analyzed by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI 5500MT® system) and observed by field emission scanning electron microscopy (FE-SEM; JSM-7400F, JEOL). Deconvolution of C 1s XP spectra was performed using a non-linear least-squares curve-fitting program (MultiPak, Version 8.0), based on a report by Gardner et al. on various carbonaceous functional groups.[14] The functional group distribution was estimated by the peak areas of XP spectra.

Figure 1 summarizes the results of the surface analysis by XPS. Aromatic C–C bonding and C–O single bonding were detected on the surface before oxidation, which shows that some hydroxy and/or ether groups were present on the freshly cleaved surface. After being held at 0.6 V for 15 h, the content of C–O bonding increased and that of C–C bonding decreased. This shows that even highly crystalline carbon such as HOPG was subjected to oxidization at 0.6 V. Assuming the cathode condition of PEFC, carbon material is unstable in PEFCs, and is oxidized through the formation of surface groups. In particular, C=O bonding mainly from carbonyl groups was detected on the oxidized surface at 0.6 V, as shown in Figure 1. Based on the fact that a redox reaction corresponding to a hydroquinone and quinone reaction takes place on carbon material at around 0.55 V,[11,12] we consider that hydroxy groups are oxidized to carbonyl groups during potential holding at 0.6 V. Furthermore, carboxyl groups and/or lactone were detected after the potential holding test above 0.7 V, which suggests that C–C bonding on HOPG was cleaved and the residual carbon atom could react with water. In our previous paper,[12] we found that a carboxyl group was further oxidized to give gaseous end-products such as CO and CO_2 during holding at 1.0 V. However, carboxyl groups were still detected on the HOPG surface when the electrode potential was increased from 0.7 to 1.0 V. Carboxyl groups are formed from carbonyl groups during the electrochemical carbon oxidation, which appear at the vulnerable sites of HOPG surface. Since carboxyl groups coexist with carbonyl groups on the surface during electrochemical oxidation above 0.7 V, it is reasonable to consider that a lactone (lacthol) group is formed, as shown in eq 3, during electrochemical oxidation according to the report by Boehm.[15]



(3)

We then attempted to identify lactone rings on an electrochemically aged HOPG surface. Of the several methods that can be used to identify lactone rings, a method that uses the chemical reaction of HBr and lactone was selected in this study. According to a report by Donnet, a lactone ring is opened by a reaction between HBr and carboxyl groups, as shown in eq 4.[16]



(4)

The pristine and electrochemically oxidized HOPGs (at 0.6 and 1.0 V) were immersed in 1.0 mol dm^{-3} aqueous HBr solution for 5 h in an ambient atmosphere, and then analyzed with XPS to detect a Br 3d signal. If lactone is formed on the surface, the peak originating from C–Br bonding should appear at around 71 eV in the resultant spectra.[17]

Figure 2 shows Br 3d spectra of HOPG after being immersed in HBr solution. The lack of a peak in Figure 2a shows that there is no reaction between HBr and the freshly cleaved HOPG surface. As mentioned before, HOPG was oxidized at 0.6 V, but no significant peaks were detected, as shown in Figure 2b. In contrast, for HOPG oxidized at 1.0 V, two peaks were detected, as shown in Figure 2c. The peak at around 69 eV was attributed to Br$^-$, which might be due to the absorption of Br$^-$ on the surface.[17] The other peak at 71 eV revealed that C–Br bonding occurred on the oxidized HOPG surface upon immersion in HBr for 5 h. This fact shows that lactone rings were formed during electrochemical oxidation at 1.0 V, which is the first finding regarding the electrochemical oxidation of carbon materials.

As mentioned previously, HOPG was finally oxidized to CO_2 and/or CO during holding at 1.0 V. Therefore, we consider that electrochemical oxidation proceeds via the formation of hydroxy, carbonyl, and carboxylic groups at different potentials.[12,13] Although the initial oxidation reaction is not yet well understood, carbonyl groups are formed by the oxidation of hydroxy groups under conditions more positive than 0.55 V, and are further oxidized to carboxyl groups between 0.6 and 0.7 V. In addition, the present study reveals that lactone groups are formed between some carbonyl groups and carboxylic groups as an intermediate in the electrochemical carbon oxidation reaction. Based on the result of XPS (Figure 1), the amount of carboxyl and carbonyl groups formed on HOPG surface was relatively small, and the frequency of lactone ring formation may be low. In terms of long-term stability, however, even a small amount of formation may have a great impact on the performance of fuel cells.

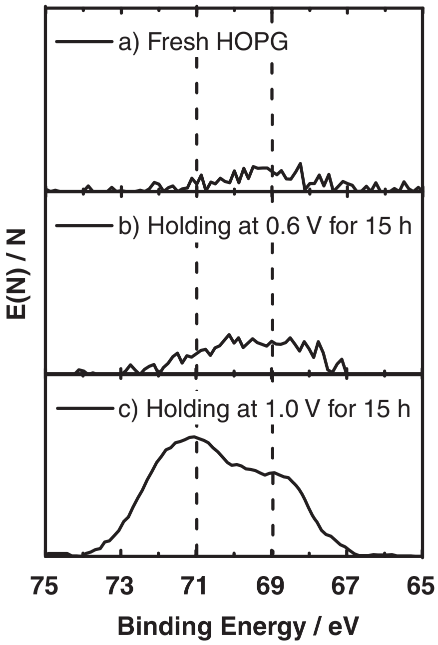


Figure 2. Br 3d XP spectra for a HOPG electrode after immersion in 1.0 mol dm^{-3} HBr aq: a) fresh, and after being held at b) 0.6 V for 15 h and c) 1.0 V for 15 h.

In conclusion, two competitive reaction pathways for CO_2 evolution are possible; one is from carboxyl groups and the other is from lactone groups in the potential range between 0.7 and 1.0 V. However, the kinetics that control CO_2 evolution are still unclear, and further studies are required.

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References

1 OSTEC, Survey and Analysis on Degradation Phenomena and Long-Term Operation Results of Polymer Electrolyte Fuel Cells, NEDO PEFC R&D Annual Report FY2005, **2005**.
2 T. Kinumoto, K. Takai, Y. Iriyama, T. Abe, M. Inaba, Z. Ogumi, *J. Electrochem. Soc.* **2006**, *153*, A58.
3 L. M. Roen, C. H. Paik, T. D. Jarvi, *Electrochem. Solid-State Lett.* **2004**, *7*, A19.
4 S.-I. Pyun, Y.-G. Ryu, S.-H. Choi, *Carbon* **1994**, *32*, 161.
5 H. Binder, A. Kohling, K. Richter, G. Sandstede, *Electrochim. Acta* **1964**, *9*, 255.
6 L. J. J. Janssen, J. G. Hoogland, *Electrochim. Acta* **1970**, *15*, 339.
7 K. Kinoshita, J. Bett, *Carbon* **1973**, *11*, 237.
8 K. Kinoshita, J. A. S. Bett, *Carbon* **1973**, *11*, 403.
9 K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, New York, **1988**, p. 322.
10 N. Giordano, P. L. Antonucci, E. Passalacqua, L. Pino, A. S. Aricò, K. Kinoshita, *Electrochim. Acta* **1991**, *36*, 1931.
11 J. Willsau, J. Heitbaum, *J. Electroanal. Chem.* **1984**, *161*, 93.
12 H.-S. Choo, T. Kinumoto, S.-K. Jeong, Y. Iriyama, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* **2007**, *154*, B1017.
13 H.-S. Choo, T. Kinumoto, Y. Iriyama, T. Abe, Z. Ogumi, *ECS Trans.* **2007**, *11*, 1003.
14 S. D. Gardner, C. S. K. Singamsetty, G. L. Booth, G.-R. He, C. U. Pittman, Jr., *Carbon* **1995**, *33*, 587.
15 H. P. Boehm, *Carbon* **1994**, *32*, 759.
16 J. B. Donnet, *Carbon* **1968**, *6*, 161.
17 S. A. Al-Bataineh, L. G. Britcher, H. J. Griesser, *Surf. Sci.* **2006**, *600*, 952.