



Electrochemical oxidation of highly oriented pyrolytic graphite during potential cycling in sulfuric acid solution

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ABSTRACT

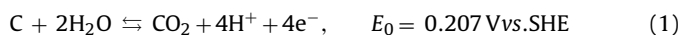
Oxidation of highly oriented pyrolytic graphite (HOPG) under potential cycling conditions is investigated to understand the stability of graphite used in polymer electrolyte fuel cells (PEFCs) under their dynamic operation conditions. Electrochemical methods, AFM and XPS are applied to examine the surface oxidation of HOPG. The current peaks corresponding to quinone–hydroquinone redox reaction begin to appear on cyclic voltammograms after potential cycling between 0.6 V and 0.8 V vs. SHE (standard hydrogen electrode), indicating that the surface of HOPG is partially oxidized to form surface functional groups containing oxygen, whereas HOPG is relatively stable during potential cycling between 0.4 V and 0.6 V. An increase in potential range to 0.8–1.0 V extends the oxidation and forms pits on the surface of HOPG that is caused by the loss of surface carbon through the oxidation to gaseous products. The high rate of potential cycling accelerates the surface oxidation of HOPG.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been intensively developed with much effort focusing on the improvement of performance for decades; but issues on durability are still remaining as a barrier for large-scale commercialization. Several degradation phenomena such as decomposition of electrolyte membrane and degradation of activity of electrode catalyst (Pt/C) have been reported [1–4]. Automotive application requires fast change in operation conditions of PEFCs; the load change due to acceleration and deceleration causes potential excursion of PEFCs and frequent start-up/shut-down causes drastic potential changes. Recent investigations revealed that the Pt/C catalyst was severely deteriorated during repeated potential cycling rather than constant potential holding [5–9]. Potential cycling is frequently adopted to accelerate degradation of the electrode catalyst and various deterioration patterns of catalyst layers have been proposed. Deterioration of carbon support is considered one of the main reasons of the catalyst deterioration. The degradation of carbon and carbon oxidation, has not been fully clarified so far.

Following carbon oxidation is well known [10]:



The standard oxidation potential values of carbon, i.e., 0.207 and 0.518 V vs. SHE (standard hydrogen electrode), indicate that carbon materials are exposed to the thermodynamically unstable conditions at the cathode of PEFCs (i.e., about 0.6–1.2 V vs. SHE). However, slow oxidation kinetics of carbon permits the use of carbon material as a catalyst support in PEFCs. Recent studies have shown that Vulcan carbon, which is commonly employed in PEFCs, is easily oxidized to form various surface-oxidized species and subsequently CO₂ under PEFCs cathode conditions [11,12]. While these studies give useful information, the details of oxidation path of carbon materials are still remaining to be clarified.

Graphite is also used as a catalyst support of PEFCs as more stable one than Ketjen black. Previously, the authors reported that highly oriented pyrolytic graphite (HOPG) as a model of graphite was oxidized to form surface functional groups containing oxygen during holding potential of HOPG at fixed value [13]. Based on this work, the effect of potential excursion on graphite oxidation is investigated in the present work employing a potential cycling method and HOPG as a model of graphite. The detailed observations of the changes in surface morphology as well as surface oxygen content

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provide an important insight into the carbon oxidation reaction upon potential cycling condition.

2. Experimental

2.1. Potential cycling test

A HOPG block (highly oriented pyrolytic graphite, Advance Ceramics, STM-1 grade, mosaic spread $0.8 \pm 0.2^\circ$, grain size $1 \mu\text{m}$)

was used as a model electrode after cleaving with adhesive tape to avoid the surface damages on basal plane. The HOPG surface, of geometric area 0.38 cm^2 , was mounted on the side of glass-made three-electrode cell. The counter electrode was Pt wire placed in a separate compartment *via* a glass frit. The reference electrode was Ag/AgCl connected to the cell by Luggin capillary, and the potential was denoted against SHE scale. Electrolyte solution was $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Electrochemical potential cycling test was carried out in N_2 by applying a triangular potential

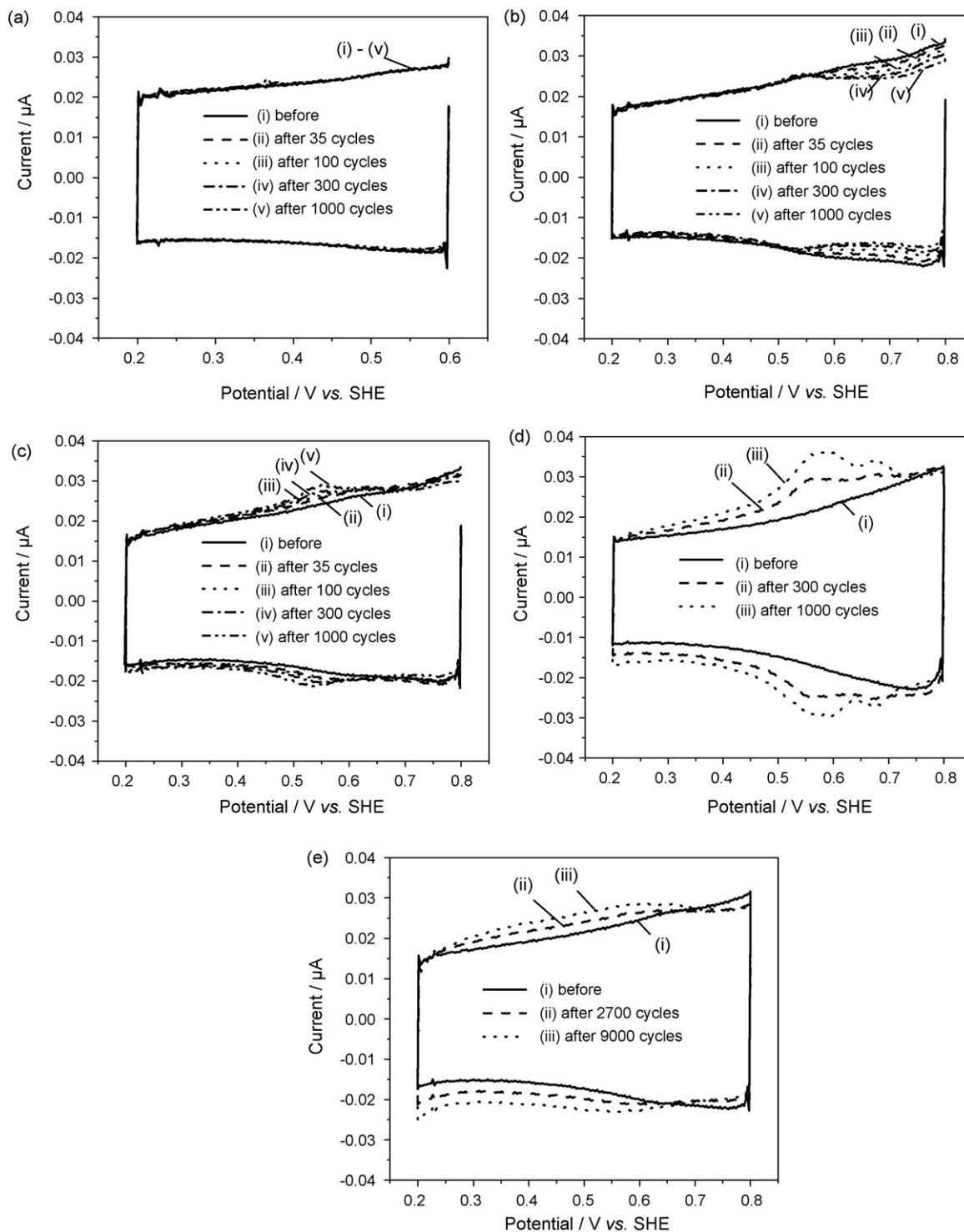


Fig. 1. CVs of HOPG electrodes at 10 mV s^{-1} before and after cycling with different cycle numbers in the potential ranges of 0.4–0.6 V (a), 0.6–0.8 V (b), 0.8–1.0 V (c), 1.0–1.2 V (d) at 10 mV s^{-1} and 0.8–1.0 V at 90 mV s^{-1} (e).

wave in the potential ranges of 0.4–0.6 V, 0.6–0.8 V, 0.8–1.0 V, 1.0–1.2 V and 0.2–0.8 V up to 5000 cycles at different sweep rates, e.g., 10 mV s⁻¹ or 90 mV s⁻¹ (VMP3[®], Princeton Applied Research). In order to investigate the oxidation of carbon during potential change, the range of potential cycling was changed stepwise under N₂ bubbling. The rate of potential cycling was set at 10 mV s⁻¹ and for comparison at 90 mV s⁻¹. All electrochemical measurements were conducted at 30 °C in aqueous 0.5 mol dm⁻³ H₂SO₄.

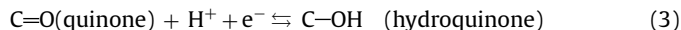
2.2. Characterization of HOPG surface

After potential cycling, the HOPG surface was measured by scanning electron microscope (SEM, S-3000H[®], Hitachi) and atomic force microscope (AFM, PicoScan[®], Molecular Imaging) with conventional contact mode. Commercially available micro-cantilever (OMCL-TR400PSA-HW, Olympus) with sharpened pyramidal SiN tip was used for AFM observations. Tip height was 2.9 μm and spring constant of the cantilever was 0.08 N m⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was performed with an ULVAC-PHI 5500MT[®] system (ULVAC-PHI) equipped with a hemispherical energy analyzer. The spectra were measured at room temperature using Mg Kα_{1,2} radiation (15 kV, 400 W). A non-linear least square curve-fitting program (MultiPak, Version 8.0) was used to analyze the resultant spectra. Deconvolution of the C 1s peak was carried out following the paper reported by Gardner et al. [14].

3. Results and discussion

3.1. Cyclic voltammetry during potential cycling

Fig. 1(a)–(d) shows the CVs of HOPG before and after cycling at 10 mV s⁻¹ in different potential ranges. The capacitance estimated from CVs in Fig. 1(a) remained unchanged after cycling up to 1000 cycles between 0.4 V and 0.6 V, which suggests that the HOPG is considerably stable in this potential range. On the other hand, as shown in Fig. 1(b), current peaks corresponding to quinone–hydroquinone redox couple in Eq. (3) appeared around 0.55 V with potential cycling between 0.6 V and 0.8 V and increased with continued potential cycling up to 1000 cycles [15].



These redox peaks indicate that surface functional groups such as alcohol and carbonyl groups are formed by electrochemical oxidation of the HOPG surface during potential cycling in this potential region. When the upper limit of the potential cycling increases from 0.8 V to 1.0 V, as shown in Fig. 1(c), the redox current peaks corresponding to quinone–hydroquinone couple increase and become clear accompanied with the increase of the capacity, which shows that the high potential range of the cycling accelerates the oxidation of HOPG surface.

Cycling between 1.0 V and 1.2 V gives the second redox current peak around at 0.68 V together with the large increase of the capacity. Considering the redox reaction of quinone–hydroquinone at around 0.55 V, this second redox peak should be related to the formation of surface oxide of higher oxidation state like carboxyl and/or lactone groups [16].

The rate of potential cycling also gives influences on surface oxidation of HOPG as shown in Fig. 1(e), which represents the results at potential cycling at 90 mV s⁻¹ in 0.8–1.0 V. The capacitance increased more at 90 mV s⁻¹ than at 10 mV s⁻¹ in 0.8–1.0 V shown in Fig. 1(c) at the identical cumulative potential cycling duration. However, the current peaks of quinone–hydroquinone

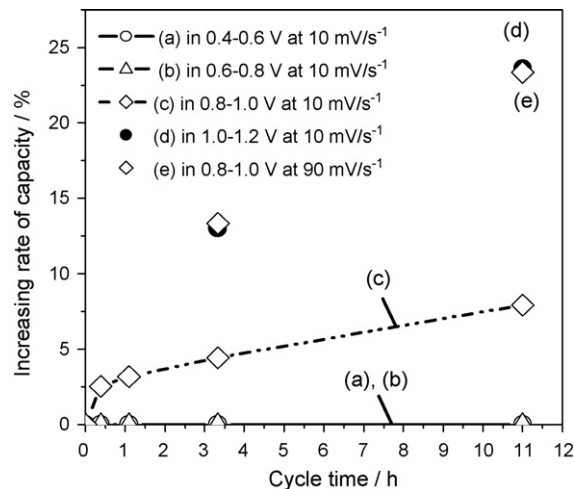


Fig. 2. Increasing rate of capacity during cycling in various potential ranges with different rates of potential cycling.

redox couple at around 0.55 V are not clearly observed at the faster potential cycling. This fact suggests that the HOPG surface is roughened more at fast potential cycling, while the surface quinone and hydroquinone groups do not increase. The reason of surface roughening is not clear yet and under investigation.

Based on CVs, the increase in capacitance was calculated from the difference in capacitances estimated from current values between 0.2 V and 0.3 V before and after potential cycling at fixed duration. As is shown in Fig. 2 the capacitance increases remarkably with potential cycling duration when the upper limit of the potential cycling is beyond 0.8 V, while the increase is negligible up to 0.8 V. When the potential cycling rate is increased from 10 mV s⁻¹ to 90 mV s⁻¹, the increase in the capacitance with the cycling duration becomes fast (compare Fig. 1(e) with (c)).

3.2. Surface morphology changes of HOPG during potential cycling

As shown in Fig. 1, the HOPG surface is gradually oxidized and roughened by potential cycling over 0.6 V. Surface morphology change of HOPG was monitored by AFM during potential cycling. Fig. 3 exhibits the AFM images and height profiles of the HOPG surfaces before and after 2000 cycles at 10 mV s⁻¹ in different potential ranges. A basal plane of freshly cleaved HOPG is flat except the stepping in several μm distances as can be seen in Fig. 3(a). The HOPG surface becomes rough after continued cycling between 0.6 V and 0.8 V (Fig. 3(b)), which indicates that the surface of HOPG is oxidized even in this relatively low potential range although the roughening is not so remarkable.

The authors have previously reported that HOPG surface is disturbed by the adsorption of oxygen and a “hillocks structure” appears on the surface [13]. The oxygen adsorption on the surface proceeds during potential cycling between 0.6 V and 0.8 V and makes the surface rough and the adsorbed oxygen almost completely covers the surface after 2000 cycles. The adsorbed state of oxygen is not clear yet but is inferred as an intermediary state of the oxidation process up to gas evolution of such as CO₂ and/or CO [17,18].

When the upper potential limit was increased from 0.8 V to 1.0 V, the surface is oxidized more and the surface became less stable

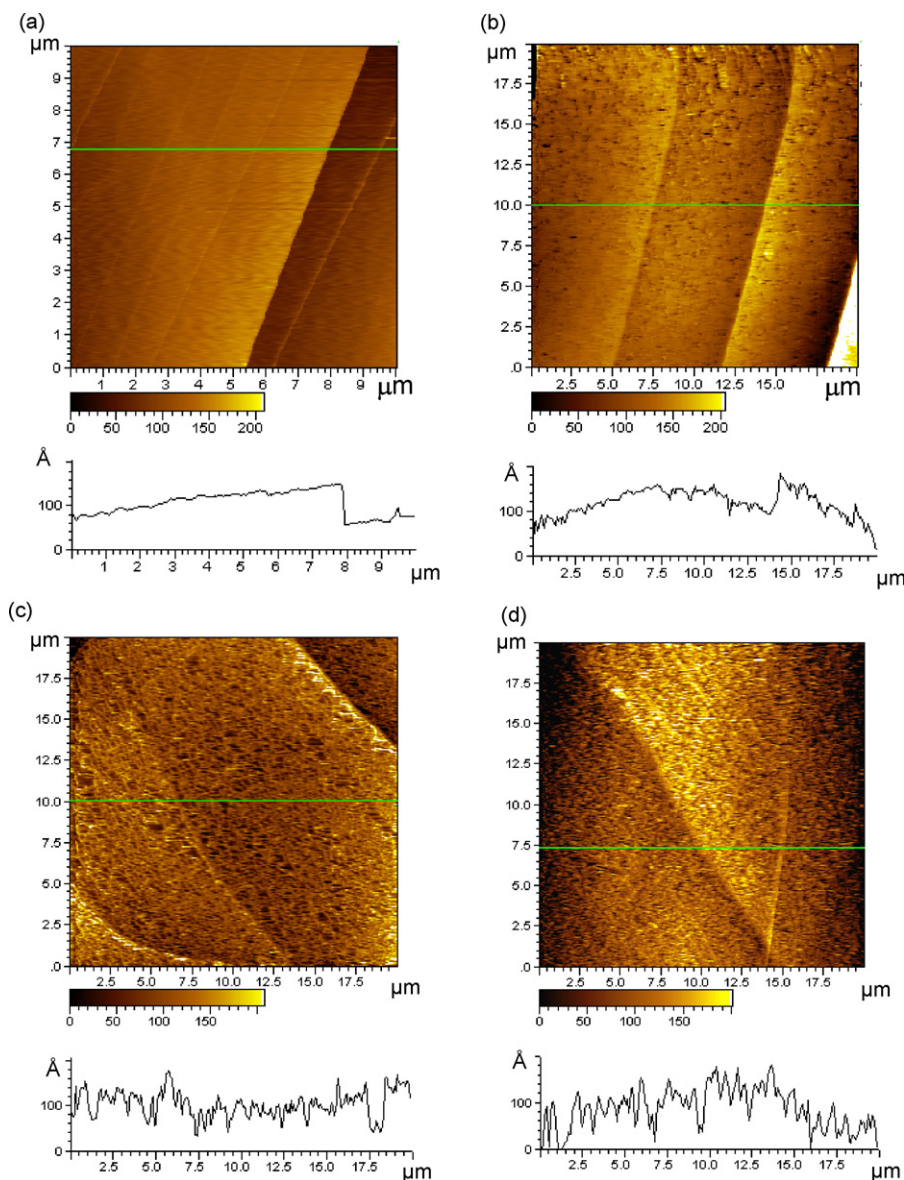


Fig. 3. AFM images and height profiles of HOPG surface, before (a) and after 2000 cycles in the potential ranges of 0.6–0.8 V (b), 0.8–1.0 V (c) and 1.0–1.2 V (d) at 10 mV s^{-1} . The sizes of images are $10 \mu\text{m} \times 10 \mu\text{m}$ (a) and $20 \mu\text{m} \times 20 \mu\text{m}$ (b)–(d).

resulting in the formation of circular pits less than $1 \mu\text{m}$ in diameter on the surface as shown in Fig. 3(c). This observation indicates that the surface oxidation proceeds up to the formation of gaseous products such as CO_2 and/or CO . Then surface carbon is lost and pits are formed. When the range of potential cycling is shifted to the more positive, the gasification proceeds more intensively. The surface morphology change is remarkable when potential is cycled between 1.0 V and 1.2 V. It is difficult at present to decide precisely the onset potential of formation of the gaseous products.

Fig. 4 shows SEM images after oxidation tests in different ways. Potential holding at 1.0 V for 22.2 h causes pits on HOPG surface as shown in Fig. 4(a). As shown in Fig. 4(b), however, the potential cycling between 0.8 V and 1.0 V for 22.2 h causes more pits on the surface though the duration exposed to the higher potential is shorter than the case when potential is held at 1.0 V. The comparison of Fig. 4(c) with Fig. 4(b) reveals the fast rate of potential cycling accelerates the pit formation, while the tex-

ture of surface change is a network of “mosaic micro-cracks” and different from that formed by the slower potential cycling. The size of “mosaic micro-cracks” seems to reflect the grain size of HOPG (STM-1). This may suggest that surface oxidation begins from grain boundary at the HOPG surface where defect density is high [19]. These results clearly show that rapid potential change accelerates the oxidation of HOPG surface. The influence of potential cycling rate on surface oxidation is still remaining to be solved.

3.3. Influence of lower potential limit during potential cycling

As described above, potential cycling accelerates oxidation of HOPG surface and influences of the lower limit of potential cycling were examined. Fig. 5 shows CVs of HOPG before and after cycling at 10 mV s^{-1} between 0.2 V and 0.8 V. The current peaks corresponding to quinone–hydroquinone redox couple are observed clearly more and more with potential cycling, though the increase in capacitance

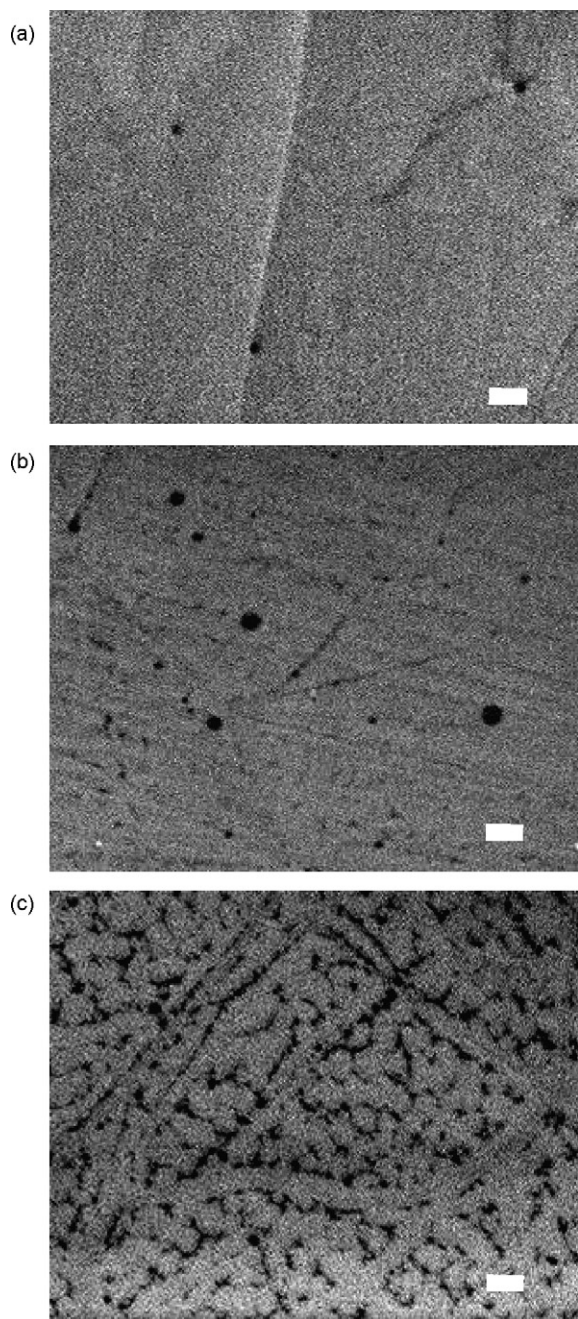


Fig. 4. Typical SEM images of the HOPG surfaces after holding at 1.0V for 22.2 h (a), and after cycling in 0.8–1.0V with a sweep rate of 10 mVs⁻¹ (b) and 90 mVs⁻¹ (c) for 22.2 h. The scale bar indicates 1 μm.

corresponding to surface area is almost unchanged. Estimating roughly the amount of surface quinone–hydroquinone groups by integration of current after subtracting the double layer charging current between 0.5V and 0.6V as a baseline, potential cycling between 0.2V and 0.8V gives more quinone–hydroquinone groups by about 3% than the potential cycling between 0.6V and 0.8V. This result indicates that reduction of quinone to hydroquinone during cycling is not important for surface oxidation and that the lower potential limit does not give a major influence on the surface oxidation.

3.4. Surface chemistry changes during potential cycling

As described above, potential cycling between 0.8V and 1.0V accelerates the surface morphology change of HOPG due to surface oxidation like pit formation. Then the introduction of oxygen to HOPG surface was roughly examined by XPS. Fig. 6 shows the C 1s spectra and deconvolution results of the HOPG just after freshly cleaved and after potential cycling between 0.8V and 1.0V. The deconvolution results to C–C, C–O, C=O, and COO are summarized in Fig. 7. Even freshly cleaved HOPG shows small peak of C–O at 285.7–286.1 eV that is ascribed to alcohol or ether group. As cycle number increased, C 1s peak decreased and became broaden and carbonyl (287.6–287.7 eV), and carboxyl groups (288.6–289.0 eV) are introduced as shown in Fig. 6(b)–(d) at the cost of C–C bond. At the initial stage of potential cycling C–O bond increases rapidly up to 100 cycles, which suggests the introduction of OH group, and the OH group increases gradually. C=O group is detected at the 100th cycle and the increase of the group is very slow. On the other hand, formation of COO group begins after C=O group accumulates. This suggests that COO group is formed by oxidation of C=O group. This is consistent with the result of CVs in Fig. 1(c), in which the introduction of redox couple ascribed to quinone–hydroquinone became remarkable after 100th cycle. With prolonged cycling above 2000 cycles, the carbonyl group is further oxidized to carboxyl group.

The formation of carboxyl groups after 2000th cycle leads to the formation of pits through further oxidation of carboxyl group to CO₂ and/or CO. This agrees well with the results of SEM observation in Fig. 4(b).

Under operation of PEFC, graphite material is exposed to air atmosphere, which means that the potential reaches about 1.0V. When PEFC is operated under fluctuating load, cathode potential can change between 0.6V and 1.0V and graphite on cathode side experiences excursion of potential like potential cycling in the present work. This work reveals that graphite is oxidized under operating conditions of PEFC, which increases hydrophilicity leading to easy wetting and flooding of cathode. The potential excursion under dynamic operation conditions accelerates remarkably the oxidation of graphite compared with constant operation conditions where the cathode potential is almost fixed. Further, oxidation of carbon support deteriorates the activity of Pt catalyst [12,20,21].

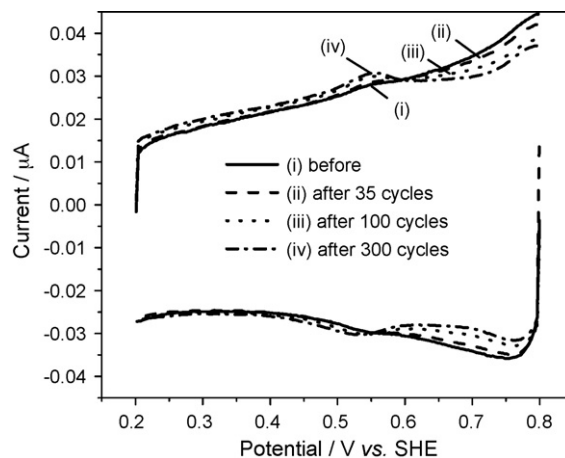


Fig. 5. CVs of HOPG electrode before and after potential cycling with different cycle numbers in the potential ranges of 0.2–0.8V at 10 mVs⁻¹.

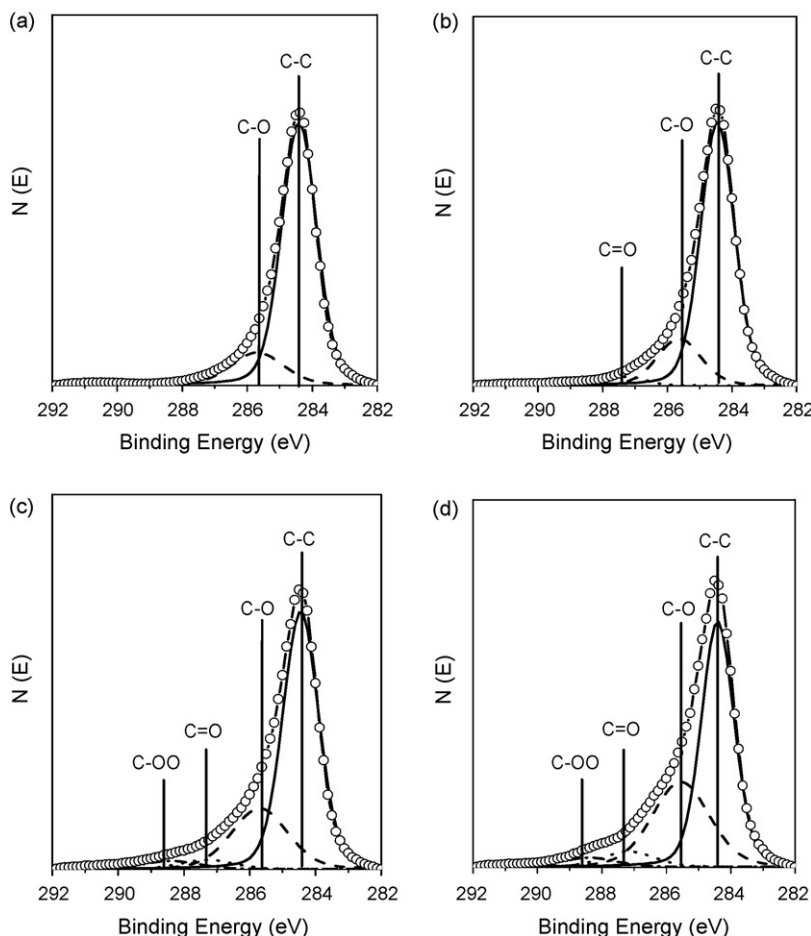


Fig. 6. XPS spectra (O) and the deconvoluted curves for C 1s spectra of HOPG before (a), and after 100 (b), 2000 (c), and 5000 (d) cycles in the potential range between 0.8 V and 1.0 V at 10 mV s^{-1} .

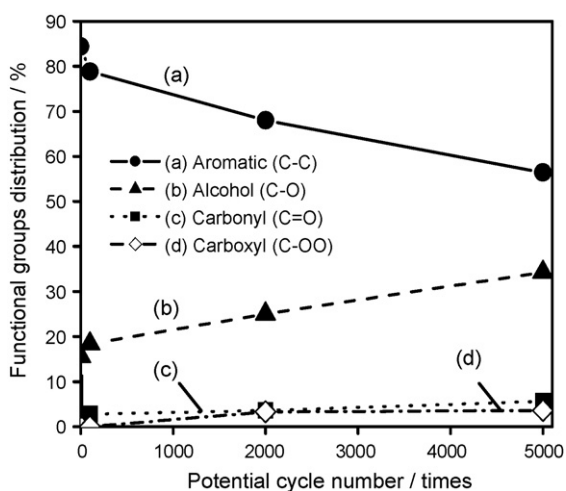


Fig. 7. Estimated contents of surface groups on the oxidized HOPG surface as a function of cycle number in the potential range between 0.8 V and 1.0 V at 10 mV s^{-1} .

4. Conclusion

Throughout the investigations of electrochemical oxidation of HOPG during potential cycling in sulfuric acid solution, the oxidation path of HOPG surface was discussed under dynamic conditions. The current peaks corresponding to quinone–hydroquinone redox reaction appeared on CVs upon cycling between 0.6 V and 0.8 V,

whereas the HOPG was relatively stable below 0.6 V, i.e., under 0.4–0.6 V cycling. AFM and SEM observations showed that the surface of HOPG was roughened through the formation of the oxidized layer during repeated potential cycling between 0.6 V and 0.8 V. While the oxidized layer was relatively stable below ca. 0.8 V, this oxidation proceeded further and a part of surface carbon was lost leading to formation of pits on the surface during potential cycling above 0.8 V. This progressive oxidation was supported by the XPS results that alcohol groups were subsequently oxidized into carbonyl and carboxyl groups with continued cycling at high potential range. The comparison of surface morphology changes revealed that oxidation reaction was accelerated by potential cycling in 0.8–1.0 V compared with potential holding at 1.0 V at the same cumulative time. The present work shows that oxidation of carbon in PEFCs is more remarkable under dynamic operation conditions.

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