

# Scanning Tunneling Microscopic and Voltammetric Studies of the Surface Structures of an Electrochemically Activated Glassy Carbon Electrode

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**The microscopic surface structures of electrochemically activated glassy carbon have been examined by scanning tunneling microscopy. Experimental results demonstrate that there are two different types of electrode surface sites, corresponding to the bundles and bundle edges of the fibrous graphite microcrystallinities. Electrochemical activation results in the formation of new void spaces of different sizes, and the structures are affected by the electrochemical activation procedures employed. The void volume resulting from cyclic polarization is usually smaller than that obtained by potentiostatic activation. Electrochemical behaviors of the activated electrode are related to both the new void structures and the size of the electroactive species employed. On the basis of the STM and voltammetric results, the microscopic structure of the activated electrode is proposed.**

Glassy carbon is usually made from polymeric resins, such as polyacrylonitrile or phenol/formaldehyde polymers, through heat treatment.<sup>1,2</sup> As suggested by Jenkins and Kawamura,<sup>1</sup> the bulk has a complex structure of interwoven graphitic ribbons, and the basic structural units are planar aromatic structures with basal and edge planes.<sup>1–3</sup> The density of glassy carbon, about 1.5 g/cm<sup>3</sup>, is much lower than that of highly ordered pyrolytic graphite (HOPG). The porosity of glassy carbon is about 35%.<sup>1,2</sup> It is impermeable for gases and liquids, suggesting that the void space is small and unconnected.<sup>1</sup> Glassy carbon electrodes have been extensively applied in electroanalysis and usually undergo a pretreatment process in order to obtain reproducible electrochemical response.<sup>3</sup> The most commonly used pretreatment methods include mechanical polishing<sup>4–6</sup> and employing electrochemical polarization.<sup>3,7,8</sup> Simple electrochemical activation is

considered to be a better pretreatment means, because the activated glassy carbon gives reproducible surfaces, improved electron transfer, and specific adsorption behavior<sup>3</sup>. However, electrochemical activation usually results in more complex surface structures than the bulk.

There have been reports on the surface structures of electrochemically activated glassy carbon.<sup>3</sup> In general, the electrode can be activated in either basic or acidic (or neutral) solutions. The smaller background current of the electrode obtained by pretreatment in basic solution resulted from a thinner monolayer surface structure. Higher background current is usually observed for the electrode pretreated in acidic (or neutral) solutions, and it has been proposed that the surface is a porous oxidized multilayer.<sup>3</sup> Several experimental methods have been used to examine the structures of the graphite oxide film obtained in acidic or neutral solutions. Ellipsometric studies showed the growth of a transparent oxidized film at a constant rate of about 45 Å per voltammetric cycle until a thickness of at least 1 μm, when cyclic-potential activation in sulfuric acid solution was employed.<sup>9,10</sup> The porosity of this transparent film could be estimated from the void fraction. The void fraction obtained by potential cycling was about 80%, but the void fraction of the film obtained by constant-potential oxidation was between zero and 70%.<sup>9,10</sup> Nagaoka and co-workers<sup>11–13</sup> suggested that electrochemically activated glassy carbon obtained by constant-potential oxidation created micropore structures and could take up ions. The average radius of the surface pores was about 10–20 Å, as measured by the Brunauer–Emmett–Teller (BET) method employing nitrogen gas as adsorbent.<sup>12,13</sup> The size of the surface pores was dependent on the anodization time employed.

The electrode surfaces of glassy carbon have been examined by scanning electron microscopy (SEM).<sup>14–16</sup> Early microscopic studies showed that the micropores were smaller than 70 Å at

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the bare glassy carbon surface.<sup>14</sup> A smooth surface was observed for the polished electrode.<sup>15,16</sup> Engstrom and Strasser<sup>15</sup> reported that there were no significant changes in the surface topography after anodization pretreatment. Picq and co-workers<sup>16</sup> found that the larger pores consistent with the fibrous stranded structure were unaltered, and smaller pores were developed during activation. On the other hand, several research groups reported studies on glassy carbon surface by scanning tunneling microscopy (STM).<sup>17–20</sup> Brown and co-workers<sup>17,18</sup> observed small graphite-like domains smaller than  $50 \times 50 \text{ \AA}^2$  at the bare glassy carbon. Elings and Wudl<sup>19</sup> reported that the ordered regions were no larger than  $20 \text{ \AA}$  at the broken surface of glassy carbon. Heiduschka and co-workers<sup>20</sup> observed the arrangement of helical and cylindrical fibers with diameters of about  $500\text{--}1700 \text{ \AA}$  at a freshly polished surface. The electrochemical pretreatment resulted in porous surface of flakes. The original structures were destroyed to a certain extent, depending on the strength of anodization.<sup>19,20</sup> The diameter of the holes (etch pits) was about  $50\text{--}100 \text{ \AA}$ ;<sup>20</sup> however, scanning microscopic images (SEM and STM) could not reflect the inner structures of those etch pits.

Our previous investigations showed that the electrodes obtained by different voltammetric methods had different adsorption behaviors for  $\text{Cu}^{2+}$  and vitamin  $\text{B}_2$  species.<sup>21–23</sup> The possible difference in void volumes, or etch pits, obtained by different voltammetric methods might affect the electrochemical behaviors, as well; however, there were very few studies on the difference in electrochemical responses of activated glassy carbon obtained by different voltammetric methods, namely activation employing cyclic and potentiostatic polarization. It has been reported that 3,4-dihydroxybenzaldehyde (DHB) could deposit at glassy carbon surfaces obtained by constant-potential activation in basic solution. Deposited DHB could catalyze the oxidation of nicotinamide adenine dinucleotide (NADH).<sup>24,25</sup> The electrocatalytic oxidation of NADH at DHB-modified PGCE was examined in this study, which provided some indirect information about the microscopic structures of electrochemically activated glassy carbon.

## EXPERIMENTAL SECTION

DHB was obtained from Aldrich, and the reduced form of NADH was obtained from Sigma. All other chemicals were of reagent grade and were used as received. Reagent solutions were prepared freshly and degassed for 5 min before use. Deionized water was obtained by purification through a Millipore system and was used throughout.

Voltammetric measurements were recorded using a BAS-CV50W voltammetric analyzer (Bioanalytical Systems Inc.). A three-electrode cell was employed, incorporating a glassy carbon working electrode, a  $\text{Ag}|\text{AgCl}$  reference electrode, and a platinum foil counter electrode. All potentials were quoted versus the  $\text{Ag}|\text{AgCl}$  reference.

Glassy carbon voltammetric electrodes (GCE) of 3.0 mm in diameter were obtained from Bioanalytical Systems Inc. Glassy carbon electrodes were polished progressively with finer emery paper, then thoroughly with  $0.3 \mu\text{m}$   $\text{Al}_2\text{O}_3$  powder on polishing cloth. The working electrode was cleaned in an ultrasonicating bath for 1 min before use.

Two different voltammetric activation methods were employed. For potentiostatic activation, the glassy carbon electrode was anodized at  $+2.0 \text{ V}$  for a short period of time ( $0.5\text{--}3.0 \text{ min}$ ) and then polarized at  $-1.0 \text{ V}$  for 0.5 min in  $0.5 \text{ M H}_2\text{SO}_4$ . The potential was then cycled between  $+1.0$  and  $-0.5 \text{ V}$  at a scan rate of  $0.1 \text{ V/s}$  for two cycles and ended at  $-0.5 \text{ V}$ . On the other hand, activated glassy carbon electrodes could also be prepared by cyclic polarization. The electrode was cycled between  $-0.3$  and  $+2.0 \text{ V}$  at  $0.1 \text{ V/s}$  in  $0.5 \text{ M H}_2\text{SO}_4$  for 10 to 15 voltammetric cycles until stable voltammograms were obtained. The DHB species were deposited at the activated electrode by potential cycling in  $1 \text{ mM DHB} + 0.2 \text{ M phosphate buffer (pH 7.0)}$  between  $-0.2$  and  $+0.3 \text{ V}$  at  $0.1 \text{ V/s}$ , as described previously.<sup>24,25</sup>

Scanning tunneling microscopic images were captured using a Nanoscope III STM/AFM instrument (Digital Instrument) with Pt/Ir tips mechanically shaped by scissors. The tip current was 1 nA, and the bias voltage employed was in the range between 0.1 and 0.5 V. Glassy carbon disks 5 mm in diameter were obtained by wire-cutting a glassy carbon rod (Atomergic Chemetals Corp.) into pieces 2 mm thick. The disk was then mounted onto a Teflon sheath. The disk electrode was polished and electrochemically activated as usual. After electrochemical measurements and washing with deionized water, the air-dried carbon disk was removed from the Teflon sheath and subjected to STM measurements.

## RESULTS AND DISCUSSION

**Scanning Tunneling Microscopic Studies.** The surface of glassy carbon obtained by different activation methods was investigated by STM. The STM images were randomly captured at different locations of the electrode surface. Two typical types of surface features were usually observed. Figure 1a shows a typical image of one type of the surface sites (designated as type I sites in this study) at a freshly polished surface. Darker areas corresponded to valleys of the surface and under low magnification were found to be about 15 nm deep. The particles corresponded to the graphitic microcrystallinities. Figure 1a reflects that the surface was rather rough at the nanometer level. The average size of the ellipsoidal particles was around 25 nm in diameter, and no apparent crystal boundary was observed for these particles, as obtained from the zoomed STM image (Figure 1b). Figure 1c shows a typical image corresponding to another type of surface sites (designated as type II sites) at the same polished surface. The fiber-shaped particles were arranged in parallel bundles with the length longer than 200 nm. Zoomed images showed that the average diameter of the fiber-shaped particles was  $<25 \text{ nm}$ . These observations indicated that the glassy carbon surface contained fibrous structures, consistent with the interwoven graphitic ribbons described by Jenkins and Kawamura.<sup>1</sup> Similar observations have been reported in the literature.<sup>17–20</sup> The two different types of typical surface sites should correspond to the bundle heads (type I sites) and bundle edges (type II sites) of the fibrous microcrystallinities.<sup>20</sup> The relative size of the two types of surface

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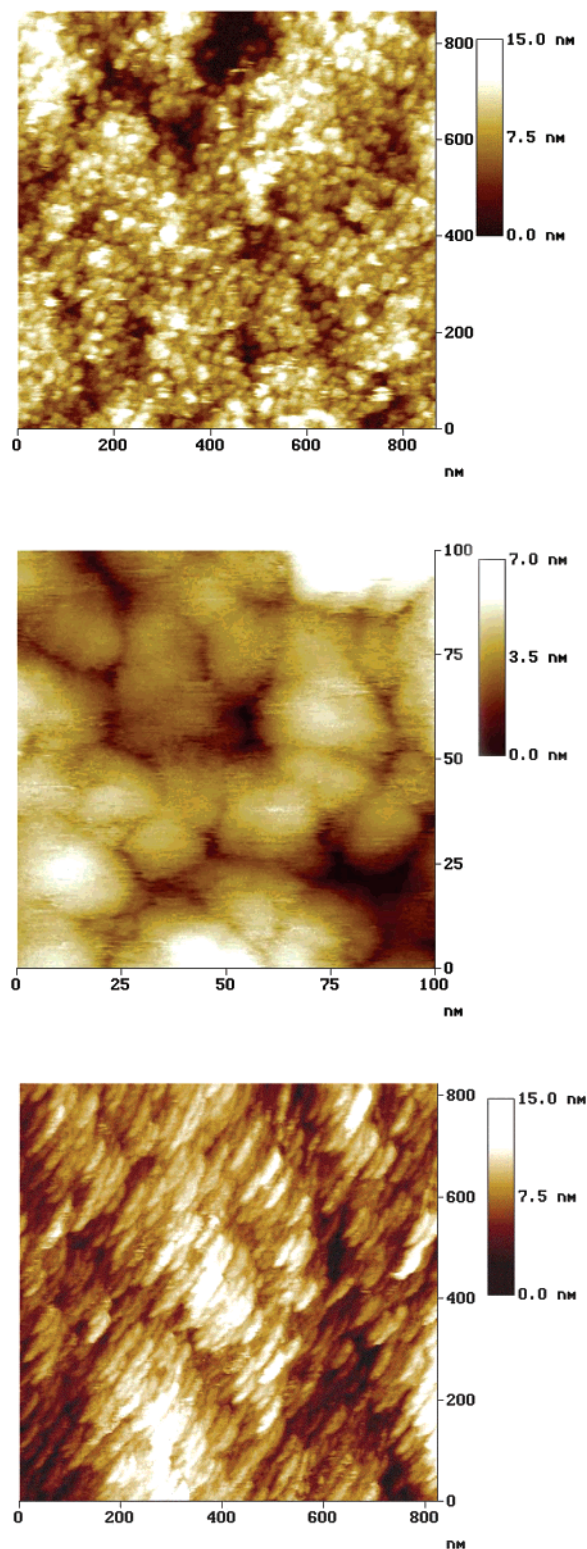


Figure 1. Scanning tunneling microscopic images of polished glassy carbon: (a) type I surface features, (b) zoomed image of type I features, and (c) type II surface features.

features varied among glassy carbon disks examined and was quite difficult to measure accurately. The graphitic bundles piled up on each other rather tightly. The valleys between the graphitic bundles corresponded to the unconnected void space with irregular shape. Most of the void volume as represented by the

darker areas was roughly estimated to be smaller than 30 nm in diameter. Some darker areas with void volume larger than 100 nm were also observed. The topographic surface of the glassy carbon was rough and porous.

The surface structures of the electrochemically activated glassy carbon electrode (PGCE) obtained by cyclic polarization were examined. The two typical types of surface sites were also observed at the activated surface. An STM image of the type I bundle heads of the activated surface showed some increase in surface roughness when compared with the glassy carbon surfaces obtained by polishing (Figure 1a). Zoomed images showed that the size of the graphitic particles reduced slightly after cyclic polarization, and the formation of small void structures was also observed. The size of the observed void space did not change very much. There was no significant difference in surface characteristics for PGCE obtained by cyclic polarization for 10 and 50 cycles. Similar results were also observed for the type II bundle edges.

On the other hand, glassy carbon could be electrochemically activated in 0.5 M  $\text{H}_2\text{SO}_4$  by the constant-potential voltammetric method, as described above. Figure 2 displays the STM images of the two typical types of surface sites at the activated surface obtained after a 1.5-min anodization, showing the newly formed void structures. A typical image of type I surface sites of the PGCE is shown in Figure 2a. Obviously, the average size of the ellipsoidal particles was much smaller than that for a polished GCE (Figure 1a). Additionally, there were increases in the void fraction and the number of individual graphitic particles when the GCE was subject to potentiostatic activation. Experimental results indicated that the surface structures of the activated electrode changed gradually as the anodization time increased. The average size of the ellipsoidal graphitic particles reduced from 25 nm on a polished surface (Figure 1b) to 20 nm on an electrode after a 0.5-min activation and then further reduced to 8 nm after a 1.5-min activation (Figure 2b). The decrease in particle size indicated that the corrosion of graphitic particles occurred when electrochemical activation was employed. The corrosion process was also evidenced by the detection of carbon dioxide during electrochemical activation of glassy carbon.<sup>26</sup> Meanwhile, darker areas corresponding to void volumes became apparently enlarged and more visible. It was roughly estimated that most of the freshly formed void volume had a diameter of about 3 nm when the anodization time employed was 1.5 min, which is much smaller than the size of the original voids before activation.

Figure 2c shows the STM image of the type II bundle edges after a 1.5-min potentiostatic anodization. It reflects that there were no significant changes in the length of the fibrous graphitic bundles when compared with those observed in Figure 1c. The corroded particles and new voids became visible in the zoomed images. It appeared that an individual particle was surrounded by the newly formed valleys, showing an ellipsoidal shape. The average particle size was  $\sim 8$  nm, which is similar to that of the type I bundles.

STM studies showed that the number of new voids or valleys increased upon activation, especially when potentiostatic activation was employed. The formation of new voids resulted from the

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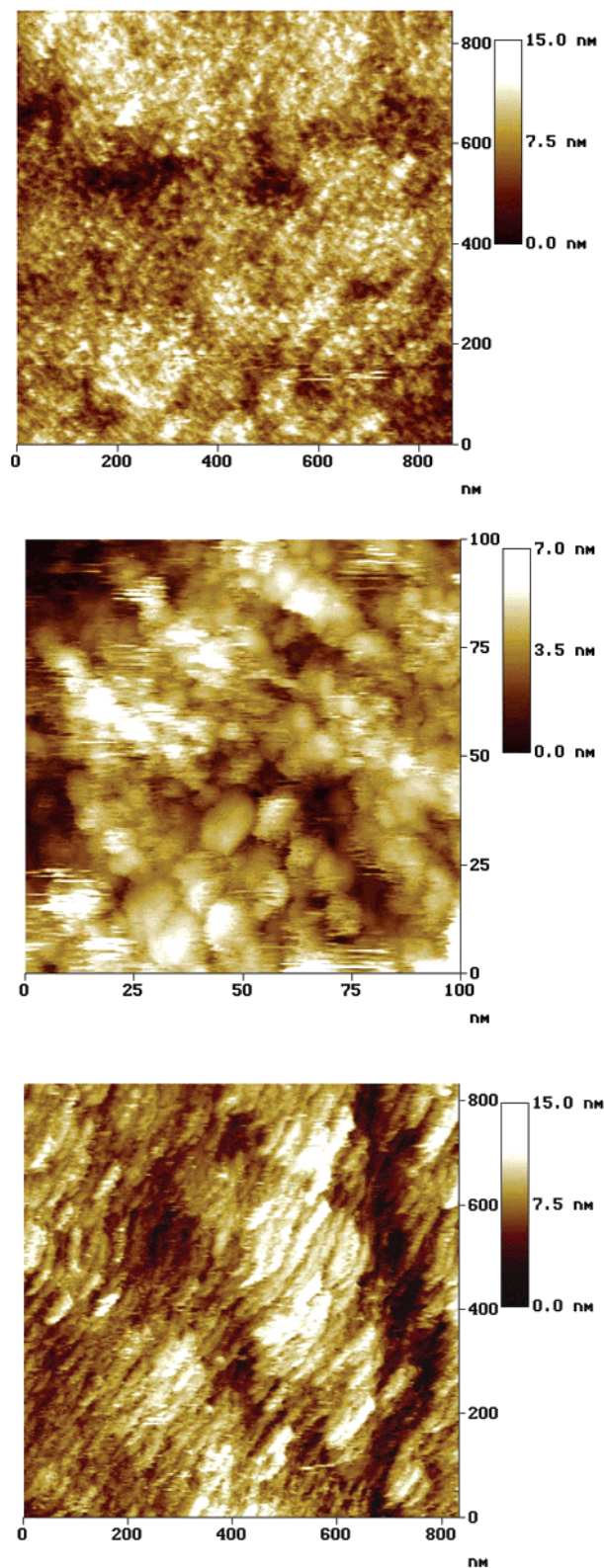


Figure 2. STM images of glassy carbon after constant-potential activation for 1.5 min: (a) type I surface features, (b) zoomed image of type I features, and (c) type II surface features.

corrosion of the graphitic particles during the anodization processes. The holes (etch pits) and void spaces became apparent as a result of activation. Many more voids at deeper crystal layers were exposed, and the size of the graphitic particles at the top

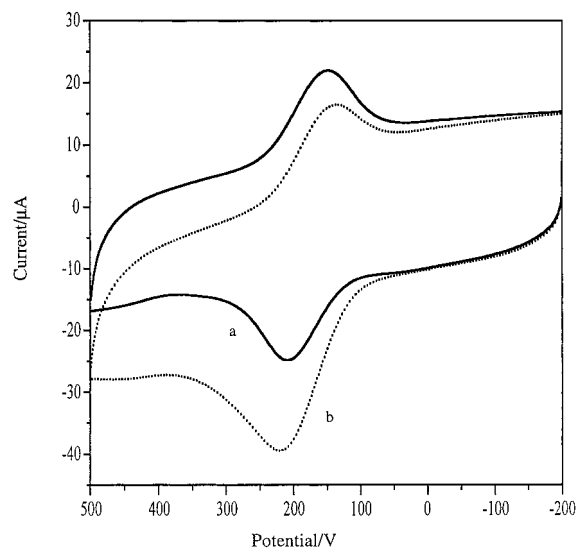


Figure 3. Cyclic voltammograms of a DHB-modified PGCE obtained by cyclic-potential activation: (a) in phosphate buffer (pH 7.0) and (b) 20 mM NADH in phosphate buffer.

layers was reduced. STM results indicated that potentiostatic activation was a more effective activation means when compared with cyclic polarization. The apparent size and depth of the void volumes obtained by cyclic polarization were much smaller than those obtained by potentiostatic activation. In general, STM reflected only a very small part of the electrode surface and did not provide detailed structural information of the interiors of the voids. It was then necessary to examine the whole surface with electroactive probes of different molecular sizes.

#### Catalytic Oxidation of NADH at DHB-Incorporated PGCE.

It has been reported that 3,4-dihydroxybenzaldehyde (DHB) could deposit at activated glassy carbon surfaces, involving electropolymerization reactions to produce stable polymeric films containing quinone moieties. The amount of deposited DHB species was found to be less than a monolayer at the electrode surface, and the deposited DHB species could catalyze the oxidation of NADH.<sup>24,25</sup> In our previous studies, cationic copper species and small organic molecules, such as DHB, were found to incorporate onto the glassy carbon electrodes obtained by electrochemical pretreatment in sulfuric acid.<sup>21–23</sup> Quasireversible redox behaviors were observed for the background voltammetric response of the activated electrodes.<sup>21–23</sup> Copper cations, chloride anions, DHB and NADH have different molecular sizes and charges, and should be suitable molecular probes to investigate the effects of surface structures of the glassy carbon obtained by different pretreatment methods on their electrochemical behaviors.

Figure 3a shows the cyclic voltammogram of a DHB-modified PGCE obtained by cyclic polarization, recorded in pure 0.1 M phosphate buffer (pH 7.0). A reversible surface wave was observed, with a formal potential at about +0.18 V. Interestingly, the peak separation was slightly smaller than that observed at a polished electrode. The saturation coverage of DHB species at this modified electrode was found to be about 0.47 nmol/cm<sup>2</sup>, assuming a two-electron process. When the same electrode was immersed in a solution containing 20 mM NADH, an increase in the anodic peak current of about 15 µA was observed in Figure 3b, indicating the catalytic oxidation of NADH at the DHB-

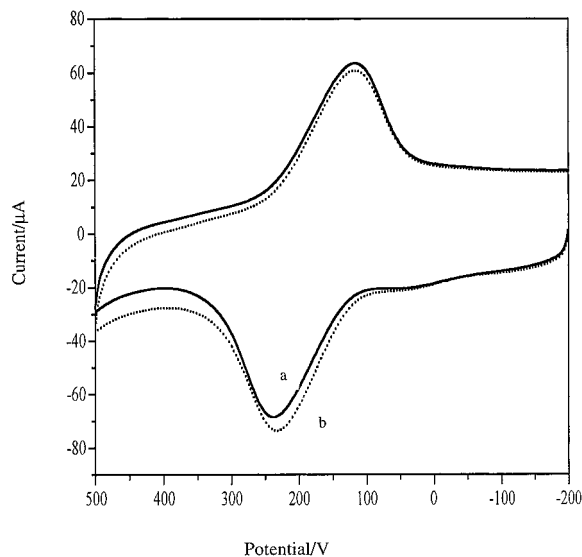


Figure 4. Cyclic voltammograms of a DHB-modified PGCE obtained by constant potential activation for 1.5 min: (a) in phosphate buffer (pH 7.0) and (b) 20 mM NADH in phosphate buffer.

modified PGCE. Figure 4a shows the voltammetric response of a DHB-modified PGCE obtained by potentiostatic activation with a 1.5-min anodization time. Interestingly, there was virtually no difference in the voltammetric characteristics for DHB-incorporated PGCE obtained by the two different activation procedures. The corresponding DHB coverage at the PGCE obtained by potentiostatic activation was about 2.38 nmol/cm<sup>2</sup>, about 5-fold larger than that for PGCE obtained by cyclic polarization. However, the increase in the catalytic current was only about 5  $\mu$ A when the DHB-loaded PGCE obtained by potentiostatic activation was immersed in 20 mM NADH (Figure 4b). This suggested that the electrocatalytic oxidation of NADH at the DHB-loaded PGCE obtained by potentiostatic activation was inefficient, even though the electrode had a much higher DHB coverage.

Additionally, the catalytic response of NADH at the two types of DHB-deposited PGCE was examined amperometrically in phosphate buffer. The electrode potential was kept at +0.3 V with stirring at 500 rpm. The catalytic current at the PGCE obtained by potentiostatic activation increased gradually and became saturated at about 0.25 mM NADH, despite the much higher DHB coverage. On the other hand, the catalytic current showed linear increase with NADH concentration for a much wider range (>0.70 mM) at PGCE obtained by cyclic polarization. Experimental results again confirmed that there was no significant catalytic effect for DHB deposited at the PGCE obtained by potentiostatic activation, and the small amount of DHB deposited at the PGCE obtained by cyclic polarization showed much higher catalytic activity.

STM results suggested that the graphitic particles became smaller and the void spaces at deeper depth became exposed when glassy carbon electrodes were electrochemically activated at constant potential. Voltammetric measurements indicated that the DHB species deposited in deeper depth of the micropore structure of PGCE obtained by potentiostatic activation were electroactive. However, experimental results showed that the increased DHB coverage on this modified PGCE did not result in an increase in catalytic oxidation of NADH. DHB<sup>27</sup> has a flat

area of about 0.619 nm<sup>2</sup>, and the minimum edgewise area is about 0.252 nm<sup>2</sup>. NADH bears negative charges and a much larger molecular size. It is possible that DHB species present at deeper depth of the micropores were inaccessible by NADH of much larger molecular size. The pronounced catalytic behaviors at PGCE obtained by cyclic polarization suggested that the DHB species were deposited on the top layers or outside the smaller voids. DHB deposited at the deeper depth of the voids did not significantly catalyze the oxidation of NADH located at top layers or outside the voids obtained by potentiostatic activation, even though the DHB species were electroactive.

On the other hand, our previous studies indicated that metal cations such as Cu<sup>2+</sup> and Pb<sup>2+</sup> adsorbed on PGCE obtained by constant-potential activation.<sup>21,22</sup> Adsorption of organic adsorbents such as benzoquinone and alizarin red S did not affect the original adsorption of these metal cations.<sup>22</sup> Different voltammetric responses were observed in solutions containing both copper sulfate and sodium chloride for PGCE obtained by cyclic and potentiostatic anodization, especially when rotating-disk electrodes were employed. Our recent studies indicated that the oxidation of deposited metallic copper at PGCE obtained by potentiostatic anodization was not significantly affected by chloride ions. This seemed to suggest that there were major differences in the microscopic structures for PGCE obtained by different means. Very small voids existed inside the larger void space generated by potentiostatic activation. Only the small metal cations could adsorb onto the void space, and the larger molecules were excluded from these micropores.

**Proposed Structural Model of GCE upon Electrochemical Activation.** It is well-known that the basic units of glassy carbon comprise basal and edge planes.<sup>1-3</sup> Literature reports suggest that the edge planes are usually more reactive than the basal planes.<sup>28-31</sup> It is likely that the void spaces are more easily formed at the original edge planes of the graphitic particles when glassy carbon is subject to electrochemical activation. More basal and edge planes become exposed when new void spaces are generated.

A simple structural model of glassy carbon is illustrated in Figure 5. The individual graphitic particles are assumed to be the basic units of sp<sup>2</sup> hybridized carbon, as shown in Figure 5a,b. There are basal and edge planes at glassy carbon crystals. Electrochemical activation results in an increase in the oxygen-containing groups at the edge planes, and carbon substrates are oxidized and then removed to leave void space.<sup>26</sup> However, the oxidation of carbon materials is not even and homogeneous for the whole edge plane. The difference in the extent of oxidation at different surfaces of the edge planes would result in newly formed void structures similar to those shown in Figure 5c,d. The activation procedures employed have a strong influence on the extent of oxidation at different activation sites, and different void structures result. Figure 5c illustrates that large void spaces corresponding to macropores are produced by the more effective

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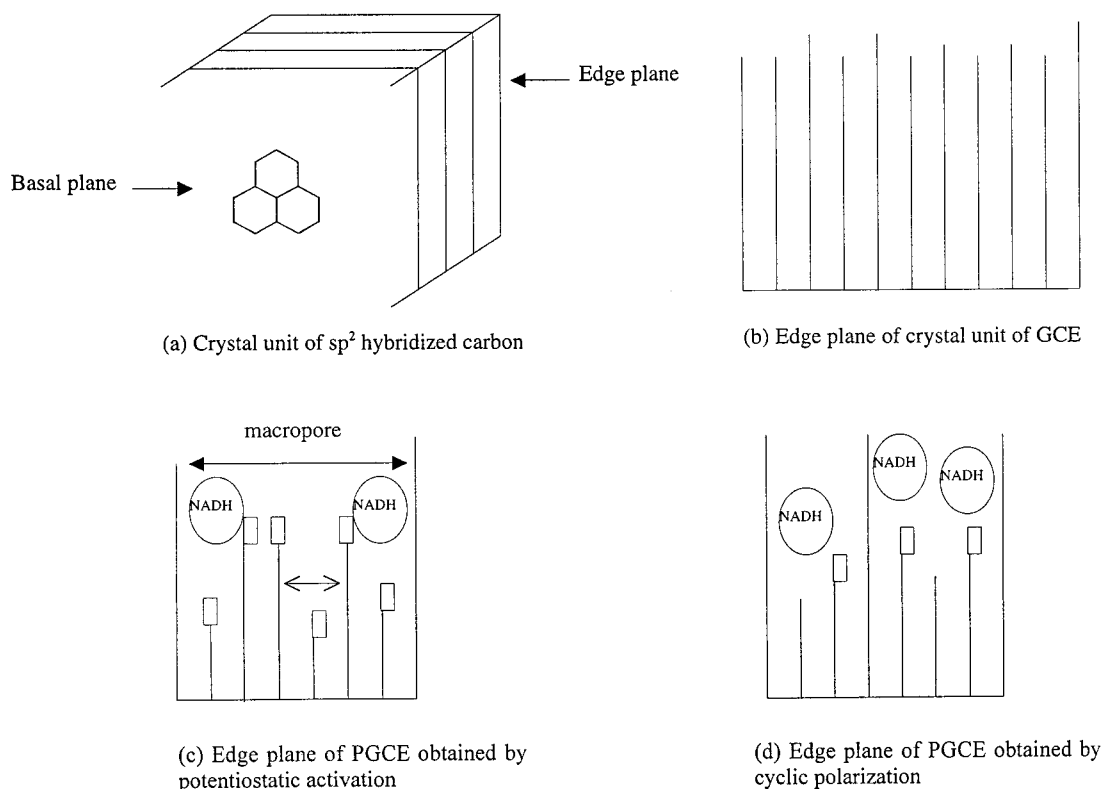


Figure 5. Structural model of glassy carbon upon electrochemical activation.

potentiostatic activation. The formation of a large void volume would result in more basal and edge planes in the interiors of the void space becoming exposed. Therefore, the resulting PGCE shows an increase in the electrochemical surface area and characteristics of both basal and edge planes. Very small void space (micropores) also exists at the bottom of the large void spaces. The size of the newly formed void space at deeper layers is small enough to be accessible only by very small metal cations and is inaccessible by larger organic adsorbents. Figure 5c also illustrates the adsorption of small DHB species in the micropores, and larger NADH molecules are excluded from the micropores. This results in the inefficient electrocatalytic oxidation of NADH at the DHB-modified PGCE obtained by potentiostatic anodization.

Figure 5d shows the types of voids obtained by cyclic polarization. Micropores are generated, and the size of the voids is smaller than the macropores created when potentiostatic activation is employed. Because cyclic polarization is a less effective means of electrochemical activation, only the upper layers of the GCE surface become corroded. Very small micropores are absent. The void space at the PGCE obtained by cyclic polarization is large enough for the adsorption of both metallic copper ions and small organic adsorbents, but it is inaccessible by large organic adsorbents. Adsorption of DHB at the micropores generated by cyclic polarization is also illustrated in Figure 5d. DHB species deposit on the top layers and are accessible by the larger NADH molecules. Consequently, efficient catalytic activity is observed.

Our proposed structural model of the electrochemically activated glassy carbon offers a reasonable explanation of experimental results; however, the model is mainly based on the qualitative changes in the STM images and indirect evidence

provided by the DHB/NADH catalytic reaction only. It is certainly desirable to examine voltammetric behaviors of redox probes of varying sizes before the structural model can be established with confidence. On the other hand, there have been reports suggesting that the microscopic void structures of the PGCE might resemble those of the supramolecular calixarenes.<sup>23,32</sup> Calixarenes are known to have hydrophobic cavities surrounded by aromatic carbon cages and relatively polar outer structures. Usually this type of supramolecule could form host-guest complexes with a number of species, such as metal cations, aromatic organic species, and surfactants involving complex interactions. The corresponding adsorption behaviors of the PGCE could be viewed as host-guest interactions. Detailed studies on the adsorption behaviors of various species at PGCE will be reported elsewhere.

## CONCLUSIONS

Experimental results showed that the fibrous graphitic microcrystallites of glassy carbon had nanometer size and that there were two types of typical surface sites corresponding to helical bundles and bundle edges of interwoven graphitic ribbons. With the increasing extent of anodization in sulfuric acid solution, the graphitic microcrystalline particles at the top layer were continuously removed, and more of the graphitic microcrystallinities at the deeper layers became exposed. The roughness of the electrode increased. New voids resulted mainly from the corroded graphitic microcrystallites. The size of the new void volume was dependent on the activation methods employed. Usually, the average void volumes obtained by cyclic polarization were smaller than those obtained by potentiostatic activation. However, very small micro-

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pores were created at the interiors of the glassy carbon. The electrochemical behaviors of the activated electrode were related to both the new void volumes and the size of the electroactive species.

#### ACKNOWLEDGMENT

The authors express their appreciation to Dr. Zhao-Xiong Xie, State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, China, for assistance in carrying out the STM

studies. This work was supported in part by the Faculty Research Grant of HKBU (FRG/99-00/II-13 and FRG/00-01/I-17) and the Research Grants Council of Hong Kong (HKBU 2049/01).

Received for review July 2, 2001. Accepted November 19, 2001.

AC010734+