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Activation of Glassy Carbon Electrodes by Polishing with Ceramics Particles

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Synopsis. Glassy carbon electrode polished with ceramics particles (TiB_2, SiC, and TiC) showed higher oxidation rate of ascorbic acid. The activation seems to depend on hardness of glassy carbon and ceramics particles and to be influenced by fresh edges formed on glassy carbon surface.

Glassy carbon electrode (GCE) has been used for voltammetry and amperometry. Renewal of glassy carbon (GC) is usually perfomed by polishing GC surface with an abrasive such as α-alumina. It was recently shown that an oxide (α-Al_2O_3, CeO_2, ZrO_2, etc.) dispersed on GC surface enhances the rate of electrochemical reaction of ascorbic acid and other compounds.[1-3] A model has been proposed to explain the enhancement. A porous thin layer of carbon embracing metal oxide particles adheres to the surface of base GC.[1-3] The current is enhanced due to additional current from an electroactive species in the porous layer. These studies are, however, limited to the experiments on metal oxides.

In this paper, activity of three types of glassy carbon electrode polished with ceramics particles (titanium boride (TiB_2), silicone carbide (SiC), and titanium carbide (TiC)) was investigated for oxidation of ascorbic acid by cyclic voltammetry.

Experimental

L-Ascorbic acid (Wako Pure Chem. Co.) was used without further purification. α-Al_2O_3 was obtained from Buehler Co. (Chicago), TiB_2 (particle size: 2 μm, hardness: 3200—3400 kg mm^{-2}) from Hermann C. Starck Co., SiC (particle size: 2 μm, hardness: 2700 kg mm^{-2}) from Fujimi Kenmazai Kogyo Co., and TiC (particle size: 2 μm, hardness: unknown[4]) from Japan New Metals Co. The supporting electrolyte was 0.1 M (1 M=1 mol dm^{-3}) phosphate buffer at pH 2.0. Twice distilled water was used throughout the experiments. Other chemicals used are of reagent grade.

Three types of GC (GC-10, GC-20, and GC-30, Tokai Carbon Co.) with a geometric area of 0.071 cm^2 were used. Each GC was polished succesively with α-Al_2O_3 of 1.0, 0.3, and 0.05 μm in diameter as a slurry with wáter, until a mirrorlike surface was obtained. After polishing, the electrode was washed with water for 15 min in an ultrasonic field. The each electrode was repolished with an aqueous slurry of an abrasive (TiB_2, SiC, or TiC) for 30 s on a polishing pad (Yanaco) under pressure and rinsed with water. The electrode was electrochemically examined immediately. GCE was deactivated by a polishing cloth.[5]

A Yanaco model VMA-010 cyclic voltammetric analyzer was employed for cyclic voltammetric measurements. The reference and counter electrodes were Ag/AgCl (Yanaco, MR-P3) and a Pt wire, respectively. The differential capacitance of GCE was evaluated from a.c. measurements with a Fuso phase sensitive amplifier.

Electrodes activated by polishing with the abrasives were immersed into a solution of 1×10^{-3} M ascorbic acid in 0.1 M phosphate buffer solution at pH 2.0 and cyclic voltammograms were recorded to examine the activity of GCE at a scan rate of 100 mV s^{-1}.

Table 1. Electrochemical Data for Ascorbic Acid Oxidation

GC	Abrasive	Size μm	E_{pa} V. vs. Ag/AgCl	$E_{pa/2}$ V. vs. Ag/AgCl	$i_{pa}{}^*/i_{pd}$
GC-10	TiC	2	0.257	0.190	0.90
	SiC	2	0.233	0.166	1.21
	TiB_2	2	0.216	0.159	1.40
	α-Al_2O_3	0.05	0.209	0.171	1.27
		0.3	0.205	0.160	1.40
		1.0	0.205	0.163	1.52
GC-20	TiC	2	0.185	0.155	1.87
	SiC	2	0.175	0.141	2.44
	TiB_2	2	0.171	0.139	2.50
	α-Al_2O_3	0.05	0.190	0.158	1.72
		0.3	0.176	0.144	2.07
		1.0	0.169	0.135	3.13
GC-30	TiC	2	0.181	0.155	2.02
	SiC	2	0.171	0.139	3.22
	TiB_2	2	0.171	0.139	3.80
	α-Al_2O_3	0.05	0.181	0.151	1.89
		0.3	0.179	0.141	2.43
		1.0	0.170	0.139	3.58

* i_{pa} is peak current value measured at about 10 s after polishing.

Results and Discussion

By preliminary experiments using GCE activated with α-Al_2O_3 (1.0, 0.3, and 0.05 μm in diameter) it was revealed that the enhancement of oxidation of ascorbic acid depends on the particle size of α-Al_2O_3 as shown in Table 1. In this study, GCE surface was activated by polishing it with ceramic particles(TiB_2, SiC, and TiC) with a same particle size of 2 μm.

Typical cyclic voltammograms of ascorbic acid solution in phosphate buffer are shown in Fig. 1. No cathodic wave was observed for deactivated and activated GCE. A broad oxidation wave was obtained at the deactivated GCE. The avarage of 20 peak potential (E_{pd}) values at deactivated GCE was 0.476 V vs. Ag/AgCl. Peak current (i_{pa}) was enhanced and peak potential (E_{pa}) shifted to a less positive potential by polishing GCE with seramics particles. Similar voltammetric behavior was observed at GCE activated with each of the ceramics. The results for oxidation of ascorbic acid are summarized in Table 1, indicating that the activation of ascorbic acid occurs at GCE activated with the ceramics particles. The presence of metal oxide particles dispersed on GC surface will not necessary for activation of ascorbic acid. The order of activation is TiB_2>SiC>TiC at the same type of GCE. TiB_2 is assumed to have the highest hardness in three abrasives examined. The results indicate that the activation depends on the hardness of ceramics particles at a constant particle size.

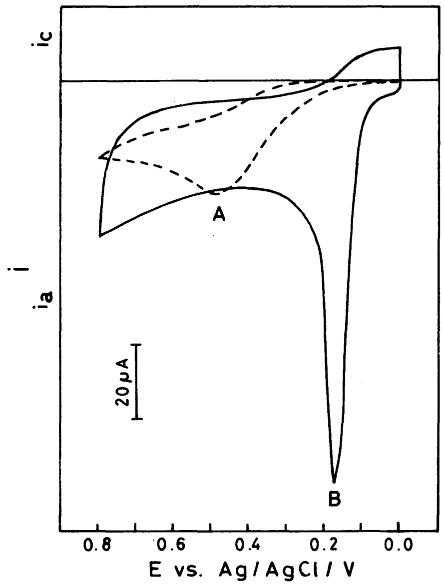

Fig. 1. Cyclic voltammograms of 1×10^{-3} M ascorbic acid at pH 2.0 at GC-30 GCE. Scan rate 0.1 V s^{-1}. (A): Deactivated by final polishing on a polishing cloth. (B): Activated by polishing with TiB_2.

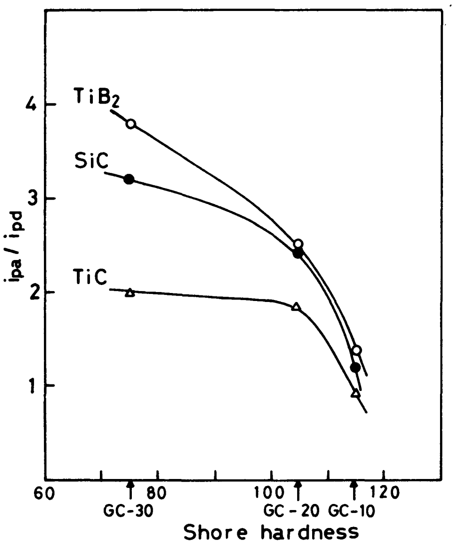

Fig. 2. Plots of the ratio of i_{pa} to i_{pd} versus the average Shore hardness of GC.

Figure 2 shows the relationship between the ratio of peak current at activated GCE(i_{pa}) to peak current at deactivated GCE (i_{pd}) and the average Shore hardness of GC. The order of oxidation activation for three types of GCE is GC-30>GC-20>GC-10. GC-30 GCE which has the lowest hardness shows the most enhanced oxidation of ascorbic acid. These results suggest that active edges are formed on carbon surface of GCE(GC-30) polished with TiB_2.

On the other hand, the differential capacitance at peak potential for deactivated GCE(GC-30) in ascorbic acid solution was 62 μF cm^{-2}. The values for GCE(GC-30) polished with TiB_2, SiC, and TiC were 570, 554, and 463 μF cm^{-2}, respectively. These values are seven to nine times greater than that for deactivated GCE and similar to that for edge orientation of pyrolytic graphite.[6] It is likely that ascorbic acid is adsorbed on fresh carbon edges. The activation of ascorbic acid oxidation will be ascribed to fresh carbon edges formed on GCE surface.

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