ELECTROANALYTICAL APPLICATION OF CONDUCTIVE DIAMOND ELECTRODES BY CONTROLLING ITS SURFACE TERMINATION

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Diamond is a very attractive material for many potential applications due to its outstanding properties. In particular, highly boron-doped conductive diamond (BDD) films prepared by CVD process have received attention from electrochemists owing to the superior electrochemical properties, including wide potential windows, low background current and the stability of the surface. Some report of BDD application in electrochemical analysis had been published. In the present studies, the effect of surface termination at BDD electrode for electrochemical oxidation of several compounds has been reported.

BDD films from CVD process have naturally H-termination since it is synthesized in H_2 -plasma atmosphere. The surface can be easily changed to be O-termination by oxidation in high potential. O terminated-BDD is known to have some advantages due to its wider potential windows and higher stability than those of H-terminated one. However, since oxygen molecule brings relatively negative charged, negative charged molecule is repelled at BDD surface, disturbing the oxidation reaction. This repulsion effect is found at oxidation of some negative charged compound, like DNA, insulin and oxalic acids. Figure 1 shows that oxidation current of oxalic acid is much higher at H-terminated than that of O-terminated BDD.

However, it is found that the oxidation current reaction at H-terminated BDD gradually decreased with time. The possible reasons of the limited stability of H-termination can be explain by the change of the part of BDD surface from H- to O-termination due to oxidation reaction in high potentials as well as the blocking of reactant or oxidation product at BDD surface due to adsorption process.

Reduction treatment is examined to recover oxidation current at BDD electrode. Figure 2 shows that oxidation current of insulin at BDD electrode can be recovered by 20 minutes of reduction treatment under N_2 atmosphere at –1.7 V (*vs.* SCE). Repeating the oxidation reaction and reduction cycles for several times shows durability of the electrode as shown in Figure 3.

While the reduction treatment is good for current recovery at insulin oxidation, recovery of oxidation current by similar method is not being succeeded for oxalic acid oxidation. As it is found that the oxidation reaction is limited by diffusion control, the only reason of decreasing current is due to oxidation of BDD surface. The result indicates that the reduction treatment cannot change surface termination from O-termination to H-terminated easily. Instead of reduce the BDD surface; reduction treatment reduced the adsorption molecules effectively at BDD surface. Therefore, current is recovered.

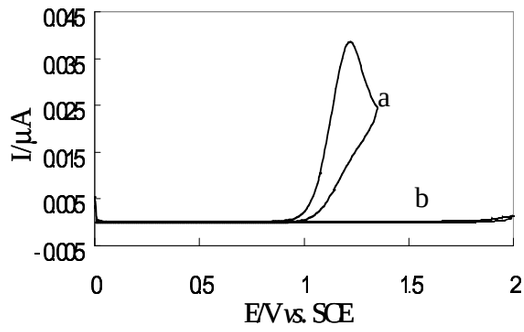

Fig. 1. Cyclic voltammogram of 0.1 mM oxalic acid in Britton Robinson buffer (pH 2.1) at (a) H-terminated and (b) O-terminated BDD.

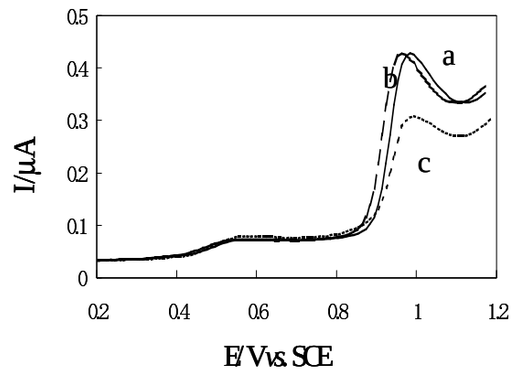

Fig. 2. Linear sweep voltammogram of 10 mM oxalic acid in Britton Robinson buffer (pH 2.1) at BDD surface for (a) the 1st cycle (b) the 2nd cycle and (c) after reduction treatment in Britton Robinson buffer under N_2 atmosphere.

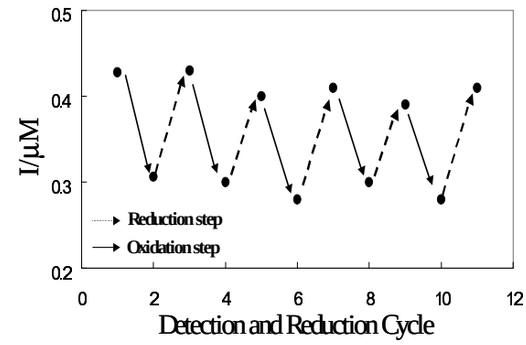

Fig. 3. Plot of insulin oxidation current before and after reduction treatment. Condition is similar to that at Fig.2.