Surface Transition Kinetics on Synthetic Metallic Diamond

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On the heavily doped diamond electrode, the reactivity for the copper deposition was changed depending on an electrochemical hysteresis of the surface. On the electrode, which underwent hydrogen or oxygen evolution, though the reduction of Cu^{2+} proceeded on both, the reduced atom was trapped only on the surface on which the hydrogen was evolved in advance. The time course of this surface transition was investigated.

The boron-doped diamond (BDD) electrode has a potential superiority for many electrochemical applications such as electrolysis and sensors because BDD has the wide potential window,[1-3] the small background current[1,4,5] and the corrosion resistivity.[2,6,7] The heavily doped BDD shows a metallic response with many electrochemical species.[4,5,7-11] However, because of the covalent structure of the surface, many examples have been reported that an electrochemical response on the metallic BDD differs from one on a simple metal electrode.[1,3,8,9,12,13] This difference is enhanced especially in the case that the reaction proceeds under short range interaction between the surface and the reactants. In these cases, the reactivity is governed by the outer most layer on the BDD. The stable structures of the outer most layer are the hydrogen terminated or the oxygen terminated surfaces.[14] The couple of these structures can exchange reversibly under high temperature or plasma treatment in vacuum chamber.[15,16] In this article, we will demonstrate a possible example that an electrochemical treatment might induce this transition under much moderate conditions. And, furthermore, the time course of this transition will be monitored by using the simplest structure sensitive reaction on BDD, the copper deposition in a neutral aqueous electrolyte.[9]

The BDD films were synthesized using the microwave plasma-assisted chemical vapor deposition (MPCVD), as reported.[13] The electrochemical responses were obtained by using a potentiostat combined with a coulometer; Model 273 EG&G PARC. A couple of the typical cyclic voltammograms for the copper deposition were shown in Figure 1. The cathodic currents observed in both (a) and (b) corresponded to the reduction of Cu^{2+}. However, the anodic current due to the electrochemical dissolution of the copper layer was only observed in Figure 1 (a). The stripping current requires a pretreatment for the electrode that is 10 min continuous hydrogen evolution in 0.1 M Na_2SO_4 aqueous solution at -1.8 V vs. Ag/AgCl. The voltammogram (a) was measured in the aqueous electrolyte containing 1 mM $CuSO_4$ and 0.1 M Na_2SO_4 into which the pretreated electrode was transferred. Similarly, the voltammogram (b); no anodic peak, was obtained in the aqueous $CuSO_4$ solution, after 10 min oxygen evolution in the Cu^{2+} free solution at +1.8 V vs. Ag/AgCl. The two voltammograms were changed reversibly depending on the pretreatment.

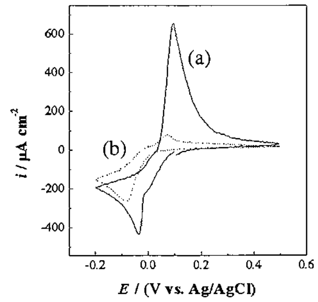

Figure 1. Cyclic voltammograms obtained in aqueous $CuSO_4$ (1 mM, 0.1 M Na_2SO_4) at a potential sweep rate of 20 mV s^{-1} on the BDD electrode (surface area, 0.12 cm^2) with pretreatment by fixing the potential at (a) −1.8 V vs. Ag/AgCl and (b) +1.8 V vs. Ag/AgCl for 10 min in Cu^{2+} free solution.

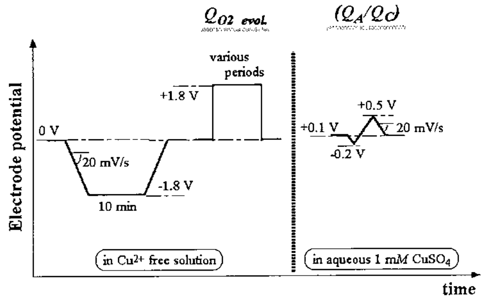

Figure 2. Schematic representation of potential program applied to the BDD electrode.

The metal deposition on the surface of the electrode is the secondary process following the preceding electron transfer. The reduced atom lands on the surface and moves to the edge of the metal ad-layer where it settles.[17] The two voltammograms in Figure 1 show that this secondary process is affected by the change on the surface induced by the gas evolution in the pretreatments. The change in the chemical species at the outer most layer has not been identified yet, but we can estimate the kinetics of this surface transition by using a specially designed electrode potential program shown in Figure 2.

Initially, the electrode potential was kept at −1.8 V vs. Ag/AgCl in the Cu^{2+} free solution for 10 min where the saturated amount of the trapping sites for the copper atom is formed on the BDD electrode surface. Then, in order to quench these sites, the potential was stepped to +1.8 V vs. Ag/AgCl within the programmed period of the time, where the charge for the oxygen evolution Q_{O2evol} was obtained simultaneously. Next, the electrode was rinsed by degassed pure water and quickly transferred into the aqueous 1 mM $CuSO_4$ electrolyte. Then, finally, the anodic-to-cathodic charge ratios (Q_A/Q_C) were obtained by using the programmed cyclic potential. This ratio (Q_A/Q_C) was *ca.* unity and zero on the surface in case of Figure 1 (a) and (b), respectively. Thus, we can investigate the time course of the change from the Cu trapping surface to the dropping one as a function of the charge for the oxygen evolution Q_{O2evol}.

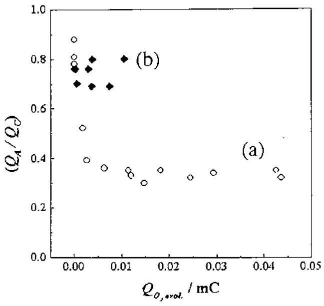

Figure 3. The relationship between the oxygen evolution charge $Q_{O2\ evol}$ and the anodic-to-cathodic charge ratios (Q_A/Q_C) when the electrode potential was held at (a) +1.8 V vs. Ag/AgCl and (b) +1.0 V vs. Ag/AgCl.

At the quenching potential of +1.8 V vs. Ag/AgCl, (Q_A/Q_C) was plotted against Q_{O2evol} in Figure 3 (a). This plot indicates that the number of the trapping sites decreases exponentially as a function of Q_{O2evol}. At +1.0 V vs. Ag/AgCl, the relationship between (Q_A/Q_C) and Q_{O2evol} was shown in Figure 3 (b). Though oxygen bubble was generated in both experiments, the decrease of the (Q_A/Q_C) was slow when the electrode potential was held at +1.0 V vs. Ag/AgCl.

It has been reported that the reaction overpotential for chlorine gas evolution on BDD increased during continuous anodic electrolysis and that the surface O/C ratio increased simultaneously.[2] This surface carbon-oxygen complex whose chemical structure has not been known yet deactivated the sites for the chlorine evolution. We suppose it is this surface carbon-oxygen complex that controls the copper deposition on the metallic BDD electrode. The sticking coefficient of the copper atom on the surface would be affected by the coulombic interaction between the negatively charged copper cluster in the solution and the surface whose charge density is modified by the surface chemical structure. This tentative conclusion implicitly suggests that the low temperature electrochemical modification of the diamond surface is also possible.

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