Fabrication and Characterization of Gold–Platinum Black Electrode

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Gold–platinum black layer was electrochemically deposited on a platinum electrode in the mixed solution of tetrachloroaurate, hexachloroplatinate, and lead acetate. The surface of the electrode after the deposition was characterized by scanning electron microscopy, X-ray microanalysis, and cyclic voltammetry. There was no evidence of the localization of gold and platinum, and the deposition ratio of gold and platinum was proportional to the concentration of tetrachloroaurate and hexachloroplatinate.

In recent years, much work and intense research activity have been devoted for the development of microbiosensors for flow injection analysis,[1] intracellular monitoring,[2] neuro-transmitter detection,[3] and the implantation monitoring.[4–6] In general, sensitivity decreases as the sensor size is reduced. Hence, compensatory technique, such as enlargement of surface area, is required to develop microsensors.[7]

Recently, it is suggested that a platinized gold electrode can stably immobilize enzyme molecules and efficiently catalyze hydrogen peroxide, which is an enzymatic reaction product.[8] We report here our development of gold–platinum black codeposited electrode, which has a large surface area.

Noble metals, such as gold and platinum, have specific properties and have different applications. In the case of gold, self-assembled monolayers of thiols on gold surface have been intensively studied.[9–12] Proteins, such as enzyme[13–15] and antibody[16,17] immobilized on gold electrode surface via thiols are also studied. While platinum, which has highly catalytic activity for hydrogen peroxide, is widely used as a biosensing transducer.[18–20] We found that our method can easily control the deposition ratio of gold and platinum.

The electrode was fabricated according to our previous procedure.[7] A microplatinum wire with a diameter of 200 μm was inserted into a glass capillary tubing and then sealed by heating. The tip of the wire was polished with emery papers to obtain a flat surface, and electrochemically cleaned by applying potential waves repeatedly (–200 ~ 1450 mV, 500 mV/s, 50 cycles) in 1 M H_2SO_4. To codeposit Au and Pt particles, the wire was immersed in a mixed solution of tetrachloroaurate (Wako) and hexachloroplatinate (Wako) in the presence of 1.6 mM lead acetate (Wako) as an inhibitor. The total concentration of tetrachloroaurate and hexachloroplatinate was 72 mM, and the mixing ratio was changed as desired. Deposition was carried out by applying a potential (–80 mV vs Ag/AgCl) for 5 min. By potential step chronocoulometry in 1 mM $K_4[Fe(CN)_6]$, the area of gold–platinum black electrode (60 mol% hexachloroplatinate and 40 mol% tetrachloroaurate) was about 36 times larger than that of flat surface electrode.

The morphology of metal black electrodes was examined with a scanning electron microscope. In the photographs

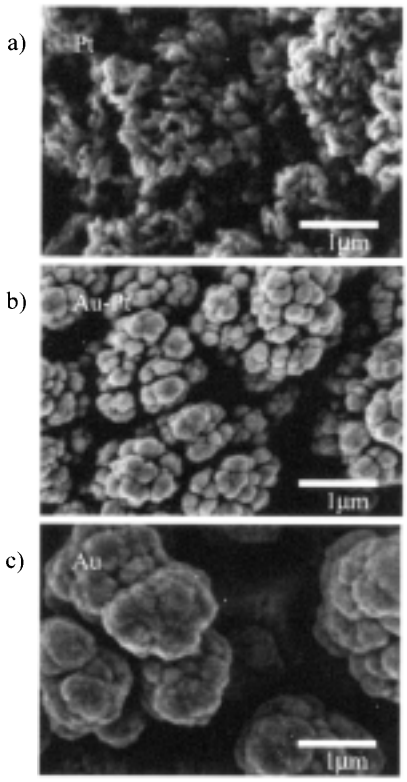

Figure 1. SEM images of metal black electrodes; a) platinum black, b) gold–platinum black, and c) gold black electrodes.

(Figure 1), all three electrodes seemed to have indented surface. However, morphology of each electrode, such as the size of grain, was seen different each other. In the case of pure platinum black, we can see porous structure with microparticles. On the other hand, cauliflower-like structure was observed in the pure gold black. Although, similar structure was observed in the gold–platinum hybrid, the size of the cauliflower-like structure was much smaller than that of the gold black. In addition, it has apparently fine grooves in each cauliflower-like structure, and such a fine structure was rather similar to the platinum black. Thus, the gold–platinum black had both the phases of gold black and platinum black. Moreover, when the gold–platinum black electrode was immersed into aqua regia ($HCl:HNO_3$ = 3:1), the whole metal black was dissolved, whilst the pure platinum black was not. We, therefore, consider that the gold and platinum were mixed in the atomic level.

Figure 2 shows the cyclic voltammogram of a metal black electrode. The gold–platinum black electrode exhibited two apparent reductive currents, which were attributed to those of gold and platinum. The composition of gold–platinum black

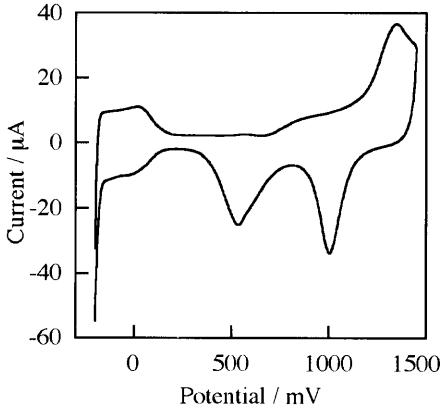

Figure 2. Cyclic voltammogram of gold–platinum black electrode measured at 500 mV/s in 1 M H_2SO_4. The electrode was prepared in a solution containing 60 mol% tetrachloroaurate and 40 mol% hexachloroplatinate.

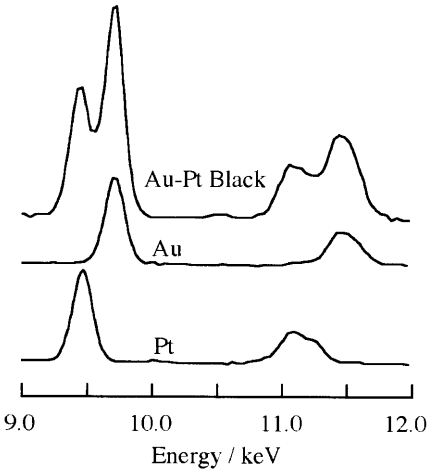

Figure 3. X-ray microanalysis of gold–platinum black at the center of electrode surface. The accelerating voltage of the electron beam was 25 kV.

electrode was further examined by X-ray microanalysis as shown in Figure 3. The peaks at 9.41 and 11.08 keV are attributed to PtLα, while those at 9.71 and 11.41 keV are to AuLα. We could never observe definite peak of lead. From the spectrum, the relative amount of deposited gold (DEP_{Au}) is estimated by the equation:

$$DEP_{Au} = 100 \times \frac{H_{Au}/H_{0Au}}{H_{Au}/H_{0Au} + H_{Pt}/H_{0Pt}} \quad (1)$$

where H_{Au} and H_{Pt} are the peak heights at 9.41KeV and 9.71KeV, respectively. H_{oAu} and H_{oPt} are the standard peak heights obtained by analyzing flat Au and Pt plates (Nilaco), respectively. The deposition ratio of gold and platinum was almost proportional to the mixture ratio of tetrachloroaurate and hexachloroplatinate as given in Figure 4.

The deposition of metal black is not uniform on the surface of base platinum electrode. At the rim of the electrode, metal complex diffuses not only from the front but also from the peripheral of the electrode. Therefore, metal is preferentially deposited at the rim. To remove apprehension that the metal

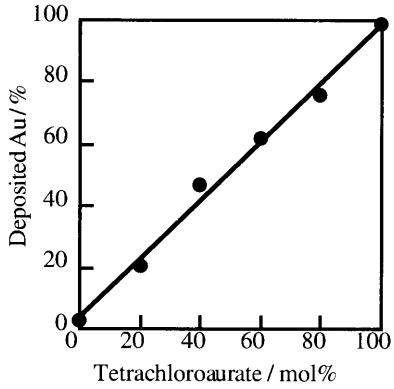

Figure 4. Composition of deposited Au at the surface of gold–platinum black electrode estimated by X-ray microanalysis.

composition on the rim differs from that on the center of the electrode, the deposition ratio of metals of each position was examined by X-ray microanalysis. As the result, we found that the deposited Au at the center and the rim were 42% and 41%, respectively.

These results indicate that the metal black was formed uniformly from the mixture of gold and platinum, and the compositions of the metals were easily controlled by changing the composition of the deposition solution.

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