Electrochemical Responses of a Graphite Electrode modified with Polyeugenol and Overoxidized Polypyrrole Composite Filmto Dopamine and Ascorbic Acid Koji Hirakawa¹, Toshihiko Imato¹, Sumio Yamasaki² and Hiroki Ohura² ¹Department of Applied Chemistry, Graduated School of Engineering, Kyushu University Hakozaki, Fukuoka 812-8581, Japan ² Department of Industrial Chemistry, Faculty of Engineering, Kyushu Sangyo Univirsity Matsukadai, Fukuoka 813-8503, Japan

Introduction A graphite electrode modified with an anodic oxidized polyeugenol (PEu) film exhibited a selective voltammetric response to dopamine (DA) with a good peak separation against ascorbic acid (AA).¹⁾ However, the PEu modified electrode showed a redox peak for a blank solution at nearly the same potential as that of DA in a phosphate media (pH: ca. 7) and as a result, the lower detection for DA was limited by the blank response. In this paper, we wish to report on an improvement of the blank response of the PEu modified electrode with a composite film of PEu and overoxidised polypyrrole (OPPy).

Experimental A PEu film modified electrode was prepared by scaning the potential of a graphite electrode in a range between 0 V and 2.4 V at 0.1 V/s for 30 cycles in a 0.1 M NaOH solution containing 10mM eugenol. After this procedure, the PEu film modified electrode was immersed in a 0.1 M NaOH solution containing 10 mM pyrrole and the electrode potential was cycled between 0 V and 0.8 V at 0.1 V/s for 10 cycles. As a result, the surface of the graphite electrode was modified with a composite film of PEu and OPPy. Electrochemical measurements were carried out by differential pulse voltammetry (DPV) under the condition of potential sweep rate 20 mV/s and pulse amplitude 50 mV.

Results and Discussion Figure 1 (A) and (B) show CVs of the pH 6.0 phosphate buffer (blank solution) obtained by using the PEu modified electrode and the PEu-OPPy composite modified electrode, respectivery. For the PEu modified electrode, a pair of redox peak (O1 and R1), which comes from quinone like surface group, is observed at a potential of ca. 0.25 V, as shown in Fig. 1(A). However, for the PEu-OPPy composite film modified electrode, such a pair of redox peak was not observed, and a background current was lower than that for the PEu modified electrode. This result may be due to the fact that the amount of quinone like surface groups in the PEu film decreases by additional modifying with the OPPy film on the PEu modified electrode.

Figure 2 (A), (B) and (C) show DPVs for a blank (pH 6.0 phosphate buffer), 5μ M DA and 5 mM AA solution obtained by using the bare graphite electrode, the PEu modified electrode and the PEu-OPPy composite film modified electrode, respectively. At the bare electrode, the oxidation peaks for DA and AA were observed at nearly the same potential each other. At the PEu modified electrode and the PEu-OPPy modified electrode, the oxidation peak of AA was observed at more negative potential, compared with the bare electrode. Furthermore, at the PEu-OPPy composite film modified electrode, the peak currents for AA and DA were 1/2 and 10 times higher than these obtained by using the bare electrode, respectively.

Figure 3 shows the DPV signals for $0.5\text{--}10\mu M$ DA and

solution obtained by using the PEu-OPPy modified electrode. The peak currents were proportional to the concentration of DA in the range. The sensitivity of the PEu-OPPy modified electrode was 5.5 μ A/ μ M and a detection limit was 0.1 μ M.



Fig. 1 Cyclic voltammograms for a blank solution obtained by using (A) PEu film modified electrode and (B) PEu-OPPy composite film modified electrode.



Fig. 2 DPVs for 5μ M DA and 5 mM AA at pH 6.0 phosphate media obtained by using (A) bare, (B) PEu and (C)PEu-OPPy modified electrode.



Fig. 3 A series of DPVs for (bottom to top) 0, 0.5, 2, 4, 8 and 10 μ M DA at pH 6.0 phosphate media obtained by using the PEu OPPy modified electrode.

1) A. Ciszewski and G. Milcarek, *Electroanalysis*, 2001, 13, 860.