Utilization of AC impedance measurements for electrochemical glucose sensing with glucose oxidase for improvement of detection selectivity

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Since the electrochemical sensing of glucose using glucose oxidase is a typical catalytic EC reaction, most reaction parameters can be easily elucidated by simple measurements. Therefore, analysis of the reaction with the impedance technique is hardly made although some papers have been published concerning impedance study for elucidation of kinetic parameters for sensor systems using specific electrodes[1]. Our previous study on ac impedance measurements of electrochemical determination of glucose oxidation using glucose oxidase and ferrocenecarboxylic acid as an electron mediator made us find that a calibration curve can be drawn from the Nyquist plots and addition of ascorbic acid does not give any changes in the curve, whereas currents due to oxidation of ascorbic acid are added to the calibration curve in the case of usual dc measurements. Those results have been concisely reported[2]. In the present paper, we would like to report results obtained by further investigations. We chose here Tris(2,2' - bipyridyl) osumium (II) chloride ($Os(bpy)_3Cl_2$) having redox potential of 0.65 V vs. Ag/AgCl as an electron mediator.

Voltammograms (A) shown in Figure 1 indicate cyclic voltammograms of the electrolyte solution containing GOx, $Os(bpy)_3Cl_2$, and glucose of different concentrations, whereas (B) and (C) indicate the voltammograms for direct oxidation of 0.5 mM uric acid and ascrobic acid at a glassy carbon electrode, respectively. The voltammograms (A) give typical electrocatalytic currents that increase with an increase in glucose concentration. Since redox potential of $Os(bpy)_3Cl_2$ is 0.65 V vs. Ag/AgCl, the current peaks are observed at around 0.73 V vs. Ag/AgCl. Therefore, if the peak currents of the glucose oxidation are used for amperometric determination of glucose concentration, the presence of ascorbic acid and uric acid in the solution should interfere the measurements, as well known.

Figure 2 shows the Nyquist plots obtained in the electrolyte solution containing GOx, $Os(bpy)_3Cl_2$, and glucose. Dc potential applied to the electrode (E_{dc}) during the measurements was 0.65 V vs. Ag/AgCl. In the absence of glucose, a straight line having ca. 45° slope was shown, indicating that the Worburg impedance due to the reversible redox reaction of $Os(bpy)_3Cl_2$ was dominant in the impedance plots. When glucose was added to the electrolyte solution, the Nyquist plots traced a semicircle and its diameter decreased as glucose concentration increased.

Figure 3(A) and (B) show the Nyquist plots obtained in the presence of 0.5 mM uric acid and 0.5 mM ascrobic acid respectively. All profiles for different glucose concentrations almost the same as those obtained for the solution in the absence of interference species. Those results indicate that introduction of ac impedance measurements into electrochemical determination of glucose with the mediator having more positive redox potential is useful for eliminating of signals by interference species. The relationship between the selectivity of detection of glucose oxidation and redox potential of mediator and interference species will be discussed, in this paper.

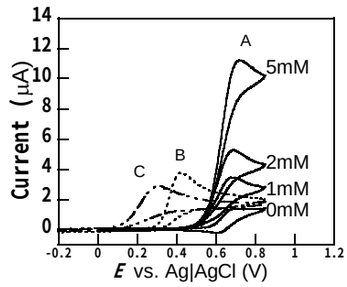

Figure 1. Cyclic voltammograms of a glassy carbon electrode taken at 5 mVs^{-1} (A) in the electrolyte solution (pH 7) containing 30 mM glucose oxidase, 0.2 mM $Os(bpy)_3Cl_2$ and glucose of given concentrations, and (B) in the electrolyte solution (pH 7) containing 0.5 mM uric acid and (C) 0.5 mM ascorbic acid.

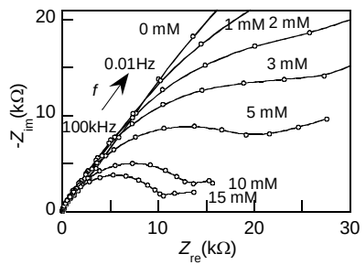

Figure 2. Nyquist plots obtained for a glassy carbon electrode polarized at 0.65 V vs Ag/AgCl in the electrolyte solution (pH 7) containing 30 mM glucose oxidase, 0.2 mM $Os(bpy)_3Cl_2$ and glucose of given concentrations.

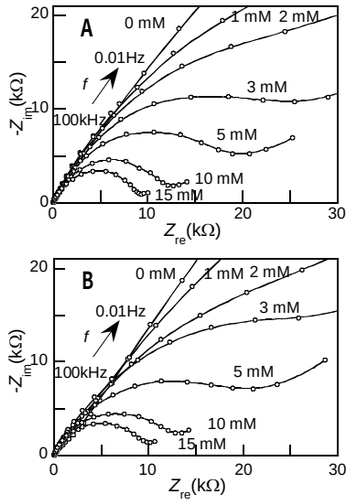

Figure 3. Nyquist plots obtained for a glassy carbon electrode polarized at 0.65 V vs Ag/AgCl in the electrolyte solution (pH 7) containing 30 mM glucose oxidase, 0.2 mM $Os(bpy)_3Cl_2$ and glucose of given concentrations in the presence of (A) 0.5 mM uric acid and (B) 0.5 mM ascorbic acid.

References

1) C. C. Jung and A. H. Hall, Anal. Chem., 67, 2393 (1995).
2) S. Kuwabata, H. Hasegawa, K. Kano, *Chem. Lett.*, **32**, 52 (2003)