Voltagmetric Detection of Oxalic Acid by Using Glassy Carbon Electrodes with Covalently Attached Nitrogen-containing Functional Groups

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We report on a novel voltammetric detection of oxalic acid by using glassy carbon electrodes with covalently attached nitrogen-containing functional groups prepared by stepwise electrolysis. A glassy carbon electrode electrooxidized in an ammonium carbamate solution was electroreduced at –1.0 V (vs. Ag/AgCl) in 1.0 M sulfuric acid for a long time. We found that the electrocatalytic oxidation wave of oxalic acid obtained by this modified glassy carbon electrode was moved to a more negative potential region than that obtained by a platinum electrode in an acidic medium. A good linearity for the peak current signals was observed in the concentration range from 0.1 to 50 mM.

Keywords Electrocatalytic oxidation, oxalic acid, voltammetric detection, glassy carbon electrode

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processes described above. A GC electrode activated by the electrolytic-oxidation/reduction processes function as electron-transfer mediators for the electrocatalytic oxidation of oxalic acid. This fact indicates that the groups introduced to the GC surface by electrolytic-oxidation/reduction processes function as electron-transfer mediators for the electrocatalytic oxidation of oxalic acid. We previously reported that there is a possibility for the formation of N-containing functional groups (i.e., primary amine and hydrazino group) on a GC electrode surface fabricated by electrolytic modification in an ammonium carbamate aqueous solution and hydrochloric acid from results obtained by X-ray photoelectron spectroscopy. The hydrazino group is electro-oxidized to a diazo group via diazene (azo group), and these electroactive species are considered to function as electron-transfer mediators of the oxidation reaction of oxalic acid.

Apparatus

Electrochemical measurements were carried out using an automation polarization system (HZ-3000, Hokuto Denko, Tokyo, Japan) with a three-electrode cell consisting of a working glassy carbon electrode, an Ag/AgCl (3 M NaCl electrolyte) reference electrode, and a Pt counter electrode. Voltammetric measurements of the sodium oxalate were carried out by using a GC electrode activated by the electrolytic-oxidation/reduction processes described above.

Results and Discussion

We evaluated the electrocatalytic activity of an NF-GC electrode with respect to the electrode reaction of oxalic acid. Figure 1 shows cyclic voltammograms (CVs) obtained when using an NF-GC electrode in 0.1 M phosphate buffer electrolyte (pH 2.1) with or without 10 mM sodium oxalate. In the case of a CV measurement of the electrolyte containing 10 mM sodium oxalate, an oxidation wave with a peak potential of +0.8 V (vs. Ag/AgCl) was observed (Fig. 1(a)). In contrast, a cyclic voltammogram of electrolyte without sodium oxalate using the NF-GC electrode is shown in Fig. 1(b), and the small and broad oxidation wave with a dominant peak at approximately +0.8 V (vs. Ag/AgCl) was measured. The potential of this small oxidation wave corresponds to that of the oxidation of oxalic acid obtained by the NF-GC electrode. This behavior obtained by the NF-GC electrode is regarded as a typical electrocatalytic oxidation of oxalic acid. This fact indicates that the groups introduced to the GC surface by electrolytic oxidation/reduction processes function as electron-transfer mediators for the electrocatalytic oxidation of oxalic acid.

Fig. 1 Cyclic voltammograms of NF-GC electrode in a 0.1 M phosphate buffer solution (pH 2.1) with 10 mM sodium oxalate (a) and without sodium oxalate (b). Scan rate, 50 mV/s.

Fig. 2 Cyclic voltammograms of sodium oxalate at different concentrations in a 0.1 M phosphate buffer solution (pH 2.1) obtained by NF-GC electrode. The sodium oxalate concentrations are 50 mM (a), 20 mM (b) and 10 mM (c). Scan rate, 50 mV/s.
The peak height for the oxidation wave of oxalic acid decreased when the pH of the electrolyte was greater than 6.0. This result means that the electrocatalytic activity for the active site of oxalic acid is significantly influenced by the pH of the electrolyte. The pH-dependent studies of the electrocatalytic activity are now in progress.

Figure 3 shows a calibration curve for sodium oxalate on the NF-GC electrode obtained by using cyclic voltammetric measurements. The oxidation peak current was proportional to the sodium oxalate concentration in the range up to 50 mM with a good correlation coefficient of 0.996. The lower detection limit was found to be 0.1 mM.

Figure 4 shows cyclic voltammograms of a bare GC (a), NF-GC (b) and Pt bulk (c) electrodes in a 0.1 M phosphate buffer solution (pH 2.1) containing 10 mM sodium oxalate. The peak potential of oxalic acid oxidation at the NF-GC electrode is at +0.8 V (vs. Ag/AgCl), which is lower than that at the bare GC electrode (+1.3 V) and Pt electrode (+0.95 V) under the same experimental conditions. This fact indicates that the NF-GC electrode is superior to the conventional electrodes concerning the electrode oxidation of oxalic acid.

Conclusions

We succeeded to prepare N-containing functional groups introduced to a glassy carbon (NF-GC) electrode by stepwise electrolysis. NF-GC electrodes have been successfully demonstrated to be able to exhibit an excellent electrocatalytic oxidation wave of oxalic acid in an acidic medium. The NF-GC electrodes are found to be suitable for the electro-oxidation of oxalic acid, which is oxidized at a lower potential than at a Pt bulk and bare GC electrodes. We also have succeeded in the voltammetric detection of oxalic acid in the concentration range from 0.1 to 50 mM by using an NF-GC electrode.

References