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Electrochemical Properties of Chlorine Dioxide Using Aminated Glassy Carbon Electrodes Fabricated by Electrolysis

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ABSTRACT

Voltammetric properties of chlorine dioxide (ClO_2) obtained by using a glassy carbon (GC) electrode fabricated by electrolyzing in ammonium carbamate aqueous solution were first reported. GC electrode surface was covalently modified with nitrogen atoms containing functional groups, which were introduced onto GC surfaces by electrochemical oxidation process in ammonium carbamate aqueous solution. The introduction of nitrogen into the GC surface structure enhanced the electrocatalytic activities of GC electrode towards the electro-oxidation of ClO_2 in an acidic medium more than a bare GC electrode does. A favorable linearity for the peak current signals in cyclic voltammograms was exhibited in the concentration range from 2.0 to 100 ppm.

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Keywords : Nitrogen Atoms Containing Functional Groups, Electrochemical Modification, Chlorine Dioxide, Electrocatalytic Activity

1. Introduction

Glassy carbon (GC) has been widely used as an electrode substrate in various electrochemical fields since it has more sustainable chemical stabilities and wider potential window than those of metal electrodes such as gold and platinum have.^{1–3} GC electrodes consisting of disordered carbon materials that are derived from polymers have been extensively utilized in the field of electrochemistry. The rich surface chemistries of GC electrodes play important roles for achieving good electrocatalysis, which allows GC electrodes to be a potential candidate for electroanalytical applications.^{4–6} In addition, the electrochemical activation of carbon electrode surfaces has attracted growing interest over several decades and their applications include electroanalytical chemistry.^{7,8} The chemical structures of carbon surface are significantly changed during the electrochemical modification reactions and consequently the interactions between materials with analytes are adapted. For example, it has been found that the reduction potential of oxygen can be significantly shifted to the potential of positive direction by using carbon alloy with nitrogen atoms.⁹

Recently, the authors' team has demonstrated that nitrogen atoms containing functional groups can easily be introduced onto GC electrode surface by the electrode oxidation of ammonium carbamate solution at a highly positive electrode potential, and we have named this electrooxidized GC electrode "an aminated GC (Am-GC) electrode".¹⁰ This electrochemical surface modification enables not only the primary amine group but also other nitrogen atoms

containing functional groups to be introduced onto the GC electrode surface.¹¹ The rates for electron transfer of various inorganic and organic compounds are accelerated to allow observation of excellent redox waves with Am-GC electrode.^{12,13} Hence, this electrochemical modification (amination reaction) of GC electrode surface improves the electrode kinetics and enhances electrocatalytic activities towards the redox reactions of some inorganic and organic compounds.^{14–16}

Among the oxychlorine compounds with oxidative activity, chlorine dioxide (ClO_2) is known to be extremely potent. Due to the presence of one unpaired electron in its molecular orbital,¹⁷ ClO_2 is a free radical.¹⁸ ClO_2 is known to have potent antimicrobial ability against bacteria, viruses, and protozoa.^{19–22} ClO_2 has been used as a disinfectant for drinking water since it has strong oxidizing capability against various microbial proteins. Furthermore, Ogata and co-workers have reported that ClO_2 inactivates the influenza virus.²³ In addition, we expect ClO_2 to also inactivate novel coronavirus (SARS-CoV-2)²⁴ as well as the influenza virus.

Backed up by such biological importance of ClO_2 , the detection of ClO_2 in water provides useful information for this purpose. Electrochemical sensing techniques for ClO_2 were required to realize the above-mentioned application in practical fields. However, only few studies have focused on the electrochemical properties and electrochemical sensors of ClO_2 .²⁵ In addition, effects of surface nitrogen containing functional groups on facilitating electro activity of ClO_2 have not been explicitly demonstrated.

In this paper, we report basic electrochemical properties of the Am-GC electrodes, which were studied by measuring cyclic

voltammetry of ClO_2 with different electron-transfer properties. The properties were also compared with results from a bare GC electrode. Moreover, we first demonstrated an electrochemical sensor based on voltammetric method of ClO_2 using Am-GC electrode as a working electrode.

2. Experimental

Ammonium carbamate ($\text{NH}_2\text{COONH}_4$, Merck, Germany), sulfuric acid (H_2SO_4 , FUJIFILM Wako Pure Chemical Corporation, Japan), and all other reagents were of analytical grade and were employed without further purifications. Chlorite ion (ClO_2^-) standard solution (certified standard solution for ion chromatography) was supplied by FUJIFILM Wako Pure Chemical Corporation (Japan). The test stock solution of chlorine dioxide (ClO_2) used was prepared by adding of the ClO_2^- into an acidic medium. Aqueous solutions were prepared with deionized water.

All electrochemical experiments were carried out in a conventional three-electrode cell constitution. An aqueous Ag/AgCl (3 M NaCl electrolyte) electrode and a platinum wire were used as a reference and a counter electrode, respectively.

The Am-GC electrode was prepared by a constant potential electrolysis as follows. A bare GC electrode (BAS Co., Ltd., Japan; diameter of 3 mm) was electro-oxidized in 0.1 M ammonium carbamate aqueous solution at +1.1 V (vs. Ag/AgCl) for 60 minutes at room temperature. This electrochemical modification process is one step with very simple and rapid modification of GC surface.

The electrochemical properties for ClO_2 were carried out with an automation polarization system (HZ-3000, Hokuto Denko Co., Ltd., Japan) by cyclic voltammetry method. Voltammetric measurements of ClO_2 were performed by using the bare GC electrode and the Am-GC electrode prepared by the electrolytic-oxidation process described above.

3. Results and Discussion

We estimated electrochemical properties of the aminated GC (Am-GC) electrode in relation to chlorine dioxide (ClO_2) measurement. We also used a bare GC electrode to measure ClO_2 for a comparison. Figure 1 shows cyclic voltammograms (CVs) of 10 ppm ClO_2 in 0.5 M sulfuric acid with the bare GC electrode and our Am-GC electrode measured under optimized conditions. In both cases, the redox wave between ClO_2 and chlorate ion (ClO_3^-)²⁶ in the cyclic voltammograms was observed by using both electrodes in acidic medium. The electrode reaction of ClO_2 has been expected as Eq. (1).

In particular, the redox wave with the Am-GC electrode (solid line) is much clearer than that with the bare GC electrode (dotted line). Indeed, the peak separation (ΔE_p) of ClO_2 for the Am-GC electrode is 68 mV, which is obviously lower than 123 mV for the bare GC electrode. This result indicates that the electron-transfer kinetics of ClO_2 is significantly different between the Am-GC electrode and the bare GC electrode. Namely, electrochemical reversibility of ClO_2 exhibits that our Am-GC electrode provides results that are comparable with those of the bare GC electrode. This may show that the nitrogen atoms containing functional groups introduced by electrode oxidation in ammonium carbamate aqueous solution function as electron-transfer mediators for ClO_2 in acidic medium. With the Am-GC electrode, capacitance much higher than that of the bare GC electrode might be owing to the effect of nitrogen atoms containing functional groups introduced onto the GC electrode surface and to preparation of highly porous-structured GC electrode surface during the electrochemical surface oxidation process of the bare GC electrode in ammonium carbamate aqueous solution.

The redox wave of ClO_2 was recorded at various sweep rates by CVs (Fig. 2a). The anodic peak current of ClO_2 oxidation linearly increases with the square root of the sweep rate from 5 mV s^{-1} to 50 mV s^{-1} (Fig. 2b), which indicates that electrode oxidation reaction is a diffusion-controlled process of ClO_2 in acidic medium. In addition, the measurement revealed that the electrode oxidation peak potential (E_{pa}) did not shift to a more positive potential direction with an increase in the sweep rate, which clearly indicates that the electrode oxidation reaction of ClO_2 with Am-GC electrode is the reversible electrochemical reaction process.

The effect for electrolyte pH on oxidation peak potentials and oxidation peak currents of ClO_2 with the Am-GC electrode were investigated by measuring cyclic voltammograms (CVs) as shown in Fig. 3a. In the case that the electrolyte pH was lower than 2.5, the shift of oxidation peak potentials of ClO_2 towards more positive values were observed. Favorable linear relationship between the oxidation peak potential and pH value was observed for the slope values of -37.6 mV per pH for ClO_2 (Fig. 3b). These facts suggest

Figure 1. Comparison of CVs obtained by using bare GC electrode and Am-GC electrode recorded in 0.5 M sulfuric acid containing 10 ppm ClO_2 . Sweep rate: 50 mV s^{-1} .

Figure 2. (a) Typical CVs at Am-GC electrode for 10 ppm ClO_2 in 0.5 M sulfuric acid at different sweep rates (A–E): 5, 10, 20, 30 and 50 mV s^{-1} . (b) The corresponding plots of oxidation peak current vs. square root of sweep rate for ClO_2 .

Figure 3. (a) CVs of 10 ppm ClO_2 using Am-GC electrode in different pH electrolyte (A–E): 0.1, 0.6, 1.0, 2.0 and 2.5. (b) The corresponding plots of their peak potentials vs. pH values.

Figure 4. CVs of Am-GC electrode in 0.1 M sulfuric acid containing various concentrations of ClO_2 in the range from 0 to 100 ppm.

Figure 5. Calibration curves of ClO_2 using the voltammetric measurements with the Am-GC electrode.

an electrode reaction of ClO_2 coupled proton transfer electrode process. In addition, peak current values were similar under various electrolyte pH conditions. The pK_a value of HClO_2 (chlorous acid) was ca. 1.9. Over this electrolyte pH range, HClO_2 and ClO_2^- (chlorite ion) were dominant species with the loss of ClO_2 owing to its chemical equilibrium. For these reasons, determination of ClO_2 is suitable for acidic conditions (the electrolyte pH is lower than 2.5) of electrolyte.

Analytical performance of ClO_2 was measured by voltammetric method for the Am-GC electrode in 0.5 M sulfuric acid electrolyte as presented in Fig. 4. The oxidation peak current increased obviously with an increase in ClO_2 concentration and the oxidation peak potential was almost unchanged (ca. +0.85 V). Therefore, an extremely stable electrochemical response of a ClO_2 sensor is expected. The oxidation peak current of ClO_2 was proportional to ClO_2 concentration in the range up to 100 ppm with favorable correlation coefficient as 0.997 (Fig. 5). The lower detection limit was found to be 2.0 ppm. Next, the Am-GC electrode proposed in this study was applied to a useful ClO_2 analysis method since simple and rapid ClO_2 in water concentration measurement was available.

4. Conclusion

We successfully demonstrated electrochemical properties of ClO_2 using the GC electrode fabricated by electrolyzing in ammonium

carbamate aqueous solution. Nitrogen atoms containing functional groups introduced onto GC surfaces by electrode oxidation of carbamic acid function as electron-transfer mediators for ClO_2 in acidic medium. Electrochemical reversibility of ClO_2 exhibited that our Am-GC electrode provides results comparable with those of a bare GC electrode. Therefore, we need to undertake a further examination to realize a quantitatively superior analytical performance. Anyhow, our approach is highly advantageous for rapid determination of ClO_2 than the bare GC electrode. This sensing platform is also expected to be used for detecting trace-level concentrations of ClO_2 in practical fields.

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