The reduction behavior of free chlorine at boron-doped diamond electrodes

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ABSTRACT

The electrochemical reduction behavior of hypochlorite ions (ClO^-) and hypochlorous acid (HClO) at the surface of boron-doped diamond electrodes is presented. The ClO^- reduction behavior is strongly affected by the dissolved oxygen through homogeneous oxygen recovery reaction between ClO^- and H_2O_2 as ORR product. As for HClO reduction, one-electron mechanism which is a peculiar characteristic of boron-doped diamond electrodes, was observed.

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1. Introduction

Free chlorine, which is defined as the concentration of dissolved gas (Cl_2), hypochlorous acid (HClO) and hypochlorite (ClO^-), has been widely utilized as a disinfecting agent in various fields such as in clinical practice, the food industry and drinking water treatment. Therefore, it is necessary to monitor and control the free chlorine concentration for public health maintenance. As one of the methods, electrochemical techniques can be used for real time monitoring of the free chlorine concentration [1]. Indeed, free residual chlorine sensors based on electrochemical reduction with platinum or gold electrodes are commercially available from many companies. However, the conditions under which systems with these sensors can be operated are constrained, since they require skillful operators and frequent calibration to make reliable measurements because the electrochemical reaction of free chlorine is affected by various factors such as pH, surface fouling and dissolved oxygen [2]. Consequently, a more reliable and versatile system is needed for the continuous monitoring of free chlorine.

The high durability and wide potential window in aqueous solutions of boron-doped diamond (BDD) electrodes makes them a promising alternative to those other electrodes [3,4]. Previously, Murata et al. have reported on utilizing the oxidation reaction for the electrochemical detection of free chlorine using BDD electrodes [5]. In that paper, the oxidation of free chlorine to form chlorate could clearly be observed due to the wide potential window of BDD although the reaction easily overlapped the oxygen evolution reaction using the other electrodes.

However, compensation for the pH dependence is also necessary with the BDD electrodes in order to determine the total free chlorine because, as with the other electrodes, it is only ClO^- that can be oxidized [6].

On the other hand, the electrochemical reduction of free chlorine at BDD electrodes has not, so far, been reported.

In this paper, the electrochemical reduction behavior of HClO and ClO^- was investigated. Here, we report on this unusual behavior, which is derived from the electrochemical properties of BDD.

2. Experimental

BDD films were deposited on silicon substrates using a microwave plasma-assisted chemical vapor deposition system. A mixture of acetone and trimethoxyborane with a boron-to-carbon ratio of 10,000 ppm was utilized as the carbon and boron sources. The detailed conditions are described elsewhere [7]. The Raman spectra of these films show no peak around 1500 cm^{-1}, assigned to sp^2-bonded carbon. The grain size, film thickness and resistivity of the BDD films were approximately 5–10 μm, 20 μm and 10^{-2} Ω cm, respectively. Electrochemical measurements were performed using a single compartment PTFE cell in an Autolab PGSTAT204 potentiostat/galvanostat system (Metrohm, The Netherlands). A Pt wire spiral and Ag/AgCl/saturated KCl were used as the counter and reference electrodes, respectively. The electrode area of BDD was 0.915 cm^2. Unless otherwise specifically noted, prior to each electrochemical measurement the BDD electrodes were cleaned by an electrochemical pretreatment comprising 10 cycles of potential cycling between −3.5 V and 3.5 V and then 20 cycles of potential cycling between −3.5 V and 0 V at a scan rate of 1 V/s in 0.1 M sodium perchlorate.

Free chlorine solutions were prepared by dissolving NaClO into electrolyte solutions, and their free chlorine concentrations and pHs

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were measured with a colorimetric free chlorine meter (Aquab AQ-202, Shibata, Japan) and a pH meter (Laqua F-74, Horiba, Japan) prior to every measurement. $HClO_4$ or NaOH was utilized to adjust the pH. All chemicals were purchased from Wako pure chemical industries, Ltd. and used as received. All the solutions were prepared using deionized water from a Direct-Q water purification system (Millipore, MA, USA).

3. Results and discussion

The equilibrium distribution of the free chlorine species, HClO and ClO^-, depends on the pH of the solution, as expressed by the following equation:

$$HClO \rightleftarrows ClO^- + H^+ \quad pKa = 7.53 \tag{1}$$

HClO can be deprotonated to form ClO^- at higher values of pH than that in Eq. (1). This equilibrium distribution of HClO and ClO^- is practically important for free chlorine sensing because the pH of tap water is usually controlled to be neutral over a range (from 5 to 9).

Fig. 1a shows linear sweep voltammograms (LSVs) of 1.4 mM free chlorine in 0.1 M $NaClO_4$ (non-degassed) with different pH from 5 to 9 using a BDD electrode. For the LSVs in the presence of free chlorine, the BDD exhibits two reduction waves at around −0.4 V and −1.3 V. As for the first reduction wave, the peak current decreases with increasing pH and almost disappears at pH 9. Fig. 1b shows the pH dependence of the peak current at the potential at which the peak or minimum |dI/dV| in the first wave occurs. The ratio of HClO to total free chlorine, which can be determined from pKa, is also displayed in Fig. 1b. The reduction current values clearly correspond to the presence of HClO. On the other hand, the second reduction wave seems to be independent of pH. Therefore, ClO^- can also be reduced in the second reduction wave although the potential significantly overlaps with the oxygen reduction reaction (ORR), which is observed in the absence of free chlorine.
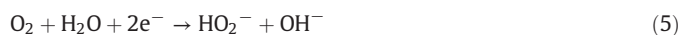
Fig. 2 shows the free chlorine concentration dependences of LSVs obtained in non-degassed 0.1 M $NaClO_4$ around pH 6 (Fig. 2a) and pH 8–9 (Fig. 2b) and therefore, most of the free chlorine is HClO for the former and ClO^- for the latter. In Fig. 2a, the peak current in the first wave increases in proportion to the concentration of HClO. In contrast, a small current in the first wave can be seen in some voltammograms in Fig. 2b due to the low fraction of HClO. On the other hand, the current in the second wave increases, dependent on the concentration of both species. Interestingly, the slope value of peak current-concentration curve of ClO^- is approximately twice the

one of first wave for HClO (Fig. 2c) while it is well known that two electrons are involved in electrochemical reduction of both species [8]. It indicates that two electrons are involved in the second wave for reduction of ClO^-, and one electron is involved in the first wave for HClO reduction. In addition, the second wave for HClO reduction also implies two electron reduction mechanism as well as ClO^- because of higher slope value than first wave.

In order to investigate influence of ORR, LSVs for 1 mM free chlorine were carried out in 0.1 M $NaClO_4$ solutions which are purged by N_2 gas and non-degassed, with approximately pH 5 (Fig. 3a) and approximately pH 9 (Fig. 3b). As for the second reduction wave, it seems to be strongly influenced with the dissolved oxygen concentration for both free chlorine species. Especially, the second reduction wave current for ClO^- in N_2-purged solution clearly showed lower net current compared to one in non-degassed solution. These results imply reduction of free chlorine is mediated by dissolved oxygen and in other words, ORR is amplified via homogeneous chemical reaction with free chlorine as follows.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$HClO + H_2O_2 \rightarrow O_2 + H_2O + H^+ + Cl^- \tag{3}$$

$$ClO^- + H_2O_2 \rightarrow O_2 + H_2O + Cl^- \tag{4}$$

Otherwise,

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \tag{5}$$

$$HClO + HO_2^- \rightarrow O_2 + H_2O + Cl^- \tag{6}$$

$$ClO^- + HO_2^- \rightarrow O_2 + OH^- + Cl^- \tag{7}$$

It has been reported that products of ORR at BDD electrodes are H_2O_2 or HO_2^- [3,4]. It has been also reported that these products of ORR can react with free chlorine to form O_2 and Cl^- [9]. Therefore, free chlorine present in the vicinity of the BDD electrode should increase ORR. As a result, two-electron reduction for a HClO or ClO^- apparently proceeds in the second reduction wave in Fig. 2 due to relatively high concentration of dissolved oxygen.

On the other hand, the first reduction wave for HClO showed almost the same peak current and potential despite the presence of dissolved oxygen. This high insensitivity to ORR is the characteristic of BDD electrode surface free of sp^2 carbon impurities [4,10]. On the other hand,
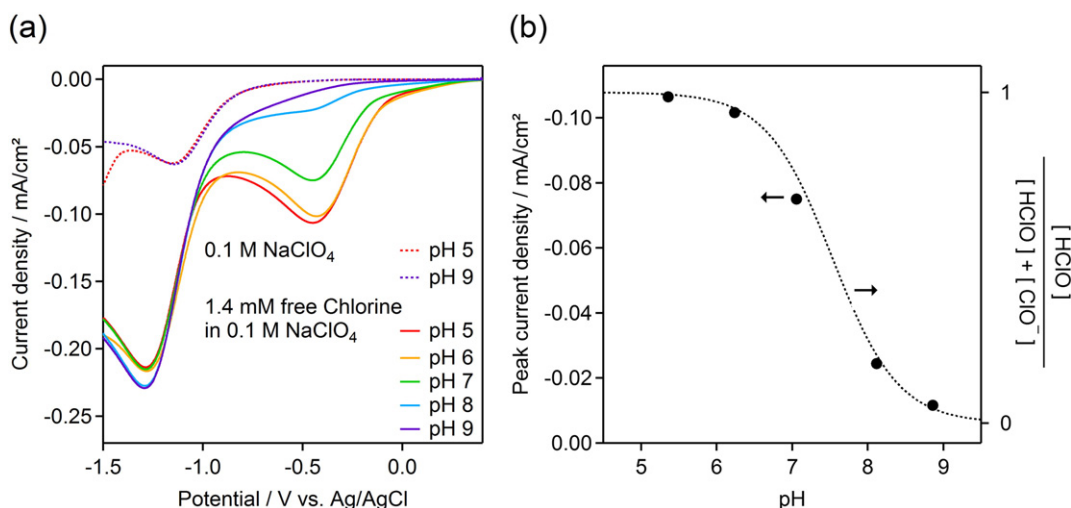

Fig. 1. (a) LSVs for 1.4 mM free chlorine in 0.1 M $NaClO_4$ with different pH and the LSVs in the absence of free chlorine in 0.1 M $NaClO_4$ at a scan rate of 20 mV/s using a BDD electrode. (b) The pH dependence of peak current in the first reduction waves of the LSVs and the ratio of HClO to HClO plus ClO^- in equilibrium.