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A Facile Electrochemical Detection of Hypochlorite Ion based on Ferrocene Compounds

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Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of ferroceneboronic acid (FcBA), 1,1'-ferrocenediboronic acid (FcDBA), ferrocenecarboxylic acid (FcCA), 1,1'-ferrocenedicarboxylic acid (FcDCA), ferrocenylmethanol (FcM), and ferrocenylethanol (FcE) were recorded on a glassy carbon electrode in the presence of hypochlorite (ClO^-) ion. The redox current of the ferrocene compounds in CV and DPV decreased with increasing the concentration of ClO^- ion in μM level. The type of substituent in the ferrocene compounds significantly affected the electrochemical response to ClO^- ion. Voltammetric and UV-visible absorption spectroscopic results suggested that the ferrocene compounds were oxidatively decomposed by ClO^- ion. Thus, the ferrocene compounds can be used as redox marker for detecting ClO^- ion in water.

Keywords: Amperometric measurement, ferrocene compounds, hypochlorite ion.

1. INTRODUCTION

Sodium hypochlorite (NaClO) is a strong oxidizer and used in agriculture, chemical and food industries, etc. [1-4]. NaClO is frequently used as disinfectant in swimming pools, water treatment and as a household bleaching agent in the concentration of typically 0.01-10 mM [5]. Such a high concentration is hazardous to human bodies. It can cause eye or nose irritation, coughing or sore throat, and even stomachache and diarrhea [6]. Therefore, it is necessary to develop a facile, sensitive, and convenient way to detect hypochlorite (ClO^-) ion in water.

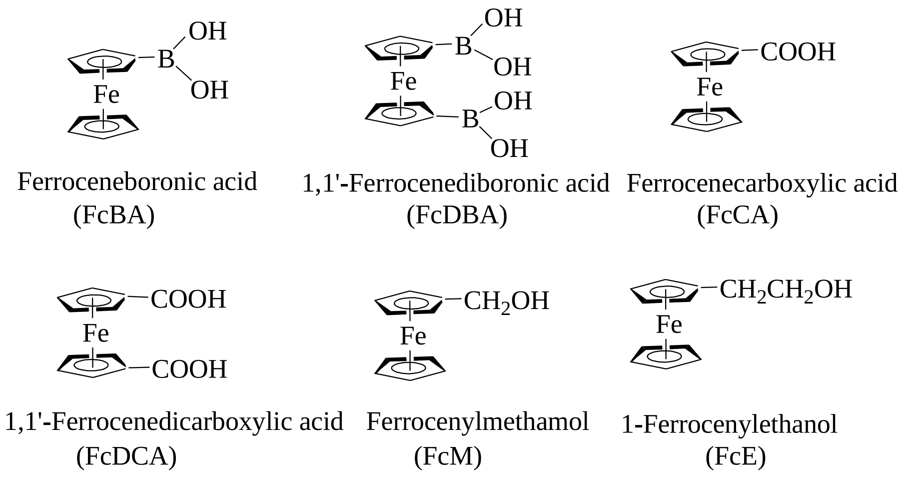
Several methods are currently available for detecting ClO^- ion, including spectrophotometry [7,8], catalyst-assisted flow-injection [9] and electrochemistry [10,11]. Among of them, electrochemical sensors can provide a low cost, quick and easy way to detect ClO^- ion. A variety of electrochemical sensors have been developed so far. For example, Ordeig and coworkers reported a method using platinum electrodes to continuously monitor ClO^- ion in tap water [12]. Endo and coworkers deposited dendrimer-stabilized gold nanoparticles on glassy carbon (GC) electrode to enhance the response of GC electrode in measuring NaClO [13]. Recently, Chen's group employed porphyrin film-modified GC electrodes and indium tin oxide-coated glass electrodes to detect ClO^- ion [14]. They found that the polymer film-coated electrodes showed selective response to ClO^- ion without interference. The linear response range to ClO^- ion was reported to be 0.01-10 mM. On the other hand, there is no threshold value for human beings to NaClO exposure. Even low exposure may be harmful to some sensitive people [6]. Therefore, in this context, we have tried to explore a facile and sensitive electrochemical method to detect ClO^- ion using ferrocene (Fc) compounds. Fc is a redox-active metal complex consisting of an iron(II) atom sandwiched with two cyclopentadienyl ligands. Fc and its derivatives are widely used as electron transfer mediators and redox markers in analytical electrochemistry because of their high stability in redox reactions and facile synthesis of derivatives [15-17]. In the present study, we have used six kinds of Fc compounds as redox active marker to detect ClO^- ion. We assume here that redox behavior of Fc compounds may change in the presence of ClO^- ion because of its strong oxidizing activity.

2. EXPERIMENTAL

2.1. Reagents

Ferroceneboronic acid (FcBA) and 1,1'-ferrocenediboronic acid (FcDBA) were purchased from Aldrich Chemical Co. (USA). Ferrocenecarboxylic acid (FcCA), 1-ferrocenylethanol (FcE), and ferrocenylmethanol (FcM) were obtained from Tokyo Chemical Industry Ltd. (Tokyo, Japan). 1,1'-Ferrocenedicarboxylic acid (FcDCA) was from Wako Pure Chemical Industry Ltd. (Osaka, Japan). Sodium hypochlorite (available chlorine 8.5-13.5%), potassium dihydrogenphosphate, and di-potassium hydrogenphosphate were from Nacalai Tesque, Inc. (Kyoto, Japan). Poly(allylamine hydrochloride) (PAH, Mw~150,000) and carboxymethylcellulose sodium (CMC, Mw~254,000) were from Tokyo Chemical Industry Ltd. (Tokyo, Japan) and Nittobo Co. (Tokyo, Japan), respectively. Fc-modified PAH (Fc-PAH) was prepared according to the reported procedure [18].

The ClO^- solutions were standardized by iodometric titration [19]. All other reagents were of analytical grade and used as received. Aqueous solutions were prepared using ultrapure deionized water (18 MΩ·cm). 0.1 M Phosphate buffer solution (pH 7.0) was used throughout this work. Structures of Fc compounds used are shown in Fig.1.



Ferroceneboronic acid (FcBA)
1,1'-Ferrocenediboronic acid (FcDBA)
Ferrocenecarboxylic acid (FcCA)
1,1'-Ferrocenedicarboxylic acid (FcDCA)
Ferrocenylmethamol (FcM)
1-Ferrocenylethanol (FcE)

Figure 1. Chemical structures of Fc compounds used.

2.2. Measurements

UV-visible absorption spectra were recorded using a Shimazu UV-3100PC spectrophotometer (Kyoto, Japan). Cyclic voltammetry and differential pulse voltammetry were carried out with an electrochemical analyzer (ALS 660B, Japan). A glassy carbon (GC) disk electrode (3 mm diameter) was used as working electrode. The surface of the GC electrode was thoroughly polished using alumina powder before use. For the preparation of layer-by-layer (LbL) film-modified electrode, the surface of polished GC electrode was first modified with *p*-aminobenzenesulfonic acid by electrochemical oxidation [20]. Then, the GC electrode was immersed alternately in 0.5 mg/mL Fc-PAH and CMC solutions (in 0.1 M 1-[4-(2-hydroxyethyl)-1-piperadinyl]ethanesulfonic acid] buffer solution, containing 0.1 M NaCl, pH 7.0) to fabricate $(\text{Fc-PAH/CMC})_5$Fc-PAH multilayer films on the surface of GC electrode, according to the reported procedure [18]. All electrochemical measurements were performed at ca. 20 °C in a glass cell using the GC electrode as working electrode, a platinum wire as a counter electrode, and a Ag/AgCl electrode (3 M NaCl) as a reference electrode.

3. RESULTS AND DISCUSSION

Fig. 2 shows cyclic voltammograms (CVs) of NaClO recorded on GC electrode in an aqueous solution at pH 7.0. The CV exhibited an irreversible cathodic peak around -0.2 V, while no redox peak was observed in the range of 0-0.6 V. The cathodic peak can be ascribed to electrochemical reduction of ClO^- ion (Equation 1)[12]. ClO^- ion has often been determined based on the electrochemical reduction at this potential. However, deaeration is essentially required in the cathodic determination of ClO^- ion owing to partial overlapping of the reduction peak and that of dissolved oxygen in sample solution. In fact, broad reduction peak centered at -0.6 V was observed without deaeration under the same experimental conditions (data not shown). Therefore, facile procedures that can be operated under aerobic conditions are highly required for determining ClO^- ion in water. For this goal, in this work, we have employed Fc compounds as redox marker for detecting ClO^- ion.

$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^- \qquad (1)$$

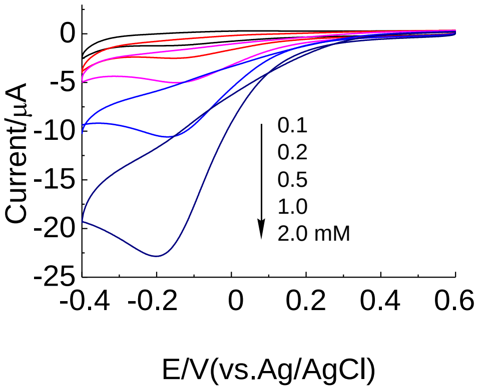


Figure 2. Typical CVs of ClO^- ion on GC electrode in 0.1 M phosphate buffer solution at pH 7.0. Scan rate: 50 mV s^{-1}.

Fig. 3 shows CVs of FcBA and FcDBA in the absence and presence of ClO^- ion. FcBA showed reversible oxidation and reduction peaks at 0.21 and 0.15 V, respectively, in the absence of ClO^- ion (Fig. 3a).

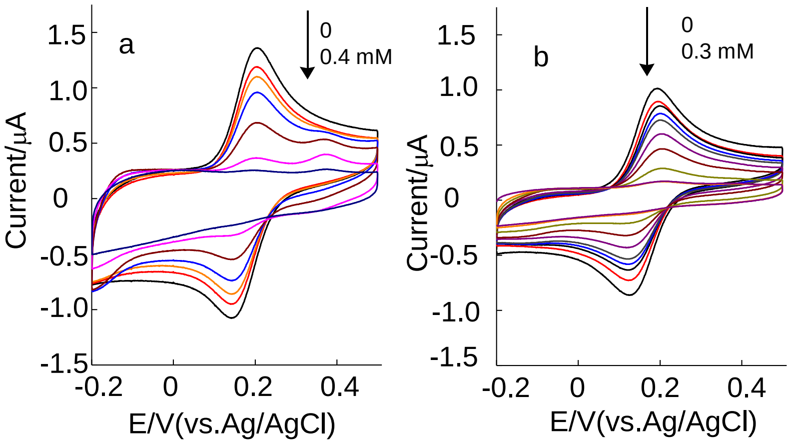


Figure 3. CVs of 0.1 mM FcBA (a) and 0.1 mM FcDBA (b) on GC electrode in the presence of ClO^- ion in 0.1 M phosphate buffer solution (pH 7.0). Scan rate: 50 mV s^{-1}.

In contrast, the magnitude of both the redox peaks decreased with increasing the concentration of ClO^- ion, suggesting that the concentration of electrochemically active FcBA decreased probably due to oxidative decomposition by ClO^- ion. We observed that the color of FcBA solution turned to light yellow, which gradually deepened with increasing concentration of ClO^- ion. Then, the color of the solution changed to light brown and finally faded upon adding higher concentration of ClO^- ion. In addition, smaller redox peaks appeared at -0.18 and 0.35 V in the presence of ClO^- ion. The appearance of the smaller peaks together with fading of FcBA solution strongly suggests that FcBA decomposed into fragments in the presence of ClO^- ion. FcDBA showed a similar response to ClO^- ion in CV (Fig. 3b); the redox peaks decreased upon addition of ClO^- ion depending on the concentration. Similar color changes and fading were also observed for the FcDBA solution in the presence of ClO^- ion, although the color changes were not as clear as FcBA.

Differential pulse voltammograms (DPV) were also recorded for evaluating ClO^- ion-dependent redox reaction of FcBA and FcDBA. Fig. 4a shows that oxidation current of FcBA at ca. 0.15 V decreased with increasing the ClO^- concentration. Smaller peaks were also observed at -0.18 and 0.35 V, in accordance to CV results. The inset in Fig. 4 plots the peak current in the DPV as a function of ClO^- concentration. The peak current inversely depended on the concentration of ClO^- ion in the range of 1-200 μM. A similar DPV behavior was observed for FcDBA in the presence of ClO^- ion (Fig. 4b). These results suggest that DPV of FcBA and FcDBA is useful for facile determination of ClO^- ion in the range of 1-200 μM.

It has been reported that scission of C-B bond in phenylboronic acids occurs to form phenol derivatives in the presence of ClO^- ion [21]. The cleavage of C-B bond in FcBA and FcDBA may be an initial reaction induced by ClO^- ion during the CV measurements, which is followed by decomposition reactions. The smaller peaks observed in CV and DPV are possibly ascribable to the redox reactions of these decomposition products, such as phenolic derivatives.

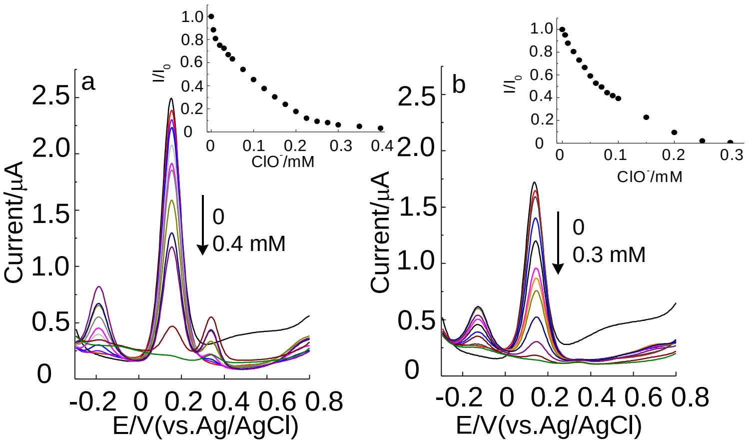


Figure 4. DPVs of 0.1 mM FcBA (a) and 0.1 mM FcDBA (b) on GC electrode in the absence and presence of ClO^- ion in 0.1 M phosphate buffer solution (pH 7.0). Inset: The change in the oxidation peak currents as a function of ClO^- ion concentration. I_0 and I denote the peak current in DPV in the absence and presence of ClO^- ion, respectively.

Fig. 5 shows UV-visible absorption spectra of FcBA and FcDBA in the absence and presence of ClO^- ion. A new absorption peak appeared at about 280 nm in the presence of ClO^- ion for both

FcBA and FcDBA probably due to the formation of hydroxyl-substituted Fc derivatives as a result of oxidative scission of C-B bond in the compounds. A similar spectral change was reported for phenylboronic acids [22].

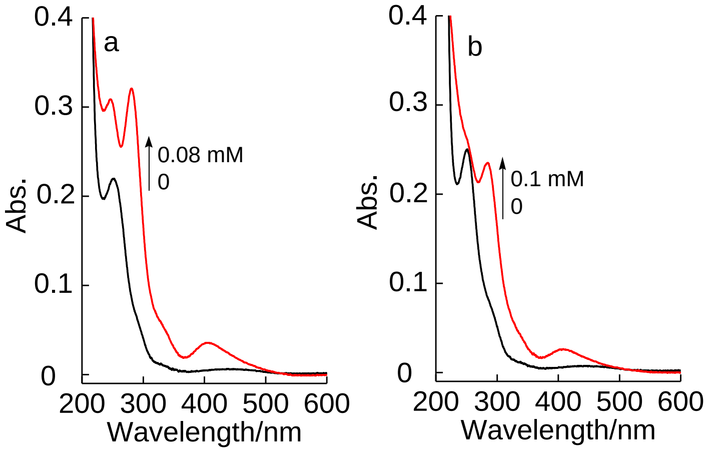


Figure 5. UV-visible absorption spectra of FcBA (a) and FcDBA (b) in the absence and presence of ClO^- ion. Concentration of FcBA and FcDBA: 0.05 mM.

In order to confirm whether Fc compounds decompose in the solutions containing ClO^- ion, we have recorded CV of Fc-modified electrode before and after treatment in 0.1 mM ClO^- ion solution. It is anticipated that redox signals of Fc-modified electrode decrease or disappear if the immobilized Fc moieties decompose.

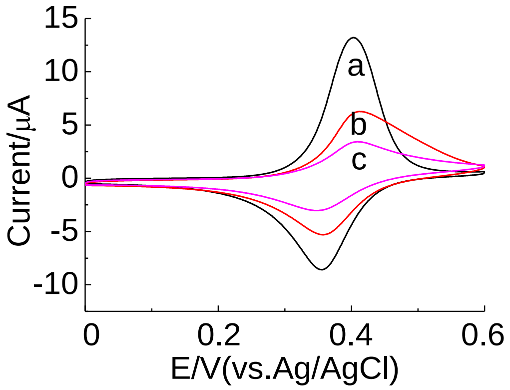


Figure 6. CVs of $(Fc\text{-}PAH/CMC)_5Fc\text{-}PAH$ film-coated GC electrode in 0.1 M phosphate buffer (pH 7.0). a: CV in buffer solution without ClO^- ion, b: CV in 0.1 mM ClO^- ion solution, and c: CV recorded in buffer solution without ClO^- ion after immersed in 0.1 mM ClO^- ion solution.

For this goal, the surface of GC electrode was coated with multilayer films composed of Fc-bearing polymer, Fc-PAH, because Fc-containing multilayer films are known to exhibit stable redox reactions [18,23-25]. Fig. 6 shows CVs of Fc-PAH film-coated electrode in buffer solution with and without ClO$^-$ ion. The LbL film-coated electrode exhibited well-defined quasi-reversible redox couple at 0.36 and 0.40 V, which originates from redox reaction of Fc moieties in the polymer film (Fig. 6a). On the other hand, the intensity of the redox peaks decreased in the CV recorded in ClO$^-$ ion solution (Fig. 6b). Then, we measured CV of the electrode in buffer solution again (Fig. 6c), in which the redox current was lower than that in the original CV. This means that the Fc moieties in the polymer film decomposed in the presence of ClO$^-$ ion and the amount of Fc moieties in the film decreased. These results support our assumption that Fc compounds irreversibly decompose in the presence of ClO$^-$ ion.

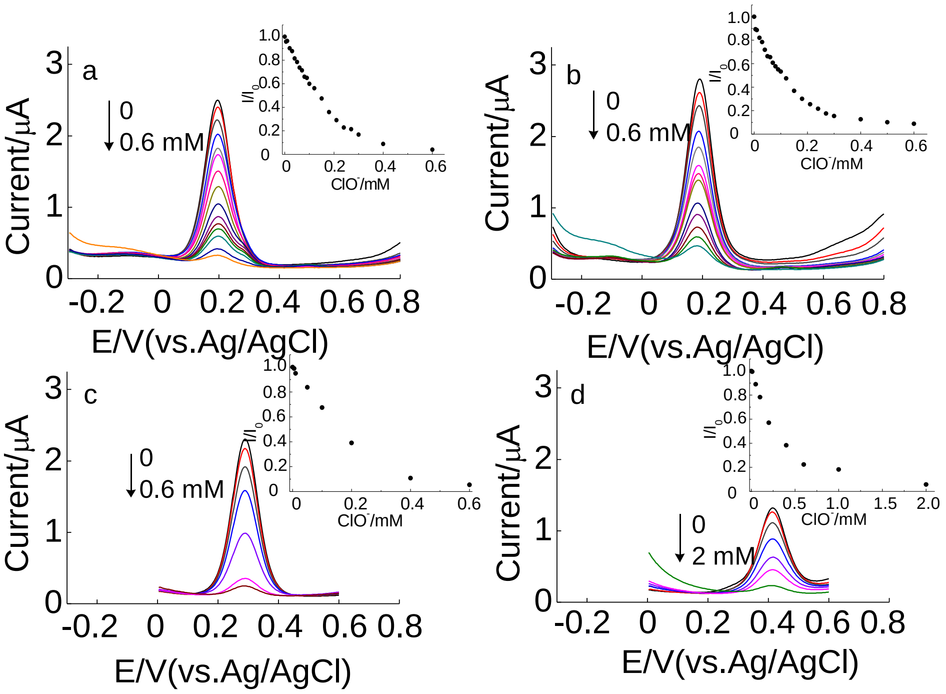


Figure 7. DPVs of FcM (a), FcE (b), FcCA (c), and FcDCA (d) in 0.1 M phosphate buffer (pH 7.0) in the absence and presence of ClO$^-$ ion. Concentration of Fc compounds: 0.1 mM. Inset: The change in the oxidation peak currents as a function of the concentration of ClO$^-$ ion.

We used four kinds of Fc compounds, in addition to FcBA and FcDBA, to evaluate the effects of the type of substituent on the response to ClO$^-$ ion. Fig. 7 shows DPVs of FcM, FcE, FcCA, and FcDCA in 0.1 M phosphate buffer at pH 7.0. All compounds tested exhibited response to ClO$^-$ ion in a similar manner as FcBA and FcDBA; the peak current in DPV decreased in response to ClO$^-$ ion, depending on the concentration. These results clearly show that boronic acid moiety in FcBA and FcDBA is not prerequisites for the response to ClO$^-$ ion. However, the type of substituent in the Fc compounds significantly affected the voltammetric response of the compounds. First, the peak potential in DPV clearly depended on the type of substituent of the compounds. Carboxylic acid-substituted FcCA and FcDCA exhibited higher oxidation potentials at 0.29 and 0.42 V, respectively, than the other compounds probably due to the electron-withdrawing effects of the substituent. Second, smaller oxidation peaks did not observe in DPVs for FcM, FcE, FcCA, and FcDCA, in contrast to those for FcBA and FcDBA, which suggests different pathway in the ClO$^-$ ion-induced decomposition of these Fc compounds from that of FcBA and FcDBA. Third, sensitivity of the compounds to ClO^- ion is different from one another. For example, the oxidation peak current in DPV of FcM, FcE, and FcCA decreased in the range of sub-mM level of ClO^- ion, while the response range of FcDCA slightly shifted in the higher concentration side. The lower limit of linear response to ClO^- ion in DPV of FcM and FcE was approximately 1 μM, which is almost comparable to those for FcBA and FcDBA. On the other hand, while the lower limit of linear response of FcCA and FcDCA were around 5 and 50 μM, respectively. In addition, FcM and FcE can be used in DPV for qualitative detection of sub-μM level of ClO^- ion, although the response is weak and less reproducible. Thus, the type of substituent has significant effects on the reactivity of the Fc compounds toward ClO^- ion.

It has been reported that platinum electrode and porphyrin-modified gold electrode exhibited amperometric response to ClO^- ion in the concentration range of 2-80 μM and 0.024-10 mM, respectively [12,14]. Therefore, the response range of our system is nearly comparable to the reported procedures.

4. CONCLUSIONS

In the present study, we offered a facile procedure to determine ClO^- ion in aqueous solution based on an electrochemical method using Fc compounds. The peak current of Fc compounds in DPV decreased in the presence of ClO^- ion in sub-mM level. Among Fc compounds tested, boronic acid-substituted compounds, FcBA and FcDBA, are more sensitive to ClO^- ion than carboxylic acid- or alkylated Fc derivatives owing to high reactivity of the C-B bond in FcBA and FcDBA to ClO^- ion. Thus, Fc compounds, especially boronic acid-substituted FcBA and FcDBA, are useful for a facile electrochemical detection of sub-mM level of ClO^- ion in water.

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