



Ferrocene-enhanced polyvinyl chloride-coated electrode for the potentiometric detection of total residual chlorine in simulated ballast water



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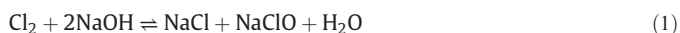
ABSTRACT

In-situ electrolytic generation of chlorine is commercially adopted as an economic and effective method for treating ballast water (BW). An in-situ and rapid method for detecting total residual chlorine (TRC) is necessary for automatic control on the electrolysis. A polymer-coated electrode fabricated by coating a glassy carbon (GC) electrode with a polyvinyl chloride (PVC) coating that contains zephiran chloride (ZephCl) was prepared in this study. This all-solid ion-selective sensor was used to detect TRC in the simulated electrolytically treated BW. Results showed that adding ferrocene (Fc) in the PVC coating could significantly improve the response speed, reproducibility and stability of the electrode. The potential of the Fc-PVC-ZephCl-GC electrode was linearly proportional to the logarithm of TRC within the range of 1 mg/L to 20 mg/L. The interference of the dissolved oxygen and the possible co-existing ions in seawater was also evaluated without evident interference found. The response mechanism of the electrode, the enhancement of Fc and the failure mechanism of the electrode were discussed. The Fc-PVC-ZephCl-GC electrode could be used as a suitable sensor for the in-situ monitoring of TRC in the electrolytic treatment of BW.

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1. Introduction

Considerable attention has been focused on ballast water (BW) treatment to reduce the ecological risks possibly initiated by discharging BW that contains invasive marine species into new environments [1–4]. Among the developed methods, electrolytic treatment by in-situ generation of chlorine [4–7] is adopted as one of the most economic and effective technologies. During electrolysis, chlorine formed on anode reacts with base generated on cathode:



Part of NaClO undergoes hydrolysis:



Therefore, Cl₂, NaClO, and HClO are all effective for sterilization in the electrolytically treated BW. The total concentration of these effective species is summed up as the total residual chlorine (TRC). Based on the equilibria shown in Eqs. (1) and (2), once the concentration of one species, such as ClO[−], is determined, the concentration of other species can also be found. This condition indicates that identifying the relationship between the concentration of ClO[−] and TRC is possible. Results show that an optimal concentration of TRC exists

in the electrolytically treated BW for sufficient sterilization [5]. When TRC is less than 5 mg/L, the efficiency of sterilization is insufficient [8]. When TRC is higher than 15 mg/L, the strong oxidation of TRC may harm the marine species that live in the discharging area, damage the ship painting, and cause serious corrosion of the ship steel beneath the painting [9–11]. Therefore, TRC should be maintained within the optimal range of 8 mg/L to 12 mg/L. A timely feedback based on an in-situ sensing of TRC is required to maintain this range. That is, once TRC in BW becomes less than 8 mg/L, the sensor can provide an electric signal to a control unit to trigger the electrolysis equipment to produce extra chlorine. When TRC in BW becomes higher than 12 mg/L, the sensor can automatically send an electrical message to the control unit to turn off the electrolysis current.

To date, many methods have been developed to detect TRC, including colorimetric methods based on N, N-diethyl-p-phenylenediamine [5,12] or o-toluidine [13], iodometric titration [14], optical methods [15], and electrochemical methods based on amperometric measurement [16–21]. Although these methods are applied in analyzing tap water, swimming pool water and wastewater, they are all ex-situ methods with their measuring procedures usually being rather complicated and time-consuming. However, these methods cannot directly provide electric responses and fulfill the demand of automatic feedback that triggers the electrolysis equipment as expected. Given these reasons, the potentiometric method based on ion-selective electrodes (ISEs) has attracted the interest of many researchers. This method is a

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more suitable method to monitor TRC in the electrolytic treatment of BW for its easy preparation and operation, low-cost measurement, and short response time.

Numerous ISEs such as acetylcholine sensitive enzyme [22], Pb(II)-ISE [23], Fe(III)/Fe(II) redox buffer [24], and potassium iodide redox electrodes [25,26], have been fabricated to detect TRC. However, these electrodes can only provide indirect potential response to TRC after several complicated sample preparation procedures. Adding a special redox buffer and adjusting the pH of the solution make these methods unsuitable for detecting the TRC in BW of massive volume. Motomizu et al. [27] first reported the use of coated wire electrode (CWE) in analyzing free chlorine. But the stability and reversibility of the electrode rapidly deteriorate due to the blocked effect of the PVC coating layer and the formation of water layer between the electronic and ionic conductors after a long immersion. Thereafter, some ion-to-electron transducer intermediate layer is introduced in the polymer coating of the CWE electrode to enhance performance. Conducting polymer [28–31], carbonaceous materials [32–34], and redox-active self-assembled monolayer [35] have been tested to improve both the stability and reversibility of the electrode. The results indicate that these all-solid state ISEs are more suitable for in-situ sensing.

Polyvinyl chloride (PVC)-coated glassy carbon (GC) electrode with zephiran chloride (ZephCl, also named benzyldimethyltetradecylammonium chloride) dissolved in the PVC matrix was tested in this study for in-situ detection of TRC. This electrode failed to provide satisfactory results. Ferrocene (Fc) was then introduced as the phase transfer catalyst and ion-to-electron transducer into the PVC coating. Fc was considered because of its high redox activity, good electrochemical reversibility and stable redox potential [36,37]. This study showed that with Fc serving as the phase transfer catalyst and ion-to-electron transducer the performance of the PVC-coated GC electrode significantly improved. The response of the Fc-enhanced electrode to the change in TRC was rapid, and the TRC of the simulated BW could be monitored for nearly one week using one electrode.

2. Experimental

2.1. Reagents and materials

Based on Eqs. (1) and (2), the effective species in electrolytically treated BW are formed by the reaction of Cl_2 with NaOH. To our knowledge, the commercial sodium hypochlorite is prepared by purging Cl_2 into the NaOH solution, following the same procedure. The effective components of the electrolytically treated BW are similar to those of the sodium hypochlorite solution with differences in NaCl and TRC concentrations. Hence, the electrolytically treated BW can be simulated by diluting the sodium hypochlorite solution with higher TRC with 3.5 wt.% NaCl solution. A series of solutions containing different TRCs was prepared by dissolving the sodium hypochlorite (Sinopharm chemical Co. Ltd., China) solution in 3.5 wt.% aqueous NaCl solution. Owing to the inaccurate concentration of the commercial sodium hypochlorite, iodometric titration was used to calibrate the concentration of hypochlorite in these solutions.

ZephCl was purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). PVC powder, Fc, tetrahydrofuran (THF), Na_2SO_4 , NaF, MgCl_2 , Na_3PO_4 , Na_2CO_3 , NaHCO_3 , NaNO_2 , NaBr, KI, KCl, CaCl_2 , and NH_4Cl are all analytical reagents. All solutions were prepared with ultrapure water (Millipore, $18.25 \text{ M}\Omega \cdot \text{cm}$).

2.2. Electrode preparation

The solution for coating casting of the PVC–ZephCl–GC electrode was prepared by dissolving 71 wt.% PVC and 29 wt.% ZephCl in 10 mL of THF with an ultrasonic cleaner for 15 min. The solution for the

Fc–PVC–ZephCl–GC electrode was prepared by dissolving 52 wt.% PVC, 32 wt.% ZephCl, and 16 wt.% Fc in 10 mL of THF.

Prior to casting, a GC electrode (4 mm in diameter) was carefully polished and rinsed with ethanol and ultrapure water using an ultrasonic cleaner for 1 min and then dried using a N_2 flux. The PVC coating was casted using a dipping method. After drying in air overnight, the PVC–ZephCl–GC and Fc–PVC–ZephCl–GC electrodes were obtained. Before each measurement, the electrode was activated by immersing in 3.5 wt.% NaCl solution for 30 min. The composition of 3.5 wt.% NaCl is close to that of the simulated electrochemically treated BW. After conditioning in this solution, the electrode will not be sensitive to Na^+ and Cl^- , which are abundant in seawater. This condition can stabilize electrode potential and shorten response time. After each experiment, the electrode was rinsed with deionized water and stored in 3.5 wt.% NaCl solution.

2.3. Potentiometric measurements

The electrochemical performance of the PVC–ZephCl–GC electrode with or without Fc addition was characterized using a two-electrode cell with the PVC–ZephCl–GC electrode or Fc–PVC–ZephCl–GC electrode serving as the working electrode and a saturated Ag/AgCl electrode (REX 217-01) with the KCl inner solution and a 3.5 wt.% NaCl solution salt bridge serving as the reference electrode. For electrochemical impedance spectroscopy measurement, a three-electrode cell with a Pt foil of 1 cm^2 serving as the counter electrode was used. All the potentials reported in this work were referred to this Ag/AgCl reference electrode. The electrolyte solutions are 3.5 wt.% NaCl solution containing different TRCs. The concerned species were dissolved in the 3.5 wt.% NaCl solution with their highest concentration set close to that of seawater to investigate the interference of the dissolved oxygen and the possible co-existing ions in seawater.

The potential response of the electrode to TRC was recorded by measuring the open circuit potential (OCP) using the two-electrode cell on a CHI 604C electrochemical workstation (CH Instrument, Shanghai, China). All measurements were conducted at room temperature ($25 \pm 0.2 \text{ }^\circ\text{C}$). Electrochemical impedance spectroscopy of the electrode was recorded using the three-electrode cell at OCP. The measuring frequency range is 0.01 Hz to 10^5 Hz with the excitation signal of 50 mV. The impedance was analyzed by fitting the spectrum using the ZsimpWin impedance analysis software.

3. Results and discussion

3.1. Response behavior

The potential responses of the PVC–ZephCl–GC electrode and Fc–PVC–ZephCl–GC electrode to the TRC change are shown in Fig. 1. The electrode potential for the PVC–ZephCl–GC electrode could not attain a stable value, and no reliable result can be obtained. By contrast, the potential of the Fc–PVC–ZephCl–GC electrode could attain a stable value in less than 50 s. This result indicates that the adding Fc could significantly improve the response behavior of the electrode.

Fig. 1 shows that the electrode potential of the Fc–PVC–ZephCl–GC electrode is linearly proportional to the logarithm of TRC ($\log c$), obeying Nernst equation. However, the slope of the linear part is 67.6 mV/decade, which deviates from the typical Nernstian slope of 59.16 mV/decade. The stability of the Fc–PVC–ZephCl–GC electrode was evaluated by performing the measurement using the same Fc–PVC–ZephCl–GC electrode in four days. After each measurement, the electrode was rinsed with deionized water and stored in 3.5 wt.% NaCl solution. The deviation of the electrode potential during four days was not evident, thereby demonstrating good electrode stability. The small potential deviation can be ascribed to the relatively low sodium hypochlorite concentration and the small memory effect of the electrode (*vide infra*).

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