Introduction

In recent years, how to monitor water quality in real time has drawn much attention from both regulatory agencies and researchers. One popular method is to use a sensor network in the setting of Internet of Things (IoT) to detect water quality factors and share the data using the internet. There are six groups of contaminants in water: microorganisms, disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals and radionuclides. Chlorine is commonly used for disinfection due to its strong oxidizing property. It is widely applied for drinking water, swimming pools, waste water, as well as bleaching and other manufacturing processes. Free chlorine is defined as the sum of hypochlorous acid (HClO), hypochlorite ion (ClO–) and dissolved chlorine gas in the water, since they all maintain a strong oxidizing property. The concentration of free chlorine in water is a commonly used index factor for the disinfectant level in drinking and swimming pool water. If the level is too low, the disinfection function will be insufficient. If it is too high, the risk of cancer due to long-time exposure will be largely increased. The United States Environmental Protection Agency (US EPA) recommends a minimum free chlorine concentration of 1 ppm and a maximum level of 4 ppm to maintain both safety and proper disinfection functions. The World Health Organization (WHO) “Drinking-water Quality Instructions” set an upper limit for chlorine at 5 ppm. Therefore, a precise detection method for the free chlorine concentration is required.

Until now, several different methods have been developed for precisely detecting free chlorine in tap water. Among them, the colorimetric method is the most commonly used. However, apart from its accuracy, the color reagent is not always safe, and the procedure of this method is not suitable for continuous monitoring. There are some other analytical methods, such as iodometric titration, optical methods or electrochemical techniques. Among them, electrochemical techniques are versatile and can provide several advantages, such as low-cost, low power consumption, fast and reproducible data acquisition and a small form factor. However, most of the current electrochemical methods use electrodes with a gas permeable membrane that requires an internal solution, and therefore contains a complicated sensor structure and requires periodically maintenance, such as a re-fill standard solution and a replace membrane. As a result, they are incompatible with miniaturized and low-power devices required for IoT applications.

In 1992, a new electrical detection method was first reported by Motomizu et al. Through potentiometric measurements with an ion-sensitive layer coated electrode (ISE), an in situ linear response of the electrode potential to the free chlorine concentration with a 0.5-ppm resolution was achieved. However, the stability and reversibility of the electrode deteriorates rapidly due to a blocking effect of the polyvinyl chloride (PVC) coating layer and the formation of a water layer between the electrode and the coating layer. Consequently, many ISEs, such as Pb(II)-ISEs, potassium iodide redox electrodes, Fe(III)/Fe(II) redox ISE and acetylcholine sensitive enzyme ISE, have been reported for free chlorine detection.
detection. These methods cost less, and the response is quicker. The preparation and operation processes are simpler. However, it is difficult for conventional ISEs to maintain accuracy with their size being miniaturized. Therefore, a new type of ISE that is both small and accurate is required for low-power IoT devices. Here, we introduce interdigitated array (IDA) electrodes for chlorine detection. IDA electrodes are known for their high sensitivity, small form factor, and rapid response. They are much cheaper compared to traditional electrodes, since they can be manufactured in large scale using semiconductor fabrication processes. IDA has already demonstrated its advantages in fields including the environmental monitoring, aerospace industries and automotive, chemical and biochemical processing. Here, we bring up the idea of combining IDA electrodes with the conventional ion selective layer (ISL) preparation process. In this study, the ISL consists of polystyrene (PS) and zephiran chloride (ZePhCl). Polyethylene ferrocene (PVFc) was then introduced into the PS membrane. The device sensitivity, selectivity and stability were tested and the mechanism for free chlorine potentiometric measurement was discussed. Results indicated that IDA electrodes with an ISE membrane can reach a potential increase of nearly 600 mV with the ClO$^-$ concentration increasing from 0 to 10 ppm. With coupling agents and plasticizer employed into the membrane, the ClO$^-$ detection achieved high sensitivity and good linearity.

**Experimental**

**Electrode preparation**

The IDA device used is shown in Fig. 1. It consists of 302 interdigitated aluminum fingers that sit on a silicon dioxide substrate; each electrode is 2.69 μm in width and 265.5 μm in length and the IDA part is connected to the outside test circuit through wire bonding.

To prevent corrosion of the aluminum IDA electrode by the solution, 100 nm HfO$_2$ is coated on top of the device through atomic layer deposition (ALD) at 250°C.

The electrode coating material is a PS-ZephCl-PVFc mixture. PS, ZephCl and PVFc are dissolved in 10 mL of tetrahydrofuran (THF) with a ratio of 2:1:1. To study the coating material property, a coating material without PVFc was prepared too.

The coating membrane was casted by dripping the coating material onto the device surface in a nitrogen glove box and followed by drying under a nitrogen atmosphere for 2 h.

**Potentiometric measurements**

PS powder, PVFc, THF, Na$_2$SO$_4$, Na$_2$CO$_3$, and ZephCl are all analytical reagents purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). All solutions were prepared with deionized water (Millipore, 18.25 MΩ·cm). A series of solutions with a free chlorine concentration from 0 – 10 mg L$^{-1}$ (ppm) was prepared by dissolving the commercial sodium hypochlorite solution in the deionized water (DI water); iodometric titration was used to determine the actual hypochlorite concentration before each test, considering that sodium hypochlorite can easily decompose.

Before each measurement, the electrode was rinsed with DI water for 30 min. All measurements were conducted at room temperature. The open-circuit potential ($V_{oc}$) was recorded using an electrochemical workstation to measure the potential response of the coated IDA electrodes with varied free chlorine concentrations. A 25-mV bias voltage was applied with the open circuit potential test mode.

**Results and Discussion**

**Potential response behavior**

As shown in Fig. 2, the potential response (without calculating the initial bias voltage) increases monotonically as the free chlorine concentration increases. The inset graph in Fig. 2 shows the raw data of the potential response with time during each measurement.

The positive correlation between the electrode potential of a PVC-ZephCl-Fc membrane coated glassy carbon electrode and the ClO$^-$ concentration was previously reported by Dai et al.\textsuperscript{20} In that study, the electrode potential was linearly proportional to the logarithm of the ClO$^-$ concentration, which followed the Nernst equation. Our result shows a total potential increase of nearly 600 mV with the ClO$^-$ concentration increasing from 0 to 10 ppm, showing a much higher sensitivity.
Theoretical analysis of response mechanism

We suspect that the PS in the coating layer is mainly used to form the membrane structure. The ZephCl can provide ion-exchange sites (both Zeph+ and Cl-). The Cl- in the membrane is free, and it can thus exchange with the ClO4- in the solution. In the meanwhile, the Zeph+, which is fixed in the membrane provides a stronger attraction to ClO4- compared to Cl- due to the larger size of ClO4-. Consequently, the ion-exchange reaction between the Cl- in membrane and the ClO4- in solution induces a diffusion of ClO4- towards the coating layer. The ferrocene in PVFc can be oxidized by ClO4- and form Fc+, which can further facilitate ClO4- diffusion into the membrane in order to maintain charge neutralization and accelerate the diffusion process. The ion exchange between the solution and the membrane can be expressed as:

\[ \text{ClO}_4^{-\text{sln}} + \text{Cl}^{-\text{m}} \rightleftharpoons \text{ClO}_4^{-\text{m}} + \text{Cl}^{-\text{sln}}. \]  

(1)

\[ \text{ClO}_4^{-} + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{OH}^{-}. \]  

(2)

\[ K_1 = \frac{[\text{ClO}_4^{-\text{m}}][\text{Cl}^{-\text{m}}]}{[\text{ClO}_4^{-\text{sln}}][\text{Cl}^{-\text{sln}}]}, \]  

(3)

\[ 2\text{Fc} + \text{ClO}_4^{-\text{m}} + \text{H}_2\text{O} \rightleftharpoons 2\text{Fc}^{+} + \text{Cl}^{-\text{m}} + 2\text{OH}^{-}. \]  

(4)

\[ K_2 = \frac{[\text{ClO}_4^{-\text{m}}][\text{Fc}^{+}][\text{OH}^{-}]}{[\text{ClO}_4^{-\text{sln}}][\text{Fc}^{+}][\text{OH}^{-}]}, \]  

(5)

\[ \frac{[\text{Fc}^{+}]}{[\text{Fc}^{+}]} = \frac{1}{K_1K_2} = \frac{[\text{ClO}_4^{-\text{m}}]}{[\text{ClO}_4^{-\text{sln}}][\text{OH}^{-}][\text{OH}^{-}]}. \]  

(6)

\[ [\text{Fc}^{+}] = \frac{K_1K_2}{1 + K_1K_2[\text{ClO}_4^{-\text{sln}}][\text{OH}^{-}][\text{OH}^{-}]}. \]  

(7)

\[ K = \frac{K_1K_2}{[\text{ClO}_4^{-\text{sln}}][\text{OH}^{-}][\text{OH}^{-}]}. \]  

(8)

Here, the subscripts sln and m represent the ions in solution and the membrane. The equilibrium between the ClO4- and the Cl- in the tested solutions can be established as Eq. (2). Also, the equilibrium constant, \( K_1 \), can be described as Eq. (3), the Fc in PVFc can be oxidized by ClO4- and the reaction is given by Eq. (4). Then, the corresponding equilibrium constant, \( K_2 \), is expressed as Eq. (5). Combining Eqs. (3) and (5), we have Eq. (6) and \( a \) is the total Fc concentration in the coating layer. Finally, the oxidized Fc concentration can be described as Eq. (7). In this case the final reaction equilibrium constant, \( K \), can be expressed as Eq. (8).

Based on the previous description and analysis, IDA is coated with 100 nm HfO2, which can be treated as a capacitor around the electrodes. The initial bias voltage causes a nonuniform distribution of the ClO4- at positive and negative charged electrodes, which results in different concentrations of Fc+. The potential change that we measure is the voltage change across the positive and negative electrodes (Fig. S1, Supporting Information). The change of the ClO4- concentration in the solution will induce a concentration change of Fc+ near the electrode surface. With the continuously accumulated Fc+ in the membrane, the capacitor will be charged, and an electrode potential shift occurs. Eventually, the electrode potential shows positive, correlated with the ClO4- concentration in the solution through Fc+.

Since all of the capacitors are connected in series, there will be the same surface charge change on each capacitor (Fig. S1). Due to small \( C_{\text{sur}} \), \( C_{\text{total}} \) is much smaller than \( C_{\text{dz}} \), and then for the same amount of surface charge, \( \Delta V_{\text{total}} \) would be much larger than \( \Delta V_{\text{dz}} \), exceeding the Nernst limit. This effect is similar in nature to recently observed steric effects of a smaller surface capacitance causing a signal beyond the Nernst limits.23 The potential change across the double layer may follow the Nernst equation if the reaction is a single step. However, in our sensor structure, because of the existence of the phase transfer catalyst, ZephCl, there is one extra step of ion transfer. The quaternary ammonium cation in the Zeph+ is hydrophilic, and the benzene is hydrophobic. Therefore, it can help transfer the ClO4- ion through the water-organic interface. With the change of the Fc+ concentration in the coating layer, the equilibrium constant of Eq. (1) will also change. In this case, the two-step process can not be simply described by the Nernst equation, and therefore the measured potential is not linearly proportional to the logarithm of the ClO4- concentration.

Meanwhile, coating membranes without ZephCl or PVFc were prepared to verify the function of ZephCl and PVFc. The same potentiometric tests were performed, but no monotonic or effective potential shift was observed with a varied NaClO concentration (Fig. S2, Supporting Information). This indicates that the diffusion and reduction of ClO4- cannot happen without PVFc or ZephCl in the coating material.

Scanning electron microscope images of ISE membranes with and without ZephCl show that there are microscopic pores in the membrane containing ZephCl, and almost no pore in the membrane without ZephCl (Fig. S3, Supporting Information). We believe that these pores increase the inner surface area of the membrane, which facilitates ion exchange between the solution and the coating membrane.

Pool water possibly contains anions, such as Cl-, SO42- and CO32-, and common cations, such as Na+, K+. Therefore, the interference from these ions should be evaluated. As shown in Fig. 3, the non-monotonic potential change is smaller than 50 mV for an interfering ion concentration changing from 1 to 10 ppm, which is much smaller compared to that of the ClO4-. Thus, the interference of these ions can be considered to be relatively small.

Stability of the electrode and improvement of coating material

To evaluate the stability of the device, the same test was repeated each day after the first test. After each test, the samples were soaked in DI water for 30 min, and then dried to store. As shown in Fig. 4, the sensing curve shifts each day and the sensitivity (mV ppm⁻¹) at low concentrations of the electrode also decays. This indicates that the performance of the electrode starts to deteriorate. From the literature, this phenomenon is likely caused by water diffusing into the coating layer and shedding the coating layer from electrode. It is most likely due to the polar nature of PS and the hydrophilic nature of ZephCl.24

After immersing the device in the test solution for about 10 days, the coating membrane showed that cracks formed on the surface. Therefore, it is critical to improve the film-electrode adhesion and the coating material quality. To prevent deterioration, a plasticizer was added into the coating layer. The morphology of the coating membranes with different amounts of plasticizer after immersing in the test solution for 10 days shows that a higher plasticizer concentration seems to yield more stable films (Fig. S4, Supporting Information).

Moreover, coupling agents are widely employed as the surface modifier to link polymers, bio-macromolecules, and other species to the surface of materials. Here, 3-aminopropyltriethoxysilane (APTES)25 is used to form a molecular layer on the IDA surface to modify the interface between the electrode...
and the coating material and to improve the film-electrode adhesion. The electrode surface is first cleaned with anhydrous ethanol, and then a molecular layer is formed by immersing electrode surface in the APTES solution in a glove box with a humidity of 25% for 30 min. For the new devices, 0.5% plasticizer A608-2 (King Technology Co., Ltd., Shenzhen, China) is added to the ISE membrane to improve the quality of the coating material.

The potential response of the modified electrode is shown in Fig. 5(A). The electrode potential is positively correlated with the ClO⁻ concentration in the solution. Moreover, a better linearity with an R-Square of a linear fitting curve of about 0.99 is observed. This result shows that the total potential variation is about 200 mV, and an average sensitivity of about 20 mV ppm⁻¹ occurs. Figure 5(B) is the stability test results. In the first 3 days, the characteristic and sensitivity are almost the same. Compared to the results without the coupling agents and the plasticizer (Figs. 2 and 4), although the sensitivity is smaller, the device stability and linearity are much improved. The potential response of the modified electrode is shown in Fig. 5(A). The electrode potential is positively correlated with the ClO⁻ concentration in the solution. Moreover, a better linearity with an R-Square of a linear fitting curve of about 0.99 is observed. This result shows that the total potential variation is about 200 mV, and an average sensitivity of about 20 mV ppm⁻¹ occurs. Figure 5(B) is the stability test results. In the first 3 days, the characteristic and sensitivity are almost the same. Compared to the results without the coupling agents and the plasticizer (Figs. 2 and 4), although the sensitivity is smaller, the device stability and linearity are much improved. The potential response of the modified electrode is shown in Fig. 5(A). The electrode potential is positively correlated with the ClO⁻ concentration in the solution. Moreover, a better linearity with an R-Square of a linear fitting curve of about 0.99 is observed. This result shows that the total potential variation is about 200 mV, and an average sensitivity of about 20 mV ppm⁻¹ occurs. Figure 5(B) is the stability test results. In the first 3 days, the characteristic and sensitivity are almost the same. Compared to the results without the coupling agents and the plasticizer (Figs. 2 and 4), although the sensitivity is smaller, the device stability and linearity are much improved.

It is noted that the sensitivity of this modified electrode seems to be lower than a non-modified electrode compared to Fig. 2. One explanation could be that, since IDA can be treated as a capacitor around the electrodes based on the previous description, an APTES molecular layer on the IDA surface reduces the capacitance of the modified electrode. Also, the plasticizer content cut the effective component of the ISL membrane. Furthermore, it is highly possible that the plasticizer added into the coating layer improves the membrane stability and makes the membrane more compact, which just restrains the ion exchange between the solution and the coating material. Although the NH₃⁺ groups of the APTES molecules can attract not only ClO⁻, but also Cl⁻, which is abundant in tap water. However, Cl⁻ itself, will not react with Fc and therefore would not interfere with the detection selectivity, as we observed.

A possible reason for this linear curve is the influence of the coupling agent APTES. Without the APTES coating, the HfO₂ coated electrode surface would be electrically neutral. According to the site binding model, the oxide surface can de-protonate in the basic pH range and acquire negative charges. In the basic environment, the HfO₂ surface is negatively charged based on...
the pK of the HfO2 surface. Therefore, at low ClO− concentrations, the HfO2 surface will not be able to facilitate ClO− diffusion into the coating material. This also helps to explain the low sensitivity below 2 ppm, as shown in Fig. 2. It is known that the thermal oxide surface can be functionalized by self-assembly monolayers (SAM), such as APTES, which carries the amine (NH2) group in the molecular structure. The dissociation constant of APTES is reported to be 10 from previous literature,28 which means that the amine group can protonate to NH+ in the basic condition. Therefore, even though the HfO2 surface remains electrically negative in the basic condition, the APTES on the surface can still facilitate ClO− ions diffusing into the coating material to compensate the initial low concentrations of [Fc−]. In this case, the potential response as well as the slope of the sensitivity curve in basic condition is enhanced. Then, with the increase of the ClO− concentration, higher pH values cause further negative charges on the HfO2 surface and electrically neutral of APTES, restraining the diffusion of ClO− into the coating material and decreasing the sensitivity curve slope. Consequently, a linear potential response in the whole detection range is observed.

Conclusions

In this work, sensitive and selective sensors based on micro-IDA electrodes have been developed for the detection of residue chlorine (ClO−). The ISL material of PS-ZephCl-PVFc-IDA is coated on the sensor devices, showing a monotonic potential response with varied TRC concentrations from 0 to 10 ppm. A large potential response of about 600 mV occurs for 10 ppm or 60 mV ppm−1, demonstrating a much higher sensitivity compared to the traditional sensing methods. The potential response mechanism is also explored. Control experiments show that ZephCl can provide ion-exchange sites, and Fc oxidation by ClO− can charge the IDA capacitor. ISE materials lacking Fc and ZephCl show irregular signals. The device also shows high selectivity to common ions in pool water, i.e., Cl−, SO42− and CO32−.

The stability of the device is evaluated by observing the sensing curve shifts for several days. It shows that sensitivity at low ClO− concentrations decays with time going on. To improve the film-electrode adhesion and the coating material quality, the film-electrode adhesion and the coating material quality, a plasticizer is added into the ISL material, respectively. Although the sensitivity reduces to 200 mV with a TRC concentration range of 0 to 10 ppm or 20 mV ppm−1, much better linearity and stability is achieved.

We believe that the micro-IDA chip with the improved ISE membrane shows a strong potential for residue chlorine detection for applications in pool water monitoring, etc. It has advantages of small size, low cost, rapid response, and low power consumption, which is particularly suitable for Internet of Things.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci.

References