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A Study on Selectivity and Temperature Coefficients of the Chloride Ion Sensors With RuO_x Thin Film

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ABSTRACT This paper investigated the response time, chloride selectivity, and temperature coefficients of the arrayed flexible ruthenium oxide chloride ion sensor in sodium chloride (NaCl) solutions with concentrations from 10^{-5} M to 1 M. The response time was 7 s in 1 M NaCl solution at room temperature, showing that the sensor had the characteristics of the fast response. The selectivity coefficients of the SO_4^{2-} ion, NO_3^- ion, CO_3^{2-} ion, ClO^- ion, and ClO_4^- ion were 0.001, 0.056, 0.004, 0.015, and 0.006, respectively. The chloride ion sensing device had the good chloride selectivity. Finally, the sensitivity was investigated with different solution temperatures from 5 °C to 50 °C. The sensitivity was increased with higher solution temperature. The temperature coefficient of the sensitivity of the chloride ion sensing device was approximately 0.681 mV/pCl °C between 5 °C and 35 °C.

INDEX TERMS Response time, chloride selectivity, temperature effect, ruthenium oxide and chloride ion sensor.

I. INTRODUCTION

The response time, the anti-interference property and temperature effects of the chloride ion sensing device were meaningful interesting subjects. The ruthenium oxide (RuO_2) was used as the sensing base, which has the advantages of high capacitive property, low electrical resistivity, high enzyme adhesion properties and high specific surface area [1], [2]. RuO_x preparation methods included the radio frequency magnetron sputtering (RFMS) system [3]–[5] and radio frequency (R. F.) sputtering system [6] to deposit the RuO_xsensing film on the different material substrates.

Manjakkal *et al.* [7] used the screen printed technology and RuO_xpastes to prepare the RuO_x sensing film on the material substrates. They investigated the performances for the different compositions electrodes of the pH sensor. Ganesan *et al.* [8] used chemical vapor deposition system to deposit the RuO_x film with different oxygen flow rates, and they used the rapid thermal annealing (RTA) to investigate the annealing effects on the RuO_x film.

Many researchers [9], [10] investigated the temperature effects for the pH sensing devices, which indicated the temperature effect of the sensor was important. However, a few researchers investigated the temperature effects for chloride ion sensor. Therefore, it was also investigated in this study. Sardarinejad *et al.* [9] investigated the temperature effects on the sensing performance of the RuO_x pH sensor, and they found the sensitivity was increased with the solution temperature increasing. The temperature coefficient of the sensitivity (TCS) was important, which could be compensated for variations and evaluated the effect of temperature on the response voltage pH sensor. Barron and Ashton [10] performed the conductivity measurement with

TABLE 1. The comparison of sensitivity and electrode structure of the chloride ion sensor with different literatures [11]–[14].

Electrode structure	Sensitivity (mV/pCl)	Detection Chloride Range (M)	Ref.
Si/p type/phosphorus ion implant/SiO_2/Cr/Au/chloride ion film	45.0	10^{-5} to 10^{-1}	[11] 2013
ITO glass/SnO_2/ chloride ion sensing film	54.0	10^{-4} to 1	[12] 2011
GC/ PEDOT	57.9	10^{-6} to 10^{-1}	[13] 2007
GC/PEDOT/PVC- TDMACl (100 µl)	62.7	10^{-6} to 10^{-1}	[13] 2007
GC/PEDOT/POT- TDMACl (200 µl)	60.0	10^{-6} to 10^{-1}	[13] 2007
GC/PEDOT/POT- TDMACl (400 µl)	52.4	10^{-6} to 10^{-1}	[13] 2007
GC/POT-TDMACl	58.0	10^{-6} to 10^{-1}	[13] 2007
PET/RuO_2/chloride ion sensing film	25.1	10^{-6} to 10^{-1}	[14] 2016

different solution temperatures, and the solution conductivity was increased with the temperature increasing. They investigated the temperature coefficient for some solvent / solute mixture-examples.

The sensitivity comparisons of the different chloride ion sensing devices [11]–[14] were shown in table 1. The poly (vinyl chloride) (PVC) powders, bis (2-ethylhexyl) sebacate (DOS) powders, ionophore {µ-[4,5-dimethyl-3,6-bis (dodecyloxy)-1,2-phenylene]} bis(mercury chloride) (ETH9033) powders, tridodecylmethy-lammonium chloride (TDDMACl) powder and tetrahydrofuran (THF) solution were used to prepare the chloride sensitive solution [11], [12], [14]. They dropped the chloride sensitive solution onto the sensing windows. The advantages of their preparation method were convenient operation. Sjöberg-Eerola *et al.* [13] used the glassy carbon (GC), poly(3,4-ethylenedioxythiophene) (PEDOT), PVC, TDMACl and electronically semiconducting poly(3-octylthiophene) (POT) to fabricate four sensing electrode structures as shown in Table 1. The sensitivity, hysteresis, selectivity and impedance spectra were investigated by potentiometric measurements and EIS at room temperature.

They used 10^{-2} M sodium chloride (NaCl), sodium fluoride (NaF), sodium sulfate (Na_2SO_4), sodium 2-furanacrylate ($NaC_7H_5O_3$), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), sodium hydrogen carbonate ($NaHCO_3$), sodium thiocyanate (NaSCN) and sodium perchlorate ($NaClO_4$)to investigate the selectivity of sensing device.

The Nersntian equation of the chloride ion sensing membrane was shown in Eq. (1) [12] at room temperature (25 °C). E is the electromotive force (EMF), E0 is the original voltage, α is the chloride ion activity, R is the gas constant (8.316 $mole^{-1}$ deg^{-1}), F is the Faraday coefficient (96487 coulomb).

$$E = E_0 - 2.303\frac{RT}{F}\log\alpha = E_0 - 0.05916\ pCl \qquad (1)$$

The meaning of pCl is $-\log\ [Cl^-] = pCl$, $[Cl^-]$ is chloride ion concentration. The unit of the pCl is M (mol/L). Such as, the $[Cl^-]$ is 1 M, the $-\log\ [Cl^-]$ is $pCl = 0$. The $[Cl^-]$ is 10^{-1} M, the $-\log\ [Cl^-]$ is $pCl = 1$ [11].

The chloride ions passed across the helmoltz double layer (HDL) and entered the chloride ion sensing film. The ETH9033 could trap the chloride ions. The chloride ion amounts were trapped in the chloride ion sensing film, which caused the response voltages of the chloride ion sensor were obtained [12].

In our previous research [14], we used the chloride ion sensing device to investigate the sensitivity at static and dynamic states, and it could be found the sensitivity was increased with the flow rate of the solutions increasing. In addition to the sodium hypochlorite (NaClO) solution, it was also applied to detect the chloride ion of the swimming pool water. However, the temperature effect could affect the response voltages variation with different chloride concentrations. Thus, we investigated TCS of the chloride ion sensing device, which could be compensated for variations and evaluated the effect of temperature on the response voltage chloride ion sensor.

The advantages of the flexible arrayed chloride ion sensor were flexibility, light weight and low cost. The flexible arrayed chloride ion sensor was the disposable sensing device, which could increase the accuracy of the chloride ion sensor [14]. The flexible arrayed chloride ion sensor has the six sensing windows, which could avoid experimental error of single sensing window, and thus we chose the arrayed flexible chloride sensor.

In this study, the sensing characteristics of response time and chloride ion selectivity were investigated at room temperature (26 ± 2 °C). Water contained different ions such as CO_3^{2-} ion, NO_3^- ion, Cl^- ion and SO_4^{2-} ion, in order to investigate completed chloride ion selectivity of the chloride ion sensing device. We used the CO_3^{2-} ion, NO_3^- ion, SO_4^{2-} ion, ClO_4^- ion and ClO^- ion to measure the response potential and investigate the chloride ion selectivity for the chloride ion sensing device. We investigated the sensitivities with different solution temperatures. The EIS was used to analyze sensitivity variations at different solution temperatures in the static state.

II. EXPERIMENTAL

A. DESCRIPTION OF THE EXPERIMENTAL ENVIRONMENT

First, we used the voltage-time measuring system to investigate response time and interference effects at room temperature (26 ± 2 °C). Then, we used the voltage-time measuring system and the EIS to investigate the sensing characteristics at different solution temperatures from 5 °C to 50 °C.

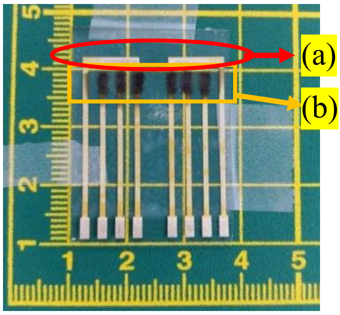

FIGURE 1. **The picture of the chloride ion sensing device (48 mm x 38 mm). (a) Differential Ag reference electrode and contrast electrode. (b) Working electrodes.**

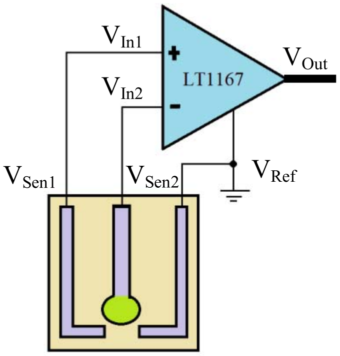

FIGURE 2. **The schematic diagram of voltage-time measurement system with instrumentation amplifier LT1167 for chloride ion sensor [14]–[16].**

B. FABRICATION OF THE CHLORIDE ION SENSING DEVICE

The screen-printed system was used to prepare the silver (Ag) paste on the PET substrate. Then, the substrate was put in the oven at 120 °C for 30 minutes. The Ag wires were used as conducted wires. R. F. sputtering system was used to prepare the RuO_x thin film on the Ag wires/PET substrate. The flow rates of argon (Ar) and oxygen (O_2) were 8 sccm and 4 sccm, respectively. The chamber pressure, sputtering power and depositing time of R. F. sputtering system were 10 mTorr, 100 W and 5 minutes, respectively. The compositions of the RuO_x thin film/Ag wires/ PET substrate were packaged with epoxy by screen printing system. Then, it was put in the oven at 120 °C for 90 minutes.

The chloride ion mixture prepared with the weight ratio of the PVC, DOS, ETH9033 and TDDMACl was 33: 66: 2: 10 (wt%), and it was used to drop on the RuO_x sensing windows of arrayed flexible pH sensor. The chloride ion sensing device was put on the table at room temperature for 3 days.

The differential reference electrode, Ag contrast electrode and chloride ion sensing electrodes (working electrodes) were used to sense chloride ions. The schematic image of flexible chloride ion sensor was shown in Fig. 1, and the dimension of chloride ion sensing device was 48 mm x 38 mm.

Many researchers used PVC, DOS, ETH9033, TDDMACl and THF to prepare chloride ion sensing devices [11], [12], [14]–[17]. They used different weight ratios to prepare chloride ion sensor, and the chloride ion sensing mixtures were mixed and dropped the sensing windows of sensing devices. The chloride ion sensing membranes were immobilized on the sensing windows by the entrapment method, and the entrapment method has the advantages of simple preparation and good adhesion.

C. CHARACTERIZATION OF THE RuO_x MEMBRANES

In order to investigate the thickness and material components of the RuO_x thin film, we used the field-emission scanning electron microscope (FE-SEM; Hitachi S4800-I, Japan) euiptted with energy dispersive spectrometer (EDS) to observe the profile of film and material components of the RuO_x thin film.

D. VOLTAGE-TIME MEASURING SYSTEM

The voltage-time measurement system was composed of 8-channel readout circuit with instrumentation amplifiers (LT1167), National Instruments data acquisition (DAQ) card, power supply, computer and analysis software (model: LabVIEW 2011). The resolution of DAQ card was 16 bits ($5V/2^{16} = 0.076$ mV), and the precision of DAQ card was 0.088 mV. We used the voltage-time measuring system to measure voltage and investigate sensing characteristics in this study.

The voltage-time measurement system for the chloride ion sensing device was shown in Fig. 2. From Eq. (2), the sensing mechanism of the chloride ion sensing electrode, differential Ag reference electrode and Ag contrast electrode [14]–[16]. V_{Out} was the output voltage of LT 1167, V_{Ref} was the voltage of the silver reference electrode, V_{Sen1} was the voltage of the silver contrast electrode, V_{Sen2} was the potential of the working electrode, V_{In1} was the voltage difference between the silver contrast electrode and the reference electrode and V_{In2} was the voltage difference between the chloride ion sensing electrode and the Ag reference electrode.

$$\begin{aligned} V_{Out} &= V_{In1} - V_{In2} = (V_{Sen1} - V_{Ref}) - (V_{Sen2} - V_{Ref}) \\ &= V_{Sen1} - V_{Sen2} \end{aligned} \tag{2}$$

E. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

We used the BioLogic SP 150 of the electrochemical impedance spectroscopy (EIS; Aurora Biotech Inc., France) to investigate charge transfer resistances (R_{ct}), solution resistance (R_s) and double layer capacitor (C_{dl}) for the sensing membrane in different concentrations of NaCl solutions between 10^{-5} M and 1 M at room temperature, the EIS measurement system was shown in Fig. 3. Moreover, R_{ct} and R_s were investigated for different temperatures between 5 °C and 50 °C. The counter electrode was platinum (Pt) electrode, the reference electrode was Ag/AgCl electrode, and the working electrode was RuO_x/chloride ion sensing film.

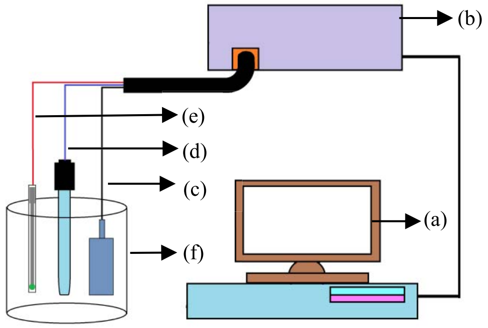

FIGURE 3. The schematic view of the analysis of electrochemical impedance spectroscopy (EIS) with the three electrode system. (a) Computer. (b) Potentiostat. (c) Counter electrode. (d) Reference electrode. (e) Working electrode. (f) Test solution can.

The EIS measurement system was set in the frequency range of sinusoidal excitation signal from 100 mHz to 10 kHz, and the amplitude of voltage was 0.7 mV.

F. MEASUREMENT OF THE TEMPERATURE EFFECTS

We investigated the variations of sensitivity, R_{ct} and R_s at different solution temperatures from 5 ± 0.2 °C to 50 ± 0.2 °C. The cooling circulating water bath contained temperature controller (TAIE FY-400, Taiwan), heating equipment, cooling device and temperature sensor in the iron box. Because the cooling circulating water bath was closed loop control, which could control exactly the solution temperature. The resolution of the thermometer (TM-906A, Taiwan) was 0.1 °C, which was used to measure the solution temperatures from 10^{-5} M to 1 M NaCl solutions. The solution temperatures were controlled from 5 ± 0.2 °C to 50 ± 0.2 °C by the cooling circulating water bath.

III. RESULTS AND DISCUSSION

A. COMPONENTS ANALYSIS OF THE RUO$_X$ MEMBRANE

The deposition time was set at 5 minutes, and we used the FE-SEM to measure the thickness of the Ag/RuOx membrane. The PET plastic substrate and chloride ion film could not endure the high temperature of the electric beam from FE-SEM. Therefore, Ag/RuO_x thin film was deposited onto the ITO glass to measure the thickness. From Fig. 4, the average thickness of the, Ag membrane and RuOx membrane were 6.9 μm and 26.94 μm. We used the EDS to investigate the chemical composition of the RuO_x membrane. From Fig. 5, the element weight ratios of Ru, Ag, O and Si were 11.92 %, 35.81 %, 51.10 %, 1.17 %. According to experiment results, the sensing membrane was the RuO_x membrane.

B. SENSITIVITY CHARACTERISTIC ANALYSIS

The chloride ion sensing device was immersed in NaCl solutions between 10^{-5} M and 1 M for 60 seconds. When chloride ions entered the sensing membrane, the response voltages were changed with different chloride ion concentrations.

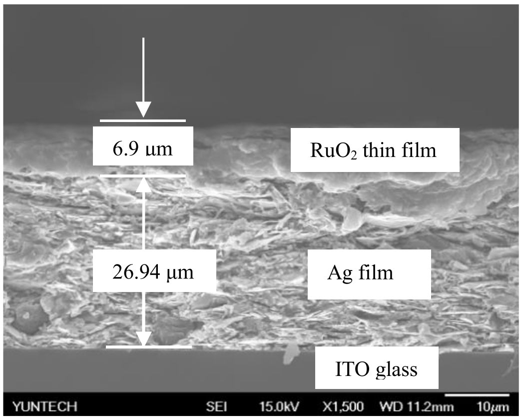

FIGURE 4. The FE-SEM image of the Ag/RuO_x membrane.

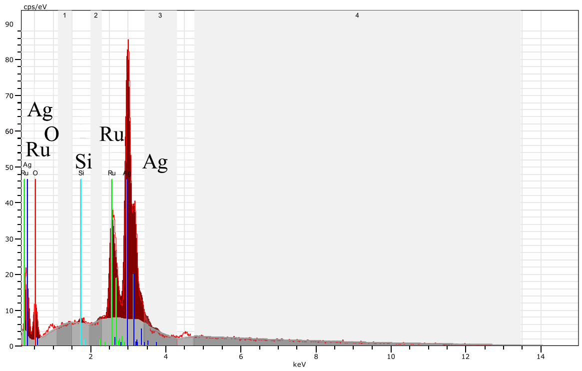

FIGURE 5. The EDS spectra of the Ag/RuO_x components analysis by EDS.

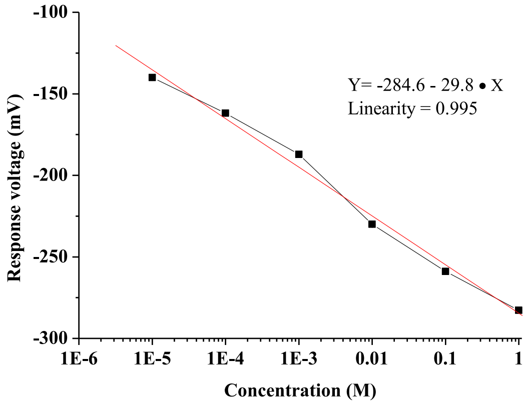

FIGURE 6. The curve of the response voltages versus different chloride concentrations for the chloride ion sensor between 10^{-5} M and 1 M NaCl solutions at room temperature.

The experimental result was shown in Fig. 6. According to Eq. (3) and Fig. 6, the response voltages were changed for different chloride ion concentrations between 10^{-5} M and 1 M. We obtained the response voltages versus chloride ion concentrations with the linear relation as follows:

$$Y = -284.6 - 29.8 \cdot X \tag{3}$$

where Y is the response voltage, X is the log of chloride ion concentration. The linearity of curve is 0.995.

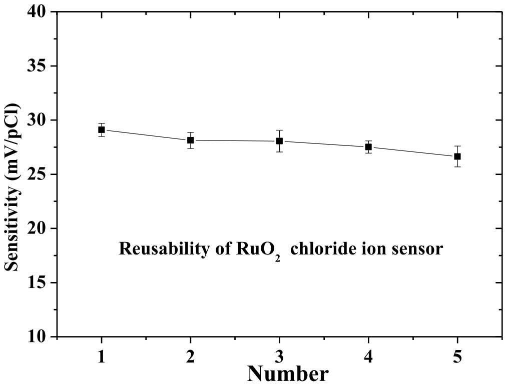

FIGURE 7. **The reusability and stability of arrayed flexible RuO$_2$ chloride ion sensor.**

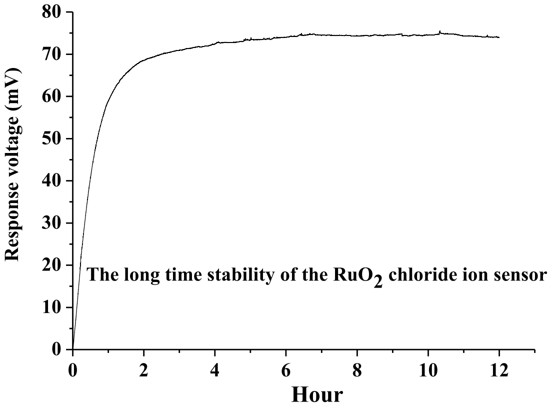

FIGURE 8. **The long time stability of the flexible RuO$_2$ chloride ion sensor in the 10^{-2} M NaCl solution.**

C. REUSABILITY AND STABILITY

We investigated the reusability and stability of arrayed flexible RuO$_2$ chloride ion sensor. From Fig. 7, we measured the five times for the reusability experiment. And we obtained that the average sensitivities were between 26.64 mV/pCl and 29.10 mV/pCl during five chloride ion concentrations. From Fig. 8, we also measured the response voltage in the 10^{-2} M NaCl solution for 12 hour. And we obtained the drift voltage with time was 0.07 mV/hr. Therefore, the RuO$_2$ chloride ion sensor had good stability in the long time measurement.

D. INVESTIGATION OF THE RESPONSE TIME

The response time was defined as the time that reaching 95% of the stable response voltage after immersing. The response voltage was stable within 60 seconds, we investigated the response time and stability for different chloride ion concentrations.

The test of response time was conducted using the chloride sensor with the membrane of PVC: DOS: ETH9033: TDDMACl = 33: 66: 2: 10 (wt%). The response mechanism of the chloride ion sensor is connected with the boundary conditions and materials of sensing film. The boundary conditions are followed Eq. (1) between the sensing film and the solution. The sensing film conditions are related to the quantity of total activates association constant and mobility of all ions in the sensing film [11]. The adsorption amounts of the chloride ion affected the response voltage variations and response time. The chloride ion sensing film contacted the higher concentration NaCl solution, which adsorbed the great amount chloride ions with the chloride ion sensing film increasing. Therefore, the response time of the chloride ion sensor was short in the higher concentration NaCl solution. The chloride ion sensing film contacted the lower concentration NaCl solution, which adsorbed the small amount chloride ions with the chloride ion sensing film. Therefore, the response time of the chloride ion sensor was long in the lower concentration NaCl solution.

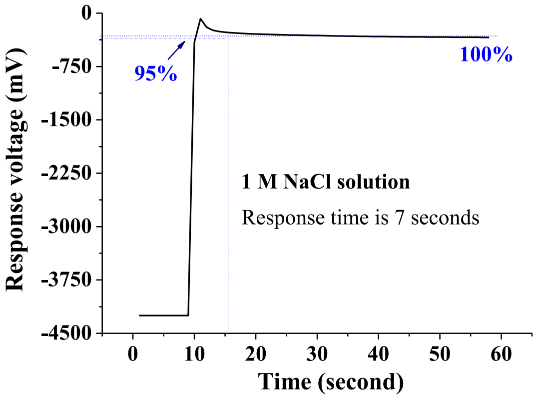

FIGURE 9. **The curve of the response voltages versus time for the chloride ion sensing device in 1 M chloride ion concentration of NaCl solution at room temperature.**

Bratov *et al.* [17] found the response time of liquid-junction potential sensor longer than 10 s. We investigated the response time for 10^{-5} M to 1 M NaCl solutions. The response voltages and response time of chloride ion sensing device in different NaCl solutions at room temperature were shown in Table 2. The response time was reduced when the chloride concentrations from 10^{-5} M to 1 M. From Table 2, for 1 M NaCl solution, it exhibited the shorter response time (7 seconds), which was illustrated in Fig. 9. The response voltage was obtained when the chloride ion sensing film of chloride ion sensing device was immersed into the NaCl solutions. The results were shown that the chloride ion sensing device had fast response.

E. INVESTIGATION OF THE CHLORIDE ION SELECTIVITY

The voltage-time measurement system was also utilized to measure the response voltages for the chloride ion selectivity. However, some researchers [11], [12], [18] investigated the ClO_4^- ion and ClO^- ion to affect their chloride ion sensing devices. Our research group [14] put the chloride ion sensing device in the sodium hypochlorite (NaClO) solution.

We used the perchloric acid ($HClO_4$) solution and deionized (D. I.) water to prepare the different $HClO_4$

TABLE 2. The response voltages and the response time of the chloride ion sensor in different chloride concentrations at room temperature.

NaCl concentration (M)	Response voltage (mV)	Response time (second)
10^{-5}	-150.08 ± 0.05	47
10^{-4}	-161.86 ± 0.06	49
10^{-3}	-177.16 ± 0.05	48
10^{-2}	-230.02 ± 0.06	20
10^{-1}	-258.91 ± 0.06	19
1	-282.74 ± 0.05	7

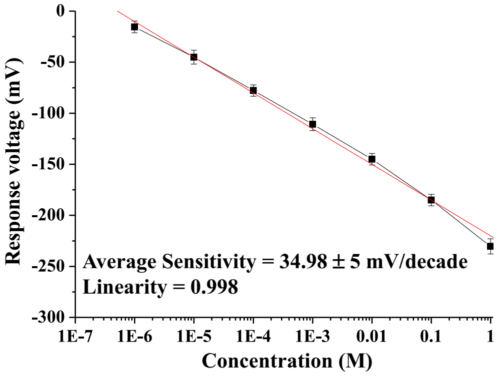

FIGURE 10. The average responses of the chloride ion sensor between 10^{-6} M and 1 M $HClO_4$ solution at room temperature.

TABLE 3. The comparisons of the average responses and chlorine residual concentrations in the different $HClO_4$ concentration solutions from 10^{-6} M to 1 M.

$HClO_4$ concentration (M)	Chlorine residual concentrations (mg/L)	Response voltage (mV)
10^{-6}	0.00	-15.57 ± 5.77
10^{-5}	0.03	-45.11 ± 6.78
10^{-4}	0.18	-77.82 ± 5.56
10^{-3}	0.58	-110.79 ± 6.35
10^{-2}	16.67	-145.02 ± 5.65
10^{-1}	35.00	-185.12 ± 5.67
1	1075,00	-230.47 ± 7.43

solutions from 10^{-6} M to 1 M. The chlorine residual concentrations and response voltages were measured and investigated by a chlorine spectrophotometer (Hach Test Kits −58700-00, U. S. A.). The response voltage of the chloride ion sensing device was varied for ClO_4^- ion, as shown in Fig. 10. The sensitivity and linearity were 34.98 ± 5 mV/decade and 0.998. From Table 3, the chlorine residual concentration ranges were 0 mg/L to 1075,00 mg/L in the 10^{-6} M to 1 M HClO4 solutions. The response voltage ranges were −15.57 mV to −230.47 mV in the 10^{-6} M to 1 M HClO4 solutions. The final dissociative substances of the ClO_4^- were Cl^- and H_2O [19]. According to Fig. 10 and previous research [14], the ClO^- ion and ClO_4^- ion affected the chloride ion sensing device.

We used the matched potential method (MPM) to investigate the selectivity coefficients in this study. The experiment results of selectivity coefficients were shown in Table 4. From Table 4, The selectivity coefficients of the SO_4^{2-} ion, NO_3^- ion, CO_3^{2-} ion, ClO^- ion and ClO_4^- ion were 0.001, 0.056, 0.004, 0.015 and 0.006, respectively. Based on the above experiments, the chloride ion sensing device demonstrated the advantages of better sensing characteristic, specificity and stability.

TABLE 4. The selectivity coefficients of the chloride ion sensor under five different interfering ions.

Interfering ions	Selectivity coefficients log $K^{pot}_{Cl^-/j}$
SO_4^{2-}	0.001
NO_3^-	0.056
CO_3^{2-}	0.004
ClO^-	0.015
ClO_4^-	0.006

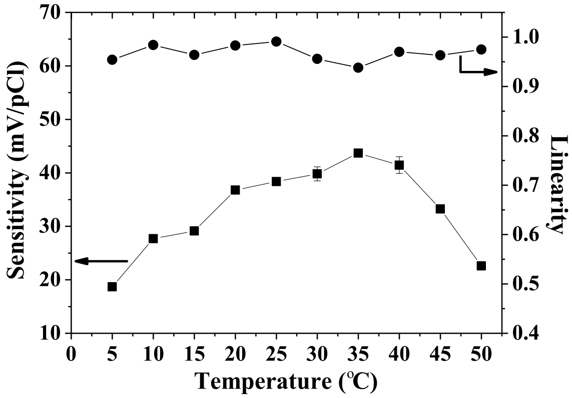

FIGURE 11. The measurement results of the different solution temperatures for NaCl solutions for the chloride ion sensing device.

F. INVESTIGATION OF THE TEMPERATURE EFFECTS

We used the temperature controlled system to maintain temperatures of NaCl solution between 5 °C and 50 °C, and the experimental results of average sensitivity and linearity with different temperatures were shown in Fig. 11, Table 2 and Table 5. The average sensitivities were 18.68 ± 0.06 mV/pCl (5 °C), 27.70 ± 0.02 mV/pCl (10 °C), 29.14 ± 0.03 mV/pCl (15 °C), 36.78 ± 0.01 mV/pCl (20 °C), 38.38 ± 0.10 mV/pCl (25 °C),

TABLE 5. The sensitivity variations of the chloride ion sensing device in different solution temperatures.

Solution temperature (°C)	Sensitivity (mV/pCl)
5	18.68 ± 0.06
10	27.70 ± 0.02
15	29.14 ± 0.03
20	36.78 ± 0.02
25	38.38 ± 0.10
30	39.80 ± 1.32
35	43.70 ± 0.02
40	41.45 ± 1.56
45	33.25 ± 0.13
50	22.61 ± 0.02

39.80 ± 1.32 mV/pCl (30 °C), 43.70 ± 0.02 mV/pCl (35 °C), 41.45 ± 1.56 mV/pCl (40 °C), 33.25 ± 0.13 mV/pCl (45 °C) and 22.61 ± 0.02 mV/pCl (50 °C) for different NaCl solution temperatures from 5 °C to 50 °C, respectively.

The increasing solution temperature would increase the mobility of the ions in solution and decrease solution viscosity. The amounts of ions in solution because of dissociation of molecules were increased with the increasing solution temperature. The electrical conductivity of a solution was dependent on these factors so the raising temperature will lead to increase the electrical conductivity [10]. It also indicated that diffusion rate and electrical conductivity would be increased so that the sensitivities were raised from 5 °C to 35 °C. The amounts of chloride ion in NaCl solution were increased when the solution temperature was increased. It could attribute to the dissociation of molecules was raised with the higher temperature [9], [20]. When the solution temperature was over than 35 °C, it could decrease the adhesion betwixt the chloride ion sensing film and RuO_x sensing windows. Thus the sensitivity was decreased over than 35 °C.

The operating temperatures of the chloride ion sensing device were between 5 °C and 35 °C. The amounts of chloride ion in NaCl solution were increased when the solution temperature was increased. It could attribute to the dissociation of molecules, which was increased with the higher temperature. TCS is an important parameter, and it could compensate temperature variations and compute the temperature effects on the output voltage of the sensors [9].

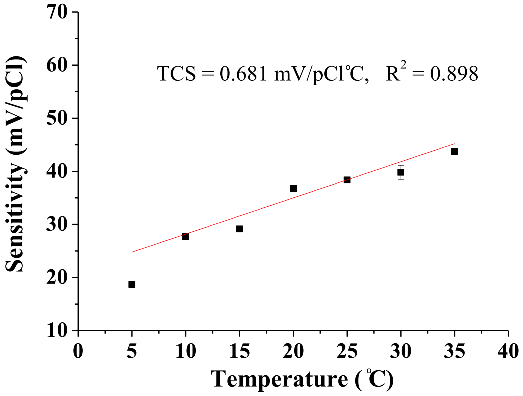

FIGURE 12. The sensitivity versus temperature for the developed chloride ion sensing device.

From Fig. 12 and Table 6, many researchers investigated the temperature coefficients of the sensitivity (TCSs) for the temperature effects of sensing devices from low solution temperatures to high solution temperatures. The amounts of hydrogen ions in pH solution were increased with the higher temperature. The sensitivities of pH sensor were increased with solution temperatures increasing. Many researchers [9], [21]–[27] investigated the sensitivity variations of the different sensing membranes of the pH sensors with different structures for different solution temperatures. The maximum operation temperature of the hydrogen ion sensor was 65 °C. The maximum operation temperature of the chloride ion sensor was 50 °C, and the best sensitivity was 43.70 ± 0.02 mV/pCl at 35 °C.

According to the experimental result, the TCS of the chloride ion sensor was approximately 0.681 mV/pCl °C from 5 °C to 35 °C. The working temperature range of the chloride ion sensor to detect chloride concentration is from 10 °C to 35 °C, it can be applied as follow:

1. Application of real water environment.
2. Detection of the chloride concentration in the concrete.
3. Application of swimming pool water (from 30 °C to 31 °C in winter and from 26 °C to 28 °C in summer).
4. Monitored the chloride concentration for aquaculture water (the fish living temperature range is from 20 °C to 24 °C, and the fish reproducing temperature range is 25 °C to 28 °C).

The electrochemical impedance technology was used to measure the electrochemical impedances of the different chloride ion concentrations between 10^{-5} M and 1 M NaCl solutions at 25 °C room temperature. From Table 7 and Fig. 13, the R_s, R_{ct} and C_{dl} were solution resistance, charge transfer resistance and double layer capacitor [28]. The R_{ct} with different chloride concentrations from 10^{-5} M to 1 M NaCl solutions were 10.66 MΩ (10^{-5} M), 5.14 MΩ (10^{-4} M), 1.96 MΩ (10^{-3} M), 1.54 MΩ (10^{-2} M), 1.29 MΩ (10^{-1} M) and 0.65 MΩ (1 M) at room temperature.

The R_{ct} of chloride ion sensing device decreased with increasing concentration of NaCl solution. Because chloride ions transmission was increased with increasing chloride ions adsorption, the R_{ct} decreased with increasing chloride ions transmission. We utilized 1 M NaCl solution to study the R_{ct} for different solution temperatures between 10 °C and 50 °C. From Table 8, the R_{ct}were 293.44 kΩ, 190.12 kΩ, 112.66 kΩ, 70.05 kΩ, 77.85 kΩ and 111.69 kΩ with different solution temperatures at 10 °C, 20 °C, 30 °C, 35 °C, 40 °C

TABLE 6. The temperature coefficient of the sensitivity varieties at different ion solution temperatures.

Temperature (°C)	Sensing membrane	Structure	Sensitivity	Temperature coefficient of the sensitivity (TCS)	Ref.
5-35	RuO_2	PET	18.68-43.70 (mV/pCl)	0.681 (mV/pCl °C)	This study
1.5-50	RuO_2	platinum/ceramic	65.66-84.50 (mV/pH)	0.338 (mV/pH °C)	[9] 2015
25-65	a-Si:H	SiO_2/p-Si/Al	50.62-59.97 (mV/pH)	0.242 (mV/pH °C)	[21] 2000
25-55	Sentron 1090 Al_2O_3	SiO_2/ p-type Si/Al	53.23-61.92 (mV/pH)	0.315 (mV/pH °C)	[22] 2001
25-55	Ta_2O_5	SiO_2	59.43-64.29 (mV/pH)	0.134 (mV/pH °C)	[23] 2000
25-65	a-WO_3	p-type Si	44.85-55.80 (mV/pH)	0.268 (mV/pH °C)	[24] 2001
5-65	$PbTiO_3$	SiO_2/p-Si/Al	54.00 (mV/pH)	0.101 (mV/pH °C)	[25] 2000
25-55	Si_3N_4	N/A	46.00-56.00 (mV/pH)	0.307 (mV/pH °C)	[26] 1997
5-65	AlN	SiO_2	48.40-57.30 (mV/pH)	0.145 (mV/pH °C)	[27] 2005

N/A: Not available.

TABLE 7. The fitting results of R_{ct}, R_s and C_{dl} with the different chloride ion concentrations between 10^{-5} M and 1 M NaCl solutions at room temperature.

NaCl solution (M)	Charge transfer resistance R_{ct} (MΩ)	Solution resistance R_s (kΩ)	Double layer capacitor C_{dl} (F)
1	0.65 ± 0.02	27.67 ± 5.46	$1.48\times10^{-10} \pm 6.1\times10^{-12}$
10^{-1}	1.29 ± 0.05	22.30 ± 3.79	$1.12\times10^{-10} \pm 6.36\times10^{-13}$
10^{-2}	1.54 ± 0.03	14.82 ± 0.21	$2.1\times10^{-10} \pm 7.78\times10^{-12}$
10^{-3}	1.96 ± 0.01	16.68 ± 0.11	$1.96\times10^{-10} \pm 5.09\times10^{-12}$
10^{-4}	5.14 ± 0.08	18.96 ± 0.66	$1.50\times10^{-10} \pm 1.48\times10^{-12}$
10^{-5}	10.66 ± 4.04	4.63 ± 1.27	$5.85\times10^{-11} \pm 4.95\times10^{-14}$

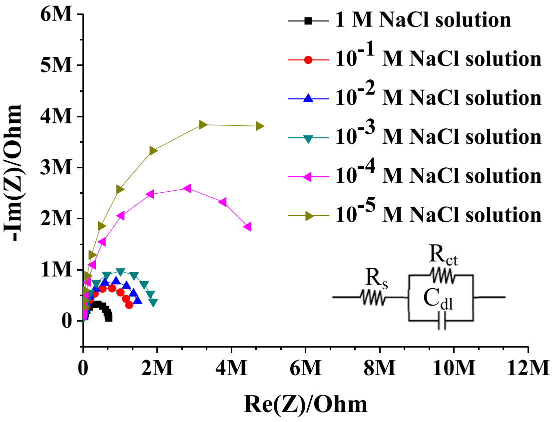

FIGURE 13. The electrochemical impedances of fitting curves in the different chloride ion concentrations from 10^{-5} M to 1 M NaCl solution at room temperature.

TABLE 8. The fitting results of R_{ct}, R_s and C_{dl} in the 1 M NaCl solution at different temperatures between 10 °C and 50 °C.

Solution temperature (°C)	Charge transfer resistance R_{ct} (kΩ)	Solution resistance R_s (kΩ)	Double layer capacitor C_{dl} (F)
10	293.44 ± 33.35	10.11 ± 4.00	$3.00\times10^{-10} \pm 2.83\times10^{-12}$
20	190.12 ± 6.98	10.52 ± 0.44	$5.79\times10^{-10} \pm 1.33\times10^{-10}$
30	112.66 ± 27.42	19.90 ± 9.56	$7.91\times10^{-10} \pm 1.21\times10^{-10}$
35	70.05 ± 12.60	8.63 ± 6.20	$7.98\times10^{-10} \pm 1.98 \times10^{-11}$
40	77.85 ± 10.33	17.59 ± 10.61	$7.85\times10^{-10} \pm 3.60 \times10^{-10}$
50	111.69 ± 2.00	17.78 ± 20.71	$6.70\times10^{-10} \pm 1.41\times10^{-12}$

and 50 °C, respectively. The R_s were 10.11 kΩ, 10.52 kΩ, 9.90 kΩ, 8.63 kΩ, 17.59 kΩ and 17.78 kΩ at 10 °C, 20 °C, 30 °C, 35 °C, 40 °C and 50 °C, respectively. The R_{ct}, R_s and C_{dl} were 293.44 kΩ, 10.11 kΩ and 3.00×10^{-10} F in 1 M NaCl solution at 10 °C. However, the smallest R_{ct} and R_s and C_{dl} were 70.05 kΩ, 8.63 kΩ and 7.98×10^{-10} F at 35 °C.

The amounts of free chloride ion in NaCl solution because of dissociation of molecules were increased when the solution temperature was increased [10], [20]. Thermal activation of spectating ions to participating ions produced the observed transitions originate, which caused the charge carriers concentration increasing with temperature. Therefore, the double layer capacitor was increased when solution temperature increased [29]. From Table 8, the R_{ct} of chloride ion sensing device was decreased when the chloride ions transmission increased from 10 °C to 35 °C. The C_{dl} of chloride sensing devices was increased when the chloride ion adsorption increased from 10 °C to 35 °C [13].

The polyvinyl chloride (PVC) was a polymer material, which could fix the chloride ionophore III (ETH9033) and tridodecylmethy-lammonium chloride (TDDMACl). There was chlorine atom in the polyvinyl chloride, and the adsorption force can increase in the link. The dioctyl sebacate (DOS) was the plasticizer, which could soften the polymer member. According to our preview paper [16], the chloride sensing mixture was similar to the colloid. The chloride sensing films were based on the RuO_x sensing windows, and the chloride sensing films and RuO_x sensing windows adhered to each other. When the solution temperature was over 35 °C, and the adhesion was lower between the chloride ion sensing film and sensing window. As a consequence, the sensitivities of the chloride ion sensing device were decreased when solution temperature was higher than 35 °C.

IV. CONCLUSION

The sensing characteristics of response time, interference effects and temperature effects were investigated at static state. The response times of the chloride ion sensing device were 47 seconds (10^{-5} M), 49 seconds (10^{-4} M), 48 seconds (10^{-3} M), 20 seconds (10^{-2} M), 19 seconds (10^{-1} M) and 7 seconds (1 M) in NaCl solutions, respectively. The response time of the 1 M NaCl solution was 7 seconds, showed that the sensor had the characteristics of fast response. The selectivity coefficients of the SO_4^{2-} ion, NO_3^- ion, CO_3^{2-} ion, ClO^- ion and ClO_4^- ion were 0.001, 0.056, 0.004, 0.015 and 0.006, respectively. It was observed that the sensor only reacted with the chloride ions. The sensitivities were raised by the thermal convection between 5 °C and 35 °C. The best average sensitivity was 43.70 ± 0.02 mV/pCl at 35 °C. The advantages of the chloride ion sensor were fast response, good specificity, good stability and better sensing characteristic at 35 °C. According to the experimental result, the TCS of the chloride ion sensor was approximately 0.681 mV/pCl °C from 5 °C to 35 °C.

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