Int. J. Electrochem. Sci., 12 **(2017)** 1506 – 1520, doi: 10.20964/2017.02.52

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Determination of Sulfate in Seawater by a Novel All-Solid-State Sulfate Sensor with H_2SO_4 Doped Polyaniline as Sensitive Membrane

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Received: 14 November 2016 / *Accepted:* 25 December 2016 / *Published:* 30 December 2016

An all-solid-state sulfate selective-electrode, with Au wire as the substrate and H_2SO_4 doped polyaniline (PANI) as the sensitive membrane, has been proposed. The effect of polymeric monomers concentration, oxidization potential, and solvent component on the electrochemical reaction has been optimized for further improving the performance of the electrode. The membrane is prepared by electro-polymerization with 0.1 M aniline hydrochloride dissolved in 1 M H_2SO_4, 0.0005 sampled interval, and setting scanning potential at 0.8 V give the excellent Nernstian linear response to sulfate in the concentration range of 8.0×10^{-5} to 1.0 M of Na_2SO_4 solutions made by freshly prepared 3.5% NaCl solution, with a slope of -26.62 mV per decade (R^2>0.99). The potentiometric response of the electrode is independent of pH in the range of 5.5-8.5. The scanning electron microscope (SEM) observation reveals that H_2SO_4 doped PANI formed cross-linked rods nearly 0.2-0.4 um in length and 0.1um in thickness on the surface of the Au wire. Bulk impedance of the electrode is about 36 Ω, much lower than the glass and poly (vinyl chloride) (PVC) electrode reported. The utility of the new sulfate electrode has been used as a sensor for the determination of sulfate concentration in seawater successfully. Particularly, the electrode is in a small size and convenient for both integrate and assembly to capture *in-situ* data in distant and inaccessible sites, which is superior to those existing jelly-like and mechanically non-robust sulfate electrodes for real-word *in-situ* monitoring.

Keywords: Sulfate determination; All-solid-state sulfate electrode; Polyaniline; *In-situ* measurement; Low impedance

1. INTRODUCTION

Sulfate (SO_4^{2-}) is the fourth most abundant ion in modern seawater and a major component of the alkalinity budget, which governs the pH of seawater [1]. The sulfate concentration of the ocean should track the oxidation history of the Earth's surface [2]. Sulfate concentrations affect several important biological processes, including carbonate mineralogy, microbially mediated organic matter remineralization, sedimentary phosphorous regeneration, nitrogen fixation and sulfate aerosol formation [3]. Steep sulfate gradients of the pore water corresponding to upward methane flux and the presence of underlying gas hydrate, deemed as an indicator of the gas hydrate [4-6]. Marine gas hydrate, primarily buried in submarine sediment, is assumed as a great potential energy source attracting much attention and efforts worldwide. Microorganism reduce sulfate to sulfide by using organic carbon in oxygen-deficient environment, then influence the composition of seawater. Rates of sulfate burial are unsteady and linked to changes in the area of marine environments suitable for evaporite formation and preservation [7]. Consequently, determination of the *in-situ* sulfate concentration in seawater, in seafloor sediments and in microbial environments is relevant to a board array of marine studies.

For a long time, gravimetry, turbidometry, indirect atomic absorption spectrometry, ion-chromatography and inductively coupled plasma optical emission spectrometry are the main methods for surveying sulfate ions [8]. These methods are either time-consuming, involve multiple sample manipulations, or feature low reproducibility [9]. Ion-selective electrodes (ISEs), majority based on potentiometric, become a routinely analytical tool in numerous fields [10-13]. Potential generated by a cell as an electrical signal under essentially equilibrium conditions [14]. Nevertheless, conventional glass-housed electrodes contain a solution interface [15, 16], ordinary liquid solution or a gel, meaning that a further miniaturization to require inner solutions of lower resistivity is quite difficult [17]. Besides, the solution filled could be replaced with a fresh portion if the glass electrode was not sealed hermetically. The elimination of internal solution and replaced with solid-state electrodes, making it is possible to decrease the diameter and reduce impedance.

Recently, a series of sulfate ISEs based on barium(II)-Rose Bengal [18], N-[4-[4-[(anilinocarbothioyl)amino]benzyl]phenyl]-N-phenylthiour-Ea [19], Nickel (II)-dioxime complex [20], 4-(4-bromophenyl)-2,6-diphenylpyrilium perchlorate [21] and surfactant modifyed zeolite (SMZ) particles [22] with a closing Nernstian behavior and relatively wide concentration range have been reported. However, such glass and PVC ISEs reported exhibit longer response time, weakly mechanical properties and integration difficulties, which usually used to assess the analytes in laboratory conditions [23-25]. For real-time capture *in-situ* data from remote spots such as ocean and glaciers, there are no sulfate sensors available still. Meanwhile, sulfate ISEs in previous works performing weakly in high sulfate concentration considering the sulfate concentrations in the modern ocean reach 28 mM [2]. Therefore, developing a novel high-precision sulfate sensor to monitoring sulfate precisely and rapidly in ocean is urgently needed.

Since the first successful preparation of coated wire electrode in the 1970s [26], nowadays, the all-solid-state electrodes have developed to conductive polymer electrode [27]. Polytrioctylthiopherene, polypyrrole, polythiopheres, polyethylenedioxy-thiophene and PANI are the most frequently used in solid state ISEs [28], for example, PANI for CN^- [29]. The electrical conductivity and thermoelectric power results suggest that the PANI is a p-type semiconductor polymer [30] behaving attractive features, such as perfect conductivity, simple synthesis procedure, good chemical stability, and anti-corrosion performance [31-33].

In this paper, a new all-solid-state sulfate ISE was fabricated by chronoamperometry method with electro-polymerized membrane of PANI which was doped by H_2SO_4. As schematically illustrated in Fig. 1, this electrochemical interaction happened when nitrogen atoms of PANI were protonated, creating positive charges that were moved in the conjugated chain [34]. The sulfate electrode consist of an Au wire coated with H_2SO_4 doped PANI as membrane. Since its miniature size and benign selectivity, the proposed electrode could be applied for the analysis of the sulfate in sampled natural seawater. Besides, it was intergerated sucessively with other ISEs as a multi-role sensor to capture *in-situ* sulfate surveying data in ocean.

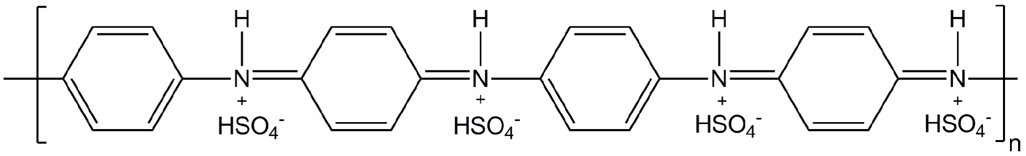

Figure 1. Chemical structure of H_2SO_4 doped PANI.

2. EXPERIMENTAL

2.1 Reagents and apparatus

Hydrogen peroxide, ethanol and sulfuric acid were purchased from Sinopharm Chemical Reagent Company, Shanghai, China. All sodium salts including sulfate, oxalic, chloride, bromide, perchlorate, thiocyanate, iodide, nitrate and aniline hydrochloride (99%) were obtained from Aladdin. Au wire (99.98%, 0.3 mm in diameter) was purchased from the Precious Materials Company of Changzhou, China. All regents were of analytical grade without purified further. And all aqueous solutions were prepared by dissolving the reagents in boiled deionized water. Working solutions of different concentrations were prepared stepwise by diluting 1 M Na_2SO_4 solution made with freshly prepared 3.5% NaCl solution.

All electrochemical studies were performed by CHID760D electrochemical workstation (Chenhua Company, China) at ambient temperature (25 ± 1 °C). Platinum electrode (Gaoss Union Electronic Technology Company, China) was utilized as auxiliary electrode and a commercial Ag/AgCl electrode (3 M KCl; Gaoss Union Electronic Technology Company, China) served as reference electrode. Ultrasonic cleaning KQ218 (Shumei Company, China) was used to clean Au wires and accelerate dissolution. Scanning electronic microscopy (SU-8010, Hitachi, Japan) was employed to observe the surfaces of the Au electrodes coated.

2.2 Pretreatment of substrate

0.3 mm Au wires, as the substrate, were polished mechanically by chamois leather doped with 0.05 mm-alumina power. And then put the Au wires into the mixture (18 ml), which the volume ratio of sulfuric acid and hydrogen peroxide was 3:1 for 10 minutes. Both of the sulfuric acid and hydrogen peroxide were analytical grade and utilized directly without any dilution. After that, the Au wires were washed ultrasonically with ethyl alcohol and deionized water for 10 minutes respectively, and dried at room temperature.

2.3 Sulfuric acid doped PANI film coating

Chronoamperometry method was used to electroplate the PANI film on Au wire in the reaction mixture, constituted by 1.9439 g aniline hydrochloride dissolved in 15 ml H_2SO_4 (1 M). The H_2SO_4 (1 M) was prepared by the concentrated sulfuric acid purchased and the reaction mixture was stored in a round-bottom flask (20 ml) with ultrasonic vibrating for 10 minutes. After that, the thin doped PANI membrane was coated on the pretreated Au substrate by electro-polymerized with a three-electrode system at ambient temperature. The working electrode was an Au wire, the reference electrode was a commercial Ag/AgCl electrode, and the auxiliary electrode was a Platinum electrode. In this procedure, the scanning number and sample interval were set 1 and 0.0005, positive initial step, the sensitivity of $1.e^{-002}$ and the potential was 0.8 V for 160s. Finally, the Au wire coated was rinsed thoroughly ethanol and deionized water successively, naturally dried in air. The proposed electrode was activated in 0.01 M sodium sulfate solution prepared by 3.5% NaCl solution for 6 h.

The selectivity of sulfate electrode was induced by the way of the ion-recognition sites incorporated directly into the conducting polymer matrix, by doping the conjugated polymer with counter ions containing ion-complexing groups or by covalent binding of ion-recognition sites to the conjugated polymer chain [35, 36]. Sulfate had been doped into PANI conjugated chain by electrochemical reaction as illustrated. Scheme of the prepared sulfate electrode with H_2SO_4 doped PANI as membrane is shown in Fig. 2.

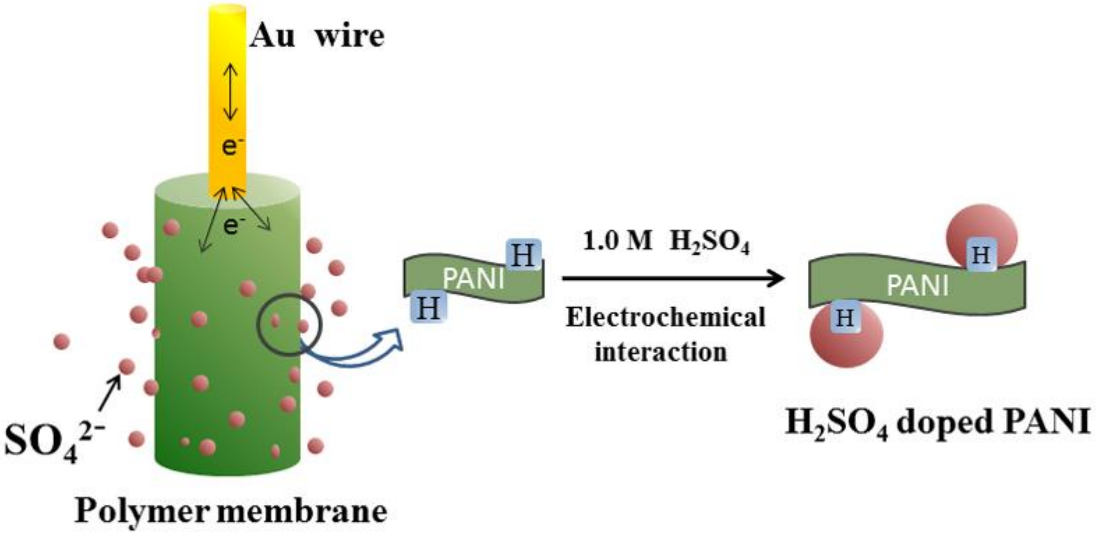

Figure 2. Scheme of the solid-state sulfate electrode with H_2SO_4 doped PANI as membrane.

2.4 Potential measurements

All potential measurements were carried about by Open Circuit Potential-Time with CHI760D electrochemical workstation. In this procedure, the reference electrode was a commercial Ag/AgCl electrode and the polymeric membrane coated Au electrode served as working electrode. Based on Nernst equation, what has to relate the measured signal to the ion activity (a) rather than concentration (c) of target analyte, possess particularistic linear correlation with electrochemical sensor potentiometric signal. Ion pairs come to being among ions of opposite charge because of the ionic interaction. As a result, the effective ion concentration would be lower than the nominal concentration, even in strong electrolyte solution. Ion activity, in fact, is regarded as the effective ion concentration in electrolyte solution. In order to describe the relationship between ion activity and concentration, f is calculated by the following equation (1):

$$f = a / c \qquad (1)$$

where f is the ratio of ion activity and concentration. However, instead of single ion activity, only mean activity coefficient $f\pm$ could be measured. According to Debye-Hückel theory (2):

$$\lg f\pm = (-A|Z^{+}\cdot Z^{-}|\sqrt{\mu}) / (1 + Ba^{0}\sqrt{\mu}) \qquad (2)$$

where μ is named as ionic strength (3):

$$\mu = \frac{1}{2} \sum (c_i \cdot Z_i) \qquad (3)$$

Where c_i is i ion concentration and Z_i is the corresponding charge number, A and B are constants as long as temperature in stationary. For 25℃, A=0.512, B=0.329. And a^0 is the sum of the effective radius between positive and negative ions, which is a constant also. In a word, the practical experimental potentiometric response slopes of ISEs lower than the ideal value corresponding to the actual ion activity existing in solution.

ISEs with polymeric membranes constitute the most numerous group of electrodes, and the selectivity of varied membranes coated is the basis for the potentiometric selectivity of respective electrodes. Normally, the conventional filmed electrodes could be regarded as a concentration cell, which potential (ΔE) is comprised by two interfacial potential difference of inside-out:

$$E_1 = E^0 + RT\ln a_i' / Z_iF \qquad (4)$$

$$E_2 = E^0 + RT\ln a_i''/ Z_iF \qquad (5)$$

$$\Delta E = E_1 - E_2 = (\ln a_i' - \ln a_i'') \cdot RT/ Z_iF \qquad (6)$$

Where a_i' and a_i'' are the ionic activity, E_1 and E_2 are the potential of external solution immersed and fixed inner solution respectively. However, for the Au electrode coated by H_2SO_4 doped PANI, the internal solution has been removed entirely. As a consequence, electrode potential is equal to the response potential of solid-state membrane to analyte.

2.5 Application

The proposed sulfate ISE was integrated and carried out a sea trial to capture *in-situ* data of sulfate in the sea area (28°25'42"N, 121°49'52"E) near Dachen Island. And the tested seawater for further laboratory analysis sampled from one meter deep submerged underwater at the same spot, being taken every five minutes in sequence for three times.

3. RESULTS AND DISCUSSION

3.1 Electro-polymerization of sulfuric acid doped PANI

The fabrication and construction of sulfate electrode based on the electro-polymerization of H_2SO_4 doped PANI as membrane coated on Au substrate was studied by Chronoamperometry, as shown in Fig. 3. Initially, the synthesized curve tended relatively smooth because there were just a few doped micro-aniline particles formed on the Au electrode. However, about 50 s later, the membrane had been polymerized little by little in synchronism with the downward sloping curve.

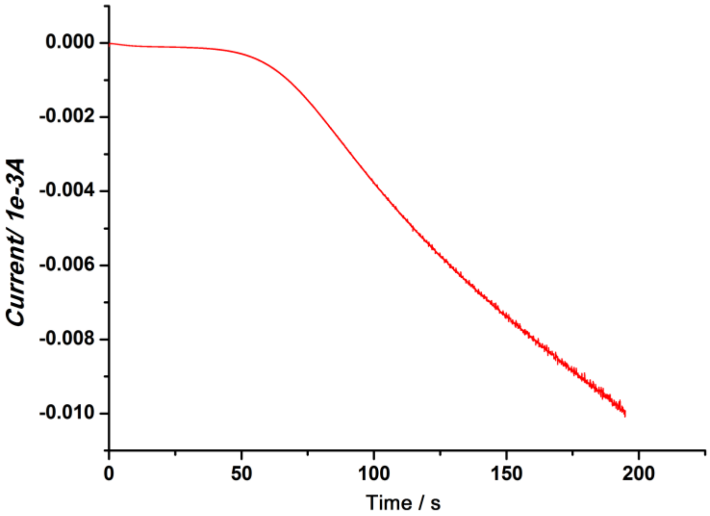

Figure 3. Electro-polymerization of membrane based on H_2SO_4 doped PANI in 0.1 M aniline sulfate reaction mixture by Chronoamperometry.

Table 1. Optimization of the membrane for the sulfate ISE proposed based on Chronoamperometry polymerization

Electrode no.	Components		Parameters			Slope	R-square	Detection
	H_2SO_4 (M)	Aniline hydrochloride (M)	Potential (V)	Sample Interval	Pulse Width (s)			
1	1	0.5	1.0	0.001	200	-26.5	0.99932	$10^{-3} – 10^{-1}$
2	1	0.67	0.8	0.001	200	-15.68	0.98744	$10^{-4} – 10^{-1}$
3	1	1	0.8	0.001	60	-25.0	0.99932	$10^{-3} – 10^{-1}$
4	1	1	0.75	0.002	100	-16.75	0.99275	$10^{-4} – 10^{-2}$
5	1	1	0.8	0.004	70	-28.66	0.96159	$10^{-4}– 10^{-1}$
6	1	1	0.7	0.005	150	-20.99	0.99134	$10^{-4}– 1$
7	1	1	0.8	0.001	180	-18.26	0.96990	$10^{-4}– 1$
8	1	1	0.8	0.005	200	-22.02	0.99520	$10^{-4}– 1$
9	1	1	0.8	0.005	180	-25.19	0.99429	$10^{-4}– 1$
10	1	1	0.8	0.005	160	-26.22	0.99419	$10^{-4}– 1$
11	1	1	0.8	0.005	140	-24.63	0.99574	$10^{-4}– 1$

The information of electro-polymerization was given in Table 1. All those preparation parameters could affect the compact-structure and composition of the membrane, as a result, influencing the Nernstian response of the sulfate electrode accordingly. In this work, any plasticizers which switched the selectivity of membrane and changed the response dramatically [37] were not be used, however, it was impossible to fabricate an ISE based on PVC and graphite without plasticizers as membrane solvent in previous works. In order to optimize the sulfate-recognition and minimize the redox interference, both of electronic and ionic transport properties of the sensitive membrane polymerized should be operated pinpoint. As the results shown, the optimized concentration of aniline hydrochloride was 1.9439 g dissolved in 1M H_2SO_4 (15 ml). The potential and time were setting at 0.8 V and 160 s respectively, with sampled interval of 0.0005, displaying the best characteristic performances. And $R^2 > 0.99$, which exhibited a perfect degree of linear correlation of the potential measured. After a good deal of experiments, we found that the optimized sulfate electrode exhibited best slope of -26.62 mV/decade of concentration closing to the theoretical calculation value after transfer to activity, shown a broad liner range of 10^{-4} M to 1 M.

3.2 SEM observation

The presence of H_2SO_4 doped PANI was further investigated using SEM as presented in Fig. 4. In Fig. 4, the Au electrode well-coated by H_2SO_4 doped PANI bars crossed and overlapped each other. Sulfate, as ion-recognition sites, incorporated directly into the PANI chains. Those cross-linked micro-bars about at the length of 0.2-0.4 um and the width of 0.1 um as shown in the photograph after amplifying 50000 times, forming a densely three-dimensional network framework. Both of the images were in the nano-cubic structure generated a conduction of particularly electrical signals to sulfate among external solutions.

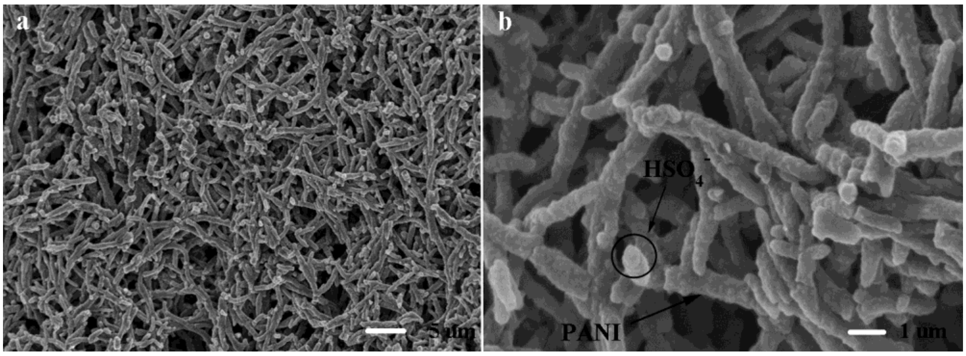

Figure 4. SEM photographs of the membrane based on H_2SO_4 doped PANI after amplifying 10000 and 50000 times.

3.3 Electrochemical impedance spectroscopy studies

The glass electrodes with liquid internal reference solution for reproducible and stable potential have high electrical resistance, up to 10^{12} Ω [38], which demand high-precision voltmeters with higher input impedance to reduce measure deviation. For this sulfate ISEs, the corresponding membrane was formed on the surface of substrate by electro-polymerization or deposition, without any internal electrolyte. As a result, the impedance of the coated wire electrodes primary depended on the properties of membrane.

Electrochemical impedance spectroscopy (EIS), in principle, provides with the information on the processes in the membrane bulk, in boundary layers, and directly at the interface. In this work, EIS was measured in 0.02 M Na_2SO_4 solution prepared by 3.5% NaCl solution, aimed to simulate the real-world concentration of SO_4^{2-} in seawater. And the operating potential was 0.70 V with frequency range: 0.01 Hz~1 MHz. The impedance spectrum, widely, interpreted with the help of respective equivalent circuits which supporting quantitative measurement by simple equations that contributing to application. A semicircle curve and Warburg diffusion were demonstrated in Fig. 5. The impedance value of the membrane polymerized was only approximately 36 Ω, corresponding to the projection of the lowest portion of the curve on X-axis. Low impedance may largely depend upon the property of PANI as semiconductor polymer [31]. Meanwhile, according to Fig. 4, the compact-structure of cross-linked micro-bars and low interface impedance between H_2SO_4 doped PANI thin membrane with Au wire substrate may also a reason that should not be ignored. Lower impedance electrode means the interference of noisy signals reduced so that the next stage circuit could obtain higher measurement accuracy [39], which is one of practical advantages of the sulfate selective-electrode proposed as well.

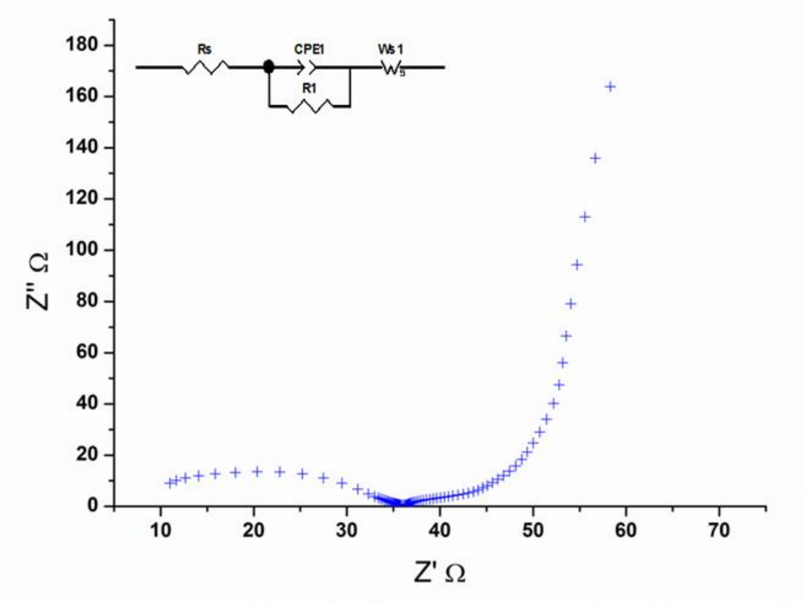

Figure 5. EIS of Au/ H_2SO_4 doped PANI in 0.02 M Na_2SO_4 solution prepared by 3.5% NaCl solution. Scanning frequency range from 0.01 Hz to 1 MHz. Z′and Z″ are the real and imaginary parts of the impedance respectively.

3.4 Response and life time

The response time of an electrode indicates the rate of steady value of potential reach, which measured during the procedure of sample or calibration solution replaced with the next tested one. This characteristic is an important analytical feature since it determines the throughput of the measuring device of a sensor. As presented in Fig. 6, the practical response time data were obtained when the sulfate selective-electrode immersed into Na_2SO_4 solutions range from 10^{-4} M to 1 M made with freshly prepared 3.5% NaCl solution. Real-time target detected signals were available less than 1 s, while the ISEs reported take about 15 s to several tens of minutes to reach a steady response [9,20]. Rapid response was bound up with the structure of the H_2SO_4 doped PANI membrane and the nature of PANI. In addition, lower interfacial resistance between substrate and membrane also contributed to the fast response. Short response time is especially valuable for water monitoring, because subsequently coupled controlling devices could intervene with minimal delay. As a consequence, the practicability of the sulfate ISE has been enhanced extensively.

In terms of the life of the solid-state sulfate electrode, the detection limit and response stability were maintained for a period of 10 days at least when the prepared electrode was stored in 0.01 M Na_2SO_4 solution prepared by 3.5% NaCl solution. It was close to the lifetime of sulfate ISEs reported recently [40, 41]. Besides, the storage periods of the prepared electrode could be prolonged to over 8 weeks when kept dry in air. The difference of the electrodes storing conditions on lifetime might be related to the slow decomposition of the polymer membrane coated during the long-term storage in aqueous solution.

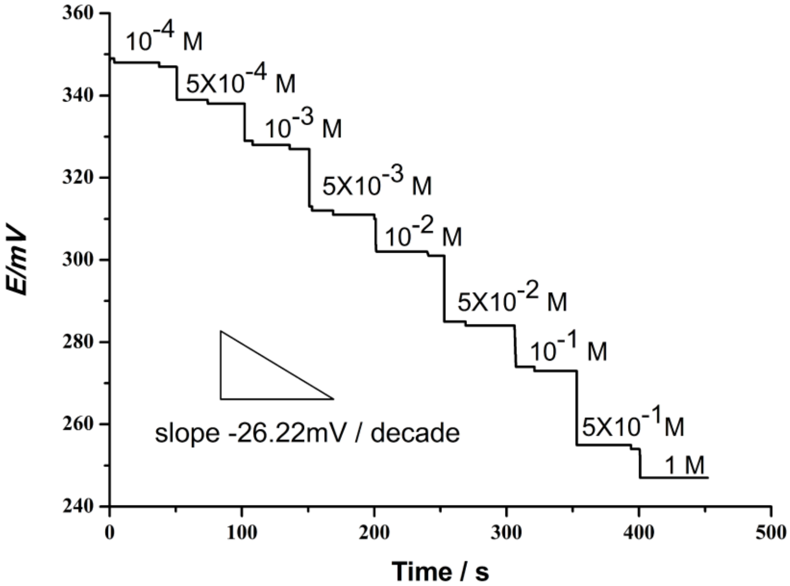

Figure 6. Dynamic response characteristics of the electrode for step changes from 10^{-4} M to 1 M Na_2SO_4 solutions made by freshly prepared 3.5% NaCl solution.

3.5 Effect of pH

Since the hydrogen ions are known to cause interference in the characteristic performances of the electrodes [42], it is essential to determine effective pH range that the electrodes perform well. The effect of pH on the potential response of the fabricated electrode was investigated in 1.0×10^{-1} M and 1.0×10^{-2} M Na_2SO_4 solutions in the pH of 2.0-10.5. The pH of the tested solutions was adjusted by dilute HCl or NaOH solutions, and the variation of potential was depicted in Fig. 7. As presented in Fig. 7, the electrode response was independent of pH in the range of 5.5-8.5. The potential response of the sulfate electrode increases gradually at pH lower than 5.5 may due to the protonation of sulfate ions. As pH values more than 8.5, the decrease in potential is attributed to the interference from OH^-.

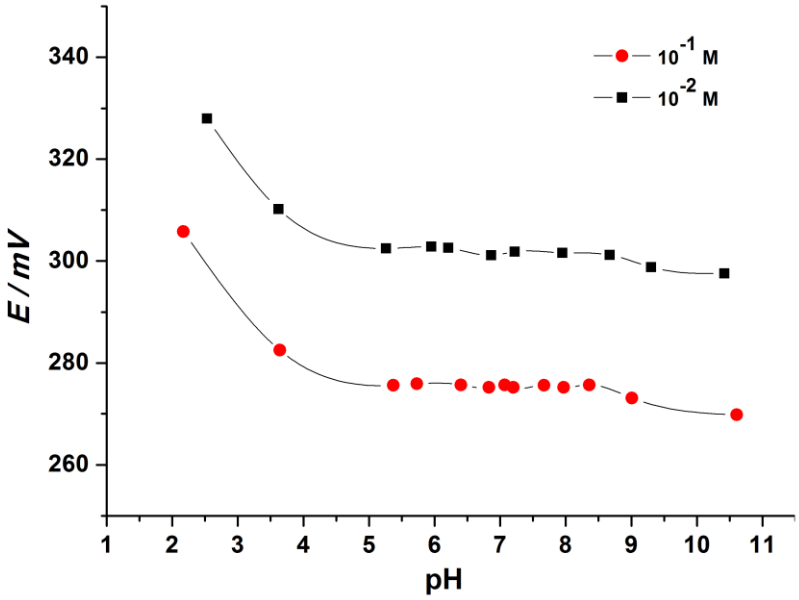

Figure 7. pH effect on response characteristics of the sulfate electrode. The pH of the solutions (10^{-1} and 10^{-2} M Na_2SO_4) were adjusted by the addition of HCl and NaOH.

3.6 Potentiometric stability of the polymeric film

Table 2. Potential of the two independent electrodes based on H_2SO_4 doped PANI as membrane

Na_2SO_4 Concentration (M)	E (mv)	
	Without scraping the membrane	With scraping the membrane
10^{-4}	345.4	344.1
5×10^{-4}	332.4	331.9
10^{-3}	317.8	321.1
5×10^{-3}	306.7	309.3
10^{-2}	297.4	298.7
5×10^{-2}	281.3	281.1
10^{-1}	271.4	271.9
0.5	256.1	256.2
1	249.5	249.1

Considering it is much harder to avoid electrodes contact with obstacles such as macadam and plant and animal materials in real-world, the characteristic performances of the electrodes may distorted inevitable. Hence, the potentiometric stability of the sensitive film becomes a determinant factor whether the sensor could be available with high-efficiency or not. Obviously, the classic glass electrodes couldn’t meet this demand appropriately considering that the glass chamber broken except integration difficulties, identical to such sensors based on PVC and graphite considering the fragile substrates. For study the characteristic stability of the H_2SO_4 doped PANI, two Au electrodes were prepared in the same way while one lateral coated membrane was scraped off. Potentiometric response of two independent H_2SO_4 doped PANI electrodes were presented in Table 2 and Fig. 8. The electrodes behave superior similar performance, which was also an obvious merit in real-world application.

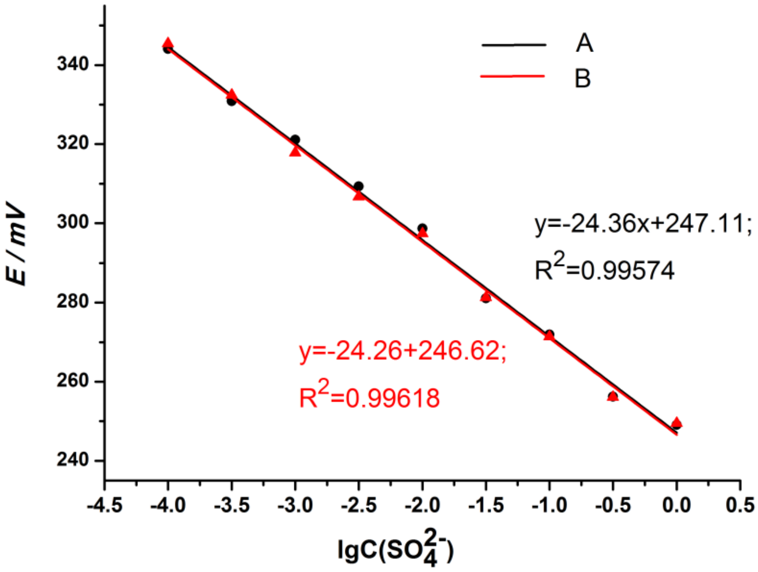

Figure 8. Potential response of the two sulfate electrodes were displayed with the concentration rang of 1.0 × 10^{-4}~1.0 M. A was the scraped electrode while B was intact.

3.7 Potentiometric reproducibility and selectivity

Excellent reproducibility is essential to substitute a malfunctioning sensor for a new one without wasting time to calibrate, especially for in-line monitoring of a practical process. In order to examine the reproducibility of the proposed electrode, four electrodes coated under same polymeric styles were prepared and the calibration curves of the sulfate ISEs are illustrated in Fig. 9. The potentiometric selectivity coefficients, used to describe the preference of the proposed electrodes to interfering ions relative to sulfate, which were calculated by using Fixed Interference Method (FIM) [43-46]. Considering there are diverse ions in real-time tested solution and the interaction between ions, therefore, measurements in mixed solutions are prefer performed with variable concentration of the target analyte ion (SO_4^{2-}) and a constant concentration of the interference [47]. Meanwhile, determination of selectivity coefficient by Matched Potential Method (MPM) has sensitive function of concentration of the interfering ion and in FIM the selectivity coefficients do not depend upon concentration substantially [48]. In this work, the concentration of the interfering ions (NO_3^-, Br^-, CH_3COO^-, I^-, Cl^-, SCN^-, ClO_4^-) was fixed at 10^{-2} M to measure the selectivity coefficients of sulfate. In Table 3, the selectivity coefficients of the electrode were compared to those reported before.

Noteworthy, this is just a gross relative comparison, since those selectivity data reported using inconsistent experimental methods such as MPM and separate solution method (SSM).

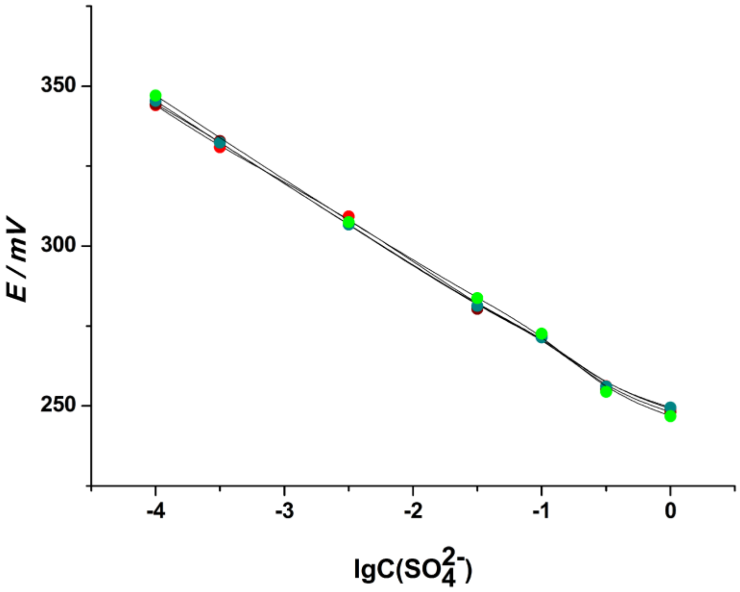

Figure 9. Reproducibility of the sulfate ISE based on H_2SO_4 doped PANI as a sensitive membrane.

Table 3. Comparison among the selectivity coefficients with previously published

Anion	[22]	[41]	[49]	[50]	[51]	[52]	This work
NO_3^-	-2.4	-0.6	2.9	-2.3	143	4.3	1.6
Br^-	-2.5	-2.5	2.2	-2.1	26.7	2.4	0.9
CH_3COO^-	-	-	-0.8	-	3.6×10^{-3}	-1.7	2.1
I^-	-2.5	3.4	-	-3.5	-	7.4	1.6
Cl^-	-2.4	-3.4	0.8	-2.3	0.43	-0.2	4.2
SCN^-	-3.8	3.1	-	-2.5	-	-	2.5
ClO_4^-	-3.1	5.9	-	-3.4	-	10.4	3.1

3.8 Analytical application

The fabricated sulfate sensor was found to perform well to determinate *in-situ* sulfate concentration in natural seawater. The sulfate concentration was measured with gravimetric method, direct potentiometry with the sulfate ISE and self-assembly electrochemical sensor. The detector part of this self-assembly sensor consist of a pH ISE, an Eh ISE, a CO_3^{2-} ISE, a solid-state Ag/AgCl reference electrode and this sulfate ISE. The integrated solid-state sulfate electrode in the self-assembly sensor was in a small size with 0.5 cm in length and 0.3 mm in diameter. The location of the self-assembly sensor placed was consistent with the position sampled.

The determination results were summarized in Table 4. It was shown that the *in-situ* sulfate concentration determined by the self-assembly sensor in sea trial was 1.89 g/L. The values determined by the direct potentiometry with the sulfate ISE were 1.91 g/L, 1.89 g/L and 1.87 g/L respectively, while those values were 1.93 g/L, 1.93 g/L and 1.91 g/L by gravimetric method. The recovery rates of the determination ranges from 97-98%, indicating that the sulfate in natural seawater can be measured with the sensor precisely.

Table 4. Results of sulfate determination in seawater by the self-assembly sensor, by direct potentiometry with the sulfate ISE and by gravimetric method

Sample no.	Self-assembly sensor (g/L)	Potentiometry (g/L)	Gravimetry (g/L)	Recovery (%)
1	1.89	1.91	1.93	98.96
2		1.89	1.93	97.92
3		1.87	1.91	97.91

4. CONCLUSIONS

A robust and ultrasensitive solid state sulfate selective-electrode, free of plasticizers, was prepared by electrochemical method with Au wire as the substrate coated H_2SO_4 doped PANI as the sensitive membrane. By doping PANI conjugated chain with sulfate, the covalent binding of sulfate-recognition sites to PANI backbone offers a better characteristic performance to sulfate. The electrode performs good potentiometric stability and fast response as 1 s attribute to its low impedance of 36 Ω, which could reduce the interference of electronic nose signals tremendously during practical application. Meanwhile, the proposed sulfate electrode behaves a Nernstian response (-26.22 mV/decade) toward sulfate in 10^{-4} M to 1 M Na_2SO_4 solutions made with freshly prepared 3.5% NaCl solution in the pH range of 5.5-8.5. The electrode is in miniature size and has been assembled as a sensor successfully for the determination of *in-situ* sulfate concentration in ocean, which contributes to solve the deficiencies and limitations of sulfate electrode existing. In addition, this sulfate electrode prepared could be convenient integrate with other electrodes as a multi-role electrochemical sensor to measure several chemical quantities simultaneously, possessing a huge substantial value and broad prospects in *in-situ* monitoring, such as ocean, lakes and sewage water.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China (Grant 41276092) and we extended thanks to the helps of Marine and Fisheries of Taizhou.

References

1. F. M. M. Morel, J. G. Hering, *Principles and Applications of Aquatic Chemistry*, Wiley, (1993) New York.
2. M. T. Hurtgen, *Science*, 337 (2012) 305.
3. U. G. Wortmann, A. Paytan, *Science*, 337 (2012) 334.

4. C. Hensen, M. Zabel, K. Pfeifer, T. Schwenk, S. Kasten, N. Riedinger, H. D. Schulz, A. Boetius, *Geochim. Cosmochim. Ac.*, 67 (2003) 2631.
5. C. Niewöhner, C. Hensen, S. Kasten, M. Zabel, H. D. Schulz, *Geochim. Cosmochim. Ac.,* 62 (1998) 455.
6. W. S. Borowski, C. K. Paull, W. Ussler Iii, *Mar. Geol*., 159 (1999) 131.
7. I. Halevy, S. E. Peters, W. W. Fischer, *Science,* 337 (2012) 331.
8. K. Krengcl-Rothensee, U. Richter, P. Heitland, *J. Anal. Atom. Spectrom.,* 14 (1999) 699.
9. M. R. Ganjali, A. Sepehri, A. Daftari, P. Norouzi, H. Pirelahi, A. Moradzadegan, *Microchim. Acta.,* 149 (2005) 245.
10. V. K. Gupta, A. Nayak, S. Agarwal, B. Singhal, *Comb. Chem. High Throughput Screening,* 14 (2011) 284.
11. E. Bakker, K. Chumbimuni-Torres, *J. Brazil. Chem. Soc.,* 19 (2008) 621.
12. A. S. A. Attas, *Int. J. Electrochem. Sci.*, 4 (2009) 9.
13. V. K. Gupta, R. N. Goyal, R. A. Sharma, *Int. J. Electrochem. Sci.,* 4 (2009) 156.
14. M. S. Frant, J. W. Ross, *Science,* 167 (1970) 987.
15. V. K. Gupta, R. N. Goyal, R. A. Sharma, *Electrochim. Acta.,* 54 (2009) 4216.
16. V. K. Gupta, L. P. Singh, R. Singh, S. Chandra, S. Kumar, B. Sethi, *Talanta,* 85 (2011) 970.
17. K. N. Mikhelson, *Ion-selective electrode*, Springer-Verlag, (2013) New York.
18. A. M. Othman, M. S. El-Shahawi, M. Abdel-Azeem, *Anal. Chim. Acta.,* 555 (2006) 322.
19. S. Firouzabadi, I. Razavipanah, R. Zhiani, M. Ghanei-Motlagh, M. R. Salavati, *Monatsh. Chem.,* 144 (2013) 113.
20. E. A. Assirey, *Desalin. Water. Treat*., 57 (2016) 3160.
21. M. R. Ganjali, L. Naji, T. Poursaberi, M. Taghizadeh, H. Pirelahi, M. Yousefi, A. Yeganeh-Faal, M. Shamsipur, *Talanta*, 58 (2002) 359.
22. A. Nezamzadeh-Ejhieh, A. Esmaeilian, *Micropor. Mesopor. Mat.*, 147 (2012) 302.
23. M. Shamsipur, M. Yousefi, M. R. Ganjali, T. Poursaberi, M. Faal-Rastgar, *Sensor. Actuat. B-Chem.,* 82 (2002) 105.
24. M. R. Ganjali, S. Shirvani-Arani, P. Nourozi, D. Salimzadeh, M. Faal-Rastegar, A. Moghimi, *Electroanal.*, 16 (2004) 1009.
25. Z.-Q. Li, G.-D. Liu, L.-M. Duan, G.-L. Shen, R.-Q. Yu, *Anal. Chim. Acta.,* 382 (1999) 165.
26. R. W. Cattrall, H. Freiser, *Anal. Chem.*, 43 (1971) 1905.
27. J. Bobacka, T. Alaviuhkola, V. Hietapelto, H. Koskinen, A. Lewenstam, M. Lamsa, J. Pursiainen, A. Ivaska, *Talanta,* 58 (2002) 341.
28. J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.,* 108 (2008) 329.
29. A. Shirmardi-Dezaki, M. Shamsipur, M. Akhond, H. Sharghi, *J. Electroana. Chem.,* 689 (2013) 63.
30. A. F. Yakuphanoglu, B. F. Şenkal, *J. Phys. Chem. C.,* 111 (2007) 1840.
31. M. R. Gizdavic-Nikolaidis, J. R. Bennett, S. Swift, A. J. Easteal, M. Ambrose, *Acta. Biomate.,* **7** (2011) 4204.
32. H. Ashassi-Sorkhabi, M. Es'Haghi, *J. Mater. Eng. Perform.,* 22 (2013) 3755.
33. A. H. Elsayed, M. M. Eldin, A. M. Elsyed, A. A. Elazm, E. M. Younes, H. A. Motaweh, *Int. J. Electrochem. Sci.,* 6 (2011) 206.
34. F. Z. Silveira, G. W. Duarte, C. G. Tachinski, R. Piletti, J. Fiori, M. Peterson, H. G. Riella, M. A. Fiori, *J. Appl. Polym. Sci.,* 128 (2013) 430.
35. F. Garnier, *Angew. Chem. Int. Edit.,* 1 (1989) 117.
36. A. Michalska, *Anal. Bioanal. Chem.,* 384 (2006) 391.
37. P. Buehlmann, E. Pretsch, E. Bakker, *J. Cheminformatics*, 98 (1998) 1593.
38. S. Lee, R. An, A. J. Hunt, *Nat. Nanotechnol.*, 5 (2010) 412.
39. C. Karl, *Working with Ion-Selective Electrodes,* Springer-Verlag, (1979) New York.
40. M. J. Berrocal, A. Cruz, I. H. Badr, L. G. Bachas, *Anal. Chem.*, 72 (2000) 5295.
41. Y. Liu, Y. Qin, D. Jiang, *Analyst,* 140 (2015) 5317.

42. V. K. Gupta, A. K. Jain, G. Maheshwari, *Talanta*, 72 (2007) 1469.
43. Eric Bakker, Ernö Pretsch, Philippe Bühlmann, *Anal. Chem.*, 72 (2000) 1127.
44. R. N. Goyal, V. K. Gupta, M. Oyama, N. Bachheti, *Talanta*, 72 (2007) 976.
45. A. K. Jain, V. K. Gupta, L. P. Singh, P. Srivastava, J. R. Raisoni, *Talanta*, 65 (2005) 716.
46. V. K. Gupta, S. Chandra, R. Mangla, *Electrochim. Acta.*, 47 (2002) 1579.
47. G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, J. D. R. Thomas, *Pure Appl. Chem.*, 48 (1976) 127.
48. V. K. Gupta, A. K. Singh, L. K. Kumawat, *Electrochim. Acta.*, 95 (2013) 132.
49. S. Nishizawa, P. Bühlmann, K. P. Xiao, Y. Umezawa, *Anal. Chem. Atca.*, 358 (1998) 35.
50. S. V. Lomako, R. I. Astapovich, O. V. Nozdrin-Plotnitskaya, T. E. Pavlova, S. Lei, V. A. Nazarov, E. B. Okaev, E. M. Rakhman'Ko, V. V. Egorov, *Anal. Chem. Atca.*, 562 (2006) 216.
51. B. Ballarin, M. Morigi, E. Scavetta, R. Seeber, D. Tonelli, *J. Electroanal. Chem.*, 492 (2000) 7.
52. M. Fibbioli, M. Berger, F. P. Schmidtchen, E. Pretsch, *Anal. Chem.*, 72 (2000) 156.