

Short Communication

## Solid-contact Polymeric Membrane Electrode for Real-Time Monitoring of Lead Adsorption

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This work demonstrates for the first time the application of solid-contact Pb<sup>2+</sup>-selective electrode in the adsorption study of Pb<sup>2+</sup> onto humic acid. Compared with other techniques, one advantage of the electrode is that it offers the possibility of real-time and continuous Pb<sup>2+</sup> monitoring. Results show that the potential stability, selectivity, and pH working range of the proposed electrode make it a convenient and promising tool for the investigation of Pb<sup>2+</sup> adsorption.

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**Keywords:** Ion-selective electrode; Solid contact; Lead; Adsorption

### 1. INTRODUCTION

Adsorption process plays a critical role in the migration and distribution, and appears to be a promising technique for the removal of these heavy metals [1, 2]. To accurately record the adsorption process, it is necessary to use a real-time technology for monitoring of concentration change. Adsorption experiments are usually carried out using batch approach, in which aliquot of the sample was taken and filtered at various time intervals, and then the adsorbate content is determined by standard analytical methods, such as atomic absorption spectrometry (AAS), anodic stripping voltammetry (ASV) and inductively coupled plasma mass spectrometry (ICP-MS). However, this approach, which is suitable in most cases, does not work when the adsorbents cannot be separated from the solution by filtration, and concentration change is inevitably prone to occur during the

filtration and/or storage before measurement. Moreover, these tests are time-consuming, thus cannot provide the adsorption information immediately and efficiently.

Ion-selective electrodes (ISEs) are in principle the appropriate techniques for real-time monitoring the heavy metals adsorption [3-7]. As simplest electrochemical sensors, ISEs have been widely used in clinical, environmental, and industrial analysis due to their simple analytical procedure and fast response. They do offer the possibility to distinguish between soluble and particulate-bound state without any previous separation procedure. In this way possible alterations in the physicochemical characteristics of the samples are avoided and thus the risk of contamination and/or losses of constituents minimizes.

In the past decade, the structure of ISEs has undergone huge changes from conventional configuration with inner reference solution to solid-contact ion-selective electrodes (SC-ISEs) [8-13]. In conventional ISEs, the ion-selective membrane is in electrical contact with the inner reference electrode through the inner solution, and these electrodes suffer from various drawbacks such as the inner filling solution drying out, electrode orientation, temperature variations and pressure range. Elimination of inner solution from the conventional arrangement has led to the development of SC-ISEs, in which a solid ion-to-electron transducer layer was introduced between the ion-selective membrane and the electronic substrate. Because of their intrinsic advantages of miniaturization, straightforward fabrication and maintenance-free, SC-ISEs are highly desirable for demanding applications such as online process analysis.

Among heavy metals that are particular hazardous to the environment, lead is a quite toxic one that can be found at elevated levels in several environmental compartments. In this work, lead adsorption onto humic acid was chosen as model system because it is very common in nature. A novel polymeric transducer, poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,7-diyl)] (F8BT), was used to construct SC-ISEs. To demonstrate the plausibility of real-time monitoring  $Pb^{2+}$  concentration by using the proposed electrodes, we assessed the electrode characteristics, such as working concentration range, response time, selectivity and long-term stability.

## 2. EXPERIMENTAL

### 2.1. Reagents

Poly (vinyl chloride) (PVC), 2-nitrophenyl octyl ether (o-NPOE), sodium tetrakis [3, 5-bis (trifluoromethyl)phenyl]borate (NaTFPB), and lead ionophore, tert-Butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide), were purchased from Sigma-Aldrich. F8BT was from Shanghai Hanshang Electronic Materials. Humic acid was from J&K Chemical. All other reagents used were of analytical-reagent grade from Sinopharm Chemical Reagent. Deionized water with specific resistance of 18.2 M $\Omega$ cm was obtained by a Pall Cascada laboratory water system.

## 2.2. $Pb^{2+}$ -Selective membrane and electrodes

The  $Pb^{2+}$ -selective membrane contained PVC, NPOE, ionophore, and NaTFPB. The membrane components (totaling 300 mg) were dissolved in THF (3.0 mL). 10~20  $\mu$ L polymeric transducer (F8BT) (5 mg/mL) was drop-casted on the Au substrate electrodes. After overnight evaporation of the solvent, the homogeneous  $Pb^{2+}$ -selective membrane cocktail was poured on the top of F8BT surrounded by PVC tubing. In order to achieve low limit of detection and high reproducibility, the fabricated SC-ISEs were conditioned in  $1.0 \times 10^{-3}$  mol/L  $Pb(NO_3)_2$  mixed with  $1.0 \times 10^{-4}$  mol/L  $HNO_3$  before use.

## 2.3. Real-time monitoring study

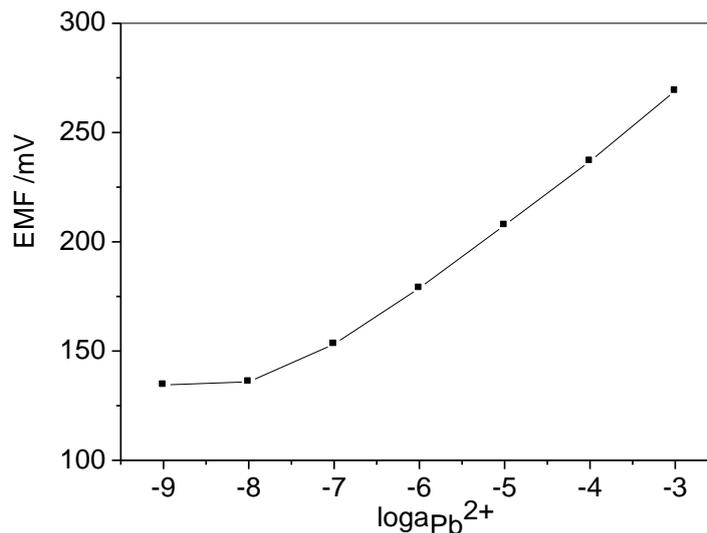
The experiments were conducted to see the effect of the amount of humic acid added under different pH on the adsorption quantity. Before monitoring the  $Pb^{2+}$  adsorption, calibration curves were taken in  $10^{-3}$  to  $10^{-9}$  mol  $L^{-1}$   $Pb(NO_3)_2$  with natural background level, including  $10^{-3}$  mol  $L^{-1}$   $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ . The adsorption were carried out using 500mL  $Pb(NO_3)_2$  solution at the fixed concentrations at room temperature under constant stirring at 200 rpm.  $Pb^{2+}$ -selective electrode and Hg/Hg<sub>2</sub>Cl<sub>2</sub> reference electrode were inserted into the solution, and the EMF was recorded every 5 seconds with a Model PXSJ-216 digital ion analyzer (Shanghai Leici Instruments Factory, China). The kinetics of the change in  $Pb^{2+}$  activity was calculated with the calibration curve.

# 3. RESULTS AND DISCUSSION

The use of conducting polymers as intermediate transducer in SC-ISEs has been extensively studied due to their commercially availability, ease of processing and fast electrochemical switching [14-18]. Here we evaluated the performance of  $Pb^{2+}$ -ISEs based on F8BT transducer.

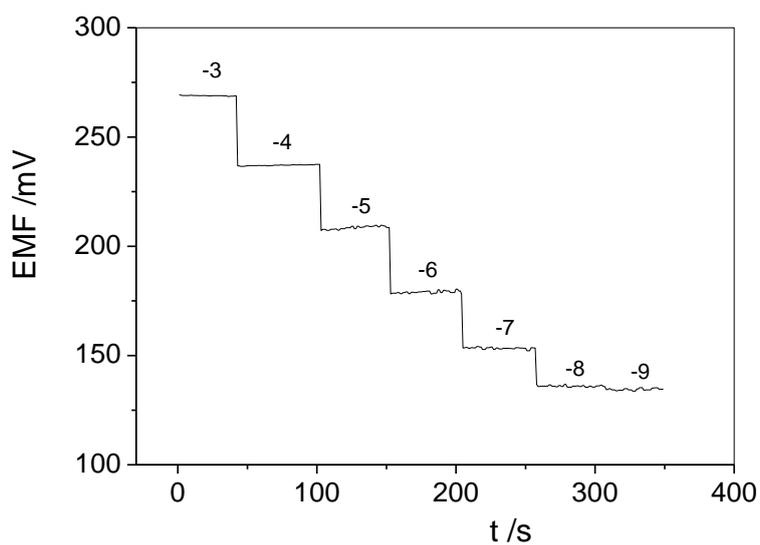
## 3.1. Potentiometric response

The calibration for the proposed  $Pb^{2+}$ -ISEs were performed at 20-21°C using a PXSJ-216 pH meter (Leici, Shanghai). The external reference electrode employed was a double-junction saturated calomel electrode (SCE) with 0.1 M LiOAc as a bridge electrolyte. The electromotive force (EMF) values were corrected for the liquid-junction potentials with the Henderson equation. The activity coefficient of ions was calculated from the modified Debye-Hückel equation. Fig. 1 indicates the solid-contact  $Pb^{2+}$ -ISEs showed a very good sensitivity towards lead ions, with slope of the calibration curve (30.1 mV/dec) close to that predicted theoretically (28.5 mV/dec) by the Nernst equation. The linear range of the proposed sensor is between  $1 \times 10^{-3}$  to  $1 \times 10^{-8}$  M. The detection limit was calculated as  $3 \times 10^{-8}$  M by extrapolating the linear parts of the calibration curve.



**Figure 1.** Calibration curve of the solid-contact  $Pb^{2+}$ -selective electrode.

3.2. Response time



**Figure 2.** Time traces of EMF response of the corresponding electrode.

Real-time monitoring system requires the use of ISEs with relatively short response times so that the ISEs can reach equilibrium in a short period of time. It has been demonstrated that the replacement of inner solution with solid transducer favors the response time of the electrode [19]. Fig. 2 represents the dynamic response of the solid-contact  $Pb^{2+}$ -ISEs based on F8BT. According to an IUPAC report on Definition and Determination of Response Time of Ion Selective Electrodes,

differential quotient response time is “the most satisfactory approach for the time being” [20]. By adopting this approach, the electrode required 10~15 s to achieve a steady state potential ( $\Delta E/\Delta t$ , less than  $0.2 \text{ mVmin}^{-1}$ ).

### 3.3. Selectivity

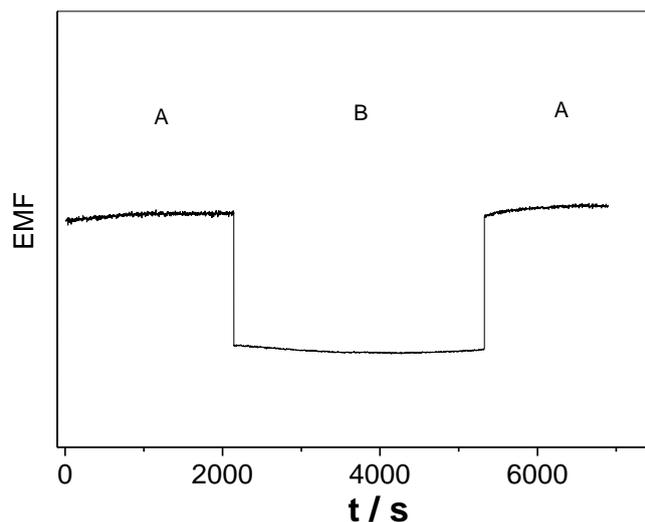
The most important parameter of any ISE is its response to the primary ion in the presence of other ions. Selectivities of ISE are quantitatively related to equilibria at the interface between the sample and the electrode membrane. The unbiased selectivity coefficients,  $K^{\text{pot}}_{Pb,J}$ , were determined by using the separate solution method (SSM) after the electrodes were conditioned in  $1 \times 10^{-3} \text{ M NaNO}_3$  for 12 h. The selectivity coefficients are illustrated in Table 1. These results indicate the proposed sensor is very selective to lead over all interfering ions ( $\log K^{\text{pot}}_{Pb,J} \leq -5$ ).

**Table 1.** Selectivity coefficients,  $\log K^{\text{pot}}_{Pb,J}$ , obtained with the F8BT-based solid-contact electrode.

Ion <i>J</i>	SC-ISE
$\text{K}^+$	$-5.1 \pm 0.2$
$\text{Na}^+$	$-6.2 \pm 0.3$
$\text{Ca}^{2+}$	$-8.5 \pm 0.5$
$\text{Mg}^{2+}$	$-9.0 \pm 0.5$
$\text{H}^+$	$-4.2 \pm 0.3$
$\text{Cd}^{2+}$	$-4.5 \pm 0.2$
$\text{Cu}^{2+}$	$-5.9 \pm 0.3$

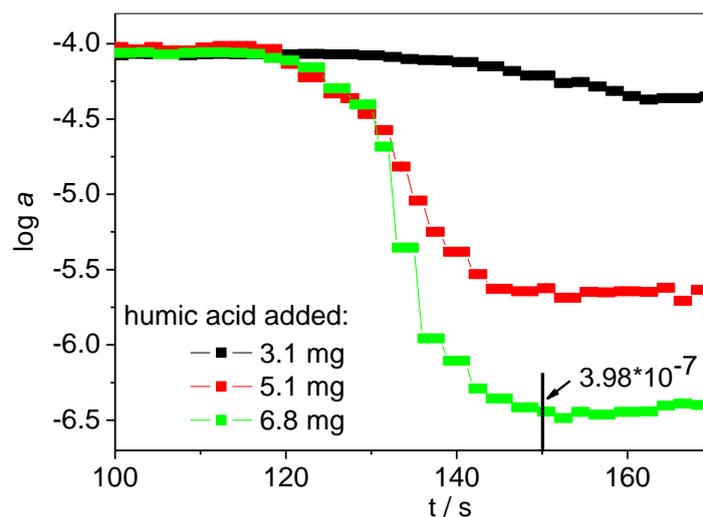
### 3.4. Long-term stability

The stability of the proposed electrodes was evaluated using water film test [21], potential signal was recorded first in a solution of the primary ions and then replaced with a solution of the interfering ions in solutions, and again in solution of primary ions. The results for the water film test are shown in Fig. 3, the electrode exhibits a stable potential response no obvious potential. Thus, it can be concluded that the undesirable water layer is successfully eliminated by the proposed electrode., indicating that undesirable water layer was eliminated in the sensor.



**Figure 3.** Water layer test of the fabricated  $\text{Pb}^{2+}$ -selective electrode performed by successively measuring the EMF responses of  $10^{-5}$  M  $\text{Pb}(\text{NO}_3)_2$ ,  $10^{-3}$  M  $\text{Cu}(\text{NO}_3)_2$  and again  $10^{-5}$  M  $\text{Pb}(\text{NO}_3)_2$ .

### 3.5. Real-time concentration monitoring



**Figure 4.** Real-time concentration change of  $\text{Pb}^{2+}$  with time monitored by the fabricated electrode.

$\text{Pb}^{2+}$  adsorption onto humic acid was investigated using the proposed solid-contact  $\text{Pb}^{2+}$ -selective electrode for real-time monitoring. Fig. 4 shows the change in concentration of  $\text{Pb}^{2+}$  in the aqueous solution with time. The initial metal ion concentrations were kept constant. The percentage of adsorption increased with increase in the humic acid added. The humic acid was intentionally added in

a large amount in order to prove that SC-ISEs are more suitable for real-time determination of adsorption kinetics. In batch adsorption tests, aliquots were usually taken from the suspension at the intervals of at least 2 minutes. In some cases, however, this timescale is too long to obtain detailed information about the kinetics of the system. As shown in the inset of Fig. 4, the  $\text{Pb}^{2+}$  adsorption reaches equilibrium within 2 min. By using the proposed SC-ISEs, the whole adsorption process, especially at the very beginning was recorded successfully. The signal fluctuation is due to the instability in the adsorption system.

#### 4. CONCLUSIONS

In this work, a new solid-contact  $\text{Pb}^{2+}$ -selective electrode was constructed and successfully employed to collect highly resolved data of  $\text{Pb}^{2+}$  adsorption process in real-time. This sensor exhibited a fast response time, good selectivity, and a low detection limit of  $3 \times 10^{-8}$  M. It was noteworthy that the new SC-ISEs can be built easily at low cost, and they are reliable and maintenance-free, having fewer limitations in temperature and pressure ranges than conventional ISEs.

#### ACKNOWLEDGEMENTS

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