



Short communication

Improved potentiometric response of all-solid-state Pb^{2+} -selective electrodeShunyang Yu ^{a,*}, Qun Yuan ^{a,b}, Fuhai Li ^{a,b}, Yongming Liu ^b^a Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, YICCAS, Yantai, Shandong 264003, PR China^b Chemistry and Chemical Engineering College, Yantai University, Yantai 264005, China

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ABSTRACT

Zero-current ion-flux has a great influence on the characteristics of the ion-selective electrodes. In this work the improvement of analytical performance of all-solid-state Pb^{2+} -selective membrane electrodes was demonstrated by adjusting the transmembrane ion flux. The study is focused on the relationship between the conditioning solution and the linear working range of the obtained electrodes for different sample matrixes. Results show that the electrode with appropriate conditioning keeps good reproducibility within linear working range. The utility of the electrode has been tested by successfully determining Pb^{2+} concentration in real water samples.

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1. Introduction

The technology of ion-selective electrodes (ISEs) has advanced greatly over the past decades [1–3]. This has been achieved mainly by reducing zero-current transmembrane ion flux effects with ISEs having a liquid internal contact [4,5]. Recently there has been a surge in the application of solid ion-to-electron transducers to replace the troublesome inner solution in conventional configuration [6–9]. From a practical application point of view, the all-solid-state ISEs thus obtained are of special interest in the field of potentiometric sensors because they are free from some limitations resulting from the presence of the inner reference solution, including the need to work in a vertical position, and maintenance requirement [10,11].

Although the coextraction process from the inner solution can be largely eliminated by the use of solid ion-to-electron transducers, transmembrane ion flux still occurs in all-solid-state ISEs similarly as observed for conventional inner solution electrodes [12–14]. As a result, the observed lower detection limit was not an intrinsic property of the electrodes but a consequence of the many parameters, such as the type of conducting polymer ion-to-electron transducer, the conditioning procedure [15–17], or the presence of interfering ions in the sample [18]. Investigating the relationship between the above parameters and the analytical characteristics of all-solid-state ISEs is fundamental to the improvement of the electrodes.

Conducting polymers are promising materials for a large variety of chemical sensors. They could act as ion-to-electron

transducers in all-solid-state ISEs for their mixed electronic and ionic conductivity and ease of processing [19–22]. More recently, we have described for the first time a novel solid transducer based on a thiophene oligomer, α, ω -dihexylsexithiophene, for the construction of all-solid-state ISEs [23]. In the present work, we investigate the influence of conditioning procedure and sample composition on the potentiometric response of the electrodes based on this transducer. The main objective of this work is to provide a procedure for the development of all-solid-state Pb^{2+} -selective electrode with good reproducibility for different sample matrixes.

2. Experimental

2.1. Reagents

Poly (vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), sodium tetrakis [3, 5-bis (trifluoromethyl)phenyl]borate (NaTFPB), the lead ionophore, tert-Butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) and α, ω -dihexylsexithiophene (DH-6T), were purchased from Sigma-Aldrich. Tetrahydrofuran (THF), chlorobenzene, $\text{Pb}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and other materials were purchased from Sinopharm Chemical Reagent and were of analytical-reagent grade. Deionized water with specific resistance of 18.2 M Ω cm was obtained by a Pall Cascada laboratory water system.

2.2. Ion-selective membranes and electrodes

The membrane was composed of 32.8 wt% PVC, 65 wt% DOS, 1.5 wt% ionophore, and 0.7 wt% NaTFPB. The membrane solution was prepared by dissolving 200 mg of the membrane components

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in 2.0 mL of THF. Au disk electrodes were used as conducting substrates. Before use they were polished with 0.3 μm alumina, rinsed with water and methylene chloride. DH-6T was applied on the Au discs by drop-casting 10–20 μL of a 50 mg/mL solution in chlorobenzene, and dried for at least 10 min. The electrode was then introduced into a fitting PVC tube at a depth of 1 mm, allowing the casting of 100 μL of membrane cocktail on the top of DH-6T layer, and left to dry for 1 h at room temperature.

The obtained all-solid-state electrodes were conditioned for 24 h. Three different conditioning solutions were used. They consisted of 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$ (ISE A), 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$ mixed with 1.0×10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$ (ISE B), and 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$ mixed with 1.0×10^{-4} mol/L HNO_3 (ISE C).

2.3. Potentiometric measurements

Membrane potentials were performed using a Model PXSJ-216 digital ion analyzer (Shanghai Leici Instruments Factory, China) in magnetically stirred solution at room temperature in the galvanic cell. $\text{Hg}/\text{Hg}_2\text{Cl}_2$ with double junction was used as reference electrode with 1.0 M LiOAc as salt bridge electrolyte. Activity coefficients were calculated according to the Debye–Hückel approximation and electromotive force (EMF) values were corrected for liquid-junction potentials with the Henderson equation.

Potential vs. logarithm of activity dependences were recorded in $\text{Pb}(\text{NO}_3)_2$ solutions (I); $\text{Pb}(\text{NO}_3)_2$ solutions with the background of 1.0×10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$ (II); and $\text{Pb}(\text{NO}_3)_2$ solutions with 1.0×10^{-4} mol/L HNO_3 background (III). Water samples from Sanyuan Lake in Yantai were first filtered through a standard 0.45 μm filter, and then treated with online UV digestion using a 1000 W UV lamp (Hanovia Ltd.) for release of the Pb^{2+} from the lead organic complexes. The analysis was carried out by direct potentiometry using standard addition method after acidification of the samples to pH 4.

3. Results and discussion

The response of the obtained all-solid-state ISEs in $\text{Pb}(\text{NO}_3)_2$ solutions (I) are presented in Fig. 1. ISE A is characterized with linear responses within the Pb^{2+} activities range from 10^{-2} to 10^{-6} mol/L, with a slope of 28.5 ± 0.5 mV/dec ($R^2=0.998$) and detection limit reaching 1.0×10^{-6} mol/L. For Pb^{2+} activities lower than 1.0×10^{-6} mol/L, an abrupt potential decrease is observed

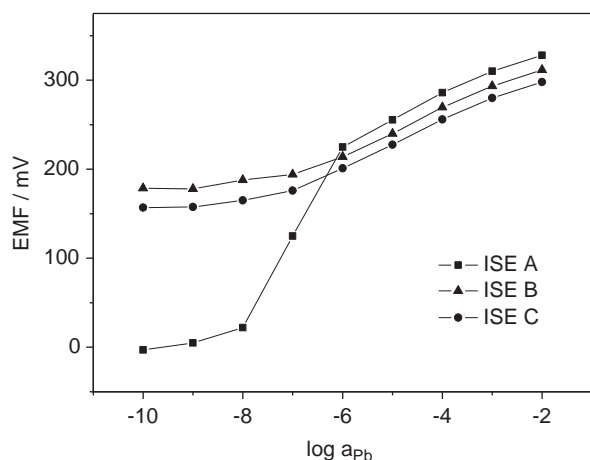


Fig. 1. Potential vs. logarithm of activity dependences of the obtained all-solid-state Pb^{2+} -selective electrodes in (I) $\text{Pb}(\text{NO}_3)_2$ solutions.

pointing to super-Nernstian behavior of the electrode. The abrupt potential decrease is attributed to a continuous Pb^{2+} ion accumulation in the DH-6T layer, resulting in a much lower concentration compared with the bulk sample solution.

Relatively low detection limits are achieved for the electrodes conditioned in 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$ mixed with interfering ions (ISE B and C). This is in agreement with previous report that interferent present in the transducer phase exerts a favorable influence on the linear working range and detection limit of the all-solid-state electrodes [24]. The linear responses of ISE B and C are obtained within the range from 10^{-2} to 10^{-7} M with the slope of 28.1 ± 0.4 mV/dec ($R^2=0.999$), and 10^{-2} to 10^{-8} M with the slope of 28.4 ± 0.4 mV/dec ($R^2=0.999$). The detection limit was close to 3.16×10^{-7} and 2.57×10^{-8} mol/L, respectively. The low detection limits of ISE B and C are attributed to the role of the interfering ions in achieving balanced transport through the ion-selective membrane phase. The interfering ions chosen at the inner side of the ion-selective membrane are hydrogen or calcium ions introduced into the DH-6T layer via conditioning process.

Under favorable conditions, when analyte ions are in relatively dilute aqueous solutions and where interfering ions are not a problem, the obtained ISE A, B, and C can be used very rapidly and easily. However, in most applications where interfering ions, pH levels, or high concentrations are a problem, the potentiometric response of electrodes may be different. It can be seen from Fig. 2 that ISE C exhibits high reproducibility in the whole working range from 10^{-2} to 10^{-8} mol/L, whereas ISE A and B are strongly affected by the ionic background of the sample below 10^{-6} mol/L. The concentrations at the outer sensing membrane surface layer depend on the sample composition and the concentration gradients in the membrane may change after contacting sample [4]. From a practical point of view, ISE C is more preferred because it works in the same way as the background composition of samples differs from one another.

It is well established that the zero-current transmembrane ion fluxes dictate the response behavior [4], and therefore any measure to make fluxes as small as possible is helpful to improve the analytical characteristics of sensors. The ion fluxes are due to the concentration gradient that originates in the coextraction of primary ions and their counterions from the inner solution into the sensing membrane and/or the exchange of primary ions by interfering ones on both sides of the membrane. In general, the backfilling solution of conventional ion-selective electrode membranes consists of the primary ion salt solution in a moderately high concentration, and coextraction of such a salt into the membrane always occurs to some extent. As for the all-solid-state ISEs, even though the conditioning is coupled with spontaneous charging/discharging leading to accumulation of primary ions and/or interfering ions in the transducer phase [17], the concentration bias is insufficient to lead to a coextraction flux. The mechanism of transmembrane ion fluxes for the all-solid-state ISEs is the exchange of primary ions by interfering ones on both sides of the membrane.

Schematic view of the process is presented in Fig. 3. Partial exchange of primary ions from the sensing membrane with interfering cations from the sample results in a counter-diffusion process and a flux of primary ions in the direction of the sample solution. On the other hand, the exchange of primary ions from the sensing membrane with interfering cations from the solid transducer phase leads to a counter-diffusion process and a flux of primary ions in the direction of the solid transducer. Since an outward flux inevitably occurs on contacting the sample solution, optimized ion exchange on the inner transducer side may counterbalance the outward flux and prevent primary ions from leaching into the sample by building up an inward concentration gradient in the membrane.

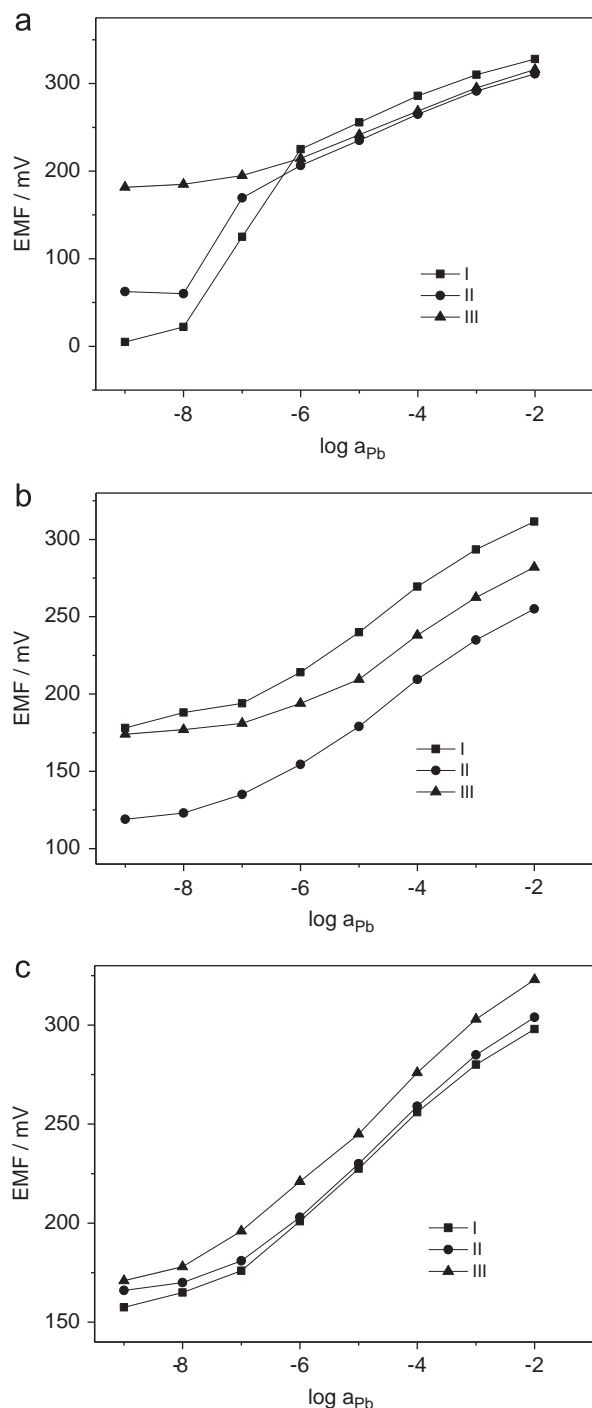


Fig. 2. Potentiometric response of the all-solid-state Pb^{2+} -selective electrodes in different matrixes: (a) ISE A, (b) ISE B, (c) ISE C.

In the case of ISE A, the exchange of Pb^{2+} in the sensing membrane with interfering H^+ from the sample counterbalances the Pb^{2+} ion accumulation towards DH-6T layer, and as a result, the super-Nernstian behavior diminishes in $Pb(NO_3)_2$ solutions with 10^{-4} mol/L HNO_3 background (III), and a low detection limit, 3.41×10^{-7} mol/L, was obtained. On the other hand, in $Pb(NO_3)_2$ solutions with the background of 10^{-3} mol/L $Ca(NO_3)_2$ (II), the counterbalance effect by partial exchange of Ca^{2+} on the sample side of the sensing membrane eliminated the super-Nernstian from 10^{-6} to 10^{-7} mol/L, but abrupt potential decrease was still observed from 10^{-7} to 10^{-8} mol/L. The selectivity coefficients of the obtained Pb^{2+} -selective ISEs determined by Separate Solution

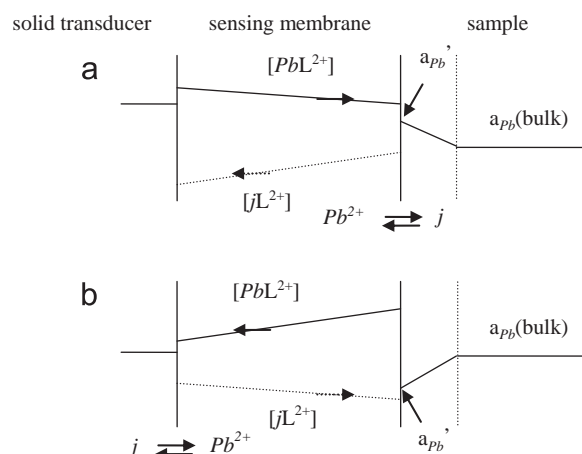


Fig. 3. Schematic representation of the influence of ion flux on the primary ion activity in the aqueous boundary layer of sensing membrane. (a) Partial exchange of primary ions by interfering ones at the sample side, and (b) exchange at inner transducer side.

Table 1
Determination of lead ion in real sample ($n=3$).

Samples	SC-ISE/ 10^{-7} M ^a	AAS/ 10^{-7} M ^a
1	7.75 ± 0.07	7.13 ± 0.02
2	6.96 ± 0.08	6.21 ± 0.02
3	7.47 ± 0.06	7.78 ± 0.03

^a Average value of three determinations \pm standard deviation.

Methods (SSM) were: $\log K_{Pb,H}^{pot} = -4.5$, $K_{Pb,Ca}^{pot} = -12.1$. Therefore stronger flux-counterbalance effect of H^+ is due to a larger amount of H^+ than Ca^{2+} engaged in exchange process. Despite bad reproducibility below 10^{-6} mol/L, ISE A showed good reproducibility from 10^{-2} to 10^{-6} mol/L.

For ISE B, good reproducibility in $Pb(NO_3)_2$ solutions (I) and $Pb(NO_3)_2$ solutions with the background of 10^{-3} mol/L $Ca(NO_3)_2$ (II) was observed with a linear responses from 10^{-2} to 10^{-7} mol/L, with a slope of 28.1 ± 0.4 mV/dec ($R^2=0.999$). However, in $Pb(NO_3)_2$ solutions with 10^{-4} mol/L HNO_3 background (III) with strong interfering background, the exchange of Pb^{2+} in the sensing membrane with interfering H^+ from the sample prevails, and an outward Pb^{2+} flux is induced, maintaining a local ion activity of as high as ca. 10^{-6} mol/L in the sample layer at the ion-selective membrane surface. As a consequence, the electrode showed sub-Nernstian behavior from 10^{-5} to 10^{-7} mol/L, and was insensitive to the sample activity changes for Pb^{2+} concentration lower than 10^{-7} mol/L.

Compared with many other analytical techniques, all-solid-state ISEs are relatively inexpensive and simple to use. In order to illustrate its accuracy in practical analysis, the comparison between the ISE C and atomic absorption spectrometry (AAS) for determining the concentration of Pb^{2+} in real samples was carried out. The results are shown in Table 1. It can be seen that the proposed electrode has a great potential for real sample analysis with high accuracy and good reliability.

4. Conclusions

Conditioning solution and sample composition were found to influence the transmembrane ion-flux, and consequently the linear working range and detection limit of the obtained all-solid-state Pb^{2+} -selective ISEs. By appropriate conditioning the electrode, the lower detection limit, and more importantly the reproducibility at

different backgrounds may be greatly improved. This effect is mainly attributed to the balanced transport through the ion-selective membrane phase by partial exchange of primary ions with interfering ions. The simple approach is of interest for real sample measurement.

Acknowledgments

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