

Short Communication

Preparation of Planar Ion-Selective Electrode Based on Conjugated Thiophene Oligomer

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Ion-selective electrodes (ISEs) are the most common electrochemical sensors in environmental and clinical analysis. However, many challenges still remain to reduce the size and cost of the electrodes for a larger scale application. In this study, a novel planar ion-selective electrode using α , ω -dihexylsexithiophene (DH6T) as the ion-to-electron transducer was developed with small size and low cost. The new electrode exhibited a response of 29.7 mV/dec and a low detection limit of 7.2×10^{-8} mol/L. Moreover, the fabricated planar electrode has wide linear range, quick response and enhanced stability.

Keywords: Ion-selective electrodes; Planar; Lead; Oligomer

1. INTRODUCTION

Solid-contact ion-selective electrodes (SC-ISEs) have sparked more and more interest over the past ten years and the research has opened up a large application area of potentiometric analysis. For SC-ISEs, an ion-to-electron transducer is added to replace conventional internal filling solution, and consequently they are released from some limitations owing to the presence of the internal solution, such as electrode orientation and maintenance requirement of internal solution. Until now, a large variety of materials, such as conducting polymers (CPs) [1,2], carbon materials [3,4], and redox-active monolayers [5] have been used as ion-to-electron transducers to obtain thermodynamically defined electrochemical interfaces.

So far, SC-ISEs are comparable or superior to the state of the art conventional electrodes with optimized internal filling solution. For large-scale applications, however, the cost of all-solid-state electrodes can be limitations [6], and the miniaturization of potentiometric systems is greatly needed. In pursuing these goals, screen-printed electrodes was applied as substrate instead of conventional substrate electrodes, such as gold, platinum disc or glassy carbon [7-9]. Screen-printed SC-ISEs were first reported in 1995 [10], and from then on, screen-printed ion-selective electrodes have been reported for environmental [11-13] and clinical applications [14,15].

In recent years, we have fabricated several all-solid-state PVC membrane electrodes based on α , ω -dihexylsexithiophene (DH6T) [16,17], poly (2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV) [18], thieno[3,2-b]thiophene (LCPT) [19], and poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,7-diyl)] (F8BT) [20] etc. This paper was an extension of our research on ion-to-electron transducer, and a planar Pb^{2+} electrode was prepared based on screen-printed Ag substrate. DH6T was used as the ion-to-electron transfer between the screen-printed substrate and ion-selective PVC membrane. This proposed electrode is demonstrated to be sufficiently sensitive, selective and reliable.

2. EXPERIMENTAL

2.1. Reagents

o-nitrophenyl octyl ether (*o*-NPOE), high molecular weight poly(vinyl chloride) (PVC), sodium tetrakis(4-chlorophenyl)borate (NaTCIPB), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH500), α , ω -dihexylsexithiophene (DH6T), and the lead ionophore, tert-butylcalix arene-tetrakis(N,N-dimethylthioacetamide) (all from Fluka) were used as received. All other reagents were purchased from Sinopharm Chemical Reagent and were of the highest purity. Distilled, deionized water was used to prepare all solutions.

2.2. Ion-selective membranes and electrodes

Membrane solutions were prepared by thoroughly dissolving 300 mg of 65.0 wt% *o*-NPOE, 32.0 wt% PVC matrix, 1.1 wt% tert-butylcalix arene-tetrakis(N,N-dimethylthioacetamide), 0.6 wt% NaTCIPB and 1.3 wt% ETH 500 in 3.0 ml of THF. 50 mg/mL DH6T in chlorobenzene were made for use.

Screen-printed Ag electrodes were used as conducting substrates for the electrodes. 20~50 μL of DH6T transducer was drop-casted on the screen-printed Ag electrode, and then dried for 3 hr. Finally 100 μL of membrane cocktail was cast on the top of DH6T, and dried for at room temperature ($22\pm 1^\circ\text{C}$).

2.3. Potentiometric measurements

All the measurements were carried out using a Model PXSJ-216 digital ion analyzer (Shanghai Leici Instruments Factory, China) at room temperature ($22\pm 1^\circ\text{C}$). Sample solutions were prepared by sequential dilution of a stock solution of 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$. The double junction $\text{Hg}/\text{Hg}_2\text{Cl}_2$ was used as a reference with 1 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. For the measurements in dilute solutions, the electrodes were conditioned in 1.0×10^{-3} mol/L $\text{Pb}(\text{NO}_3)_2$ for 2 days and then in 1.0×10^{-9} mol/L $\text{Pb}(\text{NO}_3)_2$ 1 day before measurements and were kept in 1.0×10^{-9} mol/L $\text{Pb}(\text{NO}_3)_2$ solution when not in use.

3. RESULTS AND DISCUSSION

Thiophene-based π -conjugated systems have attracted researchers' extensive attention as intermediate transducer in SC-ISEs because they are ion-to-electron transductive, and commercially available. Here we evaluated the performance of screen-printed Pb^{2+} -ISEs based on DH6T transducer. DH6T is a conjugated hexyl-substituted thiophene oligomer, and the hexyl side chains increase solubility. It is chemically and electrically stable in air [21]. On the one hand, the strong aggregation among thiophene units is favorable for the formation of π -dimers, which makes DH6T a high-mobility semiconductor. On the other hand, ions can diffuse in or out of the oligomer through chemical doping. Thus, DH6T is supposed to be an effective ion-to-electron transducer for the preparation of all-solid-state ISEs.

There are three practical considerations with ISE measurements that must be taken into account, including the linear range, selectivity, and lifetime.

3.1. Potentiometric response

Figure 1 shows the calibration plot of the fabricated electrode.

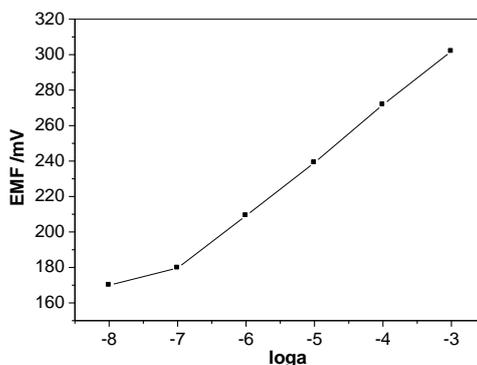


Figure 1. Calibration plot of the proposed planar Pb^{2+} electrode.

The potential values of the electrode response was studied within the activity range of 1.0×10^{-3} - 1.0×10^{-9} mol/L. Linear response was obtained within the activity range from 1.0×10^{-3} to 2.5×10^{-8} mol/L. The slope of the calibration plot was 29.7 mV/dec approach Nernstian (28.5 mV/dec). The low detection limit (the intersection of the Nernstian and sub-Nernstian lines) was 7.2×10^{-8} mol/L. In the Pb^{2+} -selective electrode, the selective membrane phase contains a high concentration of Pb^{2+} -ionophore complex, usually on the order of \sim mmol/L [22]. In that case, the trans-membrane ion flux could make Pb^{2+} ions enriched in the boundary layer. The proposed planar Pb^{2+} electrode was insensitive to the sample activity changes for the activity less than 1.0×10^{-8} mol/L.

Response time was defined by the time required when the potential drift is less than 0.5 mV/min after dilution. The absence of internal filling solution favors the response time. In the activity range from 1.0×10^{-3} to 1.0×10^{-7} mol/L, the new EMF value was stable after 10~15 s after successive dilutions.

3.2. Selectivity

The response to the main ions in the solution containing different interfering ions, that is, the selectivity of ion-selective electrode is one of the most important measurement parameters [23]. Selectivity of ISE is quantitatively related to equilibria at the interface between the ion-selective membrane and the sample. Bakker's separate solution method was used to determine the unbiased selectivity coefficients, $K^{\text{pot}}_{\text{Pb},J}$, after the electrodes were conditioned in 1×10^{-3} mol/L NaNO_3 for 12 hr. The selectivity coefficients of the planar Pb^{2+} electrode are illustrated in Table 1.

Table 1. Selectivity coefficients, $\log K^{\text{pot}}_{\text{Pb},J}$, of the DH6T-based planar electrode.

Ion <i>J</i>	Pb^{2+} -ISE
K^+	-5.7 ± 0.2
Na^+	-6.5 ± 0.1
Ca^{2+}	-9.5 ± 0.5
Mg^{2+}	-10.5 ± 0.5
H^+	-5.4 ± 0.2
Cu^{2+}	-4.2 ± 0.2
Cd^{2+}	-5.5 ± 0.2

These results showed the screen-printed Pb^{2+} -ISE based on DH6T transducer gave good $\log K^{\text{pot}}_{\text{Pb},J}$ towards the examined interfering ions.

3.3. Lifetime

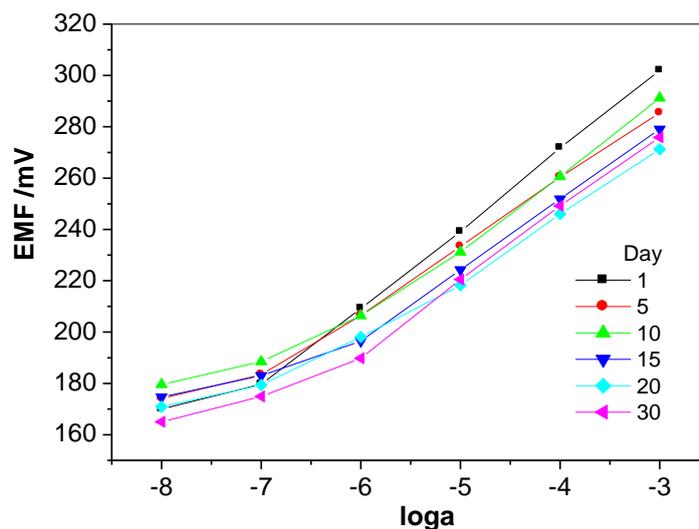


Figure 2. Potential stability of the DH6T-based planar Pb^{2+} electrode.

The potential stability of the proposed planar Pb^{2+} electrodes based on DH6T transducer was studied in term of reproducibility for long-term measurements. The calibration curves of the proposed electrode obtained by periodically measured in $\text{Pb}(\text{NO}_3)_2$ solution of 1×10^{-3} to 1×10^{-8} mol/L were presented in Figure 2. The electrodes were stored in 10^{-9} mol/L $\text{Pb}(\text{NO}_3)_2$ solution between measurements. The potential drift was less than 1mV within 24 hr, and less than 10% in 30 days, demonstrating a strong stability of the electrodes. That could be contributed to the introduction of DH6T, which affords effective ion-to-electron transduction, and stable interface as well.

4. CONCLUSIONS

We have shown an all-solid-state planar Pb^{2+} -selective electrode made from α , ω -dihexylsexithiophene (DH6T) transducer on screen-printed substrate. Besides basic parameters, the electrode exhibited many other advantages, such as cost effectiveness, simplicity, and easy to miniaturize. DH6T was proved to be a good choice for the fabrication of planar ISEs, as well as SC-ISEs we have shown before.

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