A Solid-contact Pb^{2+} -selective Electrode with Carbon Nanotubes by Electrodeposition as Ion-to-electron Transducer

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ABSTRACT

A novel all-solid-state polymeric membrane Pb^{2+} -selective electrode was developed by electrodepositing the CNTs films on the glassy carbon (GC) electrode, and characterized by electrochemical impedance spectroscopy (EIS), chronopotentiometry, and water layer test. The results showed that the electrodeposited CNTs films formed a well interconnected spaghetti-like structure on the GC substrates and increased the low-frequency capacitance of electrode from the EIS curves. The electrode has excellent ion-to-electron transducing ability, showing a Nernstian response of 29.0 mV per decade in the Pb^{2+} concentrations range of 10^{-3} – 10^{-8} M. No water film was observed on the surface of the electrode for long-term measurements. The research demonstrated a new strategy for the fabrication of robust potentiometric ion sensors.

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1. Introduction

The Ion-selective electrodes with a solid-contact configuration (SC-ISEs) have made very rapid progress over the past decades, and were widely utilized in medical, environmental, and industrial analysis.^{1–3} Owing to the intrinsic advantages of easy preparation, fast response, and no risk of solution leakage,^{4,5} SC-ISEs are expected to improve the electrode characteristics, compared with conventional electrodes with a liquid contact. In order to improve the potential instability and irreproducibility of SC-ISEs, different novel materials between electrode support and ion-selective polymeric membrane have been investigated, such as redox-active monolayers,⁶ carbon materials,^{7–11} and conducting polymers (CPs),¹² etc.

To obtain the satisfactory performance of SC-ISEs, good adhesion with matrix polymer, high chemical stability, and proper ion to electron transduction must be met for the inner contact materials. Carbon nanotubes (CNTs) as solid-contact in the Ion-selective electrodes have several outstanding properties, which have been widely studied as a key element in electromechanical actuators,^{13,14} super capacitors,^{15,16} batteries¹⁷ and electrochemical sensors.^{18–20} Though CNTs have been tested as transducers in potentiometric analysis, many investigations were focused on the development of new methods for the fabrication of CNTs conductive layer. Spraying is widely used to make layers of CNTs. However, this method is time-consuming, poor adhesion with the matrix, and not suitable for large area substrate processing.^{21,22} There is a need in the development of simple and versatile techniques for large area applications. Comparing with spraying method, electrodeposition showed many advantages of film uniformity, rigid control of film thickness and deposition rate, firmly bonded with the substrate, etc.

In this paper, the SC-ISE was fabricated by electrodepositing the CNTs film on the glassy carbon (GC) substrate, and the electrology characteristics were tested. 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. In addition, the stability of all-solid-contact electrode and the influence of the interfacial water layer were presented.

2. Experimental Methods

2.1 Reagents

The reagents with Poly vinyl chloride (PVC), 2-nitrophenyl octyl ether (o-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and the lead ionophore, tert-butylcalix arene-tetrakis (N,N-dimethylthioacetamide) were supplied by Sigma-Aldrich. Single-walled carbon nanotubes (SWCNTs) were purchased from XFNANO Materials Tech. Co. All other reagents were purchased from Sinopharm Chemical Reagent. Deionized water with specific resistance of 18.2 MΩ cm was obtained by a Pall Cascada Laboratory Water System.

2.2 Ion-selective membranes and electrode

The working SC-ISE was prepared by electrodepositing the CNTs on the distal end of GC rod. Firstly, Purified CNTs were dispersed in the solution of 100 mg of sodium dodecyl sulfate (SDS) and ultrasonicated for 4 h to produce a uniform suspension. 10 mg $\text{Mg}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was added into the suspension to increase the deposition rate and improve the adhesion of the powder particles to substrate. Then, the polished and well-rinsed GC disk electrode with the area of 0.07 cm² was used as substrate, connecting to the positive potential, and the cathode was the platinum electrode. Two electrodes were parallel kept at the distance of 2 cm in the suspension, and DC electric voltage of 40 V was applied. After deposition the as-deposited CNTs film electrode was washed with methanol to remove excess dispersed materials and dried in the air at 60°C for 2 h. As the CNTs film was dry, a piece of PVC tube was put on the tip of GC electrode [4], as shown in Fig. 1. Finally, 100 μL of ion selective membrane cocktail consisting of 37 wt% PVC, 61 wt% o-NPOE, 1.3 wt% lead ionophore and 0.7 wt% NaTFPB dissolved in the THF was cast on the top of CNTs film surrounded by the PVC tube. Among them, lead ionophore in the polymeric membrane selectively extracts lead ions into the organic membrane phase via the coordination interaction. The structure of the lead ionophore was shown in Fig. 2. NaTFPB can decrease the membrane resistance, reduce anion interference and improve selectivity of the electrode. The plasticizer, o-NPOE, the membrane solvent, not only dissolves ionophore and ion-exchanger and gives a homogeneous organic phase but also influences the dielectric constant of the membrane

Figure 1. (Color online) Scheme of solid-contact electrode with a layer of CNTs.

Figure 2. The structure of the lead ionophore.

phase and the mobility of the ligands and their complexes. PVC is used as the membrane matrix, which provides for mechanical stability and elasticity. The electrode was dried for 1 h at room temperature.

2.3 Electrochemical tests

Membrane potential was measured with a Model PXSJ-216 digital ion analyzer (Shanghai Leici Instruments Factory, China) in the magnetically-stirred galvanic cell at room temperature. Hg/Hg₂Cl₂ was used for reference electrode with saturated KCl (3 M) as inner filling solution and 1 M LiOAc solution as salt bridge electrolyte. Potentials were measured with a custom-made 16-channel electrode monitor at room temperature (20–21°C) in stirred solutions with a pH of 4 in the galvanic cell: SCE/1 M LiOAc/sample solution/ISE membrane/CNT layer/GCE as shown in Fig. 3. The detection background for Pb²⁺ solution contains 1.0×10^{-3} M CaCl₂ and 1.0×10^{-4} M HNO₃ in order to keep the ionic strength of the solutions constant. The electrode was immersed in the 1.0×10^{-3} M Pb(NO₃)₂ solution for 12 h and then in the 1.0×10^{-9} M Pb(NO₃)₂ solution for 2 days. After immersion, the potentiometric property was tested in the different concentration of Pb(NO₃)₂ solutions that had the background of 1.0×10^{-2} M NaCl.²³ Pb²⁺ ion pretreatment is essential for condition the membrane, which can assure the Pb²⁺ ion activity constant in the membrane phase. Potentiometric detection for Pb²⁺ solution with different concentrations was not only achieved in a cell. After measurement of one solution, the electrode was transferred into another solution. The proposed solutions were prepared by stepwise dilution of the stock solution.

Figure 3. The electrochemical cell.

Figure 4. SEM image of electrode surface, showing an entangled network of CNTs.

Chronopotentiometry was measured on the solid-contact Pb²⁺-ISE by applying a constant current of +1 nA for 60 s, following by −1 nA for 60 s in 1.0×10^{-1} M Pb(NO₃)₂ solution. Chronopotentiometry and electrochemical impedance spectroscopy (EIS) were performed by CHI660C Electrochemical Workstation (Shanghai Chenhua Instruments Company, China) with an Ag/AgCl/3 M KCl as reference electrode and the area of platinum plate is 0.07 cm² as counter electrodes in the deaerated 1.0×10^{-1} M Pb(NO₃)₂ solution. EIS data were recorded at open circuit potential with an AC amplitude of 100 mV and a frequency range of 100 kHz to 10 MHz.²³

3. Results and Discussion

Taking advantage of the material compatibility between the GC and CNTs, a layer of about 30 μm thick network of CNTs was electrodeposited onto the distal end of the polished GC rod. The SEM image of the CNTs films is shown in Fig. 4. It can be seen that the films formed a well interconnected spaghetti-like structure. Randomly dispersed but homogeneous 3D networks of CNTs were electrodeposited on GC substrates. The thickness of CNT films increased with the increase of applied electric field and deposition time. The addition of SDS as a dispersant in the solution can prevent the agglomeration of CNTs because the dodecyl sulfate ions were adsorbed on the surface of CNTs, forming a stable suspension in solution. Mg²⁺ were added into the suspension as electrolyte for electrodeposited. SDS can also provide negative charge on CNTs surface. As the DC field was applied, it can force the negatively

Figure 5. EIS data for the Pb^{2+} -selective electrodes: (a) GC/CNTs/ Pb^{2+} -selective membrane and (b) GC/ Pb^{2+} -selective membrane.

charged CNTs moving towards the anode, which accelerated the CNTs deposited onto the GC rod. The SDS can make the enhancement of binding force and a good contact of the CNTs and GC. In addition, because the charged CNTs in the suspension during electrodeposition process were driven by a uniform dc electric field, the film formed on GC is dense and uniform with a very strong adhesion to GC.

The EIS was performed to characterize the quality of CNTs contact. Figure 5 shows the EIS of the Pb^{2+} -selective electrode. It can be seen that EIS of the GC/CNTs/PVC electrode were recorded at open circuit potential in the $1.0 \times 10^{-1} \text{ M Pb(NO}_3)_2$ solution with an ac amplitude of 100 mV and a frequency range of 100 kHz to 10 MHz. The semicircle diameter of high-frequency is equals to the bulk membrane resistance coupled with the contact resistance between the GC substrate and PVC membrane. With electrodeposition of CNTs layers between the GC and PVC membrane, the resistance is decreased from 0.19 M to 0.07 M owing to the charge transport across the interface facilitated by the CNTs inner contact. Similar effects have been observed for PVC electrodes with polyaniline nanoparticle-based contact, and polyacrylate electrodes with poly(3-octylthiophene) (POT) contact.^{24,25} The absence of low-frequency semicircle of SC-ISE indicated that the CNTs contact increased low-frequency capacitance, and the ion-to-electron transduction across the CNTs film increased due to the charge conductivity of the CNTs.

Figure 6 shows the potentiometric response of the electrode measured in the concentration range of 1.0×10^{-3} to $1.0 \times 10^{-8} \text{ M Pb(NO}_3)_2$ solution. The results showed a Nernstern slope of $29.0 \pm 0.8 \text{ mV}$ per decade ($R^2 = 0.999$) by linear regression used CNTs as transducers. The electrochemical equation for the EMF response is $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$. And as shown in Fig. 6(b), the electrode without CNTs showed a near-Nernstern slope of 27.8 mV per decade over a wider concentration range of 1.0×10^{-3} to $1.0 \times 10^{-8} \text{ M Pb(NO}_3)_2$ solution. Figure 7 shows the dynamic potentiometric response of the solid-contact Pb^{2+} -selective electrode. The response time is about 5–10 s at the Pb^{2+} concentrations ranging from 1.0×10^{-3} to $1.0 \times 10^{-8} \text{ M}$ used CNTs as transducers, indicating that the absence of an inner solution will increase the response time of the electrode.^{26,27} The response time of the electrode without CNTs was longer and reached approximately 20 s for Pb^{2+} concentration below $1.0 \times 10^{-7} \text{ M}$.

Figure 8 shows EMF responses obtained according to Bakker's method²⁸ toward the ions of GC/CNTs/ Pb^{2+} -selective membrane. The selectivity coefficients ($\log K^{\text{pot}}_{\text{Pb},j}$) of the Pb^{2+} -ISE were calculated from the EMF values by Nicolsky–Eisenman equation.

Figure 6. Calibration curve of (a) GC/CNTs/ Pb^{2+} -selective membrane and (b) GC/ Pb^{2+} -selective membrane.

Figure 7. Dynamic potentiometric response of (a) GC/CNTs/ Pb^{2+} -selective membrane and (b) GC/ Pb^{2+} -selective membrane.

Figure 8. (Color online) EMF responses obtained according to Bakker's method toward the ions of GC/CNTs/ Pb^{2+} -selective membrane.

The results are shown in Table 1. Thus, the electrodeposition of CNTs for the ISE can avoid the potential drift and the ion leakage from the inner water layer formed between the GC substrate and ion-selective membrane.

Table 1. Selectivity coefficients ($\log K^{\text{pot}}_{\text{Pb},J}$) of GC/CNTs/ Pb^{2+} -selective membrane and the coated-disk electrode (CDE).

Ion J	Slope [mV decade^{-1}]	($\log K^{\text{pot}}_{\text{Pb},J}$) of SC-ISE
Ca^{2+}	17 ± 2	-12.0 ± 0.4
Na^+	29 ± 2	-5.8 ± 0.2
H^+	29 ± 2	-4.0 ± 0.2
Cu^{2+}	14 ± 2	-4.9 ± 0.2
Cd^{2+}	12 ± 2	-5.4 ± 0.2
Mg^{2+}	15 ± 2	-2.3 ± 0.2

Figure 9. Water layer test of solid-contact Pb^{2+} -selective electrode measuring the EMF responses of $1.0 \times 10^{-5} \text{ M Pb(NO}_3)_2$, $1.0 \times 10^{-3} \text{ M Cu(NO}_3)_2$ and again $1.0 \times 10^{-5} \text{ M Pb(NO}_3)_2$.

The stability of the SC-ISE was measured with the protocol developed by Pretsch and his colleagues.²⁹ Potential measurements were initially done in the $\text{Pb(NO}_3)_2$, then in $\text{Cu(NO}_3)_2$, and finally in $\text{Pb(NO}_3)_2$ solution. The results are shown in Fig. 9. The undesirable water layer was eliminated in the electrode because no obvious potential drift was observed, which may be owing to the formation of intermixed layer between the CNTs contact, and the ion-selective membrane addition would enhance the adhesion of the GC substrate and CNTs.

The SC-ISE uses CNTs as excellent ion-to-electron transducers and it did not show any evidence of the formation of a water layer between the transducer and the ion-selective membrane. Figure 10 shows a schematic representation of the electrodes studied where the CNTs networks play the role of the ion-to-electron transducer with no redox reaction. The high hydrophobicity of the CNTs based transducer layer may be attributed to the absence of the water film. This property makes the instrumental response of the SC-ISE very stable and insensitive to electroactive reagents. The CNTs can act as active ion-to-electron transducers in SC-ISE. The principles of ion-to-electron transduction in CNTs are not based on a redox reaction but on the high charge transfer of CNTs. The sensing capacity of CNTs relies on the extreme sensitivity of the nanotube electrical properties to changes in local chemical environments.

4. Conclusion

A solid-contact Pb^{2+} -selective electrode based on the CNTs inner contact and PVC ion-selective membrane was prepared by electrodeposition method. The CNTs films showed a spaghetti-like structure on the GC substrates, and could effectively reduce the contact resistance and increase the capacitance of the electrode. A Nernstian slope of $29.0 \pm 0.8 \text{ mV decade}^{-1}$ ($R^2 = 0.999$) is obtained

Figure 10. Schematic representation of the electrodes studied in this work, showing the different layers and the role of CNTs as ion-to-electron transducers.

from the chronopotentiometric measurements. Undesirable water layer can be effectively eliminated in this electrode. It is expected that the CNTs film by electrodeposition as ion-to-electron transducer is a promising approach for the fabrication of solid-contact ISEs.

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