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An all-solid-state polymeric membrane Pb^{2+}-selective electrode with bimodal pore C_{60} as solid contact

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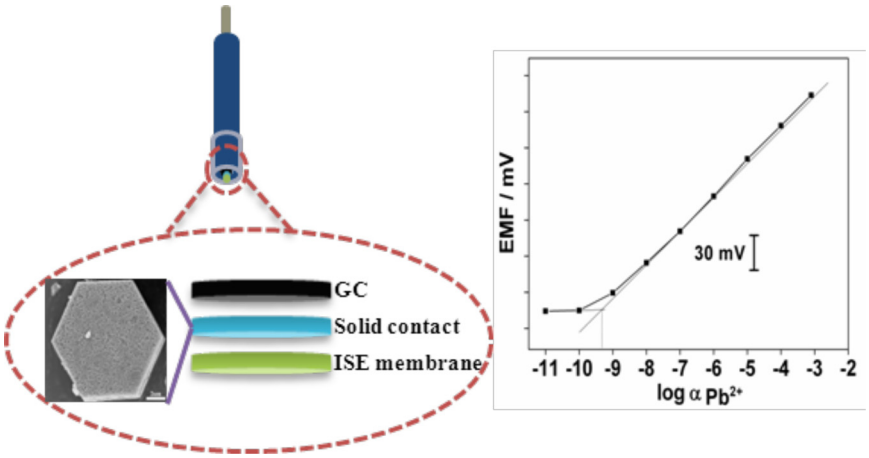
HIGHLIGHTS

- An all-solid-state Pb^{2+}-ISE with bimodal pore C_{60} as solid contact is developed.
- The bimodal pore C_{60}-based solid contact is prepared by electrochemical deposition.
- The electrode shows an excellent potential stability with a LOD of 5.0×10^{-10} M.

GRAPHICAL ABSTRACT



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ABSTRACT

An all-solid-state polymeric membrane Pb^{2+} ion-selective electrode (Pb^{2+}-ISE) based on bimodal pore C_{60} (BP-C_{60}) as solid contact has been developed. A BP-C_{60} film can be readily formed on the surface of a glassy carbon electrode by electrochemical deposition. Cyclic voltammetry and electrochemical impedance spectroscopy have been employed to characterize the BP-C_{60} film. The large double layer capacitance and fast charge-transfer capability make BP-C_{60} favorable to be used as solid contact for developing all-solid-state ISEs. The all-solid-state BP-C_{60}-based Pb^{2+}-ISE shows a Nernstian response in the range from 1.0×10^{-9} to 1.0×10^{-3} M with a detection limit of 5.0×10^{-10} M. The membrane electrode not only displays an excellent potential stability with the absence of a water layer between the ion-selective membrane and the underlying BP-C_{60} solid contact, but also is insensitive to interferences from O_2, CO_2 and light. The proposed solid-contact Pb^{2+}-ISE has been applied to determine Pb^{2+} in real water samples and the results agree well with those obtained by anodic stripping voltammetry.

1. Introduction

All-solid-state ion-selective electrodes (ASS-ISEs) with solid inner contacts have been received much attention since the beginning of the 1970s with the invention of coated wire

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electrodes (CWEs), which consist of a metallic conductor covered with an ion-selective membrane [1]. Unfortunately, coated wire electrodes show long-term potential instability, which is attributed to the lack of a well-defined interface between the ionically conductive sensing membrane and the electronically conductive conductor and the formation of a thin water layer between them [2,3]. By incorporation of appropriate redox-active compounds to the ISE membranes [4,5] or using conducting polymers (CPs) such as polypyrrole, poly(3-octylthiophene), polyaniline and poly(3,4-ethlyenedioxythiophene) as solid contacts [6], the potential stabilities of all-solid-state ISEs can be largely improved. However, these methods may still suffer from problems of the presence of the water layers, undesired side reactions with redox interferences and sensitivity to light, dissolved oxygen and CO_2 [6,7]. It is therefore highly desired to develop alternative materials as solid contacts in order to obtain stable and reliable potential responses for all-solid-state ISEs.

In recent years, carbon-based nanomaterials such as graphene [8,9], three-dimensionally ordered macroporous carbon [10], colloid-imprinted mesoporous carbon [11] and carbon nanotubes [12] have been used as solid contacts for the fabrication of ASS-ISEs. Due to the large double layer capacitances and hydrophobic properties of carbon materials, these ASS-ISEs possess high potential stability, and show the absence of an interfacial aqueous layer between the polymeric sensing membrane and the underlying solid contact. In addition, these carbon materials based ASS-ISEs have excellent resistance to O_2, CO_2, light and redox interferences. Therefore, carbon-based materials have become more attractive as solid contacts for fabricating ASS-ISEs [13].

Fullerenes (C_{60}), as three-dimensionally electron-acceptor carbon-based materials, have been reported to be efficient charge-transfer mediators [14]. Fullerene derivatives [2] and pristine C_{60} [15] have been employed as solid contacts for preparing ASS-ISEs. Interestingly, bimodal pore C_{60} (BP-C_{60}), which is prepared by introducing multiple pores in pristine C_{60} crystals, shows a larger surface area than that of the pristine C_{60}. BP-C_{60} can be applied in high-power solar cells and capacitors, large hydrogen storages, and highly sensitive chemical and physical sensors [16]. However, BP-C_{60} has not been used as solid contact for ASS-ISEs.

Herein, we report on the use of BP-C_{60} with macro- and meso-pore architectures as solid contact to develop an all-solid-state polymeric membrane Pb^{2+}-ISE. The BP-C_{60} film was prepared on a glassy carbon electrode by an electrodeposition method. The electrodeposition technique offers a straightforward fabrication process for preparing solid contacts, and has advantages of high efficiency and good reproducibility as compared with the drop-casting method which has been commonly employed for the preparation of carbon-based solid contacts for ASS-ISEs [17]. In the studies reported here, the electrochemical properties of the BP-C_{60}-based solid contact were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), and the potentiometric performance of the proposed membrane electrode with BP-C_{60} as solid contact was investigated.

2. Materials and methods

2.1. Reagents

C_{60} powders (99.5% pure) were purchased from JC nano Materials Tech Co., Ltd. (Nanjing, China), lead ionophore IV, [*tert*-butylcalix[4]arene-tetrakis(*N*,*N*-dimethylthioacetamide)], tetradodecylammonium tetrakis-(4-chlorophenyl)borate (ETH 500), sodium trakis[3,5-bis(trifluoro-methyl)phenyl]borate (NaTFPB), 2-nitrophenyl octyl ether (*o*-NPOE) and poly(vinyl chloride) (PVC) were purchased from Sigma–Aldrich. Carbon tetrachloride (CCl_4), isopropyl alcohol (IPA), benzene, tetrahydrofuran (THF), $Pb(NO_3)_2$ and other materials were purchased from Sinopharm Chemical Reagent and were of analytical-reagent grade. Deionized water (18.2 MΩ cm specific resistance) was obtained with a Pall Cascada laboratory water system.

2.2. Electrodeposition of BP-C_{60} on the GC electrode

The BP-C_{60} materials with macro- and meso-pore architectures, including BP-C_{60} (I) and BP-C_{60} (II), were synthesized respectively in the mixture solvents of CCl_4 and benzene with the weight ratios of 2:8 and 1:9 by the liquid–liquid interfacial precipitation method [16]. A BP-C_{60} suspension was prepared by adding 1 mL toluene containing 0.15 mg mL^{-1} BP-C_{60} into acetonitrile of 3 mL with stirring. The BP-C_{60} film with a thickness of approximately 50 μm was electrodeposited on the GC electrode in the mixture solution containing BP-C_{60} at 5 V for 10 min. For comparison, the pristine C_{60} modified GC electrode was also prepared under the same conditions. The above-prepared electrodes are denoted as GC/BP-C_{60} (I), GC/BP-C_{60} (II) and GC/C_{60} electrodes, respectively.

2.3. Fabrication of the all-solid-state Pb^{2+}-selective electrodes

The membrane cocktail components (totaling 250 mg), including lead ionophore IV (1.00 wt.%), NaTFPB (0.44 wt.%), ETH 500 (1.00 wt.%), PVC (32.52 wt.%), and *o*-NPOE (65.04 wt.%), were dissolved in tetrahydrofuran of 2 mL. All-solid-state Pb^{2+}-ISEs (GC/BP-C_{60} (I)/Pb^{2+}-ISEs) were prepared by drop-casting 100 μL of the membrane cocktail on the GC/BP-C_{60} (I) electrodes. After being dried for 12 h at room temperature, the electrodes were conditioned in 1.0×10^{-3} M $Pb(NO_3)_2$ for 1 day and in 1.0×10^{-9} M $Pb(NO_3)_2$ for 2 days. For comparison, the coated disc electrodes (GC/Pb^{2+}-ISEs) were prepared by covering bare GC electrodes with the above mentioned membrane cocktail. For the selectivity measurements using the separate solution method [18], the electrodes were conditioned in 1.0×10^{-3} M NaCl overnight.

2.4. Apparatus and measurements

The electromotive force (EMF) measurements were carried out at room temperature using a CHI 660C electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China). Hg/Hg_2Cl_2 with 0.1 M LiOAc as salt bridge electrolyte was used as reference electrode. All EMF values were corrected for liquid junction potentials according to the Henderson equation, and activity coefficients were calculated according to the Debye–Hückel approximation.

CV was carried out in a 0.1 M KCl solution by using the CHI 660C electrochemical workstation with a conventional three-electrode system, consisting of the GC/BP-C_{60} electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (3 M KCl) electrode as the reference electrode. The cycles were recorded between −0.5 and 0.5 V with a scan rate of 100 mV s^{-1}.

EIS measurements for the GC/BP-C_{60} electrode were carried out in a 0.1 M KCl solution with an excitation amplitude of 10 mV and a frequency range of 2 Hz–10 kHz. For the GC/Pb^{2+}-ISE and GC/BP-C_{60} (I)/Pb^{2+}-ISE, EIS measurements were recorded in 1.0×10^{-3} M $Pb(NO_3)_2$ with an excitation amplitude of 100 mV and a frequency range of 0.01 Hz–100 kHz.

Chronopotentiometric measurements were carried out for the GC/Pb^{2+}-ISE and the GC/BP-C_{60} (I)/Pb^{2+}-ISE in 1.0×10^{-3} M Pb$(NO_3)_2$ by applying a constant current of +1 nA for 60 s followed by a current of −1 nA for 60 s.