Short communication

Using sp²-C dominant porous carbon sub-micrometer spheres as solid transducers in ion-selective electrodes

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ARTICLE INFO

Article history:
Received 5 September 2014
Received in revised form 13 October 2014
Accepted 27 October 2014
Available online 31 October 2014

Keywords:
Solid-contact ISEs
Transducers
Porous carbon sub-micrometer spheres
Potential stability

ABSTRACT

Potential stability is one of the most intractable challenges for solid-contact ion-selective electrodes (SC-ISEs) with regard to the classic inner-reference ISEs. Among the well-established electrode structures for SC-ISEs, solid-contact transducer layer is the most crucial component. Herein, we introduce porous carbon sub-micrometer spheres (PC-SMSs) as a promising solid-contact material for fabrication of highly stable K⁺-SC-ISE. Systematic characterizations including contact angle, electrochemical impedance spectroscopy and cyclic voltammetry demonstrate that the PC-SMSs disclose high hydrophobicity and large interfacial capacitance, which efficiently eliminate the water-layer and stabilize the potential of K⁺-SC-ISEs. The developed PC-SMSs electrode also exhibits good long-term stability as well as anti-interferences from O₂ and CO₂.

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1. Introduction

Ion selective electrodes (ISEs) featured by low-cost and ion sensing are frequently used in environmental monitoring, research laboratories and clinical analysis [1–3]. Conventional inner-reference ISEs with good potential stability remain the popular ion sensor devices. However, several frequently mentioned drawbacks, such as leaching of inner reference solution, susceptibility to the temperature and miniaturization challenging have limited the development of conventional ISEs [4]. Wire coated electrode (CWE) prepared by directly coating the ion-selective membrane (ISM) on a platinum wire pioneered the first solid-contact ion-selective electrodes (SC-ISEs) [5]. CWE opens the research area of SC-ISEs, but poor potential stability becomes the main obstacle for its practical applications. Lately, detailed studies demonstrate that the lack of “block” interfaces between the electrode and ISM layer dominates the factor of potential instability [6]. The crucial characteristics for the “block” interface have been distinguished including sufficiently reversible and fast ion-to-electron transduction, high exchange currents and anti-interferences [7]. Conducting polymers (CPs), for example, the representative poly(3,4-ethylenedioxythiophene) with large redox capacitance and fast ion-to-electron transduction have been extensively investigated during the past decades [8–10]. Further developed more lipophilic and solution prepared CPs, such as polyoctylthiophene and other alkylthiophenes have further improved the potential stability [11–14]. Nevertheless, light and gas sensitivities and redox interferences as well as inadequate hydrophobicity remain the challenges for the CPs based SC-ISEs [7,15,16].

With regard to the redox-type transducers, another attractive transducer is the carbon-based nanomaterial based on the electric double layer capacitance. For example, Buehlmann and coworkers first proposed a three-dimensionally ordered macroporous carbon (3DOM) as the solid-contact layer, which exhibits high ionic and electric conductivity. The long-term potential drift is only 11.7 μV h⁻¹ and also displays few responses to the gas and light [17]. Recently, carbon nanotubes (CNTs) and graphene have also been utilized to be effective and promising transducers [18,19]. Their remarkable capacitances based on large surface area result in high exchange current density and thus a closely nonpolarizable interface because of the asymmetric ion-to-electron transduction process. Very recently, mesoporous carbon transducers by a colloid imprinted way further exhibit the promising scale-up fabrication of SC-ISEs based on carbon based materials [20].

In this work, we introduce another carbon based materials, i.e., porous carbon sub-micrometer spheres (PC-SMSs) as a solid-contact transducer for fabrication of a highly stable K⁺-SC-ISE. The prepared PC-SMSs show uniform structural size distribution and high hydrophobicity (137° contact angle). PC-SMSs also exhibit good electric conductivity as well as high capacitance (12 mF), which meets the crucial requirements for the development of SC-ISEs with superior performances. Additionally, simple preparation process would make PC-SMSs as an effective solid-contact material in scale-up fabrication of SC-ISEs.
2. Experimental

Valinomycin was obtained from Acros. Bis(2-ethylhexyl)sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KTClPB), high molecular weight poly(vinyl chloride) (PVC) and dopamine hydrochloride (THF, 99.8%) were obtained from Fluka. Ammonia, methanol, and tetrahydrofuran (THF, 99.8%) were obtained from Shanghai Chemicals, China.

PC-SMSs were prepared using the method proposed by Ai et al. [21]. Briefly, in a typical synthesis of SMSs with size of ca. 620 nm, 0.5 mL NH₄OH (28–30%) was mixed with 40 mL ethanol and 90 mL water under mild stirring at room temperature for 0.5 h. Then 10 mL dopamine water solution (0.05 g mL⁻¹) was injected into the mixture solution and the reaction was proceeded for 30 h to obtain the PDA SMSs. After centrifugation and washed with water for 3 times, the resulted PDA SMSs were carbonized at 800 °C for 1 h in Ar at a rate of 5 °C min⁻¹ to obtain the carbon SMSs. Finally, carbon SMSs were mixed with KOH at a weight ratio of 1:4, followed by thermal treatment at 700 °C for 1 h in Ar at a rate of 5 °C min⁻¹. After cooling down, the resulting powder was washed with 1 M HCl for 3 times and then washed with water for 3 times to remove the excess KOH. Scanning electron microscopy (SEM) images were performed by a field emission scanning electron microscopy (FE-SEM, XL30ESEM-FEG). Transmission electron microscopy (TEM) images were obtained by using a JEOL 2000 transmission electron microscope operating at 200 kV. Contact angle measurements combined with an optical CCD were performed at a contact angle apparatus (Changchun optics and fine mechanic instrument).

The membrane cocktail was a THF solution containing ca. 15% (w/w) potassium ion-selective membrane (K⁺-ISM) component, which consisted of 1.0% valinomycin, 0.5% KTClPB, 65.2% DOS and 33.3% PVC (w/w). PC-SMSs (5 mg) were dispersed in a mixture containing ethanol (0.49 mL) and nafion (11 μL, 5%) respectively, resulting in a concentration of ca. 10 mg·mL⁻¹. An aliquot of 4 μL was dropped onto the surface of a polished glassy carbon electrode (GCE, 3 mm diameter), dried in the air. The procedure was repeated four times. PC-SMSs/K⁺-ISE was prepared by depositing K⁺-ISM (ca. 30 μL) onto the PC-SMSs film. For comparison, K⁺-CWE was fabricated by directly coating the ISM onto a GC electrode. All the prepared electrodes were dried in air over night and then conditioned in 0.01 M KCl solution for 24 h before and between the measurements.

Electrochemical measurements including cyclic voltammograms, electrochemical impedance spectroscopy, chronopotentiometry and open circuit potentials were performed using the CHI 660A electrochemical workstation with a three-electrode electrochemical cell. The working electrodes are modified GCE electrode, and the auxiliary electrode is a Pt wire. The reference electrode is Ag/AgCl electrode (3 M KCl). The analytical performance of the K⁺-SC-ISEs (PC-SMSs/K⁺-ISE) was studied in the concentration range of 10⁻⁹ to 10⁻¹ M KCl. The activity coefficients were calculated by using the extended Debye–Hückel equation.

3. Results and discussion

Fig. 1a schematically illustrates the preparation process of PC-SMSs, which just consists of three simple steps including the synthesis of PDA SMSs, carbonizing the PDA SMSs and the synthesis of PC-SMSs. The PC-SMSs which used dopamine as a carbon precursor contain little sp³-C in the matrix, exhibiting enhanced conductivity. As can be seen from a typical SEM image (Fig. 1b), the resulting PC-SMSs are uniformly spherical in shape with diameters of ca. 650 nm. Both high resolution TEM images (Fig. 1c and d) manifest the porous surface that provides a highly large surface area after etching by KOH. Solid-contact materials with high hydrophobicity are expected to be beneficial for suppressing the undesirable water layer at the SC|ISM interface [22,23]. After coating the PC-SMSs dispersion on a cleaned GC electrode, the wetting property of the PC-SMSs film was checked by a contact angle (CA) measurement. The
advancing CA was obtained by forming a 5 µL drop of water on the surface. As shown in the inset of Fig. 1d, the PC-SMSs film has a CA of 137° between a 5 µL water droplet and the film, and the droplet stayed statically over 30 min, indicating high hydrophobicity and stability of the film.

Electrochemical investigations of the PC-SMSs film were carried out by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in 0.1 M KCl solution. Fig. 2a illustrates the complex impedance plot for GC/PC-SMSs where the spectrum is dominated by a ca. 90° capacitive line extending down to low frequencies. The value for double-layer capacitance estimated by an equivalent electrical circuit (not shown) was 12.01 mF, which agrees with the calculated result of the CV well (~12.8 mF, represented in the inset). The remarkable results would derive from the morphology of PC-SMSs. The absence of a high-frequency semicircle indicates a fast charge transfer across the GC[PC-SMSs and the PC-SMSs|KCl interfaces as well as fast charge transport in PC-SMSs layer, confirming the excellent electroconductivity of sp²-C dominant structure. To further verify the excellent electrical characterization of developed ISE, impedance measurements for the PC-SMSs/K⁺-ISE and K⁺-CWE were also recorded. As can be seen in Fig. 2b, each electrode shows a high-frequency semicircle represented by total bulk resistance and the result is 7.5 MΩ and 6.0 MΩ for the PC-SMSs/K⁺-ISE and the K⁺-CWE, respectively. The slight difference of resistance of the two electrodes may have arisen from the uncertainty in making membranes of the same thickness. By contrast, the low-frequency parts of two electrodes are obviously distinct. The K⁺-CWE exhibits a second semicircle due to a large charge transfer resistance in parallel with the small double-layer capacitance at the GC|ISM interface, whereas the low-frequency resistance of the PC-SMSs/K⁺-ISE in the impedance spectrum sticks to the real impedance axis and doesn’t change with frequencies, indicating a high low-frequency capacitance. Current-reversed chronopotentiometry was found to be a fast and convenient method to critically evaluate the potential stability of SC-ISEs. We used it to quantify the low-frequency capacitance of the PC-SMSs/K⁺-ISE and the K⁺-CWE, thus examining their potential stability. As shown in Fig. 2c, a potential jump (IR) related to the resistance (R) of the ISM is followed by a potential drift. A drastic potential drift appears when a current of ±1 nA was applied to the K⁺-CWE, indicating the poor capacitance. The PC-SMSs/K⁺-ISE, however, shows little potential drift under more harsh conditions with a current of ±10 nA. The calculated ΔE/Δt value for the PC-SMSs/K⁺-ISE is 4.8 µV·s⁻¹ corresponding to a capacitance value of 2083 µF from the fundamental capacitor equation, \( I = C \cdot \Delta E / \Delta t \). The decrease of capacitance value after coverage with the ISM can be attributed to the difference of the contacting medium that has an effect on ion-to-electron process [7]. In spite of that, the value was still much higher than those measurement results for other well-established transducers [18,19,24–28], which can be seen clearly in Fig. 2d. Additionally, the resistance values estimated from the potential jump for the PC-SMSs/K⁺-ISE and K⁺-CWE are 7.67 MΩ and 6.14 MΩ respectively, in agreement with the results from the impedance measurements.

Open-circuit potentiometric measurements were used to check the main analytical performance of the developed electrode. Firstly, water layer test was applied to check the aqueous layer at the SC|ISM interface. The PC-SMSs/K⁺-ISE was sequentially exposed to 0.1 M KCl, 0.1 M NaCl, and then back to 0.1 M KCl. As shown in Fig. 3a, there is no noticeable positive or negative potential drift during the whole test, suggesting the absence of an undesirable water layer, which resulted from the highly hydrophobic characterization of the PC-SMSs. Besides, the intermediate-term stability was calculated by the last step of the test and the value obtained corresponds to 14.9 µV·h⁻¹ for 20 h. The interference of O₂ and CO₂ on the potential response was tested by immersing the developed electrode in 0.1 M KCl solution and alternating saturation with N₂, O₂ and CO₂ in the sequence shown in the inset of

![Fig. 2. a) Electrochemical impedance plots of GCE/PC-SMSs in 0.1 M KCl. Frequency range, 10 kHz to 0.01 Hz; Eac, 0.2 V; \( \Delta E = 100 \text{ mV} \). Inset: cyclic voltammograms in 0.1 M KCl; scan rate: 0.01 V·s⁻¹. b) Electrochemical impedance plots of the PC-SMSs/K⁺-ISE and K⁺-CWE. Frequency range, 100 kHz to 0.3 Hz; Eac, 0.2 V; \( \Delta E = 100 \text{ mV} \). c) Chronopotentiometric results. Upper part: PC-SMSs/K⁺-ISE; applied current: 10 nA for 60 s and – 10 nA for 60 s; bottom part: K⁺-CWE; applied current: 1 nA for 60 s and – 1 nA for 60 s; solution: 0.1 M KCl. d) \( C_{\text{fr}} \) of PC-SMSs/K⁺-ISE compared to previous SC-ISEs based on chronopotentiometric results.](http://example.com/figure2.png)
supposed to account for such a promising long-term potential stability of the developed electrode [30].

4. Conclusions

Herein we developed a new type of SC-ISE by using sp²-C dominant PC-SMSs as promising transducers. The porous structure of PC-SMSs provides great interface area for ion-to-electron transfer while the high proportion of sp²-C benefits the electroconductivity. Because of the high hydrophobicity of PC-SMS film, the undesirable interfacial water layer was effectively suppressed. Thus the developed ISEs exhibited excellent long-term potential stability and remarkable interference immunity. Furthermore, the simplicity in synthesis and construction of ISEs makes the PC-SMSs based electrodes promising for miniaturization and mass fabrication.

Conflict of interest

The authors declare that there are no conflicts of interest.

Acknowledgments

The authors are most grateful to the NSFC (no. 21205112, 21105096, 21175130 and 21225252), Ministry of Science and Technology of the People’s Republic of China (2012YQ170003) and Department of Science and Technology of Jilin Province (no. 201215091 and 20120308).

References


Fig. 3. a) Water layer test for PC-SMSs/K⁺-ISE. Inset: CO₂ and O₂ interference test. b) Time response of the PC-SMSs/K⁺-ISE. Inset: calibration curve for the PC-SMSs/K⁺-ISE in the varied concentration of KCl solution.