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SENSORS and ACTUATORS B Chemical

An all-solid-state potentiometric microelectrode for detection of copper in coastal sediment pore water

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ABSTRACT

Potentiometric microelectrodes are regarded as promising probes for ion sensing when only limited sample volumes are available. In this work, an all-solid-state ion-selective microelectrode (ISµE) has been developed by coating ionophore-based ion-selective membrane on a poly(3,4-ethylenedioxythiophene)-poly(sodium 4-styrenesulfonate) modified gold wire with a diameter of 14 µm for detection of copper. Under the optimized conditions, the proposed all-solid-state Cu^{2+}-ISµE shows a Nernst response toward Cu^{2+} in 0.5 M NaCl in the range from 2.5×10^{-7} to 2.5×10^{-4} M with a detection limit of 4.0×10^{-8} M. Additionally, the Cu^{2+}-ISµE has been used for monitoring the vertical distribution profile of Cu^{2+} in coastal sediment pore water with a small volume (e.g., 300 µL). The results agree well with those obtained by anodic stripping voltammetry, which indicates that the proposed potentiometric technique based on the all-solid-state ISµE is promising for detection of Cu^{2+} in coastal sediment pore water. The method for the preparation of the ISµE can be extended to detect other heavy metal ions in sediments by using different ion-selective membranes.

1. Introduction

Dissolved heavy metals in contaminated sediment pore waters are indicative of their bioavailabilities for benthic organisms and consequently, implicate possible human exposure through the aquatic food chain transfer [1]. Moreover, the environmental behaviors of heavy metals are directly associated with their concentrations in the sediment pore water [2]. Therefore, it is highly desired for reliable measurements of heavy metal ions in sediment pore water.

The general procedures for detection of heavy metal ions in sediment pore water are based on the on-the-spot extraction of the pore water by centrifugation and squeezing combined with the subsequent laboratory chemical analysis [1,3]. In recent years, DET (diffusive equilibration in thinfilms) and DGT (diffusive gradient in thinfilms) techniques have been proposed for determination of heavy metal ions in sediment pore water [4–6]. However, these techniques suffer from problems of complex and time-consuming procedures.

Electrochemical microsensors have shown a promising application in solving the challenges in environmental chemistry and marine science [7]. As a simple, field-portable, and widespread electrochemical

methodology, potentiometry based on polymeric membrane ion-selective electrodes (ISEs) is widely used for selective and sensitive detection of cations and anions in biological and environmental samples [8]. One unique feature of these ISEs is that the drastical decrease in sample volume does not deteriorate the detection limit of the electrode [9,10]. Therefore, an ion-selective microelectrode (ISµE) is a promising probe for ion sensing when limited sample volumes are available. More importantly, the ISµE shows a great potential for *in situ* measurement of heavy metal ions in pore water.

Since the discovery in 1960s, various kinds of the potentiometric microelectrodes have been developed [11–13]. Among them, the glass micropipettes with the diameters from a few tens of µm to a few tens of nm have been used to develop the potentiometric microelectrodes to monitor ion activities in matrixes such as living organisms [11] and pore waters [14]. Additionally, the glass micropipette-based potentiometric microelectrodes have also been applied to map the ion fluxes in plant tissues and investigate corrosion processes [15–18]. They have also been adopted as probes of scanning electrochemical microscopy (SECM) [19–21]. However, such kind of the microelectrodes suffers from problems of difficult handling, fragility and short lifetimes [11]. In

recent years, all-solid-state potentiometric microelectrodes with the ease of preparation and robustness have been developed [11,22]. For example, Tóth and coworkers proposed an all-solid-state potassium-selective microelectrode with polypyrrole as solid contact [22]. Brown and coworkers prepared a glass nanopore-based all-solid-state ion-selective microelectrode to probe the distribution of ionic species at the micro- or submicrometer-length scale [23]. However, most of these potentiometric microelectrodes were used to detect the common electrolytes such as K^+, Na^+, Ca^{2+}, Li^+ and Cl^-. The aim of this work is to develop an all-solid-state ISμE for detection of heavy metal ions in coastal sediment pore water. For this purpose, the ISμE has been prepared by coating ionophore-based ion-selective membrane on a poly (3,4-ethylenedioxythiophene)-poly(sodium 4-styrenesulfonate) modified gold wire. By using Cu^{2+} as a model of heavy metals, the characterists for the Cu^{2+}-ISμE have been investigated.

2. Experimental section

2.1. Materials

All the information of the chemicals is available in the Supporting Information.

2.2. Fabrication of the gold microelectrode

A gold wire with a diameter of 14 μm (Alfa Aesar, 99.9%) was attached to a copper wire by using a graphite-filled silver glue, and then dried for 4 h at 80 °C. The gold wire was carefully inserted in a glass capillary tube (with a diameter of 1.0 mm), and the copper wire was fixed by casting non-conducting epoxy glue at the stem end of the capillary tube [24,25]. The glass was then flame-fuse sealed around the gold wire from the tip (Fig. S1). Finally, the sealed end was polished with sand paper and a 0.05 μm aluminum oxide suspension. The microelectrode was immersed in 1.0 M HNO_3 for 15 min, and then cleaned ultrasonically in deionized water and ethanol, respectively. The prepared gold microelectrode is denoted as the AuμE eletrode. The voltammetric characteristics of the AuμE are illustrated in Fig. S2, which shows a sigmoid-shaped voltammogram [22].

2.3. Preparation of the all-solid-state Cu^{2+}-ISμE

The conducting polymer poly(3,4-ethylenedioxythiophene)-poly (sodium 4-styrenesulfonate) (PEDOT(PSS)) was deposited on the surface of the AuμE electrode by galvanostatic electrochemical polymerization to prepare the AuμE/PEDOT(PSS) electrode [26,27]. More details are shown in the Supporting Information. 250 mg of the membrane components, including 1.00 wt% Cu^{2+} ionophore (ETH1062), 1.02 wt% sodium tetrakis[3,5-bis (trifluoromethyl) phenyl]borate (NaTFPB), 65.32 wt% 2-nitrophenyl octyl ether (o-NPOE), and 32.66 wt % poly(vinyl chloride) PVC, was dissolved in 2 mL of tetrahydrofuran (THF). Then, 0.8 μL of the Cu^{2+}-selective membrane cocktail solution was applied on the surface of the PEDOT(PSS) film. After being dried, the all-solid-state Cu^{2+}-ISμE, denoted as the AuμE/PEDOT(PSS)/Cu^{2+}-ISE, was conditioned in a 10^{-3} M $CuCl_2$ solution for 1 h. For comparison, the AuμE/Cu^{2+}-ISE was prepared by coating the ion-selective membrane on the bare AuμE.

2.4. Apparatus and measurements

Electromotive force (EMF) measurements were carried out at room temperature using a CHI 760C electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China). An Ag/AgCl/3 M KCl microelectrode with a diameter of 10 μM was used as the reference electrode [28]. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.1 M KCl solution by using a three-electrode system, composed of the AuμE, AuμE/

PEDOT(PSS) or AuμE/PEDOT(PSS)/ISE electrode as working electrode, the Ag/AgCl/3 M KCl microelectrode as reference electrode and a Pt wire as counter electrode.

2.5. Sample analysis

In order to investigate the vertical distribution profile of Cu^{2+} in coastal sediment pore water, the sediment samples were collected on January 12, 2018 (Fig. S3). Details of the sample preparation are available in the Supporting Information. Before analysis, the samples were acidified to pH 2.0 with HNO_3. The standard addition method was applied to determine the concentration of Cu^{2+} in 300 μL of each sample solution by using the proposed all-solid-state Cu^{2+}-ISμE [29]. For comparison, the concentrations of Cu^{2+} in the coastal sediment pore water were also determined by the 797 V A computrace via anodic stripping voltammetry (ASV, Metrohm Ltd., Switzerland).

3. Results and discussion

Due to its high conductivity, large redox capacitance and good thin film-forming properties [30], the PEDOT(PSS) film has been studied and used as the ion-to-electron transducer in the design of the solid-contact ISEs [26,31]. SEM images of the AuμE and AuμE/PEDOT(PSS) electrodes reveal that the AuμE electrode shows a smooth surface with a diameter of 14 μm, while the AuμE/PEDOT(PSS) electrode shows a compact and rough morphology (Fig. S4) [32]. CV and EIS measurements were also carried out to evaluate the electrochemical characteristics of the AuμE and AuμE/PEDOT(PSS) electrodes [33,34]. As shown in Fig. 1A, a capacitive process with a near-rectangular shape from −0.5 to 0.5 V was observed except the oxygen reduction peak at ca -0.35 V [35]. The symmetrical shape of the CV reveals that the PEDOT(PSS) film has a high reversibility for the doping process [36]. Moreover, the anodic currents at 0 V vary linearly with increasing the scan rate (Fig. S5), indicating that both ion and electron transports in the PEDOT(PSS) film are fast. Fig. 1A also shows that the capacitive current of the bare microelectrode is only at 10^{-10} A levels, which is due to the high resistance of the microelectrode. However, when the AuμE is modified with the PEDOT(PSS) film, more than 100-fold increase of the capacitive current can be observed. This phenomenon is similar to the conventional electrode [37] and indicates that the presence of PEDOT(PSS) film enhances the redox capacitance of the electrode.

The impedance spectra of the AuμE, and AuμE/PEDOT(PSS) electrodes were compared. As shown in Fig. 1B, both electrodes show near 90° capacitive lines with the absence of the high-frequency semicircle, which indicates that there are fast charge transfers at the interfaces for both electrodes. However, according to the equation, C = -1/(2πfZ″), where f is the lowest frequency used to record the spectra (0.01 Hz), Z″ is the impedance at this frequency [33,34], the redox capacitance of the AuμE/PEDOT(PSS) electrode (252.8 ± 11.9 nF) was found to be much higher than that of AuμE (1.0 nF). This phenomenon is in accordance with that obtained by CV. Therefore, the PEDOT(PSS) film with a sufficiently high bulk (redox) capacitance was employed for preparing the all-solid-state Cu^{2+}-ISμE [26]. It should be noted that the diffusion resistance (R_D) of the AuμE/PEDOT(PSS) is calculated to be 11.1 ± 2.8 KΩ when fitting the equivalent circuit (Fig. 1B) [26]. According to the equation $R_D = \tau_D/C_L$, a diffusion time constant (τ_D) of 2.9 ± 0.7 ms can be obtained. The low frequency relation process described by the time constant increases with the thickness of the PEDOT(PSS) film and might be connected with the long-term drift of the electrode potential [38].

The impedance spectrum of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE was also investigated (Fig. 1C). The bulk capacitance of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE was calculated to be 197.3 ± 22.2 nF when fitting the equivalent circuit (average error, χ^2 = 0.06) [39], which is lower than that of the AuμE/PEDOT(PSS) (252.8 ± 11.9 nF). However, due to the thin polymeric membrane applied (a few micrometers) and the
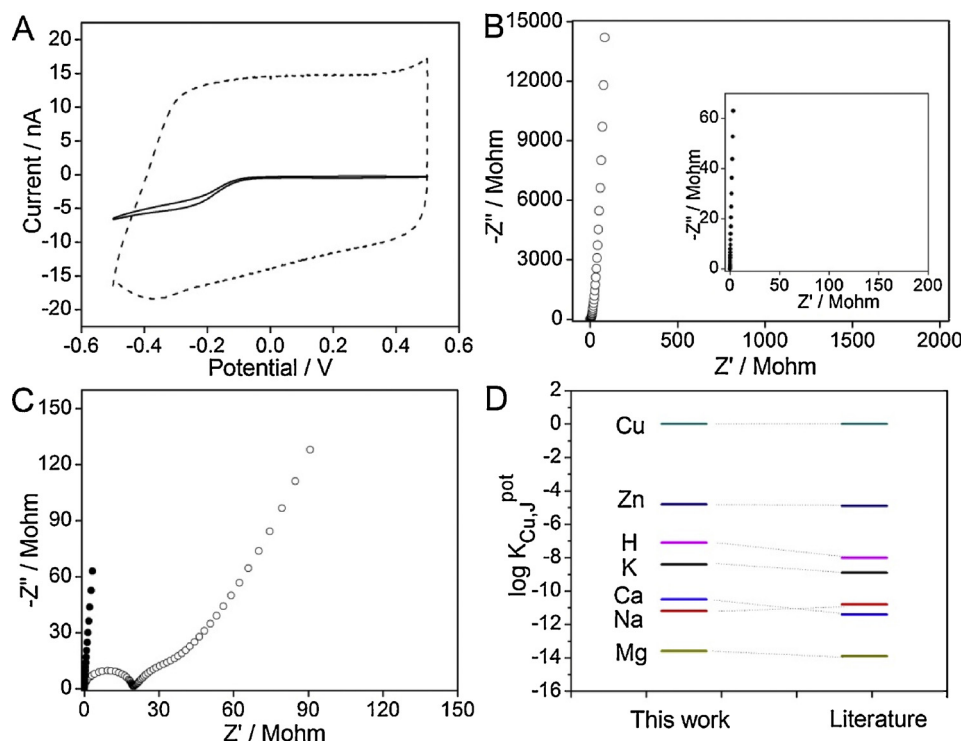
Fig. 1. (A) Cyclic voltammograms of the AuμE (line), and AuμE/PEDOT(PSS) electrodes (dash). (B) Impedance spectra for the AuμE (○) and AuμE/PEDOT(PSS) electrodes (●) in 0.1 M KCl solution recorded at the open-circuit potentials. The inset shows magnification of the impedance spectrum of the AuμE/PEDOT(PSS) electrode. (C) Impedance spectra for the AuμE/PEDOT(PSS) electrode (●) and AuμE/PEDOT(PSS)/Cu^{2+}-ISE (○) in 0.1 M KCl solution recorded at the open-circuit potentials. Scan rate, 50 mV s^{-1}; frequency range, 0.01 Hz-10 kHz; excitation amplitude, 100 mV. (D) Comparison of the selectivity coefficients for the present Cu^{2+}-selective membrane obtained with the separate solution method [40] and reported in the literature [41].

high charge transfer process of the AuμE, such capacitance decrease is quite low.

The selectivity was examined by the separated solution method [40]. As shown in Fig. 1D, the selectivity coefficients of the Cu^{2+}-selective membrane are consistent with those in the literature [41]. Moreover, according to the determined selectivity coefficients toward sodium ions, a theoretical detection limit can be evaluated to be 8×10^{-13} M for copper ions in the presence of 0.5 M sodium ions [42].

The potentiometric performance of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE was investigated in deionized water (Fig. 2A-a). The electrode exhibits a stable response with a slope of 30.7 ± 1.3 mV/decade ($R^2 = 0.997$). The detection limit calculated as the intersection of the two lines is 1.6×10^{-8} M (Fig. 2B-a). In the background solution of 0.5 M NaCl, the proposed all-solid-state Cu^{2+}-ISμE shows a linear response in the range of 2.5×10^{-7}–2.5×10^{-4} M with a slope of 28.1 ± 1.8 mV/decade ($R^2 = 0.999$) (Fig. 2A-b). In the presence of high concentrations of interfering ions, the primary ions in the outer boundary layer of the membrane can be replaced. Therefore, substantial fluxes of copper ions from the membrane into the sample could

be generated and deteriorate the detection limit of the electrode [43]. Indeed, the detection limit found for the proposed electrode in 0.5 M NaCl is 4.0×10^{-8} M, which is higher than that obtained in deionized water (Fig. 2B-b). Interestingly, the detection limit for the microsensor is lower than that of the conventional all-solid-state bulk Cu^{2+}-ISE (4.0×10^{-7} M) under the same conditions (Figs. 2A-c and B-c). This phenomenon may be attributed to the small size of microelectrode, which makes the ion diffusional transport more efficient. In this case, the primary ions leaching from the membrane into the sample solution, which deteriorates the detection limit of the microelectrode, could be expelled via the rapid diffusion process at the membrane/solution interface [43,44].

The effect of sample pH on the Cu^{2+}-ISμE response was investigated. According to the determined selectivity coefficients of the Cu^{2+}-ISμE toward H$^+$ (log K_{ij}^{pot} = -7.1), the Cu^{2+}-ISμE was insensitive to sample pH. Indeed, as shown in Fig. S6, a stable EMF value was obtained in 10^{-5} M CuCl$_2$ in the presence of 0.5 M NaCl over a wide pH range. Additionally, the short-term potential stability was investigated. According to the chronopotentiograms (Fig. S7), the potential drift of
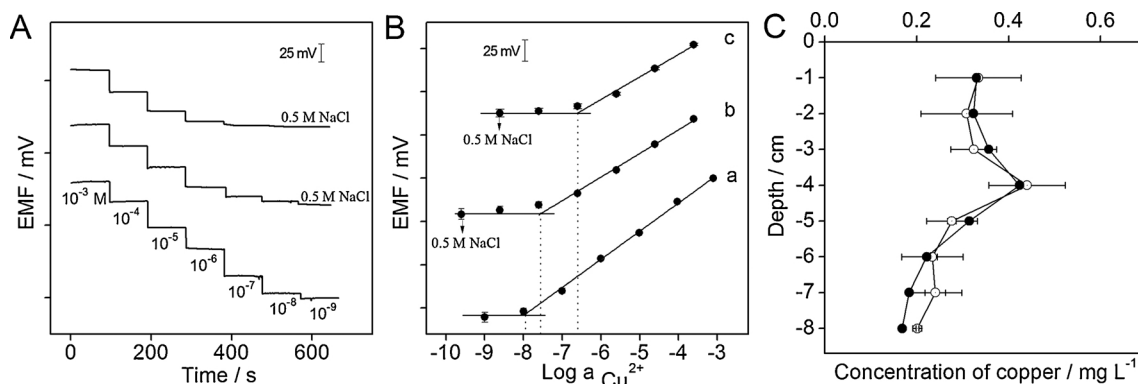

Fig. 2. (A) Potential time traces of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE in CuCl$_2$ at different concentrations in the absence (a) and presence (b) of 0.5 M NaCl, and of the conventional solid-contact Cu^{2+}-ISE in CuCl$_2$ in the presence of 0.5 M NaCl (c). (B) Calibration curves of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE in CuCl$_2$ in the absence (a) and presence (b) of 0.5 M NaCl, and of the conventional solid-contact Cu^{2+}-ISE in CuCl$_2$ in the presence of 0.5 M NaCl (c). (C) Copper concentration profiles in pore water obtained by the proposed sensor (hollow circle) and ASV (solid circle). Error bars represent one standard deviation for three measurements.

the AuμE/PEDOT(PSS)/ Cu^{2+}-ISE was calculated to be 38.3 ± 7.5 μV s^{-1} when using the applied currents of ± 0.01 nA, indicating that the microelectrode could obtain a stable potential response. Indeed, a solid-contact microelectrode with a potential drift of 0.063 mV min^{-1} has been reported by using PEDOT nanowires as ion-to-electron transducer [45]. Moreover, several other solid-contact microelectrodes have also been developed and show acceptable stabilities and reproducibilities [13,22]. The reproducibility of the AuμE/PEDOT(PSS)/Cu^{2+}-ISE were evaluated (Fig. S8). Experiments reveal that the proposed electrode exhibits good reproducibility.

In order to demonstrate the feasibility of the proposed AuμE/ PEDOT(PSS)/ Cu^{2+}-ISE for environmental analysis, the contents of copper ions in the coastal sediment pore water samples were detected by the standard addition method. The volumes of the pore water samples obtained from the coastal sediment core were very limited, especially when the depths were up to 6 cm. Therefore, the proposed potentiometric technique based on the all-solid-state ISμE is promising for detection of Cu^{2+} in the sediment pore water samples with small volumes. The depth profile of copper in pore water is shown in Fig. 2C, which shows the observed copper concentrations in the range of 0.15 to 0.45 mg L^{-1} and a peak concentration of 0.42 mg L^{-1} at the depth of 4 cm. Fig. 2C also shows that the depth profile of copper determined by the proposed Cu^{2+}-ISμE is in close agreement with those obtained by ASV.

4. Conclusions

In this work, an all-solid-state ISμE based on the electrodeposited PEDOT(PSS) has been developed for detection of copper ions in coastal sediment pore water. The proposed sensor shows favorable potentiometric performance in terms of detection limit, selectivity, and potential stability. Additionally, the all-solid-state Cu^{2+}-ISμE is promising for detection of Cu^{2+} in the sediment pore water samples with small volumes. The proposed method is versatile and can be used for detection of other heavy metal ions in sediments by using different ion-selective membranes. With the introduction of the solid-contact pototentiometric microsensors for pore water analysis, the perturbation of the profiles of the heavy metal ions in the sediment pore water can be avoided. Thus, the electrode shows potential promise for *in situ* measurements of heavy metal ions in pore water. The related studies are currently in progress in this laboratory.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2018.09.125.

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