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A solid-contact Pb^{2+}-selective polymeric membrane electrode with Nafion-doped poly(pyrrole) as ion-to-electron transducer

Tanji Yin · Dawei Pan · Wei Qin

Abstract Conducting polymer poly(pyrrole) (PPy) doped with Nafion was successfully used as ion-to-electron transducer in the construction of a solid-contact Pb^{2+}-selective polymeric membrane electrode. The Nafion dopant can effectively increase the capacitance of the conducting polymer and improve the mechanical robustness of the coating. The transducer layer, PPy-Nafion, characterized by cyclic voltammetry and electrochemical impedance spectroscopy, exhibits a sufficiently high bulk (redox) capacitance and fast ion and electron transport process. The new Pb^{2+}-selective polymeric membrane electrode, based on PPy-Nafion film as solid contact, shows stable Nernstian characteristics in Pb(NO$_3$)$_2$ solution within the concentration range of 1.0×10^{-7}–1.0×10^{-3} M, and the detection limit is 4.3×10^{-8} M. The potential stability of the electrode and the influence of the interfacial water layer were also evaluated by chronopotentiometry and potentiometric water layer test, respectively. The results show that the solid-contact Pb^{2+}-selective electrode, based on PPy-Nafion film as ion-to-electron transducer, can effectively overcome the potential drift and reduce the water layer between the PPy-Nafion transducer layer and the ion-selective membrane.

Keywords Solid contact · Ion-selective electrode · Lead · Poly(pyrrole) · Nafion

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Introduction

Potentiometric ion-selective electrodes (ISEs) have attracted much attention for directly determining ions in medical, environmental, and industrial analysis due to their attractive features including small size, portability, low energy consumption, and low cost [1, 2]. However, the conventional polymeric membrane electrodes with the inner filling solutions suffer from ion fluxes of primary ions between the inner aqueous solution and the sample solution, which may deteriorate the lower detection limits [3] and the selectivity coefficients of the ISEs [4]. Many empirical approaches have been used to decrease these ion fluxes including adjusting the composition of the inner solution [5, 6], lowering the concentration of ionic sites, and increasing the thickness and polymer content of the membrane [7]. Coated-wire ISEs offered a way to eliminate the influence of the inner solution. However, the main drawback of coated-wire ISEs is the poor potential stability resulting from the high charge-transfer resistance and low double-layer capacitance at the interface between the electronic conductor and the ion-selective membrane [8, 9]. To improve potential stability, solid-contact ISEs are fabricated by utilizing electroactive materials with electronic and ionic

conductivities to act as ion-to-electron transducer between the electronic conductor and the ion-selective membrane [10–13]. Among the electroactive materials available today, the electrically conducting polymers with excellent and unique properties have attracted much interest [2, 14]. Poly (pyrrole) (PPy) doped with different anionic dopants are one of the most promising ion-to-electron transducers for solid-contact ISEs. For example, PPy doped with calcium complexing ligand Tiron was applied as solid contact for the construction of all-solid-state ISEs, e.g., calcium-selective electrode [15]. Pandey et al. [16] developed PPy doped with tetraphenylborate as solid contact in K^+-ISEs to obtain reversible ion transfer at the interface between conducting polymer and the ion-selective membrane. Electropolymerized PPy doped with different anions, such as $Fe(CN)_6^{4-}$, Cl^-, NO_3^-, ClO_4^-, CH_3COO^-, were used as solid contact in pH-selective electrodes [17].

Nafion has been widely used as cation exchanger and applied to fabricate different kinds of chemically modified electrodes. It contains a hydrophobic fluorocarbon chain and hydrophilic $—SO_3^-$ groups. Nafion can act as a molecular dopant in the electrochemical synthesis of the conducting polymer PPy and improve the stability to the electrochemical cycling [18]. In addition, the adhesion of the PPy doped with Nafion is much better than that of conducting polymer doped with other anions such as perchlorate ions [18]. However, Nafion-doped conducting polymer PPy have not been reported as effectively ion-to-electron transducer in the construction of solid-contact electrodes.

Lead, one of the most toxic metallic pollutants, can damage nervous system and cause the abnormal function of the brain and many other organs. Moreover, exposure to excessive lead also causes blood disorders in mammals. Therefore, it is necessary to develop efficient methods to detect Pb^{2+} ion. Inductively coupled plasma mass spectrometry, as a powerful technique, is widely used for the determination of metal ions. However, it is rather expensive, time-consuming, and not suitable for on-site analysis. Potentiometry with ISEs is a very promising method for trace Pb^{2+} level analysis [19, 20], owing to its advantages such as low cost, simple analytical procedure, and fast response.

In the present work, we developed an electroactive film, PPy-Nafion, as ion-to-electron transducer to design a solid-contact Pb^{2+}-selective polymeric membrane electrode. The electrochemical properties of the transducer layer PPy-Nafion was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The potential stability of the new solid-contact electrode and the influence of water layer between the PPy-Nafion transducer layer and the Pb^{2+}-selective membrane were also investigated.

Experimental

Chemicals

Lead ionophore [IV *tert*-Butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide)], sodium trakis[3,5-*bis*(trifluoro-methyl)phenyl]borate (NaTFPB), 2-nitrophenyl octyl ether (*o*-NPOE), and high molecular weight poly(vinyl chloride) (PVC), tetradodecylammonium tetrakis-(4-chlorophenyl) borate (ETH500) were purchased from Fluka (Buchs, Switzerland). Nafion-perfluorinated resin solution (5 wt.% in a mixture of lower aliphatic alcohols and water) and pyrrole (98%) were obtained from Aldrich. All other chemicals were of analytical reagent grade. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

Fabrication of solid contact Pb^{2+}-selective electrode

The glassy carbon (GC, 3 mm in diameter) electrode was polished with 1.0, 0.3, and 0.05 μm alumina slurries, rinsed with deionized water, and then cleaned ultrasonically. Nafion-doped PPy film was electrodeposited potentiostatically on the polished bare GC working electrode in an acetonitrile solution containing 0.1 M pyrrole and 0.25 wt.% Nafion. A constant potential of 1.0 V (vs. Ag/Ag/Cl) was applied to produce polymerization charges of 2.5 mC. After polymerization, the PPy-Nafion modified GC electrode was rinsed with acetonitrile to remove residual pyrrole monomer and Nafion, and dried with N_2 before further use.

The membrane components (totaling 100 mg) for the solid-contact Pb^{2+}-ISE, including lead ionophore (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 (THF; 1.5 ml) and poured into a glass ring (i.d. 20 mm) fixed on a glass plate. After overnight solvent evaporation, a disk of 5-mm diameter was punched from the membrane and glued to the PPy-Nafion modified GC electrode with THF. For comparison, Pb^{2+}-selective coated disk electrode was prepared by applying the ion-selective membrane directly on the polished bare GC electrode with THF. The above-prepared electrodes are denoted as the GC/PPy-Nafion/Pb^{2+}-ISE and GC/Pb^{2+}-ISE electrodes, respectively. For the measurements in dilute solutions, the electrodes were conditioned for 2 days in $1.0×10^{-5}$ M $Pb(NO_3)_2$ and then overnight in $1.0×10^{-9}$ M $Pb(NO_3)_2$. For the selectivity measurements using the separate solution method [21], the electrodes were conditioned in $1.0×10^{-3}$ M $NaNO_3$ for 1 day.

EMF measurements

The electromotive force (EMF) measurements were carried out at room temperature using a CHI660C electrochemical

workstation (Shanghai Chenhua Apparatus) with Ag/AgCl (3 M KCl) as reference electrode in the galvanic cell: Ag/AgCl (3 M KCl)|sample solution |Pb^{2+}-ISE membrane|PPy-Nafion/GC. All EMF values were corrected for liquid junction potentials according to the Henderson equation, and the ion activities were calculated by the Debye–Hückel approximation.

CV and EIS

The CV measurements were carried out in 0.1 M KCl solution with a conventional three-electrode system comprising a PPy-Nafion modified GC working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl (3 M KCl) reference electrode. The cycles were recorded between −0.5 and 0.5 V with a scan rate of 100 mV/s.

EIS was performed at the open-circuit potential in the frequency range 100 kHz–10 mHz by using a sinusoidal excitation signal. An excitation amplitude of 10 mV was applied in 0.1 M KCl solution while studying the GC/PPy-Nafion electrode. For the GC/Pb^{2+}-ISE and GC/PPy-Nafion/Pb^{2+}-ISE electrodes, an excitation amplitude of 100 mV was used in 1.0×10^{-3} M Pb(NO$_3$)$_2$ solution in order to enhance the signal-to-noise ratio.

Chronopotentiometry

Chronopotentiometric measurements were carried out on the GC/Pb^{2+}-ISE and the GC/PPy-Nafion/Pb^{2+}-ISE electrodes in 1.0×10^{-3} M Pb(NO$_3$)$_2$ solution by applying a constant current of +1 nA for 100 s followed by a current of −1 nA for 100 s.

Results and discussions

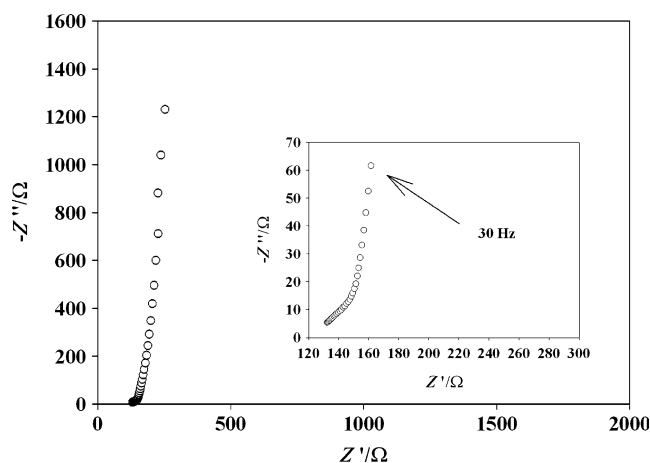## Characterization of the GC/PPy-Nafion electrode

In order to evaluate the performance of the PPy-Nafion film as ion-to-electron transducers in the design of solid-contact ISEs, the GC/PPy-Nafion electrode was characterized by CV and EIS. Figure 1 shows the cyclic voltammograms of a bare GC electrode and the GC/PPy-Nafion electrode recorded in 0.1 M KCl at a scan rate of 100 mV/s. The potential scan range of −0.5 to +0.5 V [vs. Ag/AgCl (3 M KCl)] was used to avoid degradation of the polymer [22]. It can be seen that the capacitive current of the GC/PPy-Nafion electrode is higher than that of the bare GC electrode. This phenomenon indicates that the high redox capacitance can be obtained with the GC/PPy-Nafion electrode. Moreover, the anodic currents at 0 V were found to vary linearly with increasing the scan rate (inset in
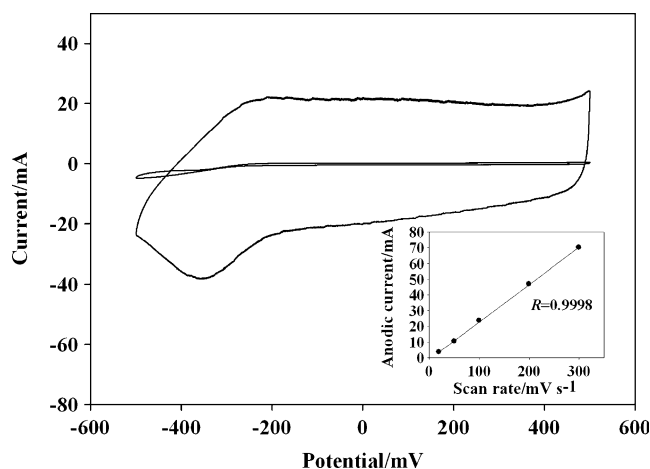

Fig. 1 Cyclic voltammograms for the bare GC electrode and the GC/PPy-Nafion electrode recorded in 0.1 M KCl at a scan rate of 100 mV/s. *Inset*: Plot of anodic current at 0 V vs. scan rate

Fig. 1), revealing that both ion and electron transports in the PPy-Nafion film are fast [22].

Figure 2 shows the electrochemical impedance spectra of the GC/PPy-Nafion electrode recorded in 0.1 M KCl solution. The impedance spectra are dominated by an approximate 90° capacitive line, and there is only a slight deviation from the capacitive line at high frequencies. These results indicate that a fast electronic transfer occurs at the interface between GC/PPy-Nafion and PPy-Nafion/solution. The equivalent circuit, which is composed of the solution resistance (R_s), the bulk capacitance (C_d), and the finite-length Warburg diffusion element (Z_D), is showed in Fig. 3. The Z_D element is described as follows by the diffusion time

Fig. 2 Impedance spectra of the GC/PPy-Nafion electrode recorded in 0.1 M KCl solution at the open-circuit potential. Polymerization charge, 2.5 mC; the frequency range, 0.6 Hz–10 kHz; the excitation amplitude, 10 mV
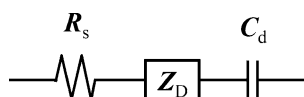
Fig. 3 Equivalent electrical circuit for the GC/PPy-Nafion electrode. R_s Solution resistance, Z_D finite-length Warburg diffusion, C_d bulk capacitance

constant (τ_D), the diffusion pseudo-capacitance (C_D), and the diffusion resistance ($R_D = \tau_D / C_D$) [23]:

$$Z_D = \tau_D / C_D \coth(jw\tau_D)^{0.5} / (jw\tau_D)^{0.5} \quad (1)$$

The impedance spectra were fitted to the equivalent circuit (Fig. 3). The solution resistance (R_{sol}) is 137 Ω, which is close to the estimated value ($R_{sol} = 150$ Ω) for the conducting polymer transducer in an identical 0.1 M KCl solution [24]. In addition, the estimated value for the bulk capacitance (C_d) of the GC/PPy-Nafion electrode is 124 μF, which is higher than that of bare GC electrode ($C_d = 1$ μF). This result is consistent with those obtained by CV. Since a sufficiently high bulk (redox) capacitance of the conducting polymer used as the solid contact is a prerequisite for obtaining a stable potential of the all solid-state potentiometric ion sensor [9], it can be concluded that PPy-Nafion can act as ion-to-electron transducers between the bare GC electrode and the ion-selective membrane and display highly stable potential for the construction of solid-contact ISEs.

Potentiometric response of the GC/PPy-Nafion/Pb²⁺-ISE electrode

After the GC/PPy-Nafion/Pb²⁺-ISE electrode was conditioned for 2 days in 1.0×10^{-5} M Pb(NO₃)₂ and then overnight in 1.0×10^{-9} M Pb(NO₃)₂, the potentiometric response was measured in Pb(NO₃)₂ solution in the concentration range of 1.0×10^{-9}–1.0×10^{-3} M. The calibration curve is shown in Fig. 4. The slope of calibration curve in the linear range of 1.0×10^{-7}–1.0×10^{-3} M is 29.1 ± 0.6 mV/decade ($n=5$, $R^2 = 0.9994$). The detection limit calculated as the intersection of the two slope lines is 4.3×10^{-8} M. The response time (see inset of Fig. 4) is less than 10 s, indicating that the absence of an inner solution favors the response time of the electrode [12, 25]. Moreover, the GC/PPy-Nafion/Pb²⁺-ISE electrode has a good reproducibility and stability. The relative standard deviation of the potentials of different electrodes was less than 10% ($n=5$) for the same concentration.

The selectivity of the GC/Pb²⁺-ISE and GC/PPy-Nafion/Pb²⁺-ISE electrodes were characterized by using Bakker's method to eliminate the influence of the inherent sensitivity limit on the response toward discriminated ions [21]. As shown in Fig. 5, the selectivity coefficients of the GC/PPy-Nafion/Pb²⁺-ISE and GC/Pb²⁺-ISE electrodes are similar.
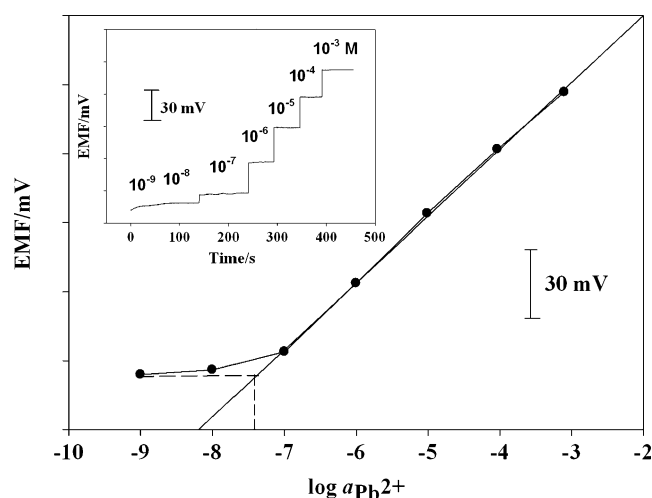

Fig. 4 Calibration curve obtained by successively increasing Pb²⁺ activities for the GC/PPy-Nafion/Pb²⁺-ISE electrode. *Inset*: Time traces of EMF response of the GC/PPy-Nafion/Pb²⁺-ISE electrode

These results confirm that the selectivity of the solid-contact ISEs is mainly determined by the composition of the ion-selective membrane, not by the type of the used solid contact.
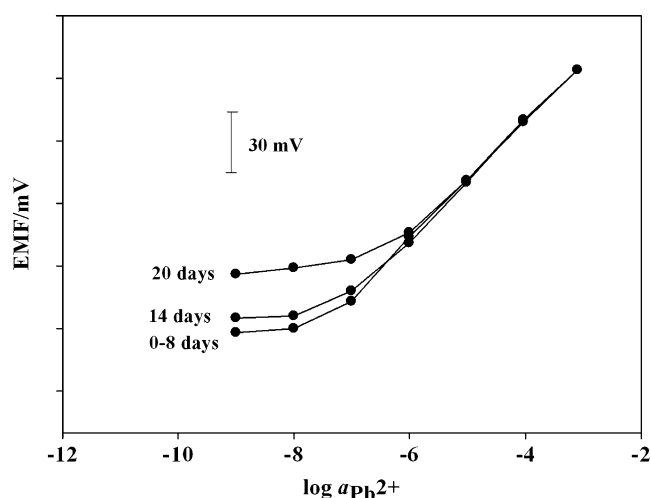
The long-term response behavior of the GC/PPy-Nafion/Pb²⁺-ISE electrode is shown in Fig. 6. Between measurements, the GC/PPy-Nafion/Pb²⁺-ISE electrode was kept in the dark in 1.0×10^{-9} M Pb(NO₃)₂ solution. During the first 14 days, the slight changes of the slope and the detection limit of the electrode occur. Afterwards, the detection limit is deteriorated by about one decade of activity values in 20 days, probably owing to ionophore leaching from the membrane [26].

Chronopotentiometry

The potential stability of the solid-contact Pb²⁺-ISE electrode was evaluated by constant current chronopotentiometry [9].
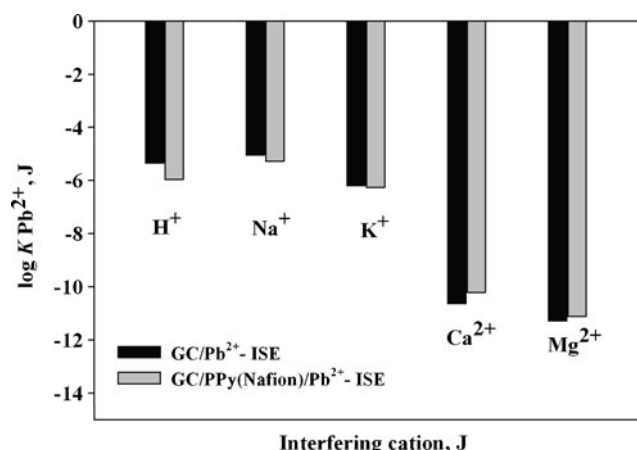
**Fig. 5** Selectivity coefficients (log $K_{Pb^{2+},J}$) of the GC/Pb²⁺-ISE and the GC/PPy-Nafion/Pb²⁺-ISE electrodes

Fig. 6 Long-term response behavior of the GC/PPy-Nafion/Pb²⁺-ISE electrode

Figure 7 shows the chronopotentiograms for the GC/Pb²⁺-ISE and the GC/PPy-Nafion/Pb²⁺-ISE electrodes recorded when a current of ±1 nA was applied in 10^{-3} M Pb(NO₃)₂. The two main characteristic, the potential jump when changing the direction of the current and the slow potential drift at long times, can be clearly observed. The total resistance (R) of the GC/PPy-Nafion/Pb²⁺-ISE electrode is approximately 0.3 MΩ, estimated by the potential jump, according to Ohm's law, $R = E/I$, where E represents the potential change and I is the applied current. Moreover, the potential drift of the GC/PPy-Nafion/Pb²⁺-ISE electrode, derived from the ratio $\Delta E/\Delta t$, is 36 µV/s for the current of 1 nA. The estimated value is lower than that of the GC/Pb²⁺-ISE electrode under the similar conditions ($\Delta E/\Delta t = 340$ µV/s). These results suggest that the potential stability can be dramatically improved by applying a
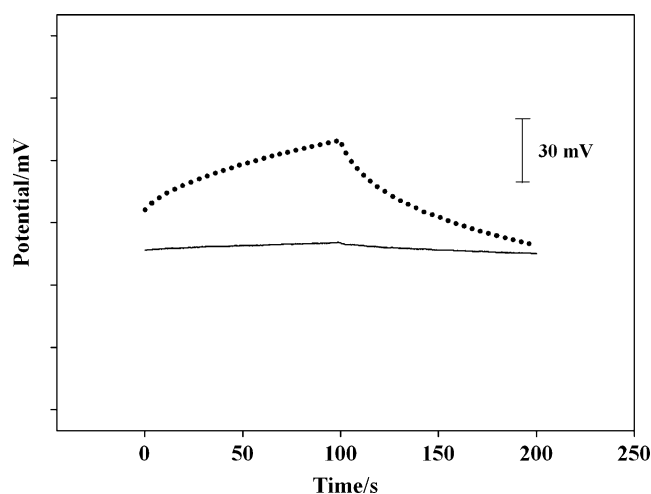
Fig. 7 Chronopotentiograms for the GC/Pb²⁺-ISE (*dotted line*) and the GC/PPy-Nafion/Pb²⁺-ISE (*solid line*) electrodes recorded in 1.0×10^{-3} M Pb(NO₃)₂. The applied current was +1 nA for 100 s and −1 nA for 100 s
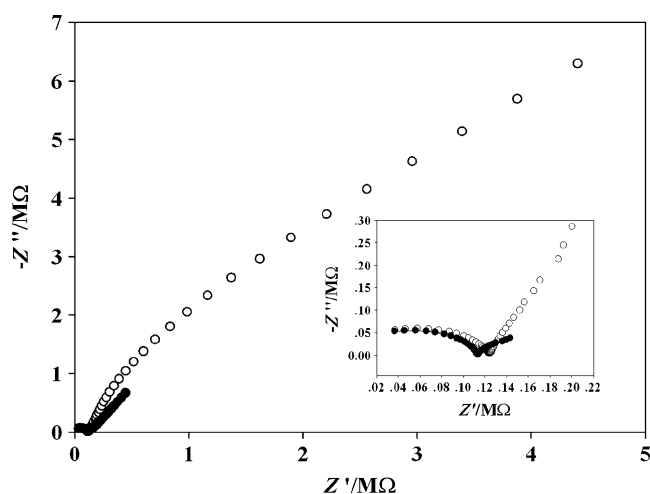

Fig. 8 Impedance spectra of the GC/Pb²⁺-ISE (*hollow circle*) and the GC/PPy-Nafion/Pb²⁺-ISE (*solid circle*) electrodes recorded in 1.0×10^{-3} M Pb(NO₃)₂ at the open-circuit potential. The frequency range, 0.01 Hz–100 kHz; the excitation amplitude, 100 mV

PPy-Nafion film as the solid contact between the GC electrode and the ion-selective membrane. In addition, according to the fundamental capacitor equation $I = C\mathrm{d}E/\mathrm{d}t$, the evaluated low-frequency capacitance of the GC/PPy-Nafion/Pb²⁺-ISE electrode is as low as 28 µF, which is due to the PPy-Nafion solid-contact layer covered with Pb²⁺-selective polymer membrane.

Impedance of the GC/Pb²⁺-ISE and the GC/PPy-Nafion/Pb²⁺-ISE electrodes

The impedance spectra of the GC/Pb²⁺-ISE and the GC/PPy-Nafion/Pb²⁺-ISE electrodes in 1.0×10^{-3} M Pb(NO₃)₂ are shown in Fig. 8. Both impedance spectra demonstrate a high-frequency semicircle, resulting from the bulk resistance of
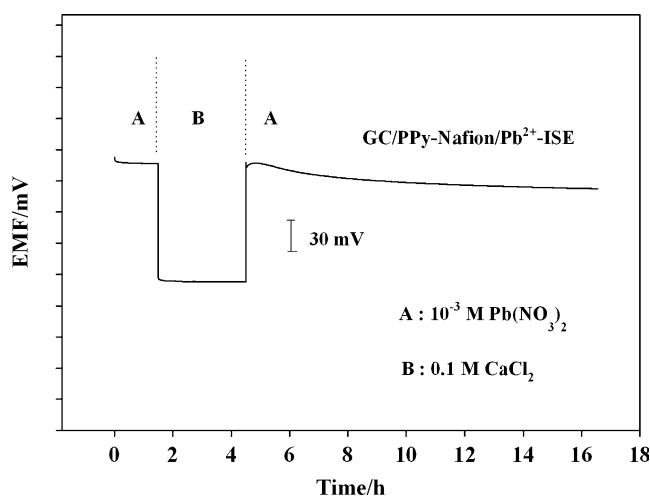
Fig. 9 Water layer test for the GC/PPy-Nafion/Pb²⁺-ISE electrode. The measurements were recorded in 1.0×10^{-3} M Pb(NO₃)₂ (**a**) and 0.1 M CaCl₂ (**b**)

the ion-selective membrane in parallel with its geometric capacitance. The GC/Pb^{2+}-ISE electrode also displays a large low-frequency semicircle, which is due to the parallel connection between the small double-layer capacitance and the large charge-transfer resistance at the "blocked" interface between the GC electrode and the ion-selective polymeric membrane. However, compared with the GC/Pb^{2+}-ISE electrode, the impedance spectrum of the GC/PPy-Nafion/Pb^{2+}-ISE electrode exhibits higher low-frequency capacitance and lower charge-transfer resistance because of the changes of the interfacial conduction, which suggests that electronically and ionically conducting PPy-Nafion layer facilitates the charge transfer across the interfaces between the electronically conducting GC electrode and ionically conducting ion-selective membrane, which is characteristic for "unblocked" interface.

Water layer test

The influence of water layer between the PPy-Nafion transducer layer and the Pb^{2+}-selective electrode was investigated by the potentiometic water layer test [27]. The potential response of the GC/PPy-Nafion/Pb^{2+}-ISE electrode was measured in 1.0×10^{-3} M Pb(NO$_3$)$_2$, 0.1 M CaCl$_2$, and again 1.0×10^{-3} M Pb(NO$_3$)$_2$, respectively. As seen in Fig. 9, a rather stable potential is initially observed when the GC/PPy-Nafion/Pb^{2+}-ISE electrode is detected in 10^{-3} M Pb(NO$_3$)$_2$ for 1.5 h. After the solution is replaced with the discriminated interfering solution (0.1 M CaCl$_2$), a potential response of the electrode is still stable for 3 h. The presence of an inner water film causes a positive drift when changing the sample solution from the primary ion to a solution of an interfering ion, because the primary ion is slowly replaced by the interfering ion in the film [27]. Figure 9 shows the absence of positive potential drift, which indicates that no undesirable water layer is formed between PPy-Nafion transducer layer and Pb^{2+}-selective membrane.

Conclusions

The work demonstrates that Nafion-doped PPy was successfully applied as effective ion-to-electron transducer in solid contact Pb^{2+}-selective polymeric membrane electrode. Nafion as a molecular dopant can effectively increase the capacitance of the conducting polymer and improve the mechanical properties of the coating. Additionally, owing to its sufficiently high bulk (redox) capacitance and the fast process of ion and electron transport, the PPy-Nafion layer has the capability to act as ion-to-electron transducer between the electrochemically active GC and the ionically active polymeric ion-selective membrane. The new Pb^{2+}-selective polymeric membrane electrode, based on PPy-

Nafion as solid contact, shows stable Nernstian characteristics within the concentration range from 1.0×10^{-3} to 1.0×10^{-7} M Pb(NO$_3$)$_2$ solution, with response times less than 10 s. Moreover, the solid-contact ISE electrode displays considerable stability, and no undesirable water layer is formed between the PPy-Nafion film and the Pb^{2+}-selective polymeric membrane.

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