



Thin polymeric membrane ion-selective electrodes for trace-level potentiometric detection

Junhao Wang^{a, c}, Rongning Liang^{a, d, **}, Wei Qin^{a, b, d, *}

^a CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China

^b Laboratory for Marine Biology and Biotechnology, Pilot National Laboratory for Marine Science and Technology (Qingdao), Shandong, 266237, PR China

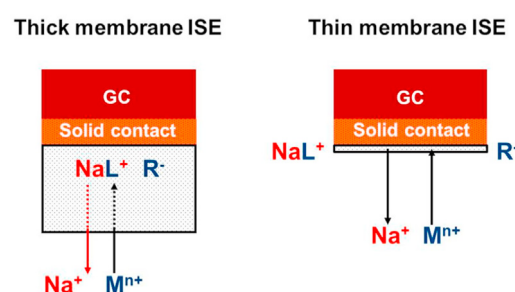
^c University of Chinese Academy of Sciences, Beijing, 100049, PR China

^d Center for Ocean Mega-Science, Chinese Academy of Sciences, Qingdao, Shandong 266071, PR China

HIGHLIGHTS

- A novel thin polymeric membrane potentiometric sensor is developed.
- The thin membrane configuration is used to improve the detection limit of the non-classical potentiometric sensor.
- The proposed sensor shows a significantly improved detection sensitivity compared to the conventional ISEs.
- The thin membrane-based concept can be extended to improve sensing performance of other polymeric membrane ISEs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 August 2020

Received in revised form

9 September 2020

Accepted 11 September 2020

Available online 13 September 2020

Keywords:

Ion-selective electrode

Thin-layer membrane

Trace-level analysis

Non-classical potentiometric sensor

Solid contact

ABSTRACT

In this work, we describe a novel method to improve the detection limits of the non-classical polymeric membrane ion-selective electrodes (ISEs) which are conditioned with highly discriminated ions instead of primary ions. It is based on a thin-layer ISE membrane with a thickness of 5 μm , which is coated on ordered mesoporous carbon used as solid contact. The diffusion of the primary ion from the surface of the sensing membrane to the bulk of the membrane could be avoided by the proposed thin membrane configuration. Since the detection sensitivity of the non-classical ISEs depends on the accumulation of the primary ion in the interfacial layer of the sensing membrane, a lower detection limit can be obtained. By using the copper ion as a model, the present potentiometric sensor shows a significantly improved detection sensitivity compared to the conventional ISE with a membrane thickness of ca. 200 μm . Low detection limits of 0.29 and 0.53 nM can be obtained in 0.01 and 0.5 M NaCl, respectively. In addition, the proposed sensor exhibits an excellent reversibility by using a neutral proton-selective ionophore incorporated in the thin membrane.

© 2020 Elsevier B.V. All rights reserved.

^{**} Corresponding author. CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China.,

^{*} Corresponding author. CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China.

E-mail addresses: rnliang@yic.ac.cn (R. Liang), wqin@yic.ac.cn (W. Qin).

1. Introduction

Nowadays, polymeric membrane ion-selective electrodes (ISEs) have played a vital role in various fields including clinical diagnosis, environmental monitoring and food analysis due to their excellent selectivity, easy preparation and high reliability [1–6]. For the

conventional ISEs, the polymeric sensing membranes are usually conditioned with the primary ions before measurements. In this case, the potentiometric measurements are performed under the classical equilibrium conditions with the Nernstian responses. The lower detection limits of these classical ISEs are unfortunately in the micromolar range. This poses serious limits to their applications in trace-level analysis. Since 1997, the improvements in the lower detection limits of ISEs have allowed the Nernstian responses at subnanomolar levels, which can be achieved by drastically reducing zero-current primary ion fluxes from the membrane in the direction of the sample [7]. During the past decades, various approaches have been utilized to improve the lower detection limits of ISEs, such as employing a chelator [8] or an ion-exchange resin in the inner solution [9], using a rotating electrode configuration [10], immobilizing the ionophore [11] and applying a solid inner contact [12–15]. Such advances have made the new wave of ISEs [16–19].

In recent years, various polymeric membrane ISEs based on the non-equilibrium response mechanism have been developed [20–22]. Unlike the classical ones, these electrodes are conditioned with the highly discriminated ions instead of the primary ions. In these systems, the potentiometric responses to the primary ions in the aqueous solution are based on the non-equilibrium ion-exchange processes between the discriminated ions in the membrane phase and the primary ions in the aqueous phase, which results in a kinetic potential response [20]. The pioneering work on the non-equilibrium potentiometry was reported by Hulanicki [23]. In that work, the chloride-conditioned anion-exchanger-based membrane ISEs were used for detection of the lipophilic perchlorate and periodate [23]. Later, the non-equilibrium mechanism was extended to sensitive measurements of polyions such as heparin and protamine, for which a reproducible and steady-state potential response can be obtained when the flux of polyion from the sample solution equals that in the ISE membrane [20]. Currently, these potentiometric polyion sensors have been routinely implemented for use in clinical detection of heparin in undiluted whole-blood samples, demonstrating that such non-classical sensing schemes can be practically useful [24]. In addition, the performances of these non-equilibrium potentiometric sensors have been further improved by introduction of current control to induce instrumentally an ion flux across the membrane [25]. Given the large number of potential applications of the non-classical potentiometric sensors, it is of interest to further enhance the sensitivity of these sensors. Recently, we described an asymmetric polymeric membrane ISE configuration to improve the detection limits of non-classical potentiometric sensors [26]. The lipophilic ion-exchanger was evenly spread onto the surface of the polymeric membrane rather than being incorporated into the bulk of the membrane matrix as for the conventional ISEs. Therefore, the diffusion of the primary ions from the surface of the sensing membrane to the bulk of the membrane could be effectively blocked. Since the detection sensitivity relies on the accumulation of the primary ions in the interfacial layer of the sensing membrane, a lower detection limit could be obtained. However, it should be noted that the ion flux from the membrane interface into the membrane bulk cannot be fully blocked because of the inherent impurities in the PVC matrix. In addition, the slow penetration of the ion exchanger from the surface layer into the membrane bulk might affect the sensor's long-term stability.

Herein, we propose a new robust method to improve the detection limits of the non-classical polymeric membrane ISEs. Unlike the conventional ISEs which have membranes of $\sim 200\ \mu\text{m}$, the proposed ISE is based on a thin membrane of $\sim 5\ \mu\text{m}$. Recently, the solid-contact ISEs with the thin polymer membranes have been exploited in the ion-transfer stripping voltammetry [27] and

coulometric transduction method [28]. Note that, the thin membrane-based ISEs have rarely been explored in potentiometric sensing. Bakker and coworkers developed the thin-layer membrane potentiometric sensors for sequential ion determination [29] and rapid identification for development of solid-contact ISEs [30]. It can be expected that the thin membrane configuration can effectively inhibit the diffusion of the primary ions from the membrane interface to the membrane bulk owing to the absence of the membrane bulk. Thus, a lower detection limit can be achieved. As a proof-of-concept experiment, copper is selected as a model. In order to support the thin Cu^{2+} -ISE membrane, ordered mesoporous carbon (OMC) is employed as the solid contact. It will be shown that such a thin ISE membrane can offer remarkably improved sensitivity for potentiometric measurement of Cu^{2+} . To the best of our knowledge, the ISEs with thin membranes have not yet been explored in the improvement of the detection limits in zero-current potentiometry.

2. Experimental

2.1. Reagents and materials

High molecular weight poly (vinyl chloride) (PVC), 2-nitrophenyl octyl ether (o-NPOE), sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), N,N,N',N'-tetrabutyl-3,6-dioxaoctanedi (thioamide) (ETH 1062, Cu^{2+} ionophore) and NaCl ($\geq 99.999\%$) were purchased from Sigma-Aldrich. OMC with a BET surface area $\geq 900\ \text{m}^2/\text{g}$ and an average pore diameter of 3.8–4 nm was obtained from Nanjing XFANO Materials Tech. Co., Ltd. All other chemical reagents were purchased from Sinopharm Reagent Co., Ltd (China). They were of analytical grade and used without further purification. Aqueous solutions were prepared with freshly deionized water ($18.2\ \text{M}\Omega\ \text{cm}$ specific resistance) obtained with a Pall Cascada laboratory water system.

2.2. Electrode preparation

The glassy carbon (GC) electrodes (3 mm in diameter) were polished with $0.05\ \mu\text{m}$ alumina slurries. Then, they were ultrasonically cleaned and rinsed with deionized water and ethanol for 10 min. The OMC suspensions were prepared by ultrasonically 1 mg of the OMC material in 1 mL of freshly distilled THF for 1 h. $6\ \mu\text{L}$ of the prepared OMC suspension was dip-coated on the GC electrodes, and then left to dry at room temperature for further use.

The conventional thick membranes of Cu^{2+} -ISE contained 1 wt% ETH 1062, 0.5 wt% ETH 5315, 1 wt% NaTFPB, 32.5 wt% PVC, and 65 wt% o-NPOE. The membrane cocktail was prepared by dissolving 360 mg of the membrane components in 3.6 mL of THF and stirred for at least 2 h to obtain a homogeneous solution. Then, $80\ \mu\text{L}$ of the membrane cocktail was drop-cast on the above OMC modified GC electrodes to prepare the proposed solid-contact thick membrane Cu^{2+} -ISEs, and then left to dry at room temperature. Different thin membrane cocktails were prepared by diluting a certain amount of the thick membrane cocktail in THF. The membrane of $5\ \mu\text{m}$ was formed by drop-casting $40\ \mu\text{L}$ of the diluted membrane cocktail obtained by diluting $100\ \mu\text{L}$ of the thick membrane cocktail in 2 mL THF. The cocktail solution for the thin membrane was also allowed to evaporate naturally at room temperature. An approximately uniform thin membrane could be obtained. The thickness of the membrane was determined visually by using a microscope after the membrane was stained with methylene blue. Prior to analysis, all the electrodes were conditioned in $0.01\ \text{M}$ NaCl. The conventional thick membranes were conditioned overnight, while the thin ones were conditioned for 1 h before measurements.

2.3. Potentiometric measurements

All the potentiometric measurements were carried out by using a high impedance input 16-channels potentiometric monitor (Lawson Laboratories, Inc., USA) at room temperature with a Ag/AgCl (3 M KCl) electrode as reference electrode in the galvanic cell: Ag|AgCl (3 M KCl)|sample solution|Cu²⁺-selective membrane|OMC|GC electrode. For potentiometric measurements, the electrodes were immersed in the background solution stirred at 1500 rpm. When the baseline potential was stable, the copper solution with a desired amount was added into the background solution. The potential difference between the baseline and the potential measured at a fixed time of 150 s after Cu²⁺ addition was used for quantification. Selectivity coefficients were determined by the separate solution method [31]. The electromotive force (EMF) values were corrected for the liquid-junction potentials with the Henderson equation. The ion activity coefficients were calculated according to the Debye-Hückel equation.

3. Results and discussion

The thin polymeric membrane based solid-contact ISEs have been mainly applied in ion-transfer stripping voltammetry [27]. Despite their great successes in the field of electrochemistry, thin membrane-based ISEs have rarely been explored in potentiometry. More recently, Bakker and coworkers subsequently brought this thin membrane configuration into potentiometric sequential cation and anion sensing [29] and rapid complication identification in the development process of the solid-contact ISEs [30]. The aim of this work is to demonstrate that thin membranes can also be successfully used in the improvement of the detection limits of non-classical ISEs.

3.1. Sensing mechanism of the thin membrane-based ISE

Traditionally, the thickness of the polymeric ISE membrane is around 100–200 μm . By conditioning the membrane in the interfering ion solution (e.g., NaCl), the highly discriminated ion (e.g., Na⁺) can be extracted in the interfacial layer of the sensing membrane. When the conditioned electrode contacts with the solution containing the primary ion, the primary ion (e.g., Cu²⁺) can displace the interfering ion rapidly owing to the strong ion-ligand interactions between the primary ion and the ionophore in the membrane phase. In this case, the response to the primary ion is quite super-Nernstian and this non-classical response was then modeled by using a steady-state approach [32] and further explained by the non-equilibrium mechanism [20]. It has been well established that under the non-equilibrium conditions, the detection sensitivity, which depends on the concentration of the primary ion accumulated in the boundary layer of the membrane phase, could be improved by many ways such as stirring the sample solution and changing the composition of the membrane phase [20,26].

The sensing mechanisms of the non-classical membrane ISEs conditioned with highly discriminated ions are shown in Fig. 1. For the conventional membrane with a thickness of 100–200 μm , the primary ions could be diffused favorably from the boundary layer into the bulk of the membrane due to the presence of the exchanger or the impurities in the membrane (Fig. 1a). In the present work, a thin membrane (of $\sim 5 \mu\text{m}$) is proposed to improve the detection sensitivity (Fig. 1b). As illustrated, the membrane thickness is much less than that of the conventional ISE one. Thus, it can be expected that after displacement of the highly discriminated ion by the primary ion in the membrane-phase diffusion layer, the further diffusion of the primary ion away from the membrane interface

into the membrane bulk as for the conventional thick membrane (Fig. 1a) would be effectively suppressed because of the absence of the membrane bulk (Fig. 1b). Additionally, according to the previous report [29,30], by reducing the thickness of the ISE membrane, a rapid diffusion process would occur. In this case, more primary ions could be rapidly accumulated in the membrane boundary layer so that an excellent detection sensitivity can be obtained.

3.2. Optimization of the proposed electrode

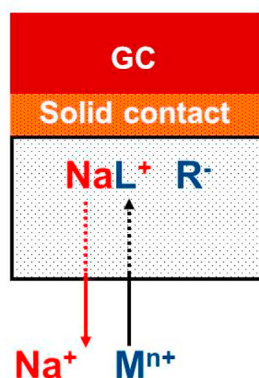
Since the thickness of the ISE membrane plays an important role in the detection sensitivity under non-equilibrium conditions, the influence of the membrane thickness was investigated. Potentiometric detection of Cu²⁺ was performed in a background of 0.01 M NaCl at the concentrations of 10^{−9} and 10^{−8.5} M with a constant stirring at 1500 rpm. As illustrated in Fig. 2, the potential responses to the low-level Cu²⁺ in the presence of 0.01 M NaCl increase with a decrease of the membrane thickness owing to the increased accumulation of Cu²⁺ in the interfacial layer of the membrane. For measurements of Cu²⁺ at 1 nM, the potential responses obtained by the thicker membranes are neglectable (curves A and B), while an obvious EMF change can be observed for the membrane with a thickness of 5 μm (curve C). These results indicate that the diffusion of the primary ion from the phase boundary into the bulk of the membrane can be effectively suppressed by using the thinner membrane. However, it should be noted that further decrease in the thickness of the sensing membrane could cause poor response reproducibility (data not shown), which is probably attributed to the fact that it is difficult to control the membrane thickness via drop-casting a rather diluted membrane cocktail solution on the OMC-modified GC electrode.

Since the EMF response of the proposed discriminated-ion-conditioned electrode is highly dependent on the accumulation of the primary ions in the interfacial layer of the membrane phase, the detection sensitivity can be largely improved by accelerating the ion fluxes in the aqueous Nernst layer. It has been well known that improvements in the detection sensitivity of the non-classical potentiometric sensors could be made by using the rotating electrode configuration which can enhance mass transfer of the analyte to the membrane/sample interface [10,26]. Hence, the effect of the stirring rate on the sensitivity was investigated. As shown in Fig. S1 in the Supporting Information, the potential response increases rapidly with increasing the stirring rate up to 1500 rpm and then increases gradually. However, larger noise levels in the potential response could be observed when the stirring rates were higher than 1500 rpm. Therefore, 1500 rpm was selected as the optimal stirring rate for the present thin membrane ISE.

3.3. Characterization of the thin membrane ISE

Under the optimized conditions, the potential responses of the proposed sensor with the thin membrane of 5 μm to Cu²⁺ at the concentrations of 10^{−9}, 10^{−8} and 10^{−7} M were tested. Fig. 3a shows the potential response of the discriminated-ion-conditioned thin membrane Cu²⁺-selective electrodes in 0.01 M NaCl. It can be seen that the proposed sensor exhibits an excellent sensitivity for Cu²⁺ detection. For a comparison, the potential response of the conventional thick ISE membrane with a thickness of 100 μm was also measured. The results are shown in Fig. 3b. Clearly, a typical non-classical potential response behavior can be observed for this conventional ISE. A strong super-Nernstian response occurs at low concentration levels of Cu²⁺. Moreover, compared to the thin membrane electrode, the conventional electrode shows a much worse detection sensitivity. For measurements of Cu²⁺ at 10^{−7} M in the presence of 0.01 M NaCl background, the EMF change obtained

(a) Thick membrane ISE



(b) Thin membrane ISE

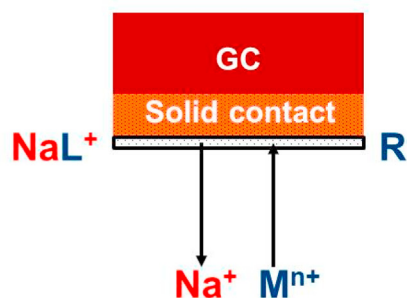


Fig. 1. Schematic illustration of the sensing mechanisms of the solid-contact (a) thick membrane and (b) thin membrane ISEs conditioned with highly discriminated ions (e.g., Na^+) for potentiometric detection of heavy metal ions (M^{n+}).

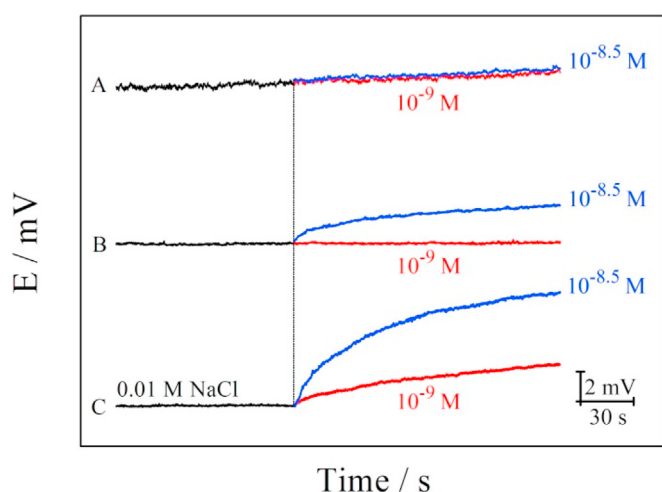


Fig. 2. Potentiometric responses to Cu^{2+} in 0.01 M NaCl measured under non-equilibrium conditions at a constant stirring rate of 1500 rpm by using the ISE membranes with different thicknesses: (A) 20, (B) 10 and (C) 5 μm .

by the thick membrane is negligible, the electrode based on the thin membrane shows a response is approximately 55 mV. These results indicate that the thin membrane configuration is favorable for the improvement of the detection limit of the non-classical ISE. Such improvement can be ascribed to the fact that the diffusion of primary ions away from the boundary layer into the bulk of the membrane can be prevented by the thin membrane configuration. In this case, the primary ions can readily accumulate in the interfacial layer of the membrane rather than diffuse further into the membrane bulk. Therefore, a lower detection limit can be achieved.

Fig. 4a displays the typical dynamic potential responses of the thin membrane ISE for measuring Cu^{2+} at concentrations ranging from 1 to 150 nM in 0.01 M NaCl. Unlike the thick membrane ISE which shows a steady-state potential response at low concentrations [26], no steady state could be reached for the thin-layer membrane. In this case, the potential difference between the baseline and the potential measured at a fixed time (i.e., 150 s) after Cu^{2+} addition was used for quantification. As shown in Fig. 4b, the potential response is proportional to the concentration of Cu^{2+} in the range of 1–100 nM. The detection limit was calculated to be 0.29 nM (3σ). The obtained detection limit could allow the

applications of the thin membrane electrode to trace-level determination of Cu^{2+} in environmental samples [33].

The selectivity coefficients for the thin ISE membrane and the conventional thick ISE membrane were determined by using the separate solution method [31]. The logarithmic Nikolskii coefficients for Cu^{2+} over discriminated ions are summarized in Table 1. It can be seen that the potentiometric selectivity coefficients of the proposed thin membrane electrode are comparable to those of the conventional thick membrane electrode based on the same membrane composition. These results suggest that the proposed thin membrane configuration cannot affect the selectivity coefficients.

Since the ionophore-based ISE shows high selectivity towards Cu^{2+} over the discriminated ions (e.g., Na^+), it is very difficult to regenerate the membrane. To improve the reversibility of the thin membrane ISE, the pH cross-sensitive electrode was designed, for which a neutral H^+ -selective ionophore (ETH 5315) was incorporated into the membrane together with the Cu^{2+} -selective ionophore [26,34,35]. The membrane restoration was made simply by stripping Cu^{2+} out of the thin membrane with an acid solution after each measurement. By using 10^{-3} M HCl as the regeneration solution, the potentiometric reversible detection of Cu^{2+} was obtained (Fig. 5). As can be seen, the potential responses are fully reversible with a relative standard deviation (RSD) of 4.2% (10 nM, $n = 5$).

In our previous asymmetric membrane configuration, the lifetime of the asymmetric membrane sensor might be affected by the diffusion of the ion exchanger from the surface layer into the membrane bulk [26]. Such diffusion could gradually change the composition of the active interfacial sensing layer. In order to inhibit the ion exchanger diffusion, a high-PVC-content membrane which could prolongs the penetration of the ion exchanger from the surface to the bulk was designed. In the present work, the ion exchanger diffusion problem can be solved because the thin membrane is homogeneous.

To validate the feasibility for seawater analysis, the proposed thin membrane electrode was used to analyze Cu^{2+} in a high electrolyte background containing 0.5 M NaCl with constant stirring at 1500 rpm. As shown in Fig. 6a, the electrode also exhibits excellent detection sensitivity towards Cu^{2+} . The potential response of the thin membrane electrode is proportional to the concentration of Cu^{2+} in 0.5 M NaCl from 1 to 100 nM. The detection limit of the electrode was calculated to be 0.53 nM (3σ), which is comparable with that obtained by the asymmetric ISE membrane

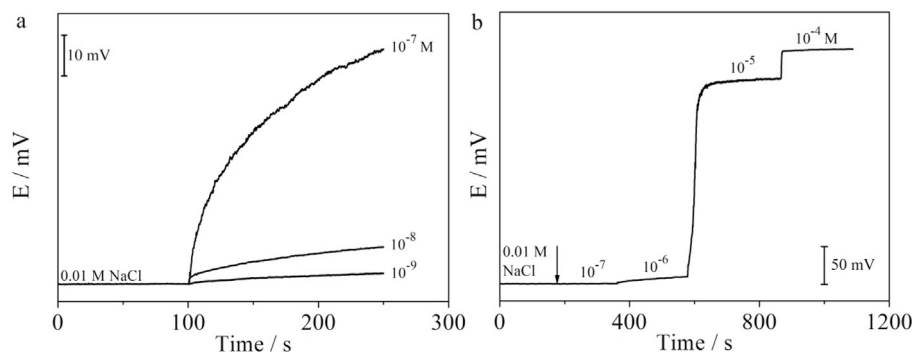


Fig. 3. Potentiometric responses of the polymeric membrane Cu^{2+} -ISEs based on (a) the thin membrane of 5 μm and (b) the conventional thick membrane of 100 μm . All the measurements were performed in 0.01 M NaCl with constant stirring at 1500 rpm.

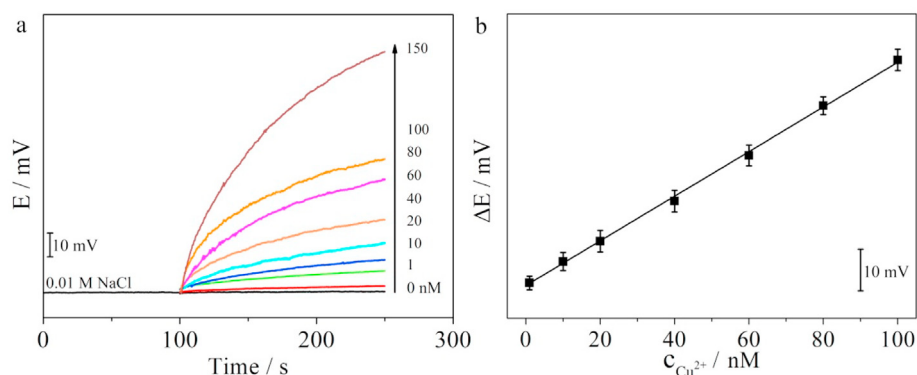


Fig. 4. Dynamic potential response (a) and corresponding calibration curve (b) of the solid-contact thin membrane ISE in a background of 0.01 M NaCl. The potential difference between the baseline and the potential measured at 150 s after Cu^{2+} addition was used for quantification. Each error bar represents one standard deviation for three measurements.

Table 1
Potentiometric selectivity coefficients, $\log K_{\text{Cu}^{2+}, J}^{\text{pot}}$, of the thin membrane ISE compared with those of conventional membrane ISE.

Ion J	$\log K_{\text{Cu}^{2+}, J}^{\text{pot}}$ ^a	
	Thin membrane	Conventional membrane
H^+	-3.2 ± 0.5	-3.3 ± 0.3
Na^+	-10.6 ± 0.2	-10.6 ± 0.1
K^+	-9.7 ± 0.2	-10.2 ± 0.2
Mg^{2+}	-11.8 ± 0.3	-12.5 ± 0.1
Ca^{2+}	-12.1 ± 0.1	-11.8 ± 0.2
Zn^{2+}	-4.5 ± 0.4	-4.9 ± 0.3
Pb^{2+}	-2.1 ± 0.6	-2.3 ± 0.4

^a Average value obtained from the three corresponding pairs of concentrations of Cu^{2+} and the respective interfering cation in the Nernstian response range \pm standard deviation.

with a rotation speed of 3000 rpm [26]. These results indicate that the thin membrane configuration is promising for trace-level analysis in high electrolyte backgrounds, particularly in marine environments. However, it should be noted that the potential responses of the proposed electrode to Cu^{2+} in 0.5 M NaCl (Fig. 6b) are smaller than those in 0.01 M NaCl (Fig. 4b). Indeed, the electrolyte background of 0.5 M NaCl could not only give a higher activity of the interfering ion (i.e., Na^+) but also induce lower activities of the primary ion (i.e., Cu^{2+}) due to the rather high ion strength. In this case, the ion exchange between Na^+ in the membrane and Cu^{2+} in the sample solution could be inhibited, thus decreasing the sensor's sensitivity.

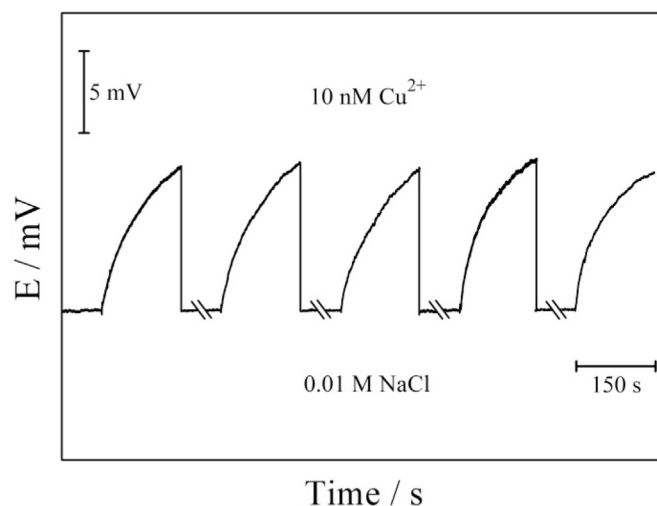


Fig. 5. Recycle potential responses of the solid-contact thin membrane Cu^{2+} ISE to 10 nM Cu^{2+} in 0.01 M NaCl background. After each measurement, the electrode was immersed in a 10^{-3} M HCl solution for 5 min for Cu^{2+} stripping and then reconditioned in a 0.01 M NaCl for 5 min to obtain the original and reproducible baseline.

4. Conclusions

A thin membrane configuration is proposed to improve the detection limit of a solid-contact polymeric membrane potentiometric sensor via suppressing the diffusion of the primary ion from the interfacial membrane layer to the membrane bulk and

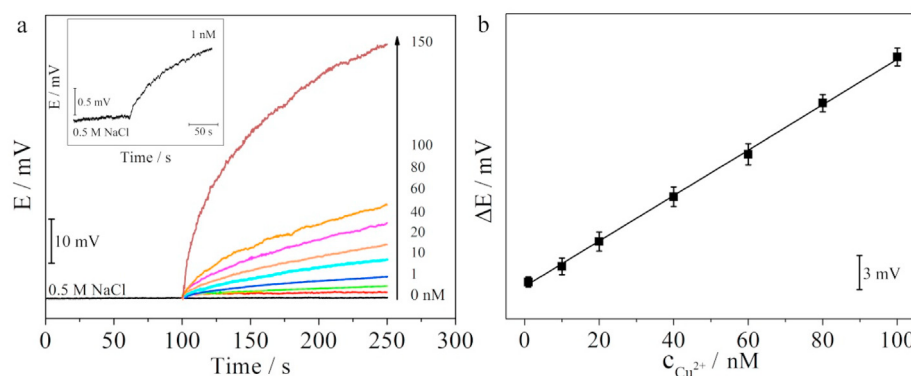


Fig. 6. Dynamic potential response (a) and corresponding calibration curve (b) of the solid-contact thin membrane ISE in a background of 0.5 M NaCl. The other conditions are as given in Fig. 4. The inset shows the potential response to 1 nM Cu^{2+} in 0.5 M NaCl.

promoting the accumulation of the primary ion in the interfacial layer. The present electrode shows a remarkably improved sensitivity for Cu^{2+} detection compared to the conventional thick membrane ISE. Since many ionophores are commercially available, the proposed solid-contact thin membrane ISE is promising to develop potentiometric sensors for trace-level measurements of a wide range of targets, especially for environmental monitoring and clinical analysis.

CRediT authorship contribution statement

Junhao Wang: Conceptualization, Methodology, Investigation. **Rongning Liang:** Conceptualization, Methodology, Writing - review & editing, Supervision. **Wei Qin:** Conceptualization, Methodology, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (21677172, 21874151), the National Key Research and Development Program of China (2016YFC1400700), the Youth Innovation Promotion Association of CAS (2014190) and the Taishan Scholar Program of Shandong Province (tsdpd20181215).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2020.09.024>.

References

- [1] E. Bakker, P. Bühlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, *Chem. Rev.* 97 (1997) 3083–3132.
- [2] J. Bobacka, A. Ivaska, A. Lewenstam, Potentiometric ion sensors, *Chem. Rev.* 108 (2008) 329–351.
- [3] E. Bakker, *Electroanalysis with membrane electrodes and liquid-liquid interfaces*, *Anal. Chem.* 88 (2016) 395–413.
- [4] M. Parrilla, M. Cuartero, G.A. Crespo, Wearable potentiometric ion sensors, *TrAC, Trends Anal. Chem.* 110 (2019) 303–320.
- [5] J.B. Hu, A. Stein, P. Bühlmann, A disposable planar paper-based potentiometric ion-sensing platform, *Angew. Chem. Int. Ed.* 55 (2016) 7544–7547.
- [6] R.N. Liang, J.W. Ding, S.S. Gao, W. Qin, Mussel-inspired surface-imprinted sensors for potentiometric label-free detection of biological species, *Angew. Chem. Int. Ed.* 56 (2017) 6833–6837.
- [7] T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch, Large improvement of the lower detection limit of ion-selective polymer membrane electrodes, *J. Am. Chem. Soc.* 119 (1997) 11347–11348.
- [8] T. Sokalski, A. Ceresa, M. Fibbioli, T. Zwickl, E. Bakker, E. Pretsch, Lowering the detection limit of solvent polymeric ion-selective membrane electrodes. 2. Influence of composition of sample and internal electrolyte solution, *Anal. Chem.* 71 (1999) 1210–1214.
- [9] W. Qin, T. Zwickl, E. Pretsch, Improved detection limits and unbiased selectivity coefficients obtained by using ion-exchange resins in the inner reference solution of ion-selective polymeric membrane electrodes, *Anal. Chem.* 72 (2000) 3236–3240.
- [10] Q.S. Ye, M.E. Meyerhoff, Rotating electrode potentiometry: lowering the detection limits of nonequilibrium polyion-sensitive membrane electrodes, *Anal. Chem.* 73 (2001) 332–336.
- [11] M. Puntener, M. Fibbioli, E. Bakker, E. Pretsch, Response and diffusion behavior of mobile and covalently immobilized H^+ -ionophores in polymeric membrane ion-selective electrodes, *Electroanalysis* 14 (2002) 1329–1338.
- [12] J. Bobacka, Conducting polymer-based solid-state ion-selective electrodes, *Electroanalysis* 18 (2006) 7–18.
- [13] T.J. Yin, W. Qin, Applications of nanomaterials in potentiometric sensors, *TrAC, Trends Anal. Chem.* 51 (2013) 79–86.
- [14] J.H. Li, T.J. Yin, W. Qin, An all-solid-state polymeric membrane Pb^{2+} -selective electrode with bimodal pore C_{60} as solid contact, *Anal. Chim. Acta* 876 (2015) 49–54.
- [15] J.B. Hu, A. Stein, P. Bühlmann, Rational design of all-solid-state ion-selective electrodes and reference electrodes, *TrAC, Trends Anal. Chem.* 76 (2016) 102–114.
- [16] E. Bakker, Y. Qin, *Electrochemical sensors*, *Anal. Chem.* 78 (2006) 3965–3984.
- [17] E. Pretsch, The new wave of ion-selective electrodes, *TrAC, Trends Anal. Chem.* 26 (2007) 46–51.
- [18] E. Bakker, E. Pretsch, *Modern potentiometry*, *Angew. Chem. Int. Ed.* 46 (2007) 5660–5668.
- [19] E. Zdrachek, E. Bakker, Potentiometric sensing, *Anal. Chem.* 91 (2019) 2–26.
- [20] B. Fu, E. Bakker, J.H. Yun, V.C. Yang, M.E. Meyerhoff, Response mechanism of polymer membrane-based potentiometric polyion sensors, *Anal. Chem.* 66 (1994) 2250–2259.
- [21] M.E. Meyerhoff, B. Fu, E. Bakker, J.H. Yun, V.C. Yang, Polyion-sensitive membrane electrodes for biomedical analysis, *Anal. Chem.* 68 (1996) A168–A175.
- [22] E. Bakker, M.E. Meyerhoff, Ionophore-based membrane electrodes: new analytical concepts and non-classical response mechanisms, *Anal. Chim. Acta* 416 (2000) 121–137.
- [23] A. Hulanicki, R. Lewandowski, Some properties of ion-selective electrodes based on poly(vinyl chloride) membranes with liquid-ion-exchanger, *Chem. Anal.* 19 (1974) 53–60 (Warsaw, Pol.).
- [24] S.A. Ferguson, M.E. Meyerhoff, Advances in electrochemical and optical polyion sensing: a review, *Sens. Actuators, B* 272 (2018) 643–654.
- [25] A. Shvarev, E. Bakker, Reversible electrochemical detection of non-electroactive polyions, *J. Am. Chem. Soc.* 125 (2003) 11192–11193.
- [26] W. Qin, R.N. Liang, X.L. Fu, Q.W. Wang, T.J. Yin, W.J. Song, Trace-level potentiometric detection in the presence of a high electrolyte background, *Anal. Chem.* 84 (2012) 10509–10513.
- [27] P.J. Greenawalt, M.B. Garada, S. Amemiya, Voltammetric characterization of ion-ionophore complexation using thin polymeric membranes: asymmetric thin-layer responses, *Anal. Chem.* 87 (2015) 8564–8572.
- [28] T.T. Han, U. Mattinen, J. Bobacka, Improving the sensitivity of solid-contact ion-selective electrodes by using coulometric signal transduction, *ACS Sens.* 4 (2019) 900–906.
- [29] G.A. Crespo, M. Cuartero, E. Bakker, Thin layer ionophore-based membrane for multianalyte ion activity detection, *Anal. Chem.* 87 (2015) 7729–7737.

- [30] T. Forrest, E. Zdrachek, E. Bakker, Thin layer membrane systems as rapid development tool for potentiometric solid contact ion-selective electrodes, *Electroanalysis* 32 (2020) 799–804.
- [31] E. Bakker, Determination of improved selectivity coefficients of polymer membrane ion-selective electrodes by conditioning with a discriminated ion, *J. Electrochem. Soc.* 143 (1996) L83–L85.
- [32] M. Maj-Zurawska, T. Sokalski, A. Hulanicki, Interpretation of the selectivity and detection limit of liquid ion-exchanger electrodes, *Talanta* 35 (1988) 281–286.
- [33] Z. Szigetia, I. Bitterb, K. Tóthc, C. Latkoczyd, D.J. Fliegeld, D. Güntherd, E. Pretsch, A novel polymeric membrane electrode for the potentiometric analysis of Cu^{2+} in drinking water, *Anal. Chim. Acta* 532 (2005) 129–136.
- [34] M. Lerchi, E. Reltter, W. Simon, E. Pretsch, Bulk optodes based on neutral dithiocarbamate ionophores with high selectivity and sensitivity for silver and mercury cations, *Anal. Chem.* 66 (1994) 1713–1717.
- [35] S. Mathison, E. Bakker, Renewable pH cross-sensitive potentiometric heparin sensors with incorporated electrically charged H^+ ionophores, *Anal. Chem.* 71 (1999) 4614–4621.