Desalination and Water Treatment
www.deswater.com

46 (2012) 168–170
August

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.677525

Taylor & Francis
Taylor & Francis Group

Electrochemical sensors for the detection of cadmium (II) based on calix [4] arene

Karima Morakchi[a,*], Abdallah Hamel[b], Rochdi Kherrat[a]

[a]*Laboratoire de recherche génie de l'environnement, faculté des sciences de l'ingénieur, Annaba BP 12, Algeria*
Tel.: +213 7 90962240; email: morakchik@yahoo.fr
[b]*Laboratoire de Traitement des Eaux et Valorisation des Déchets Industriels, Faculté des sciences, Université Badji-Mokhtar, Annaba BP 12, Algeria*

Received 6 September 2011; Accepted 20 February 2012

ABSTRACT

In the present work, we report on the elaboration of a polymeric membrane including calix [4] arene as an ionophore to functionalise cadmium (II) ion-sensitive electrode. The phenomena occurring at the electrode/solution interface have been investigated by electrochemical impedance spectroscopy and cyclic voltammetry methods. Several conditions were optimised to enhance the sensitivity of the ion sensor; in particular, polarisation was adjusted to $-0.2\,\mathrm{V}$/SCE. The cadmium concentrations that can be detected are in the range 10^{-8}–10^{-3} M and the low detection limit is about 10^{-6} M.

Keywords: Calix [4] arene; Modified electrode; Electrochemical impedance; Electrochemical sensor

1. Introduction

The selective measurement of ion activities in aqueous solutions by potentiometric devices like ion-selective electrodes (ISEs) and chemically modified field effect transistor is nowadays well established [1,2]. The physicochemical properties of the chemical sensors are based on selective recognition of the sensing ionophore for guest species. A variety of organic supramolecules and polymeric compounds have been used as sensitive membranes for ion detection [3,4]. The use of calix [*n*] arene as a recognition reagent in electroanalysis has given rise to vivid interest during the last years [5]. In particular, calix [4] arene macrocyclic molecules are able to recognise ions and organic molecules according to a key-lock inter-action mechanism [6]. Calixarenes are synthetic substrates showing structural similarities with crown ether and cyclodextrin compounds. They can be utilised for molecular recognition as a direct consequence of their vase-like structure and internal cavity. The vast majority of studies on calixarenes are focused on the calix [4] arene because they possess open and rigid structures that are desirable for molecular recognition [7,8]; however, the shape and size of the cavity are adjusted by changing the value of n, where $n = 4, 6, 8, \ldots$ [9]. The calixarene is a molecule that is actually used in the detection of heavy metals (nickel, copper, cadmium) [10,11]. In this work, we describe the possibility of using calix [4] arene as an ionophore for Cd^{2+} ion detection. A polymeric layer deposited on platinum electrode has been characterised by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry methods. Impedance spectroscopy is commonly used to characterise the electrical response of a material as a function of frequency [12].

---

*Corresponding author.

2. Experimental

2.1. Composition and deposition of the membranes

Calix [4] arene derivatives were synthesised at the "Claude Bernard University" Lyon France [13]. For the preparation of Cd(II)-sensitive membranes, a typical procedure was applied using calix [4] arene, polyvinyl chloride (polymer), dioctylphthalate (plastiser) in the ratio of 8:67:33 (w/w/w), respectively, diluted in 0.5 ml chloroform; 5 µl of polymeric membrane was deposited on the platinum electrode; the solvent was then evaporated in ambient air. The sensors were then soaked for 1 h in 10^{-2} M $CdCl_2$ solution to achieve appropriate conditioning of PVC/ionophore membrane. The supporting electrolyte chosen for these measurements was (KNO_3 10^{-1} M, pH $\approx$ 6.7).

2.2. Measuring system

The measurement set-up used an electrochemical cell with three electrodes: auxiliary platinum electrode, saturated calomel electrode (SCE) and the modified platinum electrode (area = 0.25 cm^2) as the working electrode. Impedance spectroscopy measurements were performed at a frequency of 100 kHz – 100 MHz and with a signal amplitude of 10 mV using an impedance analyser (Voltalab 40 from Radiometer Analytical, SA, France) and a PGZ 301 as a potentiostat. The whole system was computer controlled. The experiments were performed in a dark and grounded metal box to eliminate electrical interferences. Solutions for testing the ion sensitivity were $CdCl_2$ in the concentration range of 10^{-8}–10^{-3} M.

3. Results and discussion

3.1. EIS studies

The measurements were performed at open-circuit potential at room temperature. The polarisation potential was maintained at −0.2 V/SCE in order to perform analysis in the accumulation mode and to avoid a dielectric breakdown. The Nyquist diagram of bare platinum Fig. 1 presents a half-circle, characteristic of a resistance in parallel with a capacity and the Warburg impedance was not observed.

All EIS spectra were fitted to equivalent circuit using the voltaMaster 4 software [14,15]. The cyclic voltammetry measurements were accomplished in KNO_3 0.1 M, pH $\approx$ 6.7 at a scanning rate of 100 mV/s. Fig. 2 depicts voltammograms obtained before and after the deposition of the polymeric layer on the platinum electrode at −0.8–0.8 V. As we can see, the bare platinum electrode gives good reversibility curve (a), while the fine layer modified electrode curve (b) exhibits a net decrease of the peak current; the current flowing through the working electrode is capacitive current I_c, which is caused by charging and discharging of the electrochemical double layer on the surface of the working electrode.

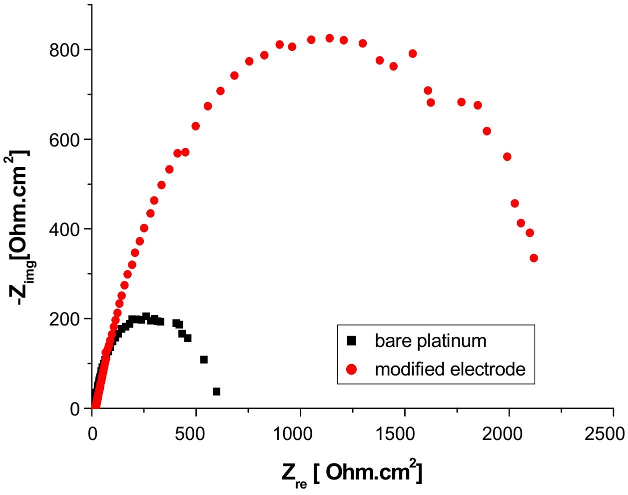

Fig. 1. Nyquist plot for bare platinum and modified electrode.

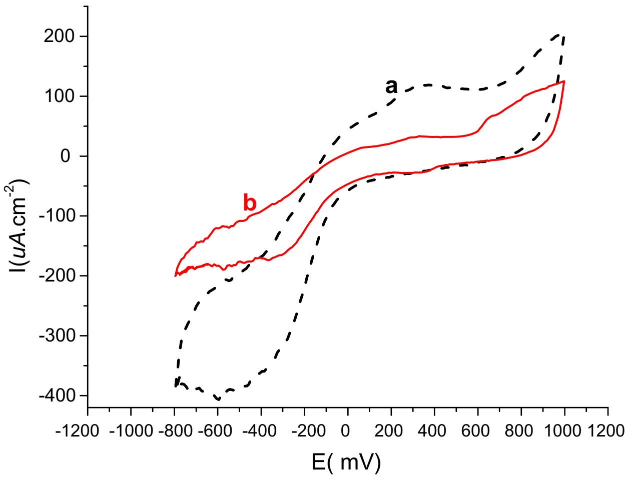

Fig. 2. Voltammograms of (a) bare platinum and (b) modified electrode. Scan rate 100 mV/s.

3.2. Impedance analysis of a membrane functionalised ISE structure

In the presence of cadmium ions, we can see in Fig. 3 that at high frequencies the impedance is not modified. However, at low frequency, the impedance of the electrochemical system decreases significantly with increasing concentrations of Cd(II). It can be

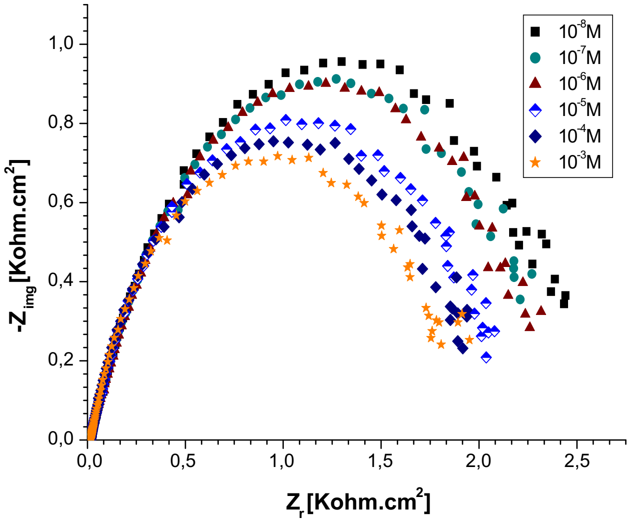

Fig. 3. Impedance spectra in Nyquist presentation in different concentrations of Cd^{2+}.

noted that the most significant variation of impedance occurs at low frequencies. The approximate form is a semicircle, characteristic of the association of a resistance in parallel with a capacity. It is important noteworthy that the semicircle decreases with increasing concentrations of cadmium, which characterises a decrease of the transfer resistance charge.

The sensitivity of functionalised platinum electrode sensors was carried out at −0.2 V/SCE polarisation and 1 Hz frequency. In these conditions, the variation of the sensor impedance $-\log Z/Z_0$ is presented as a function of p[Cd^{2+}] Fig. 4. From the obtained data, it is seen that the sensor presents a dynamic range from 10^{-6} to 10^{-3} M with a detection limit of about 10^{-6} M.

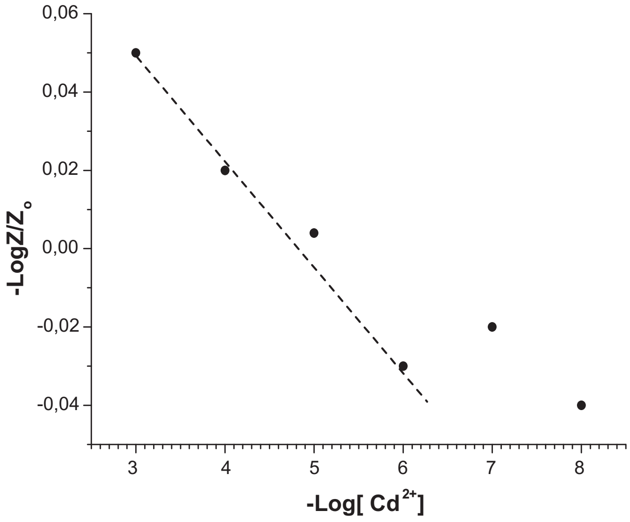

Fig. 4. Response of functionalised platinum electrode for Cd^{2+} ions measurements performed in KNO_3 0.1 M, pH = 6.7 with a frequency of 1 Hz and at −0.2V vs. SCE.

4. Conclusion

In this work it has been shown that it is possible to functionalise the ISE sensor for Cd(II) ion detection with a polymeric membrane including calix [4] arene as an ionophore. The platinum electrode has been characterised by impedance spectroscopy and cyclic voltammetry methods.

The cadmium's low detection limit is about 10^{-6} M. This result can be obtained in specific conditions (polarisation −0.2 V/SCE, frequency 1 Hz) of measurements.

References

[1] M.B. Ali, A. Abdelghani, H. Ben Ouada, N. Jaffrezic-Renault, R. Lamartine, Optical and electrochemical studies of thiacalix [4]arene film supported on Si/SiO^2 for ion-sensitive sensor, Mater. Sci. Eng. C21 (2002) 29–34.

[2] P. Bergveld, Development of an ion-sensitive solid-state device for neurophysiological measurements, IEEE Trans. Biomed. Eng. 17 (1970) 70–71.

[3] M.B. Ali, R. Kalfat, H. Sfihi, J.M. Chovelon, H. Ben Ouada, N. Jaffrezic-Renault, Sensitive cyclodextrin–polysiloxane gel membrane on EIS structure and ISFET for heavy metal ion detection, Sens. Actuators, B 62 (2000) 233–237.

[4] R. Mlika, h. Ben Ouada, F. Mhenni, G. Gamoudi, R. Kalfat, N. Jaffrezic-Renault, Thin sensitive organic membranes on selective iron-ion sensors, Synth. Met. 90 (1997) 239–243.

[5] N. Sakly, M. Souiri, F. Fekih Romdhane, H. Ben Ouada, N. Jaffrezic-Renault, Platinum electrode functionalized with calix [4]arene thin films for impedimetric detection of sodium ions, Mater. Sci. Eng. C21 (2002) 47–53.

[6] P. Linnane, S. Shinkai, Calixarenes: Adaptable hosts par excellence, Chem. Ind. 20 (1994) 811–814.

[7] W.M. Hassen, C. Martelet, F. Davis, S.P.J. Higson, A. Abdelghani, S. Helali, N. Jaffrezic-Renault, Calix[4]arene based molecules for amino-acid detection, Sens. Actuators, B 124 (2007) 38–45.

[8] M.M. Stone, A.H. Franz, C.B. Lebrilla, Non-covalent calixarene-amino acid complexes formed by MALDI-MS, J. Am. Soc. Mass Spectrom. 13 (2002) 964–974.

[9] C.J. Liu, J.T. Lin, S.H. Wang, J.C. Jiang, L.G. Lin, Amine, chromogenic calixarene sensors for amine detection, Sens. Actuators B 108 (2005) 521–527.

[10] M. Regayeg, F. Vocanson, A. Duport, B. Blondeau, M. Perrin, A. Fort, R. Lamartine, New calixarenes for nonlinear optics: Synthesis and conformation of functionalized *p*-nitrocalix[4] arenas, Mater. Sci. Eng. C21 (2002) 131–135.

[11] H. Halouani, I. Dumazet-Bonnamour, R. Lamartine, Synthesis of novel chromogenic bi-and tri-functionalized calix[4]arene, Tetrahedron Lett. 43 (2002) 3785–3788.

[12] A. Rouis, R. Mlika, J. Davenas, H. Ben Ouada, I. Bonnamour, N. Jaffrezic-Renault, Impedance spectroscopic investigations of ITO modified by new Azo-calix[4]arene immobilised into electroconducting polymer (MEHPPV), J. Electroanal. Chem. 60 (2007) 129–138.

[13] I. Dumazet-Bonnamour, H. Halouani, F. Oueslati, R. Lamartine, Calixarenes for metal cations extraction, Compte Rendue Chimie 8 (2005) 881–891.

[14] S. Zougar, K. Morakchi, A. Zazoua, S. Saad, R. Kherrat, N. Jaffrezic-Renault, Characterization of ammonium ion—sensitive membranes in solution with electrochemical impedance spectroscopy, Mater. Sci. Eng. C28 (2008) 1020–1023.

[15] K. Morakchi, A. Zazoua, A. Hamel, S. Zougar, R. Kherrat, N. Jaffrezic-Renault, Fonctonalization of ISE sensor for metal ion detection, Mater. Sci. Forum 609 (2009) 249–254.