

Detection of heavy metal ions by ISFETs in a flow injection analysis cell

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Abstract

An ion-selective field-effect transistor (ISFET) is chemically modified with a photopolymerizable and cyanopropyl modified polysiloxane containing *N,N,N',N'*-tetrabutyl-3,6-dioxaoctane-dithioamide as Cd^{2+} ionophore. This CHEMFET has a Nernstian response (30 mV/decade) to a change of cadmium activity in aqueous solutions. Selectivity coefficients of the CHEMFET towards potassium, calcium, copper, and lead are given. Preliminary results of the CHEMFET in a flow injection analysis cell without wire bonding and polymeric encapsulation are presented.

Introduction

Synthetic receptor molecules that selectively bind charged guests store chemical information. Integration of these molecular receptors and field-effect transistors into one chemical system gives a device that registers changes of substrate activity in aqueous solutions [1]. However, some serious problems have been recognized, for example, the mechanical stability of the membrane, the interference of CO_2 on the potentiometric response, and the (relatively) high drift rate of ISFETs. The attachment of the membrane can be improved by chemically [2, 3] anchoring the membrane to the surface of the gate oxide. The interference of CO_2 in the response of the chemically modified FET (CHEMFET) can be eliminated by introduction of an intermediate buffered hydrogel layer [4, 5]. This approach leads to a sensor concept in which each layer can be applied by photopolymerization and is anchored covalently to an underlying layer. One of the remaining problems, the relatively high drift rate of ISFETs, is less important when CHEMFETs are used in flow systems [6, 7].

Previously, we have shown that an accurate sensor for the selective detection of potassium ions in aqueous solution can be constructed by the incorporation of highly potassium-selective calixarene-based crown ethers in the membrane of a

CHEMFET [1]. However, the detection of heavy metal cations with CHEMFETs is virtually unknown. Schneider *et al.* [8] have used *N,N,N',N'*-tetrabutyl-3,6-dioxaoctane-dithioamide in a PVC-based ion-selective electrode to detect Cd^{2+} ions in aqueous solution.

This paper reports the use of such a dithioamide in the photopolymerizable siloxane membrane materials we have developed recently [9]. Selectivity measurements are given for the aforementioned CHEMFETs used as encapsulated sensors. The first experimental results of these CHEMFETs used in a flow injection analysis cell without polymeric encapsulation and wire bonding [7] are also presented.

Experimental

Chemicals

Commercial 3-methacryloxypropyltrimethoxysilane (MEMO) (Janssen Chimica), ethylene glycol dimethacrylate (EGDMA, Merck-Schuchardt), 2-hydroxyethyl methacrylate (HEMA, Merck-Schuchardt) and 2,2-dimethoxy-2-phenylacetophenone (Janssen Chimica) were used. Polyvinylpyrrolidone (PVP) with an average molecular weight of 360 000 Dalton (Janssen Chimica) was used. *N,N,N',N'*-Tetrabutyl-3,6-dioxaoctane-dithioamide and potassium tetrakis(4-chlorophenyl) borate (KTCBP) were obtained from Fluka. The siloxane membrane material was made

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by emulsion polymerization of methacryloxypropyl and cyanopropyl modified methylsiloxanes and dimethylsiloxane (ABCR chemicals), as described previously [6, 9]. The polysiloxane was synthesized from a mixture containing 2.8 mol% methacryloxypropyl and 10 mol% cyanopropyl siloxane. Dichloromethane (CH_2Cl_2) of HPLC grade (Aldrich) was used. Tetrahydrofuran (THF) was freshly distilled from benzophenone/sodium before use. The metal salts and the nitric acid used were of analytical-reagent grade (Merck-Schuchardt) and solutions were prepared with doubly distilled, deionized, CO_2 -free water.

CHEMFETs

The ISFETs were fabricated as described previously [2], but because of the architecture of the new flow injection analysis cell their detailed structure has been changed [7]. Surface silylation of a wafer with MEMO was performed as described before [4]. A hydrogel was applied on wafer scale on the gate oxide of the ISFET by photopolymerization with a mask aligner of a mixture of EGDMA, HEMA, PVP, water, and photoinitiator in a w/w ratio of 0.4:100:10:40:4, respectively. The resulting polyHEMA layer had dimensions of $800\ \mu\text{m} \times 800\ \mu\text{m} \times 15\ \mu\text{m}$. The encapsulated sensors were prepared by mounting the ISFET on a printed circuit board. After wire bonding and encapsulation with a room-temperature vulcanizing silicone rubber the sensor was soaked in a solution of 10 mM cadmium nitrate and 0.1 mM nitric acid for 1 hour. The unmounted ISFET chips for use in the flow cell were also soaked in this solution.

The ion-sensitive membranes were prepared by dissolving a 5% mixture of cadmium ionophore (1.7 wt.%), KTCPB (0.6 wt.%), photoinitiator (2.2 wt.%) and siloxane material (95.5 wt.%) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (100:1, w/w). Fifteen microliters of this solution was applied to both the encapsulated and the flow cell ISFETs. After evaporation of the solvent, photopolymerization of the membranes was achieved by irradiation with UV light for two minutes. The response of the CHEMFETs was measured with a source and drain follower type of ISFET amplifier (Electro Medical Instrumentation, Enschede, Netherlands) in a constant drain-current mode ($I_d = 100\ \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5\ \text{V}$) [10]. The signal of the

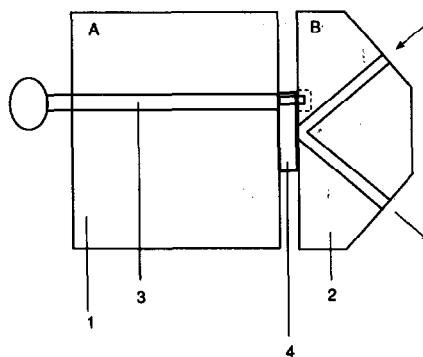


Fig. 1. Side view of the detailed structure of the flow injection analysis cell: 1, 2, Perspex; 3, contact wire (hook); 4, CHEMFET.

ISFET amplifier was recorded with an Apple II computer.

Measurements

The experimental set-up to measure the encapsulated sensors has been described before [11] and used without modification. The encapsulated sensors were conditioned overnight in a solution of 10 mM cadmium nitrate and 0.1 mM nitric acid. The selectivity coefficients were determined by the fixed interference method (FIM). All solutions were adjusted to pH 4 (nitric acid), unless stated otherwise.

The flow injection system has been reported previously [7] and was used with minor adjustments. An autosampler (Skalar, sampler 1000) and a pump (Gilson, minipuls 3), both controlled by the Apple computer, were added in order to automate the complete measurement cycle. The flow injection system consisted of one flow injection cell and a calomel reference electrode.

In the flow injection cell (for a detailed description see ref. 7) a thin silicone rubber ring was applied between part B and the CHEMFET to ensure a watertight seal (Fig. 1). This appeared necessary because the mechanical strength of the siloxane membrane material was less than that of the plasticized PVC membranes used before [7]. The cell was closed again by holding the two blocks together with four pins with springs and nuts (not shown in Fig. 1).

Results and discussion

To examine the characteristics of the cadmium ionophore *N,N,N',N'*-tetrabutyl-3,6-dioxaoctane-

dithioamide in the polysiloxane membrane material functionalized with 10% cyanopropyl groups a calibration curve was measured with the encapsulated sensors in the presence of 100 mM calcium nitrate. This sensor (Fig. 2) exhibited a Nernstian response (29 mV/decade) to a change of cadmium activity in the aqueous solution.

The potentiometric selectivity coefficient ($\log K^{\text{pot}} = -4.2$) of this cadmium sensor to calcium is similar to the results of Schneider *et al.* [8]. If potassium nitrate (100 mM) is used as interfering ion, the slope (30 mV/dec.) and the selectivity coefficient ($\log K^{\text{pot}} = -3.0$) are also comparable. With copper(II) nitrate (10 mM) as the interfering salt we also found a Nernstian response (25 mV/dec., $\log K^{\text{pot}} = -1.9$) to cadmium ions, in contrast to the anion response found by Schneider [8]. A possible reason for this different behaviour could be the different membrane materials, a plasticized PVC membrane [8] compared to the polysiloxane containing a tetraphenyl borate that we used. Further research is needed to explain this difference.

The last interfering salt examined was lead(II) nitrate. The slope of the sensor was still Nernstian (25 mV/dec.). This selectivity coefficient ($\log K^{\text{pot}} = -1.5$) was not published by Schneider [8].

The influence of the nitric acid was tested by lowering the pH from 4 to 3. The calibration curves measured in the presence of 100 mM potassium nitrate were identical, whether the pH was 4 or 3.

The drift of the cadmium sensor was measured over a period of ten hours in 10 mM cadmium nitrate and was less than 0.25 mV/hour. The noise level (peak to peak) in a solution of 10 mM cadmium nitrate was of the order of 0.05 mV.

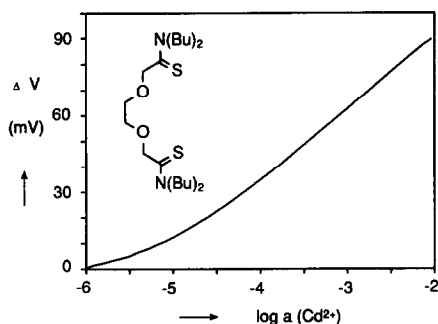


Fig. 2. Cd^{2+} response of a dithioamide-based CHEMFET (0.1 M $\text{Ca}(\text{NO}_3)_2$).

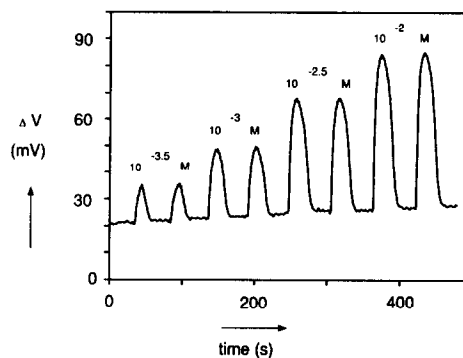


Fig. 3. Response of a Cd^{2+} CHEMFET in the flow injection analysis cell. Carrier, 0.1 mM $\text{Cd}(\text{NO}_3)_2 + 100$ mM KNO_3 ; injection, $10^{-3.5}$ – 10^{-2} M $\text{Cd}(\text{NO}_3)_2 + 100$ mM KNO_3 .

Preliminary results concerning the use of this cadmium sensor in the aforementioned flow cell were obtained by the injection of several samples containing cadmium nitrate in 100 mM potassium nitrate (pH 3) into a carrier solution of 100 mM potassium nitrate and 0.1 mM cadmium nitrate (pH 3).

A typical response is given in Fig. 3. At a flow rate of 1.3 ml/min (injected volume 220 μl) the detector response was selective and Nernstian to a change of activity of cadmium nitrate, which is identical to the results obtained in measurements performed with the encapsulated sensors.

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