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NITRATE AND BICARBONATE SELECTIVE CHEMFETS

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SUMMARY

The development of durable anion selective CHEMFET micro sensors is described. Selectivity in these sensors is either obtained from differences in hydration energy of the anions (the Hofmeister series, giving nitrate selectivity) or by introduction of a new class of uranyl salophene ionophores (bicarbonate selectivity). The durability of the nitrate sensor was enhanced by using polysiloxane membranes in which cationic tetraalkylammonium sites were covalently bound to the membrane matrix.

INTRODUCTION

We have studied various Chemically Modified Field Effect Transistors (CHEMFETs, Figure 1) as microsensors for sensing of cations, like for example sodium [1], potassium [2], and heavy metal ions like lead, copper, silver, and cadmium [3]. In these devices a membrane with an ion selective calix[4]arene derivative was placed over the gate oxide of the CHEMFET. These CHEMFETs differ from the earlier reported Membrane Field Effect Transistors (MEMFETs) in that a hydrophilic polyhydroxyethyl methacrylate (polyHEMA) layer is positioned between the gate oxide of the CHEMFET and the ion selective membrane.

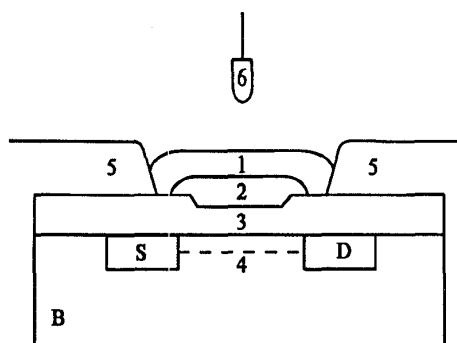
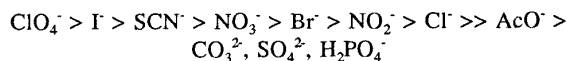


Figure 1. Chemically Modified Field Effect Transistor (CHEMFET); 1: Hydrophobic membrane, 2: PolyHEMA hydrogel, 3: SiO₂ gate oxide, 4: Channel, 5: Insulating resin, 6: Reference electrode, B: Bulk, S: Source, D: Drain.

This polyHEMA layer is conditioned in a pH buffered solution of the primary ion that will be detected, and eliminates undesired pH response and CO₂ interference.

In general, the selective detection of anions is more demanding than the detection of cations, because of their greater differences in hydration energies. Therefore it is more difficult to attract anions into the membrane. A simple anion selective membrane, containing positively charged ionic sites, like for example a plasticized PVC membrane with tetraoctylammonium bromide, shows a selectivity governed by the relative hydration energies, as is given in the well-known Hofmeister series:



Because of the selectivity of nitrate over other common anions like nitrite, chloride, sulfate, and phosphate, various nitrate sensors have been made based on this principle. To change the selectivity for other ions, it is necessary to add an ionophore to the membrane which can selectively bind to the target anion. Uranyl salophenes are a promising new class of neutral anion binding molecules that can be used as ionophore.

URANYL SALOPHENES AS IONOPHORES

Uranyl (UO₂²⁺) has a pentagonal bipyramidal coordination structure with the two oxygen atoms at the apical positions. When bound by a salophene, four coordination sites are occupied by the nitrogen and oxygen atoms of the salophene unit. The fifth coordination site is available for anion binding [4]. Besides the selectivity of the uranyl binding site based upon the Lewis acid character of uranyl, it is possible to introduce additional binding sites at the phenolic part of the salophene that enhance the selectivity. Compound 1 (Chart 1) possesses two extra amide moieties that can intensify anion binding by the formation of hydrogen bonds.

CHEMFET measurements using membranes incorporating 1 showed a high selectivity of this ionophore for bicarbonate (Figure 2 and Table 1).

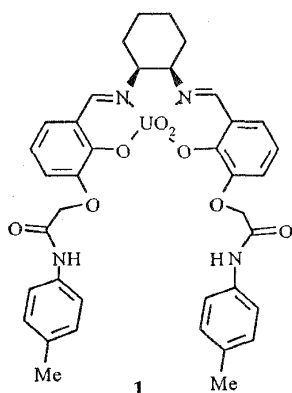
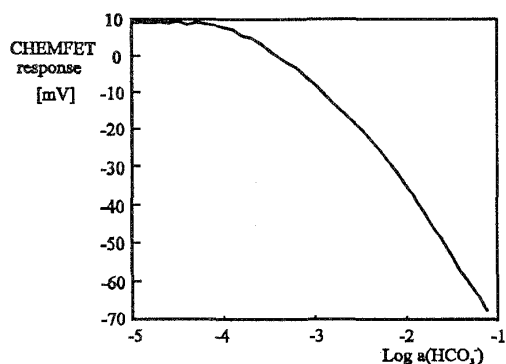


Chart 1

Figure 2. CHEMFET response for HCO_3^- in the presence of 0.1 M. SO_4^{2-} .

Interfering ion	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	HPO_4^{2-}
$\text{Log } K_{\text{HCO}_3^-}^{\text{pot}}$	-1.7	-1.4	-1.2	-2.0	-2.1

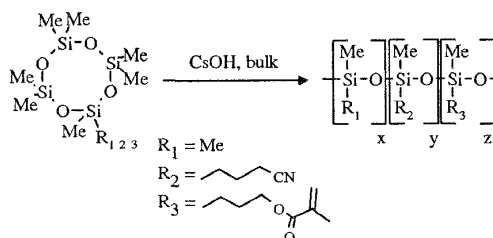
Table 1. Selectivity data (FIM) of CHEMFET with ionophore 1.

NEW MEMBRANE MATERIALS

The use of PVC as membrane material in ion sensors has some major disadvantages. Upon prolonged contact with the analyte solution the plasticizer slowly dissolves into the contacting aqueous solution, causing an increase in noise and finally resulting in a failure of the sensor. Also the ionophore and lipophilic cationic sites in the membrane will slowly leak into the sample solution causing lower selectivity and sensitivity. Therefore it is very difficult to make sensors based on PVC membranes that show a required longterm stability. Besides these problems, the use of PVC is not very compatible with IC manufacturing methods. Covalent binding of the membrane with the silicon chip is not well possible, neither as patterning of the membrane with photolithographic techniques.

Polysiloxane membranes appear to be very promising

in sensing devices. Simple polysiloxanes, however, like poly(dimethylsiloxane), are too apolar to be used for ion selective membranes. By introducing polar side chains (e.g. cyanopropyl groups) to the polysiloxane backbone the polarity is enhanced. Recently a reproducible synthesis for well-defined siloxane copolymers was published [5]. Anionic copolymerization of cyclotetrasiloxanes monofunctionalized with either methyl, cyanopropyl, or methacryloylpropyl resulted in polymers with various amounts of cyanopropyl groups (Scheme 1).



Scheme 1.

The methacrylate moiety is in principle available for cross-linking of the polymer, but can also be used for anchoring of the membrane to the (surface methacrylated) polyHEMA layer. Via the polyHEMA layer the ion selective membrane is covalently bound to the CHEMFET silicon surface. This enhances the durability of the sensor. It was also shown that ionophores for cations and lipophilic anions can be bound via the methacrylate moieties, leading to a further increase in durability [6].

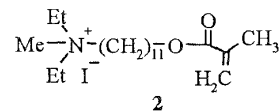


Chart 2.

For the development of a durable nitrate selective CHEMFET, the quaternary ammonium compound 2 (Chart 2) was synthesized. This compound was covalently bound in the polysiloxane membrane by photopolymerization. The CHEMFET response of a polysiloxane membrane with 25 % of cyanopropyl moieties and 0.5 wt% 2 is shown in Figure 2. This sensor shows good nitrate selectivity, governed by the Hofmeister series, and is stable upon prolonged exposure to a flow of tap water.

ACKNOWLEDGEMENT

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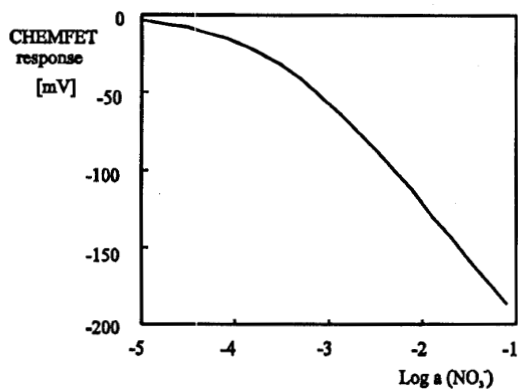


Figure 3. Nitrate selective CHEMFET with polysiloxane membrane and covalently bound ammonium site.

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