

Enhanced performance of potassium CHEMFETs by optimization of a polysiloxane membrane

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Abstract

In a way to enhance performance of CHEMFETs based on chemically modified polysiloxane membrane matrix, the effect of the polarity of polysiloxane material on the membrane homogeneity in relation to the covalent binding of the ionophore was investigated. Potassium sensors with the membrane based on the new polysiloxane showed a response with a Nernstian slope in a whole investigated range of cation activity. A new polysiloxane as the membrane matrix improved its homogeneity and increased the yield of functioning CHEMFETs.

Introduction

Since the introduction of the ion-sensitive field-effect transistor (ISFET), much attention has been given to improving the sensitivity and selectivity of these devices. Chemical modification of the membrane which is deposited on the top of gate offers the possibility of changing the ion selectivity of the so-called CHEMFET [1]. However, a widespread use of FET-based sensors has been restricted largely due to the limited lifetime under continuous flow conditions [2]. Four main problems are encountered with CHEMFETs using solvent polymeric membranes, e.g., plasticized PVC, deposited on top of the gate: (i) a limited lifetime due to leakage of the encapsulation of the total device; (ii) a limited lifetime due to poor fixation of the membrane to the surface; (iii) an unstable output signal occurs due to the undefined electrical potential difference at the membrane-insulator interface, and (iv) a limited lifetime due to leaching out of membrane constituents.

The encapsulation problem and the membrane fixation to the gate surface can be solved by using specially designed flow cells which allow only contact of the sample solution with the membrane at the gate area [3]. Moreover, the introduction of a buffered poly(2-hydroxyethylmethacrylate) (polyHEMA) layer between gate surface and the polysiloxane-sensing membrane

will account for a stable potential at the gate surface and the inner interface of the sensing membrane [4]. By functionalization of the gate oxide, the polyHEMA layer and the polysiloxane-sensing membrane with methacrylate groups, covalent attachment of the layers using photopolymerization could be achieved. This leads to a stable multilayered structure [1].

Although by these means solutions have been found for the first three problems, the leaching out of the electroactive components from the membrane has not been solved yet [1, 3]. However, the presence of a methacrylated functionality in the polysiloxane prepolymer also allows the covalent binding of ionophores provided with a pendant methacrylate group, Fig. 1.

We have investigated the effect of covalent binding of potassium ionophore (2) in CHEMFETs with polysiloxane membranes of different compositions. The effect of polarity of the membrane and membrane homogeneity in relation to the response and lifetime of CHEMFETs with covalently bound ionophore are discussed.

Experimental

Chemicals

Potassium selective ionophores: hydroxymethylphenyl hemispherand (1) and methacryloxymethylphenyl hemispherand (2) were synthesized according to ref. 5. Anionic sites, potassium tetrakis[3,5-bis(trifluoro-

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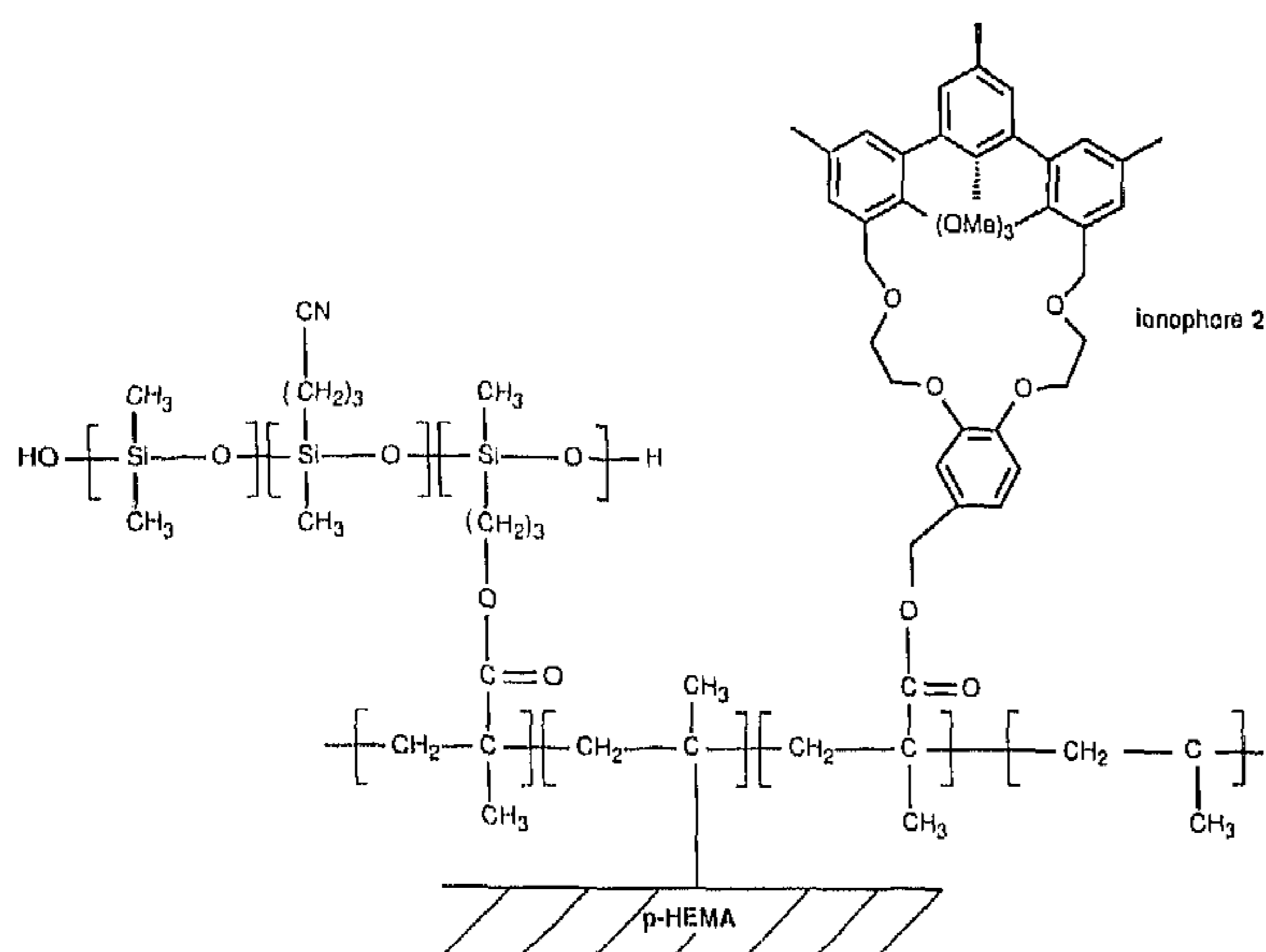


Fig. 1. Schematic representation of the sensing membrane after photocrosslinking.

methyl) phenyl]borate (KTTFPB), purchased from Fluka, was used. Photocurable polysiloxanes, containing 2.8 and 10 mol% cyanopropyl groups were made using an emulsion polymerization [6]. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. The chloride salts of potassium, sodium, calcium, and the hydrochloric acid used were of analytical-reagent grade (Merck-Schuchardt). All solutions were prepared with double-distilled, deionized, CO₂-free water.

CHEMFETs

The ISFETs were fabricated as described previously [5]. The CHEMFETs used in this study contain an intermediate hydrogel layer of polyHEMA between the gate oxide and the sensing membrane. The polyHEMA layer was anchored chemically to the gate oxide as described before in refs. 4 and 7. After mounting on printed circuit boards, the CHEMFETs were wire bonded and encapsulated with epoxy resin (Hysol H-W796/C8 W795) or with silicone rubber (Dow Corning 3140 RTV). Before the membrane was applied on top of the polyHEMA layer the CHEMFETs were conditioned in a buffered (pH=4) 0.1 M KCl solution for at least 1 h. A standard membrane consists of 1 wt.% ionophore, 3 wt.% 2,2'-dimethoxy-2-phenylacetophenone as photoinitiator, 40 mol% anionic sites and 96 wt.% polysiloxane in 0.6 ml of THF. The membrane composition was modified to study the sensor performance. A droplet of this solution was casted on the polyHEMA surface of an encapsulated CHEMFET. The CHEMFETs were left for 30 min at room temperature in order to evaporate the solvent. Then the CHEMFETs were photocured in a nitrogen-purged quartz tube using a UV lamp (100 W high pressure mercury lamp, Blak-Ray B-100A) for 2 min. The distance between the lamp and the CHEMFET was approxi-

mately 10 cm. Before the measurements were started the membranes were conditioned in a buffered (pH=4) 0.1 M KCl solution for one night.

CHEMFET measurements

The CHEMFETs were measured in a constant drain-current mode ($I_d = 100 \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5 \text{ V}$) [8].

Polymer analysis

The polymer mol. wt. (M_w) and polydispersity (M_w/M_n) were determined by using a GPC setup consisting of a Waters pump (model 510) and detector (RI 411) combined with a HP1050 Ti injector. The column setup consisted of four columns filled with $\mu\text{styrigel}$ of size 10^5 , 10^4 , 10^3 and 500 \AA , respectively, in combination with a 500 \AA guard column. THF (Merck p.a.) was used as a solvent. Polystyrene in THF was used for calibration. The percentage extractable material was determined by measuring the weight loss of a photocured polysiloxane membrane after washing with an excess of dichloromethane and drying under vacuum. An HPLC analysis was used for determining the efficiency of the covalent binding of the ionophore [9].

Results and discussion

CHEMFET sensors with polysiloxane membranes were prepared by casting a standard solution, using a polysiloxane containing 2.8 mol% of cyanopropylsilyl groups, on top of a precondition polyHEMA layer. The schematic structure of the sensing membrane with the covalently attached potassium-selective ionophore 2 is shown in Fig. 1. A number of sensors prepared with this polysiloxane showed potassium responses with an almost nernstian slope in a horticulture feeding solution containing 30 mM Na⁺, 10 mM Mg²⁺, 10 mM Ca²⁺, 20 mM NO₃⁻, 10 mM SO₄²⁻, 10 mM H₂PO₄⁻ and 10 mM Cl⁻. The durability test under flow conditions showed that CHEMFETs with covalently attached ionophore 2 gave a considerably more stable response than CHEMFETs with the free ionophore 1 (Table 1).

Although these results are encouraging, it is necessary to further improve the lifetime of these sensors. One

TABLE 1. Response (mV/pK) of potassium sensors under continuous flow condition using a free-potassium ionophore 1 and a chemically attached ionophore 2

Time in flowcell (days)	0	7	18	22	28
ionophore 1	55.2	31.4	21.9	12.9	11.0
ionophore 2	53.3	51.3	47.1	42.7	42.6

TABLE 2. Average molecular weight (M_w), average polydispersity (M_w/M_n) and percentage of extractable polysiloxane oligomers and ionophore 2 after UV irradiation of methacrylated polysiloxane copolymer

Polysiloxane (% of cyanopropylsilyl groups)	Molecular weight (M_w) ^a (10^3 g)	Polydispersity ^a	% of extractable oligomers ^b	% free ionophore ^b
2.8 mol%	222	3.9	3	42
10 mol%	36	1.6	22	8

^aBefore UV curing.

^bAfter UV curing.

of the parameters which is relatively unexplored is the compatibility of electroactive components and the polysiloxane membrane matrix. In the preparation of CHEMFETs using the polysiloxane containing 2.8 mol% of cyanopropylsilyl groups, a precipitate occurs, during the evaporation of the THF, before irradiation of the prepolymer. Therefore, we investigated whether this precipitation influences the lifetime of the sensor and the efficiency of the covalent binding of the ionophore.

However, it appeared that a further decrease in the concentration of the membrane components in the polysiloxane matrix was restricted by the concurrent decrease of the potassium response. Therefore, as an alternative possibility to prevent precipitation of the membrane components, the effect of increasing the polarity of the polysiloxane prepolymer was examined.

A polysiloxane membrane of higher polarity was made by increasing the amount of cyanopropylsilyl groups from 2.8 to 10 mol%. The polymer parameters of a number of batches of polysiloxanes were evaluated for their mol. wt., polydispersity, and percentage of extractable material after photocrosslinking of the prepolymer. Based on the polydispersity and mol. wt. values, we found that the reproducibility of the synthesis of a new polysiloxane containing 10 mol% or cyanopropylsilyl groups is better in comparison with the previous, low polar (2.8 mol% cyanopropylsilyl groups) polysiloxane. Furthermore, increasing of the polysiloxane polarity leads to an increase in the amount of low mol. wt. oligomers as extractable material after photopolymerization of the prepolymer (Table 2).

Next we investigated the efficiency of covalent binding of the ionophore in different polysiloxane matrices. HPLC analysis showed that the polysiloxane with 10 mol% of cyanopropylsilyl groups a larger amount of ionophore 2 is bound upon photocuring. This indicates that by increasing the prepolymer polarity the electroactive compound precipitation is reduced.

Based on this new polysiloxane material of higher polarity, several membrane compositions with different amounts of electroactive components were prepared. The obtained membranes were transparent and showed no precipitates under the microscope. The responses of CHEMFETs on these membrane compositions are

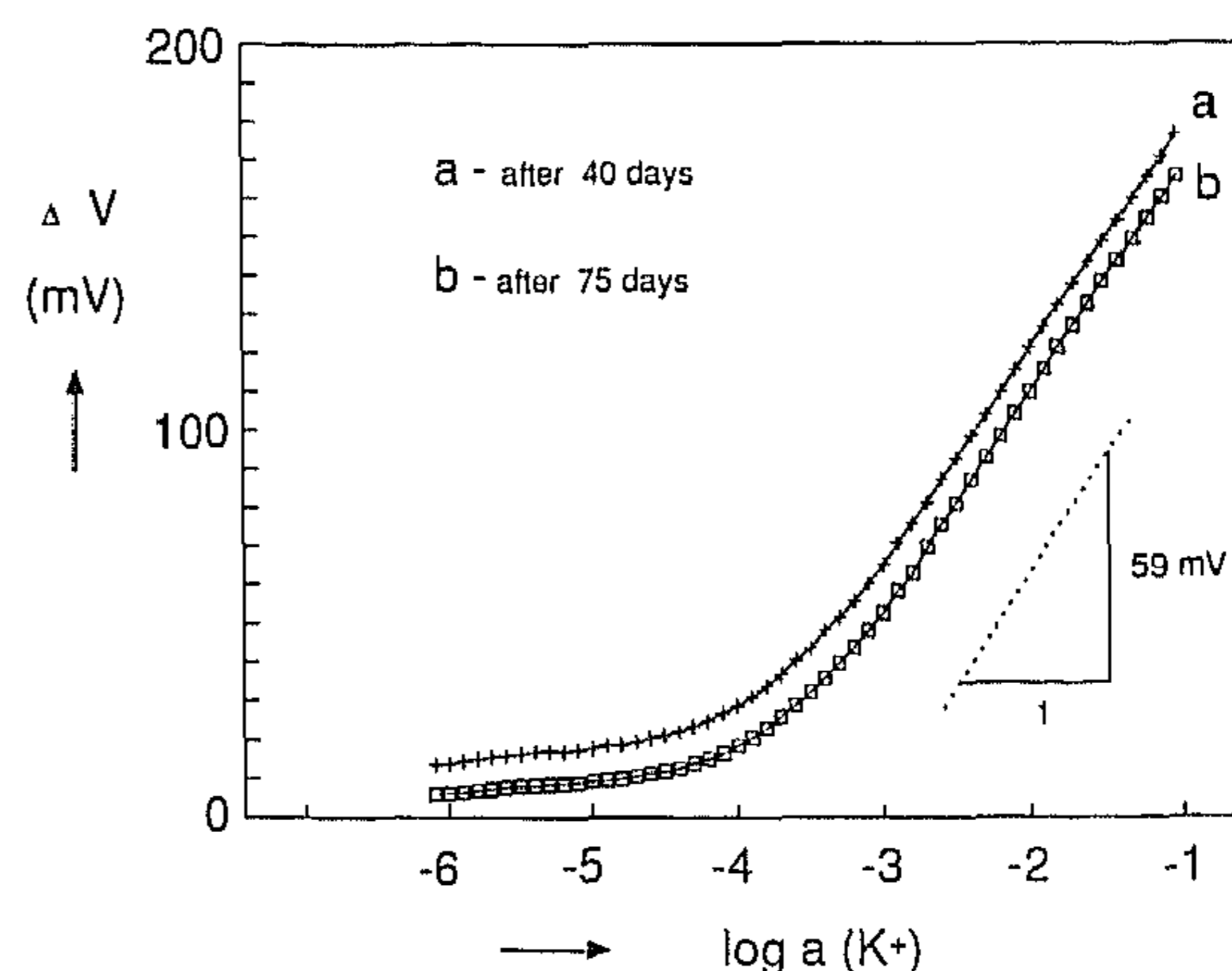


Fig. 2. K^+ -responses of CHEMFETs after different times.

shown in Fig. 2. The potassium response has a Nernstian slope in the whole investigated range of potassium activity in contrast to the sensors which are based on the low polar polysiloxane membranes.

To evaluate the long-term performance of potassium CHEMFETs with this new polysiloxane prepolymer, we prepared a number of sensors and selected the sensors functioning with a response of at least 50 mV/pK for lifetime tests. Using the new polysiloxane as a membrane material the yield of functioning sensors increases to 60% in comparison with only 20% for CHEMFETs based on low polar polysiloxane (2.8 mol% or cyanopropylsilyl groups). The selected sensors were washed in tap water continuously. In spite of the lower concentration of electroactive compounds in the membrane, these sensors still showed a satisfying response and selectivity after 75 days as displayed in Fig. 2.

Conclusions

It was shown that using a new polysiloxane with 10 mol% of cyanopropylsilyl groups as sensing-membrane matrix improved its homogeneity and increased the yield of functioning CHEMFETs. This is an important step towards mass production of sensors for use in practical applications like continuous monitoring of the irrigation water in greenhouses.

References

- 1 D.N. Reinhoudt, Application of supramolecular chemistry in the development of ion-selective CHEMFETs, *Sensors and Actuators B*, 6 (1992) 179–185.
- 2 O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf and W. Simon, Lifetime of neutral carrier-based liquid membranes in aqueous samples and blood and the lipophilicity of membrane components, *Anal. Chem.*, 63 (1991) 596–603.
- 3 H.H. van den Vlekkert, U.H. Verkerk, P.D. van der Wal, A. van Wingerden, G.W.N. Honig, H.A.J. Holterman, J.R. Haak and D.N. Reinhoudt, Multi-ion sensing device for horticultural applications based on chemical modifications and special packaging of ISFETs, *Sensors and Actuators B*, 6 (1992) 34–37.
- 4 E.J.R. Sudholter, P.D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D.N. Reinhoudt, Modification of ISFETs by covalent anchoring of poly(hydroxyethyl methacrylate) hydrogel, *Anal. Chim. Acta*, 230 (1990) 59–65.
- 5 P.D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, E.J. Sudholter and D.N. Reinhoudt, New membrane materials for potassium-selective ion-sensitive field-effect transistors, *Anal. Chim. Acta*, 231 (1990) 41–52.
- 6 P.L.H.M. Cobben, Sensors for heavy metal ions based on ISFETs, *Thesis*, University of Twente, Enschede, The Netherlands, 1992.
- 7 E.J.R. Sudholter, M. Skowronska-Ptasinska, P.D. van der Wal, A. Van den Berg and D.N. Reinhoudt, *Eur. Patent Applic. No. 285 591* (1986).
- 8 P. Bergveld, The operation of an ISFET as an electronic device, *Sensors and Actuators*, B1 (1981) 17–29.
- 9 U.H. Verkerk, H.H. van den Vlekkert, G.W.N. Honig, H.A.J. Holterman, J.F.J. Engbersen and D.N. Reinhoudt, Development of chemically modified ISFETs as durable sensors for continuous flow measurements, *Sensors and Actuators B*, 13/14 (1993) 221–225.