The sensors for the intelligent micro washing system

Work report 4, 8-Aug-95
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1. Introduction

In work report 2 it was shown that the correlation coefficient of the conductivity towards the water hardness is large. According to the statistics of 44 Dutch cities over the year 1986 a coefficient of 0.852 was found. If the actual hardness is wanted (this means the concentration of calcium and magnesium in the water), two selective sensors are needed.
With the same data it was tried to see what the contribution of Ca^{2+} to the hardness is. The next lines are a MathCad 4.0 calculation:

The Vectors 'Ca' and 'Mg' contain the average Ca $^{2+}$ and Mg $^{2+}$ ion concentrations of the tap water of 44 Dutch cities over the year 1986.

The total average concentrations are:

$$\text{mean}(Ca) = 56.493 \cdot \frac{mg}{liter} \qquad \text{mean}(Mg) = 5.823 \cdot \frac{mg}{liter}$$

The water hardness is defined here as the total Ca^{2+} and Mg $^{2+}$ concentrations:

$$Hardness := Ca + Mg \qquad \text{mean}(Hardness) = 62.316 \cdot \frac{mg}{liter}$$

The calcium concentration is quite a value for the hardness because:

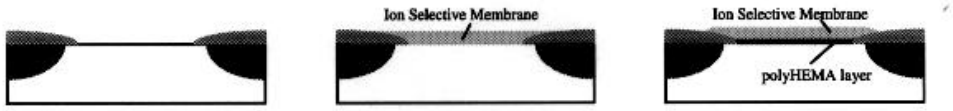
$$\text{corr}(Hardness, Ca) = 0.994$$

So it seems that the average concentration of calcium in the Dutch drinking water is 56.5 mg/litre and the magnesium concentration is 5.8 mg/litre. So the average concentration of calcium is ten times higher than the magnesium concentration.
The correlation of the calcium concentration to the hardness is 0.994. From this it can be concluded that measuring calcium gives a good indication of the hardness (and it is not necessary to determine the magnesium concentration as well).

This work report starts with the description of the known method for developing ion selective membranes. A summary of the theoretical properties of ChemFETs is given in the second section, where the membrane model by Albert van den Berg [3] is summarised as well. In the third section, a fabrication and testing of a calcium ChemFET is described. This research was performed to be able to conclude something about the usability of modified ISFETs in the integrated sensor-array.

2. Developing ChemFETs

The bare ISFET of figure 2.1a gives a response on a proton (H^+-ion) concentration. By applying an ion-selective membrane to the device, an ion selective FET is obtained. The simplest version is the MemFET (figure 2.1b)



[a] ISFET [b] MemFET [c] ChemFET

Fig. 2.1: Schematic structure of the ISFET and ISFET-based devices

The behaviour of the membrane-electrode interface is the result of the selectivity of a receptor in the membrane. This receptor is called an ionophore and is carried by the membrane matrix material which is usually poly(vinylchloride) (PVC). The ion to be determined (primary ion) diffuses into the membrane and links to the ionophore to form a complex. The concentration of the primary ion will be kept constant by a buffer mechanism.
In a following section it will be shown that applying a polyHEMA layer containing the primary ion improves the properties of the MemFET. To distinguish the polyHEMA MemFET from the normal MemFET the first one is often referred to as ChemFET (figure 2.1c).

2.1. Boundary stability

There are two boundaries in a device without a polyHEMA layer: between sample and membrane and between membrane and ISFET. Each interface introduces a boundary potential E_B at equilibrium given by [1,2]:

$$E_B = -\frac{RT}{z_i F} \ln \frac{a_1}{a_2} \qquad (2.1)$$

where
T : absolute temperature [K];
F : the Faraday equivalent ($9.6487 \cdot 10^4$ C mole^{-1});
R : the gas constant (8.314 JK^{-1}mole^{-1});
z_i : the charge number of the ion;
a_i: the activity in medium i of the primary ion.

At the membrane/sample interface the activities a_1 and a_2 are equal to the calcium concentrations in the electrolyte and membrane respectively. When the amount of calcium in the membrane is buffered, the potential E_B is proportional to the logarithm of the concentration in the sample.

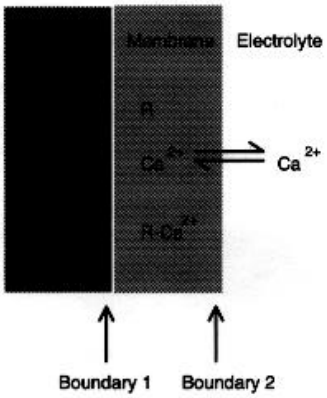


Fig. 2.2: The boundaries in the MemFET

The buffering is done by a system of a receptor and negative charge (figure 2.2.). To make the ion diffuse into the membrane the membrane must be negatively charged or be supplied with ion exchanger sites (perm selectivity). A membrane with ion exchangers is called a neutral carrier based membrane. An example of such a membrane is a membrane with NaTPB (SodiumTetraPhenylBorate).
After the attraction of ions, the specific selectivity is obtained by addind selective ionophores (receptors).

If the ion is I^{z+} with valence z, and the receptor is referred to as R, then the association constant in the membrane is defined as:

$$K_{as} = \frac{[I^{z+}][R]}{[I^{z+}R]} \tag{2.2}$$

With the condition:

$$[TPB^-] = \frac{1}{2} z \cdot [R] \tag{2.3}$$

half of the total amount of receptors will be filled so $[R] = [I^{z+}R]$, and the association becomes:

$$[I^{z+}] = \frac{K_{as}[I^{z+}R]}{[R]} \approx K_{as} \tag{2.4}$$

so the amount of calcium in the membrane is being buffered.

2.2. The use of polyHEMA

At the membrane-ISFET interface however, the activity of calcium in the ISFET is not defined and the membrane potential will be unknown.

This is one reason why a polyHEMA hydrogel layer is added between the selective membrane and the ISFET (figure 2.1c). The improvements are:

- The possibility of holding a defined amount of calcium to define the boundary potential;
- Without a polyHEMA layer it seemed that CO_2 molecules diffused through the membrane, react with water and caused an undesired pH-response. With a pH-buffered polyHEMA layer, the CO_2 response is minimised.

2.3. The process

The fabrication of ChemFETs begins with the normal ISFET process. Before the cutting of the wafer the polyHEMA layer is spinned on and photolithographically paterned. The ISFET is packaged in the regular way (glued on a dip-stick and partially covered with Hysol). To put Ca^{2+} ions in the polyHEMA layer, the dipsticks are soaked in a calciumchloride solution. After a while the concentration in the polyHEMA layer can be assumed to be equal to the concentration of this solution. The solution is pH-buffered to avoid CO_2 responses of the ChemFET.
After this step which is called "conditioning", the membrane is "casted" by writing with a small capillary. The capillary contains the cocktail which defines the ion selective membrane.

The cocktail contaminants are:

a	Solvent:	0.75 ml Tetrahydrofuran (THF);
b	Membrane matrix:	poly(vinylchloride) (PVC);
c	Plasticizer;	
d	Ionophore;	
e	Additive:	SodiumTetraPhenylBorate (NaTPB).

Normally the amounts of contaminants b, c and d are 33 : 66 : 1 wt.%, together 0.1g. Appendix A gives examples of commercially available cocktails and cocktail-contaminants.

3. Theory

The system containing the reference electrode, a sample solution and the ChemFET can be seen as an electrochemical cell. A description for this cell can be:

Ag / AgCl / Cl^- / (salt bridge) / /	• Reference half - cell
Ca^{2+} /	• Sample
Membrane / PolyHEMA / ISFET	• Membrane electrode half - cell

The total cell potential (the electromotive force at zero current) is the sum of all local potential differences generated at all boundaries. In the best case only the potential at the sample-membrane interface is dependent on the Ca^{2+}-ion concentration. This membrane potential E_M can be found from integration of the electrochemical free energy from phase α to β and was mentioned before as equation (2.1):

$$E_M = -\frac{RT}{z_i F} \ln \frac{a_i^\beta}{a_i^\alpha} \tag{3.1}$$

where ion i is the ion which is present on both sides of the phase interface [2].

3.1. Sensitivity

For a buffered membrane the activity in the membrane a^β is constant and using

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b) \tag{3.2}$$

equation (3.1) reduces to:

$$E_M = E_0 + s \ln a_i^\alpha \tag{3.3}$$

with

$$s = \frac{RT}{z_i F} \tag{3.4}$$

the Nernstian slope. This slope is $25.69/z_i$ mV for the use with the natural logarithm and $59.16/z_i$ mV with the 10th logarithm. For the total cell potential the constant E_0 can be expanded to a E'_0 including all other constant potential drops in the cell.

3.2. Selectivity

The previous mentioned model for the sensitivity implements the selectivity to only one species. In practice such ideal electrode behaviour is not observed. It is necessary to observe other contributions to the measured cell potential due interfering ions in the sample solution. A semi empirical approach is given by the extended Nicolsky-Eisenmann equation [1]:

$$E_M = E_0 + s\ln\left[a_i^{\alpha} + \sum_j K_{ij}^{Pot}\left(a_i^{\alpha}\right)^{z_i/z_j}\right] \qquad (3.5)$$

where K_{ij}^{Pot} is the potentiometric selectivity factor for species j. This factor can be determined in three ways:

- *Separate Solution Method (SSM)*
  The cell potential is measured for the ion of interest i and the interfering ion j, both in pure single electrolyte solutions. Equation (3.5) results in:

  $$E_i = E_0 + s\ln\left[a_i^{\alpha}\right]$$
  $$E_j = E_0 + s\ln\left[K_{ij}^{Pot}\left(a_j^{\alpha}\right)^{z_i/z_j}\right]$$

  and the selectivity factor becomes:

  $$K_{ij}^{Pot} = e^{\frac{(E_i - E_j)z_iF}{RT}} \frac{a_i^{\alpha}}{\left(a_j^{\alpha}\right)^{z_i/z_j}} \qquad (3.6)$$

  The problem with this method is that the obtained selectivity is sometimes not representative for mixed sample solutions.
- *Fixed Interference Ion Method (FIM)*
  Selectivity factors are obtained by graphically evaluating the electrode function of the measuring ion in solutions of a fixed concentration of the interfering ion. The value of a_i is obtained from the intersection of the extrapolated parts of the linear portions of the response curves corresponding to E_i and E_j. At the intersection point E_i and E_j are equal and (3.6) reduces to:

  $$K_{ij}^{Pot} = \frac{a_i^{\alpha}}{\left(a_j^{\alpha}\right)^{z_i/z_j}} \qquad (3.7).$$

- *Fixed Primary Ion Method (FPM)*
  The concentration of the interfering ion J is varied at a constant concentration of the primary ion. This method is used to determine pH dependencies.

In table A8 in appendix A some selectivity factors are given. It can be seen that the factor K_{CaH}^{Pot} is the worst, but is still $10^{-1.6}$ which means that the selectivity towards Ca^{2+} is about 40× the selectivity towards H^+.

3.3. Response time

Response times of the ion selective electrode are only measurable if the time constant of the response function of the electrode is much larger than the time constants of the electrochemical cell and the set-up.
For neutral carrier based membranes modified with ion-exchanger sites the response time can be represented by an exponential function [1]:

$$E_t = E_\infty + s \log\left[1 - \left(1 - \frac{a_i^0}{a_i}\right) e^{-\frac{t}{\tau'}}\right] \qquad (3.8)$$

with

$$\tau' = \frac{\delta^2}{2D'} \qquad (3.9)$$

where:
E_t : the cell potential at time t [mV];
E_∞ : equilibrium potential at $t = \infty$ [mV];
s : Nernstian Slope (equation 3.4);
a^0_i, a_i : activities of the primary ion in the bulk of the sample solution at $t < 0$ and $t \geq 0$ [mole/l] respectively;
D' : mean diffusion coefficient in the stagnant layer [m^2/s];
δ : thickness of the stagnant layer [m].

So the dynamic response characteristics are governed by the transport processes in the stagnant layer. This means that the response time depends on the shape and condition of the membrane surface as well as the composition of the sample.
In data books the 90% response time is given. This 90% response time can be expressed as:

$$t_{90\%} = \tau' \ln\left(\frac{1 - \frac{a_i^0}{a_i}}{1 - 10^{-\frac{E_\infty}{10s}}}\right) \qquad (3.10)$$

resulting from the equations (3.8) and (3.9).

3.4. Life time

The lifetime of an electrode is limited by mechanical influences, electrical shunts, chemical events, poisoning and loss of neutral carrier op plasticizer from the membrane into the sample solution. The theoretical models that predict lifetime are based on the kinetics of the loss of components from the membrane into the sample solution. Table 3.1 summarises the rate constants of processes that take place.

Table 3.1: Rate constants of kinetic processes involved in the transfer of membrane components to the sample solution [1]

Kinetic process	Rate constant [cm/s]
a: Interfacial exchange reaction	k'
b: Diffusion through a stagnant boundary layer	$\frac{D_s}{k\delta_s}$
c: Linear diffusion in the sample	$\frac{1}{k}\sqrt{\frac{D_s}{\pi t}}$
d: Spherical diffusion in the sample	$\frac{D_s}{k \cdot r_0}$
e: Linear diffusion in the membrane	$\sqrt{\frac{D_m}{\pi t}}$

k' : exchange reaction rate constant of the first order [cm/s];
k : partition coefficient between membrane and sample;
D_s : diffusion coefficient in the sample [cm^2/s];
δ_s : thickness of the stagnant boundary layer in the sample [cm];
r_0 : radius of the formally spherical membrane [cm];
D_m : diffusion coefficient in the membrane [cm^2/s].

The process with the smallest rate constant will be rate controlling. In reference [1] some examples are given using the ETH 1001 calcium ionophore.

3.5. The membrane model

To learn about the membrane behaviour, the membrane model of Albert van den Berg was used [3]. This model describes the membrane potential of a membrane located between two electrolytes. In the ChemFET case, one of them is the polyHEMA hydrogel and the other is the sample.

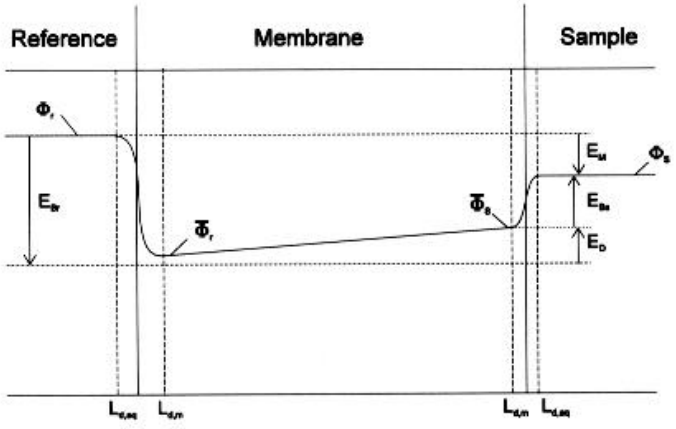


Fig. 3.1: Membrane potential distribution

In figure 3.1 the hydrogel is the reference side and the corresponding (constant) boundary potential drop is E_{Br}. At the sample-membrane interface the boundary

potential is E_{Bs}. The result is that in the membrane a diffusion potential appears E_D. The total membrane potential is:

$$E_M = E_{Bs} + E_D + E_{Br} \qquad (3.11).$$

The layers $L_{d,aq}$ and $L_{d,m}$ are assumed to be small.

First the activities of the charge carriers in the membrane are calculated for both the sample and the reference boundary. To calculate this, the electro neutrality of the interface is used:

$$\sum_{i=1..nc} \bar{a}_{c_i} + \sum_{i=1..nx} \bar{a}_{X_i} + \sum_{i=1..nl} \bar{a}_{Lc_i} - \sum_{i=1..na} \bar{a}_{a_i} - \sum_{i=1..ny} \bar{a}_{Y_i} = 0 \qquad (3.12)$$

with (from left to the right) the total amounts of free cations, not ion-paired cationic sites, ligand-cation complexes, free anions and not ion-paired anionic sites. The line above the activities a refer to the situation in the membrane.
With one type of ligand L, one anionic site Y, two cations (one of them is primary ion) and two anions 3.12 reduces to:

$$\sum_{i=1..2} \bar{a}_{c_i} + \sum_{i=1..2} \bar{a}_{Lc} - \sum_{i=1..2} \bar{a}_{a_i} - \sum_{i=1..2} \bar{a}_{Y} = 0 \qquad (3.13)$$

The activities of ions in the membrane edges are related to the activities in the solution by the partition equations. For anions:

$$\bar{a}_a = k_a \cdot a_a \cdot e^{\frac{F}{RT} E_B} \qquad (3.14)$$

for cations:

$$\bar{a}_c = k_c \cdot a_c \cdot e^{-\frac{F}{RT} E_B} \qquad (3.15)$$

where

k_c, k_a : the partition coefficients for cations and anions respectively;
a_a, a_c : the activities of anions and cations in the solution;
E_B : the boundary potential.

The total activity of the ligand-cation complexes is a function of the total activity of the anionic sites [3]:

$$\sum \bar{a}_{Lc} = \frac{L_{tot} \sum \beta \bar{a}_c}{1 + \sum \beta \bar{a}_c + K_L \sum \bar{a}_Y \sum \beta \bar{a}_c} \qquad (3.16)$$

which is itself a function of the total ligand-cation complex activity:

$$\sum \bar{a}_Y = \frac{Y_{tot}}{1 + \sum K_Y \bar{a}_c + K_L \sum \bar{a}_{Lc}} \tag{3.17}$$

with

L_{tot}, Y_{tot} : total amount of ligand and anionic site;
β : association constant for ligand-cation complexes;
K_L : association constant for ligand-cations complexes with anionic sites;
K_Y : association constant for cation-anionic sites complexes;

From equations (3.16) and (3.17) the total activities in the membrane for anionic sites and ligand-cation complexes can be evaluated as a function of the primary ion. Equation (3.13) now gives an implicit expression of the activity of the primary ion in the membrane and the membrane potential can be calculated using the partition equations (3.14) and (3.15).

The diffusion potential can be derived from the activities in the membrane using the Henderson equation [2]:

$$E_D = \frac{RT}{F} \cdot \frac{\sum_i \mu_{ci} \Delta \bar{a}_{ci} + \sum_i \mu_{Lci} \Delta \bar{a}_{Lci} - \sum_i \mu_{ai} \Delta \bar{a}_{ai}}{\sum_i \mu_{ci} \Delta \bar{a}_{ci} + \sum_i \mu_{Lci} \Delta \bar{a}_{Lci} + \sum_i \mu_{ai} \Delta \bar{a}_{ai}} \cdot \ln\left(\frac{\sum_i \mu_{ci} \bar{a}_{ci}(r) + \sum_i \mu_{Lci} \bar{a}_{Lci}(r) + \sum_i \mu_{ai} \bar{a}_{ai}(r)}{\sum_i \mu_{ci} \bar{a}_{ci}(s) + \sum_i \mu_{Lci} \bar{a}_{Lci}(s) + \sum_i \mu_{ai} \bar{a}_{ai}(s)} \right) \tag{3.18}$$

with

μ_x : the mobility of ion x;
(r), (s) : at the reference side, sample side respectively;
Δa_x : activity drop across the whole membrane.

Now the whole membrane potential can be calculated using equation (3.11). Appendix B gives an implementation of the model for a system containing:

- one ligand $L_{tot} = 10^{-2}$, $\beta_{prim} = 10^4$, $\beta_{sec} = 10^{-2}$;
- one anionic site $Y_{tot} = 10^{-3}$, $K_L = 1$, $K_Y = 10^4$;
- Ca^{2+} as primary ion $a_{c.ref} = 0.1$ M, $k_c = 10^{-5}$;
- Na^+ as secondary ion $a_{c.sample} = 0.5$ M;
- Cl^- as counter ion. $k_a = 10^{-5}$.

Figure 3.2 gives the result of a simulation where the primary ion was changed and the membrane potential was simulated.

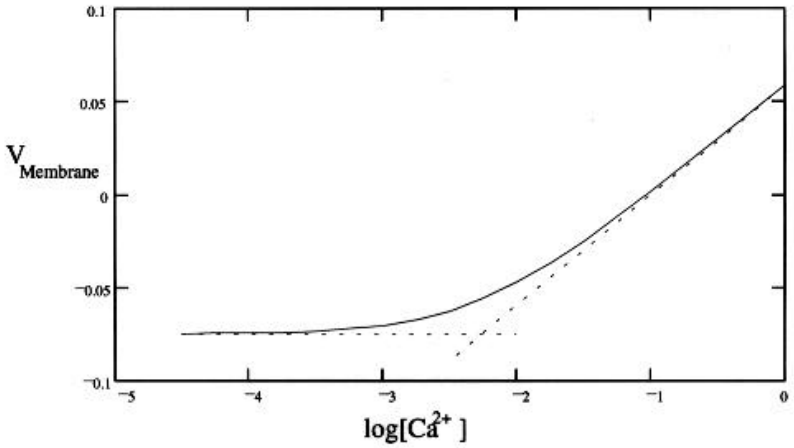


Fig. 3.2: Simulated membrane potential

The Nernstian slope is 59/2 mV as predicted with equation (3.4), the selectivity $Kpot_{CaNa}$ can be found from the asymptotes using equation (3.7).
Other simulation experiments listed in the thesis of van den Berg [3] were successfully repeated using this model, but they will not be given here. This model can not be used to explain the measurements quantitatively because the factors like L_{tot}, β_{prim} and β_{sec} are not known, only their global ranges. The model is suitable for simulating trends and phenomena.

3.6. Expected problems

If the sensor is being used in the washing liquor, lipophillic contaminants in the sensor will reduce lifetime. The soap in the detergent will penetrate the membrane and remove the lipophillic structures like for example TPB. Actually, the PVC membrane has some lipophillic groups itself and the ionophores are lipophilic as well to avoid leakage into the sample solution. An idea of the lipophilicity of a molecule can be obtained by the knowledge that oxygen and nitrogen atoms decrease lipophilicity while carbon increases this behaviour.
With PVC membranes lifetimes of 80 hours are reported (under non-soap conditions). If this value is dramatically reduced in detergent we must find another membrane material or restrict to measuring in the supply water.
At the chemical technology department research is performed on new membrane materials. A popular one is polysiloxane. There are three options:

- The receptor (ionophore) is kept in the polysiloxane by capture in the polymer branches. Low quality can be expected but little research has to be done.
- The receptor is bonded to the polysiloxane. To do this, some new research must be done.
- The receptor is used to make cross links in the polysiloxane. This is hard to do and requires a lot of specific research. At the department of chemical technology this is currently performed for other receptors.

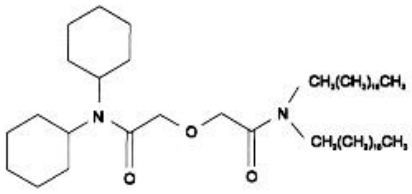
It seems that if the PVC membrane gives a bad lifetime it is worth trying the first option.

4. Experimental

From appendix A a membrane composition was chosen according to the price and the properties of the compounds. Calcium ionophore IV was chosen because there are some references to literature [8] and combined a low price with good selectivities.

4.1. Fabrication of the ChemFET

The systematical name for this ionophore is *N,N -dicyclohexyl - N',N' -dioctadecyl - 3 - oxapentanediamide* and is sometimes referred to with the code ETH 5234.



N,N - Dicyclohexyl - N',N' -dioctadecyl - 3 - oxapentanediamide

Fig. 4.1: Ionophore ETH 5234

The composition is $C_{52}H_{100}N_2O_3$ and the molecular weight is 801.37 g/mole. It's high lipophilicity can be understood by noticing that the hydrophilic nitrogen and oxygen atoms are shielded by the xylene groups and the long carbon chains.

First, Ta_2O_5 ISFETs with polyHEMA were packaged (type JHGL 26-1-1995, 0.05 mV/hour drift) and tested by watching the green light on the ISFET amplifier. To condition the polyHEMA, 200 ml solvent was made using Yokogawa 4.01 pH-buffer with 0.1 M $CaCl_2$ (99.5%). The ISFETs were soaked for 4½ hours.

The membrane cocktail composition was chosen as in table A7 of appendix A, were the components were added in the order of table 4.1.

Table 4.1: Membrane cocktail composition using Calcium Ionophore IV

Additive	Potassium tetrakis (4-chlorophenyl)borate	2.1	wt.%	1.55 mg	Fluka 60591
Ionophore	Calcium Ionophore IV	5.0	wt.%	5.0 mg	Fluka 21198
Polymer	Poly(vinyl chloride) high molecular weight	33.0	wt.%	33.0 mg	Fluka 81392
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	66.0	wt.%	66.0 mg	Fluka 73732
Solvent	Tetrahydrofuran		fill to 0.75 ml		Fluka 87369

Casting was done by writing with a small capillary and repeated three times in one hour. After one night of drying the devices were soaked in 0.1 M $CaCl_2$ for another night to exchange the sodium in the membrane by calcium and to put the membrane structure in a steady state.

The price of an ISFET based ion sensor is hard to calculate because it is hard to find the costs of the fabrication of the semiconductor device. The price of the membrane is almost completely dependent on the ionophore when making small amounts (less than a hundred).

4.2. Response time

To use the automatic titration set-up it is necessary to have an impression of the response time. One device was placed in a 0.1 M NaCl solution, the membrane potential was monitored by connecting the output of the ISFET amplifier to the auxiliary input of a potentiostat. With a 1 ml pipette a 1 M $CaCl_2$ solution was applied (figure 4.2).

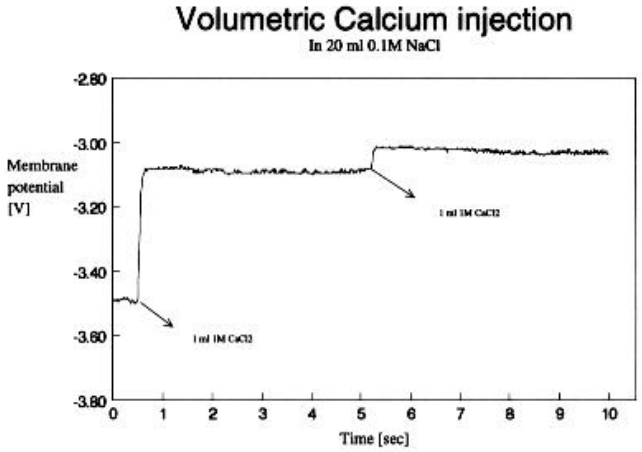


Fig. 4.2: Step response of Calcium ChemFET

To determine the time-constant of the response the 90% response time (equation (3.10)) is used. The 90% response time is obtained from figure 4.3 and is 0.58 seconds, so the time constant is $\tau' = 0.69$ seconds.

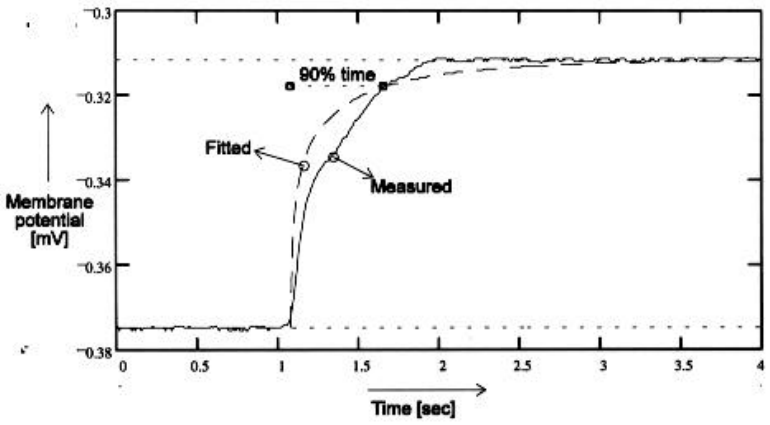


Fig. 4.3: 90% Response time and fitted response

4.3. Drift measurement

From figure 4.4 the drift of two ChemFETs during 12 hours can be found. The value of about 0.1 mV per hour does not differ significantly from that of the bare ISFET.

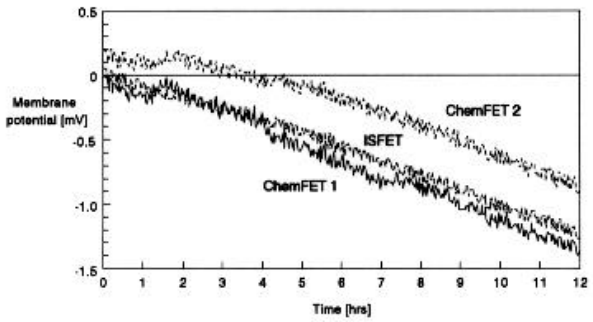


Fig. 4.4: Drift measurement with second set of ChemFETs and one ISFET

4.4. Concentration response

With the automatic titration set-up, it is possible to expose the ChemFETs to a number of different primary ion concentrations. In section 3.2. it was shown that this can be combined with a selectivity measurement. First, sodium was chosen as a secondary ion and the calcium concentration was changed.

If the concentration NaCl is 1 M and assuming a selectivity factor $\log(K_{pot})$ of -5.9 [4], then a Nernstian relation relative to calcium can be expected at calcium concentrations above 1 μM. However, the amount of calcium in the used sodium results in an initial concentration of some micro-molars, so the selectivity measurement can not reliably performed with the used set-up.

The first calcium scan was performed with four ChemFETs (one was broken) in 40 ml of 1 M NaCl. In figure 4.5A the measured response is set on a logarithmic x-axis because this should give a straight line in case of a Nernstian behaviour.

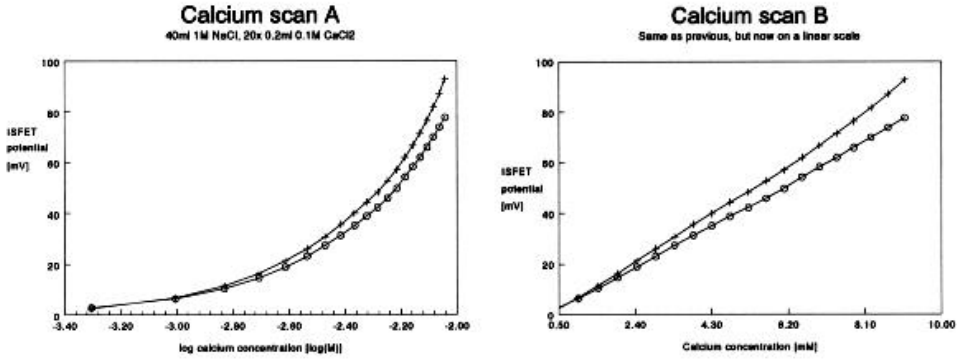


Fig. 4.5: Calcium scan with first set of ChemFETs

From this graph it appears that the theoretical slope of about 30 mV/decade can not be observed. Instead, the measured data on a linear scale shows a straight line which might indicate an ohmic contact.

A second batch of ChemFETs was produced to repeat the concentration scan. Two scans were made with a bare ISFET as a reference. The first one (figure 4.6A) showed a 25.34 mV per decade Nernstian response at first instance, but skipped to an ohmic response after 10 mM of $CaCl_2$. It must be noted that the leakage current through the reference electrode was high: 50 nA.

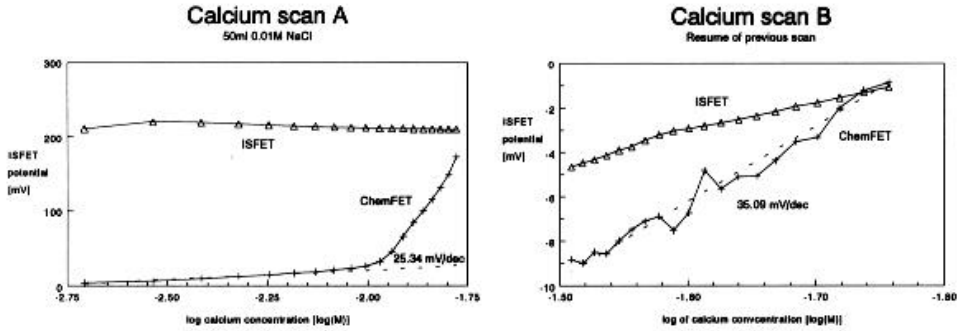


Fig. 4.6: Calcium scans with second set of ChemFETs and one ISFET

It was assumed that the ohmic contact was due to a wet dipstick-connector. The devices were repositioned, and with the same electrolyte another successive scan was made. Again an almost Nernstian response was observed (35.09 mV/dec., see figure 4.6B).

4.5. Life-time and durability test in a washing machine

Only a few of the total number of assembled ChemFETs did work at first instance (three of ten). With these devices successful measurements (like figure 4.6B) were performed during three days. The devices were wet for about 30 hours in total and dried sometimes completely between measurements.

This lifetime of will probably be reduced in a washing machine: 30 hours in sodium- and calcium-chloride are not equal to 30 washing cycles because the washing liquor is a much more aggressive and heated environment. Therefore two ChemFETs and some structures containing polysiloxane were placed in the washing machine like described in work report 3. Six washes were performed: three white washes (60°C, Dobbelman detergent) and three coloured washes (40°C, Dreft Colour detergent).
The membranes were optically inspected afterwards. The polysiloxane showed no damage and was still hard to remove using tweezers. The poly(vinylchloride) membranes were still on the ISFETs, and were as easy removable as fresh ones. So polysiloxane shows a better bonding to the substrate than PVC, although no problems were observed.
As reported in the previous work report, the used two-component epoxy (Hysol) has a granulated structure after washing, probably due to the high pH. Besides that an overall cover of chalk was deposited on the sensor strip, which could change the behaviour of the devices.

5. Conclusions

The fabrication and testing of calcium ChemFETs was primary done to get an impression of the possibilities of membrane-covered ISFETs in the integrated washing sensor project. The aim of this project is to integrate existing sensors, so attention must be paid to the measurement set-ups for these membranes rather than the development of new ones.
A secondary point of interest was to measure calcium which has a major contribution to the water hardness.

A membrane model given in the Ph.D. thesis of Albert van den Berg was successfully evaluated. This model can be used for modelling trends and effects in membrane processes. For qualitative calculations models for selectivity, life-time and response time are present.

In the experimental part some ChemFETs showed a Nernstian response to the calcium concentration. Selectivity measurements were not performed because they would require very pure chemicals. The response time is less than one second and lifetime of 30 hours were recorded at room temperature in sodium- and calciumchloride solutions. The used ChemFETs were based on Ta_2O_5 ISFETs instead of the mainly used SiO_2-based devices.

Some ChemFETs were placed in a washing machine for six wash cycles. The structure of these devices were not modified. No measurements were performed using these washed sensors.

The advantage of ChemFETs is that they give a very selective response and so no advanced circuitry (like neural networks or fuzzy logic) is necessary to interpret the signal.
Disadvantages come from the fact that they have uncertain life-times and that they are hard to put in the operational mode. This makes the device not convenient to start a number of experiments with for example differential measurements, pseudo-references and temperature behaviour. Besides that, the membrane has the price of a non-disposable sensor but the properties are of a disposable one.

Appendix A: Ionophore cocktails

The chemicals are taken from: Fluka Chemika, Selectophore [4]. The numbers refer to the order numbers.

Table A1: Calcium Ionophore I

Solvent	Tetrahydrofuran (THF)			87369	100 ml *f*30,-
Ionophore	Calcium Ionophore I	3.3	wt.%	21192	50 mg *f*378,-
Plasticizer	Bis(1-5) decane-1,10-dihyl diglutarate	63.7	wt.%	30585	250 mg *f*59,80
	or: Bis(1-butylpentyl) adipate (BBPA)	63.7	wt%	02150	5 ml *f*47,70
	or: Bis(2-ethylhexyl) sebacate (DOS)	63.7	wt%	84818	5 ml *f*29,30
Additive	Potassium tetrakis (4-chlorophenyl)borate	2.1	wt%	60591	250 mg *f*25,90
Polymer	Poly(vinyl chloride) high molecular weight	30.9	wt%	81392	10 g *f*37,10

Table A2: Calcium Ionophore I, Cocktail A*

Solvent	Tetrahydrofuran			87369	100 ml *f*30,-
Ionophore	Calcium Ionophore I	10.0	wt%	21048	0.1 ml *f*152.40
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	89.0	wt%		
Additive	Sodium tetraphenylborate (TPB)	1.0	wt%		
Polymer	Poly(vinyl chloride) high molecular weight			81392	10 g *f*37,10

* Reference [5]

Table A3: Calcium Ionophore I, Cocktail B

Solvent	Tetrahydrofuran	3×wt		21191	0.1 ml *f*85.-
Ionophore	Calcium Ionophore I	8.6	wt%		
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	76.5	wt%		
Additive	Sodium tetraphenylborate (TPB)	0.7	wt%		
Polymer	Poly(vinyl chloride) high molecular weight	14.0	wt%		

Table A4: Calcium Ionophore II*

Solvent	Tetrahydrofuran			87369	100 ml *f*30,-
Ionophore	Calcium Ionophore II	1.0	wt%	21193	50 mg *f*113.20
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	65.6	wt%	73732	5 ml *f*38,90
Additive	Potassium tetrakis (4-chlorophenyl)borate	0.6	wt%	60591	250 mg *f*25,90
Polymer	Poly(vinyl chloride) high molecular weight	32.8	wt%	81392	10 g *f*37,10

* Reference [6]

Table A5: Calcium Ionophore II, Cocktail A

Solvent	Tetrahydrofuran				87369	100 ml *f*30,-
Ionophore	Calcium Ionophore II	5.0		wt%	21196	0.1 ml *f*118.80
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	94.0		wt%		
Additive	Sodium tetraphenylborate (TPB)	1.0	86.0	wt%		
Polymer	Poly(vinyl chloride) high molecular weight		14.0	wt%	81392	10 g *f*37,10

Table A6: Calcium Ionophore III*

Solvent	Tetrahydrofuran	87369	100 ml *f*30,-
Ionophore	Calcium Ionophore III	21186	5 mg *f*132,40
Plasticizer			
Additive			
Polymer	Poly(vinyl chloride) high molecular weight	81392	10 g *f*37,10

* Reference [7]

Table A7: Calcium Ionophore IV*

Solvent	Tetrahydrofuran			87369	100 ml *f*30,-
Ionophore	Calcium Ionophore IV	5.0	wt%	21198	50 mg *f*149,70
Plasticizer	2-Nitrophenyl octyl ether (o-NPOE)	66.0	wt%	73732	5 ml *f*38,90
Additive	Potassium tetrakis (4-chlorophenyl)borate	46.0	mol%#	60591	250 mg *f*25,90
Polymer	Poly(vinyl chloride) high molecular weight	33.0	wt%	81392	10 g *f*37,10

* Reference [8]

Relative to the ionophore

Table A8: Properties:

Ionophore:	Selectivity coefficients	Stability [mV/h]	Lifetime log P_{TLC}	90% Response time [sec]
Calcium Ionophore I	$\log K^{Pot}_{CaH} = -2.9$ $\log K^{Pot}_{CaNa} = -3.7$ $\log K^{Pot}_{CaK} = -3.7$ $\log K^{Pot}_{CaMg} = -4.7$	0.01	7.5	
Calcium Ionophore I, Cocktail A	$\log K^{Pot}_{CaNa} = -5.5$ $\log K^{Pot}_{CaK} = -5.4$ $\log K^{Pot}_{CaMg} = -4.9$			<5
Calcium Ionophore I, Cocktail B	as cocktail A			
Calcium Ionophore II	$\log K^{Pot}_{CaH} = -1.6$ $\log K^{Pot}_{CaLi} = -3.3$ $\log K^{Pot}_{CaNa} = -3.7$ $\log K^{Pot}_{CaK} = -4.0$ $\log K^{Pot}_{CaMg} = -4.9$		7.2	2.5
Calcium Ionophore II, Cocktail A	$\log K^{Pot}_{CaNa} = -5.6$ $\log K^{Pot}_{CaK} = -7.2$ $\log K^{Pot}_{CaMg} = -6.7$			<5
Calcium Ionophore III				
Calcium Ionophore IV	$\log K^{Pot}_{CaH} = -3.1$ $\log K^{Pot}_{CaLi} = -5.8$ $\log K^{Pot}_{CaNa} = -5.9$ $\log K^{Pot}_{CaK} = -7.5$ $\log K^{Pot}_{CaMg} = -4.4$		22.6	1.2

Appendix B: Implementation of the membrane model

The following is a complete listing of a MathCad 4.0 file:

Math parameter:

$TOL := 1 \cdot 10^{-5}$

Physical constants:

Faraday constant $F := 96485.309$

Temperature $T := 298$

Gas constant $R := 8.314510$ $\frac{R \cdot T}{F} = 0.0257$

Ranges:

$i := 0..18$ Number of points

Activities:

$a_{a,r} := \begin{pmatrix} 10^{-1} \\ 0 \end{pmatrix}$ $a_{c,r} := \begin{pmatrix} 10^{-1} \\ 0 \end{pmatrix}$ 0.1 M primary cation and anion in the polyHEMA layer

$a_{a,s_{0,i}} := 10^{-0.25 \cdot i}$ $a_{c,s_{0,i}} := 10^{-0.25 \cdot i}$ a variable amount of primary ions in the sample solution

$a_{a,s_{1,i}} := 0.5$ $a_{c,s_{1,i}} := 0.5$ a constant amount of secondary ions in the sample solution

Variables and constants:

$k_c := \begin{pmatrix} 10^{-5} \\ 10^{-5} \end{pmatrix}$ $k_a := \begin{pmatrix} 10^{-5} \\ 10^{-5} \end{pmatrix}$ Partition coefficient cations and anions

$\beta := \begin{pmatrix} 10^{4} \\ 10^{-2} \end{pmatrix}$ Association constant of the complex by free ligand Molecules

$K_Y := 10^4$ Ion-pair formation constant of anionic sites Y with cations

$K_L := 1$ Association constant of ligand-cation complexes with anionic sites

$Y_{tot} := 10^{-3}$ Total activity of cationic sites

$L_{tot} := 10^{-2}$ Total activity of ligand Molecules in the membrane

$\mu_a := 1$ $\mu_c := 1$ $\mu_{Lc} := 1$ Mobilities

Partitio n equations:

$am_c(E_B, a_c, k_c) := k_c \cdot a_c \cdot \exp\left(-\frac{F \cdot E_B}{R \cdot T}\right)$ $am_a(E_B, a_a, k_a) := k_a \cdot a_a \cdot \exp\left(\frac{F \cdot E_B}{R \cdot T}\right)$

$ns := 0..1$ The number of ions is 2

The model:

$$eq1\left(E_B, a_c\right) := \frac{1}{\sum_{ns} \beta_{ns} \cdot am_c\left(E_B, a_{c_{ns}}, k_{c_{ns}}\right)} + 1 \qquad eq2\left(E_B, a_c\right) := 1 + \sum_{ns} K_Y \cdot am_c\left(E_B, a_{c_{ns}}, k_{c_{ns}}\right)$$

$$eq4\left(E_B, a_c\right) := \sqrt{\left(\frac{eq2\left(E_B, a_c\right)}{2 \cdot K_L} + \frac{Y_{tot} - L_{tot}}{2 \cdot eq1\left(E_B, a_c\right)}\right)^2 + \frac{L_{tot} \cdot eq2\left(E_B, a_c\right)}{K_L \cdot eq1\left(E_B, a_c\right)}}$$

$$eq3\left(E_B, a_c\right) := -\frac{eq2\left(E_B, a_c\right)}{2 \cdot K_L} + \frac{L_{tot} - Y_{tot}}{2 \cdot eq1\left(E_B, a_c\right)}$$

$$am_{Lc}\left(E_B, a_c\right) := if\left(eq3\left(E_B, a_c\right) - eq4\left(E_B, a_c\right) > 0, eq3\left(E_B, a_c\right) - eq4\left(E_B, a_c\right), eq3\left(E_B, a_c\right) + eq4\left(E_B, a_c\right)\right)$$

$$am_Y\left(E_B, a_c\right) := \frac{Y_{tot}}{eq2\left(E_B, a_c\right) + K_L \cdot am_{Lc}\left(E_B, a_c\right)}$$

$$Err\left(E_B, a_c, a_a\right) := \sum_{ns} am_c\left(E_B, a_{c_{ns}}, k_{c_{ns}}\right) - \sum_{ns} am_a\left(E_B, a_{a_{ns}}, k_{a_{ns}}\right) + am_{Lc}\left(E_B, a_c\right) - am_Y\left(E_B, a_c\right)$$

Solve E_B from $Err(E_B) = 0$

$E_B := -1$

Boundary potential membrane/polyHEMA interface

$$E_{B.r} := root\left(Err\left(E_B, a_{c.r}, a_{a.r}\right), E_B\right)$$

$$E_{B.r} = -0.059$$

Boundary potential membrane/sample interface

$$E_{B.s_i} := root\left[Err\left[E_B, \begin{pmatrix} 10^{-0.225 \cdot i} \\ 0.1 \end{pmatrix}, \begin{pmatrix} 10^{-0.25 \cdot i} \\ 0.1 \end{pmatrix}\right], E_B\right]$$

$$am_{c.r_{ns}} := am_c\left(E_{B.r}, a_{c.r_{ns}}, k_{c_{ns}}\right) \qquad am_{a.r_{ns}} := am_a\left(E_{B.r}, a_{a.r_{ns}}, k_{a_{ns}}\right)$$

$$am_{c.s_{ns,i}} := am_c\left(E_{B.s_i}, a_{c.s_{ns,i}}, k_{c_{ns}}\right) \qquad am_{a.s_{ns,i}} := am_a\left(E_{B.s_i}, a_{a.s_{ns,i}}, k_{a_{ns}}\right)$$

Henderson approximation for diffusion potential :

$$E_{D_i} := \frac{R \cdot T}{F} \cdot \frac{\begin{array}{l} \sum_{ns} \mu_c \cdot \left(am_{c.r_{ns}} - am_{c.s_{ns,i}}\right) \cdots \\ + \mu_{Lc} \cdot \left[am_{Lc}\left(E_{B.r}, a_{c.r}\right) - am_{Lc}\left[E_{B.s_i}, \begin{pmatrix} 10^{-0.25 \cdot i} \\ 0.1 \end{pmatrix}\right]\right] \cdots \\ + -\sum_{ns} \mu_a \cdot \left(am_{a.r_{ns}} - am_{a.s_{ns,i}}\right) \end{array}}{\begin{array}{l} \sum_{ns} \mu_c \cdot \left(am_{c.r_{ns}} - am_{c.s_{ns,i}}\right) \cdots \\ + \mu_{Lc} \cdot \left[am_{Lc}\left(E_{B.r}, a_{c.r}\right) - am_{Lc}\left[E_{B.s_i}, \begin{pmatrix} 10^{-0.25 \cdot i} \\ 0.1 \end{pmatrix}\right]\right] \cdots \\ + \sum_{ns} \mu_a \cdot \left(am_{a.r_{ns}} - am_{a.s_{ns,i}}\right) \end{array}} \cdot \ln\left[\frac{\begin{array}{l} \sum_{ns} \mu_c \cdot am_{c.r_{ns}} \cdots \\ + \mu_{Lc} \cdot am_{Lc}\left(E_{B.r}, a_{c.r}\right) \cdots \\ + \sum_{ns} \mu_a \cdot am_{a.r_{ns}} \end{array}}{\begin{array}{l} \sum_{ns} \mu_c \cdot am_{c.s_{ns,i}} \cdots \\ + \mu_{Lc} \cdot am_{Lc}\left[E_{B.s_i}, \begin{pmatrix} 10^{-0.25 \cdot i} \\ 0.1 \end{pmatrix}\right] \cdots \\ + \sum_{ns} \mu_a \cdot am_{a.s_{ns,i}} \end{array}}\right]$$

The complete membrane potential becomes:

$$E_{M_i} := E_{B.s_i} - E_{D_i} - E_{B.r}$$

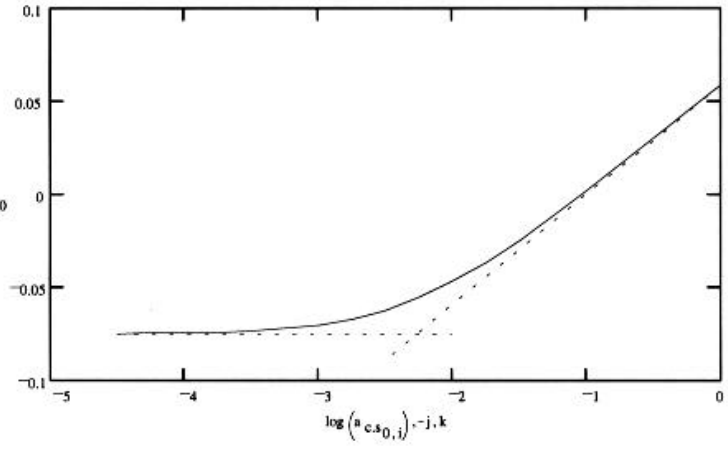
$j := 0, 0.5 .. 2.5$ $k := -4.5, -4 .. -2$

Membrane potential [V] versus l og(Ca^{2+}) activity [log(M)]

E_{M_i}

$\frac{R \cdot T}{F} \cdot \ln\left(10^{-j}\right) + E_{M_0}$

$E_{M_{18}}$



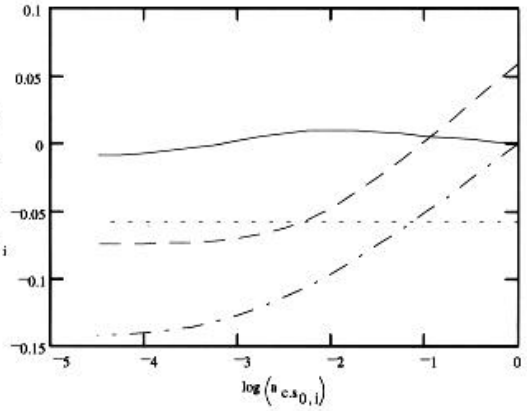
Separate contributions of diffusion and interface potentials to the total membrane potential

E_{D_i}

$E_{B.r}$

E_{M_i}

$E_{B.s_i}$



Total membrane potential

Diffusion potential

Sample/membrane interface

Membrane/reference interface

Appendix C: References

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