

Superposition of Sensitivities in Sensors with Hydrophobic Polymers on Field-Effect Devices

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A potentiometric solid state sodium sensor with a hydrophobic membrane was investigated concerning the interface membrane/solid support. The formation of a potential difference at this interface dependent on the composition of the external solution was verified. Therefore a superposition of sensitivities of two interfaces in series was observed. Impedance spectroscopy was used to investigate the membrane properties and to determine the exchange current density at the membrane/solid support interface using a simplified structure.

1. Introduction

Starting with Bergfeld's paper⁽¹⁾ in 1970, much attention has been given to the development of ion-sensitive field-effect transistors (ISFETs). Different sensitive insulating layers such as SiO₂, Si₃N₄, Al₂O₃ and Ta₂O₅ were used for the determination of pH. The deposition of an additional sensitive layer on top of the insulator or directly on the silicon⁽²⁾ results in a variety of sensors. Several inorganic layers, *e.g.*, chalcogenides,⁽³⁾ silver halides⁽⁴⁾ or LaF₃,⁽⁵⁾ were successfully tested for the measurement of different ions. Since the number of suitable inorganic sensitive materials is restricted, polymer membranes have been extensively investigated for use as sensitive layers.

The interface between the insulator and the sensitive membrane may cause different problems. Janata and Moody⁽⁶⁾ have shown that the interface between the gate oxide and the sensitive layer lacks a thermodynamically well-defined potential difference. This capacitive contact is stable in the case of an ISFET because of the negligible stray capacitances and leak currents. When using organic materials as sensitive layers, the penetration of gases such as CO₂ or organic acids⁽⁷⁾ that change the pH at the insulator/membrane interface causes additional problems. Because of the pH sensitivity of the insulator, this results in a change of gate voltage and loss of selectivity. The application of a buffered hydrogel between the insulator and the membrane was proposed to solve this problem.^(8,9)

Polymer membranes used as sensitive layers are highly hydrophobic materials; therefore, penetration of inorganic ions through the membrane would not be expected. But even for a hydrophobic polymer like polyurethane, a slight influence of the electrolyte on the electrical membrane properties was found.⁽¹⁰⁾ Thus the question arises whether or not a very slow change of the ion concentration at the insulator/membrane interface occurs after a change of electrolyte composition leading to drift of the sensor and loss of sensitivity and selectivity. It was the aim of this study to clarify if such an additional potential difference at the insulator/membrane interface caused by diffusion of inorganic ions in hydrophobic membranes can be a problem in solid-state sensors.

Polyglutamate, a hydrophobic polymer with a high resistivity, was selected to be the object of investigation. The films were prepared by the Langmuir-Blodgett (LB) technique because of the well-defined and reproducible preparation conditions. A sodium sensor was realized using a sodium ionophore as a dopant for the polymer, as was demonstrated in ref. 11. As support, a Si/SiO₂/Si₃N₄/LaF₃ multilayer structure which was known to be a very stable and selective fluoride ion sensor⁽⁵⁾ was used. The application of this sensor is very advantageous judging from the strong evidence of the experiments performed. The structure was subjected to an examination of its sensitivity to sodium as well as fluoride. Impedance spectroscopy was used to characterize the sensor system in detail.

2. Materials and Methods

The sensor system for the sensitivity measurements was prepared by thermal vapor deposition of a 250 nm layer of LaF₃ at a pressure of about 5×10^{-3} Pa and a rate of 0.3 to 0.5 nm/s. The samples were hydrophobized by treating with a silylating agent (hexamethyldisilazane in chloroform). In the second step LB film deposition was performed using a film balance with a control system (Lauda FL1, Germany) providing constant surface pressure and a processor-controlled film lift. Figure 1 shows the molecular structure of the polyglutamate (PG). Mixed LB films were prepared by physically mixing PG and a sodium ionophore (Na⁺-ionophore III, Fluka AG, Switzerland) in chloroform as described in ref. 11. The molecular amount of the sodium ionophore in the mixed film was 10% with respect to the monomer units of PG. The film deposition was accomplished from a chloroform solution of 1 mg/ml at a surface pressure of 20 mN/m and a lift velocity of 8 mm/min. Milli-Q-water served as a subphase at a temperature of 20°C.

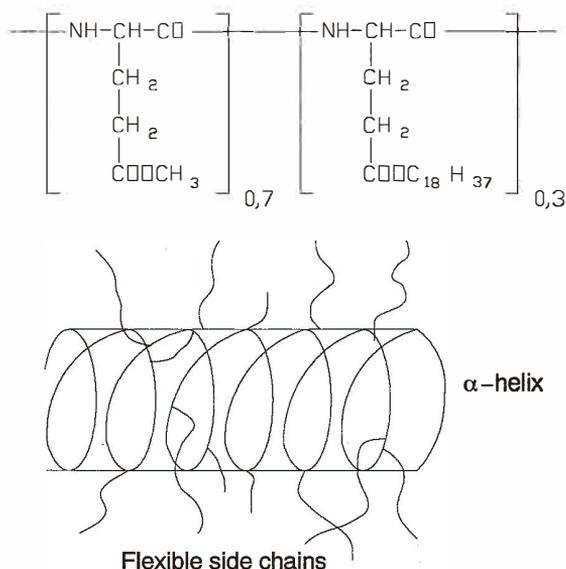


Fig. 1. Molecular structure of poly[(γ -methyl-L-glutamate)-co-(γ -n-octadecyl-L-glutamate)] (PG). Schematic view of the α -helical conformation.

Then the sensor was mounted in an electrochemical cell that was part of a flow system (Fig. 2) and was equilibrated for half an hour with 0.1 M NaF.

The computer-controlled equipment consisted of a precision LCR meter (4284A, Hewlett-Packard), a seven-port valve (Knauer, Germany) and a peristaltic pump (IPC-S, Ismatec, Switzerland).

The measurement procedure was to change the solution while the potential was being monitored using a high-frequency capacitance-voltage measurement (HF-CV) with a computer-controlled constant capacitance mode.⁽¹²⁾ The solution flow rate was 250 μ l/min. Sodium sensitivity measurements were performed as a matter of routine between the fluoride sensitivity measurements to prove the membrane integrity. A detailed investigation of the sodium sensor behavior was performed without use of the flow system.

Impedance measurements were carried out using an impedance spectrometer for electrochemical purposes (IM5d, Zahner Elektrik, Germany). Membranes of thicknesses ranging from 10 to 50 layers were prepared on a square platinum-covered silicon carrier with an edge length of 15 mm. The film deposition parameters were the same as for the LaF₃-covered samples. The active area was a circle with a diameter of 8 mm.

The samples were brought into electrolyte contact and after a delay time of 10 minutes to two hours, depending on the film thickness, equilibrium was established (constant electrical potential). Then the measurement was carried out under open circuit potential conditions.

The compositions of the solutions used for the impedance spectroscopy and for the sensitivity measurements are given in connection with the results.

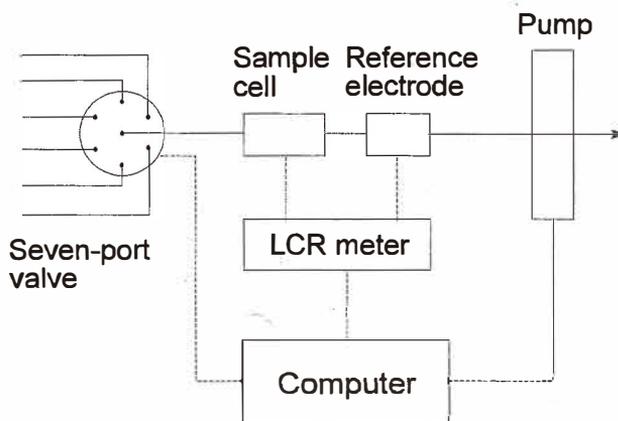


Fig. 2. Flow system for fluoride sensitivity measurements. Solid lines: electrolyte flow; dotted lines: electric connections or computer interface cables.

3. Results

3.1 Sensitivity measurements

Mixed LB-films of PG and Na⁺-ionophore III on top of Si/SiO₂ structures are known to show a reversible shift of the characteristic CV curves of about 50 mV/ ΔpNa ,⁽¹¹⁾ as shown in Fig. 3. These curves were obtained after electrolyte contact of 5 min. By kinetic investigations using a constant capacitance mode CV-technique,⁽¹⁴⁾ the sensor response time could be determined to $t_{50} < 1$ min. In view of the following experiments the influence of different counter ions such as Cl⁻, F⁻ and SO₄²⁻ was investigated. Figure 4 shows that no significant influence of these counter ions on the sensor characteristic could be detected. In particular, further measurements prove that no potential change is induced by fluoride ions (Fig. 5). Measurements with a constant fluoride background concentration (curve a) and varying concentration of fluoride (curve c) resulted in the same potential shift. With the sodium concentration held constant while varying the fluoride concentration (curve b), no significant potential shift could be observed.

Thin layers of LaF₃ are known to result in a very selective fluoride ion sensor. The deposition of the LB film on top of a Si/SiO₂/Si₃N₄/LaF₃ structure should again result in a sodium sensor, but if there is diffusion of fluoride ions through the LB film to the LaF₃/LB film interface, an additional fluoride ion sensitivity will be detectable. First of all the behavior of the Si/SiO₂/Si₃N₄/LaF₃ structure without the LB film was investigated in the flow system described above. For concentrations higher than 10⁻⁵ mol/l fluoride, a Nernstian sensitivity of 58 mV/ ΔpF was found (Fig. 6). The limit of detection was determined to be 8×10^{-7} mol/l. The dynamic response of the fluoride ion sensor without LB film is fast and depends on the fluoride ion concentration.⁽¹³⁾ For concentrations higher than pF5 the response time t_{50} is in the range of seconds.

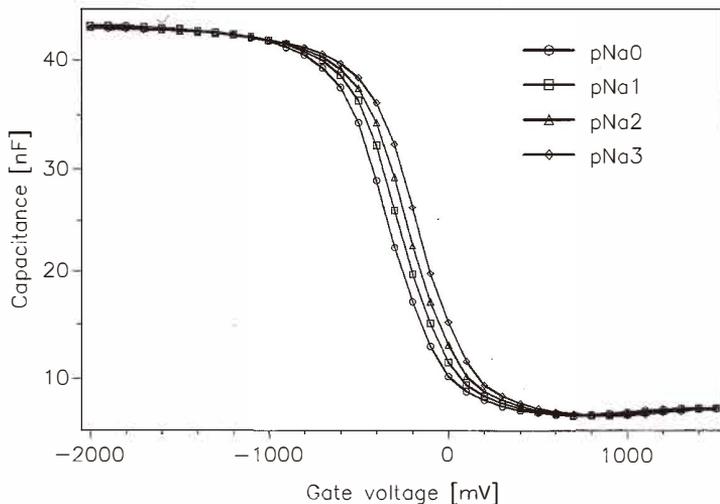


Fig. 3. Shift of the CV curves of a sodium ion sensor of the Si/SiO₂/PG structure with 20 monolayers of PG and Na⁺-ionophore III. Variation of the NaF concentration in 0.05 M TRIS buffer (pH8). Lines are introduced to guide the eyes.

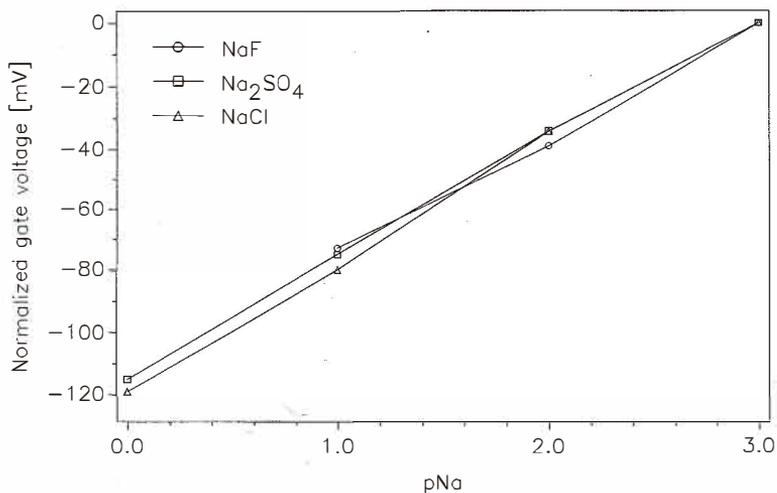


Fig. 4. Influence of different counter ions on sodium sensitivity of the Si/SiO₂/PG structure. Variation of the NaF, Na₂SO₄ and NaCl concentrations in 0.05 M TRIS buffer (pH8). Lines are introduced to guide the eyes.

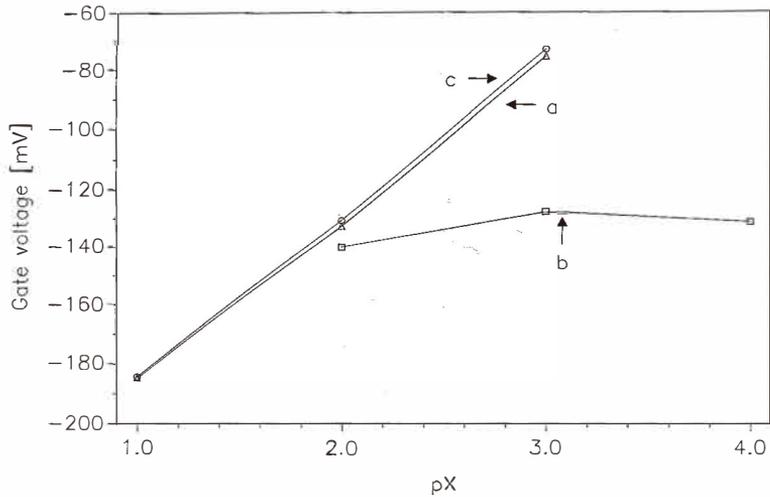


Fig. 5. Sensitivity of the Si/SiO₂/PG structure to (a) sodium at constant fluoride concentration (0.001 M), (b) fluoride at constant sodium concentration (0.01 M), (c) sodium fluoride. All solutions with 0.05 M TRIS buffer (pH8). Lines are introduced to guide the eyes.

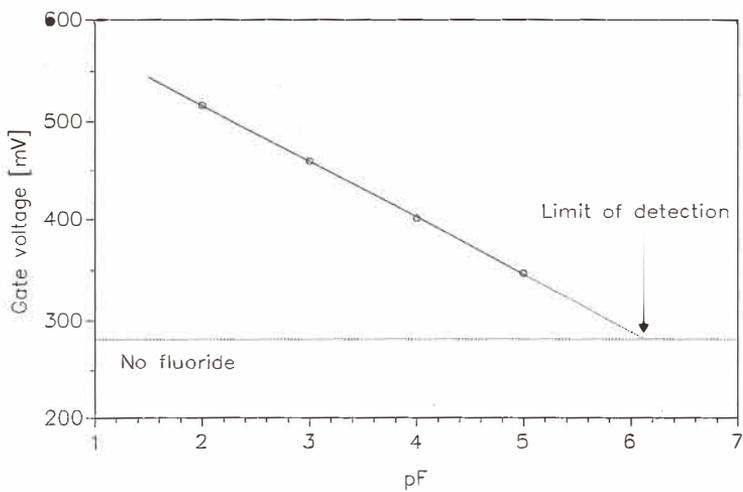


Fig. 6. Sensitivity of the Si/SiO₂/Si₃N₄/LaF₃ structure (fluoride sensor). Variation of the NaF concentration in 1 M NaCl.

Sensitivity measurements of the complex Si/SiO₂/Si₃N₄/LaF₃/LB structure for short times (5 min in each stagnant solution) and a low concentration of supporting electrolyte lead to a result comparable to that of the system without the LaF₃ layer, i.e., no sensitivity to fluoride, but a sodium sensitivity was found corresponding to the typical sodium sensitivity of this LB membrane (Fig. 7).

However, using higher concentrations of the supporting electrolyte in the flow system, a small sensitivity to fluoride was found. It should be noted that the influence of the fluoride ion concentration on the potential depended to a great extent on the kind of inert salt used. In Na₂SO₄ the sensitivity is in the range of 15 to 20 mV per decade, whereas in NaCl a sensitivity of about 40 mV per decade can be found (Fig. 8).

It was clearly shown that this is not a change of film behavior with time, because the influence of the supporting electrolyte is a reversible effect. It should be noted that the rate of potential change due to a stepwise concentration change is comparatively slow with t_{90} in the range of 10 min.

The behavior of the sensor structure is clearly illustrated for measurements with a change of the NaF concentration in solutions with a low inert salt content (Fig. 9). For low concentrations there is only a fast sodium sensitivity, but for the change to the 0.1 M NaF solution, the fast response to Na⁺ is followed by a slow drift in the opposite direction. This is obviously attributable to the F⁻-ion sensitivity found at constant sodium concentrations. These results allow us to associate the effects due to fluoride of the structure Si/SiO₂/Si₃N₄/LaF₃/LB clearly with the LaF₃/LB film interface.

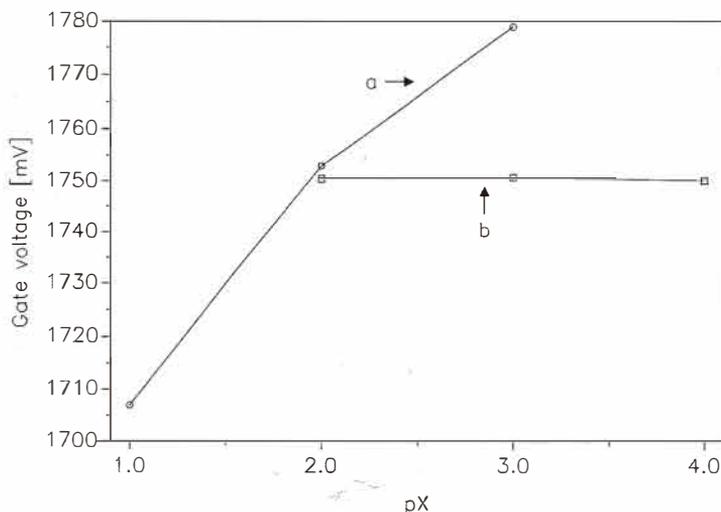


Fig. 7. Sensitivity of the Si/SiO₂/Si₃N₄/LaF₃/LB structure to fluoride and sodium, respectively at low background concentrations. Variation of (a) NaCl and (b) NH₄F in 0.05 M TRIS buffer (pH8). Lines are introduced to guide the eyes.

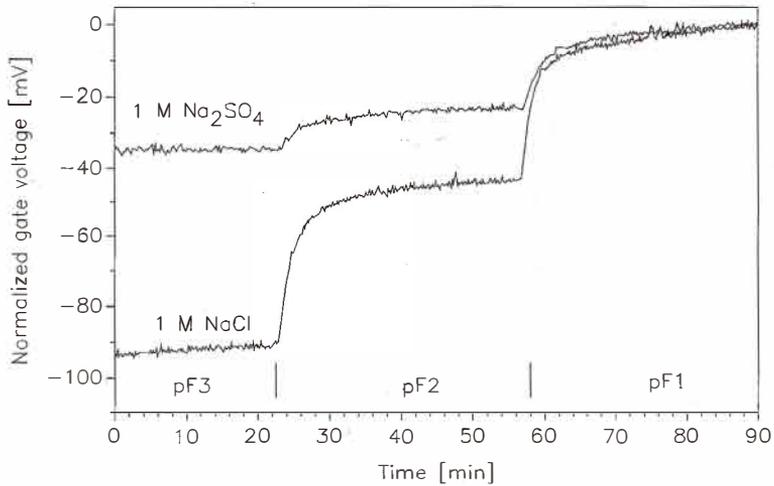


Fig. 8. Response to fluoride of the Si/SiO₂/Si₃N₄/LaF₃/LB structure; 20 monolayers. Variation of the NaF concentration at 1 M NaCl and 1 M Na₂SO₄.

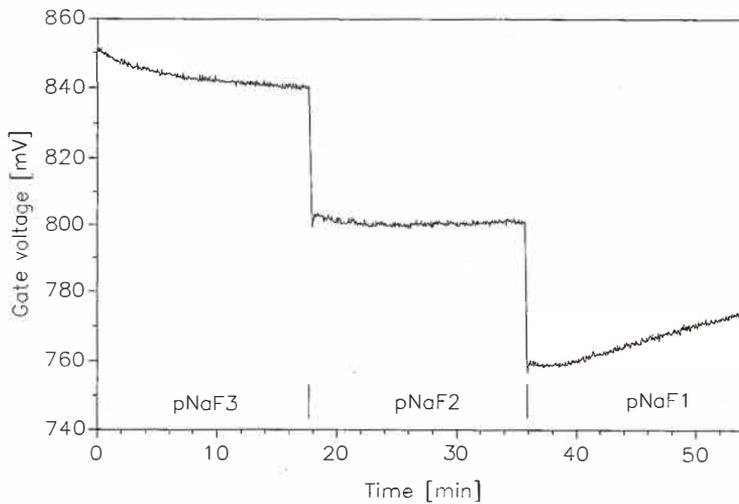


Fig. 9. Response to sodium fluoride of the Si/SiO₂/Si₃N₄/LaF₃/LB structure. Variation of NaF in 0.05 M TRIS buffer (pH8).

3.2 Impedance spectroscopy

Impedance spectroscopy is a very suitable method for the characterization of bulk properties of thin films as well as interfaces. We used a simplified structure of Si/Pt/LB/electrolyte with an electrical contact with the platinum to avoid the high impedance of the insulator in series. In a very simple model the structure can be represented by a parallel RC combination for the bulk of the membrane, a parallel RC combination for the Pt/LB-film interface in series and the electrolyte resistance (Fig. 10). The spectra obtained provide only well-defined information about the electrolyte resistance in the high-frequency range, while a correlation to physical properties is difficult for low frequencies because of the poorly resolved spectrum (Fig. 11). A variation of the experimental conditions was necessary to obtain more detailed information.

The bulk impedance of a nonpermeable membrane should not be affected by changing the electrolyte properties. On the contrary, assuming a distribution equilibrium between electrolyte and membrane, the membrane resistance should decrease with increasing salt concentration.

Figure 11 shows the impedance dependence of the electrolyte concentration. In the low-frequency part a drastic reduction of the impedance with increasing concentration can be observed.

In another experiment the electrolyte composition was varied, keeping the conductance of the electrolyte approximately constant. Even in this case the low-frequency impedance is reduced by nearly 50 percent upon changing from MgSO_4 to NaCl (Fig. 12).

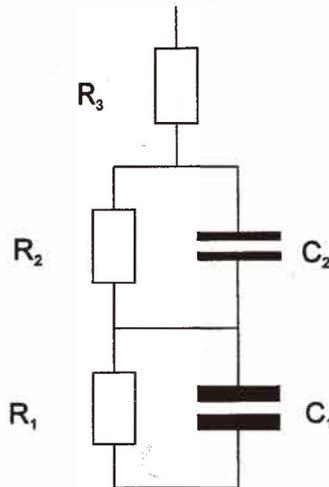


Fig. 10. Equivalent circuit for the Pt/LB system. R_1 : exchange resistance; C_1 : double layer capacitance (constant phase element, see below); R_2 : membrane resistance; C_2 : membrane capacitance; R_3 : electrolyte resistance.

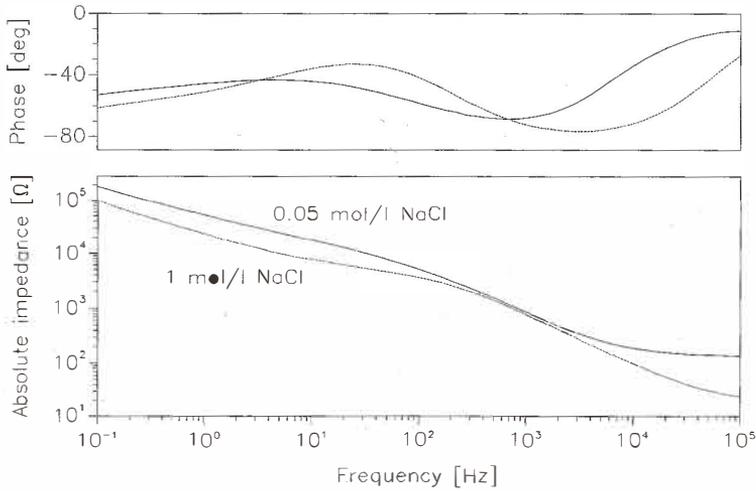


Fig. 11. Dependence of the impedance spectrum of the Pt/LB structure on the salt concentration; 10 monolayers. Variation of the NaCl concentration.

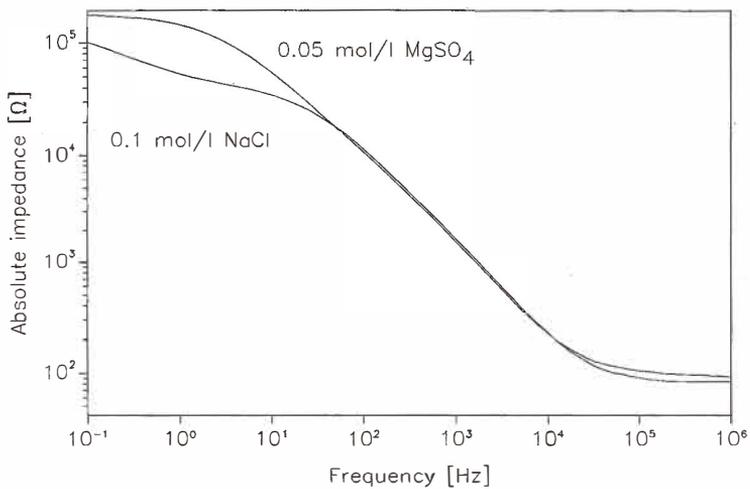
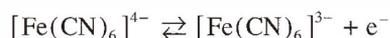


Fig. 12. Comparison of the impedance spectra of the Pt/LB structure with different electrolytes; 20 monolayers.

These effects can only arise from a soaking process that causes a response in the membrane resistance to a change of the electrolyte composition. The electrolyte uptake depends on the dissolved salt; i.e., there are specific distribution coefficients of the salts between the membrane and the electrolyte. Similar results were obtained for cellulose acetate membranes, which are, in contrast, hydrophilic.⁽¹⁴⁾

For further characterization of the sensitive layer/supporting layer interface we tried to follow the kinetics of an electrochemical reaction at the interface. It is well known that the exchange reaction



at a platinum electrode influences the impedance of the Pt/electrolyte phase boundary because of its concentration-dependent exchange current. It was our aim to investigate whether this reaction can be found even with the membrane-covered platinum.

Figure 13 shows a large impedance decrease, though the total amount of charge carriers in the solution is approximately constant, in the low-frequency range with each increment of the FeII/FeIII concentration caused by the high concentration of the supporting electrolyte. Therefore we have proof of the possibility of an electrochemical reaction in the LB-covered system and the equivalent circuit described above.

The numerical evaluation of the spectra with the proposed equivalent circuit yields the electrical parameters of the membrane bulk, which is represented by one RC circuit.

The resistances for a 10-layer film are 7.9, 7.7 and 3.6 GΩcm in 0.05, 0.1 and 1 M NaCl solutions, respectively. The resistance of the membrane in contact with 0.05 M MgSO₄ is

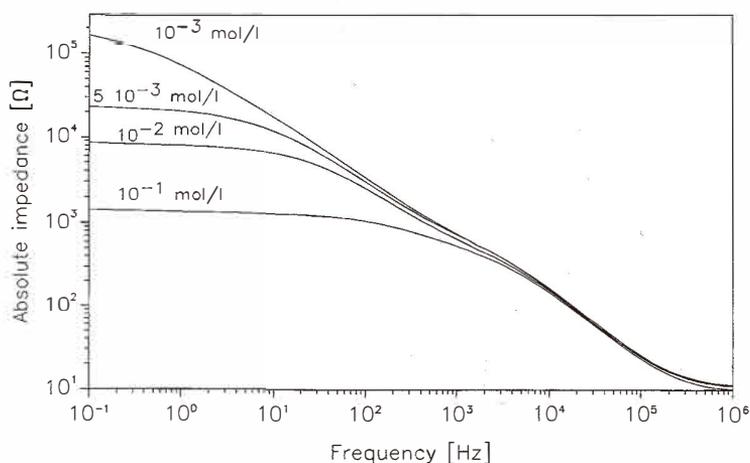


Fig. 13. Impedance spectra of the Pt/LB structure; 20 monolayers. Variation of the concentration of FeII/FeIII ($K_3[\text{Fe}(\text{CN})_6]/K_4[\text{Fe}(\text{CN})_6]$ 10:1; concentrations are total iron) in 1 M NH_4NO_3 .

22 G Ω cm. The dielectric constant could be determined to be 9, having no appreciable variation with the electrolyte composition.

The experimental results have shown that the Pt/membrane interface is influenced by an electrochemical reaction, and therefore it can be represented by the second RC combination. The capacitive component is due to a Helmholtz double layer formed by the electrolyte in polymer pores near the platinum. To fit the spectra satisfactorily, the corresponding capacitor must be represented by a constant phase element. The resistor corresponds to the exchange reaction; i.e., the reciprocal resistance is proportional to the reaction rate. The comparison of the resistances of film-covered and uncovered platinum in Fig. 14 shows an increase of the exchange resistance of up to three orders of magnitude; i.e., the reaction rate is drastically reduced by the film. As already described for the fluoride ion sensitivity, we also found an influence of the inert supporting electrolyte on the exchange rate.

4. Discussion

Mixed LB films of PG with Na⁺ ionophore III deposited on field effect structures yield promising sodium sensors. However, even for this hydrophobic material there was a fluoride ion sensitivity when a fluoride-sensitive interlayer was used. The slow response to fluoride indicates that there must be a change in fluoride ion activity at the LaF₃/PG interface. This means that there is ion uptake into the hydrophobic membrane. The experiments using the redox system show the possibility of transport of even larger ions

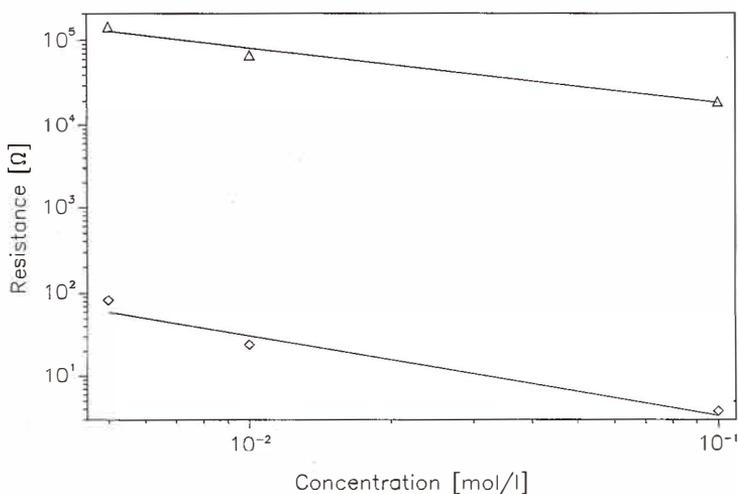


Fig. 14. Comparison of the exchange resistance of LB-covered and uncovered platinum. Variation of the FeII/FeIII concentration in 1 M NH₄NO₃. Δ : 30 monolayers; \diamond : uncovered platinum.

through the membrane.

On the other hand, we have shown that the sensitivity to fluoride is much lower with the membrane compared to the uncovered LaF_3 . This can be explained by assuming that the distribution coefficient of the ions between the membrane and the electrolyte is much smaller than unity.

The change in the exchange current density of the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system comparing covered and uncovered Pt leads to the same result. From these measurements a distribution coefficient of about 10^{-3} can be estimated.

The permeation of electrolyte through hydrophobic membranes might be somewhat surprising and we had to consider the argument that the effects found at the supporting interlayer are due to defects in the membrane. However, the fact that a change in the supporting (inert) electrolyte leads to a reversible alternation of the response of the sensor structure to fluoride cannot be explained by pinholes in the membrane. On the other hand, it is well known for hydrophilic membranes that the distribution coefficient can be influenced by a second electrolyte in mixed solutions. Therefore, the sensor behavior can be explained considering a small uptake of fluoride ions dependent on the kind of the supporting electrolyte. This is also supported by the observation that the exchange current density of the redox system also changes with the supporting electrolyte.

As a consequence a superposition of potential formation at two interfaces in series (supporting layer (insulator)/LB film and LB film/electrolyte) was proven. The fact that potential formation at the supporting layer/membrane interface depends on the inert electrolyte and that, consequently, the state of the membrane is influenced by it should be internalized.

From the slow response to a change in fluoride ion concentration a very small diffusion coefficient of about $10^{-15} \text{ cm}^2/\text{s}$ can be estimated, considering the very small thickness (10 layers \triangleq 17.5 nm) of the LB film.

Although the results presented in this paper are obtained for a specific system, it can be generalized that even for hydrophobic membranes a small uptake of electrolyte can occur. This results in a change of the ion concentration at the solid support/polymer interface and as a consequence, it can result in a potential change. For membranes with a smaller distribution coefficient or a higher thickness these effects will be slower and smaller.

However, in this case the time constant and the amount of the second potential formation are on the order of magnitude of typical drift phenomena of ISFETs. Very often the problem of a superposition of sensitivities has been ignored in the literature.

Acknowledgments

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