Development of a New Matrix Based on a Silicone Ladder Polymer for Ion-sensing Membranes

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A silicone ladder-type polymer was successfully utilized for a matrix of an ion sensing membrane to fabricate an ion-sensitive field-effect transistor. An ion sensing membrane was readily fabricated by mixing a silicone ladder-type oligomer with a quaternary ammonium salt, casting onto the gate of the field-effect transistor, and polymerizing with heating. Since no acid catalysts were needed to prepare the ion sensing membrane, it was possible to keep the quaternary ammonium salt in the matrix without decomposition. The ion-sensitive field-effect transistor based on the silicone ladder-type polymer and the quaternary ammonium salt showed a linear response with a slope of \(-58.1\, \text{mV decade}^{-1}\) very close to the theoretical Nernstian response over an \(\text{NO}_3^-\) range between \(3.0 \times 10^{-6}\) and \(1.0 \times 10^{-3}\) M. The time required to reach 90% total response was within 5 s, when the \(\text{NO}_3^-\) concentration was changed from \(1.0 \times 10^{-3}\) to \(3.0 \times 10^{-3}\) M. The newly fabricated ion-sensitive field-effect transistors have kept their original sensitivity for more than half a year.

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Introduction

To date, plasticized poly(vinyl chloride)(PVC) has been used as the most popular matrix for liquid-membrane-type ion sensors.\(^1\)\(^-\)\(^3\) This is certainly because plasticized PVC membrane matrices can be easily prepared by incorporating ionophores. This feature is favorable to fabricate the ion sensor or to evaluate the properties of ionophores. However, from the viewpoint of practical use, there remain some significant problems with regard to plasticized PVC membrane matrix. Most plasticizers used to maintain an ionophore inside the matrix are relatively polar, so that they are amenable to be effused into the external solution with time, leading to the gradual loss of sensitivity. Besides this, plasticized PVC membranes are apt to peel off the solid surface, such as the gate of an ion-sensitive field-effect transistor (ISFET), due to its poor adherence to inorganic materials.\(^4\) Thus, since the durability of plasticized PVC membranes is usually poor, it is difficult to maintain the original ability to attain the accurate determination of ion concentrations with a sufficient selectivity.\(^5\)

Sol-gel glass derived with hydrolysis of metal alkoxides has been used in order to improve the durability of the membrane and to keep detecting materials for longer periods.\(^6\)\(^,\)\(^7\) Since the sol-gel glass can be prepared at relatively low temperatures, it is beneficial and practical to create the various sol-gel derived organic/inorganic hybrid composite materials. Indeed, the sol-gel glass membrane, prepared from silicon alkoxide has been successfully applied to the ion sensor.\(^8\)\(^-\)\(^10\)

Recently, we have paid attention to silicone ladder-type polymer materials\(^11\)\(^,\)\(^12\) (referred to as SLP in this report), by which thin films can be readily prepared. For example, SLP has been used in protective coatings for electrical parts.\(^13\) SLP is obtained by polymerization of silicone ladder type-oligomer (referred to as SLO in this report) (Fig. 1(a)). SLP is supposed to be obtained via the condensation reaction of SLO molecules. Upon condensation, the elimination of either hydroxy group or alkoxy group may be responsible for successive bindings to form SLP.

Importantly, SLO is soluble in various organic solvents, such as alcohol, ester, ketone and aromatics. This suggests that most of the ionophores are homogeneously incorporated into the matrix during polymerization. Since both hydroxy and alkoxy groups are present on SLO molecules, it may be possible to immobilize various organic compounds that bear either silicon alkoxy groups or silanol via the condensation reaction. Therefore, it was predicted that both plasticizers as well as hydrolysis would be unnecessary to fabricate SLP membranes.

Fig. 1 Silicone ladder oligomer (SLO) (a), and quaternary ammonium salt (QAS: dimethyloctadecyl-3-trimethoxysilylpropyl-ammonium chloride) (b).
Materials

SLP (Glass Resin®, GR-100) was obtained from Showa Denko (Tokyo, Japan). QAS (dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride) was obtained from Shin-Etsu Silicone (Tokyo, Japan). Sodium nitrate, sodium sulfate, sodium chloride, sodium bromide, sodium dihydrogenphosphate, sodium acetate, sodium benzoate and sodium perchlorate were of guaranteed reagent grade. SLO (Glass Resin®, GR-100) was obtained from Showa Denko (Tokyo, Japan). QAS (dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride) was obtained from Shin-Etsu Silicone (Tokyo, Japan). Sodium nitrate, sodium sulfate, sodium chloride, sodium bromide, sodium dihydrogenphosphate, sodium acetate, sodium benzoate and sodium perchlorate were of guaranteed reagent grade.

ISFET fabrication

In this work, the commercially available metal oxide semiconductor field-effect transistor (MOSFET) chip was employed to fabricate the ISFET.14–16 Figure 2 shows the schematic drawing of the ISFET. A MOSFET 2SK241 was purchased from Toshiba Co. (Tokyo, Japan). A copper disk (7-mm in diameter, 2-mm in thickness) connected to a gate terminal with solder was stuck to one end side of a glass tubing (7-mm in external diameter, 4-mm in internal diameter, 100-mm long) with a silicone-type adhesive. Both SLO and QAS were dissolved in 2-propanol (2 ml). The total weight of SLO and QAS was kept at 100 mg. The contents of QAS were 20, 30, 40 and 50 wt%. A mixture of SLO and QAS was cast on the copper disk (the other side of the glass tubing) and this disk was allowed to stand for one day at room temperature. Subsequently, the copper disk coated with the mixture was put in an oven and kept at 70°C for three days to complete polymerization. The thickness of the membrane was estimated by a microscope to be about 20 µm.

Measurements

The potential measurement was carried out at room temperature with an ISFET/pH meter (BAS Co., Tokyo, Japan). The potential was monitored with respect to a double-junction-type Ag/AgCl reference electrode with 3 M KCl as an internal solution and 1 M CH₃CO₂Li as an external solution. The applied voltage (Vₒ) and the current (Iₒ) between a source and a drain were 5 V and 400 µA, respectively.

The test solution was stirred with a constant rotation speed. The concentrations of the test solutions were changed by injection of higher concentration solutions. The activity coefficient of anions (γ) was calculated according to the Davies equation:17 log γ = −0.511(1/Vₒ)(1 + 0.33α(Vₒ/2)) − 0.10I, where I = ionic strength, α = ion size parameter. The selectivity for NO₃⁻ was evaluated according to the IUPAC recommendations,18 which employ the fixed interference method (FIM). The background anion concentrations were 1.0 × 10⁻¹ M for SO₄²⁻, Cl⁻, Br⁻, H₂PO₄⁻, CH₃CO₂⁻ and C₆H₅CO₂⁻ and 1.0 × 10⁻¹ M for ClO₄⁻. The ion concentrations were checked by an ion chromatograph (Model IC7000, Yokogawa Electric Co., Tokyo, Japan) using an anion-exchange column packed with 5-µm poly(vinyl alcohol) substrate (ICS-A23, 4.6 × 75 mm, Yokogawa Electric Co.). Each sample size was 50 µl. The column was eluted with 3.0 mM Na₂CO₃ aqueous solution at a flow-rate of 1.0 ml/min. The column temperature was kept at 40.0°C throughout the experiments.

Results and Discussion

Properties of the membranes

To obtain the more durable and sensitive membrane, we have first evaluated the conditions to prepare the membranes based on SLP and QAS. The contents of QAS added into the membrane varied from 20 to 50 wt%. When QAS contents were 20, 30 and 40 wt%, the resulting membranes were transparent and colorless, indicating that the membranes are homogenous. In relation to this, no cracks were observed on those membranes when viewed in the microscope. However, when QAS contents were 50 wt%, the membrane took on an opaque appearance, possibly indicating the occurrence of an undesirable phase separation.

ISFET response

As stated above, the membranes based on SLP and QAS were expected to be available for an anion sensing membrane for an ISFET. Based on this expectation, the selectivity screening for NO₃⁻, Cl⁻ and SO₄²⁻ was carried out. For this purpose, the membrane containing 40 wt% of QAS was employed.

Figure 3 shows the potential response of the ISFET with SLP membrane for the following ions: NO₃⁻, Cl⁻ and SO₄²⁻.
shown, for NO$_3^-$ the ISFET exhibited a linear response with slope of $-58.1 \text{ mV decade}^{-1}$, almost corresponding to the theoretical Nernstian response, ranging in concentration of $3.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M. The observed range was comparable with or wider than that of the best NO$_3^-$-selective electrode so far. So we can conclude that this ISFET functions as an ion sensor favorable to NO$_3^-$ over a wide concentration range.

Subsequently, the relationship between the contents of QAS and sensitivity for NO$_3^-$-ISFETs based on SLP and QAS (QAS contents, $\square$: control (= 0); $\triangle$: 20 wt%; $\bullet$: 30 wt%; $\bigcirc$: 40 wt%; $\blacktriangle$: 50 wt%).

In the case of the membrane with the QAS content of 20 wt%, a Nernstian response was not obtained in the NO$_3^-$ concentrations lower than $1.0 \times 10^{-4}$ M. On the other hand, when QAS content was 50 wt%, the Nernstian response range became narrow, as compared to that observed with the membrane with QAS of 30 and 40 wt% contents. These results suggest that QAS contents suitable for the determination of NO$_3^-$ are between 30 and 40 wt%.

Furthermore, the ISFETs based on SLP and QAS (the contents of 30 or 40 wt%) have kept the good sensitivity (slopes of $-60.6 \text{ mV decade}^{-1}$ ranging in concentration of $3.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M) for more than half a year after the fabrication.

**Effect of pH on potential response**

Figure 5 shows the pH dependence of the potential response of the ISFET based on SLP and QAS (content 40 wt%) at various pHs in the presence of $1.0 \times 10^{-3}$ M of NO$_3^-$ . All tested solutions were prepared with 0.1 M H$_3$PO$_4$–NaOH buffer solutions. As shown in Fig. 5, it was confirmed that the effect of pH on the potential response was negligibly small at pHs between 2 and 9. This feature is also favorable for the practical use.

**Response time**

The times required to reach 90% total response ($t_{90}$) of ISFETs based on SLP and QAS (QAS contents; 20, 30, 40 and 50 wt%) are shown in Fig. 6. At contents of 30 and 40 wt%, it was found that the $t_{90}$ value was within 5 s, when the NO$_3^-$ concentrations were changed from $1.0 \times 10^{-3}$ to $3.0 \times 10^{-1}$ M. The $t_{90}$ value observed may be regard to be short enough for practical use. By contrast, the $t_{90}$ values observed in the ISFET with 20 and 50 wt% of QAS were longer than 10 s. These results also suggest that the optimal QAS contents are between 30 and 40 wt%.

It is noticeable that SLP membranes with QAS of 30 and 40 wt% contents exhibit the optimal conditions for both sensitivity (Fig. 4) and the $t_{90}$ values. It is also supposed that the homogenous membranes can be fabricated depending on the QAS contents, as stated above, taking into consideration that the fabrication of the homogenous membrane is essential for a practical and efficient ion sensor. SLP with an ability to give the homogenous thin film may be useful and feasible to fabricate ion sensing membranes. When QAS content was 20 wt%, the number of the ion exchange sites may be insufficient for the sensitive detection of NO$_3^-$ . In the case of higher contents, such as 50 wt%, it was observed that QAS in the membrane partly deposited on the membrane surface. Such
deposited QAS may interfere with sensing of NO$_3^-$.

**Ion selectivity**

Figure 7 shows the selectivity coefficients for NO$_3^-$ against various interfering ions, which are usually used to evaluate the selectivity for ion sensors. The values were evaluated using the ISFET, of which QAS contents were 30 and 40 wt%. In the case of the ISFET with the QAS content of 30 wt%, the ion selectivity coefficients with respect to SO$_4^{2-}$ ($K_{\text{pot}(\text{NO}_3^-\text{,SO}_4^{2-})}$) and H$_2$PO$_4^-$ ($K_{\text{pot}(\text{NO}_3^-\text{,H}_2\text{PO}_4^-)}$) were determined to be $2.7 \times 10^{-5}$ and $2.4 \times 10^{-5}$. By contrast, the selectivity for NO$_3^-$ against ClO$_4^-$, Br$^-$ and C$_6$H$_5$COO$^-$ seemed to be insufficient ($K_{\text{pot}(\text{NO}_3^-\text{,ClO}_4^-)} \approx 3.2 \times 10^{-6}$, $K_{\text{pot}(\text{NO}_3^-\text{,Br}^-)} \approx 7.9 \times 10^{-2}$ and $K_{\text{pot}(\text{NO}_3^-\text{,C}_6\text{H}_5\text{COO}^-)} \approx 5.8 \times 10^{-2}$) from the viewpoint of the selectivity coefficient that is normally expected to be smaller than $1.0 \times 10^{-2}$. The value of $K_{\text{pot}(\text{NO}_3^-\text{,Cl}^-)}$ was $1.0 \times 10^{-2}$, which would be sufficient enough for the practical use. In the case of the anion-exchanger-type ion sensors, it is well-known that the selectivity usually follows the Hofmeister series.$^{21}$ The selectivity determined in this study was also found to follow the Hofmeister series.

To improve the selectivity, it might be advisable to employ different kinds of ionophores. As stated above, since SLO is soluble in various organic solvents, it would be feasible to incorporate any kind of ionophore into the SLP matrix. Based on this property, various kinds of ionophores would be able to be used for the fabrication of an ion sensing matrix on the MOSFET in order to improve the selectivity.

**Application to NO$_3^-$ determination**

As stated above, from the viewpoint of the practical application to natural waters, it seems that the newly developed ISFET possesses sufficient performance. Thus, the ISFET based on SLP with QAS of 30 wt% content was applied to determination of NO$_3^-$ in natural water.

On the basis of the potentiometric ISFET method, the NO$_3^-$ concentration in rainwater was determined to be $2.0 \times 10^{-5}$ M on the average by ten times repetitive measurements. The coefficient of variation was 1.8%. The NO$_3^-$ concentration in the same water determined by means of ion chromatography was $2.1 \times 10^{-5}$ M. Thus it was demonstrated that the value obtained by the potentiometric method using newly fabricated ISFET was in good agreement with that based on the ion chromatography.

**Conclusion**

In this study, we have newly developed SLP film as a matrix of ion sensing membranes. As our first application of such film to the ion sensor, we fabricated an ISFET based on SLP and QAS and evaluated its capability in detail. As a result of a series of evaluations, the ISFET based on SLP and QAS proved to successfully function as an NO$_3^-$ sensor. Based on the confirmed readiness for preparation of ion sensing membrane and its durability, we conclude that SLP is available as a practical matrix material for ion sensors.

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**References**