Neutral-Carrier-Type Ion-Sensing Membranes Based on Sol-Gel-Derived Glass

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Typical neutral carriers, valinomycin and a bis(12-crown-4) derivative have been encapsulated in sol-gel-derived glasses to afford a novel type of ion-sensing membranes based on neutral carriers for ion-sensitive field-effect transistors (ISFETs). The neutral-carrier-based sol-gel-derived glass membranes, when incorporated in the ion sensors, showed high sensitivity, high selectivities, and fast potential response.

A most popular membrane material for neutral-carrier-type ion sensors is plasticized poly(vinyl chloride) (PVC). However, since special plasticizers are generally required for the PVC-based ion-sensing membranes, exudation of the membrane plasticizers often causes sensor deterioration and contamination of measuring samples. Also, plasticized PVC membranes are not very suitable for ion-sensitive field-effect transistors (ISFETs) and solid-state ion-selective electrodes, since they are easy to peel off from the surface of ISFET gates and metal electrodes due to their poor adhesiveness to inorganic materials. On the other hand, sol-gel-derived glasses are gaining increasing interest as functional glasses, into which various organic materials can be incorporated at relatively low temperature.[1] We have been interested in sol-gel-derived glasses as a membrane material for neutral-carrier-type ion-sensing membranes due to their low toxicity, high processibility, and high adhesiveness to inorganic materials. Here we report the applications of sol-gel-derived glass ion-sensing membranes containing valinomycin and bis(12-crown-4-methyl) α-dodecyl-α'-methylmalonate [bis(12-crown-4)] to Na^+- and K^+-ISFETs.

Neutral-carrier-containing sol-gel-derived glass membranes were fabricated on ISFET gate surface with an initial tetraethoxysilane (TEOS)/diethoxydimethylsilane(DEDMS) ratio of 1/3.[2] The resulted membranes were quite hard to remove from the gate surface. Potential measurements were carried out at 25 °C, by using an ISFET meter. Figure 1 shows typical potential response to metal ion activity changes for the K^+- and Na^+-ISFETs based on sol-gel-derived glass membranes of valinomycin and bis(12-crown-4), respectively. The K^+-and Na^+-ISFETs show Nernstian response to K^+- and Na^+-activity changes, respectively, in their wide activity ranges. The membrane systems fabricated with higher composition ratios of TEOS and DEDMS gave the poorer sensitivity and/or the narrower activity ranges for the Nernstian or sub-Nernstian response, probably due to the high-degree crosslinking of the resulting glass membranes. The potential response was quite fast for both K^+ and Na^+ sensors, response times (t_{90}) being within 3 s. The selectivities for the K^+ and Na^+ sensors based on the neutral-carrier-type membranes are summarized in Figure 2. The selectivity coefficient for K^+ with respect to Na^+ in the valinomycin-based K^+ sensors is 2 X 10^{-4} and that for Na^+ with respect to K^+ in the bis(crown ether)-based Na^+ sensor is 3 X 10^{-3}. The selectivities are comparable to those for ISFETs based on their corresponding plasticized PVC membranes.[3,4] The high performance for the ISFETs based on neutral-carrier-type sol-gel-derived glass membranes has lasted so far for at least a month.

Thus, neutral-carrier-containing glass membranes fabricated by a sol-gel method are applicable to K^+- and Na^+-ISFETs, affording high sensitivity, high selectivities, and fast sensor response. A study was under way to test the ion sensors for their practical applicability, especially in clinical analyses.

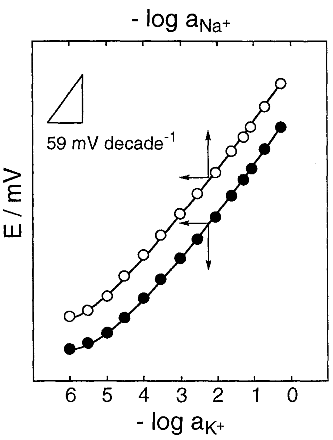

Figure 1. Potential response of K^+- and Na^+-ISFETs based on sol-gel-derived glass membrane of valinomycin(●) and bis(12-crown4)(○) to K^+ and Na^+ activity changes.

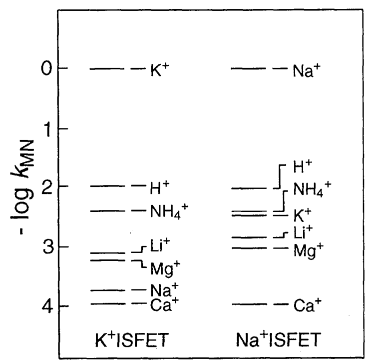

Figure 2. Selectivity coefficients of K^+- and Na^+-ISFETs based on neutral-carrier-type sol-gel-derived glass membrane.

References and Notes

1 Chemical Processing of Advanced Materials, ed by L. L. Hench and J. K. West, Wiley, New York (1992).
2 TEOS(12.5 μl, 5 X 10^{-5} mol), DEDMS(35.5 μl, 1.5 X 10^{-4} mol), ethanol(38.8 μl), and 0.1 M(1M=1 mol dm^{-3}) HCl aqueous solution (12.0 μl) were mixed and the mixture was then allowed to stand for 36 h to give a viscous sol-gel solution. An aliquot (1 μl) of the sol-gel solution was placed on the gate surface of a commercially available pH-ISFET, which was then heated 50 °C for 2 days.
3 L. A. R. Pioda, V. Stankova, and W. Simon, *Anal. Lett.*, **2**, 665(1969).
4 H. Tamura, K. Kimura, and T. Shono, *Anal. Chem.*, **54**, 1224 (1982).