Chemical modification of sol-gel-derived glass by a neutral carrier for ion sensors

Keiichi Kimura,* Takenobu Sunagawa and Masaaki Yokoyama

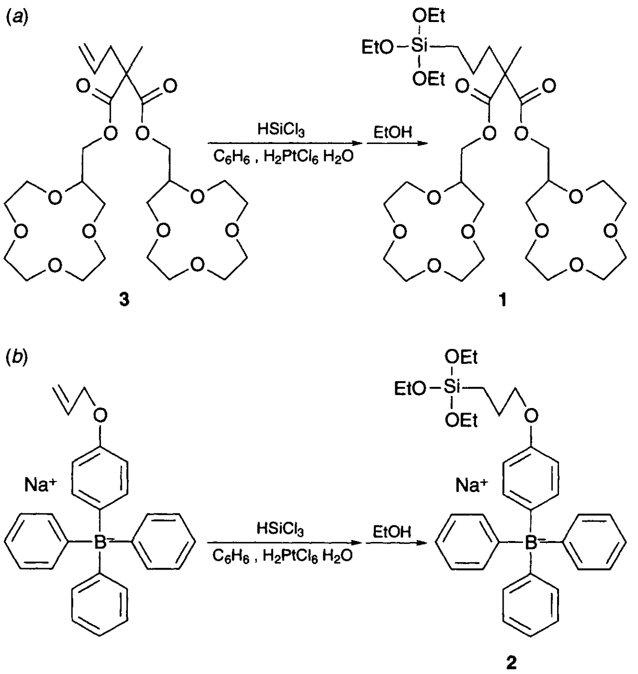
Chemical Process Engineering, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

An alkoxysilyl bis(crown ether) derivative is incorporated as a neutral carrier into sol-gel-glass-based ion-sensing membranes by chemical bonding; ion sensors based on neutral carriers exhibit high sensitivity, high ion selectivities and fast potential response in spite of the chemical immobilization of the neutral carrier molecules on the sol-gel glass.

Neutral carrier-based ion sensors are used widely due to their high ion selectivities, especially on clinical ion assay. Most neutral carrier-type ion-sensing membranes are made by dispersing neutral carriers in plasticized poly(vinyl chloride) (PVC). The PVC-based ion-sensing membranes still possess some toxicity and poor biocompatibility mainly due to the extrusion of the neutral carriers and plasticizers from the membranes. Immobilization of neutral carriers on membranes by chemical bonding is one of the best ways to prevent the extrusion of neutral carriers and thereby improve the toxicity and durability of the neutral carrier-based ion-sensing membranes.[1–4]

Sol-gel-derived glass is a candidate for use as biologically inactive supports of ion-sensing membranes. Sol-gel glass membranes simply encapsulating neutral carriers have proved to be excellent ion-sensing membranes for neutral carrier-type ion sensors, especially for ion-sensitive field-effect transistors (ISFETs).[5] However, neutral carrier-dispersed sol-gel glass membranes may still be able to extrude neutral carriers. This prompted us to immobilize neutral carriers on sol-gel glass by chemical bonding, aiming at low toxicity, high biocompatibility and high durability of the ion sensors. In sol-gel preparation, silanol groups which were formed by acid-catalysed hydrolysis of alkoxysilane are condensed with another alkoxysilane to yield highly crosslinked polysiloxanes.[6] Neutral carriers, when incorporated with alkoxysilyl groups, are expected to be chemically bound to the sol-gel-derived glass.

Here we describe the first successful formation of sol-gel-derived glass membranes chemically modified by a neutral carrier for high-performance neutral carrier-type ion sensors. The sol-gel glass is prepared using alkoxysilyl-substituted bis(12-crown-4) derivatives **1** together with the tetraphenylborate salt **2** for use in Na$^+$-ISFETs. Hydrosilylation of its corresponding 2-allyl derivative **3** with trichlorohydrosilane in the presence of hydrogen hexachloroplatinate, followed by treatment with ethanol, afforded bis(2,5,8,11-tetraoxacyclododecylmethyl) 2-[3-(triethoxysilyl)propyl]-2-methylmalonate **1** (Scheme 1).† The allyl derivative **3** was prepared by a previously reported method.[7] Similarly, sodium triphenyl{4-[3-(triethoxysilyl)propyl]phenyl}borate, which is a precursor for the chemical immobilization of the ion sites, was obtained by treating equimolar amounts of sodium triphenyl(4-allyloxyphenyl)borate with trichlorohydrosilane followed by ethanol. By using solutions of tetraethoxysilane (TEOS), diethoxydimethylsilane (DEDMS) **1** and **2**,‡ sol-gel glass membranes containing the alkoxysilyl bis(12-crown-4) derivative **1** and the sodium salt **2** were formed on the gate surface of a commercially available pH-ISFET which had previously been coated with polythiophene as polymer electrolyte.[8] In separate experiments, IR spectroscopy of the neutral carrier-type sol-gel-derived glass confirmed that the neutral carrier and sodium tetraphenylborate used for the membrane formation were immobilized in the sol-gel–glass membrane by chemical bonding (Fig. 1). Typical potential responses of the Na$^+$-ISFET based on sol-gel-derived glass membranes chemically modified by the neutral carrier and the ionic site to Na$^+$ activity changes are shown in Fig. 2. The ion sensor exhibited high Na$^+$ sensitivity, that is, Nernstian response to Na$^+$ activity changes (59 mV decade^{-1}, at 25 °C) over a wide concentration range (1×10^{-5} to 1 mol dm^{-3}).



Scheme 1 Syntheses of (*a*) the neutral carrier and (*b*) the ionic site used for the chemical immobilization on the sol-gel glass membrane

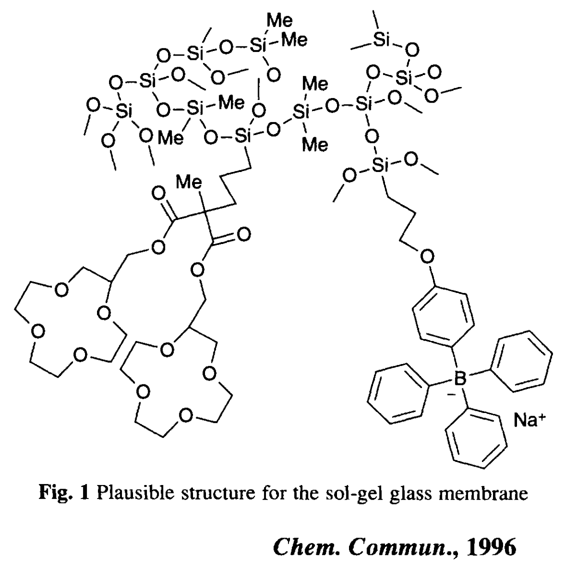


Fig. 1 Plausible structure for the sol-gel glass membrane

Since high-mobility neutral carriers are generally required for the efficient cation-exchange and rapid establishment of membrane potentials in the neutral carrier-type ion-sensing membranes, their chemical immobilization on the membrane support often causes a large decrease in the sensitivity, namely, a non-Nernstian response, without addition of special plasticizer.[1–3] This is not the case with the present ion-sensing membranes. It should also be noted that the response time for the ion sensor is quite short irrespective of the chemical bonding of the neutral carrier on the sol-gel glass, *i.e.* t_{90} is 3 s on changing the sample Na^+ activity from 1×10^{-3} to 3×10^{-3} mol dm^{-3}. The selectivity coefficient for Na^+ with respect to K^+ is 6×10^{-3} for the Na^+-ISFET based on neutral carrier-immobilized sol-gel–glass membranes, the Na^+ selectivity being similar to those for previously reported Na^+ sensors based on bis(12-crown-4) derivatives. In a preliminary comparison of the sensor durability between the Na^+-ISFETs based on the sol-gel-derived glass membranes of the present chemically-immobilized bis(12-crown-4) and previous corresponding neutral carrier-dispersed systems, the high performance of the sensor properties such as sensitivity and selectivity lasted for at least several months in the present system, whereas significant deterioration occurred after only one month in the latter system due to the easy extrusion of the dispersed neutral carrier and ion site.

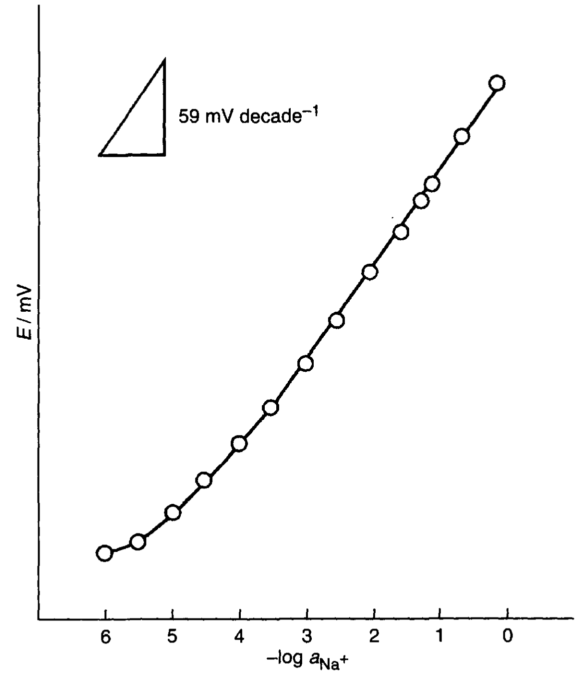


Fig. 2 Typical potential response to Na^+ activity changes of Na^+-ISFETs based on sol-gel-glass membrane chemically modified by the bis(12-crown-4) derivative **1**

Thus, the sol-gel-derived glass membranes chemically modified by the neutral carrier are promising neutral carrier-type ion-sensing membranes for durable and less toxic neutral carrier-type ion sensors.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. We also thank the Suzuken Memorial Foundation and the Salt Science Research Foundation for financial support.

Footnotes

† ^1H NMR ($CDCl_3$) δ 0.1 (2 H, t, $SiCH_2$), 1.2 (9 H, t, $SiOCH_3C\mathit{H}_3$), 1.4 (3 H, s, $CH_2CC\mathit{H}_3$), 1.6–1.9 [4 H, m, $SiCH_2(CH_2)_2C$], 3.4–4.1 (40 H, m, $SiOC\mathit{H}_2CH_3$, OCH_2 and OCH). This compound was subjected to the following sol-gel reaction without purification due to the easy polymerization.

‡ TEOS (22 μl, 1.2×10^{-4} mol), DEDMS (62 μl, 3.5×10^{-4} mol), ethanol (69 μl) and 0.1 mol dm^{-3} HCl (21 μl), **1** (1 mg) and **2** (0.2 mg) were mixed and the mixture allowed to stand for 36 h to afford a viscous solution. An aliquot (1 μl) of the solution was placed on the gate surface of a commercially available pH-ISFET tip. Heating at 60 °C for 2 d afforded a sol-gel-derived glass membrane of about 0.2 mm thickness.

References

1 J. Tietje-Girault, I. MacInnes, M. Schroder, G. Tennant and H. H. Girault, *Electrochim. Acta*, 1990, **35**, 777.
2 S. Daunert and L. G. Bachas, *Anal. Chem.*, 1990, **62**, 1428.
3 G. G. Cross, T. M. Fyles and V. V. Suresh, *Talanta*, 1994, **41**, 1589.
4 J. A. J. Brunink, R. J. W. Lugtenberg, Z. Brzozka, J. F. J. Engbersen and D. N. Reinhoudt, *J. Electroanal. Chem.*, 1994, **378**, 185.
5 K. Kimura, T. Sunagawa and M. Yokoyama, *Chem. Lett.*, 1995, 967.
6 L. L. Hench and J. K. West, *Chemical Processing of Advanced Materials*, Wiley, New York, 1992.
7 H. Tamura, K. Kimura and T. Shono, *Anal. Chem.*, 1982, **54**, 1224.
8 J. Bobacka, M. McCarrick, A. Lewenstam and A. Ivaska, *Analyst (London)*, 1994, **119**, 1985.

Received, 27th November 1995; Com. 5/07722B