Properties of Alkali-free Magnesium Phosphate Glass Membranes Containing Silver Oxide and Their Application to the Ammonia Selective Electrode

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Synopsis. The properties of magnesium phosphate glass and the potential response of its membrane to ammonia were studied. The most suitable glass composition for the ammonia selective electrode is $5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$. The potential-concentration curve of the electrode exhibits a slope of about 48 mV/decade for the ammonia-concentration range of (10^{-2}—10^{-6}) mol/dm^3.

Various types of alkali silicate glasses containing Al_2O_3 or B_2O_3 have been investigated as materials of the ion selective electrode, and they were used for the measurement of alkali metal ions, Ag^+, Cu^+,[1,2] and the ammonium ion.[3] The ammonia selective electrode consists of a hydrophobic gas-permeable membrane and pH electrode.[4,5] Truesdell and his co-workers[6] found that the glass containing P_2O_5 and Fe_2O_3 as the major constituents can be applied to the ion-selective electrode for alkaline earth cations. According to Eisenman's suggestion,[7] the replacement of aluminium in the sodium-almino-silicate glass by phosphorus would be expected to lead to anion-exchange properties and a response to anionic substances. This paper will describe the composition of alkali-free magnesium phosphate glasses, the durability of glasses against water, and the application of the electrode membrane to ammonia.

Experimental

Preparation of Glass Membrane. Orthophosphoric acid (85%), silver carbonate, tetramagnesium tricarbonate dehydroxide, and aluminium hydroxide were used to prepare the alkali free magnesium phosphate glasses. Mixtures of the chemicals were placed in a quartz evaporating dish and evaporated to dryness. The cake was finely powdered, it was then melted at 1350 °C for 90 min in a platinum crucible, and the melt was poured into a circular hollow of a graphite plate. The final composition of the glass usually deviates from the initial composition because of the loss of phosphoric acid by vaporization during melting.[8] From the determination of P_2O_5 as $Mg_2P_2O_7$ or $AlPO_4$ by the gravimetric method, the volatillization loss of P_2O_5 was found to be about 5 weight % of the initial orthophosphoric acid content from 45 to 55 mol% P_2O_5 glass. Therefore, under all the experimental conditions, the orthophosphoric acid content in the initial materials were established to be about 5 weight % in excess of the calculated amount. To form the electrode, disks (11—12) mm in diameter and (0.4—0.6) mm thick were cut from the glass pellet.

Measurement of the Membrane Potentials. The cell scheme used for the investigation was as follows:

SCE | 0.1 mol/dm^3 $NaNO_3$ | Glass membrane | Sample soln containing 5×10^{-4} mol/dm^3 NaOH | Agar bridge | 0.1 mol/dm^3 $NaNO_3$ | SCE

(Ion-selective electrode)

The membrane potentials for ammonia and other anions or compounds were measured in a solution containing 5×10^{-4} mol/dm^3 sodium hydroxide at pH about 10.4 at 20 °C.

Table 1. Durability of glasses against water

Glass composition	Solubility in water (mg mm^{-2})	Ratio
$5Ag_2O$–$50P_2O_5$–$45MgO$	3.87×10^{-3}	1.00
$5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$	1.45×10^{-3}	0.37
$25Ag_2O$–$50P_2O_5$–$20MgO$–$5Al_2O_3$	3.11×10^{-3}	0.80
$5Ag_2O$–$50P_2O_5$–$35MgO$–$10Al_2O_3$	1.08×10^{-3}	0.28

From the dissociation constant[9] of the ammonium ion, $K=a_{H^+}\cdot a_{NH_3}/a_{NH_4^+}=10^{-9.25}$, the concentration of the ammonium ion becomes very small at pH values above 10.0. Therefore, the temperature being constant, we can write the glass membrane potential, E, as the following equation:

$$E = \text{Const} - K\log a_{NH_3}, \quad (1)$$

where a_{NH_3} denotes the activity of ammonia and K is the slope of the calibration graph.

The activities of various anions were derived from the concentration by means of the activity coefficients tabulated by kielland.[10]

Durability of Glass against Water. Glass film (about 0.3 g) (surface area, 3×10^2 mm^2) was weighted and placed in a 100-ml portion of distilled water, and then allowed to stand for 60 d at about 30 °C. The durability was measured by the weight loss per unit of area of the glass membrane.

Results and Discussion

Glass-forming Region and Durability of Glass against Water. A glass-forming region in the MgO–P_2O_5 system was found at the composition with a MgO contents of less than 55 mol %. This was in agreement with that found in the previous studies.[11] The same result was observed with the Ag_2O–P_2O_5 system.

Table 1 shows the durability of various glasses against water. With an increase in the amount of Al_2O_3 in the glass composition, the solubility of glass decreased. It can be decided that the durability of glasses is produced by the formation of the –P–O–Al– linkage.[12] However, the melting point for the glass formation becomes very high when the Al_2O_3 content increases to more than about 15 mol %.

Potential Response of the Magnesium Phosphate Glass Membrane Electrode. Figure 1 shows the potential response of the $5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$ glass membrane for various anions or compounds in solutions containing 5×10^{-4} mol/dm^3 sodium hydroxide.

In the case of the alkali silicate glass electrode, cation exchange is the basis for the Nicolsky-Eisenman interpretation.[7] As is shown in Fig. 1, on the contrary, it became clear that this glass shows the properties of the anionic response.

The response for ammonia was linear over the range of (10^{-2}—10^{-5}) mol/dm^3, and had a slope of a 48 mV/decade change in the ammonia concentration at 20

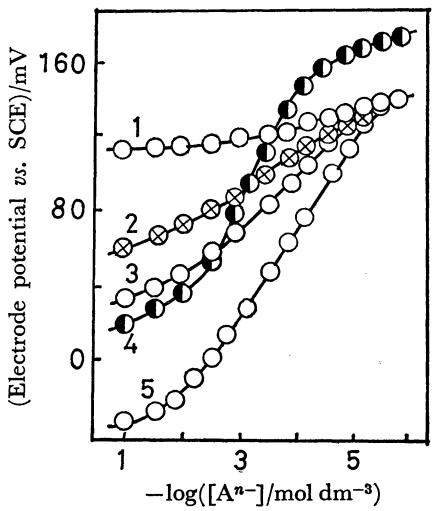

Fig. 1. Potential response of the $5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$ gass electrode.
Here, 5×10^{-4} mol/dm^3 sodium hydroxide was used as the electrolyte solution except for the measurement of hydroxide ion.
1: SO_4^{2-}, 2: Cl^-, 3: NO_3^-, 4: OH^-, 5: NH_3.

°C. Below 10^{-5} mol/dm^3 and above 10^{-2} mol/dm^3, however, the a_{NH_3}-potential graph deviates from linearity.

When the ammonia concentration increases from 10^{-6} to 10^{-2} mol/dm^3, the electrode potential attains a constant value within a minute, but the concentration of ammonia decreases in the same concentration range, the dynamic response time[13] becoming 10 to 20 min.

Response Behavior of Glass Membranes of Various Compositions. The glass electrode containing only MgO and P_2O_5 shows a small response to ammonia. This suggests that no carrier ions which produce the potential response to ammonia, such as the silver ion, are present in the glass composition.

Both the selectivity coefficient of ammonia for other anions and the durability against water decrease with an increase in the Ag_2O content in the glass composition. For the variation in Ag_2O content, the selectivity coefficient of ClO_4^- is found to be $10^{-1.5}$ in Ag_2O content of 15 mol% and $10^{-1.0}$ at 25 mol%, while that of NO_3^- is found to be $10^{-1.5}$ at 15 mol% and $10^{-1.2}$ at 25 mol% respectively.

From these results, it can be concluded that the glass composition of $5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$ is the most suitable for an ammonia selective electrode.

Selectivity Coefficient of Ammonia for the Other Anions or Compounds. The method for the determination of the selectivity coefficients, $K_{NH_3\cdot A}$, is based on the electrode-potential measurements in a mixed solution containing ammonia and the interfering ion, A.[14] The electrode potential of the mixture is expressed by the following equation:

$$E' = \text{Const} - K\log(a_{NH_3}+K_{NH_3\cdot A}\cdot a_A), \quad (2)$$

where $K_{NH_3\cdot A}$ is the selectivity coefficient for A over ammonia and a_A is the activity of an interfering anion or compound A. In the case of $E=E'$, by combining Eqs. 1 and 2 $K_{NH_3\cdot A}$ is obtained by means of the following equation:

$$K_{NH_3\cdot A} = a_{NH_3}/a_A. \quad (3)$$

Therefore, the values of $K_{NH_3\cdot A}$ are obtained by measuring the electrode potential in solutions containing a fixed quantity (10^{-2} mol/dm^3) of the interfering anion or compound and a varied concentration of ammonia.

The selectivity coefficient and the potential slope for each anion or compound obtained using the $5Ag_2O$–$50P_2O_5$–$40MgO$–$5Al_2O_3$ glass electrode are listed in Table 2.

Table 2. Selectivity coefficient for anions or compounds

Anions or compounds	Slope (mV/pC)	Selectivity coefficient
NH_3	48	1
ClO_4^-	37	1.6×10^{-2}
NO_3^-	38	2.1×10^{-2}
OH^-	45	7.4×10^{-2}
Cl^-	32	8.4×10^{-3}
SCN^-	44	8.4×10^{-2}
$CH_3CO_2^-$	30	6.5×10^{-3}
SO_4^{2-}	12	1.4×10^{-3}
$S_2O_3^{2-}$	38	2.1×10^{-2}
Pyridine	33	9.8×10^{-3}
Ethylenediamine	40	5.8×10^{-2}
Triethanolamine	39	5.2×10^{-2}
Urea	14	2.5×10^{-3}

In comparing the pH glass electrode coated by a hydrohobic gas-permeable membrane,[4] the preparation and the operation of the electrode is more simplified, and the effect of interfering species, such as pyridine and urea, is less.

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