Development of Hydrogen Ion Selective Electrode with Lithium Phosphate Glasses for the Use in Solutions Containing Hydrofluoric Acid

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In order to determine reproducible and stable potential response conditions of the hydrogen ion in hydrofluoric acid solutions, lithium phosphate glass membranes of various constituents were developed. The glass membranes contained various metal oxides: Ag_2O, Li_2O, P_2O_5, MgO, BeO, WO_2, and Al_2O_3. The response characteristics of the glass electrode depend strongly on the glass compositions. For the examination of the selectivity coefficient and the electrode function of hydrogen ion activities, the glass composition of 10 Ag_2O : 20 Li_2O : 50 P_2O_5 : 10 MgO : 10 WO_2 is the most suitable one. The potential response is linear over the hydrogen ion activities of ($10^{0.3}$—10^{-4}) mol/dm^3, and has a slope of 44.5 mV/decade change in the hydrogen ion activity at 20 °C. The dynamic response time was within a minute in the range 10^{-1} to 10^{-4} mol/dm^3. The intereference of the various cations on the activity of about 0.1 mol/dm^3 can be ignored during the determination of the hydrogen ion activities at pH below 3. Physical and chemical properties, such as glass transition temperature, softening temperature, thermal expansion, membrane resistance, and chemical durability were measured and compared with those of other glasses.

It is well known that various types of the ion selective glass electrode are available; almost all of these are made of alkali silicates.[1,2] However, these electrodes show a serious disadvantageous point: They are earsily corroded chemically by hydrofluoric acid. Some anomalous behavior of the common glass electrode in solutions containing hydrofluoric acid has been discussed.[3] In the hydrofluoric acid solution, the hydrogen ion activities have been measured with a metallic antimony electrode or the cation exchange membrane electrode.[4]

Phosphate glasses containing iron oxide[5] have been investigated as materials of the cation selective membrane electrode for alkaline earth cations. Moreover, it is known from the literature[6] that the glasses made from aluminium and lithium metaphosphate were studied and their potential responses to hydrogen ions were found. However, the chemical durability and the dependence of the potential response in the hydrofluoric acid solutions have not been published in detail.

We have already studied the properties of alkali-free magnesium phosphate glasses and their application to the ammonia selective electrode.[7] In the present work, we studied the physical and chemical properties of the lithium phosphate glasses containing various metal oxides, such as Ag_2O, MgO, BeO, WO_2, and Al_2O_3, and the application of the electrode membrane to determine the hydrogen ion activities in the hydrofluoric acid solution.

Experimental

Preparation of the Glass Membrane. Orthophosphoric acid (85%), silver carbonate, lithium carbonate, tetramagnesium tricarbonate dehydroxide, tungsten dioxide, aluminium hydroxide, and beryllium oxide were used to prepare the glasses. All the chemical except silver carbonate were of a reagent grade. The preparation procedures of the phosphate glasses and the glass membrans have been described previously.[7] The chemical compositions of some of the tested glasses are shown in Table 1.

Glass Transition Temperature, Softening Temperature, and Thermal Expansion of Lithium Phosphate Glasses. Glass transition temperature (T_g, °C) softening temperature (T_s, °C) and thermal expansion (α, cm °C^{-1}) were measured with a Shimadzu TM-30 type dilatometer. All dilatometer measurements were carried out at 3 °C/min of the sample heating rate.

Chemical Durability and Membrane Resistance of the Glasses. The chemical durability of the tested glasses was measured by the following method. A glass film (surface area, about 3×10^2 mm^2) was weighted and placed in a 100 ml portion of 0.5 mol/dm^3 hydrofluoric acid and 0.6 mol/dm^3 sulfuric acid mixtures, allowed to stand for 60 d at about 30 °C, and the weight loss per unit area of the glass membrane was measured.

The resistance of the lithium phosphate glass membrane was measured by a Toa Denpa SM-9E type megaohm meter, because the resistance of the tested glass membrane is relatively low compared to that of the alkali silicate glasses.

Measurements of the Membrane Potentials. The glass elec-

TABLE 1. COMPOSITION OF THE GLASSES

Glass No.	Ag_2O	Li_2O	P_2O_5	MgO	WO_2	BeO	Al_2O_3
1	10	30	50	10	—	—	—
2	10	30	50	—	10	—	—
3	5	25	50	10	10	—	—
4	10	20	50	10	10	—	—
5	20	10	50	10	10	—	—
6	10	20	50	—	—	20	—
7	10	25	50	10	—	—	5

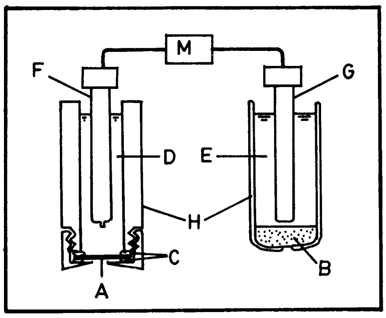

Fig. 1. Construction of the electrode.
A: Glass membrane, B: agar bridge, C: O-ring (Silicone rubber), D: , E: internal filling solution (0.1 mol/dm^3 $NaNO_3$), F: internal reference electrode (SCE), G: reference electrode (Ag/AgCl), H: plastic tube, M: ion meter.

trode was prepared by tightening the glass disk with a Silicone rubber O-ring and a plastic holder at the end of the cyclindrical plastic tube, which was filled with 0.1 mol/dm³ $NaNO_3$ solution. The Ag/AgCl reference electrode was a double junction type, DKK 4400, with a salt bridge of 0.1 mol/dm³ $NaNO_3$ internal solution; the acid error of the reference electrode is removed.

Figure 1 shows the completed assembly of the electrode system for the determination of hydrogen ion activity. The responses of each glass membrane were observed by measuring the potential *vs.* a Ag/AgCl reference electrode with a DKK IOC-10 ion-meter connected with a Sekonic model SS-250F recorder. In order to obtain a reproducible electrode potential, the electrodes were polished with waterproof silicon carbide paper No. 1000, and then preconditioned before use in distilled water for 1 d. The hydrogen ion activities for the proper quantities of nitric acid or nitric acid in the solution containing hydrofluoric acid and sodium nitrate mixtures were measured with a commercially available pH electrode, and then the electrode potentials which has been measured by the glass membranes tested in the same composition of the solutions were converted into the hydrogen ion activities. The activities of various cations except for hydrogen ion were calculated from the concentration by means of the activity coefficients tabulated by Kielland.[8]

Results and Discussion

Physical and Chemical Properties of Glasses. Some physical and chemical properties, such as glass transition temperature, softening temperature, thermal expansion, membrane resistance, and chemical durability of some lithium phosphate glasses in hydrofluoric acid solution are summarized in Table 2.

When we compared the values of T_g and T_s of those of the tested glasses and the usual silicate glasses, the tested glasses showed much lower values. However, all the values of the thermal expansion among these glasses were very similar.

When some Ag_2O is included in the glass constituents, the mixtures are easily glass forming, and show very low resistance.[9] However, the presence of Al_2O_3 has a negative effect on the chemical durability and the glass completely dissolved after standing for 60 d. The tested glasses which contain MgO or WO_2 were found to be more soluble in the hydrofluoric acid solution, but the glasses containing both MgO and WO_2 gave better results as for the chemical durability. Contrary to this result, however, the glasses containing both MgO and WO_2 increased in membrane resistance.

Potential Response of the Lithium Phosphate Glass Membranes. Figure 2 shows the potential response of the $10Ag_2O : 50P_2O_5 : 20Li_2O : 10MgO : 10WO_2$ glass membrane (Glass No. 4) to hydrogen ion activities in the solution containing 0.01 mol/dm³ sodium nitrate and 0.05 mol/dm³ hydrofluoric acid.

The potential response for the two experimental conditions was observed on the same calibration curve. The response for the hydrogen ion activity was linear over the range of ($10^{0.3}$—10^{-4}) mol/dm³. The average slope was computed as 44.5 mV/decade change at 20 °C. Responses of the electrodes are reproducible, and electrode potentials are the same within 2 mV. The dynamic response time[10] for the change of the hydrogen ion activity was within a minute in the range 10^{-1} to 10^{-4} mol/dm³, but was a few minutes above 10^{-1} mol/dm³. Therefore, the steady state is defined as a potential stable to less than 1 mV drift in 2 min.

At the hydrogen ion activities below 10^{-6} mol/dm³, however, the slope of the electrode potential *vs.* hydrogen ion activities falls to almost zero, and the electrode ceases to be functional. The tested glass membranes responded to the hydrogen ion activities within a certain range, but the slope was smaller than the value predicted by the Nernst expression.

From the dissociation constant[11] of the hydrofluoric acid, $a_{H^+} \cdot a_{F^-} / a_{HF} = 10^{-3.2}$, the hydrofluoric acid mole-

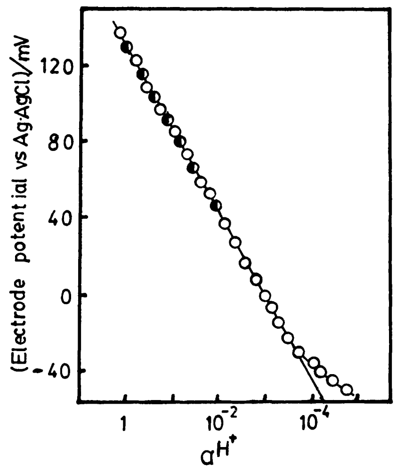

Fig. 2. Electrode response as a function of the hydrogen ion activities.
Electrode membrane: $10\,Ag_2O : 50\,P_2O_5 : 20\,Li_2O : 10\,MgO : 10\,WO_2$ glass.
○: Nitric acid, ◐: nitric acid in the solution containing 0.01 mol/dm³ $NaNO_3$ and 0.05 mol/dm³ HF.

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES OF THE GIASSES

Glass No.	Transition temperature T_g/°C	Softening temperature T_s/°C	Thermal expansion $\alpha \times 10^7$/cm °C^{-1}	Chemical durability mg mm^{-2}	Membrane resistance MΩ cm^{-1}
1	296	329	132.3	$1.0_8 \times 10^{-1}$	1.71
2	240	323	147.7	$1.5_0 \times 10^{-1}$	5.89
3	352	390	116.1	$2.3_8 \times 10^{-2}$	6.52
4	333	371	121.3	$1.9_9 \times 10^{-2}$	6.71
5	317	352	139.8	$2.1_8 \times 10^{-2}$	8.18
6	—	—	—	$6.2_8 \times 10^{-2}$	1.45
7	—	—	—	Dissolve	2.24

TABLE 3. ELECTRODE FUNCTION OF HYDROGEN ION ACTIVITIES AND SELECTIVITY COEFFICIENT OF VARIOUS CATIONS

Glass No.	Electrode function mV/pH	Selectivity coefficient $\times 10^2$				
		Li^+	Na^+	K^+	Ca^{2+}	Al^{3+}
1	42.5	1.86	2.58	2.55	1	1.51
2	29.4	—	—	—	—	—
3	36.8	6.74	7.90	2.82	2.51	3.16
4	44.5	3.73	2.51	1.32	1.58	0.79
5	38.6	33.7	50.1	23.3	15.8	7.94
6	31.4	17.7	15.8	8.61	6.32	1.58
7	21.3	—	—	—	—	—

cules exist at pH values below 3.0. Therefore, when the measurements of the pH value are performed with a commercially available pH electrode in the hydrofluoric acid solution, a reproducible electrode potential cannot be expected over long times, due to the dissolution of the electrode surface. However, the electrode potentials of the lithium phosphate glasses are more stable and reproducible than that of the alkali silicate glasses.

Response Behavior of Glass Membrane of Various Compositions. The response characteristics of lithium phosphate glass electrodes depend upon the glass composition. Therefore, the experiments of the electrode response were carried out with the glasses containing fixed quantities of P_2O_5 at 50 mol% and a varied quantities of the other metal oxide.

The glasses not containing Ag_2O show a small potential response to hydrogen ion activity and an unstable electrode potential in the hydrofluoric acid solution. Therefore, the presence of Ag_2O in the glass structure may contribute to the greater mobility of cations in the glass membrane and to the reproducibility of the electrode potential.[2] However, the presence of Al_2O_3 decreases the chemical durability in the hydrofluoric acid solution and the glass electrode is not responded to the hydrogen ion activities for the same behavior as in the case of silicate glasses.[12]

The electrode function of the hydrogen ion activities and the selectivity coefficients of the other cations for the lithium phosphate glass electrodes are shown in Table 3.

Selectivity Coefficient of Hydrogen Ion for the Other Cations. The interferences of various cations on the concentration of about 0.1 mol/dm^3 can be ignored for the measurement of the hydrogen ion activities at pH values below 3.

The selectivity coefficients of lithium phosphate glass electrodes with respect to a number of cations were determined by the mixed solution method.[13] Values of the selectivity coefficient are obtained by measuring the electrode potential in solutions containing fixed quantities of the interfering ion (0.1 mol/dm^3) and a varied activity of the hydrogen ion.

It is apparent that the selectivity coefficients for the interfering cations and the electrode function of hydrogen ion activities are better for glass electrode No. 4 than the others.

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