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Alkali-free Magnesium Phosphate Glasses as Nitrate-ion-selective Materials for Solid-state Electrochemical Sensors

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Ion-selective electrochemical sensors which respond to nitrate-ion activities have been developed. The sensor material consists of alkali-free magnesium phosphate glasses containing CuO, Al_2O_3, and SiO_2. The response characteristics have been observed strongly on the glass composition. Studies of the selectivity coefficient and the electrode function of nitrate-ion activities have shown that the most suitable glass composition is $10CuO:55P_2O_5:15MgO:10Al_2O_3:10SiO_2$. The potential response is linear over the nitrate-ion activities of $(10^{-1}$—$10^{-5})$ mol/dm^3, and it has a sub-Nernstian response of about 54 mV/decade change at 20 °C. The order of the selectivity is $NO_3^- > ClO_4^- > I^- > NO_2^- > Cl^- > SO_3^{2-} \gg SO_4^{2-}$. Therefore, its use to determine the nitrate-ion activities in a solution containing perchlorate ions is suggested. The physical and chemical properties, such as the glass transition temperature, the softening temperature, the thermal expansion, the membrane resistance, and the chemical durability, were measured and compared with those of other glasses.

Solid electrodes for the determination and monitoring of nitrate ion have not been commercially available. Liquid ion-exchanger electrodes have been made, and used for the determination of nitrate-ion activities in various sample solutions.[1,2] However, common anions such as iodide and perchlorate interfere seriously, and the loss of the liquid ion-exchanger in the liquid electrodes can be expected. Some investigations of selective nitrate-ion solid-type sensors have been made. One of the solid-type sensors was made of PVC film, which included the optimum proportion of the nitrate-selective liquid-ion-exchanger in the PVC matrix,[3] and another was made by the film of the nitron-nitrate precipitate in the araldite matrix.[4]

There have been relatively few studies of the ion-selective electrode behavior of phosphate glasses.[5,6] Phosphate glasses containing iron oxide[5] have been investigated as materials of the cation selective membrane electrode for alkaline-earth cations. On the other hand, it has been suggested that the replacement of aluminium in the sodium alumino silicate glass by phosphorus can be expected to lead to anion-exchanger properties.[7]

We have already investigated some phosphate glass membranes as materials of ammonia-selective electrodes[8] and that of the hydrogen-ion-selective electrode in the hydrofluoric acid solution.[9] However, it is an important fact that some anion-responsive glass electrodes have apparently not been reported on to date.

In this investigation, the physical and chemical properties of alkali-free magnesium phosphate glasses containing various metal oxides, such as CuO, Ag_2O, Al_2O_3, and SiO_2, were measured, and a systematic check of the response behavior of those glass electrode was made. After several modifications of the glass compositions, some promising results were obtained for the solid-state nitrate-ion-selective sensors.

Experimental

Preparation of the Glass Membrane. The materials used were the following reagents. Orthophosphoric acid (85%) and tetramagnesium tris(carbonate)dihydroxide were used in all the systems. Dicopper(II) carbonate dihydroxide, silver carbonate, aluminium hydroxide, and silicon dioxide were used in the composition of each glass. The sample were prepared by melting it in a platinum crucible at 1200 °C for an hour; after melting, the glasses were annealed at a temperature 20 °C higher than the respective glass transition temperature for 20 min and then cooled.

The preparation of the phosphate glasses and the glass membranes has been described previously.[8]

The chemical compositions of some of the tested glasses are listed in Table 1.

Measurements of Physical and Chemical Properties. The glass-transition temperature (T_g, °C), the softening temperature (T_s, °C), and the thermal expansion (α, cm °C^{-1}) were measured with a Shimadzu TM-30-type dilatometer. The chemical durability of glass against water and the membrane resistance were measured by the method previously described in the literature.[9] The physical and chemical properties of some of the magnesium phosphate glasses containing CuO, Ag_2O, Al_2O_3, and SiO_2 are summarized in Table 2.

Reagents and Solutions. All the reagents were of an analytical grade unless otherwise specified. Sodium, potassium, and ammonium nitrate were used as nitrate standard solutions. Chloride, iodide, perchlorate, sulfate, nitrite, and sulfite salts of sodium were used as the sources of interfering anions. The water was twice-distilled. The activities of various anions were calculated from the concentration by means of the activity coefficients tabulated by Kielland.[10]

Measurements of the Membrane Potentials. The sensor element is sealed in the end of a cylindrical plastic tube, with one surface of the disk exposed to the test solution and the other to the internal-reference solution (0.1 mol/dm^3 $NaNO_3$). A double-junction-type saturated calomel reference electrode makes contact with the internal-reference solution (0.1 mol/dm^3 $NaNO_3$). The responses of each sensor are investigated by measuring the potential *vs.* SCE with a DKK IOC-10 ion-meter connected with a Sekonic model SS-250F recorder.

The electrode potential is strongly affected by prior conditioning in regard to its electrical resistance and the response

TABLE 1. COMPOSITION OF THE GLASSES

Glass No.	CuO	Ag_2O	P_2O_5	MgO	Al_2O_3	SiO_2
1	10	—	55	35	—	—
2	10	—	55	25	10	—
3	—	—	55	25	10	10
4	5	—	55	20	10	10
5	10	—	55	15	10	10
6	20	—	55	5	10	10
7	5	—	47	28	10	10
8	—	5	55	20	10	10

time. Thus, each sensor disc was polished on both sides with silicon carbide paper and then preconditioned in twice-distilled water for one day before use.

The membrane potentials for nitrate-ion and other anions are measured in a solution containing a 10^{-4} mol/dm^3 sulfuric acid solution at 20 °C. The steady state of the membrane electrode is defined as a potential stable to a drift of less than 1 mV in 2 min in the stirred solution (600 min^{-1}). With stirring, the electrode potentials are read the same within 2 mV. As a result of determining the effect of the potential response on the membrane thickness, it can be said that the response rate and the reproducibility of the electrode potential are absolutely not affected within a thickness of 1 mm.

Results and Discussion

Physical and Chemical Properties of Glasses. As shown in Table 2, with the addition of the Al_2O_3 and SiO_2, the values of T_g and T_s of the tested glasses are increased. On the contrary, the values of the thermal expansion decrease with an increase in their metal oxides in the glass compositions. On the other hand, it was observed that the chemical durability of the glass with a lower P_2O_5 content (No. 7 glass) was rather worse than that of the other ultra-phosphate glasses. This fact suggest that the ultraphosphate glass corresponding to the network-forming structure seems to stabilize structurally more than the metaphosphate glass corresponding to the straight-chain structure.[11] Moreover, the addition of silicon dioxide may also be conducive to the advancement of the chemical durability because of its tendency forms network-forming.

Potential Response of the Magnesium Phosphate Glass Membrane. The potential response curves of some of the alkali-free magnesium phosphate glass membranes for the nitrate ion activities are shown in Fig. 1. The response characteristics of a magnesium phosphate glass membrane depend strongly upon its glass composition. In particular, glasses not containing Ag_2O or CuO show a small electrode function of the nitrate-ion activities, and the electrode potentials show an unstable behavior.

As shown in Fig. 1, when we compare the electrode function of the metaphosphate glass membrane (No. 7 glass) and the other ultraphosphate glass membrane containing copper(II) oxide, the latter is better than the former. Threfore, the suitable quantity of the P_2O_5 contents in the glass membrane, determined by means of an analysis of the nitrate-ion activities, was fixed at 55 mol%, with varied quantities of the other metal oxides.

Among the glasses examined, the 10CuO : 55P_2O_5 : 15MgO : 10Al_2O_3 : 10SiO_2 glass membrane is the best in terms of stability, reproducibility, rapidity of response, and magnitude of the electrode function with nitrate-ion activities.

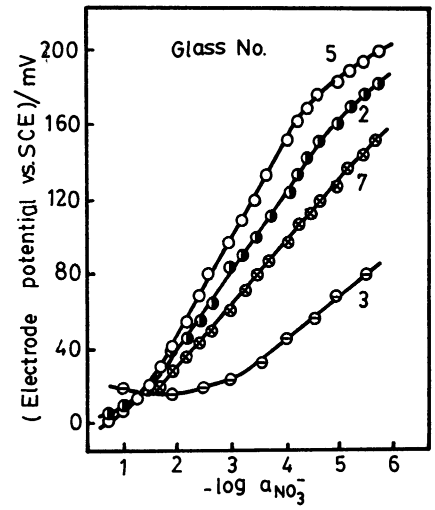

Fig. 1. Electrode response of some glasses as a function of the nitrate ion activities.
Glass compositions used in this figure were described in Table 1.

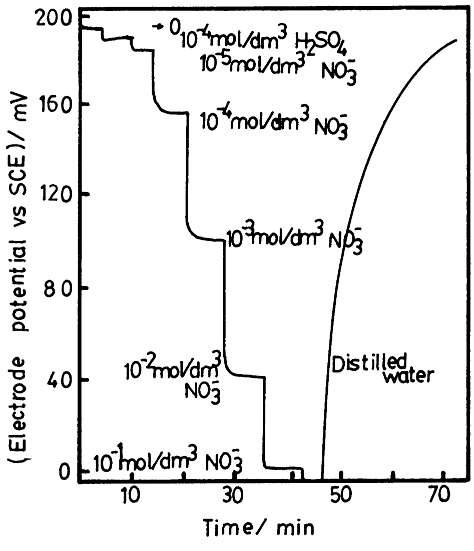

Fig. 2. Response characteristics of the No. 5 glass electrode with the nitrate ion concentration.

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES OF THE GLASSES

Glass No.	Transition temperature T_g/°C	Softening temperature T_s/°C	Thermal expansion α×10^7/cm °C^{-1}	Chemical durability mg mm^{-2}	Memberane resistance MΩ cm^{-1}
1	508	552	125.7	2.04×10^{-2}	4.53
2	546	621	100.6	2.43×10^{-3}	6.31
3	637	717	91.2	8.87×10^{-3}	3.71
4	—	—	—	1.53×10^{-2}	6.68
5	589	678	99.7	8.51×10^{-3}	5.27
6	563	632	102.4	7.32×10^{-3}	3.79
7	568	628	91.7	4.73×10^{-2}	7.77
8	574	646	120.5	3.82×10^{-3}	8.93

The potential response of nitrate-ion activities for this glass membrane was linear over the range of (10^{-1}—$10^{-4.5}$) mol/dm^3, and the slope of the potential-concentration relationship shows a sub-Nernstian response of about 54 mV/decade change at 20 °C. However, when the range of the nitrate-ion activities is below $10^{-4.5}$ mol/dm^3 or above 10^{-1} mol/dm^3, the slope becomes small.

Figure 2 shows the response characteristics of the No. 5 glass electrode operated in the following manner. The electrode was first placed directly in twice-distilled water, to which a solution of 10^{-4} mol/dm^3 sulfuric acid was added, then the electrode was exposed to increasing concentrations of nitrate ions in the order of 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} mol/dm^3 with the addition of the value-calculated sodium-nitrate solution. After recording the potential of the nitrate-ion activities to 10^{-1} mol/dm^3, the electrode was carefully washed with distilled water and then immersed in the twice-distilled water. The response rate with an increase in the concentration of nitrate-ion activities was observed to be somewhat faster than that with a decrease in the concentration of nitrate ions.

In solutions containing 10^{-1} and 10^{-4} mol/dm^3 of nitrate ions, equilibrium was reached within about 1 and 3 min respectively. However, after the electrode has been exposed to a nitrate concentration of 10^{-1} mol/dm^3, and then to concentrations decreasing to 10^{-5} mol/dm^3, the dynamic response time needed for reaching the equilibrium potential was more than 5 min. It is clear that 95% of the response times are about one minute expect in the case of nitrate-ion concentrations of less than 10^{-4} mol/dm^3.

Interferences of Diverse Anions and the Selectivity Coefficient of Nitrate Ion for the Other Anions. There were essentially no effects of the cations on the determination of nitrate ions when the magnesium phosphate glass electrode was used.

The effect of common anions on the determination of nitrate-ion activities was determined by means of the potential-concentration curve, and the order of magnitude of the selectivity, as regards all of the glass electrodes examined, was defined as: $NO_3^- > ClO_4^- > I^- > NO_2^- > Cl^- > SO_3^{2-} \gg SO_4^{2-}$. Therefore, sodium sulfate or sulfuric acid is used to adjust the ionic strength. The electrode function of the nitrate-ion activities and the selectivity coefficients of some of the coexisting anions for the magnesium phosphate glass electrodes are listed in Table 3. The selectivity coefficients were determined by the mixed solution method.[12] The values of the selectivity coefficients are calculated by means of the electrode potential, with fixed quantities of the interfering ion (0.1 mol/dm^3) and a varied activity of the nitrate ions.

The selectivity coefficients of ClO_4^- and NO_2^- with the No. 5 glass electrode are smaller than that of the liquid ion-exchanger nitrate-ion selective electrode,

Table 3. Electrode function of nitrate-ion activities and selectivity coefficients of various anions

Glass No.	Electrode function mV/pa$_{NO_3^-}$	Selectivity coefficient×10^2				
		Cl^-	ClO_4^-	SO_4^{2-}	NO_2^-	SO_3^{2-}
1	31.1	—	—	—	—	—
2	42.0	3.98	15.8	0.63	1.26	2.09
3	21.3	—	—	—	—	—
4	41.6	4.57	11.7	0.59	11.2	8.73
5	54.2	3.36	7.52	0.67	3.98	1.84
6	38.5	6.31	3.16	1.58	9.32	5.25
7	35.3	16.5	21.9	5.25	10.7	7.41
8	42.6	12.6	63.1	5.01	25.1	14.5

and the electrode potentials of mixed nitrate-perchlorate solutions indicate that the effect of the perchlorate ion on a concentration of about 0.01 mol/dm^3 can be neglected for the determination of nitrate ions at concentrations above 7.5×10^{-4} mol/dm^3.

As is obvious from the results shown in Table 3, Nos. 1, 3, and 7 glasses can not be used as ion-selective electrodes because of their poor chemical durability and small electrode function. Moreover, No. 8 glass is also observed to have a poor selectivity for the other anions.

The selectivity coefficient and the electrode function show that the No. 5 glass is better for use as an ion-selective glass sensor for nitrate-ion activities than the other glasses.

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