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Novel guidelines for the development of pM-selective glass electrodes from oxide glasses

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There have been no guidelines for developing pM-selective (M = alkali metal ions) glass membrane electrodes. One of the key points for developing pM-selective glasses is to make glasses not responsive to changes in pH, since pM-measurements can be disturbed by the pH of the solution. As hydrogen-bonded protons in glasses are mobile and their mobility is thought to be responsible for pH-sensitivity, glasses for pM-selective electrodes should contain no hydrogen-bonded protons and no non-bridging oxygen. In this paper, guidelines for developing pH-selective glasses are proposed by using pNa-selective glasses in the Na_2O–Al_2O_3–SiO_2 system as examples.

1. Introduction

Since the discovery by Cremer [1] that the potentials of glass electrodes blown in bulb form are sensitive to changes in the acidity of the solution in which the bulbs are immersed, intensive studies on the glass electrode and its many possible applications have been carried out [2]. Today, glass electrodes are widely used under various conditions for pH measurements and control in the fields of industry, commerce and research.

Curiously, the reason why commercial glasses for pH meters exhibit good responses to hydrogen-ion activities in solution has not been clearly elucidated as yet, despite the time elapsed since the discovery of pH response glass electrodes. There have been numerous attempts to give a theoretical interpretation of the function of the glass electrode. These theories have been divided into several groups such as ion adsorption, diffusion potential and phase boundary theories [2]. Recently, a new theory (the dissociation mechanism) has been proposed by Baucke [3]. On the other hand, from a practical point of view, numerous efforts for the development of pH- as well as pM (M = cations other than H^+)-response glass electrodes have been made to prepare a vast number of glasses with different compositions by trial and error. It is known that the most extensively characterized cation-sensitive glass electrodes are those in which cation selectivity is produced by the addition of Al_2O_3 [4]. The responses to H^+ and other cations such as Na^+, K^+ and Ca^{2+} are summarized as systematic functions of glass composition empirically deduced by trial and error [4]. However, it seems that in a practical sense why a glass with a particular composition shows a selectivity to a particular cation is not known.

Generally, most commercial oxide glasses, membrane electrodes prepared from which have been widely used for pH measurements, contain a small amount of water as –OH groups in the structures, although they are produced by melting at a high temperature above 1000 °C. Protons or water molecules in glasses were first studied extensively by Scholze [5–7]. For a long time, however, it was believed that protons in oxide glasses could not act as electrical charge carriers, because protons were considered to form very strong O–H bonds in oxide glasses [8–10]. Recently, Abe and co-workers [11–13] found that the protons of O–H bonds in glasses with non-bridging oxygens become mobile under an applied d.c. voltage, as a result of weakening of O–H bonds due to the formation of hydrogen bonding (–O–H ... O–) with neighbouring non-bridging oxygen ions of the glasses. The mobilities of protons in some phosphate glasses which have a large amount of non-bridging oxygen ions are estimated to be about 10^8 times higher than those in silica glasses which have only bridging oxygen ions and no non-bridging oxygen ions. Generally, the concentrations of protons in conventionally prepared silicate glasses are in the order of 10^{-1} to 10^{-4} mol dm^{-3}. The mobilities of protons in some types of glass are much higher than those of Na^+ or Ag^+ ions, but in the other types of glass they are in the reverse order [13].

As was described above, it is known that there exist two types of protons in glasses [5–7], one type is hydrogen-bonded and mobile and the other is free of hydrogen-bonding and substantially immobile [11–13]. The presence and the mobility of mobile protons are dependent on the composition of the glass.

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Based on this information, the proposition is that glasses with mobile protons should display good pH responses and those without mobile protons should not.

The development of pM response glass electrodes (M: cations such as Na^+ and Ca^{2+}) is required in many industrial fields. One of the most important and difficult problems for this development is how to make the glass electrode insensitive to pH, because hydrogen ions are inevitably present in aqueous solution. Our suggestion for the development of glasses for pNa-response and, in addition, for pH-nonresponse is that the glasses should contain Na^+ ions, which are usually mobile, and no mobile protons. SiO_2 glasses contain essentially no mobile protons and no Na^+ ions. Binary Na_2O–SiO_2 glasses involve both Na^+ ions and mobile protons. A type of glass with mobile Na^+ ions and no mobile protons is found in Na_2O–Al_2O_3–SiO_2 glasses in which the Na_2O/Al_2O_3 molar ratio equals unity.

As was reported in previous papers [12, 13] the presence of mobile and "immobile" protons in glasses is easily proved by the appearance of O–H stretching vibrations for mobile and "immobile" protons in infrared spectra.

In the present work, as the first of a series of studies on the development of pM-response electrodes, a type of glass with the composition of $20Na_2O$–$20Al_2O_3$–$60SiO_2$ (in mole %), which is expected to contain mobile Na^+ ions and no mobile protons, was prepared and the Nernstian responses of the glass membrane against the concentrations of Na^+ ions were examined potentiometrically. Prior to the examination, the absence of mobile protons in the glass was ascertained by infrared spectroscopic measurements.

2. Experimental procedures

2.1. Preparation of glass membranes

A glass with the composition of $20Na_2O$–$20Al_2O_3$–$60SiO_2$ (in mole %) was prepared as follows. A batch of $20Na_2CO_3$–$40Al(OH)_3$–$60SiO_2$ (in mole %) was melted at around 1550 °C for 2 h in an alumina crucible to form a transparent glass. The glass was annealed and subsequently cut and polished into discs with a thickness of 0.3 mm and a diameter of 12 mm. A glass disc thus prepared was connected to one end of a Teflon tube in such a way that the disc was compressed between Teflon O-rings by a Teflon cap with screws. A KCl-saturated solution was introduced into the tube, in which a KCl-saturated calomel internal electrode was inserted, and then the tube was sealed. Part of the glass electrode is shown in an inset in Fig. 1. Other glasses with different compositions of $20Na_2O$–xAl_2O_3–$(80-x)SiO_2$ (in mole %) were also prepared, so that infrared spectra of their membranes were compared with those of the glass discs prepared for the pNa-selective electrode.

2.2. Measurements of infrared absorption spectra of glasses

The infrared absorption spectra were measured with an IR spectrophotometer (Hitachi model 270) connected to a microcomputer, at room temperature using optically polished platelike glass specimens with a thickness of 0.8 mm.

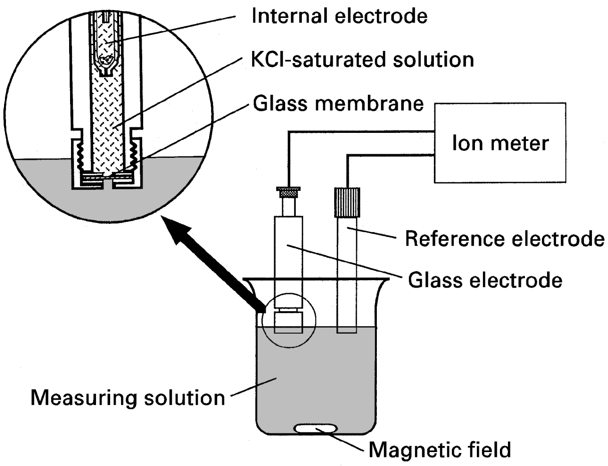

Figure 1 Schematic diagram of a cell used to measure potentials of the pNa-response glass electrode.

2.3. Measurements of potentials in glass membrane electrode

A potentiometric cell consisting of a glass membrane electrode made of a thin membrane of glass and a saturated KCl-calomel reference electrode is schematically shown in Fig. 1. The electrode potentials at 25 °C were measured within the accuracy of 0.1 mV with an ion meter. The potentials were reproducible to ± 0.4 mV. Sodium nitrate of reagent grade was used for the preparation of measuring solutions containing Na^+ ions.

The pH values of the sample solutions were adjusted by mixing suitable amounts of monoethanol amine and HCl.

3. Results

3.1. Infrared spectra of glass membranes

Infrared spectra of thin membranes of $20Na_2O$–xAl_2O_3–$(80-x)SiO_2$ (in mole %), which were prepared in the present work, and of $60SiO_2$–$25Li_2O$–$5BaO$–$7TiO_2$–$3La_2O_3$, which is prepared for commercially available pH response electrodes, are illustrated in Fig. 2. Absorption bands due to O–H stretching vibrations are observed at two different positions. Bands at $\nu_{OH} = 3500\ cm^{-1}$ (Band-1) are ascribed to the hydrogen-bonding free O–H stretching vibration and those at $\nu_{OH} = 2900\ cm^{-1}$ (Band-2) to the hydrogen-bonding O–H vibration [5–7]. Pure silica glasses, in which oxygen ions are all in a state of "bridging" ions (–O–), give only Band-1 absorption. Introduction of Na_2O into SiO_2 glasses results inevitably in the formation of non-bridging oxygen ions, which give Band-2 absorption. Addition of Al_2O_3 to Na_2O–SiO_2 glasses leads to a decrease in absorbance of Band-2. Band-2 absorption completely diminishes and Band-1 absorption increases under the condition

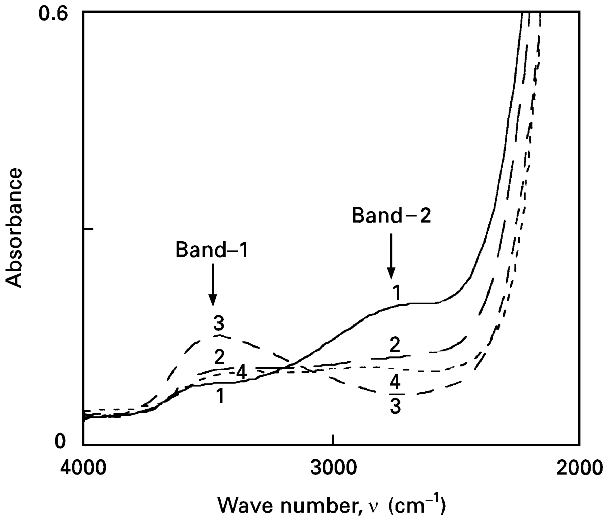

Figure 2 Infrared spectra of thin membranes of glasses with different composition (thickness ~0.8 mm).

1. $20Na_2O$-$80SiO_2$ (glass 1)
2. $20Na_2O$-$10Al_2O_3$-$70SiO_2$ (glass 2)
3. $20Na_2O$-$10Al_2O_3$-$60SiO_2$ (glass 3)
4. $25Li_2O$-$5BaO$-$7TiO_2$-$3La_2O_3$-$60SiO_2$ for commercially available pH-response electrodes (glass 4).

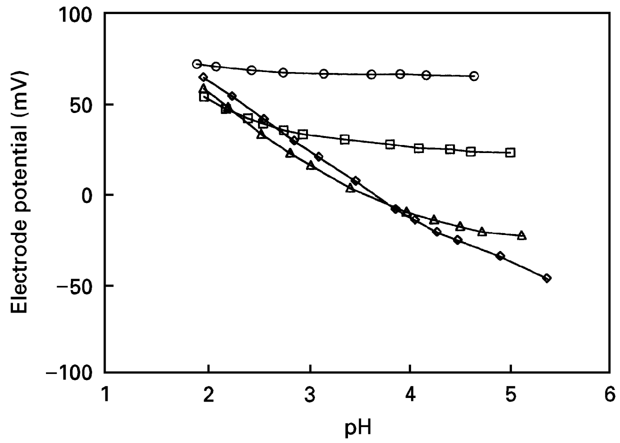

Figure 3 Plots of potentials against pH at constant Na$^+$-ion concentrations for glass 3, ○ 1; □ 0.1; △ 0.01; ◇ 0.001 (mol dm^{-3}).

of Na_2O/Al_2O_3 molar ratio equal to unity [5–7]. It has been pointed out that the mobility of protons increases markedly with increasing absorbance due to the hydrogen-bonding O–H vibration (Band-2) [11]. Thus, according to our expectation, glasses 1, 2 and 4 should function as pH-response electrodes, and glass 3, in which no mobile proton is detected, as a pNa-response electrode. In fact, glass 4 is used for commercially available pH-response electrodes. However, glass 1 and glass 2 are not applicable to pH measurements, because they respond also to pNa and are not chemically stable.

3.2. Potentials versus concentrations of Na$^+$ for glass 3

Potentials measured with concentrations of Na$^+$ ions kept constant while pH values are varied, are shown in Fig. 3. The potentials are independent of pH values in the concentration range of Na$^+$ higher than 0.1 mol dm^{-3}, while the dependence of the potentials on pH becomes predominant with decreasing Na$^+$-ion concentration. In Fig. 4 the potentials versus the concentrations of Na$^+$ (0.01, 0.1, and 1 mol dm^{-3}) at pH = 5 are plotted where the pH dependence of the potentials is negligible. The straight line linking the three experimental points shows a slope of 59 mV per decade of Na$^+$-ion concentration corresponding to the Nernstian response at 25 °C. The measurements were also carried out in pH-buffered solutions containing Na$^+$ ions at very low concentrations of 10^{-2}–10^{-7} mol dm^{-3}. The results are depicted in Fig. 5. It is obvious that the electrode shows

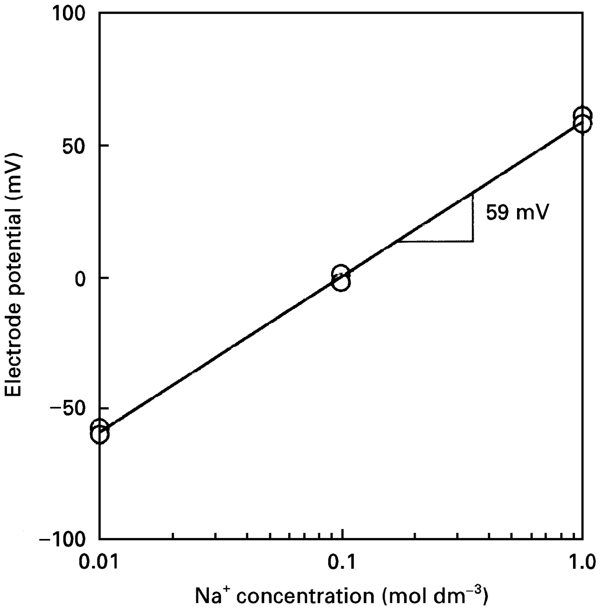

Figure 4 Plot of potentials against Na$^+$-ion concentrations ≧ 0.01 mol dm^{-3} at pH 5 for glass 3.

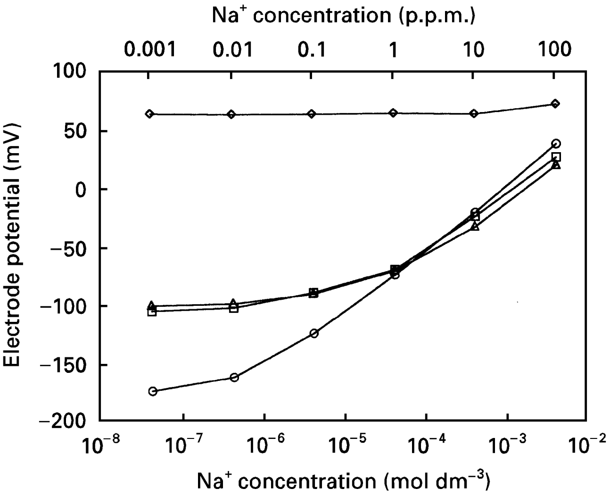

Figure 5 Plots of potentials against Na$^+$-ion concentrations <0.01 mol dm^{-3} at constant pH values for glass 3; (○) pH 10 solution: 0.01 mol dm^{-3} monoethanol amine; (□) (pH 10 + 0.01 mol dm^{-3} KCl) solution: 0.01 mol dm^{-3} monoethanol amine + 0.01 mol dm^{-3} KCl; (△) pH 7 solution: 0.01 mol dm^{-3} monoethanol amine adjusted to pH 7 by addition of HCl; (◇) pH 3 solution: 0.01 mol dm^{-3} monoethanol amine adjusted to pH 3 by addition of HCl.

a satisfactory Nernstian response at pH 7 and 10. By contrast, the electrode works as a pH-selective electrode at a higher H^+-ion concentration range of $pH < 3$. The dependence of the emf on pH, especially at low pH values, may be ascribed to the presence of small amounts of mobile protons, which may not be detected by the infrared spectroscopic measurements and/or the presence of "immobile" protons, which are not really immobile, but less mobile by 10^8 times than the mobile protons [11].

4. Discussion

In order to interpret qualitatively the behaviour of the present pNa-response glass electrode, we accepted Dole's treatment [14] that the potential of the glass electrode originates from the junction between the glass, which is regarded as a kind of solution, and the aqueous solution, because we realized that H^+ ions move in the glass, as do the Na^+ ions. The Henderson and Planck liquid junction equations were used. These equations are based on assumptions of constant mobility through the boundary, of homogeneous solvent and of the validity of the perfect gas laws, all three of which are not true for the glass-water junction [14]. According to the Henderson and Planck equations the potentials at boundaries between the glass electrode film and a given solution (E_I) or a reference solution (E_{II}) are given by Equations 1 and 2, respectively.

$$E_I = (RT/F)\ln(\mu_H C_H^I + \mu_{Na} C_{Na}^I)/(\mu_H C_H^G + \mu_{Na} C_{Na}^G) \quad (1)$$

$$E_{II} = (RT/F)\ln(\mu_H C_H^G + \mu_{Na} C_{Na}^G)/\mu_H C_H^{II} \quad (2)$$

From Equations 1 and 2 the potential of the cell (E_G) is derived as

$$E_G = (RT/F)\ln(\mu_H C_H^I + \mu_{Na} C_{Na}^I)/\mu_H C_H^{II} \quad (3)$$

where C_H^I and C_H^{II} are H^+ ion-concentrations in a given solution (I) and a reference solution (II), respectively; μ may be thought of as the mobility of the ion in the boundary layer [14], i.e. μ may be regarded as an "average" of μ values of the particular ion in the solution and in the glass. It can be said that the mobility of the particular ion in the glass is reflected strongly in the "average" mobility. Thus, the lower the mobility of the particular ion in the glass becomes, the lower the "average" mobility. From Equation 3 it is evident that the ideal pNa response is accomplished under the condition of $\mu_H C_H^I \ll \mu_{Na} C_{Na}^I$, and the ideal pH response is for $\mu_H C_H^I \gg \mu_{Na} C_{Na}^I$. Thus, as we proposed initially, the only way to meet the requirement for a good pNa membrane electrode is to reduce the ratio $\mu_H C_H^I/\mu_{Na} C_{Na}^I$, i.e. decrease the mobility of H^+ ions in the glass and raise the mobility of Na^+ ions in the glass as much as possible, since the mobilities of H^+ and Na^+ ions in solution may be regarded as constant under different conditions. This equation explains qualitatively the experimental observations of the glass electrode for Na^+ ions.

The above experimental results indicate that a glass in which protons are mobile exhibits good pH responses and one in which protons are "immobile", while Na^+ ions are naturally mobile, is selective to Na^+ ions. The glass with mobile protons is essentially selective to hydrogen ions and, thus, the immobility of protons in the glass is a requisite for the selectivity to cations other than hydrogen ions.

As was described above, it has been found that the mobility of protons in glasses increases markedly with decreasing $\text{wavenumber}_{OH}\,\text{cm}^{-1}$ for the hydrogen-bonding O–H vibration [11, 12] and recently, Abe *et al.* [13] also found that the mobilities of H^+ and Na^+ ions in glasses are proportional to their concentrations to the *n*th power (where $n \simeq 2$ for H^+ and $\simeq 4$ for Na^+; *n* values being dependent on the glass composition). Based on these findings, we propose that an essential principle for the development of glass membrane electrodes selective to cations other than hydrogen ions is to adjust the composition of the glasses in such a way that the mobility of "mobile protons" should be reduced, that is, ν_{OH}, should be increasesd and the amount of "mobile" protons in the glasses, ν_{OH} of which appears at around $2800–2900\,\text{cm}^{-1}$, should be reduced, while the mobility and the amount of the mobile cations in question should be increased as much as possible in the glasses. For pNa-selective glasses we recommend Na^+ ion-containing glasses without non-bridging oxygen ions, for example, Na_2O-Al_2O_3-SiO_2 glasses having the Na_2O/Al_2O_3 molar ratio of unity which are known as glasses having no non-bridging oxygen [11] and no Band-2 absorption; the glasses have no mobile protons. The opposite condition is the case for glass electrodes for hydrogen ions. Mixing of different kinds of alkali ions in glasses should result in decreased mobilities of the respective alkali ions in the glasses owing to a mixed alkali effect [14] and, as a result, the alkaline errors of glass electrodes for hydrogen ions will be reduced. However, it is desirable that the glasses should have chemical durability and lower electrical resistance for their practical use.

We consider that if cations in solution, which are not originally present in the glass, can penetrate the glass and are mobile in it, then the glass should respond to the cations. The penetrable or diffusing cations should have the analogous radii to those of the cations originally in the glass. As an example, a disturbance of the function of the pNa-selective glass electrode due to potassium ions, which have a slightly larger radius than sodium ions, is illustrated in Fig. 5 (compare the data for pH 10 with those for pH 10 +0.001 M KCl). The disturbance occurs ultimately at the concentration ratios of Na^+ and K^+ ions less than 10^2. Thus, it is impossible for hydrogen ions in solution, whose ionic radius is many times smaller than those of the cations in glasses, to penetrate into the glasses, if they originally contain no "mobile protons", which work as favourable sites for their diffusion.

5. Summary

Hydrogen-bonded protons, which exist in glasses having non-bridging oxygens, are mobile. We assert that the pH-response of glasses results from the existence of mobile protons in the glasses which are bound as

–OH groups and present generally in concentrations of 10^{-1} to 10^{-4} mol dm^{-3} and that the higher the mobility of the protons relative to those of alkali ions in the glasses, the less the measured pH value is disturbed by the alkali ions in solution. On the contrary, a principle for developing glasses for pM-selective electrodes ($M =$ cation other than H^+) which are disturbed by the pH of solution as little as possible is that the glasses should contain as many mobile M cations as possible and as few mobile protons as possible. A glass electrode made of a glass with the composition of $Na_2O/Al_2O_3 = 1$ (in mole ratio) in the Na_2O-Al_2O_3-SiO_2 system, in which protons are "immobile" and Na^+ ions are mobile, displayed a good pNa-response even in substantially lower concentrations of Na^+ ions.

The M^+-containing glasses in which oxygens consist entirely of bridging oxygens (not non-bridging oxygens) are recommended for pM-selective glasses.

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