MOBILE PROTONS IN SUPERPROTONIC CONDUCTORS OF PHOSPHATE GLASSES AND pH-ELECTRODE GLASSES

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Abstract In oxide glasses, strongly hydrogen-bonded protons which give IR absorption band at around 2900 cm^{-1} are very mobile, while hydrogen-bonding free protons which give its band at around 3600 cm^{-1} are immobile or much less mobile. The mobilities of protons increase with the strength of the hydrogen bonding. The superprotonic conductors of oxide glasses are developed for the phosphate glasses containing a large amount of mobile protons and molecular water. The theories of potential development of pH-glass electrodes which are long pending problem are discussed in terms of the mobile protons of the glasses. We assert that the presence of the mobile protons is indispensable for its pH-response.

INTRODUCTION

Recently, mobile protons in glasses and high proton-conducting glasses have much attraction from a view point of scientific and/or technological point. A series of studies on protonic conduction in oxide glasses have been reported by us.¹⁻²⁷ We pointed out that high proton-conducting membranes of inorganic glasses will be demanded for solid electrolytes of hydrogen-oxygen fuel cells.^{1,2} The presence of an amount of high mobility protons is a requisite condition for developing fast proton-conducting glasses or superprotonic conductors of glasses; we assert that it also plays an essential role in the potential development of pH-electrode glasses.⁴¹⁻⁴⁹ High mobility protons in glasses give important effects on their electrical properties and applications

Unfortunately, however, it has been long believed that protons in glasses are substantially immobile,²⁹ and they have no essential role on the (d.c) electrical conduction of the glasses. On the other hand, as we have reported since 1982,^{1,2} strongly hydrogen-bonded protons in glasses have been found to be very mobile, although protons free from hydrogen-bonding are substantially immobile. The mobility of the hydrogen-bonded protons in pH-glasses has been evaluated to be much higher than that

of alkali-ions.⁴⁹

The role of protons in protonic and superprotonic conductors of phosphate glasses, and that of pH-electrode glasses are reviewed in the present paper.

PROTONIC CONDUCTION IN GLASSES

These were presented at 17th ICG¹² and 3rd ISIPM²⁸, and summarized as follows.

(a) Protonic Conduction in Glasses

Without Molecular Water

Normally melt-quenched glasses contain substantially no molecular water, but contain hydroxyl groups (-OH) as an impurity in which hydrogen-bonding free protons

(immobile) and strongly hydrogen-bonded protons (mobile) are present.

Fig.1 shows IR absorption spectra for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses which is a typical example given by Scholze.³⁰ It is interesting that the peak wavenumber of the absorption band due to hydroxyl groups depends strongly on the glass structure or composition. The band-1 shown in Fig.1 is hydrogen-bonding free, and the band-2 is strongly hydrogen-bonded. The specimen-6 gives only one band (band-1) as in silica glass, and no band-2. We found that protons of band-1 is "immobile" (less mobile) under an electrical d.c. field and those of band-2 is "mobile".

Generally, alkaline earth phosphate glasses, $\text{MO}-\text{P}_2\text{O}_5$, give strong absorption at around 2900 cm^{-1} (band-2); the peak absorption wavenumber (ν_{OH}) shifts to lower one with increasing ionic radius of M-ion.

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The results obtained so far are briefly summarized as follows.

- (1) There exist two types of protons in oxide glasses, "immobile (or less mobile) protons" and "mobile protons". The IR absorption bands due to O-H stretching appear at $\nu_{\text{OH}} \approx 3600\text{ cm}^{-1}$ (band-1, free from hydrogen bonding) and $\nu_{\text{OH}} \approx$

FIGURE 1. Typical example of IR absorption spectra of $20\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(80-x)\text{SiO}_2$ glasses (after Scholze³⁰).
(1) $x=0$, (2) $x=5$, (3) $x=10$, (4) $x=12$,
(5) $x=15$, (6) $x=20$.

2900 cm⁻¹ (band-2, strongly hydrogen-bonded) which shift depending on glass structure and compositions. (It has been known that glasses containing non-bridging oxygens have band-2.)

- (2). The **protonic conductivities** (σ , S/cm) are not proportional to the concentration of protons, but are proportional to the **square** of the concentration of carrier protons ($[H^+]$, mol/l).

$$\sigma = A_H [H^+]^2 \quad \text{..... (1)}$$

- (3) The constant, A_H (a mobility term) increases considerably with the wavenumber (ν_{OH}); it increases approximately by one order with the shift of 100 cm⁻¹ of ν_{OH} .

$$\log A_H = - 0.00970 \nu_{OH} + 17.1 \quad \text{..... (2)}$$

Where, A_H is a proportional factor in the equation (1), a measure of mobility, of plotting of conductivity at 417K (150 C) vs square of concentration of mobile protons.

Thus, it is surprising that the mobilities of the protons in Ba(PO₃)₂ glasses

($\nu_{OH} \approx 2800 \text{ cm}^{-1}$) are 10⁷~10⁸ times higher than those of SiO₂ glasses ($\nu_{OH} \approx 3650 \text{ cm}^{-1}$).

- (4) It is very effective for the preparation of high proton-conducting glasses that the glasses contain **phosphates**.
- (5) .The experimental **activation energies** for the protonic conduction (E_H) which are obtained from Arrhenius plots are expressed by the following equation.

$$E_H = E_0 + E_1 \quad \text{..... (3)}$$

$$E_0 = B_0 + B_1 \nu_{OH} \quad \text{..... (4)}$$

$$E_1 = -B_2 \log[H^+] \quad \text{..... (5)} \quad (B_0, B_1, \text{ and } B_2 \text{ are const.})$$

E_0 is the value for $[H^+] = 1 \text{ mol/l}$; this is considered to be related to breaking of O-H bond; E_1 depends on the hopping distance or proton concentration)

- (6) Both protonic conductivity and activation energy of a given glass can be **evaluated** (by applying the above experimental equations) from the IR absorption spectrum of a given glass plate, **without the electrical measuring**.

As an example of the estimation of activation energy in protonic conduction of a given glass, we have applied the above equations to PbO-SiO₂ glasses.⁷ The nature of electrical charge carriers of the lead silicate glasses was a long pending question. Milnes (1962)³¹, Cohen (1973)³², Melling (1979)³³, Dutta (1988)³⁴ et al. supported the view that the Pb²⁺ were assumed to be the charge carriers. On the other hand, Hugheses (1968)³⁵ suggested that the carriers are not Pb²⁺ but either H⁺ ions or electrons. Topping (1974)³⁶ also suggested H⁺ ions are quite likely to be the dominant charge carriers. By contrast with the different results so far obtained, we estimated the activation energies (E) using the above equations, in which ν_{OH} of PbO-SiO₂ glasses

was substituted, and concluded that the current carriers are the hydrogen-bonded (mobile) protons.⁷

(b) Superprotonic Conduction in Glasses with Molecular Water

We have pointed out that glasses containing no molecular water give no superprotonic conductivities such as 10^{-1} to 10^{-5} S/cm at room temperature.^{12-a} The first superprotonic conductors of inorganic gel-glasses^{12-b} containing a large amount of molecular water and mobile protons were prepared by us for zirconium phosphate systems by a common sol-gel processing.^{12,13,15} The conductivities are shown in Fig. 2.¹⁵ The mobility of protons of SiO_2 glasses (or A_H) is very low as estimated from equation (2), and then, phosphates were selected. The first developed superprotonic conductors of $\text{ZrO}_2\text{-P}_2\text{O}_5$ gel-glasses have several weak points such as difficulty of glass formation and conductivity drop above 100 C, and since then, the system glasses in $\text{ZrO}_2\text{-P}_2\text{O}_5\text{-SiO}_2$ ^{20,21} and $\text{P}_2\text{O}_5\text{-SiO}_2$ ²⁶ have been tried. These silica-containing glasses are stable up to about 400C, and give high conductivities. However, it is widely known that sol-gel derived glasses are hardly prepared into large bulky forms such as 5 cm x 5cm membranes owing to the crack formation during sol-gel preparation; this is a common weak point of the sol-gel processing.

Recently we are now trying to develop a new processing for producing larger specimens of superprotonic conductors of transparent oxide glasses³⁷ which is not from sol-gel processing. The current carriers of the glasses are not H_3O^+ but H^+ ; the glasses contain no connective micro-pores such as those in sol-gel derived gel-glasses and in perfluorosulfonic polymers (Nafion^R); the absorption edges of these transparent and colorless glasses are around 230 nm in the ultraviolet region.

Concepts of some applications of the glasses to clean energy fields are shown in Fig. 3-5, where photocatalytic semiconductor of titania is used as an example. The photocatalytic splitting of water into hydrogen and oxygen using a semiconductor of TiO_2 were first found by Honda & Fujishima³⁸; it operates with ultraviolet light.

FIGURE 2. Arrhenius plots of protonic conductivities for sol-gel derived zirconium phosphate glasses. (Atomic ratios P/Zr for ZrP and ZrPP are 4 and 3, respectively.)

Recently, the oxide photocatalysts which operate with visible light^{39, 40} have been developed. The place where the function of the system of Fig.4 and/or Fig.5 is most effective will be outer space which is irradiated by very strong solar rays including ultraviolet light. In Fig.5, the O_2 and H_2 which are produced by photolysis are used for the H_2 - O_2 fuel cell, from which electric energies are available to result in the formation of H_2O .

FIGURE 3. Electrolysis of water.
(SPGM: superprotonic conductors of
glassy membranes)

FIGURE 4. Electrochemical photolysis
of water.

FIGURE 5. Concept of circulation type of the system. Combination of water
photolysis & its use to H_2 - O_2 fuel cells.

Summaries :

- (1) Protonic conductivity increases considerably with the introduction of **molecular water** into glasses. The activation energy decreases in proportion to $\log [\text{H}_2\text{O}]$.
- (2) Superprotonic conductors of glasses were developed by sol-gel processing for the systems of $\text{ZrO}_2\text{-P}_2\text{O}_5$, $\text{ZrO}_2\text{-P}_2\text{O}_5\text{-SiO}_2$, and $\text{P}_2\text{O}_5\text{-SiO}_2$, all of which contain a large amount of molecular water and mobile protons. Some of them are stable at around 400 C.
- (3) Preparation of superprotonic conductors of oxide glasses via another new route is in progress.

These membranes have a potential use for the proton-conducting electrolytes such as for those of electrolysis and photolysis of water and $\text{H}_2\text{-O}_2$ fuel cells.

ROLE OF PROTONS IN pH-ELECTRODE GLASSES

We have reported a series of studies on the mechanisms of pH-electrode glasses.⁴¹⁻⁴⁹ The pH-electrode glass membranes commercially obtained are regarded as a kind of hydrogen ion (H^+) sensors. In spite of the lapse of about one century since the discovery of pH-responsive glass electrodes, theories or mechanisms for the origin of the potential development of the glass electrodes seem to remain unsolved. Most theories presented so far for the potential development are mainly based on the assumption that hydrogen ions (protons) in the aqueous solution do not diffuse through the glass membrane. That is to say, all recent theories for pH-glass electrodes are originated from the hypotheses accepting the immobility of protons in the glasses, and then they are complicated and seem to be somewhat mysterious.

Table 1 gives major theories (mechanisms) for the development of pH-glass electrode potential. At the initial stage of the discovery after Cremer⁵⁰, it has been supposed that glass membrane is permeable to H^+ ions. Dole⁵¹ assumed that pH-glass electrodes are semi-permeable membranes only to hydrogen ions and derived the electrode potential equation based on diffusion potentials. However, in 1941-1962, Haugard⁵², Schwabe⁵³ and Hammond⁵⁴ concluded "as a result of their experiments" that H^+ ions do not permeate through the glasses. Since then, theories excluding the H^+ -diffusion have been widely proposed up to the present. Nevertheless, we like to assert that H^+ ions diffuse through the glass membranes during measurement of pH.

In recent text books⁵⁵ so far published, theories excluding the H^+ -diffusion are described. For example, in ref.(55-a) the following sentences appear:

"It was formerly believed that the potential of the glass electrode arose from the migration of H^+ through the glass. If H^+ could do this, and

other ions could not, then a potential analogous to a liquid junction potential would develop across the membrane and a Nernstian response to H^+ would be expected. However, it has apparently been demonstrated that H^+ does not in fact traverse the membrane, and other ideas (which are unfortunately more difficult to explain) have been developed."

In contrast, we assert that hydrogen ions of glasses having non-bridging oxygens are mobile, that is, the strongly hydrogen-bonded protons of glasses are mobile, and they are responsible for the potential development of the glass electrode...

Mobility of Hydrogen Ions in pH-Electrode Glasses

The diffusion theories that hydrogen ions of solution diffuse into the glass-membrane have been disproved by the Hammond's experiment.⁵⁴ He concluded that hydrogen ions do not diffuse into the glass membrane and cations other than hydrogen ions carry the current across the membrane. Recently, however, we have pointed out that his conclusion is not correct.⁴¹

It has been often believed that hydrogen ions (protons) in oxide glasses are hardly mobile²⁹ or their mobilities in them are much lower than those of alkali ions. The mobility ratio of H^+ ion to Li^+ ion (μ_H/μ_{Li}) in a commercial pH-responsive glass ("Li-glass") has been reported by Baucke and Gach⁵⁶ to be about 1/ 56. In contrast, according to our calculation by using eq.(2), μ_H is evaluated to be much higher than μ_{Li} (μ_H/μ_{Li} ratio $\cong 10^3$)⁴⁹. In their experiment, the glass membrane was subjected to an electrical field of 6000 V cm⁻¹ in a dilute sulfuric acid in such a way that the hydrogen ions in the solution were introduced into the specimen. It is apparent that, as shown in Fig.6, the introduced H^+ ions replaced by Li^+ ion result in the increase of H^+ -concentration of the glass; these increased H^+ ions are not intrinsic hydrogen ions which are originally present in the glass, but extrinsic ones. The concentration of the intrinsic $H^+_{(2)}$ ions, which give IR band -2 in Fig.1 and are mobile, should remain constant before and after the voltage is applied.

As seen in Fig.7, the pH-glass contains the highest concentration of mobile protons (band-2). On the assumption that hydrogen ions in solution diffuse into pH-glass membranes during measurement of pH, it is proposed that the potential, E, is expressed by eq. 6, when H^+ - and alkali (M^+)- ions are present in the solution.^{43, 46, 49}

$$E = (RT/F)\ln(\mu_H^s C_H^I + \mu_M^s C_M^I) + \text{constant} \quad \dots\dots\dots (6)$$

Where, C_H^I and C_M^I are concentrations of H^+ and M^+ in test- I solution, respectively, μ_H^s and μ_M^s are mobilities of H^+ and M^+ of the pH-glasses, respectively. Therefore, the important factor for the response to M^+ ions of solution is the mobility of M^+ ions of

TABLE 1.

"Major Mechanisms for pH-Glass Electrode Potential"

{Year}	{Proposed by}	{Origin of Potential}
1906	Cremer	Membrane or diffusion potential;
1931	Dole	Glass membrane is permeable to H^+
1909	Haber	Phase boundary or Donnan potential
1923	Horovitz	Ion adsorption or ion exchange
1937	Haugaad	between Na^+ and H^+ .
1941	Haugaad	Disproved H^+ -diffusion through
1961	Schwabe & Dahms	membrane by chemical analysis
1962	Hammond	Disproved H^+ -diffusion by tritium
1967	Nicolsky	Ion exchange theory
1986	Cheng	Double-layer and double-capacitor
		model
		Disproved "Ion exchange theory"
		($H^+ \rightleftharpoons Na^+$)
1976-96	Baucke	Dissociation mechanism
1997--	Abe	H^+ -diffusion through membrane
		(Presence of mobile H^+ in pH-glass)

Fig. 6. Schematic representation of H^+ - and Li^+ -ions in pH-electrode glass structure. ($H^+_{(1)}$: hydrogen-bonding free, and immobile proton, $H^+_{(2)}$: strongly hydrogen-bonded, and mobile proton, $O_{(1)}$: bridging oxygen, $O_{(2)}$: non-bridging oxygen.⁴⁹

FIGURE 7. IR spectra (1 mm thick).

(a): pH-electrode glass.
 (b): Window glass
 (c): 20Na₂O-20Al₂O₃-60SiO₂ glass
 (d): SiO₂ glass.
 The Nernstian slope (E/pH , in mV) is:
 (a) = 57, (b) = 43, (d) = 4

the glasses, but not their concentration. We assert; that the reason why the potential of glass electrodes originates in response to pH comes from the fact that high mobility protons are present in the glasses, and that the reason why $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glasses shown in Fi. 7 exhibit less pH-response and better pNa-response comes from the lack of mobile protons (band-2) of the glasses. When the mobile protons are decreased, the glasses become less pH-responsive.⁴³ Even the silicon wafers when hydrogens are introduced by annealing in a H_2 gas atmosphere, becomes pH-responsive.⁴⁷

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