

Electrical conduction due to protons and alkali-metal ions in oxide glasses

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The activation energy for dc electrical conduction due to alkali ions of binary alkali silicate glasses and due to protons of binary alkaline-earth phosphate glasses decreases linearly with the logarithm of their concentrations (in mol/l). The activation energy is discussed in relation to the ionic radius and concentration. Hydrogen-bonded protons are much more mobile than sodium ions in the case of calcium phosphate glasses. The conduction mechanism due to protons is suggested to be different from that due to alkali ions.

I. INTRODUCTION

It is known that the electrical charge carriers in most oxide glasses were monovalent ions such as alkali ions and silver ions, or electrons and/or holes in glasses containing transition metals. High proton conducting glasses, if developed, have a high potential for use as a solid electrolyte for H_2 - O_2 fuel cells and for H_2 -gas sensors. For a long time, it was believed that protons in oxide glasses were not able to function as electrical charge carriers because protons were considered to form very strong O-H bonding in oxide glasses; it was asserted that protons become mobile under the condition that an oxide glass contains a large amount of molecular water.^{1,2} Recently, however, protons, which exist as -OH groups in glasses, have been found by us to be a species of electrical charge carriers;³⁻⁶ the mobility of the protons in alkali-free phosphate glasses such as BaO- and SrO- P_2O_5 glasses has been found to increase to as much as 10^8 times that of SiO_2 glass.⁴

It is important for glass scientists and technologists to know how the electrical conductivity (σ) and the experimental activation energy (E) of a glass depend on the concentration of the species of electrical charge carriers. It is clear that an agreed consensus has not emerged and that the conduction mechanism in glass is still under active discussion,⁷ although numerous experimental data on electrical conduction due to alkali ions in oxide glasses have been reported by many investigators.

Comparison between protonic and ionic conduction due to alkali ions is discussed in this paper. We assert that protons in oxide glasses are divided into two main types, one is "mobile" and the other is "immobile" under a dc electrical field; the former mobile protons are hydrogen bonded and the latter immobile ones are free from hydrogen bonding; the mobility increases with the strength of hydrogen bonding.

We show that experimental activation energy for electrical conduction in oxide glasses decreases with the logarithm of concentrations of electrical charge carriers such as alkali-metal ions and protons. So, when discussing experimental activation energies of glasses with different species of carriers, we must compare them at the same

concentration of respective carriers such as at 1 mol/l carriers. According to this idea, activation energy data are arranged, and we found that there exists a simple linear relation between E and ionic radius of alkali-metal ions of binary alkali-silicate glasses when compared at the same alkali concentration of 1 mol/l. The aim of this paper is to give an approach on the ionic conduction by comparing electrical conduction due to protons with that due to alkali-metal ions.

II. EXPERIMENTAL

dc conductivity measurements and sample preparation for various phosphate glasses were followed from our earlier paper.³ The specimens of glass discs (about 4 cm diam. \times 0.4 cm thick) were cut from the sample glass blocks, ground, and polished with $< 1 \mu m$ Al_2O_3 paste. Gold electrodes with double guard rings were evaporated onto the samples in order to avoid surface conduction due to water in ambient atmosphere. The dc conductivity measurements were made with a vibrating reed electrometer (impedance = $10^{16} \Omega$) over a temperature range from 100 to 200 °C. The time required for steady-state conduction depends on the conductivity and temperature of the sample. Usually, it was established within 30 min at 100 °C and within 1 min at 200 °C.

The protonic conductivity measured was reproduced once more by the experiment and the Arrhenius plots of the conductivity gave essentially straight lines. So, the conductivity measured is the intrinsic protonic conductivity; it is not due to the surface protonic conductivity nor the conductivity due to ambient water that entered the materials.

The concentration of protons in glasses was determined by infrared spectroscopy using the absorbance at the absorption peak due to OH vibration, the molar absorption coefficient, and the thickness of platelike glass specimens; the method followed was from our previous paper.⁸

Conductivity data for alkali-silicate glasses have been often plotted against mol % of alkali-metal ions in many references. In this paper, we replotted them against a concentration of mol/l of alkali-metal ions.

III. RESULTS AND DISCUSSION

Generally, the electrical conductivity (σ) depends on temperature as shown by Eq. (1) and on the number (N) of electric charge carriers per unit volume by Eq. (2);

$$\sigma = \sigma_0 \exp(-E_{dc}/RT), \quad (1)$$

$$\sigma = N\mu ze, \quad (2)$$

where E_{dc} is the apparent (experimental) activation energy for dc electrical conduction, R is the gas constant, T is temperature in degrees K , σ_0 is the preexponential term called the frequency factor, z is the charge number ($z=1$ for alkali ions and protons, respectively), e is the electronic charge, and μ is the mobility. When we consider the effect of variables such as composition, structure, and temperature on the electrical conductivity, we are concerned with two separate contributors, i.e., the concentration of charge carriers and their mobility. It is very convenient if the conductivity of a glass can be evaluated from the chemical composition, but Eq. (2) is not applicable to this evaluation, because we cannot know the "true" numbers of carriers (N) but can know only the "chemical concentration" (nominal concentration) of the carriers such as alkali ions and protons.

The activation energy for cationic migration (E_A) in alkali-silicate glasses is given by Eq. (3) according to the Anderson-Stuart (AS) model⁹ based on the strong electrolyte theory,

$$E_A = E_b + E_s, \quad (3)$$

where E_b and E_s are electrostatic binding and strain energies, respectively.

On the other hand, according to Ravaine-Souquet (RS) model^{10,11} based on the weak electrolyte theory, Eq. (4) is given for sodium silicate glasses,

$$E_A(\sigma) = \Delta H/2 + E_m, \quad (4)$$

where ΔH is the enthalpy of the reaction, $\text{Na}_2\text{O} = \text{Na}^+ + \text{ONa}^-$, and E_m is the migration energy.

Martin and Angell¹² identify the dissociation energy of the RS model ($\Delta H/2$) with the binding energy of the AS model (E_b), and the migration energy (E_m) with the corresponding elastic strain energy (E_s); there could be no substantial difference between the AS and RS models. However, it has not been elucidated so far how the above terms such as E_b , E_s , and E_m depend on the carrier concentration.

We assume that electrical conduction due to ions in oxide glasses can be regarded as a rate process; in some cases it is rate controlled by the elemental process of ionic transportation (in other words, migration), and in other cases by the elemental process of breaking of O-M bonding.

A. Protonic conduction in alkali-free phosphate glasses

It has been revealed by infrared spectroscopy^{13,14} that there are two types of hydroxyl groups in oxide glasses; one is free from hydrogen bonding ($\nu_{\text{OH}} \approx 3650 \text{ cm}^{-1}$)

and another is hydrogen bonded ($\nu_{\text{OH}} \approx 2800 \text{ cm}^{-1}$), where ν_{OH} is the peak wave number for a given glass of the IR absorption band due to fundamental O-H stretching vibration. The values of ν_{OH} due to hydrogen bonding is known to decrease with the strength of hydrogen bonding. Examples of the IR absorption band due to O-H stretching for alkali-free phosphate glass plates have been presented in Refs. 3, 5, 6, and 15.

By plotting the concentration of hydrogen-bonded protons against dc electrical conductivity for various alkali-free oxide glasses, Abe and co-workers^{3,4} have found that the electrical conductivity (σ) is proportional not to the concentration of mobile protons but to the "square" of the concentration, as shown in Eq. (5); from experimental facts on H-D isotope effect, etc., protons in the alkali-free phosphate glasses have been proved to be the species of electrical charge carriers of the glasses;^{5,6} the species is not H_3O^+ but H^+ ,

$$\sigma_{417} = A_H [\text{H}^+]^2, \quad (5)$$

where σ_{417} is electrical conductivity at a temperature of 417 K, $[\text{H}^+]$ is the concentration of mobile protons in mol/l, which is obtained by infrared spectroscopic determination⁸ of the hydrogen-bonded protons, and A_H is a constant which is a measure of the mobility of the protons, depending on the glass composition or structure (the notation A_H has been described as A_0 in Refs. 3 and 4). From Eq. (2) and (5), the mobility of the protons must be proportional to $[\text{H}^+]$. It is noted that the term A_H varies significantly with ν_{OH} , as shown by Eq. (6),⁴

$$\log_{10} A_H = -0.00970\nu_{\text{OH}} + 17.1. \quad (6)$$

The value of ν_{OH} is known to decrease with the strength of hydrogen bonding. Therefore, Eq. (6) indicates that the protons of O-H groups free from hydrogen bonding in glasses are hardly mobile, whereas those of hydrogen bonded O-H are very mobile; for example, A_H at $\nu_{\text{OH}} \approx 2800 \text{ cm}^{-1}$ is approximately 10^8 times higher than that at $\nu_{\text{OH}} \approx 3650 \text{ cm}^{-1}$. It is known that SiO_2 glass has no nonbridging oxygen ion and no hydrogen-bonded proton; the impurity protons in silica glasses are free from hydrogen bonding ($\nu_{\text{OH}} \approx 3650 \text{ cm}^{-1}$).¹³ Hence, we assert that protons in silica glasses are hardly mobile under a dc electrical field; on the other hand, protons in some phosphate glasses containing a large amount of nonbridging oxygen ions are very mobile.

We found for some phosphate glasses that protons are much more mobile than Na^+ ions. Figure 1, for example, shows that protons are more mobile than sodium ions in a calcium phosphate glass when concentration ratio of $[\text{Na}^+]/[\text{H}^+]$ is less than ~ 10 ; the conductivity increased with $[\text{H}^+]$ as shown by Eq. (5), and did not depend on $[\text{Na}^+]$ within the concentration range of $x=2$ ($[\text{Na}^+] = 1 \text{ mol/l}$). ($x=2$ in Fig. 1 corresponds to $[\text{Na}^+] = 1 \text{ mol/l}$.) When $[\text{Na}^+]$ becomes much higher in the glass, say, $[\text{Na}^+]/[\text{H}^+] > 20$, the conductivity begins to increase with $[\text{Na}^+]$.

It is well known that the ionic conductivity of alkali containing glasses falls markedly when more than one alkali is present;¹⁶ plausible explanations for the mixed al-

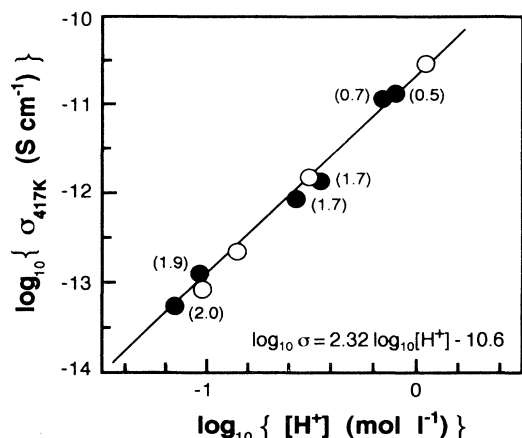


FIG. 1. Effect of added sodium ions on protonic conduction of calcium phosphate glass. Molar composition of base glass: [45 CaO 55P₂O₅ with a small amount of protons indicated in the abscissa of the figure.] Na₂O content: x mol Na₂O was added to the above glass. Open circle: electrical conductivity due to hydrogen-bonded protons ($\nu_{\text{OH}}=2850 \text{ cm}^{-1}$) at $x=0$. Black circle: electrical conductivity for Na₂O containing glass specimen. (The numerical number in parentheses indicates value of x ; $x=2$ mol is estimated to equal to $[\text{Na}^+]=1 \text{ mol/l}$.)

kali effect have been presented recently.^{17,18} The mixed H⁺-Na⁺ effect is not seen in Fig. 1; this may be ascribed by a great difference in mobility between H⁺ and Na⁺ in the calcium phosphate glass.

The experimental activation energy (E_{H}) for the conduction due to protons has been found by us to be expressed by Eqs. (7), (8), and (9);⁴

$$E_{\text{H}} = E_{0,\text{H}} + E_{1,\text{H}}, \quad (7)$$

$$E_{0,\text{H}} \propto \nu_{\text{OH}}, \quad (8)$$

$$E_{1,\text{H}} \propto -\log_{10}[\text{H}^+]. \quad (9)$$

The value of $E_{0,\text{H}}$ is that of E_{H} at $[\text{H}^+]=1$ (mol/l). It is evident that $E_{0,\text{H}}$ is the term of the energy required to overcome binding forces, because as an experimental result $E_{0,\text{H}}$ is expressed in Eq. (8) to be proportional to ν_{OH} , which is considered as a first approximation to be proportional to the O-H binding energy. The $E_{1,\text{H}}$ is regarded to be a term of proton concentration dependence of E_{H} .

The rate-controlling step for the protonic conduction is not the migration step because of the very small ionic radius, but the bond-breaking step between O and H in the hydroxyl groups.

B. Electrical conduction in binary alkali silicate glasses

In contrast to some data of protonic conduction in glasses, a number of data for electrical conductivities and the activation energies of binary alkali oxide-silica glasses have been presented recently by many investigators. However, the mechanism for the electrical conduction has not been elucidated yet, although a few tentative

models such as those of Anderson-Stuart⁹ and Ravaine-Souquet^{10,11} have been proposed so far.

It was found by us that the experimental activation energy (E_{M}) for the electrical conduction due to alkali ions (M^+) decreases linearly with $\log_{10}[\text{M}^+]$, as shown in Fig. 2, which was obtained by replotting the plots of E_{M} vs mol% of alkali ions in Ref. 19 to those of E_{M} vs $\log_{10}[\text{M}^+]$ ($[\text{M}^+]$: mol/l of alkali ions); the relations were expressed by the same formula as those for the protonic conduction as mentioned above by Eqs. (7) and (9).

$$E_{\text{M}} = E_{0,\text{M}} + E_{1,\text{M}}, \quad (10)$$

$$E_{1,\text{M}} \propto -\log_{10}[\text{M}^+], \quad (11)$$

where the value of $E_{0,\text{M}}$ is that of E_{M} at $[\text{M}^+]=1$ (mol/l) or $\log_{10}[\text{M}^+]=0$. It was found for alkali-silicate glasses that $E_{0,\text{M}}$ increases linearly with increasing ionic radius (r_{M}) of alkali ions (Fig. 3); this result indicates that $E_{0,\text{M}}$ for the alkali ions is not a term concerning with the binding energy of O-M but a term with migration of alkali ions, since, if it is the activation energy for alkali migration or transportation through the interstices of the glass network or the energy required to open up the "doorways,"⁹ it should be decreased with decreasing radius of the alkali ions. The electrical conduction process due to alkali-metal ions at $[\text{M}^+]=1$ is assumed to be rate controlled by the migration step.

It is interesting that $E_{0,\text{M}}$ decreases to be nearly zero when extrapolated to $r_{\text{M}}=0$. However, the corresponding activation energy of protons in O-H groups dissolved in SiO₂ glass, i.e., the activation energy at $[\text{H}^+]=1$ (mol/l) in H₂O-SiO₂ glass, has been estimated to be very high (150 kJ/mol),⁴ in spite of its very small ionic radius ($r_{\text{M}} \approx 0$). This implies that the mechanism of the protonic conduction is different from that due to alkali-metal ions, and that the rate-controlling step for the protonic

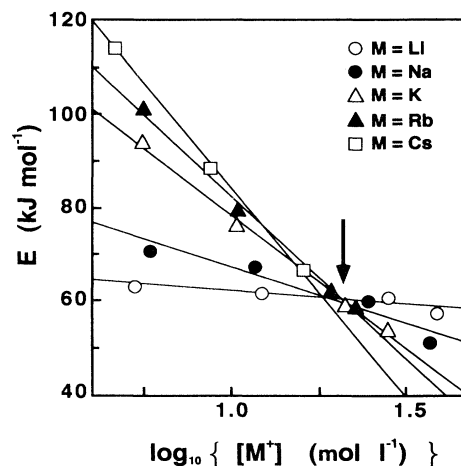


FIG. 2. Dependence of experimental activation energy (E) for dc electrical conduction on concentration of alkali ions $[\text{M}^+]$ in binary alkali-silicate glasses. (The plotting after Charles (Ref. 19) of E vs mol% of alkali ions was replotted by us to E vs mol/l.)

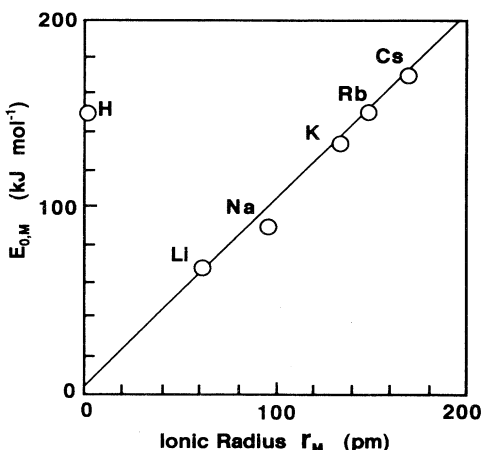


FIG. 3. Dependence of activation energy ($E_{0,M}$) in Eq. (10) on ionic radius of alkali ions (r_M) in binary alkali-silicate glasses, where $E_{0,M}$ is the activation energy at $[M^+] = 1$ (mol/l). (The value for proton was estimated by extrapolation of the linear relation of $E_{0,H}$ vs ν_{OH}).⁴

conduction is not migration step as for alkali ions but is the breaking step of O-H bonding.⁴ Once O-H bonding is broken, protons are considered to be transported by hydrogen bonding through adjacent nonbridging oxygen to next O-H sites.¹⁵ The point of intersection of various linear curves in Fig. 2, which lies at around $\log_{10}[M^+] = 1.3$, pointed by an arrow in the figure, corresponds nearly to the composition of alkali disilicate, $M_2O_2SiO_2$. It is reasonable to consider for M_2O $mSiO_2$ glasses with $m > 2$ that the rate-controlling step of the electrical conduction process is the migration (or the doorways) step of alkali ions (M^+). Addition of alkali oxide (M_2O) to SiO_2 glass having no nonbridging oxygen results in the formation of binary M_2O - SiO_2 glass having nonbridging oxygen. However, in the composition region of low alkali content at $m > 2$, silica network consisting of Si-O-Si linkage without nonbridging oxygen remains in a part of the glass structure. In order for dc electrical currents to flow in this region of low alkali content, the electrical charge carriers of alkali ions must migrate through the interstices, "bottleneck," of the silica network in which no nonbridging oxygen exists; the larger the ionic radius of the alkali-metal ions, the more difficult the migration.

This situation does not hold for the binary M_2O $mSiO_2$ glasses when $m < 2$. Figure 4 gives plots of the experimental activation energy (E_M) at a constant concentration of $\log_{10}[M^+] = 1.5$ against the ionic radius of alkali ions (r_M). Contrary to the results of the glasses with $m > 2$, E_M at $m < 2$ decreases almost linearly with r_M . That is, the rate-controlling step of the electrical conduction process in alkali-rich compositions at $m < 2$ is not the step of the ionic migration, but that of the breaking of O-M bonding. In that composition region of $m < 2$, the structural unit of every SiO_4 group is considered to have more than one nonbridging oxygen. That is, every alkali ion is adjacent to each other, thereby, the activation energy for the transportation of alkali ions to the neighboring sites of SiO_4 groups or for the doorway should be

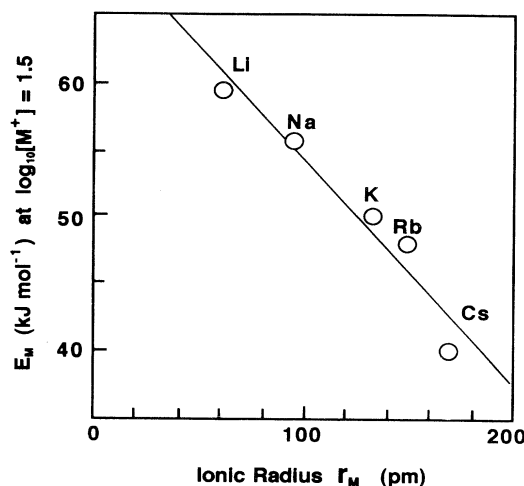


FIG. 4. Dependence of activation energy (E_M) in Eq. (10) on ionic radius of alkali ions (r_M) in binary alkali-silicate glasses, where the values of E_M at $\log_{10}[M^+] = 1.5$ are plotted.

very small, irrespective of their ionic radius; the alkali ions need not any more to migrate through the interstices of the silica network consisting of bridging oxygens. In this case, the breaking of O-M bonding is the rate-controlling step. By analogy from Eq. (8) in protonic conduction, E_M may be expressed in relation to ν_{OM} , the peak wave number of the far IR absorption band at around $100 \sim 400 \text{ cm}^{-1}$ due to O-M stretching vibration.

The conductivity dependence on concentration of mobile protons is shown by quadratic relation as expressed by Eq. (5). We found for ionic conduction in the Na_2O - SiO_2 system that this quadratic relation holds for

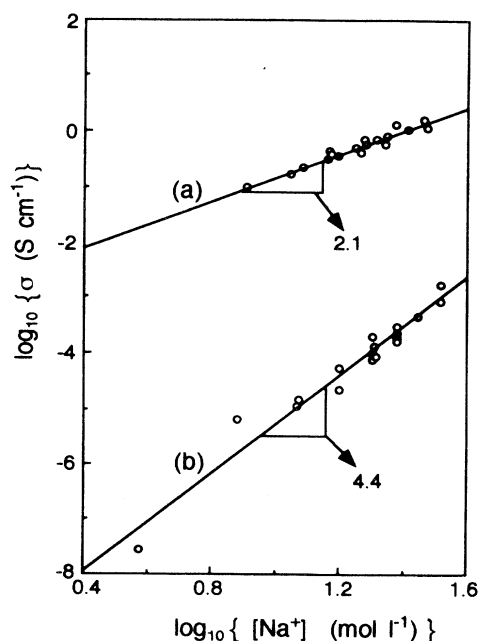


FIG. 5. Plots of $\log_{10}\sigma$ vs $\log_{10}[Na^+]$ for the Na_2O - SiO_2 system at 1200°C (a) and 300°C (b). These data were replotted from Refs. 20 and 21, respectively.

the melts at high temperature such as 1200 °C, but it does not hold for the glasses at a low temperature such as 300 °C. Figures 5(a) and 5(b) are plots of the logarithm of conductivity vs logarithm of chemical concentration of Na^+ ($=[\text{Na}^+]$), where the former data were replotted from plots of resistivities vs $[\text{Na}^+]$ in Ref. 20 and the latter data were from plots of the logarithm of conductivity vs $[\text{Na}^+]$ in Ref. 21. It is interesting that the quadratic relation holds for the molten state of the $\text{Na}_2\text{O-SiO}_2$ system; it is reasonable to consider that almost all of the chemical concentration of Na^+ ions for the molten state are mobile ions under a dc electrical field, whereas for the rigid glassy state some Na^+ ions are located at immobile sites, and the other ones are at mobile sites. The ratio of immobile Na^+ to mobile Na^+ in glasses will be discussed further elsewhere by referring to much more data.

IV. SUMMARY

It is found for a calcium phosphate glass that the mobility of hydrogen-bonded protons is found to be much higher than that of Na^+ ions. dc electrical conduction

due to alkali ions in $M_2\text{O } m\text{SiO}_2$ glasses is discussed by comparing with the data of protonic conduction. The electrical conduction process is regarded to be rate controlled by the elemental step of breaking O-M bonding and the migration step of the charge carriers. The rate controlling at $m > 2$ is the migration step of alkali ions through interstices of the silica network, and that at $m < 2$ the O-M bond breaking step appears. Protonic conduction is rate controlled by the O-H bond-breaking step. Experimental activation energies for alkali-metal ions and protons decrease linearly with the logarithm of the carrier concentration. The conductivities are suggested to be proportional to the square of the concentration of mobile alkali-metal ions or mobile protons. The mobilities are considered to increase with the carrier concentrations.

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