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Effect of sorbed water on the electrical resistance of polysodium phosphate thin films

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Measurements have been made of complex impedance and sorbed water of polysodium phosphate. The resistance and its activation energy decreases with an increase in the amount of sorbed water. The amount of sorbed water is strongly affected by the Na_2O/P_2O_5 mol ratio. The humidity dependence of the activation energy and the resistance is lowered by decreasing the average chain length of polysodium phosphate. This results in an increase in the amount of sorbed water. Especially, in low humidity conditions, the decrease in the resistance and the activation energy are achieved by increasing the concentration of the strongly acidic PO–H group. These improvements can not be achieved by increasing the Na_2O/P_2O_5 mol ratio. In a humid atmosphere, the resistance of the film, in which the Na_2O/P_2O_5 mol ratio is less than 0.8, is inversely proportional to the concentration of the strongly acidic PO–H group.

1. Introduction

In recent years there has been great interest in the development of humidity sensors. For humidity sensors using porous metal oxides [1–4] the admittance is usually enchaned by the sorption of water. Upon exposure to the atmosphere, strongly bound water molecules quickly occupy the available sites of porous metal oxides. Once the first layer has been formed, subsequent layers of water molecules are physically adsorbed and the physisorbed water dissociates due to the electrostatic field in the chemisorbed layer

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Charge transport occurs when the hydronium ion releases a proton to a neighbouring water layer [5]. A porous metal oxide is a material adequate for a conventional humidity sensing device. However, the usual metal oxide has the disadvantage of having an impedance of $10^8\,S^{-1}\,cm$ or more in the low humidity region. In order to overcome this disadvantage, the addition of a mobile alkali ion and/or dissociative proton into the porous metal oxide was considered. Previously, it has been reported [6] that sintered zircon with sodium phosphate and phosphoric acid is desirable in a humidity sensor with respect to sensitivity and stability. In addition, the admittance is affected by the concentration of sodium phosphate as an additive. Furthermore, it was confirmed that the admittance is affected by the concentration of the dissociative protons which exist on the zircon surfaces which have been sintered with phosphoric acid [7]. This paper presents the results of a study investigating the effects of the composition of sodium phosphate polymer on water adsorptivity and the resistivity of polymer thin films.

2. Experimental details

2.1. Materials

Sodium phosphate (Na_2HPO_4) and phosphoric acid were used. The raw materials were weighed in the prescribed mol ratio and mixed. The mixed samples were melted and condensed at temperatures near 1000° C for 3 h. The melts were quenched rapidly by pouring them on a large copper plate. The solid melts were then pulverized. 0.2 g of powder was dissolved in 5 ml of distilled water and permitted to stand for at least 1 week. The prepared solution was coated on the substrate (α-Al_2O_3) with a pair of gold electrodes by the dipping method and dried in air at 100° C. The structure of the sensor element is illustrated in Fig. 1.

2.2. Measurements

The structure and the concentration of polysodium phosphate protons were examined by the pH titration method with 0.1 N NaOH solution [8]. The amount of sorbed water was determined by gravimetrical measurements.

Humidity–impedance characteristics were measured with impedance meters (Hewlett Packard 4276A and 4277A) in the range from 10^2 to 10^6 Hz. Humidities (%r.h.), ranging from 0 to 90, were prepared by mixing dry and moist air in controlled proportions.

3. Results

3.1. Structure of polysodium phosphate

By quickly chilling melts in the Na_2O/P_2O_5 system, a continuous series of water soluble glasses were produced. Van Wazer [9] reported that the sodium phosphate glasses can be divided into two groups. Case I is where the Na_2O/P_2O_5 mol ratio is equal to or greater than unity and Case II where the range is between pure P_2O_5 and $Na_2O \cdot P_2O_5$. In Case I there are no branching points and hence the PO_4 groups must be interlinked into chains or rings. Furthermore, the average chain length decreases with the increasing Na_2O/P_2O_5 mol ratio [10]. In the composition range between pure P_2O_5 and Na_2O/P_2O_5, the melts have a

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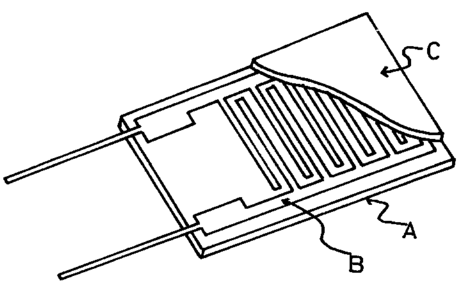
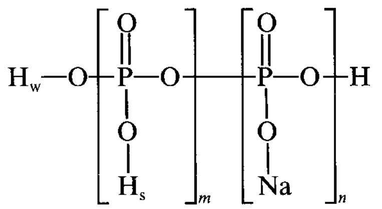


Figure 1 Schematic illustration of sensor. A–alumina substrate; B–gold electrode; C–polysodium phosphate.

three-dimensional structure [9] which are destroyed when the melts are dissolved in water. When viscosity measurements of a polysodium phosphate solution were recorded, an initial decrease was observed, after which the viscosity remained constant for 1 week. Such a decrease is caused by the hydrolysis and degradation of the sodium phosphate polymer's branch points. It seems that only straight chain or unbranched ring phosphate ions exist in aqueous solution. During the titration of the polysodium phosphate solutions, two distinct neutralization points were confirmed at pH 4.5 and 9.0 with no neutralization points observed in the range between pH 4.5 and 9. It appears that the ring phosphate is the minor product. From the titration curves, the concentration of the strongly ionized protons, which refers to a proton from a phosphorus atom, can be estimated by the pH 4.5 point. The weakly ionized protons, which refers to a proton from the ends of polyphosphate chains can be estimated by the pH 9.0 point. As shown in Fig. 2, the concentration of both types of hydrogen decreases with an increase in the Na_2O/P_2O_5 mol ratio. The existence of the strongly ionized proton can not be confirmed in Case I ($Na_2O/P_2O_5 \geqslant 1.0$). For simplicity, it is assumed that the polymer, when dissolved in water, consists only of the straight chain phosphate molecule. The structure of the polymer can then be expressed as follows



$$\mathrm{H_w{-}O{-}\left[P(=O)(O{-}H_s){-}O\right]_m{-}\left[P(=O)(O{-}Na){-}O\right]_n{-}H}$$

The H_w refers to a weak acidic proton and the H_s refers to a strong acidic proton. The m and n indicate the number of individual units, and their sum equals the average chain length. These numbers were estimated from the titration results and are shown in Fig. 3. It is clear that the chain length of the polymer increases with the prescribed mol ratio of Na_2O/P_2O_5 in Case II. In Case I, any distinct neutralization points in the titration curves can not be confirmed. Therefore the average chain length (m) was estimated from the mol ratio of raw materials by the use of the $Na_2O/P_2O_5 = (m + 2)/m$, [10] relation assuming that the ring sodium phosphate is the minor product.

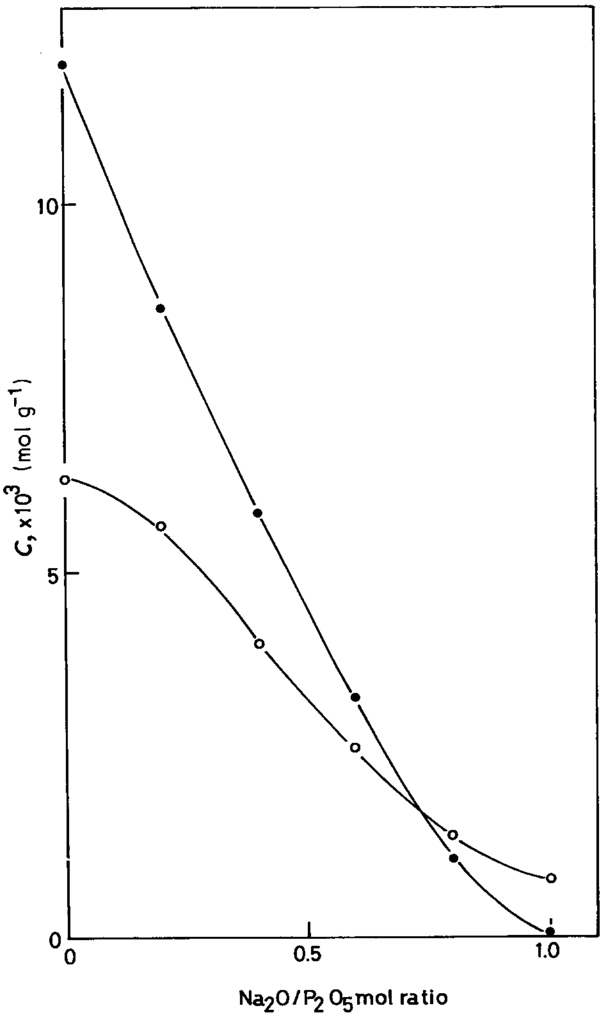


Figure 2 Mol ratio dependence of protons. (●) strongly ionized proton (C_{HS}); (○) weakly ionized proton (C_{HW}).

3.2. Electrical properties

Complex impedance analysis has been employed to evaluate the impedance measurements since it seems that the impedance consists of both resistive and capacitive components. Complex impedance plots are shown in Fig. 4. In the low humidity region, the high frequency results are represented by nearly perfect circular arcs; all of which pass through origin. The low frequency results are represented by straight lines. The resistance components, R_p, are easily estimated from the intercepts of straight lines and/or circles to the real axis. The humidity dependence of R_p is shown in Fig. 5. For all samples, R_p decreases with an increase in humidity. In Fig. 6, the relationship between the logarithm of R_p and the Na_2O/P_2O_5 mol ratio is shown. It is clear that the mol ratio dependence of R_p is complex and the maximum point of R_p is shifted in the direction of the increase in the mol ratio with a decrease in the humidity.

3.3. Amount of sorbed water

In Fig. 7, the relationship between the amount of sorbed water (ΔW_{H_2O}) and the Na_2O/P_2O_5 mol ratio is shown. At 20% r.h. or below, the weight change caused by water sorption in the sample in which the Na_2O/P_2O_5 mol ratio is greater than 1.0 can not be measured. The amount of sorbed water decreases in relation to an increase in the mol ratio. At each humidity, the mol ratio corresponding to the point in which the amount of sorbed water is at minimum is

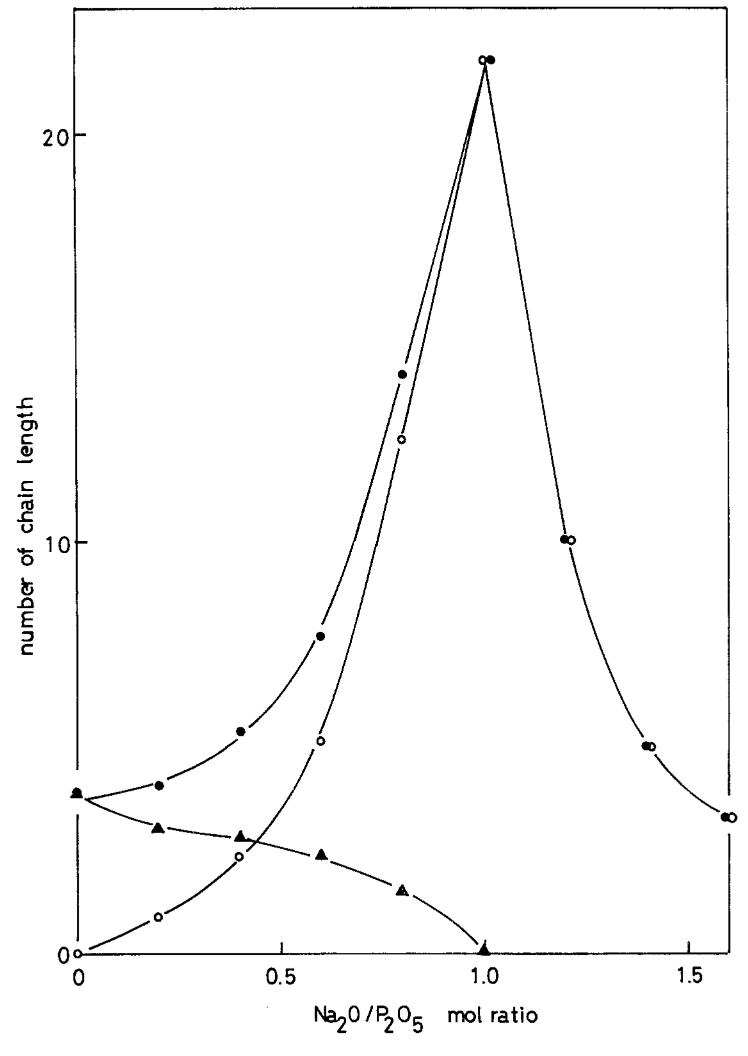


Figure 3 Mol ratio dependence of *n* and *m*. (▲) *n*; (○) *m*; (●) *m* + *n*.

approximately equal to the mol ratio in which R_P is at a maximum.

4. Discussion

In general, the resistivity, R, is expressed as

$$R = (ne\mu)^{-1} \quad (1)$$

where n is the carrier concentration, μ is the carrier mobility and e is the element of charge, respectively. It is expected that the resistivity is inversely proportional to the carrier concentration when the carrier mobility is constant. If it is assumed that the dominant charge carriers are protons, the two processes for the charge

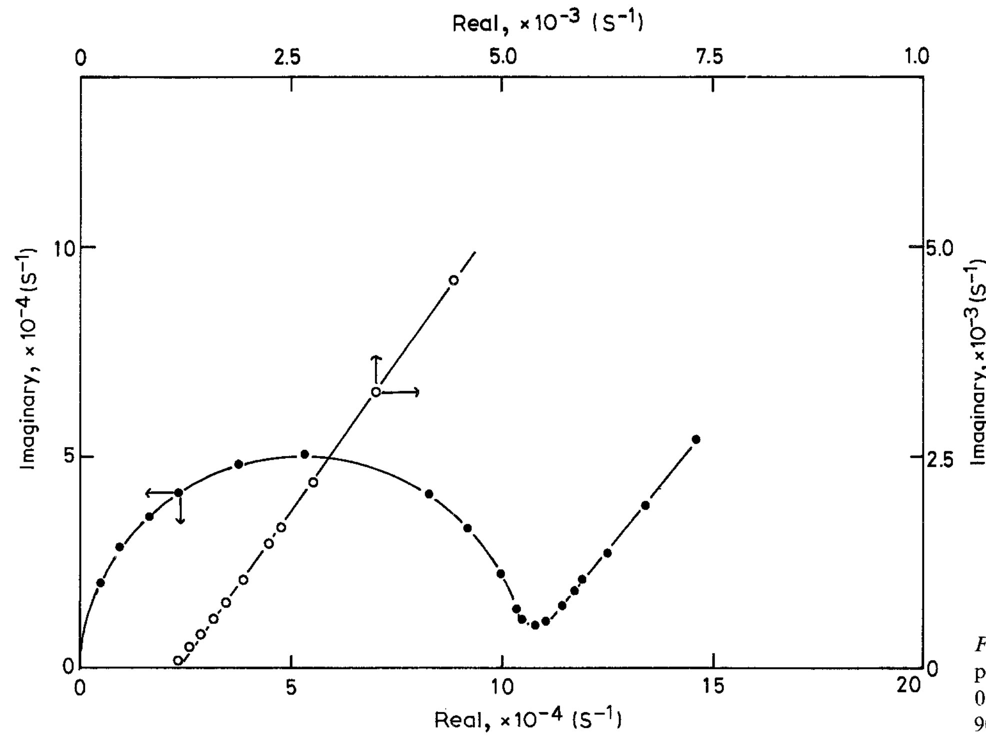


Figure 4 Complex impedance plots for the film (Na_2O/P_2O_5 = 0.4). Humidity (●) 40% r.h.; (○) 90% r.h.

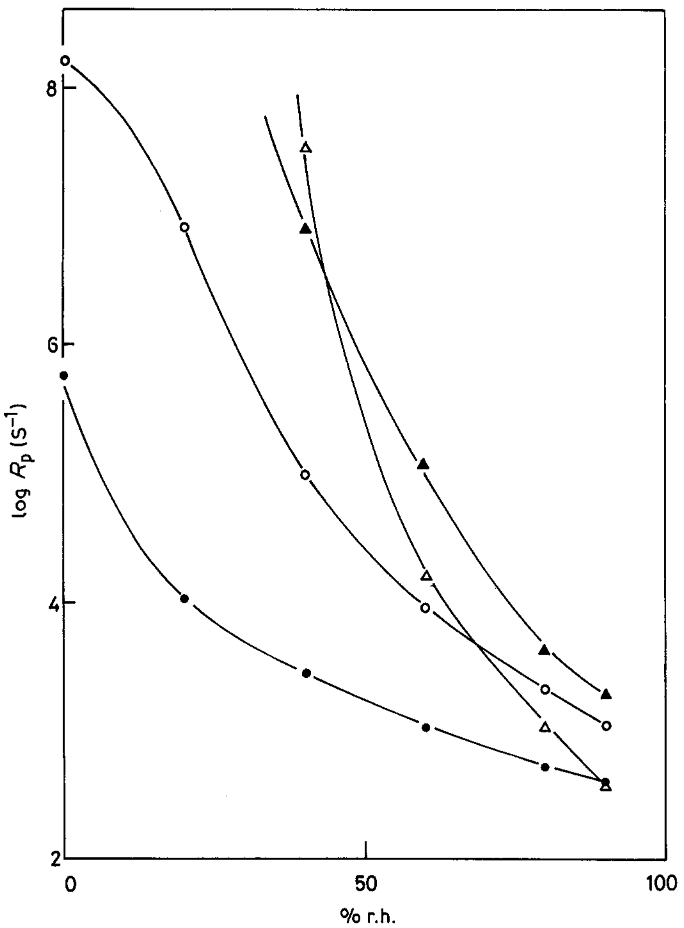


Figure 5 Humidity dependent of R_p. Na_2O/P_2O_5 mol ratio: (●) 0.0; (○) 0.4; (▲) 0.8; (△) 1.2.

carrier creation can be, the dissociation of sorbed water ($2H_2O \rightleftharpoons H_3O^+ + OH^-$) and the dissociation of PO–H groups ($PO{-}H \rightleftharpoons PO^- + H^+$). For the former case, the extent of dissociation can be approximated from the equilibrium constant, K, for the dissociation reactions

$$K = \frac{(H^+)(OH^-)}{(H_2O)} = \exp(\Delta Sd/k)\exp(-\Delta Hd/kT) \quad (2)$$

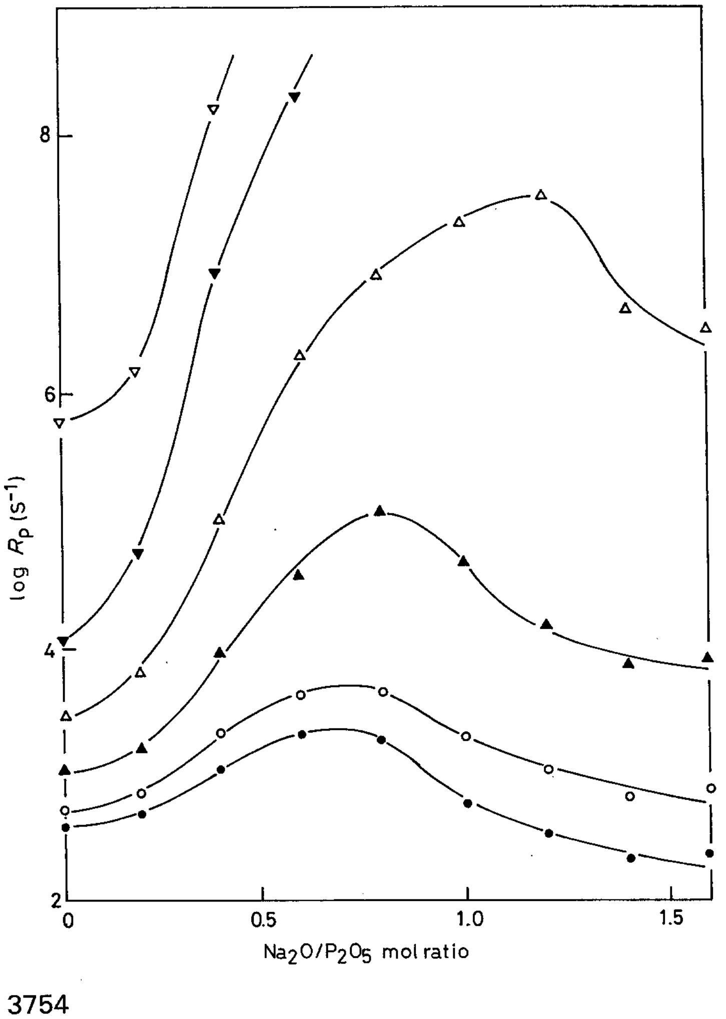


Figure 6 Relationship between R_p and Na_2O/P_2O_5 mol ratio. Humidity: (▽) 0% r.h.; (▼) 20% r.h.; (△) 40% r.h.; (▲) 60% r.h.; (○) 80% r.h.; (●) 90% r.h.

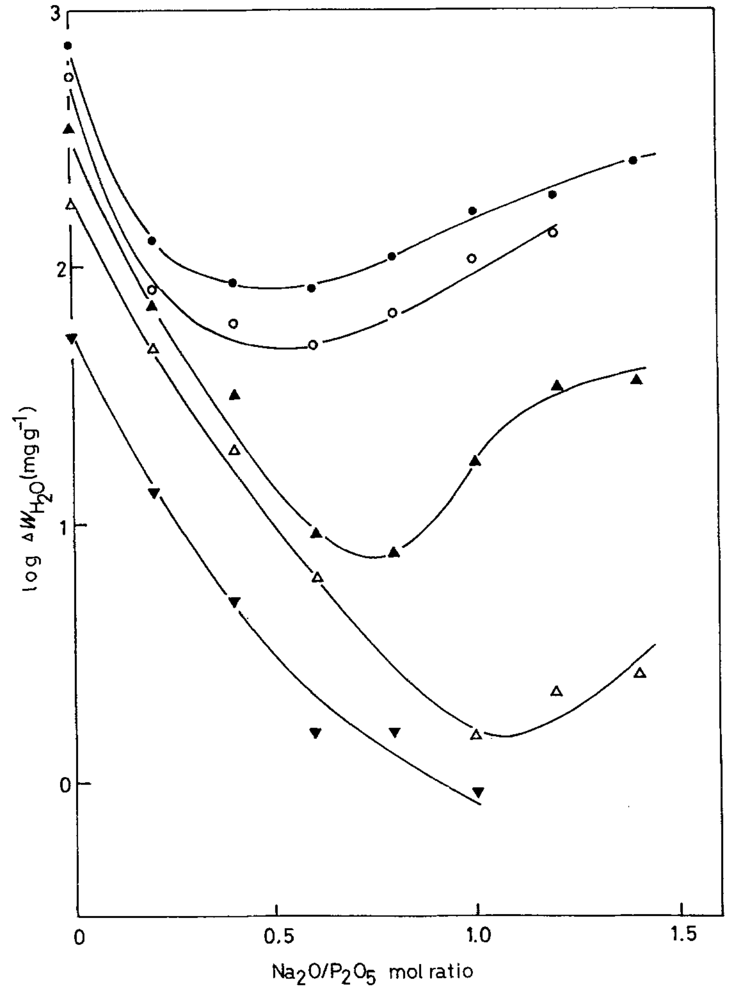


Figure 7 Relationship between ΔW_{H_2O} and Na_2O/P_2O_5 mol ratio. Humidity: (▼) 20% r.h.; (△) 40% r.h.; (▲) 60% r.h.; (○) 80% r.h.; (●) 90% r.h.

Considering the requirement for electrical neutrality, the carrier concentration (n) can be expressed as

$$n = (H_2O)^{1/2} \exp(\Delta Sd/2k) \exp(-\Delta Hd/2kT) \quad (3)$$

where ΔSd and ΔHd are the carrier formation entropy and enthalpy, respectively. For the latter case, the carrier concentration (n) can be expressed as

$$n = (PO\text{-}H)^{1/2} \exp(\Delta Sp/2k) \exp(-\Delta Hp/2kT) \quad (4)$$

When the sample in which the Na_2O/P_2O_5 mol ratio in water is less than 0.8, the solution was acidified with the sample. It is expected that the mobile proton is produced by the dissociation of PO–H groups and the sorption of water. Especially in humid atmosphere, the Grotthuss-type proton transport may predominantly occur. For simplicity, it is assumed that the mobile proton produced by the dissocation of strongly acidic PO–H groups and the concentration of this dissociated proton is much larger than that produced by the dissociation of sorbed water. While it is difficult to estimate the concentration of the mobile proton at each humidity, the concentration of the mobile protons in humid atmosphere can be approximated by the concentration of protons in the water solution and/or the concentration of the strongly

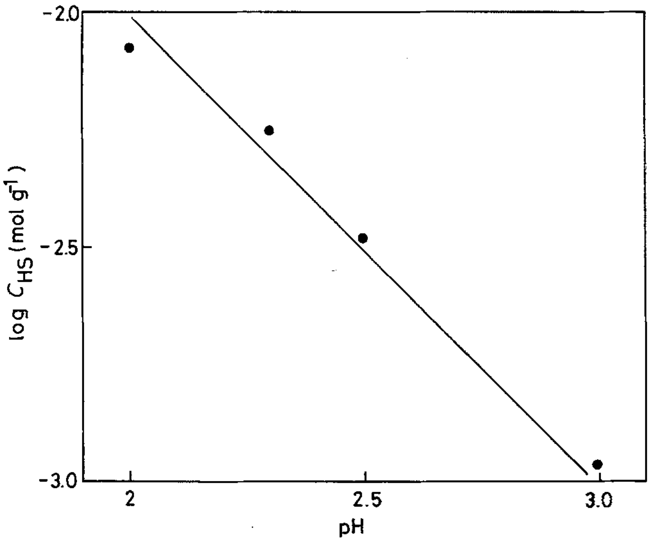


Figure 8 Relationship between C_{HS} and pH of solution.

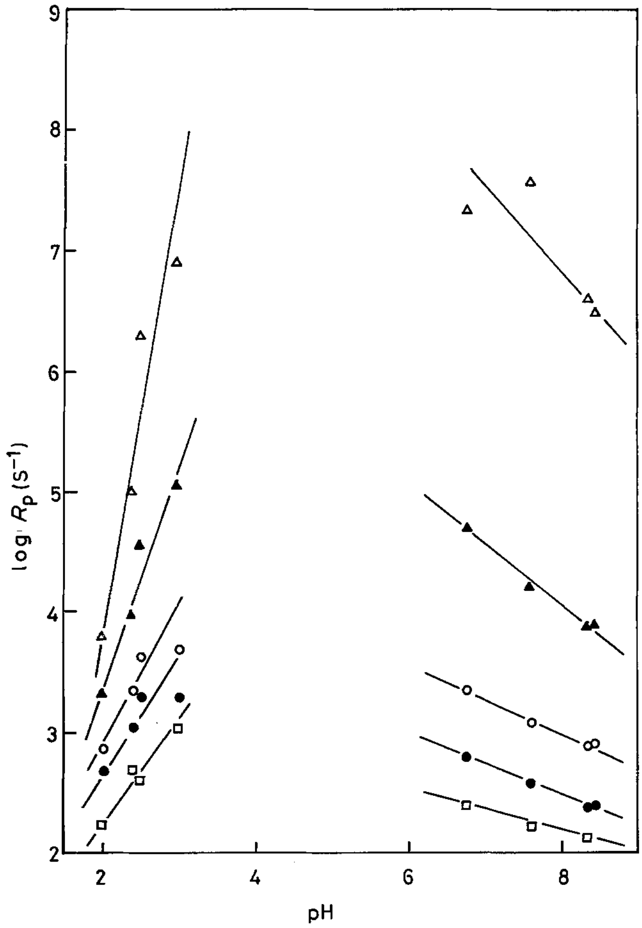


Figure 9 Relationship between R_p and pH. Humidity: (△) 40% r.h.; (▲) 60% r.h.; (○) 80% r.h.; (●) 90% r.h.; (□) solution.

acidic PO–H group which is estimated from the results of the pH titration curves. In Fig. 8, the relationship between the pH and the logarithm of concentration of strongly acidic PO–H groups is shown. In this case, the value of the pH was measured by using 50 ml deionized water with 0.1 g of sample. It is clear that the slope of the line is almost equal to -1. This indicates that the dissociation of strongly acidic PO–H occurs in solution. In Fig. 9, the relationship between the logarithm of R_p at each humidity and the pH value of the solution with the corresponding sample. In addition, the resistance of the 50 ml solution with 0.1g of sample is shown in Fig. 9. It is obvious that the slope of the line in the relationship between the logarithm of the resistance of the solution and the pH value is nearly equal to unity and a similar relationship between the logarithm of R_p at 90 %r.h. and the pH value is confirmed. This indicates that R_p is inversely proportional to the concentration of the strongly ionized protons in a humid atmosphere ($\geqslant 80$ %r.h.), and strongly acidic protons dissociate completely acting as the charge carrier for the sample in which the Na_2O/P_2O_5 mol ratio is less than 0.8. On the other hand, the slope of the line in Fig. 7 increases with a decrease in humidity. If the carrier migration path consists of the sorbed water layer (continuous water layer) and the concentration of carrier is limited by the solubility product of the sample, it is expected that the carrier concentration is linearly proportional to the amount of sorbed water. To examine this hypothesis; the relationship of the logarithm of R_p and the logarithm of the amount of sorbed water is shown in Fig. 10 for the sample in which the Na_2O/P_2O_5 mol ratio is 0.4. While the value of R_p decreases with an increase in the sorbed water, the slope of the line is estimated to be ≈ -2 in the range where the water content is 1 wt% or above. In the range of lower water contents, the slope of the curve increases with decreases in the water content. At the high water contents, charge transport occurs when the hydronium ion releases a proton to a neighbouring water molecule (Grotthuss chain reaction), while at the low contents, H_3O^+ diffusion and H^+ transfer occur and the continuous layer of sorbed water can not be formed. In addition, at low water contents, the degree of freedom of sorbed water may be hindered by the PO–H and/or PO–Na groups. The distinction between the observed slope and the predicted slope in the relationship between the logarithm of R_p and the logarithm of the water content may be realized qualitatively in terms of the variation of movability of the charge carrier with water content, i.e. the alternation from the Grotthuss chain reaction to H_3O^+ diffusion and H^+ transfer with decrease in the water content. On the other hand, for the sample in which the Na_2O/P_2O_5 mol ratio is equal to or greater than unity, any strongly acidic protons can not be detected and 50 ml ion-exchanged water is made basic with 0.1g of sample. In addition, the pH value increases with an increase in the Na_2O/P_2O_5 mol ratio. In this case, the dissociation reaction can be expressed as

$$Na_{m+2}(PO_3)_3 \rightleftharpoons xNa^+ + Na_{m+2-x}(PO_3)_m^{-x} \quad (15)$$

Therefore, it is expected that the mobile carriers are Na^+ and OH^- instead of H^+. In Fig. 9, the relationship between the logarithm of R_p at each humidity and the pH value of the solution with each corresponding sample is shown. Furthermore, the resistance of the

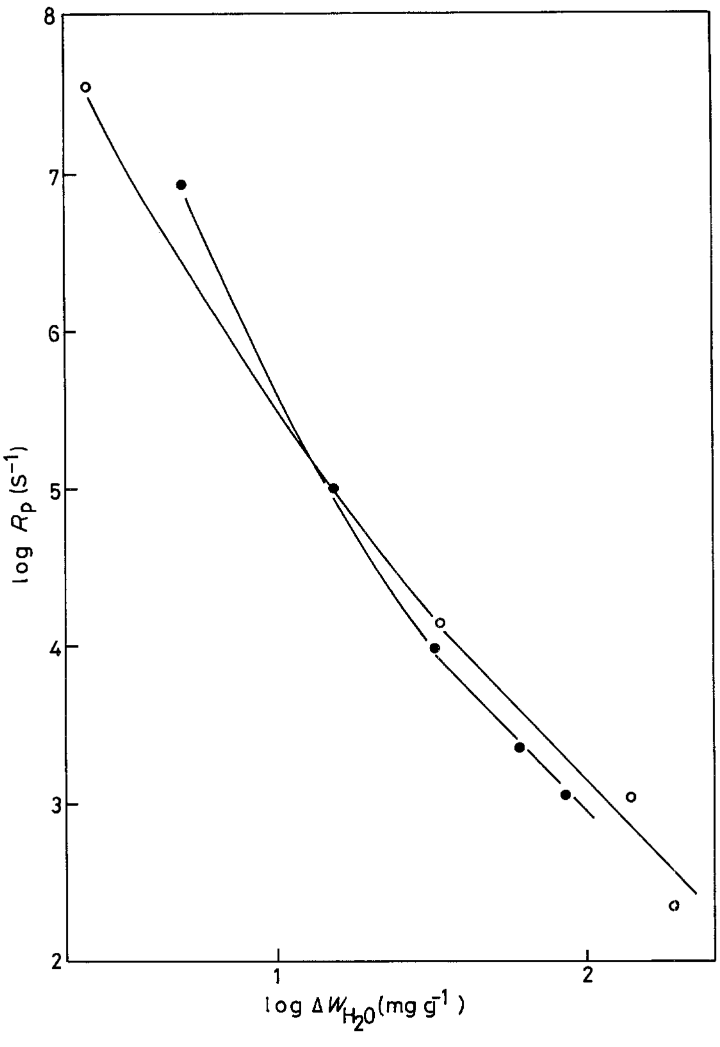


Figure 10 Relationship between R_p and ΔW_{H_2O}. (○) Na_2O/P_2O_5 1.2; (●) Na_2O/P_2O_5 0.4

50 ml solution with 0.1g of sample is also shown in this figure. At each humidity, a linear relationship was confirmed and the slope of the line decreased with an increase in humidity approaching the value of the slope of the line confirmed in the solution. While R_p is inversely proportional to the concentration of strongly ionized protons for the sample in which the Na_2O/P_2O_5 mol ratio is less than 0.8, for the sample in which the Na_2O/P_2O_5 mol ratio is larger than unity, the slope of the line at 90 %r.h. was estimated to be approximately $-1/3$. This indicates that the dissociation process of the sodium ion is complex and the charge carrier is not only the OH^- ion but also the dissociated Na^+ ion and/or the counter anion. As previously mentioned, if the concentration of carrier is limited by the solubility product of the sample, it is expected that

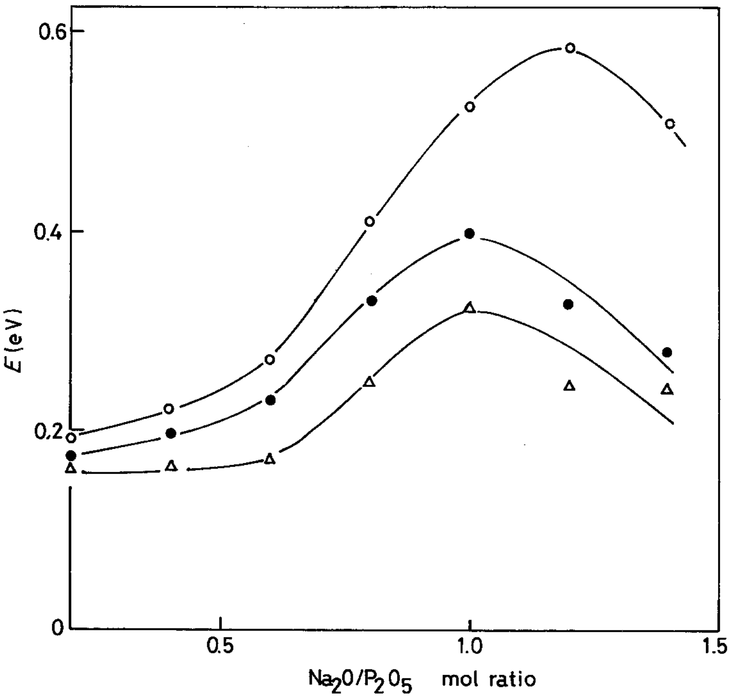


Figure 11 Mol ratio dependence of activation energy of R_p. Humidity: (○) 40% r.h. (●) 60% r.h.; (△) 80% r.h.

the carrier concentration is linearly proportional to the amount of sorbed water. But, as shown in Fig. 10, this expected relationship can not be confirmed. It means that a continuous layer of sorbed water can not be formed in low humidity regions.

The temperature dependence of resistance for all samples can be expressed as

$$R_p = R_0 \exp(-E/kT) \qquad (6)$$

where R_0 is the pre-exponential factor and E is the activation energy. To confirm the temperature dependence on resistance, the activation energy was estimated using Equation 5 from the resistance measured in the temperature range from 30 to 45° C. The relationship between the activation energy and the Na_2O/P_2O_5 mol ratio is shown in Fig. 11. With varying composition, the value of E has a maxima at each humidity and decreases with an increase in humidity. It is lowered with an increase in the water content. This tendency can be qualitatively interpreted in terms of the alternation of charge transport mechanism as previously mentioned.

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