A humidity sensor using alkali salt-poly(ethylene oxide) hybrid films

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Impedance-humidity characteristics of alkali salt doped poly(ethylene oxide) were studied. Complex-plane impedance analyses have been performed. At each humidity and temperature combination, the resistance corresponding to the ionic migration in the bulk of the film has been estimated. The sensor, composed of poly(ethylene oxide) doped with an alkali salt having a high propensity for complex formation between poly(ethylene oxide) and the alkali cation, has a good impedance variation in the range 10^7 to $10^3 \Omega$ by the humidification and desiccation process, and no apparent hysteresis can be observed. The impedance variation is interpretable in terms of the expansion of the free volume by the plasticizing effect of sorbed water.

1. Introduction

There has been great interest in recent years in the development of humidity sensors. Many types of material, such as porous oxides [1, 2] and polymers [3, 4], have been proposed for humidity sensors. In humidity sensors using polymer thin films, the admittance is usually enhanced by the sorption of water. A hydrophilic polymer is an adequate material for conventional humidity-sensing devices which require fast response, reproducibility and durability. Generally, the sorption of water in the polymer occurs predominantly by water diffusion, and so the sensor is composed of surface electrodes and a thin film of polymer formed on the substrate.

Polyethers such as poly(ethylene oxide) and poly(ethylene succinate) are hydrophilic polymers and dissolve many types of inorganic salt to high concentrations. Complexes of poly(ethylene oxide) with alkali salts have received some attention because of the possible applications as solid electrolytes in which conduction is considered to arise from essentially cationic migration. Since poly(ethylene oxide) is a hydrophilic polymer, it is expected that the conduction of complexes of poly(ethylene oxide) with alkali salts varies considerably with water sorption.

This paper presents the results of a study of the humidity dependence of the impedance for poly(ethylene oxide)-alkali salt hybrid films.

2. Experimental details

2.1. Sensor preparation

Poly(ethylene oxide) (PEO, molecular weight 5×10^7) and various alkali salts were used. Both samples were dissolved in acetonitrile in the prescribed molar ratio. The prepared solution was coated on the substrate (α-Al_2O_3) with one pair of gold electrodes by the dipping method. The coated film was dried in a nitrogen atmosphere at 150° C for 12 h. The structure of the sensor is illustrated in Fig. 1.

2.2. Measurements

Humidity-impedance characteristics were measured with impedance meters (10^2 to 10^6 Hz, Hewlett Packard 4276A and 4277A) to avoid electrode polarization. Relative humidities (r.h.), ranging from 0 to 90% were prepared by mixing dry and moist air in controlled proportions in the temperature range of 30 to 50° C.

3. Results and discussion

In our previous paper [5] it was reported that the sensor composed of PEO-$LiClO_4$ film had a good impedance variation in the range of 10^7 to $10^3 \Omega$ by the humidification and desiccation process, and a superior sensitivity over the whole humidity range. A similar humidity dependence of impedance could not be confirmed for some polymers such as polymethylmethacrylate, polyvinylacetate and polyvinylpyrrolidone doped with $LiClO_4$, and sensitivity in the low-humidity region was absent.

In Fig. 2, the impedance-humidity relationships for PEO-$LiClO_4$ are shown. The impedance at 10^3 Hz decreases exponentially with an increase in humidity. The response time was estimated to be within 60 sec in the humidification and desiccation process.

The sensor durability is shown in Fig. 3 for PEO-$LiClO_4$. The sensitivity did not change for more than 100 days. The humidity dependence of impedance depends not only on the polymer species, but on the species of alkali salt used as the dopant. The impedance-humidity relationships are shown in Figs. 4 to 6. It is clear that the impedance is dependent on the species of alkali salt in the humid atmosphere, but not dependent in a dry atmosphere. In general, it is confirmed that the impedance decreases with an increase in the anion radius of the alkali-salt dopant.

It is well known that cyclic ethers (crown ethers) are effective complexing agents for alkali-metal cations. In addition, complex formation between high molecular weight polyethers and alkali salts is known to occur. In all of these cases the dominant interaction is
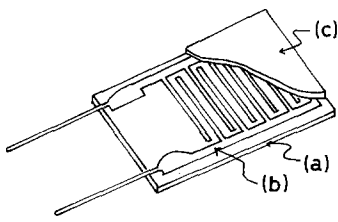
Figure 1 Schematic illustration of sensor: (a) alumina substrate, (b) gold electrode, (c) hybrid film.

the coordination of ether oxygen atoms to alkali cations. The formation of solid polyether salts fits into this pattern. Schriver *et al.* [6] indicated that the formation of solvent-free complexes closely relates to the lattice energies of the alkali salts, and is restricted to the salts of a particular cation which are below a threshold lattice energy. The propensity to form a complex is found for alkali salts having small cations and large anions, such as ClO_4^- and Cl^-. The ion radius of pure alkali salts and the probabilities of complex formation with PEO, reported by Schriver *et al.* [6], are summarized in Table I.

It is clear that alkali salts can be classified into two categories; complex-forming salts and non-complex forming salts. Fig. 7 shows the relation between the reciprocal of the ion radius of the salt ($1/r$) and the observed resistance* for PEO–alkali salt films with the same salt concentration observed at 90% r.h. In the films with the alkali salt having complex-forming ability with PEO, a lower resistance is achieved in humid atmospheres.

Complex impedance has been employed to analyse impedance measurements, since it seems that the impedance consists of resistance and capacitance com-
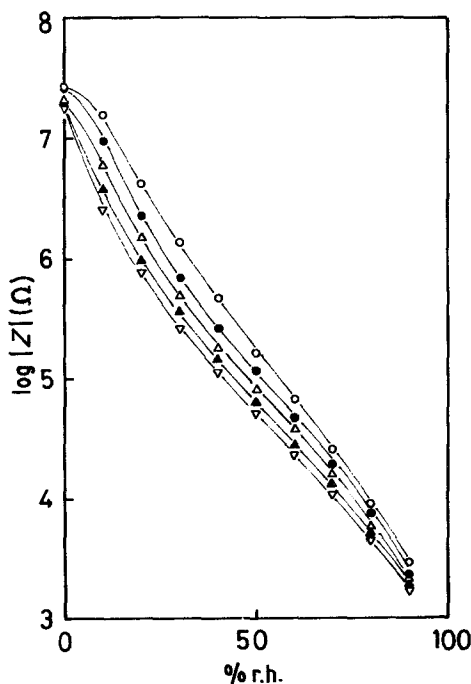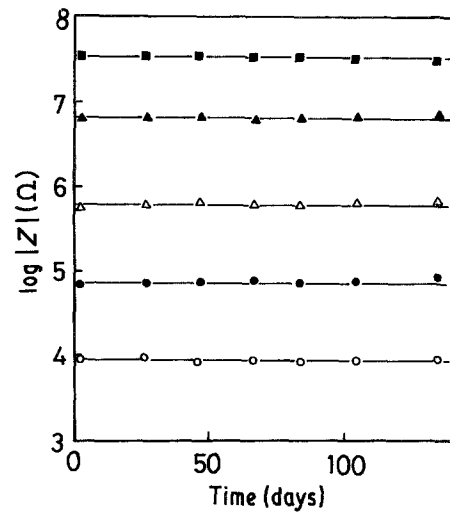

Figure 3 Impedance changes for PEO–LiClO$_4$ after storage at room temperature: (■) 0% r.h., (▲) 20% r.h., (△) 40% r.h., (●) 60% r.h., (○) 80% r.h.

ponents. The high-frequency results are represented by nearly perfect circular arcs, all of which pass through the origin. In addition, at low frequencies a second arc or spur observed in the high-humidity region may arise from electrode polarization. It is expected that these arcs arise from ionic migration in the bulk of the hybrid film, in which case the intercepts represent the d.c. resistance for the bulk excluding the electrode polarization effect. The capacitance component inserted in parallel with the d.c. resistance component (R_p) can be estimated. The estimated resistance R_p and capacitance C_p are shown in Fig. 8 as a function of humidity. The resistance decreases with an increase in humidity for each hybrid film, while no humidity dependence of the capacitance can
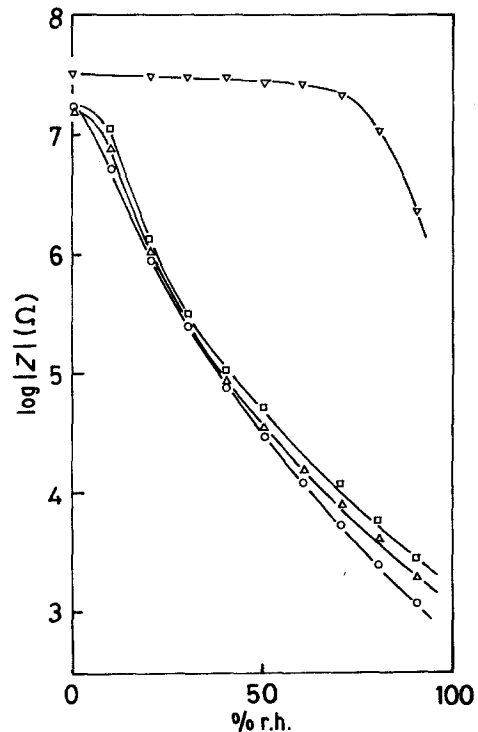

Figure 2 Humidity dependence of impedance for PEO–LiClO$_4$ (Li/O = 0.2) at 10^3 Hz: (○) 30°C, (●) 35°C, (△) 40°C, (▲) 45°C, (▽) 50°C.

Figure 4 Humidity dependence of impedance at 10^3 Hz and 30°C: (○) PEO–LiClO$_4$, (△) PEO–LiBr, (□) PEO–LiCl, (▽) PEO–LiF.

*The d.c. resistance component (R_p) obtained from complex impedance analyses.

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TABLE I Characteristics of alkali-metal salts

Alkali salt	Ion radius of salt (nm)	Propensity to form PEO–metal complex
LiF	0.204	No
LiCl	0.249	Yes
LiBr	0.264	Yes
LiI	0.290	Yes
LiClO$_4$	0.304	Yes
NaF	0.233	No
NaCl	0.278	No
NaBr	0.293	Yes
NaI	0.319	Yes
NaClO$_4$	0.333	Yes
KF	0.269	No
KCl	0.314	No
KBr	0.329	No
KI	0.355	–
KClO$_4$	0.369	–

Figure 6 Humidity dependence of impedance at 10^3 Hz and $30°$ C: (●) PEO–KI, (□) PEO–KCl, (▽) PEO–KF.

be observed. Thus the observed result indicated that the sorption of water mainly influences the resistance component for the bulk of the hybrid film. In addition, the good linear relationship between the logarithm of R_p and the reciprocal of the absolute temperature was confirmed for all hybrid films. The temperature dependence of resistance is expressed as

$$R_p = R_0 \exp (E/kT) \tag{1}$$

where R_0 is the pre-exponential factor which is inversely proportional to the carrier concentration, E is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

The R_p values of the film in the absence of alkali salt were higher than $10^7 \Omega$ in a humid atmosphere. The initial direct current was higher but it decayed to a much lower steady-state value between 10 min and 1 h. These results shows that the hybrid films are predomi-
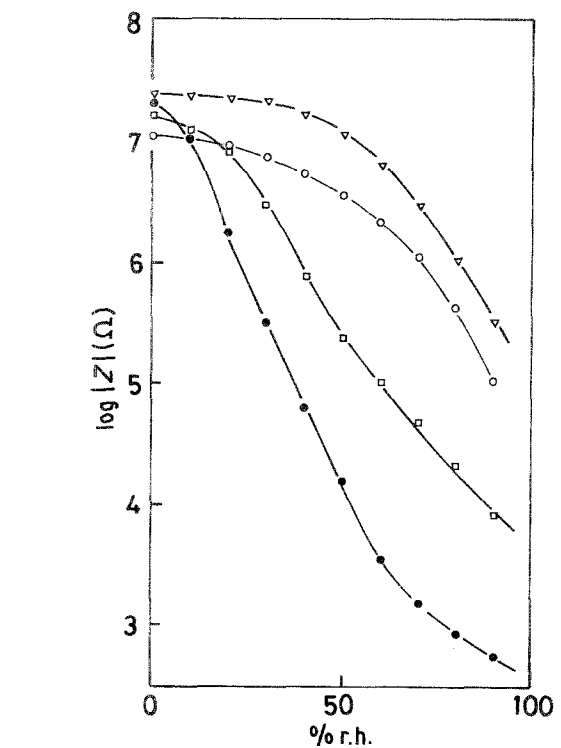
nantly ionic conductors, and that the main carrier is the alkali cation [6].

In the case of scarcely dissociated ionogenic compounds giving rise to two ions, the number of carriers will be approximately proportional to the square root of the initial salt concentration and consequently the ionic conductivity ($1/R_p$) should increase linearly with the square root of the added salt concentration at constant mobility and activation energy. This
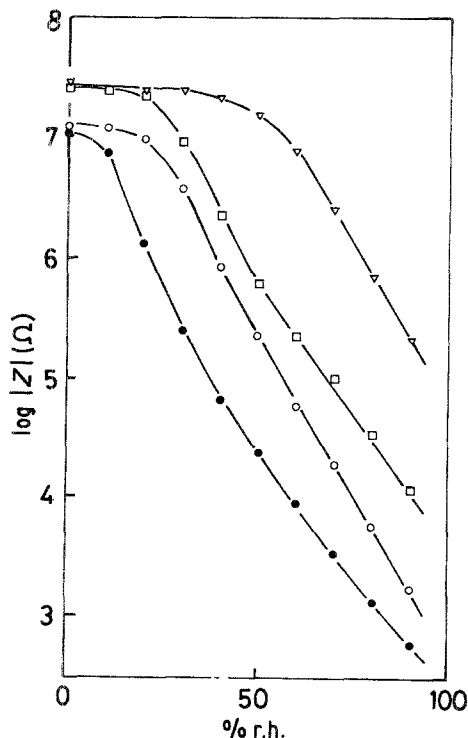

Figure 5 Humidity dependence of impedance at 10^3 Hz and $30°$ C: (●) PEO–NaI, (○) PEO–NaClO$_4$, (□) PEO–NaCl, (▽) PEO–NaF.
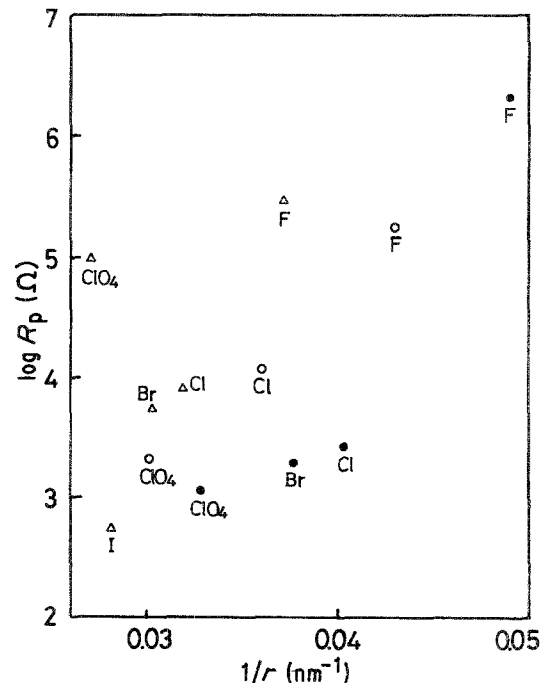

Figure 7 Relationship between R_p at 90% r.h. and ion radius for pure alkali salts: (△) potassium salts, (○) sodium salts, (●) lithium slats. The counterions are shown in the figure.
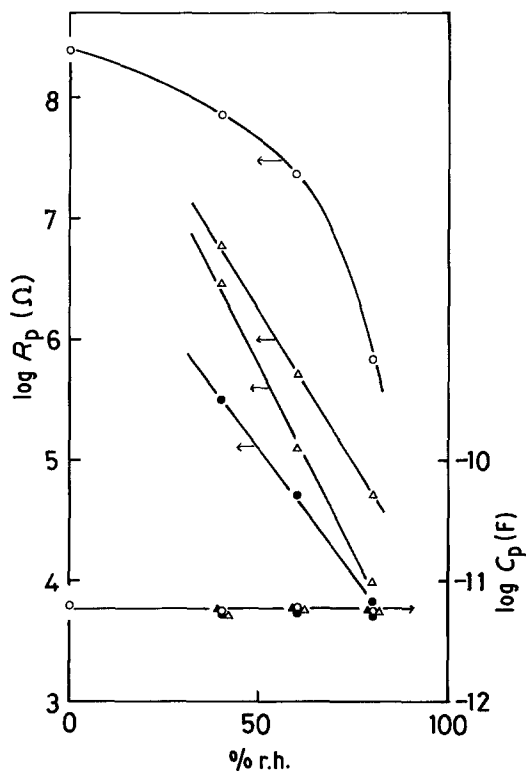
Figure 8 Humidity dependence of R_p and C_p: (●) PEO–LiClO$_4$, (▲) PEO–LiCl, (○) PEO–KCl, (△) PEO–KI.

prediction is confirmed for PEO–KCl films at 80% r.h. as shown in Fig. 9. If, on the other hand, nearly complete dissociation is attained, the conductivity should be proportional to the salt concentration. The latter situation is reflected in the behaviour of PEO–LiClO$_4$ films at 90% r.h. as shown in Fig. 9. In the low-humidity region, a slight deviation between the observed results and the predicted relation was confirmed. It seems that this deviation may be caused by the increase in the activation energy with a decrease in the salt concentration. The relationship between the activation energy and humidity is shown in Fig. 10.
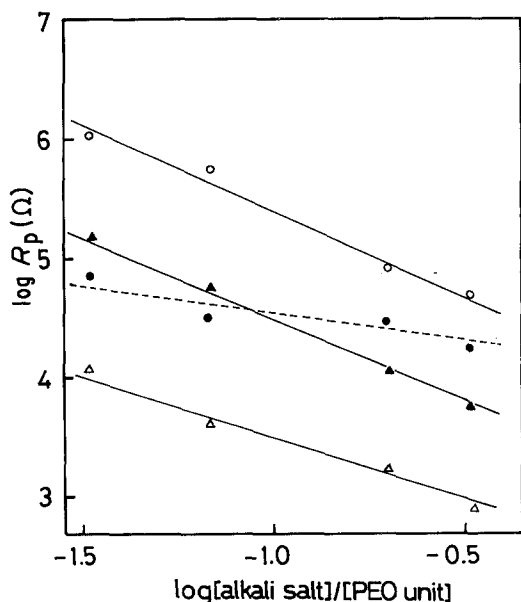

Figure 9 Relationship between impedance and concentration of alkali salt (molar ratio). Relative humidity: (○) 50%, (▲) 70%, (△) 90%, (●) 80%. (○, ▲, △) PEO–LiClO$_4$; (●) PEO–KCl.
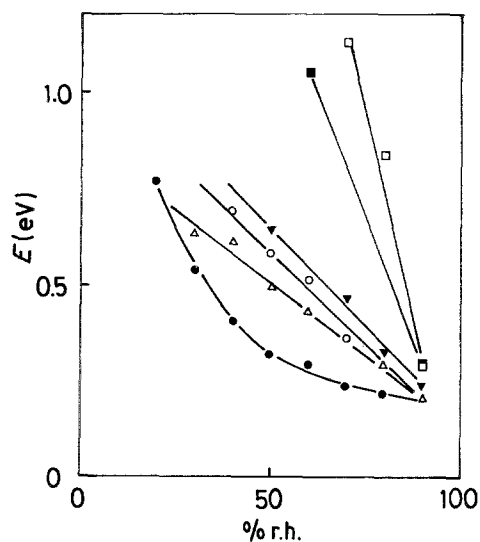

Figure 10 Humidity dependence of activation energy: (○) PEO–LiCl, (●) PEO–LiBr, (△) PEO–LiClO$_4$, (□) PEO–KCl, (■) PEO–KBr, (▼) PEO–KI.

The activation energy decreases with an increase in humidity. In addition, the hybrid films having the higher propensities toward complex formation are taken to the lower activation energy in a humid atmosphere.

While the activation energy of resistance is affected considerably by the species of alkali salt, the distinct effect of the species of alkali salt on the relationship between activation energy and resistance has not been confirmed. The relationship between the resistance at 30° C and the activation energy is shown in Fig. 11. For each system, a good linear relation is confirmed and the value of R_0 in Equation 1 is not constant but is a function of the activation energy. This relation can be expressed in the following equation instead of Equation 1:

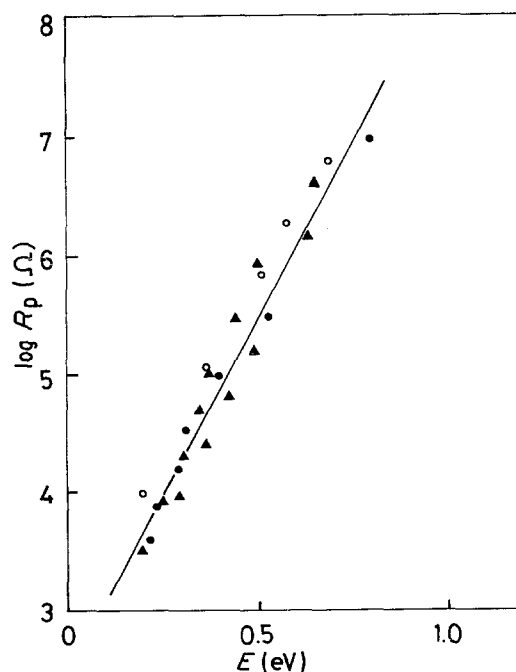$$R_p = R^* \exp\left(-E/kT^*\right) \exp\left(E/kT\right) \qquad (2)$$

Figure 11 Relationship between resistance and activation energy: (○) PEO–LiCl, (●) PEO–LiBr, (△) PEO–LiClO$_4$.

where R^* and T^* are constant and poorly dependent on humidity. The empirical equation expressed as Equation 2 is known as the Meyer–Neldel rule [7, 8]. The value of R^* is determined by the extrapolation of the linear log R_p against E plot to the intercept, and when the values of R^*, R_p and E are substituted in Equation 2, we obtain the value of T^*. The values of R^* and T^* are estimated to be 3.4 × $10^2\,\Omega$ and 470 K for the film with lithium salt, 1.5 × $10^3\,\Omega$ and 450 K for the film with sodium salt, and 1.0 × $10^2\,\Omega$ and 470 K for the film with potassium salt, respectively.

It seems that the hybrid films are predominantly ionic conductors as mentioned above, and the ionic conduction is caused by the hopping of dissociated ions which is enhanced by the sorption of water.

Ion transport is in general governed by the jump probability of an ion into the trapping and/or hopping sites [9]. The jump frequency, W_j, depends upon the potential barrier and is expressed as

$$W_j = v_0 \exp(\Delta S/k) \exp(-\Delta H/kT) \qquad (3)$$

where v_0 is the vibrational frequency for an ion, ΔS is the entropy of migration and ΔH is the enthalpy of migration. The conductivity, σ, is given by

$$\sigma = na^2 e^2 W_j/kT \qquad (4)$$

where n is the number of ion per unit volume, a is the jump distance and e is the charge. The resistance, R, is expressed as

$$R = (na^2 e^2 v_0)^{-1} kT \exp(-\Delta S/k) \exp(\Delta H/kT) \quad (5)$$

This induced relationship is comparable to Equation 2 and the $\Delta S/k$ and ΔH terms correspond to E/kT^* and E, respectively.

In the case where the ion transport is governed by the jump probability of an ion into the adjacent hopping and/or trapping sites, it is expected that the orientation polarization caused by the ion migration can be observed and the dielectric dispersion can be expressed by the Debye relation formula [10] and the activation energy of dielectric relaxation is nearly identical with that of d.c. conduction [11]. Generally, the complex dielectric constant, ε, of many systems is given by

$$\varepsilon = \varepsilon' - i\varepsilon'' \qquad (6)$$

$$\varepsilon' = \varepsilon_\infty \left(1 + \frac{l}{1 + \omega^2\tau^2}\right) \qquad (7)$$

$$\varepsilon'' = \frac{l\omega\tau}{1 + \omega^2\tau^2} \qquad (8)$$

and the loss tangent, tan δ, is expressed as

$$\tan \delta = \frac{l\omega\tau}{l + 1 + \omega^2\tau^2} \qquad (9)$$

where ε_∞ is the infinite-frequency dielectric constant, i is the imaginary operator, ω the angular frequency, τ is the relaxation time and l is the after-effect constant. According to the Debye relation formula, the relaxation time τ is expressed as

$$\tau = 1/2\,\pi f_m \qquad (10)$$

At the frequency f_m, the loss tangent reaches its maxi-

mum (tan δ_m). As shown in Fig. 12, the relationship between the resistance and f_m for PEO–LiClO$_4$ is expressed as

$$1/R \propto f_m \qquad (11)$$

In this case, the values of R and f_m were obtained at each temperature and humidity. Thus, the observed result indicates that the variation of R and f_m is based on the same ground, i.e. the migration of mobile ions, and both characteristics have the same temperature and humidity dependencies.

As described above, for hybrid films the dissolved state of the alkali salt can be classified into two categories: the dispersed state as alkali salt and the dissociated state (polyether–cation complex). The latter is predominantly found for alkali salts having small cations and large anions, and the cation is completely surrounded by the ether oxygens; therefore the unpaired electrons on the other oxygen act as the hopping site (shallow trapping site) and the cation is able to migrate through the space surrounded by the ether oxygens. In this case, the activation energy refers to that for ion migration and is poorly dependent on the lattice energy of the alkali salt.

In the former case (the dispersed state as alkali salt), the mobile carriers are produced by the dissociation of an alkali salt so that the activation energy for conduction should be correlated with the dissociation energy of the alkali salt. It is expected that the activation energy for the former case is larger than for the latter case. Actually, the activation energy of impedance for PEO–KCl and PEO–KBr is larger than that for PEO–LiClO$_4$ etc., as shown in Fig. 10.

It is considered that the sorbtion of water results in an increase in the dielectric constant of the hybrid film, an expansion of the free volume by the plasticizer effect and the formation of a shallow trapping site. The increase in the dielectric constant is responsible for the decrease in the dissociation energy of the ion-pair. The expansion of free volume and the formation of shallow trapping sites lead to an increase in ion mobility, i.e. a decrease in the potential barrier height for ion migration.
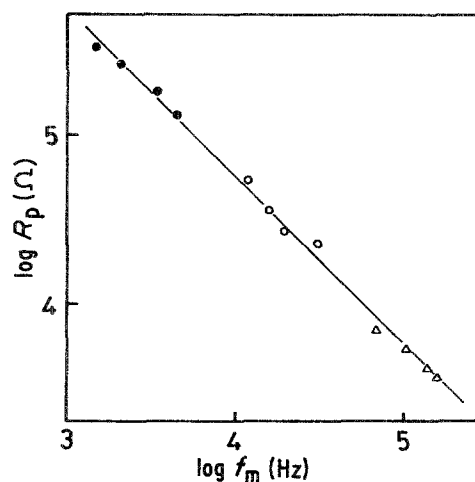
As previously mentioned, the capacitance is not

Figure 12 Relationship between resistance and f_m for PEO–LiClO$_4$. Relative humidity; (●) 40%, (○) 60%, (△) 80%.

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dependent on humidity; in addition, the value of the pre-exponential factor in Equation 2 depends on the concentration of the alkali salt but not on the humidity. It seems that the decrease in activation energy is caused mainly by an expansion of the free volume by the plasticizing effect of sorbed water for PEO doped with alkali salts having a high propensity toward complex formation.

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