

Temperature Dependence of Ionic Conductivity of Crosslinked Poly(propylene oxide) Films Dissolving Lithium Salts and Their Interfacial Charge Transfer Resistance in Contact with Lithium Electrodes

Masayoshi WATANABE, Kohei SANUI, Naoya OGATA, Fumio INOUE,*
Tadahiko KOBAYASHI,* and Zentaro OHTAKI*

*Department of Chemistry, Sophia University, 7-1 Kioi-cho,
Chiyoda-ku, Tokyo 102, Japan*

**Department of Electrical and Electronic Engineering,
Sophia University, 7-1 Kioi-cho, Chiyoda-ku,
Tokyo 102, Japan*

(Received March 27, 1984)

ABSTRACT: Temperature dependence of ionic conductivity of crosslinked poly(propylene oxide) (PPO) films dissolving lithium salts, LiBF_4 , LiClO_4 , and LiSCN , and their interfacial charge transfer resistance in contact with lithium electrodes were determined by complex impedance method on the assumption of an equivalent circuit. It was found that the temperature dependence of the ionic conductivity and the interfacial charge transfer resistance corresponding to the electrode reactions ($\text{Li} \rightleftharpoons \text{Li}^+ + e$) obeyed the WLF-type equation and the Arrhenius equation, respectively. The WLF parameters obtained were $C_1 \approx 9-15$ and $C_2 \approx 35-75$, and the activation energy for the electrode reactions was $0.57-1.2 \text{ eV}$, depending on the kinds of the incorporated salts.

KEY WORDS Ionic Conductor / Poly(propylene oxide) / Complex Impedance Method / Ionic Conductivity / Interfacial Charge Transfer Resistance / WLF-Type Equation / Arrhenius Equation /

A relatively high ionic conductivity has been recently reported in polymer complexes formed by alkali metal salts and polyethers such as poly(ethylene oxide) and poly(propylene oxide).¹⁻¹² The discovery that the ionic conductivity reached $10^{-4}-10^{-5} \text{ Scm}^{-1}$ at moderate temperatures in some complexes has accelerated their research on account of their potential application as solid electrolytes to batteries.^{2,12} From the view point of their battery application, there are several important properties which should be evaluated in addition to the ionic conductivity. Among them the interfacial charge transfer resistance in contact with electrode materials and the transference number of ions are considered to be of great importance, because these values

may often dominate the internal resistance and electromotive force of batteries. However, our knowledge about the ion conductive behavior including electrode reactions in the polyether complexes is only at a very early stage.¹²

In this article we investigated the ionic conductivity of the crosslinked poly(propylene oxide) (PPO) films dissolving lithium salts, LiBF_4 , LiClO_4 , and LiSCN , and their interfacial charge transfer resistance in contact with lithium electrodes. In order to evaluate these two different contributions to the resistance of the PPO complexes, complex impedance of a cell, lithium/PPO complex/lithium, was measured over a wide range of frequency. The bulk resistance and the interfacial charge transfer resistance were esti-

mated from the corresponding components of an equivalent circuit required to account for the complex impedance diagrams. Their temperature dependences were interpreted in terms of the WLF-type equation and the Arrhenius equation.

EXPERIMENTAL

Samples

Triol-type PPO (mol.wt. = 3000) was obtained from Asahi Denka Co. and was dried under reduced pressure at 80°C for 8 h before use. With respect to the functional groups, stoichiometric amount of PPO and freshly distilled tolylene-2,4-diisocyanate (TDI) were mixed sufficiently and were casted on glass substrates. Crosslinking reaction occurred at 65°C under dry nitrogen atmosphere for 72 h. Unreacted PPO and TDI were removed from the network films by extraction with acetone. The resulting network films obtained with thicknesses of 0.4–0.9 mm were dried sufficiently and were cut into disks with 13 mm in diameter. The disks were dipped in an acetone solution of the dried lithium salt until equilibrated and were dried under reduced pressure at 90°C for 72 h. Since the potential difference over the disks could be neglected after the drying at an elevated temperature the salt might dissolve homogeneously in the network films. The concentration of the lithium salt in the disks was determined from weight change of the disks before and after the dipping and was represented by the molar ratio of the lithium salt to the repeating unit of PPO ([Salt]/[PO unit]).

Methods

The PPO complex sandwiched between lithium electrodes for electrical contacts was packed in a sealed cell with stainless steel terminals which were in contact with the measuring device. The diameter of the electrodes was the same with the PPO complex. The cell assembly was all carried out under dry

argon atmosphere. Impedance measurement was employed with a Hewlett-Packard 4800A vector impedance meter equipped with a Takeda Riken TR5821 frequency counter over the frequency range of 5 Hz to 550 kHz. The oscillation levels were 2.7 mV, 27 mV, 270 mV, and 2.7 V depending on the sample impedance ranges of 1–10 k Ω , 10–100 k Ω , 0.1–1 M Ω , and 1–10 M Ω , respectively. In this range of the oscillation levels, the response of impedance was nearly linear. Temperature of samples was regulated with a Yashima Work BT-10 thermostated oven.

Differential scanning calorimetry (DSC) was measured by using a Rigaku Denki 8085 DSC apparatus at a heating rate of 20°C min⁻¹.

RESULTS AND DISCUSSION

Behavior of Complex Impedance Diagrams

We assumed here that the equivalent circuit shown in Figure 1(a) described the impedance behavior of the present cell system. Meanings of C_g , R_b , R_e , and C_e are cited in the figure caption. On the assumption of $C_g \ll C_e$, which is often the case in an electrolyte cell system, the general profile of the corresponding imped-

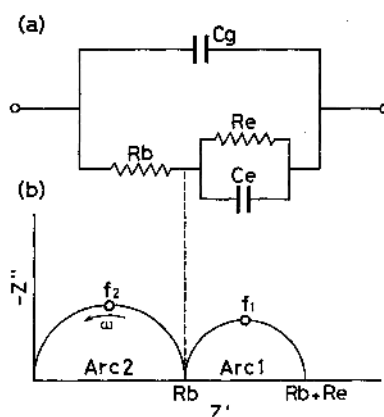


Figure 1. Equivalent circuit (a) and corresponding complex impedance diagram (b). R_b , bulk electrolyte resistance; C_g , geometrical capacitance; R_e , electrolyte/electrode interfacial resistance; C_e , electrolyte/electrode interfacial capacitance.

ance diagrams is expressed by Figure 1(b). At low frequencies C_g is considered to be open, and thus, the equivalent circuit can be symbolized by R_b in series with the parallel combination of R_e and C_e . The impedance (Z) is represented by:

$$Z = R_b + \frac{R_e}{1 + i\omega R_e C_e} \quad (1)$$

The profile of the complex impedance diagram, so called Cole-Cole plots, based on eq 1 is expressed by arc 1, as shown in Figure 1(b). In the figure, the horizontal axis is a real part of Z , defined as resistance (Z'), and the vertical axis is an imaginary part of Z , defined as reactance (Z''). The Z' values at low and high frequency ends of the arc 1 coincide with $R_b + R_e$ and R_b , respectively. f_1 is the characteristic frequency of the parallel combination of R_e and C_e , and is represented by:

$$f_1 = 1/2\pi R_e C_e \quad (2)$$

At the higher frequencies the equivalent circuit is symbolized by the parallel combination of R_b and C_g , its Z is expressed by:

$$Z = \frac{R_e}{1 + i\omega R_e C_g} \quad (3)$$

The locus of eq 3 corresponds to arc 2, as shown in Figure 1(b). f_2 is related to R_b and C_g , as follows:

$$f_2 = 1/2\pi R_b C_g \quad (4)$$

Figure 2 shows the complex impedance diagrams of the PPO complexes in contact with lithium electrodes at 70°C. Since two arcs corresponding to the arcs 1 and 2 were observed in each complex impedance diagram, R_b , R_e , f_1 , and f_2 could be estimated. Substituting these values to eq 2 and 4, we could calculate the values of C_g and C_e . Thus, all the values of the components in the equivalent circuit were obtained, as shown in Table I. C_g was in the order of 10^{11} F in each PPO complex. The values corresponded to the relative dielectric constant (ϵ_r) of 13–14. The ϵ_r values nearly

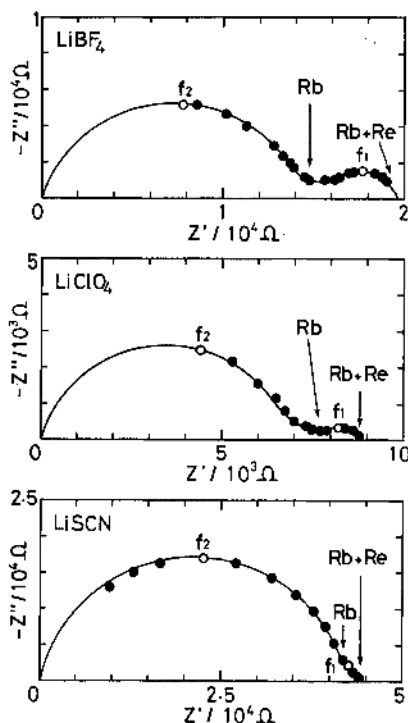


Figure 2. Complex impedance diagrams of PPO complexes ($[Salt]/[PO \text{ unit}] = 0.05$) in contact with lithium electrodes at 70°C. Sample thickness: PPO-LiBF₄, 0.84 mm; PPO-LiClO₄, 0.39 mm; PPO-LiSCN, 0.88 mm.

coincided with the findings by Wetton *et al.* that the magnitude of ϵ_r in the PPO-ZnCl₂ complex reached of the order of 10^1 at 10–40°C.¹³ R_e was considerably smaller than R_b , whereas R_e became very large in the cell with platinum electrodes. Thus, it is obvious that lithium electrodes operate as ion-reversible electrodes to the PPO complexes and that R_e corresponds to the interfacial charge transfer resistance. C_e which reached 10^{-7} – 10^{-8} F corresponds to double layer capacitance resulting from the polarization of ionic carriers at the interface.

In Figure 3 are shown the complex impedance diagrams for the PPO-LiBF₄ complex at 90, 80 and 60°C. Taking the results at 70°C in Figure 2 into consideration, it is seen that the measurable range in the complex impedance

Table I. Values of components in equivalent circuit at 70°C

Salt	R_b/Ω	f_2/Hz	C_g/F	R_e/Ω	f_1/Hz	C_e/F
LiBF ₄	1.48×10^4	5.5×10^5	2.0×10^{-14}	4.7×10^3	6.0×10	5.6×10^{-7}
LiClO ₄	7.60×10^3	5.5×10^5	3.8×10^{-14}	1.2×10^3	2.5×10^2	5.3×10^{-7}
LiSCN	4.20×10^4	2.0×10^5	1.9×10^{-14}	2.7×10^3	1.5×10^3	3.9×10^{-8}

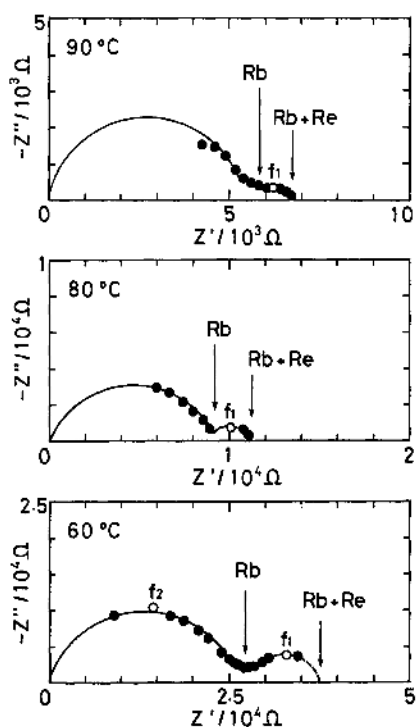


Figure 3. Complex impedance diagrams for PPO-LiBF₄ complex ([Salt]/[PO unit]=0.05) with the thickness of 0.84 mm in contact with lithium electrodes at 90, 80, and 60°C.

diagrams varied with the temperature change. At 90°C the impedance plots cited mainly on the arc 1, whereas at 60°C R_b and R_e increased and the measurable plots were mainly concerned with the arc 2. f_1 and f_2 became low with decreasing temperature.

Temperature Dependence of Ionic Conductivity

Figure 4 shows the relation between the logarithm of the ionic conductivity (σ) calculated from R_b and the reciprocal of absolute temperature ($1/T$). The temperature depen-

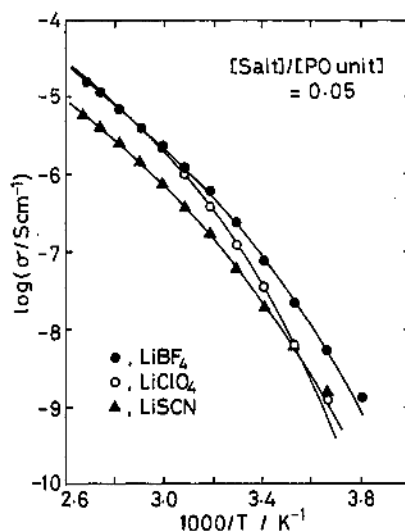


Figure 4. Relation between logarithm of ionic conductivity and reciprocal of absolute temperature.

dence did not obey the Arrhenius theory with a temperature-independent activation energy, but showed a marked deviation from a single Arrhenius behavior. The PPO complexes were transparent, amorphous, and elastic materials, and their glass transition temperatures (T_g) were lower than the measuring temperature range. It was expected that the transport of ionic carriers was related to segmental motion of the amorphous main chain. Thus, the temperature dependence of σ was expressed by the WLF-type equation:¹⁴

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (5)$$

By using T_g 's determined from DSC measurements, the data sets of C_1 , C_2 , and $\sigma(T_g)$ were so calculated as to best linearize the correlation between $1/(T - T_g)$ and $1/\log[\sigma(T)/\sigma(T_g)]$.

Table II. WLF parameters for PPO complexes

Salt	T_g °C	C_1	C_2		$\sigma(T_g)$ Scm ⁻¹
			°C		
LiBF ₄	Onset	-40	12.0	53.7	3.9×10^{-14}
	Center	-30	10.1	64.1	3.1×10^{-12}
	End	-21	8.8	75.0	6.6×10^{-11}
LiClO ₄	Onset	-34	15.0	33.4	2.2×10^{-17}
	Center	-24	11.5	43.5	5.6×10^{-14}
	End	-14	9.4	53.4	8.0×10^{-12}
LiSCN	Onset	-47	14.6	47.0	5.8×10^{-17}
	Center	-33	11.3	60.9	1.1×10^{-13}
	End	-19	9.2	76.6	1.6×10^{-11}

$\sigma(T_g)$. Table II shows the WLF parameters obtained. Onset, center, and end temperatures of the heat capacity change in the DSC charts, which was experienced in glass transition zone, were used as T_g for each calculation. Some deviation in the WLF parameters was noticed depending on the used T_g , however, their values were considered comparable to the universal values of $C_1=17.4$ and $C_2=51.6$ for the temperature dependence of the relaxation times of amorphous main chain. This implied that the temperature dependence of the ionic mobility which correlated to the segmental mobility of the PPO main chain dominated the temperature dependence of σ .

Temperature Dependence of Interfacial Charge Transfer Resistance

Since R_e is known to be proportional to the area in contact with electrodes,¹⁵ R_e per unit area is used as normalized R_e and is expressed by ρ_e . Figure 5 shows the relation between $\log \rho_e$ and $1/T$. It was found that the temperature dependence of ρ_e obeyed the Arrhenius equation:

$$\rho_e = \rho_{e0} \exp(E_a/kT) \quad (6)$$

where ρ_{e0} is a constant, and k is the Boltzmann constant. ρ_{e0} was 1.4×10^{-12} , 3.5×10^{-15} , and $9.4 \times 10^{-6} \Omega\text{cm}^{-2}$ for PPO-LiBF₄, PPO-

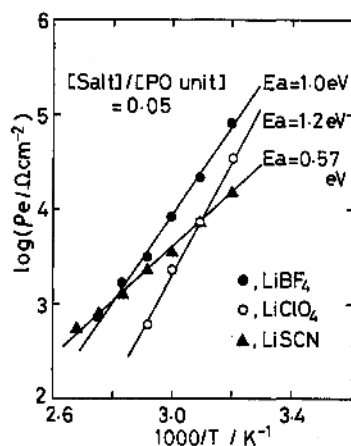


Figure 5. Relation between logarithm of normalized interfacial charge transfer resistance in contact with lithium electrodes and reciprocal of absolute temperature.

LiClO₄, and PPO-LiSCN complexes, respectively. The activation energy (E_a) ranged from 0.57 to 1.2 eV, depending on the kinds of the incorporated salts. Since the charge transfer resistance was based on the electrode reactions, $\text{Li} \rightleftharpoons \text{Li}^+ + e$, the E_a values seemed to correspond to the activation energy for the electrode reactions.

CONCLUSION

It was concluded that the temperature dependences of the ionic conductivity and the interfacial charge transfer resistance, corresponding to the electrode reactions ($\text{Li} \rightleftharpoons \text{Li}^+ + e$), for the PPO-lithium salt complexes in contact with lithium electrodes obeyed the WLF-type equation and the Arrhenius equation, respectively. The WLF parameters obtained were $C_1 \approx 9-15$ and $C_2 \approx 35-75$, and the E_a values were 0.57-1.2 eV, depending on the kinds of the incorporated salts.

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