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New Lithium Salt Ionic Conductor Using Poly(vinyl alcohol) Matrix

Takaki KANBARA, Minoru INAMI, Takakazu YAMAMOTO,* Atsushi NISHIKATA,† Tooru TSURU,† Masayoshi WATANABE,†† and Naoya OGATA††
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227
†Department of Metal Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152
††Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102

Poly(vinyl alcohol) (PVA) forms transparent homogeneous composites with lithium salt ($LiClO_4$, $LiBF_4$, and $LiCF_3SO_3$) up to 50-60 wt-% of the lithium salt in the composites. The composites show electrical conductivity of 10^{-6} - 2×10^{-4} S cm^{-1} at 50 wt-% of the lithium salt at 20 °C. Temperature dependence of the electrical conductivity obeys Arrehnius type equation in most cases with activation energies of 50-107 kJ mol^{-1}.

Preparation of polymer electrolytes and application of the polymer electrolytes to making devices (e.g., solid electrolyte battery and electrochromic devices) are the subject of recent interest.1-4) We now report that PVA, one of the most widely used polymers, can dissolve a large amount of lithium salts in its matrix and the PVA-lithium salt composites show good ionic conductivity. It is reported that a lithium salt, LiI, forms an adduct ($LiI \cdot 4CH_3OH$) with methanol and the adduct shows good ionic conductivity ($\sigma = 3.4 \times 10^{-4}$ S cm^{-1}).5)

A dimethyl sulfoxide (DMSO, 15 cm^3/1 g of PVA) solution containing PVA (average molecular weight = 25000, 88% hydrolyzed) and $Li[CF_3SO_3]$ was spread over a glass plate, and most of DMSO was removed by evaporation under vacuum at room temperature for 15 h. The film thus obtained was heated at 70 °C under vacuum for 12 h. The transparent and flexible film (thickness = 0.1 - 0.3 mm) thus obtained were mechanically strong and contained about 3.5 wt-% of DMSO as determined by GLC after thermolysis of the composite film at 455 °C by applying high frequency electromagnetic wave for 3 s. Since drying up of DMSO solutions of lithium salts under vacuum at room temperature recovered DMSO-free lithium salts, DMSO in the composite film seems to remain mainly as an adduct with PVA. Complete remove of DMSO was difficult. By using $LiBF_4$ and $LiClO_4$, similar composite films were obtained.

X-Ray diffraction pattern of the composite film showed no peak assigned to the lithium salt, revealing that PVA and the lithium salt formed homogeneous composite. It is noteworthy that PVA and the lithium salt forms homogeneous film up to about 1.5 g of the lithium salt per 1 g of PVA. Addition of a larger amount of the lithium salt afforded turbid film.

Thin gold electrodes (1 cm x 1 cm) were placed on both surfaces of the film by evaporation under vacuum, and electrical conductivity of the composite film was measured by a complex impedance method over a frequency range of 1 x 10^{-1} - 1 x 10^{5} Hz. Cole-Cole plot for the composite film showed normal patterns for the polymer electrolytes.[1-3] Electrical current observed on application of DC voltage through the gold or platinum electrodes steeply decreased with time, indicating that the electrical conduction of the composite films was originated from ionic conduction. On the other hand, use of Li plates as active electrodes showed only minor decrease of electric current with time on application of DC voltage, revealing Li^+ was the main cation species responsible to the ionic conduction.

Figure 1 shows electrical conductivity (σ) of the PVA-lithium salt composite films on the content of the lithium salt. As seen in Fig. 1, the composite shows good electrical conductivity at 20 °C in spite of high glass transition temperature (85 °C[6]) of PVA. The electrical conductivity is comparable to or higher than reported polymer electrolytes. One of interesting features of the

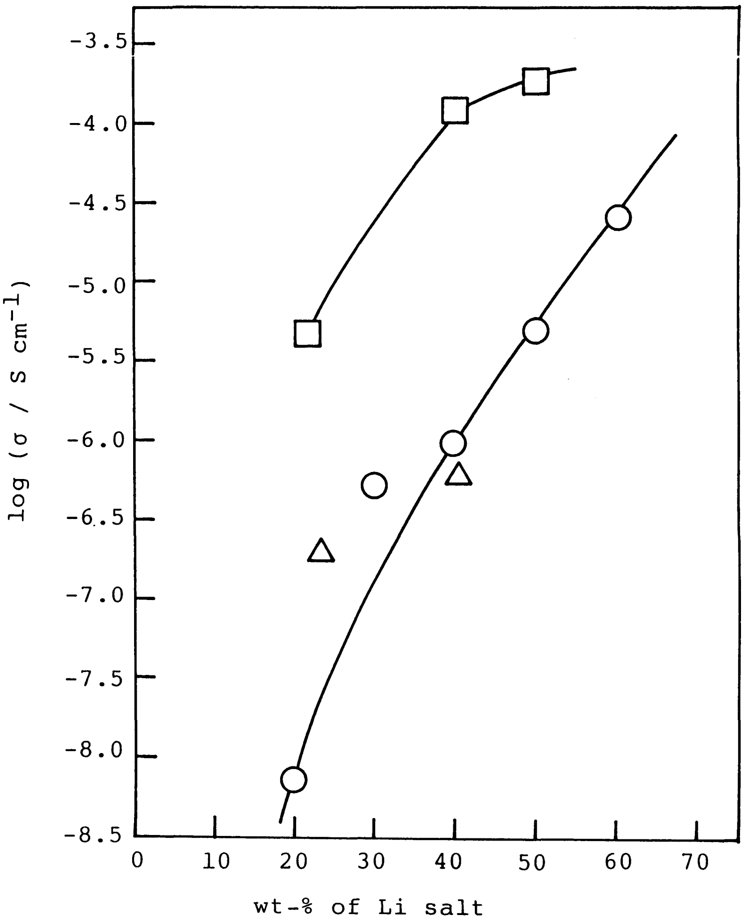

Fig. 1. Electrical conductivity (σ) of PVA-Li salt composite film as a function of Li salt content at 20 °C.

○: $Li[CF_3SO_3]$

△: $LiBF_4$

□: $LiClO_4$

PVA-lithium salts is that the electrical conductivity increases with increase in the content of the lithium salt. On the contrary, most of polymer electrolytes containing lithium salt are reported to show maximum electrical conductivity at certain ratio between polymer and lithium salt and addition of a large amount of lithium salt causes decrease of the electrical conductivity.[2,3] Since the present PVA-lithium salt electrolytes show good electrical conductivity at high concentration of the lithium salt, these polymer electrolytes seem to be especially useful to make devices which need high concentration of electrolyte.

Figure 2 shows temperature dependence of the PVA-lithium salt electrolytes. As shown in Fig. 2, the temperature dependence obeys Arrehnius type equation in most cases.

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (1)$$

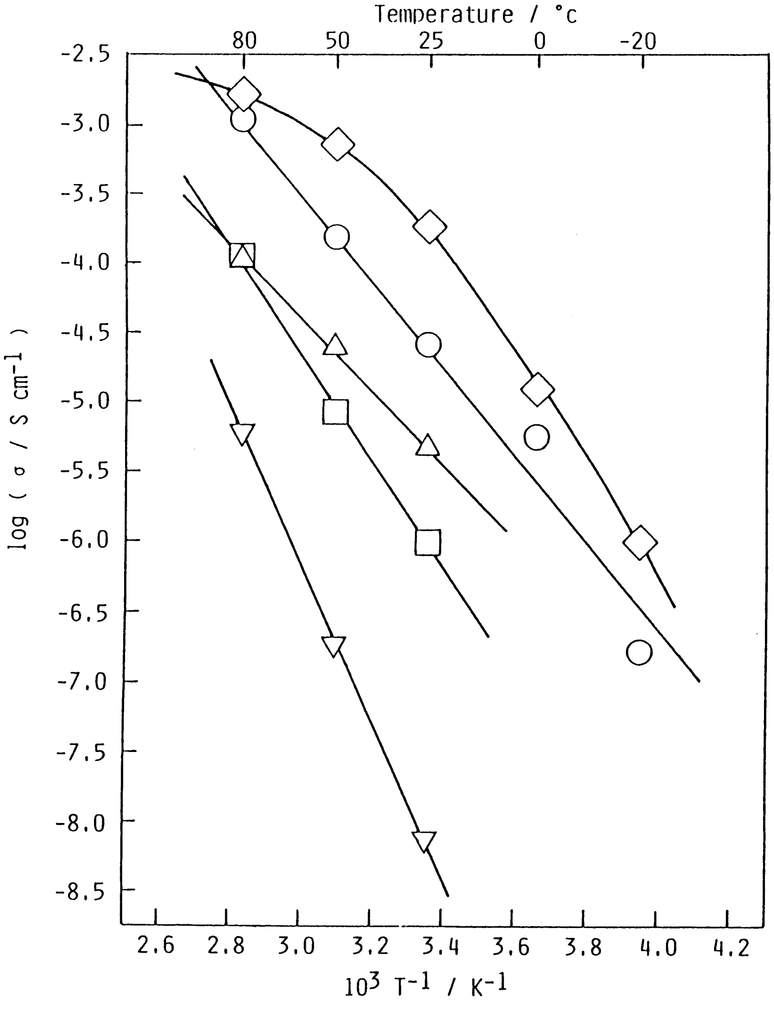

Fig. 2. Temperature dependence of the σ value.
▽: PVA-Li[CF_3SO_3] (19.9 wt-%)
□: PVA-Li[CF_3SO_3] (39.6 wt-%)
△: PVA-Li[CF_3SO_3] (49.7 wt-%)
○: PVA-Li[CF_3SO_3] (60.0 wt-%)
◇: PVA-$LiBF_4$ (49.9 wt-%)

Table 1 summarizes the E_a value obtained from the slope of the line shown in Fig. 2.

Apparent E_a value increases on lowering temperature in most of reported polymer electrolytes and the reported polymer electrolytes show very low electrical conductivity at low temperature like -20 °C.[2,3] However, as described above, the present PVA-lithium salt electrolytes show constant E_a value over a wide range of temperature and they show moderate electrical conductivity even at -20 °C. This is another merit of the present polymer electrolytes.

Table 1. E_a value of the electrolytes

Lithium salt	$Li[CF_3SO_3]$				$LiBF_4$
wt-%	19.9	39.6	49.7	60.0	49.9
Ea value kJ/mol	107	75.8	50.1	75.8	56.3[a)]

a) For a temperature range of -20 - 25 °C.

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References

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3) E. Tsuchida, Kagaku, 38, 418 (1983); N. Kobayashi, M. Uchiyama, K. Shigehera, and E. Tsuchida, J. Phys. Chem., 89, 987 (1985); N. Kobayashi, H. Ohno, and E. Tsuchida, Nippon Kagaku Kaishi, 1986, 441.

4) K. Aoki, H. Yonekura, and K. Orihara, Polym. Prepr. Jpn., 38, 652 (1989).

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6) J. Brandrup and E. H. Immergut, "Polymer Handbook," Interscience, New York (1966), p. III-72. Usually polymer electrolytes show low electrical conductivity at temperature lower than the glass transition temperature of the polymer.

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