CHEMISTRY LETTERS, pp. 2263-2266, 1990.

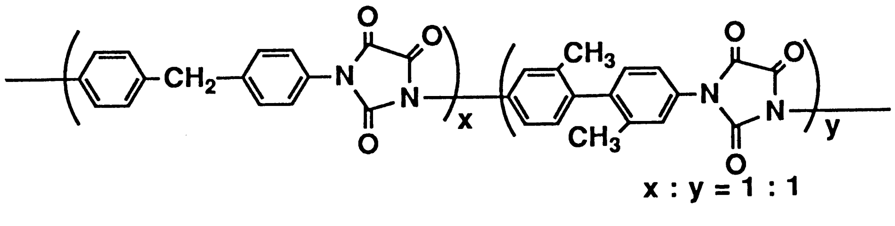
Preparation of a Thermally Stable Polymer Solid Electrolyte Using Poly(parabanic acid) Matrix

Takaki KANBARA, Minoru INAMI, Takakazu YAMAMOTO,*
Atsushi NISHIKATA,† and Toru TSURU†
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

Poly(parabanic acid) (PPA) forms transparent homogeneous composites with lithium and sodium salt ($LiClO_4$, $LiBF_4$, $Li[CF_3SO_3]$, $NaClO_4$, and $NaBF_4$) up to 30-60 wt% of the salt in the composite. The composites show electrical conductivity of 1.7×10^{-5} S cm^{-1} at 50 wt% of $Li[CF_3SO_3]$ at 20 °C. The composites are thermally stable up to about 180 °C, and temperature dependence of the electrical conductivity obeys Arrhenius type equation in most cases with activation energy of 0.6 - 1.0 eV.

Preparation of polymer solid electrolytes and their applications are of current interest for the development of advanced electrochemical devices.$^{1-6)}$ The most commonly used polymer matrixes for preparation of polymer electrolytes are poly(ethylene oxide), poly(propylene oxide) and their network polymers, which have low glass transition temperature (T_g). On the other hand, it was recently reported that poly(vinyl alcohol) (PVA) with relatively high T_g (85 °C) could dissolve large amounts of lithium salts in its matrix and the PVA-lithium salt composites showed good ionic conductivity.$^{7)}$

Poly(parabanic acid) (PPA)



Since advance of electronic devices used under various conditions requires polymer solid electrolytes usable at high temperatures, we have examined usability of thermally stable polymers as the matrix of alkali metal ion conducting polymer solid electrolyte. Among the polymers tested, poly(parabanic acid) (PPA) with T_g of 350 °C[8] has been found to be especially suitable since it can contain high concentration of alkali metal salts homogeneously in contrast to other thermally stable polymers like usual type polyimides. The polymer solid electrolyte has much higher thermal stability than the previously reported polymer electrolytes.

DMF ($1.5\ cm^3/1$ g of PPA) solution containing PPA ($[\eta] = 1.0\ g\ dl^{-1}$; 1 dl = 100 cm^3) and $Li[CF_3SO_3]$ was poured on a poly(ethylene) plate, and most of DMF was removed by evaporation under vacuum at room temperature for 12 h. The film thus obtained was heated at 120 °C under vacuum for 12 h. The yellowish transparent film (thickness = 0.1 - 0.3 mm) thus obtained virtually contained no DMF as checked by GLC after thermolysis of the composite film at 455 °C by applying high frequency electromagnetic wave for 3 s. Use of other alkali metal salt ($LiBF_4$, $LiClO_4$, $NaBF_4$, and $NaClO_4$) gave similar composite films. The composite treated at room temperature under vacuum contained 5 - 10 wt% of DMF and this composite showed electrical conductivity of about one order of magnitude higher than that of the composite treated at 120 °C. Thin gold electrodes (1 cm x 1 cm) were placed on both

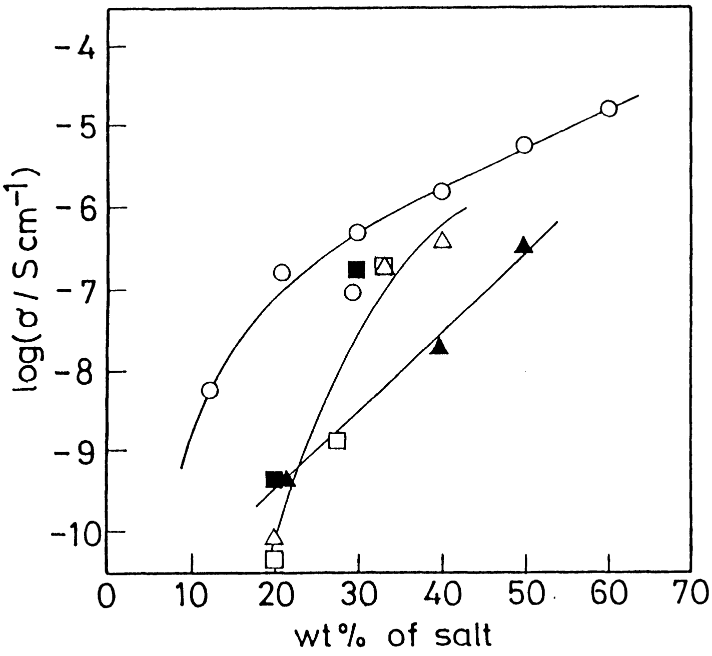


Fig. 1. Electrical conductivity (σ) of PPA-alkali metal salt composite film as a function of alkali metal salt content at 20 °C. Wt% of salt = (wt of salt) / (wt of PPA + wt of salt):

○ : $Li[CF_3SO_3]$,
△ : $LiBF_4$,
□ : $LiClO_4$,
▲ : $NaBF_4$,
■ : $NaClO_4$.

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 films showed normal patterns for the polymer solid electrolytes.[1-3,5] Treatment of the film and the measurement were carried out under dry N_2. Electrical current observed on application of d.c. voltage through the gold or platinum electrodes steeply decreased with time, indicating that the electrical conductivity of the composite films was originated from ionic conduction.

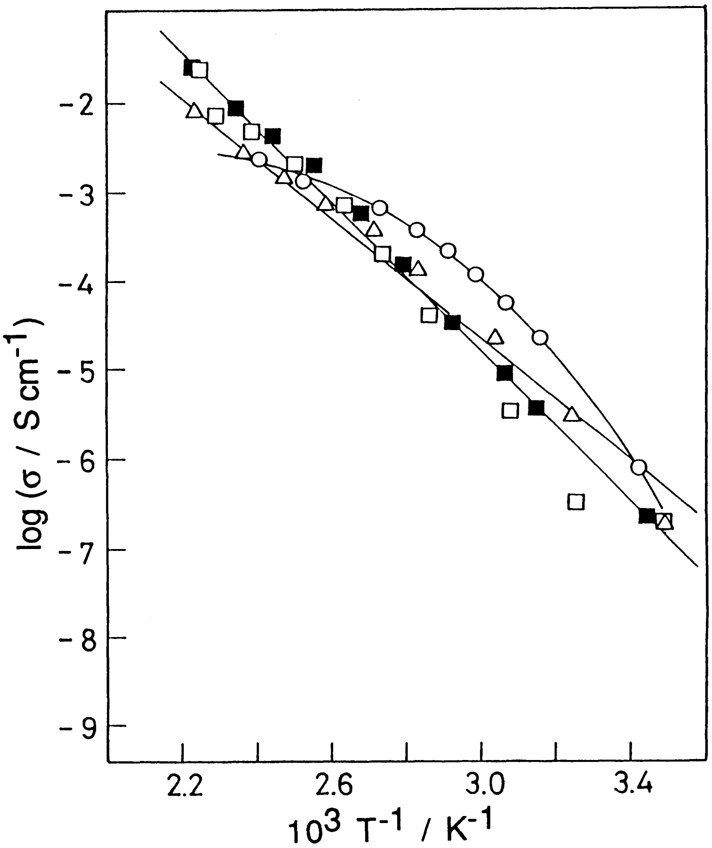


Fig. 2. Temperature dependence of the σ value.

○ : Li[CF_3SO_3] (40 wt%),
△ : $LiBF_4$ (35 wt%),
□ : $LiClO_4$ (35 wt%),
■ : $NaClO_4$ (35 wt%).

Figure 1 shows dependence of electrical conductivity (σ) of the PPA-alkali metal salt composite films treated at 120 °C on the content of the alkali metal salt. As shown in Fig. 1, the composite films show moderate electrical conductivity at 20 °C at a high concentration range of the salts. The electrical conductivity is comparable or somewhat lower compared with those of reported polymer electrolytes.[1-5]

The σ value of the PPA-alkali metal salt composite increases with increase in the content of the salt; this is in contrast to the observation that most of the polymer solid electrolytes containing lithium salt 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.[2-5]

X-Ray diffraction pattern of the PPA-Li[CF_3SO_3] composite film showed no peaks assigned to Li[CF_3SO_3] up to about 1.5 g of Li[CF_3SO_3] per 1.0 g of the polymer, revealing that PPA could dissolve the lithium salt homogeneously up to very high concentration. Addition of a larger amount of the salt afforded turbid film. It is inferred that the composites can contain large amounts of carrier ions and increase of carrier ions causes increase of ionic conductivity, in spite of the high T_g (350 °C) of PPA.

Figure 2 shows temperature dependence of the electrical conductivity of the PPA-alkali metal salt composite films treated at 120 °C. As depicted in Fig. 2, the temperature dependence obeys Arrhenius type equation over a wide temperature range (20 through 175 °C) in most cases. The apparent activation energies (E_a) obtained from the slope of the line in Fig. 2 are 0.69 and 0.89 eV for PPA-$LiBF_4$ (33 wt%) and PPA-$NaClO_4$ (33 wt%) composites, respectively. The same σ value was observed both in heating and cooling runs. It is noteworthy that most of the PPA-alkali metal salt composite films have very high thermal stability up to about 180 °C.

These results indicate the present polymer solid electrolytes is especially useful for making devices which operate at high temperatures.

This research was partially supported by grant-aid No. 02750627 from Ministry of Education, Science and Culture, Japan.

References

1) M. B. Armand, *Solid State Ionics*, **9/10**, 745 (1983).
2) F. Boino, S. Pantaloni, S. Passerini, and B. Scrosati, *J. Electrochem. Soc.*, **135**, 1961 (1988).
3) B. L. Pake, M. A. Ratner, and D. F. Shriver, *J. Phys. Chem. Solids*, **42**, 493 (1981).
4) Z. Ogumi, Y. Uchimoto, and Z. Takehara, *J. Electrochem. Soc.*, **136**, 625 (1989).
5) M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi, and Z. Ohtaki, *J. Appl. Phys.*, **57**, 123 (1985).
6) E. Tsuchida, *Kagaku*, **38**, 418 (1983).
7) T. Kanbara, M. Inami, T. Yamamoto, A. Nishikata, T. Tsuru, M. Watanabe, and N. Ogata, *Chem. Lett.*, **1989**, 1913.
8) A. Wakamatsu, *Petrotech*, **11**, 422 (1988); Y. Keumi, *Plastics*, **37**, 84 (1986).

(Received August 31, 1990)