Preparation and Properties of Polymer Solid Electrolytes Using Poly(vinyl alcohol) and Thermally Resistive Poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)] as Matrix Polymers

Takakazu Yamamoto,* Minoru Inami, and Takaki Kanbara

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Poly(vinyl alcohol) (PVA) and heat-resistive poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)] (poly(parabanic acid), PPA) with a T_g of 350 °C dissolve alkali metal salts such as Li[CF$_3$-SO$_3$], LiBF$_4$, LiClO$_4$, and NaBF$_4$ in high concentrations (1.0–1.5 g/g of the polymer). Complex impedance analysis of the polymer electrolytes thus obtained gives normal patterns usually observed for polymer electrolytes. The PVA-based polymer electrolytes have the electric conductivity (σ) of $10^{-5.5}$–$10^{-3.5}$ S cm^{-1} at 20 °C and at 1 g of Li salt/g of PVA, whereas the PPA-based polymer electrolytes exhibit the σ value of 10^{-7}–$10^{-5.5}$ S cm^{-1} under the same conditions. Temperature dependence of the σ value obeys Arrhenius type equation for both types of polymer electrolytes; the activation energies are in the range 50–107 kJ mol^{-1}. The PPA–lithium salt polymer electrolytes exhibit good heat resistance at 170 °C and σ value of about 10^{-2} S cm^{-1} at 170 °C. IR spectrum of the PVA–Li[CF$_3$SO$_3$] composite shows absorption bands originating from PVA and Li[CF$_3$SO$_3$] and no apparent shift of the ν(OH) band of PVA is observed. [(n-C$_4$H$_9$)$_4$N]Y (Y = BF$_4$, PF$_6$) shows relatively low solubility in PVA (ca. 0.25 g/g of PVA). T_g of PVA and PPA is lowered by making the composite with the lithium salt.
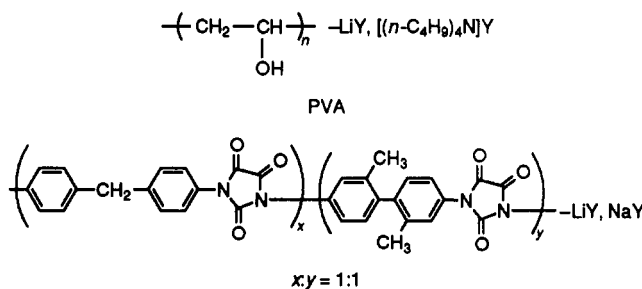
Introduction

The preparation of polymer solid electrolytes and their application to devices (e.g., solid electrolyte battery and electrochromic devices) are the subject of recent interest.[1–5] The most commonly used matrix polymers for the polymer electrolytes are poly(ethylene oxide), poly(propylene oxide), and their network polymers and copolymers, which have low glass transition temperature (T_g). Several other polymers having ester groups and amine groups in the main chain and/or side chain have been also used as the matrix polymer.

To expand the scope of the polymer electrolyte and as a part of our program to investigate conductive polymers,[6] we have examined the solubility of electrolytes in various polymers and found out that poly(vinyl alcohol)[7] with a high content of OH groups and heat-resistive poly[arylene-(1,3-imidazolidine-2,4,5-trione-1,3-diyl)][8] (poly(parabamic acid), PPA)serve as good matrix polymer toward alkali

poly(parabanic acid) (PPA, TM-1 type with [η] = ca. 1.0 g dL⁻¹)

metal and ammonium salts and afford good polymer electrolytes. The main chain of poly(parabanic acid) contains a five-membered ring resembling propylene carbonate, an excellent organic solvent for various electrolytes, and constituted of two amine nitrogens and three

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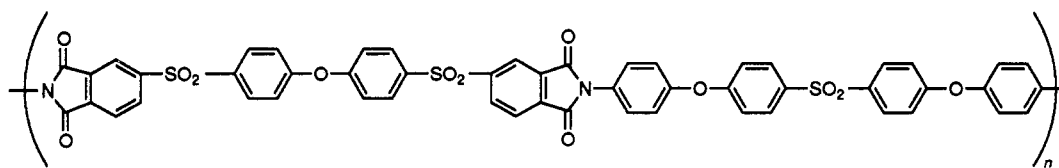
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Chart 1

carbonyl groups instead of two ethereal oxygens and one carbonyl group in propylene carbonate,and the good

propylene carbonate   five–membered unit in poly(parabanic acid)

solubility of electrolytes in poly(parabanic acid) is related to the presence of the five-membered ring in the polymer chain.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA, M_n = 25 000, 88% hydrolyzed) was purchased from Polysciences Ltd. and dried under vacuum by heating the powdery polymer at about 70 °C for 24 h. Poly[arylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl)][6b,9] (poly(parabanic acid), PPA TM-1 type with [η] = ca. 1.0 g dL^{-1}) was kindly donated from Tonen Chemical Corp. Commercially available alkali metal and ammonium salts were dried under vacuum. Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were dried, distilled, and stored under nitrogen. Lithium foil (thickness = 0.38 mm) was purchased from Aldrich Chemical Co.

Preparation of Polymer Solid Electrolyte. All of the procedures were carried out under N_2 or Ar or in a vacuum by using the Schlenk technique[10] to avoid the moisture in air.

A DMSO (15 mL/1 g of PVA) solution containing PVA and Li[CF$_3$SO$_3$] 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 for the PVA–Li[CF$_3$SO$_3$] (1:1 wt/wt ratio) composite, as determined by GLC after thermolysis of the composite film at 455 °C by applying high-frequency electromagnetic wave for 3 s. The IR spectrum of the composite film did not show observable absorption originated from DMSO. Since drying up 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 removal of DMSO was not possible. By using LiBF$_4$, LiClO$_4$, and [N(n-C$_4$H$_9$)$_4$][BF$_4$], similar composite films were obtained.

A DMF (1.5 mL/1 g of PPA) solution containing PPA and Li[CF$_3$SO$_3$] was poured on a polyethylene 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. The film was flexible and mechanically strong. Use of other alkali metal salts (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 % DMF as measured with gas–liquid chromatography (GLC), and this composite

showed electrical conductivity of about 1 order of magnitude higher than that of the composite treated at 120 °C and contained no DMF. Formation of Li[CF$_3$SO$_3$] composites with polysulfoneetherimide (PSEI, Chart 1, [η] = 0.5 g dL^{-1}) by using DMF, N,N-dimethylacetamide, and N-methyl-2-pyrrolidone as the solvent, was kindly carried out by Tonen Chemical Corp.

Analysis and Measurements. IR spectra were measured with KBr pellets prepared under nitrogen by using JASCO IR-810 spectrometer. X-ray diffraction pattern was recorded on a RIGAKU RAD-IVC system. Complex impedance analysis was made by using an NF electronic Instruments 5020 frequency analyzer, a Hewlett-Packard 3312A function generator, NF Model LI-574A autophase lock-in applifier, and a Toho Technical Research 2000 potentiostat/galvanostat or Hokuto Denko HA-301 potentiostat/galvanostat. They were controlled by a computer. Some of the complex impedance data were also taken at Department of Metal Materials of Tokyo Institute of Technology and Sophia University. Thin gold electrodes (1 cm × 1 cm) were plated on both surfaces of the composite film by sputtering using an Eiko Engineering IB-3 ion coater, and the complex impedance analysis was carried out with this sample under nitrogen by using the apparatus described above. Measurement of dc conductivity for a Li/polymer electrolyte/Li junction was made by pressing the Li foils to the polymer electrolyte film. Stability test of the PVA– and PPA–lithium salt polymer electrolytes against lithium foil at 80 °C was kindly carried out by Yuasa Battery Co. Ltd. DSC analysis was carried out with a Shimadzu DT-30 thermal analyzer. The sample (PVA or PVA–lithium salt composite) was heated to high temperature (190 °C for PVA and 120 °C for the PVA–lithium salt, respectively) and then cooled rapidly to about −50 °C. DSC measurements were carried out with samples thus treated.[5h] Such treatment has been reported to make a glass state of polymer electrolytes and make T_g point clearer in the DSC measurement.[5h] Without such treatment, only T_m was observed in the first run of the DSC measurement; however, in repeated second and third runs both the T_g and T_m were observed at the same temperatures observed with the such treated samples. In the case of PPA and its composite, the sample was rapidly cooled to −50 °C after heating to 250 (composite) or 400 °C (PPA) and then used for the DSC measurement.

Results and Discussion

PVA-Based Polymer Electrolyte. When LiBF$_4$ is used as the electrolyte, the PVA matrix forms homogeneous and transparent polymer electrolyte films up to about 1.5 g of LiBF$_4$/g of PVA. X-ray diffraction pattern (Figure 1) of the composite film shows no peak assignable to the Li salt. As shown in Figure 1, the diffraction peak of PVA is broadened by making the composite, revealing that PVA becomes amorphous by dissolving the lihtium salt. The PVA–lithium salt composite films remain transparent even after leaving them for 4.5 years at room temperature.

It is noteworthy that the PVA–LiBF$_4$ system forms the homogeneous film with such a high concentration of LiBF$_4$; 1.5 g of LiBF$_4$/g of PVA corresponds to 1 mol of LiBF$_4$/2.4 mol of the −CH$_2$–CH(OH)− monomer units of PVA. Weppner and co-workers reported that LiI formed an adduct with methanol having OH group to give LiI(CH$_3$-

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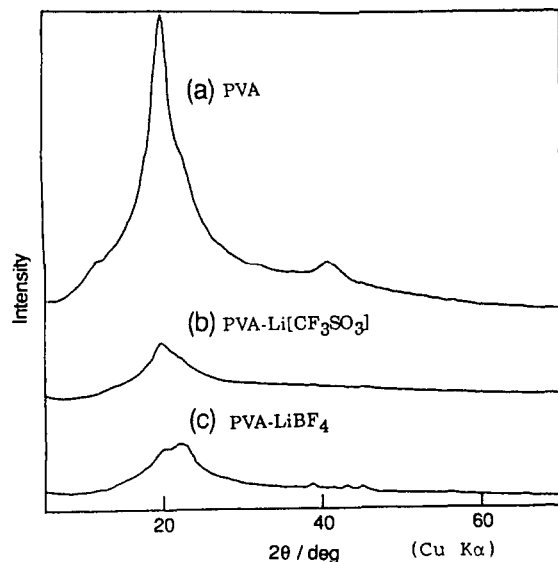
Figure 1. X-ray diffraction patterns of (a) PVA film, (b) PVA-Li[CF$_3$SO$_3$] (1.5 g/g of PVA) composite film, and (c) PVA-LiBF$_4$ (1.0 g/g of PVA) composite film.
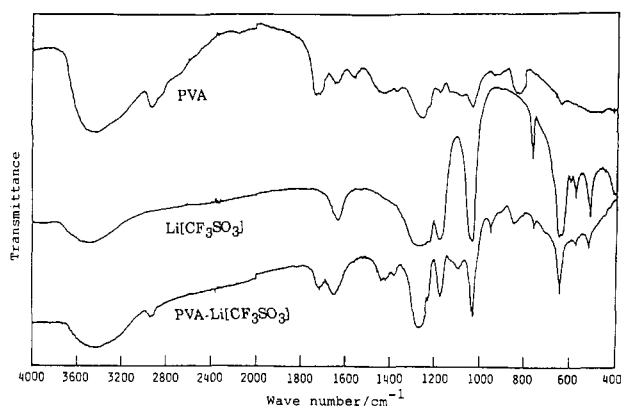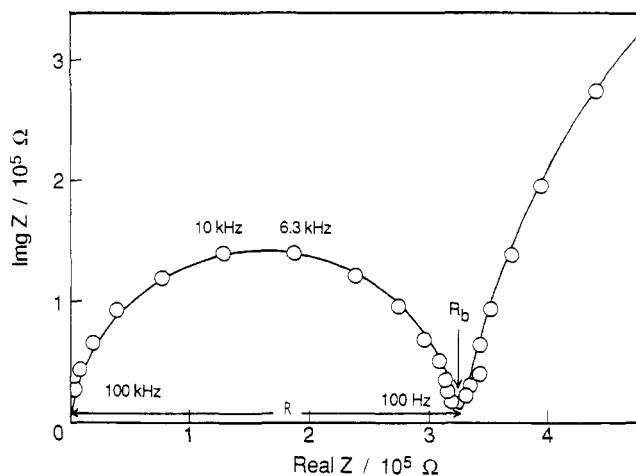

Figure 2. Comparison of the IR spectrum of the PVA-Li[CF$_3$SO$_3$] composite with those of PVA and Li[CF$_3$SO$_3$].
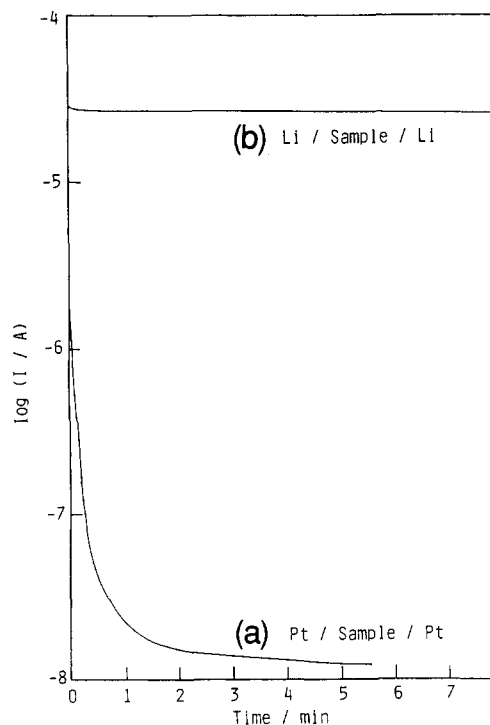

Figure 3. Complex impedance diagram (Cole-Cole plot) for the PVA-Li[CF$_3$SO$_3$] (0.62 g/g of PVA) composite film.

Figure 4. Time dependence of dc current for (a) Pt/PVA-LiBF$_4$ (1.0 g/g of PVA)/Pt junction and (b) Li/PVA-LiBF$_4$ (1.0 g/g of PVA)/Li junction. At room temperature.

OH)$_4$ and the adduct showed good ionic conductivity.[11] Addition of a larger amount of LiBF$_4$ to the PVA matrix gives a turbid heterogeneous film. The other lithium salts and [N(n-C$_4$H$_9$)$_4$][BF$_4$] have somewhat lower solubility in the PVA matrix, although their solubility in PVA is also considerably higher than their solubility in polymer matrices used for usual polymer electrolytes.

Figure 2 shows IR spectra of original PVA and the PVA-Li[CF$_3$SO$_3$] composite. The IR spectrum of the PVA-Li[CF$_3$SO$_3$] is essentially a superposition of the IR spectra of the original PVA and Li[CF$_3$SO$_3$] and no apparent shift of ν(O-H) band of PVA is observed, indicating that the interaction between the OH group of PVA and the Li salt is not strong. Other PVA-lithium salt polymer electrolytes also give rise to similar superposed IR spectra showing absorption bands originating from PVA and the lithium salt.

Figure 3 exhibits an example of Cole-Cole plot (complex impedance plot) for the PVA-lithium salt composite films, and the plot shows a normal pattern usually observed for polymer electrolytes.[1-5] The electrical conductivity of the polymer electrolytes reported in this paper is calculated from the R value shown in Figure 3.
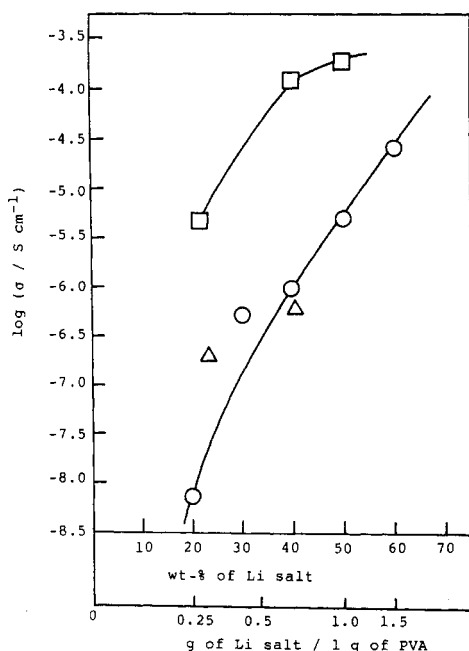
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Electrical current observed on application of dc voltage through gold or platinum electrode (blocking electrode) steeply decreases with time as exhibited by curve a in Figure 4, indicating that the electrical conduction of the composite film is originating from ionic conduction. Use of Li plate as an active electrode shows only minor decrease in the electric current with time on application of the dc voltage for short time (b in Figure 4), suggesting Li$^+$ at least participate in the ionic conduction. However, prolonged measurement revealed that the electric current decreases in an accelerating mode with time and after 18 and 30 min the electric current decreases to about 30 and 3%, respectively, of the initial value presumably due to polarization or moving of the anion species, thus suggesting that the anion species also participates in the ionic conduction. That the PVA-lithium salt composites serve as good solid electrolyte for double layer capacitor (*vide*

Figure 5. Electrical conductivity (σ) of the PVA–Li salt composites at 20 °C: Li[CF$_3$SO$_3$], $\triangle$, LiClO$_4$; $\square$; LiBF$_4$.

Figure 6. Temperature dependence of the σ value for the PVA–Li[CF$_3$SO$_3$] composite (g of Li[CF$_3$SO$_4$]/g of PVA: 0.25 ($\triangledown$), 0.66 ($\square$), 0.99 ($\triangle$), and 1.5 (O)) PVA–LiBF$_4$ composite (1.0 g/g of PVA, $\lozenge$), and PVA–LiClO$_4$ composite (1.0 g/g of PVA, ●).

infra) supports that both Li$^+$ and the anion move in the composites.

Figure 5 shows dependence of the electrical conductivity (σ) of the PVA–lithium composite film on the content of the lithium salt; all of the data shown in Figure 5 were taken for the homogeneous composite films. As shown in Figure 5, the composite shows good electrical conductivity at 20 °C in spite of the high glass transition temperature (85 °C[12]) of PVA. The electrical conductivity is comparable to or higher than those of the reported polymer electrolytes. One of interesting features of the PVA–lithium salt composites is that the electrical conductivity increases with increase in the content of the lithium salt over a wide range of the salt concentration. On the contrary, many 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 in the electrical conductivity.[3,5,6]

Figure 6 shows temperature dependence of the σ value of PVA–lithium salt electrolytes. As shown in Figure 6, the temperature dependence obeys Arrhenium type equation in most cases:

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

and the E_a values calculated from the slopes of the linear lines in Figure 6 are summarized in Table 1.

Figure 7 exhibits DSC curves of PVA, PVA–Li[CF$_3$-SO$_3$] composite, and PVA–LiBF$_4$ composite (cf. Experimental Section); the T_g and T_m values observed for PVA (curve a) are in close agreement with the reported value.[12] As shown by curves b and c, T_g and T_m values of PVA are lowered by making the polymer electrolyte. This observation is in contrast to a trend that the formation of polymer electrolytes by using usual matrix polymers generally leads to increase in T_m and indicates that
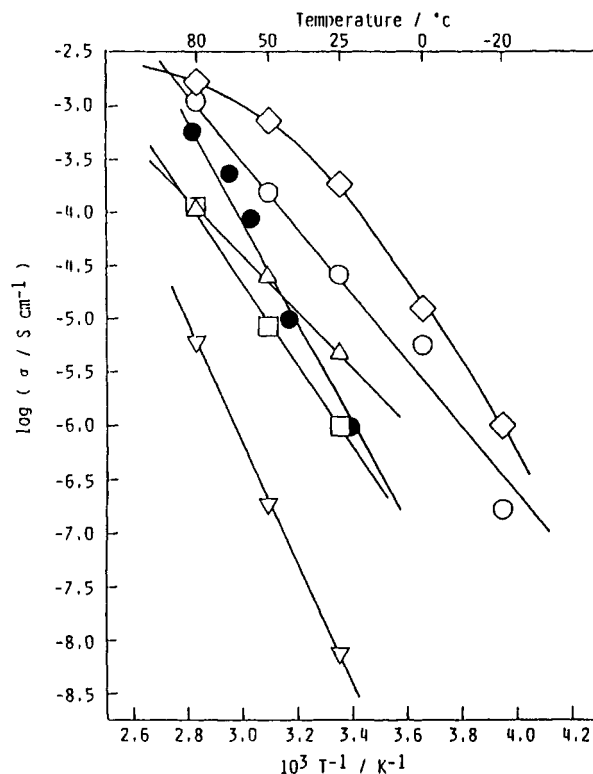
Table 1. Activation Energy E_a of the Polymer Electrolyte

polymer	salt (g/g of polymer)	E_a/kJ mol^{-1}
PVA	Li[CF$_3$SO$_3$], 0.25	107
PVA	Li[CF$_3$SO$_3$], 0.66	72
PVA	Li[CF$_3$SO$_3$], 0.99	50
PVA	Li[CF$_3$SO$_3$], 1.5	60
PVA	LiBF$_4$, 1.0	72[a]
PPA	LiBF$_4$, 0.54	65
PPA	LiClO$_4$, 0.54	89
PPA	NaClO$_4$, 0.54	80

[a] For a temperature range of –20 through 25 °C.

micromovement of the PVA chain becomes easier by making the composite, presumably owing to the decrease in the crystallinity of PVA (Figure 1). As discussed above, PVA becomes amorphous-like by dissolving the lithium salt (Figure 1), and the lowering of T_g and T_m values of PVA is related to the lowering of the degree of crystallinity. The lowering of T_g is expected to make the moving of ions in the polymer electrolytes more easily. However, the T_g is still higher than 20 °C where the conductivity shown in Figure 5 is measured, and the PVA–LiBF$_4$ composite with higher T_g than that of the PVA–Li[CF$_3$SO$_3$] exhibits higher conductivity. Moreover, as described above, the temperature dependence of the σ value obeys Arrhenius type equation in most cases and distinct change of the E_a value around T_g is not observed. These results suggest that the lowering of T_g is important for the migration of ions in the polymer electrolyte while the ions can also move even in the polymer matrix having a rather stiff region; the polymer electrolyte may be constituted of amorphous parts containing a high concentration of lithium salt and rather stiff parts containing a lower concentration of lithium salt, and the ions may move mainly through the amorphous parts.

(12) Brandrup, J.; Immergut, E. H. *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.
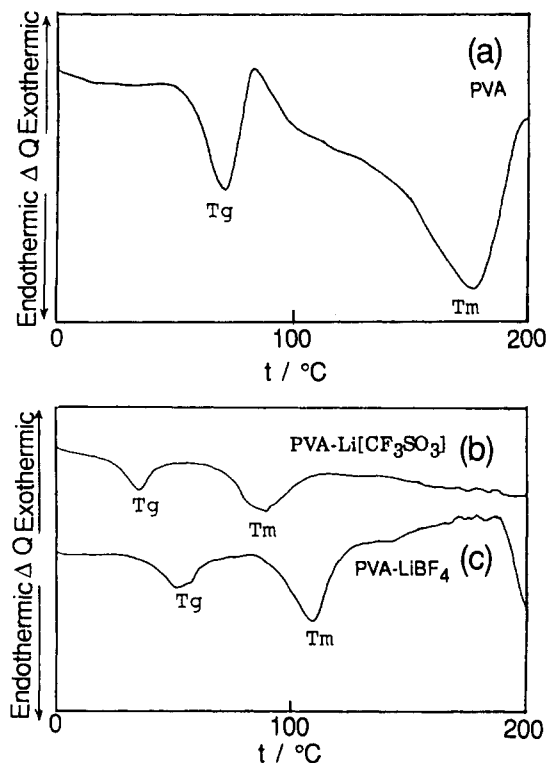
Figure 7. DSC curves of (a) PVA, (b) PVA–Li[CF₃SO₃] (1.5 g/g of PVA) composite, and (c) PVA–LiBF₄ (1.0 g/g of PVA) composite.

[(n-C₄H₉)₄N][BF₄](Bu₄NBF₄) and [(n-C₄H₉)₄N][BF₄]-(Bu₄NPF₆) have lower solubility in PVA and the Bu₄NY (Y = BF₄, PF₆) salts form homogenous PVA–Bu₄NY composites up to only about 0.25 g of Bu₄NY/g of PVA; addition of a higher amount of Bu₄NY makes a turbid heterogeneous composite. The homogeneous PVA–Bu₄-NBF₄ (0.11 g of Bu₄NBF₄/g of PVA) and PVA–Bu₄NPF₆ (0.11 g of Bu₄NPF₆/g of PVA) composites give only low electrical conductivity of 7 × 10⁻¹⁰ and 1 × 10⁻¹⁰ S cm⁻¹, respectively; the turbid PVA–Bu₄NBF₄ (0.43 g of Bu₄-NBF₄/g of PVA) and PVA–Bu₄NPF₄ (0.43 g of Bu₄NBF₄/g of PVA) composites give higher but still low electrical conductivity of 4 × 10⁻⁹ and 6 × 10⁻¹⁰ S cm⁻¹, respectively. Larger ionic radius of R₄N⁺ [13] than Li⁺ may account for the lower solubility of Bu₄NY and the lower ionic conductivity. Application of dc voltage to the PVA–Bu₄-NY composite film through blocking electrodes also leads to a rapid decrease in the dc current with time and the Cole–Cole plot for the PVA–Bu₄NY composite exhibits the normal pattern.

PPA-Based Polymer Electrolyte. PPA having a polyimide-like structure and high thermal stability with T_g of 350 °C[9] dissolves the lithium and sodium salts in as high as 0.7–1.5 g/g of PPA. The composites obtained look homogeneous, and the X-ray diffraction pattern of the PPA–Li[CF₃SO₃] composite (Figure 8b) shows no peak assignable to solid Li[CF₃SO₃] up to 1.5 g of the salt/g of PPA; on the other hand, addition of an excess amount of the lihtium salt gives heterogeneous film as shown in Figure 8c. The homogeneous PPA–lithium salt composite films remain homogeneous even after leaving them for 4 years at room temperature.

In contrast to PPA, use of a typical, soluble, and highly thermally stable polyimide PSEI (cf. Experimental Sec-

(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
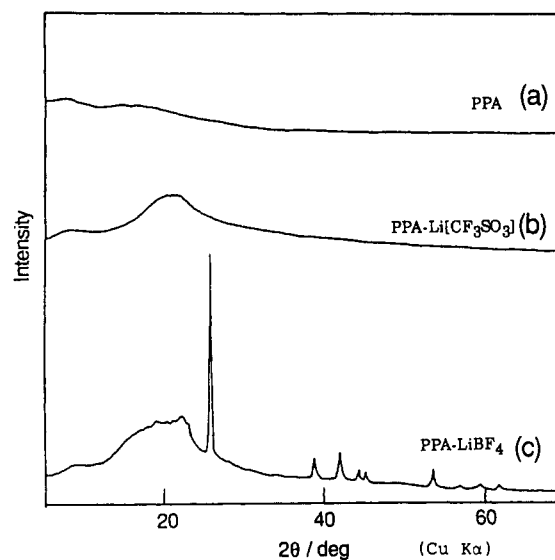
Figure 8. X-ray diffraction patterns of (a) PPA film, (b) PPA–Li[CF₃SO₃] (1.5 g/g of PPA) composite film, and (c) PPA–LiBF₄ (1.0 g/g of PPA) composite film.
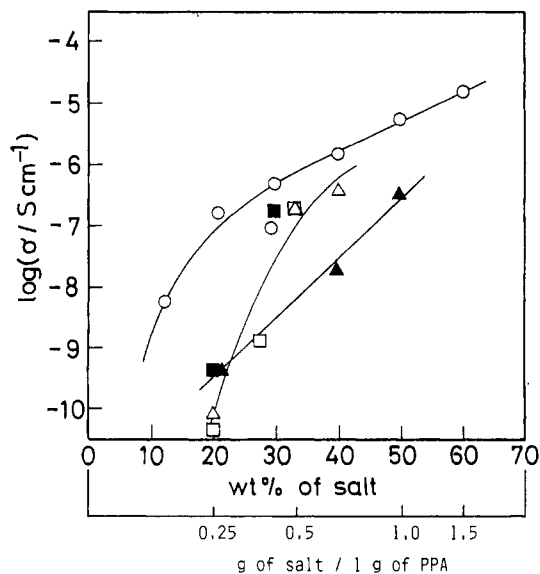
**Figure 9.** Electrical conductivity (σ) of the PPA–alkali metal salt composite at 20 °C: ○, Li[CF₃SO₃]; △, LiBF₄; □, LiClO₄; ▲, NaBF₄; ■, NaClO₄.

tion) instead of PPA did not give such a homogeneous composite; dissolution of the polymer and Li[CF₃SO₃] (0.16–0.5 g/g of PSEI) in DMF, *N,N*-dimethylacetamide, or *N*-methyl-2-pyrrolidone (cf. Experimental Section), and drying up the solvent gave only a heterogeneous and brittle composites.

Complex impedance plots for the PPA-based polymer electrolytes also exhibits normal pattern. Electrical current observed on application of dc voltage through the gold or platinum electrodes also decreases steeply with time.

Figure 9 shows dependence of electrical conductivity of the PPA–alkali metal salt composite films on the concentration of the salt; all of the data shown in Figure 9 were also taken for the homogeneous composite films. As shown in Figure 9, the composite film shows moderate electrical conductivity at 20 °C at a high concentration range of the salt, and the electrical conductivity is comparable or somewhat lower compared with those of reported polymer electrolytes.[1–5] The σ value of the PPA–
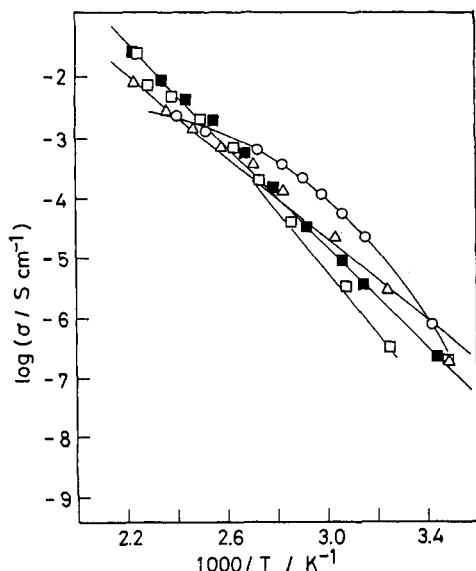
Figure 10. Temperature dependence of the σ value for the PPA–Li[CF$_3$SO$_3$] (0.67 g/g of PPA, O), PPA–LiBF$_4$ (0.54 g/g of PPA, △), PPA–LiClO$_4$ (0.54 g/g of PPA, □) and PPA–NaClO$_4$ (0.54 g/g of PPA, ■) composites.

alkali metal salt composite also increases with increase in the content of the salt.

Figure 10 depicts temperature depencence of the electrical conductivity of PPA–alkali metal salt composite films. The temperature dependence obeys Arrhenius type equation over a wide temperature range (20–170 °C) in most cases. The activation energy (E_a) obtained from the slope of the line in Figure 10 are also given in Table 1. 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 170 °C. The composite film does not melt in the temperature range shown in Figure 10. DSC curves of the PPA–lithium composites (Figure 11) also reveal that the T_g of PPA matrix is lowered by making the composite, and the PPA–lithium salt composites have T_m of higher than about 220 °C.

Features of the PVA and PPA Polymer Electrolytes and Scope. As described above, PVA and PPA dissolve the alkali metal salt in high concentrations, and the polymer electrolytes exhibit moderate conductivity ($\sigma = 10^{-5}$–$10^{-3.5}$ S cm^{-1} at 20 °C) in spite of high T_g of PVA and PPA (85^{12} and 350 °C,^{9} respectively). Use of such a polymer as PPA with very high T_g as the matrix polymer of the polymer electrolyte has no precedent.

The ionic conductivity of the polymer electorlyte can be expressed by the following equation:

$$\sigma = en_+\mu_+ + en_-\mu_- \tag{2}$$

where e, n_+, n_-, μ_+, and μ_- are the charge of ion, concentrations of cation and anion, and mobilities of cation and anion, respectively. The moderate value of σ and considerably high n_+ and n_- values for the present polymer electrolytes compared with those of usual polymer electrolytes [e.g., poly(ethylene oxide)-based polymer electrolytes] suggest lower mobility of the carrier in the present polymer electrolytes than that in the usual polymer electrolytes; lower σ value of the PPA-based polymer electrolyte than that of the PVA-based polymer electrolyte (except for the composite with Li[CF$_3$SO$_3$]) at the same salt concentration is reasonably explained by a lower μ_+ and μ_- values in PPA than that in PVA owing to the high
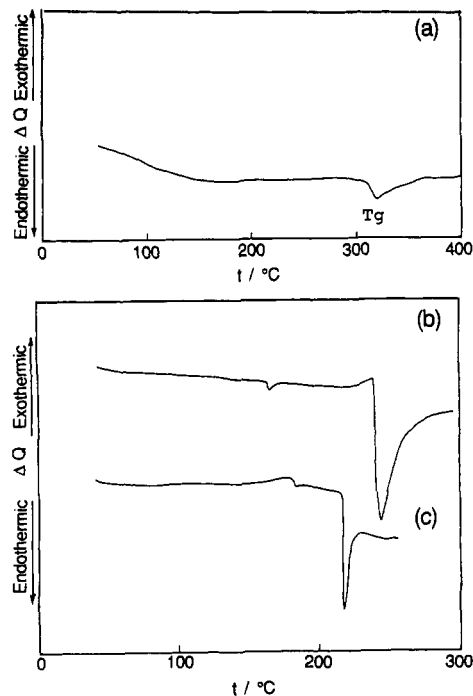
Figure 11. DSC curves of (a) PPA, (b) PPA–Li[CF$_3$SO$_3$] (1.5 g/g of PPA), composite, and (c) PPA–LiBF$_4$ (0.5 g/g of PPA) composite.

T_g of PPA. The high solubility of the salt in PVA may be related to the presence of the OH group in high concentrations, although the IR spectrum of the PVA-based polymer electrolyte shows no apparent shift of the ν(OH) band. It was recently reported that the solubility of salts in poly(ethylene oxide) can be related to the concentration of terminal OH group of the polymer.^{14}

Application of eq 2 for the PVA–Li[CF$_3$SO$_3$] and PPA–Li[CF$_3$SO$_3$] composites with 50 wt % of salt corresponding to about the n_+ and n_- values of about 2 × 10^{21} cm^{-3} and en$_+$ + en$_-$ value of about 6 × 10^2 C cm^{-3} (2 × 1.6 × 10^{-19} C × 2 × 10^{21} cm^{-3} at complete dissociation of Li[CF$_3$SO$_3$]) gives the μ_+ + μ_- value of 0.8 × 10^{-8} cm^2 V^{-1} s^{-1} [σ/(en$_+$ + en$_-$) = 5 × 10^{-6} S cm^{-1} (Figure 5)/6 × 10^{2}C cm^{-3} = 0.8 × 10^{-8} cm^2 V^{-1} s^{-1}] and 1 × 10^{-8} cm^2 V^{-1} s^{-1}, respectively. As shown in Figures 5 and 9, the σ value increases more steeply compared with the increase in the concentration of the lithium salt, [LiY], indicating that the μ_+ + μ_- value and/or degree of the dissociation of LiY increases with increase in [LiY]. At 60 wt % of Li[CF$_3$SO$_3$] in the PVA–Li[CF$_3$SO$_3$] composite, the σ value (Figure 5) and the en$_+$ + en$_-$ value of about 8 × 10^2 C cm^{-3} at complete dissociation of Li[CF$_3$SO$_3$] give the μ_+ + μ_- value of 4 × 10^{-7} cm^2 V^{-1} s^{-1}, which roughly agrees the value estimated from charge–discharge behavior of a double capacitor using the PVA–Li[CF$_3$SO$_3$] solid electrolyte (*vide infra*).

The fact that the polyimide PSEI does not dissolve the lithium salts in contrast to the high solubility of the salt in PPA indicates the importance of the 1,3-imidazolidine-2,4,5-trione unit in dissolving the salt and that the imide group does not work as an effective group to dissolve the salt. Other thermally stable polymers with such cyclic units like the 1,3-imidazolidine-2,4,5-trione with many nitrogen and oxygen atoms or the 1,3-dioxa-2-one in propylene carbonate may also dissolve the salts and give good polymer electrolytes.

(14) Ohno, H.; Sasayama, H.; Satoh, H.; Wang, P. *Polym. Prepr. Jpn.* **1990**, *39*, 3206.

Since the PVA-based polymer electrolytes can contain the salts in high concentrations they are expected to serve as excellent electrolytes for solid electrolyte double-layer capacitors. The double-layer capacitor usually requires a large amount of mobile ions for making effective double layer to give a large value of capacitance, and the solid electrolyte double-layer capacitors using the PVA-based polymer electrolytes actually show excellent charging–discharging behaviors with essentially the same capacitance as that of double-layer capacitor using liquid electrolytes.[15] The double-layer capacitor shows normal repeated charge–discharge curves,[15] excluding a possibility of occurrence of special reactions like evolution of H_2 and oxidation of PVA due to moving H^+ originated from the OH group of PVA. The conceivable contribution of the movement of H^+ to the ionic conduction will lead to the evolution of H_2 and oxidation of PVA ($2H^+ + 2e \rightarrow H_2$; $-CH_2-CH(OH)- \rightarrow -CH_2-CO- + 2H^+ + 2e$), however, indication of occurrence of such reactions has not been observed, revealing migration of H^+ essentially does not contribute to the ionic conduction in the present PVA–Li salt composite.

The capacitance of the double-layer capacitor estimated from charge–discharge profile of the capacitor remains essentially constant at a relatively small charging and discharging electric current range. However, further increase in the charging and discharging current causes decrease in the capacitance, presumably due to the difficulty for the cation and anion to follow the large electric current. A rough value of mobility of ions estimated from

a limiting electric current, beyond which the capacitance begins to decrease, and structure of the double-layer capacitor[15] has an order of 10^{-7} cm^2 V^{-1} s^{-1} at 50 °C for the capacitor using the PVA–Li[CF$_3$SO$_3$] electrolyte (wt % of Li[CF$_3$SO$_3$] = 60), the value roughly agreeing the mobility of ions estimated according to eq 2 (*vide ante*).

The temperature dependence of the conductivity of the present polymer electrolyte obeys, in most cases, the Arrhenius type equation in contrast to that of the usual polymer electrolytes,[1-5] which usually show temperature dependence following a WLF type equation. The PPA-based polymer electrolytes have high thermal stability up to 170 °C (Figure 10), and they are expected to serve for making solid electrolyte devices working at high temperatures. Thermal treatment of lithium foil–PVA-based polymer electrolyte film junction at 80 °C led to degradation of both the lithium foil and the polymer electrolyte film. However, lithium foil–PPA-based polymer electrolyte film junction exhibited good thermal stability at 80 °C and no apparent degradation was observed for either the lithium foil and the polymer electrolyte.

(15) Kanbara, T.; Inami, M.; Yamamoto, T. *J. Power Sources* **1991**, *36*, 87. For the structure of the capacitor, see this reference; separating part between two carbon–clay composite electrodes of the capacitor is constituted of the PVA-Li[CF$_3$SO$_3$] composite and has a diameter of 1.0 cm and thickness of 0.025 cm. This capacitor shows the limiting electric current of 100 μA cm^{-2} at 50 °C.