

# Conductivity enhancement of polyacrylonitrile-based electrolytes by addition of cascade nitrile compounds

Hiromori Tsutsumi<sup>\*</sup>, Akiko Matsuo, Kimio Takase, Shizuka Doi, Atsushi Hisanaga, Kenjiro Onimura, Tsutomu Oishi

*Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan*

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## Abstract

A cascade nitrile compound ( $[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CN})_2]_2$ , ED4CN) made by addition of acrylonitrile to alkyldiamine (1,2-diaminoethane), has been used as a plasticizer for solid polymer electrolytes. The ionic conductivity of a polymer electrolyte using this type of plasticizer in polyethylene oxide (PEO)- and polyacrylonitrile (PAN)- $\text{LiClO}_4$  complex was measured. Addition of ED4CN to PEO-based electrolytes did not enhance the conductivity of them. However, interaction between ED4CN and lithium ions in the complex was confirmed by infrared spectroscopy. The peak assigned to the stretching vibration of nitrile group in ED4CN shifted to high-energy side. The shift indicated that the nitrile groups interacted with the lithium ions in the PEO-based electrolytes. Conductivity enhancement was observed in the PAN-based electrolytes containing ED4CN. Conductivity of the electrolyte containing ED4CN was about 10 or 23 times larger than that of the electrolyte without ED4CN. Addition of ED4CN to a PAN- $\text{LiClO}_4$  electrolyte decreases the glass transition temperature of the complexes. Conductivity enhancement of the PAN-based electrolyte with ED4CN containing lithium salt in high concentration was also confirmed. Other low molecular weight additives, tetraethylsulfamide (TESA) and a cascade nitrile compound, ( $[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CN})_2]_2$ , TE4CN) were also used and their possibility for a conducting enhancer of PAN-based electrolytes was tested. TESA was effective; however, TE4CN was inactive for a conductance enhancer of the PAN-based electrolytes. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Solid polymer electrolyte; Polyethylene oxide; Polyacrylonitrile; Plasticizer; Cascade molecule; Conductive enhancer

## 1. Introduction

Development of portable electric equipment, such as mobile telephone, notebook computer, has been remarkable in the last decade. Power sources for such devices are normally various batteries, nickel–cadmium, nickel–hydrogen, and lithium-ion batteries. Performance of the batteries affects the performance of the devices with them. A high performance battery with high energy density, high power density, and high quality is indispensable for further development of the portable electric equipment. A battery has a cathode, an anode, and an electrolyte in the cell container. When a liquid electrolyte is used in the battery, the container should prevent the leak of the liquid elec-

trolyte from the battery. The weight of the container decreases specific energy density of the battery. Using solid polymer electrolytes will lighten the weight of the container. Solid polymer electrolyte is an essential material for a thin-film battery with high performance. Many solid polymer electrolyte systems, such as polyethylene oxide (PEO)-based, polyacrylonitrile (PAN)-based electrolytes, have been prepared and characterized [1–8]. Enhancement of conductivity for the solid polymer electrolytes has been accomplished by various methods. Addition of low molecular weight compounds is one of the techniques for conductance enhancement of the electrolytes. Many compounds have been added to the polymer electrolyte systems. For example, preparation of the electrolyte systems containing propylene carbonate (PC), ethylene carbonate (EC), various dialkylphthalate, or other compounds and their applications to lithium or lithium-ion batteries have been investigated [9–18].

<sup>\*</sup> Corresponding author. Tel.: +81-836-85-9282; fax: +81-836-85-9201.

*E-mail address:* tsutsumi@po.cc.yamaguchi-u.ac.jp (H. Tsutsumi).

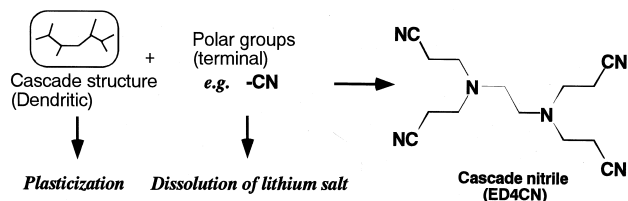


Fig. 1. Concept of a cascade nitrile compound as a conductive enhancer for solid polymer electrolytes.

Recently, a large number of dendritic or cascade molecules based on branched structures has been synthesized. Their properties attributed to their unique structures have been reported [19]. We have prepared the cascade molecules and used them as a conductivity enhancer for PEO- and PAN-based solid polymer electrolytes [15,16]. A dendritic or cascade molecule precludes densely packing due to steric hindrance itself and has a large number of terminal functional groups on its surface. Our approach to enhancement of conductivity of a solid polymer electrolyte is the addition of dendritic or cascade structure materials as a plasticizer. We think that such molecule will act as a good and bulky plasticizer to enhance polymer segment movements and/or as a dissolution enhancer of the salt in the polymer matrix. Schematic presentation of our conductive enhancer is shown in Fig. 1. Primary results of ED4CN as a conductive enhancer were reported in our previous paper [16].

In this paper, we report that possibility of cascade nitrile compounds (ED4CN and TE4CN, see Fig. 2) as a conductive enhancer for PEO- and PAN-based electrolytes. Addition of tetraethylsulfamide (TESA) that reported as a plasticizer for PEO–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte [10] to PAN-based electrolytes was also investigated.

## 2. Experimental

All chemicals for the experiments were used as received unless otherwise mentioned. Fig. 2 shows structure of the cascade nitrile compounds (ED4CN and TE4CN) added to the electrolytes. The cascade compounds with terminal nitrile groups were prepared by addition of acrylonitrile to the corresponding diamine [20]. PAN were parched from Aldrich and used without further purification. Typical procedure to prepare PAN-based electrolytes is as followed.

PAN (2.653 g, 50 mmol based on the repeating unit) and ED4CN (680 mg, 2.5 mmol) was dissolved into PC by heating about 120°C. Lithium perchlorate (LiClO<sub>4</sub>, 0.266 g, 2.5 mmol) was added into the homogeneous PC solution, after the solution was cooled below 100°C. After the dissolution of LiClO<sub>4</sub>, the solution was poured into an Al foil dish (3 cm diameter). The PC in the solution was removed by heating under dynamic vacuum. The amount

of remaining PC in the electrolyte film was estimated by measuring the weight of the film. For example, composition of a complex film is presented as (PAN)<sub>20</sub>(LiClO<sub>4</sub>)<sub>1</sub>(ED4CN)<sub>1</sub>(PC)<sub>x</sub>. This means that the film is containing 1 mol of lithium salt (LiClO<sub>4</sub>), 1 mol of ED4CN, and *x* mol of PC per 20 mol of acrylonitrile (monomer) units.

PEO (M<sub>w</sub> = 100 000, Aldrich) was also used for a matrix polymer. An acetonitrile solution containing PEO, Li salt, and low-molecular weight compounds (for example, ED4CN) was cast and the acetonitrile was removed by heating in a vacuum oven. In this case, remaining of solvent in the film was not observed.

A sample film for conductance measurement was sandwiched with two stainless plates (13 mm in diameter) and the sample was placed in a sealed cell under dry condition. Conductivity of the electrolyte was measured with an LCR meter (HIOKI 3531 Z Hi tester, 10–100 mV<sub>p-p</sub>, 1–10 kHz) under various temperature conditions.

DSC measurements of samples were performed with a differential scanning calorimeter (SSC5200, SEIKO) with heating rate at 10 K min<sup>-1</sup> and cooling rate at 5 K min<sup>-1</sup> in the temperature range from –100°C to 120°C.

X-ray diffraction patterns were recorded with an X-ray diffraction meter (XD-D1, Shimadzu).

## 3. Results and discussion

### 3.1. PEO-based electrolytes containing ED4CN

PEO-based electrolytes with and without ED4CN were prepared and their characterization was performed with conductivity, DSC, and X-ray diffraction measurements. Fig. 3 shows the temperature dependence of conductivity for the PEO–LiClO<sub>4</sub> electrolytes with and without ED4CN. Three curves in Fig. 3 are very similar to each of them. Structural consideration of the complex films was per-

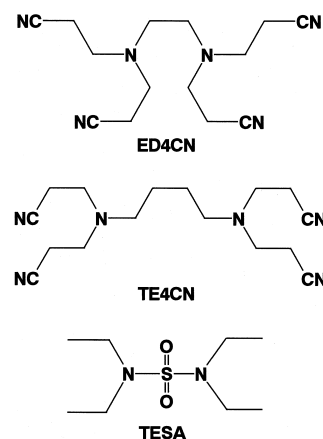


Fig. 2. Structure of cascade nitrile compounds (ED4CN and TE4CN) and tetraethylsulfamide (TESA).

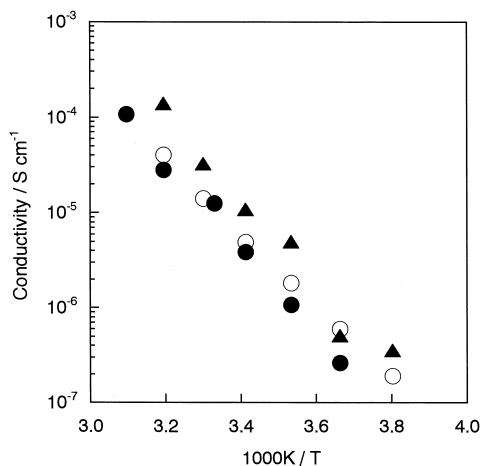


Fig. 3. Temperature dependence of conductivity for PEO-based electrolytes, (PEO)20(LiClO<sub>4</sub>)1(ED4CN)<sub>x</sub> film. (○)  $x = 0$ , (●)  $x = 1$ , (▲)  $x = 2$ .

formed by X-ray diffraction measurements of them. Fig. 4 shows the diffraction patterns of the films at room temperature (20–25°C). The patterns are very similar to each of them. Glass transition temperatures ( $T_g$ ) of the complex films were recorded by DSC measurements. The results are listed in Table 1.  $T_g$  of ED4CN was  $-54.3^\circ\text{C}$ . Addition of ED4CN to PEO matrix induced increase in  $T_g$  of the PEO complex films, for example,  $T_g$  of (PEO)-20(LiClO<sub>4</sub>)1(ED4CN)<sub>x</sub> was  $-42^\circ\text{C}$  ( $x = 0$ ) and  $-33.1^\circ\text{C}$  ( $x = 1$ ). Thus, ED4CN does not act as a plasticizer for the (PEO)20(LiClO<sub>4</sub>)1 complex. However, conductivity for the PEO–LiClO<sub>4</sub> electrolyte containing ED4CN is almost the same as that of the electrolyte without ED4CN. The results suggest that some complementary mechanism for maintaining conductivity in the PEO–LiClO<sub>4</sub> electrolyte with ED4CN should be considered.

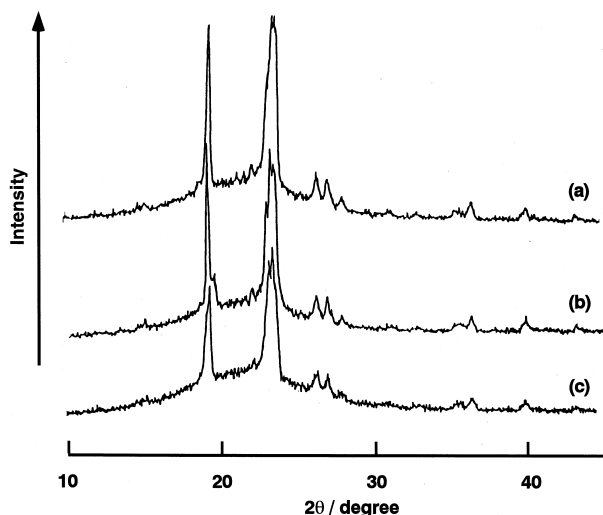


Fig. 4. X-ray diffraction patterns of PEO-based electrolytes (PEO)20(LiClO<sub>4</sub>)1(ED4CN)<sub>x</sub> film. (a)  $x = 0$ , (b)  $x = 1$ , (c)  $x = 2$ .

Table 1

Glass transition temperature of PEO-based electrolytes

Electrolyte	Glass transition temperature ( $^\circ\text{C}$ )
(PEO)20(LiClO <sub>4</sub> )1	$-42.0$
(PEO)20(LiClO <sub>4</sub> )1(ED4CN)1	$-33.1$
(PEO)20(LiClO <sub>4</sub> )1(ED4CN)2	$-27.4$

Interaction between lithium (Li) ion and nitrile groups in ED4CN was observed by FTIR measurements of the complex films. Fig. 5 shows the extended spectra in the region from 2300 to 2200  $\text{cm}^{-1}$  of the complex films. This peak is attributed to the stretching vibration of the triple bond between carbon and nitrogen in the nitrile group. Fig. 5(a) is the spectrum of ED4CN. The peak at  $2244\text{ cm}^{-1}$  and the shoulder at  $2249\text{ cm}^{-1}$  were observed. Addition of LiClO<sub>4</sub> into the PEO matrix containing ED4CN shifted the main peak at  $2244$  to  $2249\text{ cm}^{-1}$  (high-energy side). The peak shift due to an induction effect [21] suggests that lithium ions in the electrolyte interact with the nitrile groups in ED4CN. We concluded that the interaction between lithium ions and nitrile groups in ED4CN supports the dissolution of the LiClO<sub>4</sub> into the PEO matrix. Increase in the number of charge carriers in the matrix maintained the conductivity for the high  $T_g$  PEO–LiClO<sub>4</sub> complex with ED4CN.

### 3.2. PAN-based electrolytes with ED4CN

PAN-based electrolytes were also prepared and their conductive behavior was investigated. As described in the Experimental Section, a small amount of PC used for solvent remained in the PAN-based electrolytes. The weight of the remaining PC in the PAN-based electrolytes was measured and the amount of the PC in the electrolytes was presented as the molar ratio based on PAN repeating unit. Fig. 6 shows the temperature dependence of the con-

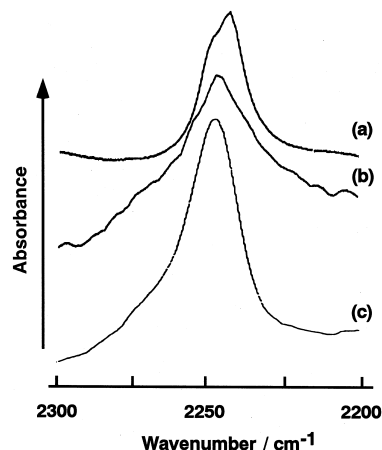


Fig. 5. IR spectra of ED4CN and PEO-based electrolytes (PEO)20(LiClO<sub>4</sub>)1(ED4CN)<sub>x</sub> film. (a) ED4CN, (b)  $x = 1$ , (c)  $x = 2$ .

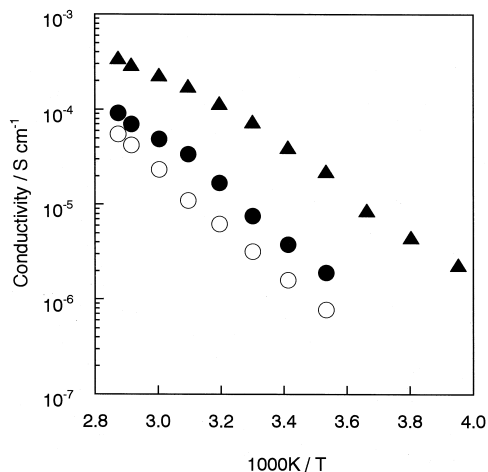


Fig. 6. Temperature dependence of conductivity for PAN-based electrolytes, (PEO)20(LiClO<sub>4</sub>)1(ED4CN)*x*(PC)*y*. (○) *x* = 0, *y* = 6.33, (●) *x* = 1, *y* = 3.30, (▲) *x* = 2, *y* = 8.23.

ductivity for the PAN–LiClO<sub>4</sub> electrolytes with and without ED4CN. Conductivity of (PAN)20(LiClO<sub>4</sub>)1(ED4CN)*x*(PC)*y* was  $3.20 \times 10^{-6}$  S cm<sup>-1</sup> (*x* = 0, *y* = 6.33),  $7.59 \times 10^{-6}$  S cm<sup>-1</sup> (*x* = 1, *y* = 3.30), and was  $7.48 \times 10^{-5}$  S cm<sup>-1</sup> (*x* = 2, *y* = 8.23) at 30°C. The conductivity for the electrolytes with ED4CN was about 10 or 23 times larger than that of the electrolyte without ED4CN. Addition of ED4CN to PAN-based electrolytes enhanced the conductance of them. The curves of the complexes with ED4CN, especially the (PAN)20(LiClO<sub>4</sub>)1(ED4CN)2(PC)8.23 complex, are slightly convex. The temperature dependence of conductivity suggests that the elastic behavior of the PAN-based electrolytes govern ion movement in them. *T<sub>g</sub>* values of the PAN-based electrolytes are listed in Table 2. *T<sub>g</sub>* of PAN is 97°C [22]. *T<sub>g</sub>* of (PAN)20(LiClO<sub>4</sub>)1(PC)6.33 complex was -54.5°C. PC in the PAN matrix acts as a plasticizer [14]. *T<sub>g</sub>* of (PAN)20(LiClO<sub>4</sub>)1(ED4CN)*x*(PC)*y* was -67.2°C (*x* = 1, *y* = 3.30) and -75.8°C (*x* = 2, *y* = 8.23). Addition of ED4CN to PAN-matrix lowers the *T<sub>g</sub>* of the PAN-based electrolytes with LiClO<sub>4</sub> and PC. The result indicates that

Table 2

Glass transition temperature of PAN-based electrolytes

(a) Glass transition temperature of PAN is 97°C and that of ED4CN is -54.3°C.

Electrolyte	Glass transition temperature (°C)
(PAN)20(LiClO <sub>4</sub> )1(PC)6.33	-54.5
(PAN)20(LiClO <sub>4</sub> )1(ED4CN)1(PC)3.30	-67.2
(PAN)20(LiClO <sub>4</sub> )1(ED4CN)2(PC)8.23	-75.8
(PAN)20(LiClO <sub>4</sub> )5(PC)9.27	-70.6
(PAN)20(LiClO <sub>4</sub> )5(ED4CN)1(PC)13.4	-75.9
(PAN)20(LiClO <sub>4</sub> )5(ED4CN)2(PC)5.82	-71.7
(PAN)20(LiClO <sub>4</sub> )10(PC)15.6	-71.7
(PAN)20(LiClO <sub>4</sub> )10(ED4CN)1(PC)8.80	-73.8
(PAN)20(LiClO <sub>4</sub> )10(ED4CN)2(PC)23.6	-78.9

ED4CN molecules in the electrolyte cooperate with PC as a plasticizer for PAN–LiClO<sub>4</sub> electrolytes.

Fig. 7 shows infrared spectra of PAN-based electrolytes with and without ED4CN. A peak at 2248 cm<sup>-1</sup> in Fig. 7(a) is assigned to the stretching vibration of free nitrile in the matrix. A peak shift from 2248 to 2270 cm<sup>-1</sup> was observed in the PAN-based electrolytes with ED4CN (Fig. 7(b) and (c)). The peak shift is induced by the interaction between Li ions (from dissolution of LiClO<sub>4</sub> in the complex) and the nitrile groups as mentioned in Section 3.1. The absorbance (*A*) ratio (*A*<sub>2270 cm<sup>-1</sup></sub>/*A*<sub>2248 cm<sup>-1</sup></sub>) is a measure of the degree of interaction between Li ions and the nitrile groups. The value of the (PAN)20(LiClO<sub>4</sub>)1(ED4CN)*x*(PC)*y* electrolytes was 0.13, (*x* = 0, *y* = 6.30), 0.30 (*x* = 1, *y* = 3.30), and 0.21 (*x* = 1, *y* = 8.20). The total amount of lithium salt is almost same for each of these films. Increase in the ratio (*A*<sub>2270 cm<sup>-1</sup></sub>/*A*<sub>2248 cm<sup>-1</sup></sub>) suggests that the number of Li ions interacting with the nitrile group in the matrix increases by addition of ED4CN. ED4CN acts as a dissolution enhancer in the electrolyte.

The complexes with high salt concentration were also prepared and characterized. Fig. 8 shows the temperature dependence of conductivity for the PAN-based electrolytes with various lithium salt concentrations. Conductivity for the (PAN)20(LiClO<sub>4</sub>)*x*(ED4CN)*y*(PC)*z* film was  $8.36 \times 10^{-4}$  S cm<sup>-1</sup> (*x* = 5, *y* = 0, *z* = 9.27),  $1.41 \times 10^{-3}$  S cm<sup>-1</sup> (*x* = 5, *y* = 1, *z* = 13.4),  $4.24 \times 10^{-4}$  S cm<sup>-1</sup> (*x* = 10, *y* = 0, *z* = 15.6), and  $1.65 \times 10^{-3}$  S cm<sup>-1</sup> (*x* = 10, *y* = 1, *z* = 8.80) at 30°C. As listed in Table 2, *T<sub>g</sub>* of the complexes with high lithium salt concentration was about -70°C. Addition of ED4CN to the complexes does not act as an effective plasticizer, but as a conductance enhancer. ED4CN supports the dissolution of lithium salts in the complexes as described above.

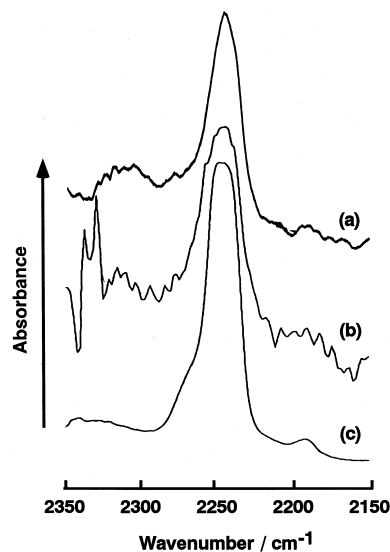


Fig. 7. IR spectra of PEO-based electrolytes (PEO)20(LiClO<sub>4</sub>)1(ED4CN)*x*(PC)*y* film. (a) *x* = 0, *y* = 6.33, (b) *x* = 1, *y* = 3.30 (c) *x* = 2, *y* = 8.23.

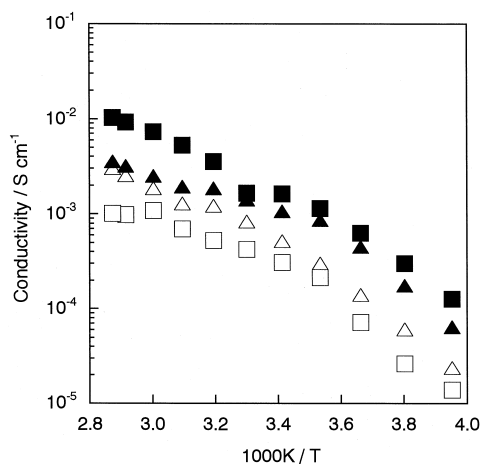


Fig. 8. Temperature dependence of conductivity for PAN-based electrolytes, (PAN)20(LiClO<sub>4</sub>)<sub>x</sub>(ED4CN)<sub>y</sub>(PC)<sub>z</sub>. (Δ)  $x = 5$ ,  $y = 0$ ,  $z = 9.27$ , (□)  $x = 10$ ,  $y = 0$ ,  $z = 15.6$ , (▲)  $x = 5$ ,  $y = 1$ ,  $z = 13.4$ , (■)  $x = 10$ ,  $y = 1$ ,  $z = 8.80$ .

### 3.3. PAN-based electrolytes with low molecular weight additives

PAN-based electrolytes containing other additives, TESA or TE4CN (see Fig. 2) were prepared and their conductive behavior was investigated. TESA is used as a plasticizer PEO–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte [10]. TESA is a nonvolatile liquid of moderate permittivity ( $\epsilon = 29$ ) and its  $T_g$  is  $-111^\circ\text{C}$  [10]. Fig. 9 shows the temperature dependence of conductivity for PAN-based electrolytes with TESA. Addition of TESA to PAN matrix containing LiClO<sub>4</sub> enhanced the PAN-based electrolytes. Conductivity of (PAN)20(LiClO<sub>4</sub>)<sub>1</sub>(TESA)<sub>x</sub>(PC)<sub>y</sub> was  $3.20 \times 10^{-6} \text{ S cm}^{-1}$  ( $x = 0$ ,  $y = 6.33$ ),  $1.08 \times 10^{-5} \text{ S cm}^{-1}$  ( $x = 1$ ,  $y = 5.36$ ) at  $30^\circ\text{C}$ .  $T_g$  values of the PAN-based electrolytes with and without TESA are listed in Table 3. Addition of TESA to PAN-based electrolytes decreased the  $T_g$  of

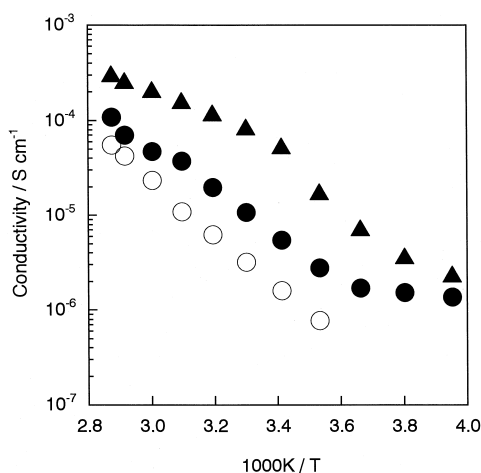


Fig. 9. Temperature dependence of conductivity for PAN-based electrolytes, (PAN)20(LiClO<sub>4</sub>)<sub>1</sub>(TESA)<sub>x</sub>(PC)<sub>y</sub>. (○)  $x = 0$ ,  $y = 6.33$ , (●)  $x = 1$ ,  $y = 5.36$ , (▲)  $x = 2$ ,  $y = 3.50$ .

Table 3

Glass transition temperature of PAN-based electrolytes with TESA and TE4CN

(a) Glass transition temperature of PAN is  $97^\circ\text{C}$ , that of TESA is  $-111^\circ\text{C}$ , and that of TE4CN is  $-54.9^\circ\text{C}$ .

Electrolyte	Glass transition temperature ( $^\circ\text{C}$ )
(PAN)20(LiClO <sub>4</sub> ) <sub>1</sub> (PC)6.33	$-54.5$
(PAN)20(LiClO <sub>4</sub> ) <sub>1</sub> (TESA) <sub>1</sub> (PC)5.36	$-78.8$
(PAN)20(LiClO <sub>4</sub> ) <sub>1</sub> (TESA) <sub>2</sub> (PC)3.50	$-63.4$
(PAN)20(LiClO <sub>4</sub> ) <sub>5</sub> (PC)9.27	$-70.6$
(PAN)20(LiClO <sub>4</sub> ) <sub>5</sub> (TESA) <sub>1</sub> (PC)7.96	$-49.8$
(PAN)20(LiClO <sub>4</sub> ) <sub>5</sub> (TESA) <sub>2</sub> (PC)11.0	$-67.2$
(PAN)20(LiClO <sub>4</sub> ) <sub>10</sub> (PC)15.6	$-71.7$
(PAN)20(LiClO <sub>4</sub> ) <sub>10</sub> (TESA) <sub>1</sub> (PC)7.45	$-50.4$
(PAN)20(LiClO <sub>4</sub> ) <sub>10</sub> (TESA) <sub>2</sub> (PC)22.8	$-49.9$
(PAN)20(LiClO <sub>4</sub> ) <sub>10</sub> (TE4CN) <sub>2</sub> (PC)2.00	$-48.8$

PAN-based electrolytes containing LiClO<sub>4</sub> in low concentration. However, the  $T_g$  of the complexes with TESA containing Li salt in higher concentration increased.

TE4CN is a cascade nitrile prepared from acrylonitrile and 1,4-diaminobutane. The structure is similar with that of ED4CN, except for the methylene chain length between one amine nitrogen and another one.  $T_g$  of TE4CN is  $-54.9^\circ\text{C}$  and its melting point (mp) is  $54.8^\circ\text{C}$ .  $T_g$  of ED4CN is  $-54.3^\circ\text{C}$  and its mp is  $66.8^\circ\text{C}$ . Their thermal properties are similar to each other. The conductive behavior of PAN-based electrolytes with TE4CN was also investigated. Fig. 10 shows the temperature dependence of conductivity for the (PAN)20(LiClO<sub>4</sub>)<sub>10</sub> complexes with ED4CN, TESA, and TE4CN. Conductivity for the complexes with TESA and TE4CN was lower than that of the electrolyte with ED4CN. As described before,  $T_g$  of the complexes with TESA and TE4CN containing Li salt in higher concentration increased (see Table 3). TESA and TE4CN were not an effective plasticizer for the complex containing LiClO<sub>4</sub> in high concentration.

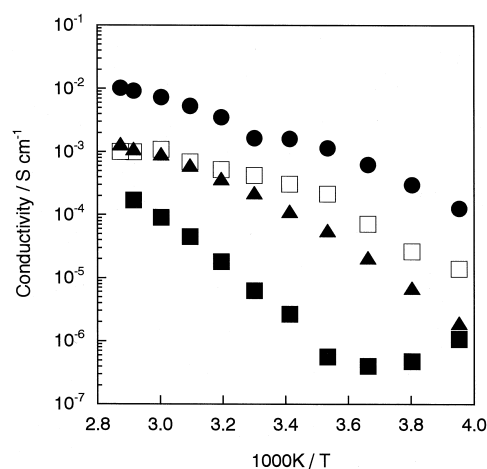


Fig. 10. Temperature dependence of conductivity for PAN-based electrolytes, (PAN)20(LiClO<sub>4</sub>)<sub>10</sub>(additive)<sub>1</sub>(PC)<sub>x</sub>. (□) none,  $x = 15.6$ , (●) ED4CN,  $x = 8.80$ , (▲) TESA,  $x = 7.45$ , (■) TE4CN,  $x = 2.00$ .

#### 4. Conclusions

Two cascade nitrile compounds (ED4CN and TE4CN) and tetraethylsulfamide (TESA) were used as a conductance enhancing additive for solid polymer electrolytes, PEO–LiClO<sub>4</sub> or PAN–LiClO<sub>4</sub> complex films.

Addition of ED4CN to a PEO–LiClO<sub>4</sub> complex film increased its  $T_g$  and ED4CN acted as a plasticizer for PEO matrix. Interaction between lithium (Li) ions and the nitrile groups in ED4CN was confirmed by FTIR measurements of the complex films. The peak assigned to the stretching vibration of nitrile shifted to the high-energy side. It suggests that Li ions in the electrolyte interact with the nitrile groups in ED4CN.

ED4CN and TESA were effective conductance enhancers in PAN–LiClO<sub>4</sub> electrolyte films. TE4CN was inactive. ED4CN and TESA acted as a plasticizer of PAN matrix with Li salt in low concentration and decreased the  $T_g$  of PAN–LiClO<sub>4</sub> matrix.

ED4CN was an effective conductance enhancer for PAN-based electrolytes with high Li salt concentration; however, TESA was inactive. ED4CN is not only a plasticizer but also a dissolution enhancer of Li salt in PAN matrix.

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