

Conductivity enhancement of PAN-based electrolytes containing cascade compounds with one amino and three or four nitrile groups

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Abstract

Conductivity enhancement of polyacrylonitrile (PAN)-based electrolytes was performed by addition of the cascade compounds with one amino and three or four nitrile groups to the matrices. The conductivity of the electrolytes with the cascade compounds was about one order higher than that of the additive-free one. DSC measurements of the electrolytes and FT-IR results from the model solution systems suggested that the additives acted as a dissolution enhancer for the lithium salt in the electrolytes. Electrochemical stability of the cascade compounds was estimated from cyclic voltammetry technique. The potential window of the compounds was over 4 V for the compounds with one amino and three nitrile groups and over 5 V for one with four nitrile groups. Polarization behavior of a lithium electrode was also investigated in the additive-free electrolyte and the electrolytes with the additives. The exchange current density of the lithium electrode in the electrolyte with the additives was about two orders higher than that in the additive-free one. Deposition and stripping processes of lithium in the electrolyte with the additive were also demonstrated with cyclic voltammetry measurements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Polyacrylonitrile; Conductivity; Cascade additive

1. Introduction

Portable power sources for cellular phone and portable computer are high-energy density secondary batteries, such as nickel hydrogen battery, lithium-ion battery. Lightening of the power sources is one of the most important points for improving portability of the electric equipment. Using polymer electrolyte as an electrolyte for the batteries is one of the most promising candidates for lightening them [1,2]. However, conductivity of polymer electrolytes, which have been prepared, is not sufficiently high for practical use of them.

Enhancing conductivity of polymer electrolytes has been performed by preparation of new polymer matrices with low glass transition temperature (T_g) and with polar groups for dissolution of an inorganic salt. Another approach for enhancing their conductivities is using gel electrolytes containing solvent, such as propylene carbonate (PC), ethylene carbonate (EC). Abraham and Alamgir reported that the conductivity of the polyacrylonitrile (PAN)-based electrolyte with PC and EC (21 mol% PAN, 38 mol% EC, 33 mol%

PC, 8 mol% LiClO₄) was $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C [3]. The conductivity is sufficiently high. However, the PAN-based electrolyte had 38 mol% of EC and 33 mol% of PC (total 63 mol%). The PC or other additives will exude from the gel electrolyte films with high composition of the low molecular weight compounds.

We have prepared several cascade compounds with terminal polar groups and added them to conventional polymer matrices, polyethylene oxide (PEO)- [4] and PAN-based [5,6] electrolytes. Addition of the cascade compounds to the solid polymer electrolytes has enhanced the conductivity of the electrolytes. Our electrolytes had the low molecular weight organic compounds in lower concentration. For example, the PAN-based electrolyte with the cascade additive compound (its conductivity was $1.06 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C) has 2.5 mol% of the additive and 34.0 mol% of PC (total 36.5 mol%) [6].

We report here on the enhancement of the conductivity of the PAN-based electrolytes by addition of the cascade nitrile compounds (see Fig. 1) to them. The enhancing mechanism by the compounds was also investigated. Furthermore, electrochemical stability of the nitrile compounds and polarization behavior of a lithium electrode in the electrolytes with them were also demonstrated.

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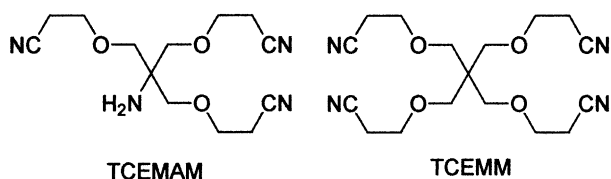


Fig. 1. Structures of cascade nitrile compounds.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) was purchased from Aldrich Co. Organic additives, tris[(cyanoethoxy)methyl]aminomethane (TCEMAM) and tetrakis[(cyanoethoxy)methyl]methane (TCEMM), were prepared by the procedure reported in the literature [7].

2.2. Preparation of PAN-based electrolytes

PAN-based electrolytes were prepared by casting the propylene carbonate (PC) solution containing PAN, lithium salt, and/or cascade nitrile compounds (TCEMAM or TCEMM). The solution was poured into an Al foil dish. The PC was removed by heating at 60–70 °C under vacuum. The amount of the remaining PC in the electrolyte film was estimated from the change of its weight. For example, composition of a complex film is presented as (PAN)20-(LiClO₄)10(TCEMAM)1(PC)4. This means that the film has 10 mol of lithium salt (LiClO₄), 1 mol of the additive (TCEMAM), and 4 mol of PC per 20 mol of acrylonitrile units in PAN. The weight ratio of the PC in the (PAN)20-(LiClO₄)10(TCEMAM)1(PC)4 complex was 14.5 wt.% and that in the (PAN)20(LiClO₄)10(TCEMM)1(PC)4 complex was 14.1 wt.%.

2.3. Measurements

A sample for conductivity measurement was sandwiched with two stainless plates (13 mm in diameter). Conductivity of the electrolyte was measured with an LCR meter (HIOKI 3531 Z Hi tester, 10–100 mV_{p-p}, 1–10 kHz) under various temperature conditions (from –20 to 70 °C).

DSC measurements of samples were performed with a differential scanning calorimeter (SSC 5220, Seiko) with heating rate at 10 K min⁻¹ and cooling rate at 5 K min⁻¹ in the temperature range from –100 to 100 °C. X-ray diffraction patterns were recorded with an X-ray diffraction meter (XD-D1, Shimadzu) with Cu K α line.

Electrochemical stability of the additives was confirmed by linear potential sweep method at 10 mV s⁻¹ scan rate. A conventional three-electrode cell with glassy carbon (\varnothing 5 mm) as a working electrode and Li foil as a reference and counter electrode was used for the measurements. The electrolyte in the cell was the PC solution containing

1 mol dm⁻³ LiClO₄ and 10 mmol dm⁻³ additive, TCEMAM or TCEMM.

Polarization behavior of a lithium electrode in the PAN-based electrolytes with and without the additives was demonstrated with a sandwich cell with the counter (Li foil, \varnothing 13 mm), reference (Li foil, 4 mm \times 2 mm, thickness 0.3 mm), and working (Li foil, 6 mm \times 5 mm, thickness 0.3 mm) electrodes [8]. Cyclic voltammetry was performed with a sandwich cell with similar configuration of the polarization measurement cell. A nickel plate was used as a working electrode and a silver wire was used as a quasi-reference electrode. The scan rate was 10 mV s⁻¹. All electrochemical measurements were recorded with a potentiogalvanostat (HA-301, Hokuto), a function generator (HB-104, Hokuto), and an X-Y recorder (XY-1100, Graphtec) at room temperature (20–25 °C).

3. Results and discussion

3.1. Conductivity for PAN-based electrolyte with additives, TCEMAM and TCEMM

Fig. 1 shows the structures of the cascade compounds with one amino and three (TCMAM) or four (TCEMM) nitrile groups. They were prepared by addition of acrylonitrile to tris(hydroxymethyl)aminomethane or pentaerythritol. Their structures and purity were checked by NMR and IR measurements. The PAN-based electrolyte films with TCEMAM or TCEMM were flexible and exudation of the PC or the additives from the films was not observed on the storage of them at room temperature for a few weeks.

Fig. 2 shows the temperature dependence of conductivity for the additive-free PAN-based electrolyte and the

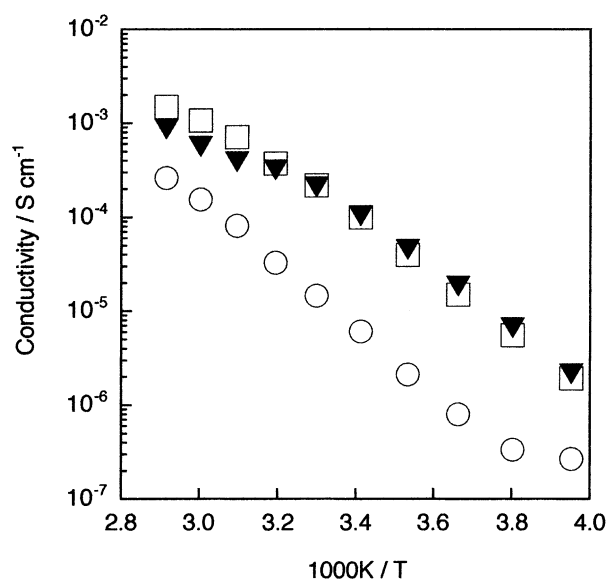


Fig. 2. Temperature dependence of conductivity for PAN-based electrolytes with or without additives, (PAN)20(LiClO₄)5(additive)_z(PC)4 complex film: (○) additive-free, $z = 0$; (▼) TCEMAM, $z = 5$; (□) TCEMM, $z = 5$.

electrolytes with TCEMAM or TCEMM. The conductivity of the (PAN)20(LiClO₄)5(additive)*z*(PC)4 film at 30 °C was $1.45 \times 10^{-5} \text{ S cm}^{-1}$ (additive-free, $z = 0$), $2.08 \times 10^{-4} \text{ S cm}^{-1}$ (TCEMAM, $z = 5$), and $2.17 \times 10^{-4} \text{ S cm}^{-1}$ (TCEMM, $z = 5$). Addition of the cascade nitrile compounds (TCEMAM or TCEMM) to PAN-based electrolytes enhanced the conductivity of them. The conductivity of the additive-free PAN-based electrolyte was about one order lower than that of the electrolytes with the cascade nitrile additives. The temperature dependence curves of the electrolytes were slightly convex. Park et al. reported that the PAN-based gel electrolyte systems with the large amount of solvents (PC and EC) showed an Arrhenius behavior [9]. When the interaction between lithium-ions and polar groups of polymer matrix is main one, it resulted in VTF-type temperature dependence of conductivity. Thus, it is suggested that the mobility of the ions in the PAN-based electrolytes with and without the additives partially depends on the mobility of the polymer chains.

Fig. 3 shows the additive concentration dependence of the conductivity at 30 and 60 °C for the PAN-base electrolytes. The conductivity at 30 and 60 °C of the PAN-based electrolytes was enhanced with increase in the concentration of the cascade nitrile compounds, TCEMAM or TCEMM.

Conductivity (σ) of a polymer electrolyte is presented as Eq. (1)

$$\sigma = \sum n_i \times e_i \times \mu_i \quad (1)$$

where n_i is the number of charge carrier of type i (cation and anion), e_i the charge of charge carrier of type i , and μ_i the mobility of charge carrier of type i [10]. Thus, enhancement of conductivity is performed by increasing in n_i and/or μ_i . Mobility of ions in a polymer electrolyte depend on the

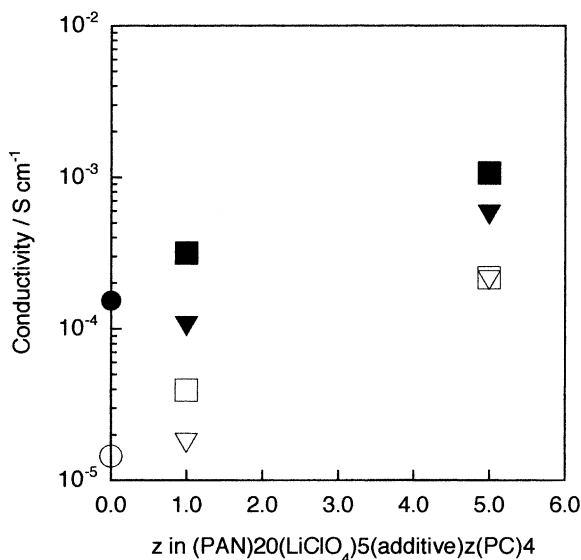


Fig. 3. Additive concentration dependence of conductivity for PAN-based electrolytes with or without additives, (PAN)20(LiClO₄)5(additives)*z*(PC)4 complex film: (○, ●) additive-free ($z = 0$); (▽, ▼) TCEMAM; (□, ■) TCEMM; open mark at 30 °C; filled mark at 60 °C.

Table 1

Glass transition temperature of PAN-based electrolytes

Sample	T_g (°C)
(PAN)20(LiClO ₄)1(PC)4	-88.2, -37.6
(PAN)20(LiClO ₄)5(PC)4	-88.7
(PAN)20(LiClO ₄)10(PC)4	-81.0
(PAN)20(LiClO ₄)1(TCEMAM)1(PC)4	-91.2
(PAN)20(LiClO ₄)1(TCEMAM)5(PC)4	-74.0
(PAN)20(LiClO ₄)1(TCEMM)1(PC)4	-80.5
(PAN)20(LiClO ₄)1(TCEMM)5(PC)4	-73.2
(PAN)20(LiClO ₄)5(TCEMAM)1(PC)4	-97.7
(PAN)20(LiClO ₄)5(TCEMAM)5(PC)4	-87.6
(PAN)20(LiClO ₄)5(TCEMM)1(PC)4	-93.9
(PAN)20(LiClO ₄)5(TCEMM)5(PC)4	-83.9
(PAN)20(LiClO ₄)10(TCEMAM)1(PC)4	-85.3
(PAN)20(LiClO ₄)10(TCEMAM)5(PC)4	-70.2
(PAN)20(LiClO ₄)10(TCEMM)1(PC)4	-85.1
(PAN)20(LiClO ₄)10(TCEMM)5(PC)4	-70.3

mobility of the polymer chains. Thus, lower glass transition temperature (T_g) polymer matrix is preferable for the polymer electrolyte matrix. T_g 's of the PAN-based electrolytes was listed in Table 1. The T_g of (PAN)20(LiClO₄)1(additive)-*z*(PC)4 film was -37.6 and 88.2 °C (additive-free, $z = 0$), -74.0 °C (TCEMAM, $z = 5$), and -73.2 °C (TCEMM, $z = 5$). The T_g of (PAN)20(LiClO₄)5(additive)*z*(PC)4 film was -88.7 °C (additive-free, $z = 0$), -87.6 °C (TCEMAM, $z = 5$), and -83.9 °C (TCEMM, $z = 5$). The T_g values of the additive-free matrices were almost equal to those of the matrices with the cascade compounds. This suggests that the PC in the matrices act as a plasticizer for the PAN-based electrolytes. It is not clear that the additives, TCEMAM and TCEMM are a plasticizer or not for the PAN-based matrix. Therefore, the conductivity enhancement of the electrolytes with the additives would be performed by other mechanisms. As presented in Eq. (1), conductivity of polymer electrolytes is enhanced by increasing in n_i in the matrix. Increase in n_i is performed by increase in concentration of the lithium salt and/or enhancing dissolution of the salt in the matrix.

We checked the interaction between the cascade nitrile compounds and the lithium salts by infrared spectroscopy of the model liquid system. The model solution consisted of PC, LiClO₄, and the cascade nitrile compound (TCEMAM or TCEMM). Interaction between lithium-ions and nitrile groups was observed by infrared spectroscopy. The CN stretching peak will be shifted to higher energy side due to an inductive effect between nitrogen atom in nitrile and lithium-ion [9]. Two overlapped peaks at 2250 and 2277 cm^{-1} were observed in the spectrum of the model solution with LiClO₄ and the additive. Appearance of the peak at 2277 cm^{-1} suggests that the nitrile groups in the additive are interactive to the lithium-ions in the solution. The R -values were estimated from Eq. (2):

$$R = \frac{A_{2277}}{A_{2277} + A_{2250}} \quad (2)$$

Table 2
The R -value in model solution

Model solution	R -value
(LiClO ₄) ₁ (TCEMAM) ₅ (PC) ₄	0.17
(LiClO ₄) ₅ (TCEMAM) ₅ (PC) ₄	0.38
(LiClO ₄) ₁₀ (TCEMAM) ₅ (PC) ₄	0.46
(LiClO ₄) ₁ (TCEMM) ₅ (PC) ₄	0.16
(LiClO ₄) ₅ (TCEMM) ₅ (PC) ₄	0.41
(LiClO ₄) ₁₀ (TCEMM) ₅ (PC) ₄	0.45

where A_{2277} and A_{2250} are absorbance of the two peaks at 2277 and 2250 cm^{-1} . The R -values are proportional to the number of the interactive lithium-ions with the nitrile groups of the additives. The estimated results are listed in Table 2. The R -value of (LiClO₄) _{y} (TCEMAM)₅(PC)₄ was 0.17 ($y = 1$), 0.38 ($y = 5$), and 0.46 ($y = 10$). It suggests that the lithium-ions in the PC solution can interact with the cascade nitrile compounds and the number of the interactive lithium-ions increases with the number of the cascade nitrile molecules in the PC solution. In the model solutions, the R -values of the solutions with TCEMAM were nearly equal to those with TCEMM. This suggests that interactivity of lithium-ions with the TCEMAM molecules in the solution is almost equal to that with TCEMM.

Fig. 4 shows the salt concentration dependence of the conductivity at 30 °C for the additive-free PAN-based electrolytes and the electrolytes with TCEMM or TCEMAM. The conductivity of the additive-free PAN-based electrolyte with high LiClO₄ concentration, (PAN)20(LiClO₄)₁₀(PC)₄, was equal to that of the (PAN)20(LiClO₄) _{y} (PC)₄ complex- ($y = 1$ or 5). This suggests that the LiClO₄ in the (PAN)-20(LiClO₄)₁₀(PC)₄ film did not dissolve completely and

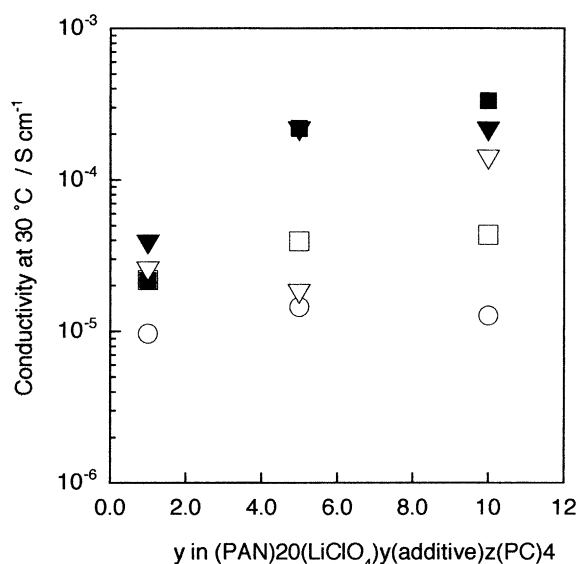


Fig. 4. Salt concentration dependence of conductivity at 30 °C for PAN-based electrolytes with and without additives, (PAN)20(LiClO₄) _{y} (additive) _{z} (PC)₄: (○) additive-free ($z = 0$); (▽, ▼) TCEMAM; (□, ■) TCEMM; open mark $z = 1$; filled mark $z = 5$.

the number of the charge carrier in the (PAN)20(LiClO₄)₁₀(PC)₄ film was low. Existence of undissolved LiClO₄ in the electrolyte film was confirmed with their X-ray diffraction patterns. Conductivity at 30 °C of the (PAN)20(LiClO₄) _{y} (additive) _{z} (PC)₄ film was $2.07 \times 10^{-4} \text{ S cm}^{-1}$ ($y = 10$, TCEMAM, $z = 5$) and $3.31 \times 10^{-4} \text{ S cm}^{-1}$ ($y = 10$, TCEMM, $z = 5$). Addition of the cascade nitrile compounds enhanced conductivity for the high-salt concentration films such as (PAN)20(LiClO₄) _{y} (additive) _{z} (PC)₄ ($y \geq 5$) film. This suggests that TCEMAM and TCEMM has high activity for dissolution of lithium salt in the electrolytes. The cascade nitrile compounds, TCEMAM and TCEMM acted as a dissolution enhancer in the PAN-based electrolytes with high-salt concentration.

3.2. Electrochemical stability of TCEMAM and TCEMM

Electrochemical stability is one of the most important properties for the electrolyte in the lithium or lithium-ion battery. We checked the electrochemical stability of the additives, TCEMAM or TCEMM, by cyclic voltammetry technique. Potential scanning from 0 to 5.0 V or 5.5 V versus Li/Li⁺ was performed by using the three-electrode cell with the PC solution containing the additives, TCEMAM or TCEMM (10 mmol dm^{-3}) and LiClO₄ (1 mol dm^{-3}). Working electrode was a glassy carbon electrode, reference and counter electrode were a lithium foil supported with a nickel mesh. The resulted voltammograms were shown in Fig. 5.

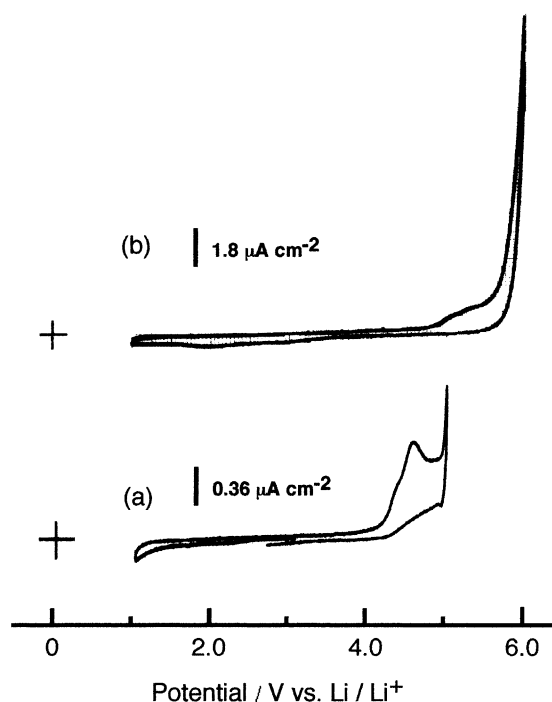


Fig. 5. Cyclic voltammograms for a glassy carbon electrode in PC solution containing 1 mol dm^{-3} LiClO₄ and 10 mmol dm^{-3} additives: (a) TCEMAM and (b) TCEMM.

No obvious peaks were observed in the region from 0 to 4.0 V in both electrolytes with the additive. In the PC solution with TCEMAM, the increase in current from 4.2 V and the peak at 4.5 V were observed. In the PC electrolyte with TCEMM, the increase in oxidative current was observed at 5.0 V. TCEMM is more stable than TCEMAM on electrochemical oxidation. TCEMAM has an amino group, which is more oxidative moiety than nitrile. Therefore, the potential window of TCEMM was about 5 V and that of TCEMAM was 4.1 V.

3.3. Polarization behavior of lithium electrode in the PAN-based electrolytes with and without additives

Plating and stripping processes of lithium on a lithium electrode in polymer electrolytes are important reactions in secondary lithium batteries. Polarization behavior of the lithium electrode in the polymer electrolytes indicates the reaction rates and reversibility of the reactions. The cell for the measurements was a sandwich cell with the working, counter, and reference (Li foil) electrodes [8]. Fig. 6 shows the polarization curves of a lithium electrode in the PAN-based electrolyte with and without the additives.

In the (PAN)20(LiClO₄)5(PC)4 complexes a large hysteresis in the polarization curves was observed in the cathodic scan. This indicates that the mass transport control (transport of lithium-ions from bulk to the lithium electrode surface) dominants in the polarization. The exchange current density was $4.57 \times 10^{-2} \mu\text{A cm}^{-2}$. The polarization behavior of lithium electrode in the PAN-based electrolytes with the additives, (PAN)20(LiClO₄)5(TCEMM)5(PC)4 and (PAN)20(LiClO₄)5(TCEMAM)5(PC)4 complex was also shown in Fig. 6. In the cathodic scan, a little hysteresis

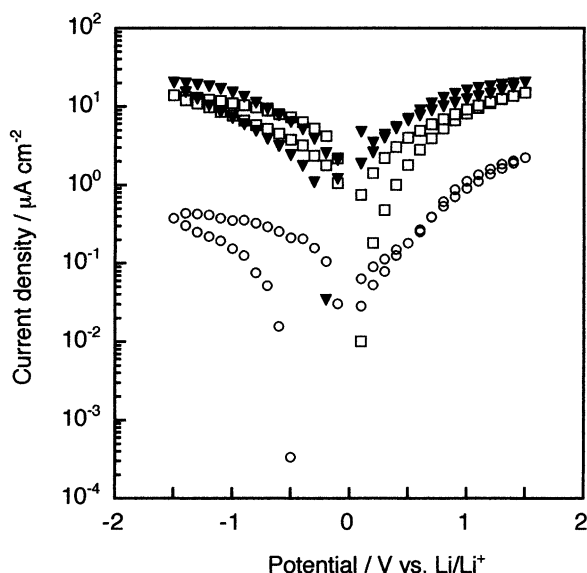


Fig. 6. Polarization curves of a lithium electrode in PAN-based electrolyte, (PAN)20(LiClO₄)5(additive)_z(PC)4 film: (○) additive-free, $z = 0$; (▼) TCEMAM, $z = 5$; (□) TCEMM, $z = 5$.

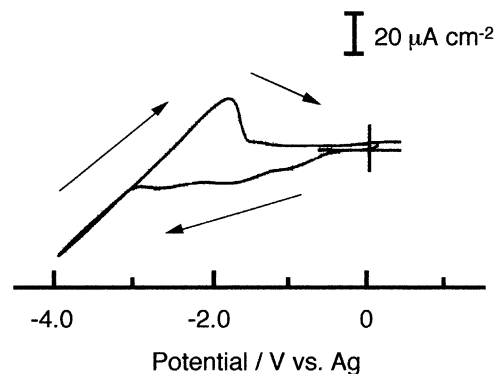


Fig. 7. Cyclic voltammogram for Ni electrode in (PAN)20(LiClO₄)5-(TCEMAM)5(PC)4 electrolyte; scan rate, 10 mV s^{-1} .

of the polarization curves was observed in the both electrolytes. The exchange current density was $1.91 \mu\text{A cm}^{-2}$ in (PAN)20(LiClO₄)5(TCEMM)5(PC)4 and $2.75 \mu\text{A cm}^{-2}$ in (PAN)20(LiClO₄)5(TCEMAM)5(PC)4 complex. The exchange current density of the lithium electrode in the PAN-based electrolytes with additives was about two orders higher than that in the additive-free electrolytes. The results suggest that the reaction rates of the deposition and stripping of the lithium on the electrode and the number of the movable ions in the electrolytes were increased by addition of TCEMAM and TCEMM to the PAN-based matrix. We think that dissolution enhancement of the lithium salt by the additive and increase in the number of the Li ions beside the electrode is the most dominant factor for the increase in current density.

3.4. Deposition and stripping lithium on Ni electrode in the PAN-based electrolytes with additives

Deposition and stripping of lithium on Ni electrode in the PAN-based electrolytes with additives were investigated by the cyclic voltammetry technique. The cell was a sandwich cell with the counter (Li foil), quasi-reference (Ag wire), and working (Ni plate) electrodes [8]. The scan rate was 10 mV s^{-1} . Fig. 7 shows the voltammogram in the (PAN)20(LiClO₄)5(TCEMAM)5(PC)4 electrolyte. Increase in cathodic current on the Ni working electrode and anodic current peak at -2.0 V were observed. The cathodic current is corresponding to the deposition of lithium on the Ni electrode and the anodic peak to the stripping of deposited lithium on the Ni plate. This would suggest that this electrolyte could be used as an electrolyte for secondary lithium batteries.

4. Conclusions

Conductivity of PAN-based electrolytes was enhanced by addition of the cascade compounds with one amino and three or four nitrile groups, TCEMAM and TCEMM.

The cascade compounds act as a dissolution enhancer of the lithium salts in the electrolyte matrix with high lithium salt concentration.

The cascade nitrile compounds, TCEMAM and TCEMM are electrochemically stable in the range from 0 to 4.0 V versus Li/Li⁺ and TCEMM is more stable than TCEMAM. Because TCEMAM has an amino group that is more easily oxidized than a nitrile group.

Addition of TCEMAM and TCEMM to the electrolytes increases the exchange current density of a lithium electrode in the PAN-based electrolytes. The results support that the reaction rates of the deposition and stripping of the lithium on the electrode and the number of the movable ions in the electrolytes were increased by the addition of TCEMAM and TCEMM.

Cyclic voltammetry for a Ni electrode in the PAN-based electrolytes with TCEMAM suggests that deposition and dissolution of lithium occur on the Ni electrode in the electrolyte matrix. This suggests that the PAN-based electrolytes with the cascade nitrile compounds will use as a polymer electrolyte for lithium secondary batteries.

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