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Conductivity Enhancement of Polyacrylonitrile-based Electrolytes by Addition of Cascade Ester Compound

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A new type conductivity enhancer for polyacrylonitrile (PAN)-based electrolytes was proposed. Conductivity of the additive-free PAN-based electrolytes was about one order of magnitude enhanced by addition of the cascade ester compound to them. It has branched backbone with four terminal ester bonds. The compound acts as a dissolution enhancer of lithium salt. The results of ^{7}Li NMR measurements of the PAN-based electrolytes suggest that the cascade compounds predominantly interact with the Li ions in the PAN matrix. Furthermore, polarization behavior of a Li electrode in the PAN-based electrolytes is also improved by addition of the cascade compound.

Key words: polymer electrolyte, lithium battery, conductivity, polyacrylonitrile, polarization behavior

1. INTRODUCTION

Power sources for portable electric equipment such as cellular phone, portable computer, and portable CD player, are high-energy density secondary batteries. Lightening of a battery and enhancing power density of it is one of the most important points for improving portability of the electric equipment. Using polymer electrolyte for the battery is one of the most promising candidates for lightening it [1, 2]. However, conductivity of polymer electrolytes is not sufficiently high for practical use of them. Enhancing conductivity of polymer electrolytes has been performed by preparation of new polymer matrixes with low glass transition temperature (T_g) and with polar groups for dissolution of an inorganic salt. Another approach for enhancing their conductivity is using gel electrolytes containing solvent, such as propylene carbonate (PC), ethylene carbonate (EC). Abraham *et al.* 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% $LiClO_4$) was 1.7×10^{-3} S cm^{-1} at 20°C [3]. Its conductivity is sufficiently high. However, the PAN-based electrolyte had 38 mol% of EC and 33 mol% of PC (total 63 mol%). PC or other additives will exude from the gel electrolyte films with large amounts of the low molecular weight compounds. We have prepared several cascade compounds with terminal polar groups and added them to conventional polymer matrixes, polyethylene oxide (PEO)-[4] and PAN-[5, 6] based electrolytes. Addition of the cascade compounds to the solid polymer electrolytes has enhanced conductivity of the electrolytes. Our electrolytes had such low molecular weight organic compounds in lower concentration. For example, the PAN-based electrolyte with the cascade additive compound (its conductivity was 1.06×10^{-3} 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 ester compound (CE4) (see Fig. 1) to them. Enhancing mechanism of CE4 was also investigated. Furthermore, electrochemical stability of the cascade compound and polarization behavior of a lithium (Li) electrode in the PAN-based electrolytes with it were also demonstrated.

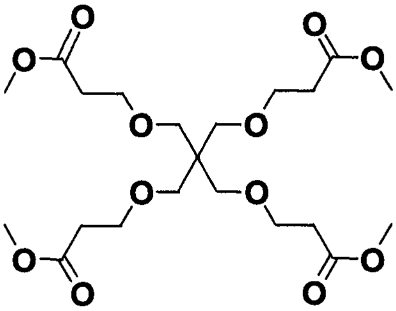

Fig. 1 Structure of CE4.

2. EXPERIMENTAL

Polyacrylonitrile (PAN) was purchased from Aldrich Co. Organic additive, CE4, was prepared by the procedure reported in the literature [7].

PAN-based electrolytes were prepared by casting the propylene carbonate (PC) solution containing PAN, lithium salt, and/or CE4. 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 $(PAN)20(LiClO_4)4(CE4)1(PC)4$. This means that the film has 4 mol of Li salt ($LiClO_4$), 1 mol of the additive (CE4), and 4 mol of PC per 20 mol of acrylonitrile units in PAN. The weight ratio of the PC in the $(PAN)20(LiClO_4)4(CE4)1(PC)4$ complex was 17.2 wt%. A sample for conductivity measurement was sandwiched with two stainless steel plates (13 mm in diameter). Conductivity of the electrolyte was measured with an LCR meter (HIOKI 3531 Z Hi tester, 10 - 100 mVp-p, 1 - 10 kHz) under various temperature conditions (from −20 to 70 ℃).

DSC measurements of samples were performed with a differential scanning calorimeter (DSC3100S, MAC Science) with heating and cooling rate at 10 K min^{-1} in the temperature range from -100 to 100 ℃. X-ray diffraction patterns were recorded with an X-ray diffraction meter (XD-D1, Shimadzu) with Cu-Kα 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 (5mmϕ) 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} $LiClO_4$ and 1 mmol dm^{-3} additive, CE4.

Polarization behavior of a Li electrode in the PAN-based electrolytes with and without the additives was demonstrated with a sandwich cell with the counter (Li foil, 13mmϕ), reference (Li foil, 4 mm × 2 mm, thickness 0.3 mm), and working (Li foil, 6 mm × 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 computer-controlled potentiogalvanostat (HZ-3000, Hokuto) at room temperature (20 – 25 ℃).

3. RESULTS AND DISCUSSION

3.1 Conductivity of PAN-based electrolytes with CE4

Fig. 2 shows temperature dependence of conductivity for additive-free PAN-based electrolytes and the electrolytes with CE4. Conductivity for the PAN-based electrolyte with CE4 was about one order of the magnitude higher than that of the additive-free PAN-based electrolyte. Addition of CE4 to PAN-based electrolyte enhanced conductivity of them. Conductivity of them is almost equal to that of the PAN-based electrolytes with the cascade nitrile compounds [5].

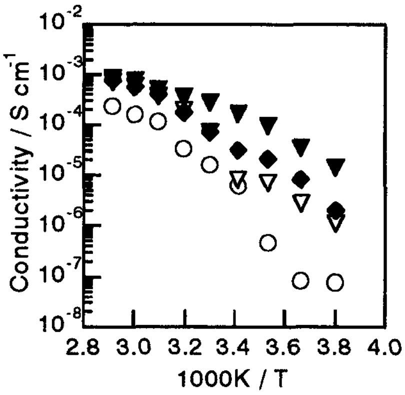

Fig. 2 Temperature dependence of conductivity for PAN-based electrolytes.
(○):(PAN)20($LiClO_4$)4(PC)4
(▽):(PAN)20($LiClO_4$)4(PC)6
(◆):(PAN)20($LiClO_4$)4(CE4)1(PC)4
(▼):(PAN)20($LiClO_4$)4(CE4)2(PC)4

Conductivity (σ) is presented as Eq. 1,

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

where n_i is the numbers of charge carrier of type i (cation and anion), e_i is the charge of charge carrier of type i, and μ_i is the mobility of charge carrier of type i [9]. Increasing in n_i and/or μ_i performs enhancement of conductivity. Increase in n_i is achieved by further addition of Li salt to polymer matrix. However, over addition of Li salt to the electrolyte matrix is not preferable to increase in n_i. Polarity of polymer matrix limits degree of dissolution of Li salt to Li ion and anion. The undissolved salt in the matrix prohibits the movement of charge carriers, Li ion and anion, in the matrix. Other approach for increasing conductivity of polymer electrolytes is enlargement of μ_i. μ_i is depended on the mobility of polymer chains in the matrix at actually used temperature. In PEO-based matrix the oxygen atoms in the PEO chains interact with the Li ions and make some complexes. Thus, the movement of the Li ions coupled with the movement of the polymer chains as a function of temperature [9]. Thus, enhancement of mobility of the polymer chains in the matrix is another proposal technique.

Fig. 3 shows X-ray diffraction patterns of PAN-based electrolytes, (PAN)20($LiClO_4$)4(additive)c(PC)4, additive-free (c=0) complex and the complexes with additive, (CE4, c=1 and CE4, c=2). Additive-free complex has some sharp diffraction peaks based on undissolved $LiClO_4$ in the matrix. The peaks disappeared with addition of CE4 to the PAN-based electrolyte. This suggests that the addition of CE4 into

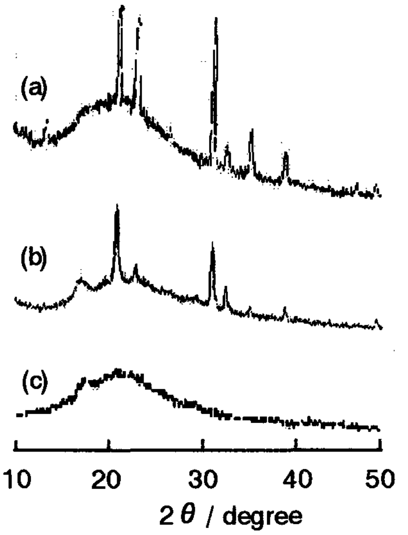

Fig. 3 X-ray diffraction patterns of PAN-based electrolytes.
(a) $(PAN)_{20}(LiClO_4)_4(PC)_6$
(b) $(PAN)_{20}(LiClO_4)_4(CE_4)_1(PC)_4$
(c) $(PAN)_{20}(LiClO_4)_4(CE_4)_2(PC)_4$

PAN matrix magnifies dissolution of Li salt in it and increase in the number of n_i in the matrix. Thus, conductivity of the PAN-based electrolyte is enhanced by addition of CE4.

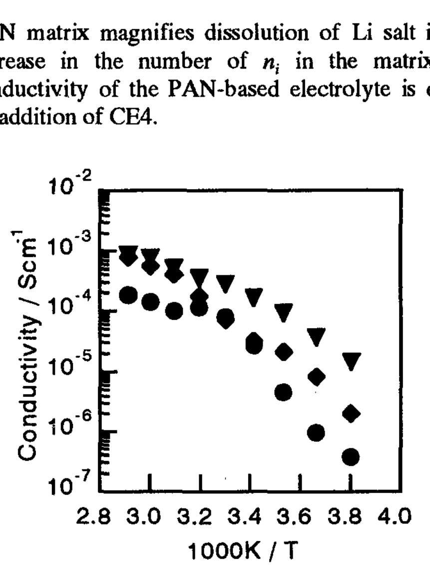

Fig. 4 Temperature dependence of conductivity for PAN-based electrolytes.
(◆):(PAN)20(LiClO$_4$)4(CE4)1(PC)4
(▼):(PAN)20(LiClO$_4$)4(CE4)2(PC)4
(●):(PAN)20(LiClO$_4$)4(CE4)3(PC)4

Fig. 4 shows temperature dependence of conductivity for the electrolytes with CE4. Increase in the amount of added CE4 to the matrix enhanced conductivity of the PAN-based electrolyte. However, over-addition (the complex with c=3) decreased conductivity of the electrolyte. Further addition of CE4 to the polymer matrix induced phase separation. Thus, lower conductivity for (PAN)20(LiClO$_4$)4(CE4)3(PC)4 complex may be related with its heterogeneous structure.

Glass transition temperature (T_g) of the electrolytes, (PAN)20(LiClO$_4$)4(CE4)c(PC)d was -97.7 (c=1, d=4), -78.4 (c=2, d=4), and -51.1 °C (c=3, d=4). It suggests that CE4 is not a plasticizer for PAN matrix and that the enhancement of conductivity for the PAN-based electrolyte with CE4 is not provided by simple increase in μ_i of charge carriers.

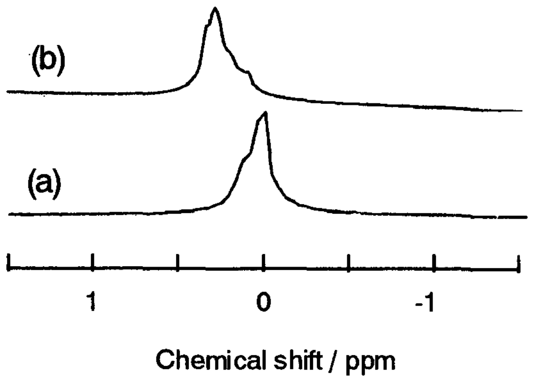

Fig. 5 ^{7}Li NMR spectra of PAN-based electrolytes at 50 °C.
(a) (PAN)20(LiClO$_4$)4(PC)6
(b) (PAN)20(LiClO$_4$)4(CE4)2(PC)4

Fig. 5 shows ^{7}Li NMR spectra of (PAN)20(LiClO$_4$)4(additive)c(PC)d complex, the additive-free electrolyte (c=0, d=6) and one with CE4 (c=2, d=4). Some overlapping peaks were observed in the spectrum of the electrolyte with CE4. This indicates that environment of Li ions in the matrix is heterogeneous and that the Li ions in the matrix will interact with the PAN matrix, the PC molecules, and the CE4. Therefore, CE4 in the PAN-based electrolyte acts as a dissolution enhancer of Li salt and not as a plasticizer.

3.2 Electrochemical stability of CE4

Electrochemical stability of CE4 was checked by linear potential sweep method with a glassy carbon electrode in the propylene carbonate solution containing CE4 and LiClO$_4$. In the potential sweep no obvious peak was observed from 1 V to 5 V *vs.* Li/Li$^+$. The stable potential window of CE4 was about 4 V. The value is sufficiently large for 3-volt class Li battery material.

3.3 Polarization behavior of a Li electrode in additive-free PAN-based electrolyte and the electrolyte with CE4

Plating and stripping reaction of Li in polymer electrolyte is a key process of Li secondary battery. Polarization behavior of the Li 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 Li electrode in the additive-free PAN-based electrolyte and the electrolyte with CE4. Cathodic polarization curves in additive-free PAN-based electrolyte shows hysteretic behavior. This indicates that plating process of Li is suppressed by the lack of Li ions near the Li electrode because of low transportation of Li ions, *i.e.*, low conductivity for the electrolyte. Exchange current density was also estimated from the polarization curves. The value is 6.68 × 10^{-2} μA cm^{-2} in the additive-free electrolyte and 2.31 μA cm^{-2} in the electrolyte with CE4. This indicates that plating and stripping rate on Li electrode in the electrolyte with CE4 is thirty-four times

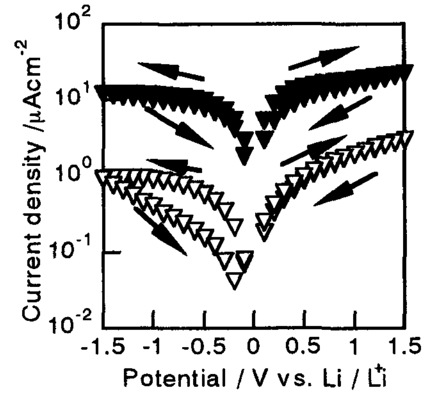

Fig. 6 Polarization curves of lithiumelectrodein PAN-based electrolytes.
(▽): (PAN)20(LiClO$_4$)4(PC)6
(▼): (PAN)20(LiClO$_4$)4(CE4)2(PC)4

higher than that in the additive-free electrolyte.

4. CONCLUSIONS

Conductivity of PAN-based electrolytes was about one order of the magnitude enhanced by addition of cascade ester compound, CE4 to them. CE4 acts as a dissolution enhancer of Li salt in the PAN matrix and not as a plasticizer. Stable potential window of CE4 was 4 V. Polarization behavior of Li electrode in the electrolyte with CE4 was improved by adding CE4 to the PAN-based electrolyte and the exchange current density of Li electrode in the electrolyte was thirty-four times higher than that in the additive-free PAN-based electrolyte.

REFERENCES

[1] J. Y.Song,Y. Y. Wang, C. C.Wan, J. Power Sources 77 (1999), 183.

[2] F. B. Dias, L. Plomp, and J. B. J. Veldhuis, J. Power Sources 88 (2000), 169.

[3] K. M. Abraham and M. Alamgir, J. Electrochem. Soc. 136 (1990), 1657.

[4] H. Tsutsumi, E. Tanaka, K. Onimura, and T. Oishi, Reactive & Functional Polymers 37 (1998), 289

[5] H. Tsutsumi, A. Matsuo, K. Onimura, and T. Oishi, Electrochemical and Solid-State Letters 1 (1998), 244.

[6] H. Tsutsumi, A. Matsuo, K. Takase, S. Doi, A. Hisanaga, K. Onimura, and T. Oishi, J. Power Sources 90 (2000), 33-38.

[7] G. R. Newkome and X. Lin, Macromolecules 24 (1991), 1443.

[8] H. Tsutsumi, M. Yamamoto, M. Morita, Y. Matsuda, T. Nakamura, and H. Asai, J. Power Sources 41 (1993) 291.

[9] D. F. Shriver and P. G. Bruce, Solid state electrochemistry, ed. P. G. Bruce, (1995), 95-118, Cambridge University Press, Cambridge.

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