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LITHIUM ION CONDUCTING POLYMERIC HYBRIDS

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Plastic solid electrolytes were prepared from inorganic lithium salts and polymer matrixes, and their ionic conductivity was discussed in relation to the ordering or the space distribution state of conduction column. When the hybrids took the micro-segregated structure with the continuous cylindrical conduction column embedded in supporting polymer matrixes, the ionic conductivity was enhanced. Thus formulated polymeric hybrids gave the ionic conductivity of 10^{-5} S/cm and excellent processibility.

INTRODUCTION

Not only the high ionic conductivity the solid electrolytes should have also the excellent processibility and adhesibility, as they could be utilized in electronic devices, such as electrochromic displays, sensors and so on. Polymeric hybrid ion conductors composed of inorganic salts and flexible polymers are the possible materialization of those requirements. Generally, inorganic salts with low dissociation energy, such as $LiBF_4$, $LiClO_4$ and $LiPF_6$ were used. Flexible and polar polymers were chosen in order to give processibility to the resulting hybrids and to accelerate the dissociation of salts.

The polymeric hybrid ion conductors can be classified into five categories as illustrated in Fig. 1 by their structural characteristics. Armand et al.[1] firstly demonstrated the binary hybrid of SYSTEM (I) composed of $LiClO_4$ and poly(ethylene oxide) (PEO). About 10^{-7} S/cm was reported[2] in this system, but the resulting hybrid was rather brittle. In order to improve the conductivity and processiblity, the authors have developed the ternary hybrids of SYSTEM (II) or (III) composed of Polymer/$LiClO_4$-Solvent or

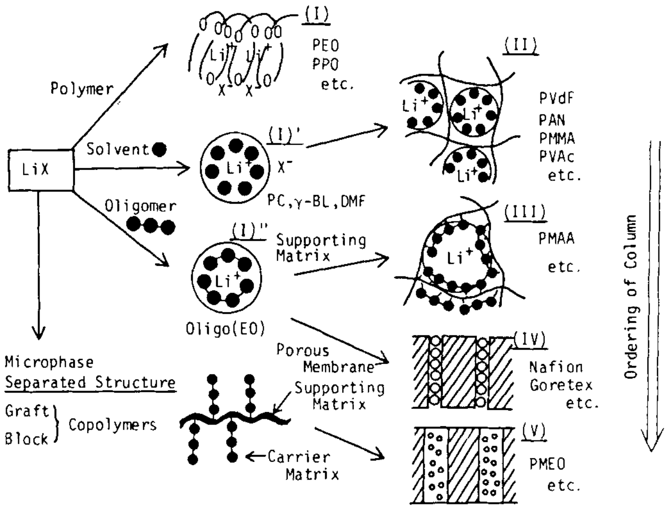


FIGURE 1 Schematic Representation of Various Li^+ Hybrid Conductors.

Polymer/$LiClO_4$-Oligomer. By the addition of solvent or oligomer, the ionic conductivity reached to 10^{-6} S/cm and the hybrids became flexible. The enhancement of ionic conductivity was brought about by the decrease of viscosity inside the conduction column, as the ionic conductivity σ_i can be expressed by the following equation[5],

$$\sigma_i = (K_o \cdot n_o)^{1/2} \cdot \frac{e^2}{6\pi r \eta} \cdot \exp(-W/2\varepsilon\kappa T) \qquad (1)$$

where the viscosity inside the conduction column is the predominant factor to determine the ionic conductivity. Here, K_o, n_o, r, η, W, ε and κ denote the intrinsic dissociation constant of LiX, LiX concentration, ion radius, viscosity, dissociation energy of LiX, dielectric constant of conduction column and Bolzman constant, respectively.

As SYSTEM (II) and (III) may have the homogeneous distribution of LiX-solvent or -oligomer clusters in the polymer network, the large amount of those additives is necessary in order to continuate the cluster domain. This usually yields too soft hybrids of which ionic conductivity slowly decays with time. Therefore in the present paper, the authors attempted to formulate distinct conduction column by using the micro-segregated structures of SYSTEM (IV) and (V).

In the present study, the ionic conductivity was measured with AC 1.0 V at 25°C and calculated from the complex impedance plots as reported previously[3,4], unless otherwise stated. The removal of water from the samples was confirmed by contacting the samples with lithium metal electrodes for 12 h.

SYSTEM (IV)

Nafion (du Pont), Flemion (Asahi Glass Co.) and related perfluoro-polyelectrolytes are known to form microsegregated structure with cylindrical ionic (polar) domain of which diameter is a few tens of A[6], as illustrated in Fig. 2. To the cylindrical pores, the $LiClO_4$-PEO_{400E} viscous solution was incorporated and the ionic conductivity of resulting hybrids was examined (Table 1). Only a few wt% incorporation of $LiClO_4$ and PEO_{400E} yielded the ionic conductivity more than 10^{-6} S/cm. When Goretex with the pore diameter of 8×10^3 A was used instead of Nafion, the salt viscous solution could not be incorporated into the pore by usual immersion or vacuum suction. By applying 3 V direct current for 12 h to the Goretex membrane of 0.1 mm thickness, the $LiClO_4$-PEO_{400E} solution could be forced to incorporate into the pore. However, such hybrid was very unstable and the contents were easily removed by pressure.

As the Nafion micropores are so small, the chemical substances therein always accept the influence of polar groups.

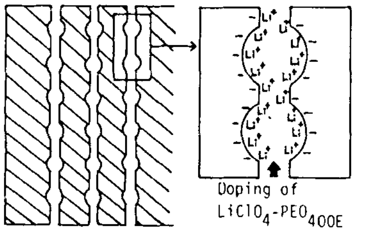
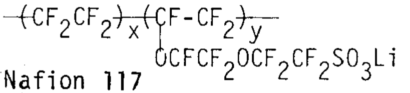
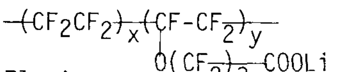


FIGURE 2 Mophology of Perfluoro-polyelectrolytes.


$$-\!\!(CF_2CF_2)_x\!\!-\!\!(\underset{\displaystyle |\atop OCFCF_2OCF_2CF_2SO_3Li}{C}F-CF_2)_y\!\!-$$

Nafion 117


$$-\!\!(CF_2CF_2)_x\!\!-\!\!(\underset{\displaystyle |\atop O(CF_2)_3COOLi}{C}F-CF_2)_y\!\!-$$

Flemion

$CH_3CO(OCH_2)_{7.8}OCOCH_3$ PEO400E

Table1 Lithium ionic conductivity of hybrid films*)

Composition (mol%)			Conductivity	Pore side
Nafion	PEO_{400E}	$LiClO_4$	$10^7 \cdot \sigma_i$ (S/cm)	(Å)
93.8	5.8	0.4	11.1	~10
98.1	1.6	0.3	6.7	
97.7	2.1	0.2	6.1	
99.2	0.7	0.1	1.7	
Goretex	Not incorporated		0	$8 \cdot 10^3$

*) PEO_{400E}-$LiClO_4$ soln immersed Nafion film

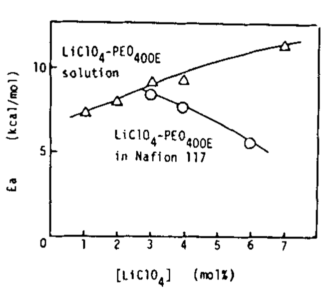


FIGURE 3 Effect of $[LiClO_4]$ on Ea

The activation energy for ionic conduction measured in homogeneous solutions such as $LiClO_4$-PEO_{400E} usually increases with increasing the salt content and therefore with the increment of viscosity. In contrast to this, the activation energy of $LiClO_4$-PEO_{400E} incorporated into the Nafion pores decreasing with increasing the salt content and it is smaller than that of homogeneous solution. This is probably brought about by the easier dissociation of salt assisted by the polar groups of Nafion, but still under consideration.

Nafion was solubilized in aqueous 2-propanol solution and mixed with $LiClO_4$ and PEO_{400E}, then it was cast to thin films. The ionic conductivity of solvent-cast system was summarized in Table 2. One can notice that the large amount of $LiClO_4$ and PEO_{400E} was necessary in order to realize the ionic conductivity of 10^{-6} S/cm similar to the incorporated systems. Probably, the microsegregated domain became vague and there was no warranty to form the continuous conduction column, when it was prepared by the solvent-casting. The

Table 2 Lithium ionic conductivity of hybrid films*)

Composition (mol%)			Conductivity
Nafion	PEO_{400E}	$LiClO_4$	$10^7 \cdot \sigma_i$ (S/cm)
81.0	18.1	0.9	0.3
72.4	26.3	1.8	1.8
68.0	30.5	15.0	15.0

*) Solubilized Nafion/PEO_{400E}/$LiClO_4$

$$\left.\begin{array}{l}\text{Solubilized Nafion}\\ PEO_{400E}\text{-}LiClO_4\end{array}\right\}\longrightarrow \text{Casting} \longrightarrow \text{Drying}$$

Table 3 Ionic conductivity of hybrid films

Composition (wt%)			Conductivity
Flemion	$LiClO_4$	PEO_{400E}	$10^7 \cdot \sigma_i$ (S/cm)
80.0	0.9	19.1	0.01
70.0	1.4	28.6	0.48
60.0	1.9	38.1	0.45
50.0	2.3	47.7	5.28
40.0	2.8	57.2	39.1
30.0	3.3	66.7	52.9

Table 4 Ionic conductivity of hybrid films

Composition (wt%)			Conductivity
Flemion	$LiClO_4$	PEO_{400E}	$10^6 \cdot \sigma_i$ (S/cm)
50.0	6.0	44.0	0.14
50.0	9.0	41.0	0.31
50.0	12.0	38.0	0.25
50.0	15.0	35.0	3.98
40.0	10.0	50.0	6.14
40.0	13.0	47.0	1.01
40.0	15.0	45.0	13.7
40.0	17.0	43.0	3.18
40.0	20.0	40.0	4.10
40.0	25.0	35.0	1.20
40.0	30.0	30.0	1.37

Table 5 Ionic conductivity of hybrid films

Composition (wt%)			Conductivity
Flemion	$LiPF_6$	PEO_{400E}	$10^6 \cdot \sigma_i$ (S/cm)
50.0	5.0	45.0	5.81
50.0	10.0	40.0	3.80
50.0	15.0	35.0	2.31
50.0	20.0	30.0	1.78
50.0	25.0	25.0	0.29
40.0	10.0	50.0	5.47
40.0	15.0	45.0	4.15
40.0	20.0	40.0	7.89
40.0	25.0	35.0	3.09
40.0	30.0	30.0	0.56

attempt to increase the content of $LiClO_4$ and PEO_{400E} was unsuccessful due to the macrophase separation.

As Flemion is known to have better elasticity and compatibility with other polymers than Nafion[7], we can expect to prepare the solvent-cast films with higher content of $LiClO_4$ and PEO_{400E}. As summarized in Table 3, the content of salt viscous solution in the hybrid film could be enriched to 60 wt%, but beyond which the macrophase separation occurred. Therefore, the ionic conductivity of those ternary hybrid systems was examined at [Flemion]=50 or 40 wt% to search for the optimum composition (Table 4 and 5). With increasing the LiX content, the ionic conductivity showed the maximum value. The similar behavior was observed in the homogeneous solution systems and the reason to show the maximum value was considered to be the summation of two effects; the increase of carrier concentration and increase of viscosity. For example, when the $LiClO_4$ content in PEO_{400E} was 10wt%, the viscosity increased to 5times comparing with pure PEO_{400E}. When the LiX content was more than 30 wt%, the micro-crystalline growth was observed in the X-ray diffraction pattern.

The effect of viscosity influenced more outstandingly on the activation energy for ionic conduction (Fig. 3). It increased expornentially with increasing the LiX content.

There seemed to be not so much difference between $LiClO_4$ and $LiPF_6$. However, when direct current of 3 V was applied to the hybrids, the ionic conductivity of $LiClO_4$ system decayed faster than that of $LiPF_6$ system with time (Fig. 4). Since those hybrid solid electrolytes are bi-ionic conductor,

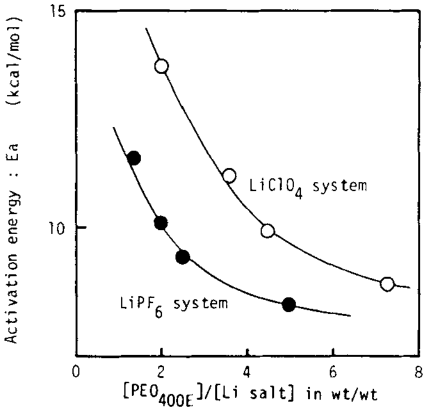


FIGURE 4 Effect of $[PEO_{400E}]/[LiX]$ Ratio on Ea of Flemion Hybrid films at [Flemion]=40wt%

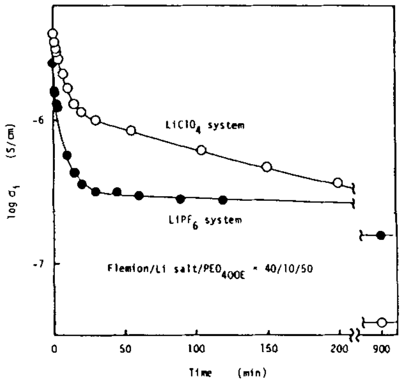


FIGURE 5 Time-decay of Ionic Ionic Conductivity with DC 3V in Flemion/LiX-PEO400E

the rapid decay at the initial stage of electrolysis may correspond to the localization of anions, which interferes the lithium ion diffusion, nearby the cathode. Therefore the slower decay and the high conductivity after reached to the constant value in the LiPF$_6$ system may be due to the larger anion radius.

As acid state Nafion or Flemion (-SO$_3$H or -COOH) dry films have the proton conductivity of about 10^{-7} - 10^{-9} S/cm, they are used as lithium salts in the present study. Those lithium sulfonate or carboxylate groups may contribute partially to the ionic conduction when they are combined with LiX-PEO$_{400E}$ either by the incorporation or solvent-casting, though the ionic conductivity of dry lithium salt films or of lithium salt films with PEO$_{400}$ (without LiX) was far less than 10^{-12} S/cm. Hence, the authors regard the -SO$_3$Li or -COOLi groups as polar function which accelerates the dissociation of LiX.

The Nafion or Flemion hybrid ion conductors obtained in this study are flexible but have reasonable mechanical strength. The microsegragated structures as illustrated in Fig. 2 or similar lamellae morphologies with 10^{-1} - 10^{0} μm polar domains can be distinguished in the case of Flemion hybrids (Flemion/LiClO$_4$/PEO$_{400E}$ = 50/9/41 - 40/30/30 by wt), from the observation by optical microscope after LiClO$_4$ and PEO$_{400E}$ are removed by dissolution into water.

SYSTEM (V)

In the ternary hybrid system of perfluoro-polyions/LiX-PEO$_{400E}$, the formation of microsegregated structure seemed to be the most important in order to realize high ionic conductivity. In such microsegregated structures, we can expect

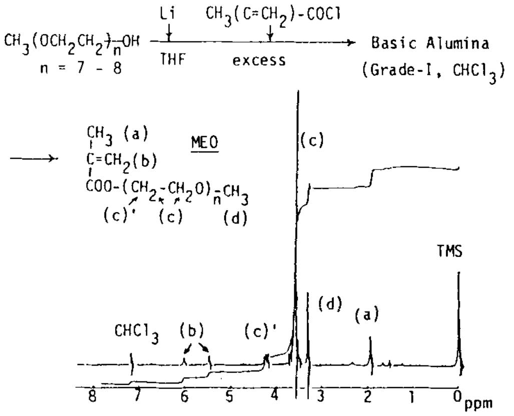


FIGURE 5 Synthesis and Characterization of Methacroyl-oligo-(oxyethylene) Macromer, MEO.

Basic alumina column was used for the removal of excess acid chloride and LiCl.

the processibility and mechanical strength to the polymer matrix and the formation of conduction column to PEO_{400E}.

It is well known that graft copolymers with rather long side chains of which chemical properties are much different from those of main-chain may form the microsegregated structures. The authors chose the methacryol oligo(oxyethylene) macromer abbreviated by MEO as the repeating units of graft copolymer, expecting that the oligo(oxyethylene) side chains and the methacrylate main-chain acted as the LiX-carrying matrix for the conduction column and the supporting matrix for keeping processibility. This macromer was easily prepared by reacting mono-endo(methoxy) oligo(ethylene oxide) lithium salt with an excess of methacroyl chloride at 0 - 5°C for 5 h. Macromers similar to MEO but with endo(hydroxy)group were not suitable because of the corrosion of lithium metal electrodes. MEO had quite high polymerizability and it polymerized spontaneously in neat even at room temperature under inert atmosphere. Hence the polymeric hybrid films were prepared by mixing LiX into the THF solution of MEO, followed by slow evaporation and polymerization in vacuo for 12 h at room temperature then for another 12 h at 60°C.

The ionic conductivity of thus obtained binary hybrids of poly(MEO) (PMEO) and LiX was summarized in Table 6. The ionic conductivity of more than 10^{-6} S/cm was accomplished without spoiling the processibility. The morphology of hybrids has been under study, but it seemed to have some segregated structure. Because the hybrid prepared by the spontaneous polymerization directly at 60°C, without giving enough period to form segregated structure, gave low conductivity.

Although this binary hybrids kept their excellent elasticity even at 50 wt% of LiX content, the mechanical strength

Table6 Ionic conductivity of hybrid films

Composition (wt%)		Conductivity
P(MEO)	$LiClO_4$	$10^6 \cdot \sigma_i$ (S/cm)
94.0	6.0	2.30
91.0	9.0	2.65
85.0	15.0	2.49
80.0	20.0	1.91
50.0	50.0	3.30
	$LiPF_6$	
94.0	6.0	1.38
91.0	9.0	3.16
85.0	15.0	2.75

Table7 Ionic conductivity of hybrid films

Composition (wt%)		Conductivity
P(MEO+BMA)*)	$LiClO_4$	$10^7 \cdot \sigma_i$ (S/cm)
97.0	6.0	0.09
91.0	9.0	0.09
88.0	12.0	0.10
85.0	15.0	1.37
80.0	20.0	2.00
75.0	25.0	5.38
	$LiPF_6$	
75.0	25.0	11.3

*) MEO:BMA=3:7 (mol ratio)

against scratching or impact force was not satisfactory. In order to improve the mechanical strength, copolymer of MEO with butyl methacrylate (BMA) was prepared by the conventional radical copolymerization in THF initiated by azobis(iso-butyronitrile) at 60°C, and the resulting copolymer P(MEO-BMA) was mixed with LiX in THF and cast to thin films. The ionic conductivity of copolymer hybrids was summarized in Table 7.

As the compatibility with LiX decreased by the incorporation of BMA units, the ionic conductivity of $LiClO_4$ hybrid was about 1 - 2 orders smaller than that of corresponding PMEO system. Beyond the $LiClO_4$ content of 20 wt%, the micro -crystalline growth was distinguished from the X-ray analysis. On the contrary, $LiPF_6$ formed better hybrid with the ionic conductivity of 10^{-6} S/cm. No X-ray diffraction pattern was observed. The difference between two salts was also influenced in the activation energy for ionic conduction; 25 ($LiClO_4$) and 16 kcal/mol ($LiPF_6$) at 20 wt%.

CONCLUSION

The ionic conductivity of hybrid films through SYSTEMS (I) to (V) is listed in Table 8. 10^{-6}-10^{-5}S/cm ionic conductivity was established in the present study. The importance

Table 8 Ionic Conductivity of Hybrid Films (25°C)

Composition(wt%)			Type	$\sigma_i \cdot 10^6$ (S/cm)	Processibility
PMEO	$LiClO_4$	Additive			
94.0	6.0	none	V	2.3	good
91.0	9.0	none	V	2.6	good
85.0	15.0	none	V	2.5	good
Nafion 93.8	0.4	PEO_{400E} 5.8	IV	1.1	-
Nafion 68.0	1.5	PEO_{400E} 30.5	IV'	1.5	good
Flemion 40.0	15.0	PEO_{400E} 45.0	IV'	15.0	good
PMAA 15.0	25.0	PEO_{400E} 60.0	III	0.24	fair
PVdF 74.1	6.2	PC 19.7	II	4.8	fair
PEO 75	25	none	I	0.1 *)	poor

*) Data taken from, J.E.Weston, B.C.H.Steel, Solid State Ionics, 2, 347 (1981)

of microsegregated structures composed of ion-carrying matrix domain and supporting matrix domain for keeping processibility was emphasized. Especially in the case of SYSTEM (V), excellent processibility and adhesibility as well as high ionic conductivity were realized. PMEO hybrids could be formulated into thin films by solvent-casting, melt flow-casting or molding. Their adhesibility was revealed to be comparable to the ordinary contact paste composed of poly(vinyl alcohol).

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