

# Ionic Conductivity of Hybrid Films Based on Polyacrylonitrile and Their Battery Application

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## Synopsis

The alternate current (AC) and direct current (DC) ionic conductivity of hybrid films composed of polyacrylonitrile (PAN), lithium perchlorate ( $\text{LiClO}_4$ ), and a plasticizer was studied. Three kinds of the plasticizer [ethylene carbonate (EC), propylene carbonate (PC), *N,N*-dimethylformamide (DMF)] were used. Suitability of these hybrid films for lithium battery was investigated. The AC conductivity, which represents bulk ionic conductivity, was dependent on the component and the composition of the hybrid films, ranging from  $10^{-4}$ – $10^{-8}$   $\text{S}\cdot\text{cm}^{-1}$ . The AC conductivity was mainly determined by the molar ratio of [plasticizer]/ $[\text{LiClO}_4]$  in the hybrid films and increased with the increase in this ratio. The effect of the plasticizer on the enhancement in the AC conductivity was in the following order: DMF > EC > PC. The hybrid films with both electrodes of lithium showed the stable DC conductivity of about 1/10 of the AC conductivity, except for the hybrid films containing DMF. The hybrid films were found to be effective as a lithium ionic conductor. The galvanic cell,  $\text{Li}/\text{sample}/\text{MnO}_2$ , at the discharge current density of  $90 \mu\text{A}/\text{cm}^2$  showed the stable electromotive force of about 3 V for 70 h.

## INTRODUCTION

Small electrical conductivity of usual polymers at low electric field is generally recognized to be ionic due to ionic impurities and/or absorbed moisture.<sup>1–3</sup> However, application of polymers to ionic conductors has up to now received little attention. On the contrary, there is considerable interest in ion conductive solids, which are called solid electrolytes, since they have high potential for application such as solid-state batteries and novel chemical sensors.<sup>4</sup> Especially, lithium ionic conductor is applicable to high energy batteries, and a new material with high conductivity and chemical stability is desired. Most solid electrolytes currently consist of crystalline inorganic materials. They are applied to electric devices as hard and brittle ceramics or compactions. Preparation of ionic conductors based on polymeric materials would offer a number of advantages over other solid electrolytes, since they can be easily processed into thin and flexible films.

In the previous paper,<sup>5</sup> we reported that the hybrid films composed of polyacrylonitrile (PAN), lithium perchlorate ( $\text{LiClO}_4$ ), and ethylene carbonate (EC) showed the high ionic conductivity of  $10^{-4}$ – $10^{-5}$   $\text{S}\cdot\text{cm}^{-1}$  at  $25^\circ\text{C}$ . In the hybrid films, the relation between the carrier mobility and the macroscopic viscosity as solid film did not obey the Walden's rule. The high conductivity was caused by that region in the film characterized by small microscopic viscosity which influences, more so than the large macroscopic viscosity, the speed of carrier migration.

In this study, the alternate current (AC) and direct current (DC) ionic con-

ductivity of the hybrid films composed of PAN,  $\text{LiClO}_4$ , and a plasticizer was studied. Three kinds of the plasticizer [EC, propylene carbonate (PC), *N,N*-dimethylformamide (DMF)] were used. Suitability of these hybrid films for lithium batteries was investigated.

## EXPERIMENTAL

### Preparation of Hybrid Films

PAN was obtained from Asahi Kasei Industry Co. Ltd. and purified by washing with pure hot water. Molecular weight of PAN from a viscosity measurement was found to be  $9.4 \times 10^4$ . Anhydrous  $\text{LiClO}_4$  was dried *in vacuo* at  $150^\circ\text{C}$  for 16 h and used. EC, PC, and DMF were purified by distillation under reduced pressure. The other materials were analytical grade commercial materials and used without further purification.

A preweighed amount of PAN and  $\text{LiClO}_4$  was dissolved in EC or PC at  $120^\circ\text{C}$  and in DMF at  $60^\circ\text{C}$ . The hybrid films were obtained by casting the solution onto a Teflon substrate and evaporating the plasticizer under reduced pressure. The amount of the plasticizer in the films was controlled by this procedure and evaluated by a Hitachi 163 gaschromatograph equipped with a Hitachi KP-1 thermal decomposition adaptor. A thickness of each film was 0.1–0.3 mm. The greatest care was taken to prevent the films from water sorption.

### Electrical Measurements

The samples for electrical measurements were cut from the hybrid films into disks of 1.0 cm in diameter, stacked between disk electrodes of 1.0 cm in diameter to form a cell, and applied to electrical measurements. The cell constitutions and the following electrical measurements were all made under dry argon atmosphere.

The AC measurements were carried out with a Yokogawa–Hewlett–Packard 4274A multifrequency LCR meter at an oscillation level of 1.0 V by using a cell,



in order to eliminate the contribution of electrode polarization from the cell impedance.<sup>6</sup> The AC conductivity was calculated from the cell impedance at 100 Hz, at which the phase angle of the cell impedance was nearly zero.<sup>6</sup> The contribution of ionic conductivity to the AC conductivity was investigated by using a polarization cell,<sup>7</sup>



where the graphite electrode is nonblocking to electrons and blocking to ions. The direct current through the cell at 1.0 V was detected with a Keithley 610C electrometer. The applied voltage was lower than the decomposition voltage of the hybrid films.

The DC ionic conductivity was measured by using a cell,



and the direct current through the cell at 3.0 V was measured with the elec-

TABLE I  
Electric Properties and Composition of Hybrid Films Containing EC

Sample code	Composition (mol %)			$\sigma$ (S-cm <sup>-1</sup> )	$E_a$ (kcal/mol)
	PAN <sup>a</sup>	LiClO <sub>4</sub>	EC		
E-1	50.7	12.7	36.6	2.14 × 10 <sup>-4</sup>	
E-2	85.3	4.5	10.2	2.11 × 10 <sup>-4</sup>	
E-3	56.5	14.1	29.4	3.21 × 10 <sup>-5</sup>	
E-4	76.5	8.5	14.9	7.81 × 10 <sup>-6</sup>	9.3
E-5	65.2	16.3	18.5	1.77 × 10 <sup>-6</sup>	10.7
E-6	52.3	22.4	25.3	1.31 × 10 <sup>-6</sup>	
E-7	69.3	17.3	13.4	8.68 × 10 <sup>-7</sup>	12.1
E-8	70.8	17.7	11.5	5.14 × 10 <sup>-7</sup>	14.1
E-9	70.5	17.6	11.9	3.23 × 10 <sup>-7</sup>	
E-10	73.0	18.3	8.7	9.38 × 10 <sup>-8</sup>	

<sup>a</sup> In unit mol %.

trometer. In order to confirm Faraday's law, the hybrid film was electrolyzed applying 3.0 V of direct current using an electrolytic cell,



The substance deposited onto the electrode was analyzed by a Shimazu AA-640-01 atomic absorption/flame emission spectrophotometer.

The discharge characteristic of a galvanic cell,



with the discharge resistance of 50 kΩ was investigated, by detecting the electromotive force of the cell with the electrometer.

### X-Ray Diffraction Patterns

The X-ray diffraction patterns were measured with a Rigaku-Denki D-3F X-ray diffractometer by CuKα line through a Ni filter.

## RESULTS AND DISCUSSION

### AC Conductive Behavior

Tables I–III show the sample code, the composition, the conductivity ( $\sigma$ ) at

TABLE II  
Electric Properties and Composition of Hybrid Films Containing PC

Sample code	Composition (mol %)			$\sigma$ (S-cm <sup>-1</sup> )	$E_a$ (kcal/mol)
	PAN <sup>a</sup>	LiClO <sub>4</sub>	PC		
P-1	31.8	8.0	60.2	7.58 × 10 <sup>-4</sup>	10.7
P-2	54.2	13.5	32.3	5.58 × 10 <sup>-5</sup>	
P-3	36.3	24.2	39.5	3.00 × 10 <sup>-7</sup>	14.0
P-4	61.8	15.5	22.7	2.60 × 10 <sup>-7</sup>	
P-5	64.6	16.2	19.2	8.85 × 10 <sup>-8</sup>	
P-6	41.5	27.7	30.8	7.96 × 10 <sup>-8</sup>	14.2

<sup>a</sup> In unit mol %.

TABLE III  
Electric Properties and Composition of Hybrid Films Containing DMF

Sample code	Composition (mol %)			$\sigma$ (S·cm <sup>-1</sup> )
	PAN <sup>a</sup>	LiClO <sub>4</sub>	DMF	
D-1	22.6	9.7	67.7	$6.13 \times 10^{-4}$
D-2	16.5	11.0	72.5	$4.22 \times 10^{-4}$
D-3	22.9	15.2	61.9	$2.84 \times 10^{-4}$
D-4	53.0	15.9	31.1	$2.40 \times 10^{-4}$
D-5	58.5	17.5	24.0	$2.49 \times 10^{-5}$
D-6	48.7	20.9	30.4	$1.06 \times 10^{-5}$
D-7	62.4	18.6	19.0	$3.97 \times 10^{-6}$
D-8	62.3	26.7	11.0	$9.52 \times 10^{-7}$
D-9	63.8	27.4	8.8	$7.94 \times 10^{-7}$

<sup>a</sup> In unit mol %.

25°C, and the activation energy for conduction ( $E_a$ ) for the hybrid films. Since the relation between reciprocal of absolute temperature ( $1/T$ ) and logarithm of the conductivity was linear over the temperature range of 15–85°C, the  $E_a$  values were calculated from

$$\sigma = \sigma_0 \exp(-E_a/RT), \quad (6)$$

where  $R$  is the gas constant. The  $E_a$  values for the hybrid films containing DMF could not be measured, because DMF came out from the films at higher temperatures and the conductivity lowered. The direct current through the polarization cell (2) decreased with time, and after 300 min reached the value which corresponded to the conductivity of about  $1/10^3$  of the AC conductivity. This result shows that the hybrid films are predominantly ionic conductors. Therefore, the AC conductivity appearing in Tables I–III represents the bulk ionic conductivity of the films without containing the electrode polarization and the resistance of the electrode reaction. Figure 1 shows the X-ray diffraction patterns of LiClO<sub>4</sub>, PAN, and three kinds of the hybrid film. The hybrid films

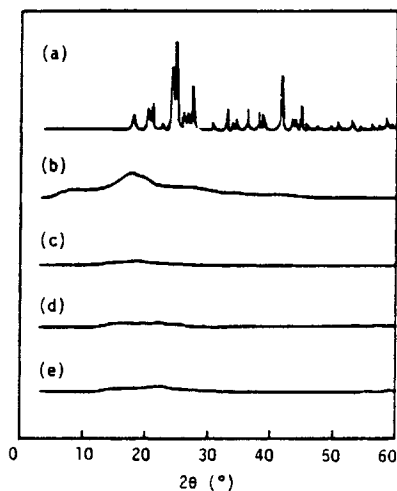


Fig. 1. X-ray diffraction patterns: (a) LiClO<sub>4</sub>; (b) PAN; (c) hybrid film containing EC; (d) hybrid film containing PC; (e) hybrid film containing DMF.

were found to be amorphous showing no diffraction peaks over the diffraction angle ( $2\theta$ ) of  $3\text{--}60^\circ$ , which denotes that  $\text{LiClO}_4$  dissolves in PAN and the plasticizer and that the hybrid films form a solid-electrolyte solution. PAN and the plasticizer which have high dielectric constants dissociate  $\text{LiClO}_4$  to generate carrier ions. The ionic conductivity is caused by the migration of the carrier ions.

The conductivity ranged from  $10^{-8}$  to  $10^{-4}$   $\text{S}\cdot\text{cm}^{-1}$ , being dependent on the composition of the hybrid films. The  $E_a$  values had a tendency that the films with the higher conductivity had the lower  $E_a$  values in the same series of the hybrid films, and ranged from 10 to 14 kcal/mol. The composition dependence of the conductivity should be noted. The conductivity was not dependent on the composition of PAN. The increase in the composition of  $\text{LiClO}_4$  did not coincide with the increase in the conductivity. Since  $\text{LiClO}_4$  dissolves in PAN and the plasticizer, the increase in  $\text{LiClO}_4$  composition enhances the number of carriers. Therefore, the above behaviors denote that the change in the carrier mobility changes the conductivity and that the mobility is not largely influenced by the composition of PAN. The increase in the conductivity corresponds best with the increase in the molar ratio of  $[\text{plasticizer}]/[\text{LiClO}_4]$  in the hybrid films, as shown in Figure 2. This is brought about by the fact that the mobility is dominated by the microscopic viscosity about the carrier ions, which is independent of the macroscopic viscosity as solid films, and the microscopic viscosity is determined by the ratio.<sup>5</sup>

The conductivity increased rapidly till the molar ratio of  $[\text{plasticizer}]/[\text{LiClO}_4]$  became about 2, and afterwards hardly changed and showed about  $10^{-4}$   $\text{S}\cdot\text{cm}^{-1}$ . As the ratio was higher than 2, the conductivity was not largely influenced by the kind of the plasticizer. On the contrary, when the ratio was lower than 2, the conductivity was dependent on the kind of the plasticizer. The effect of the plasticizer on the enhancement in the conductivity at a constant  $[\text{plasticizer}]/[\text{LiClO}_4]$  was in the following order:  $\text{DMF} > \text{EC} > \text{PC}$ . The saturated concentration of  $\text{LiClO}_4$  to the plasticizer was found to be  $[\text{plasticizer}]/[\text{LiClO}_4] \sim$

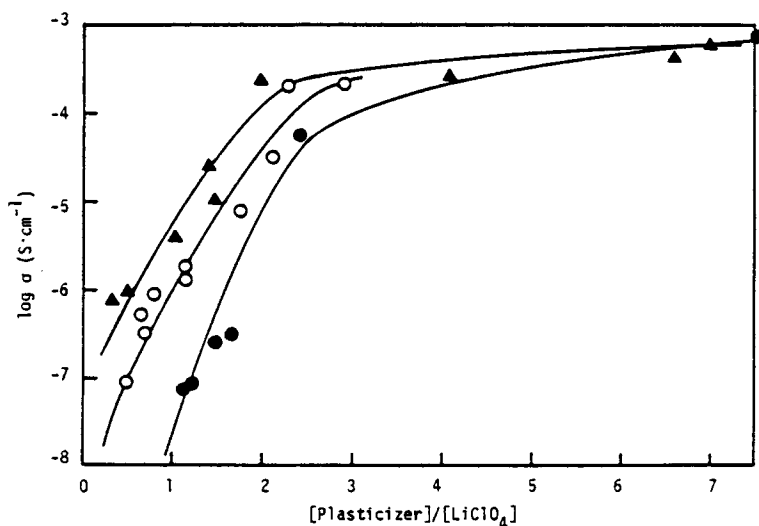


Fig. 2. Relation between  $[\text{plasticizer}]/[\text{LiClO}_4]$  and AC conductivity ( $\sigma$ ): (○) hybrid film containing EC; (●) hybrid film containing PC; (▲) hybrid film containing DMF.

2 at about room temperature. Therefore, in this region,  $\text{LiClO}_4$  cannot dissolve in the plasticizer contained, and PAN contributes to the dissolution of  $\text{LiClO}_4$  into the hybrid films. The plasticizing effect of the plasticizer on PAN is considered in the following order:  $\text{DMF} > \text{EC} > \text{PC}$ . The higher the plasticizing effect, the lower the microscopic viscosity for carrier migration. So the difference of the conductivity between three kinds of the hybrid films at a constant  $[\text{plasticizer}]/[\text{LiClO}_4]$  may be observed.

### DC Conductive Behavior

It is important to investigate the DC conductive behavior of the hybrid films with reversible electrodes of lithium, for applying the films to the electrolyte of lithium batteries. Figure 3 shows the time dependence of the DC conductivity for the cell (3) at 3.0 V. In all kinds of the hybrid films, initial decay of the DC conductivity was large. The reverse electromotive force of 0.3–0.5 V was observed, when the polarized cell was shorted. The polarization of the films in addition to the resistance of the electrode reaction leads to this decay. After 100 min, the stable DC conductivity of about 1/10 of the AC conductivity was observed in the hybrid films except for the films containing DMF. This indicates that the electrode reaction (oxidation and reduction of lithium) and the carrier migration in the films occurs constantly in the cell. For the cell of the hybrid films containing DMF, the DC conductivity continued to decrease gradually with time. With opening the cell, the surface of the electrode lithium in contact with the films turned black. It was reported<sup>8</sup> that the decomposition voltage of DMF in DMF solution of  $\text{LiClO}_4$  was 1.75 V. Since the decomposition voltage is lower than the applied voltage of 3.0 V, the decomposition compounds corrode lithium to form an insulative layer, which results in the continuous decrease in the DC conductivity. Consequently, the hybrid films containing DMF are not suitable for the electrolyte of the battery.

When the electrolysis of the cell (4) was continued, silver gray substance became to deposit onto the surface of the Pt cathode. The deposited substance showed the absorption at 670.8 nm in the atomic absorption analysis. This in-

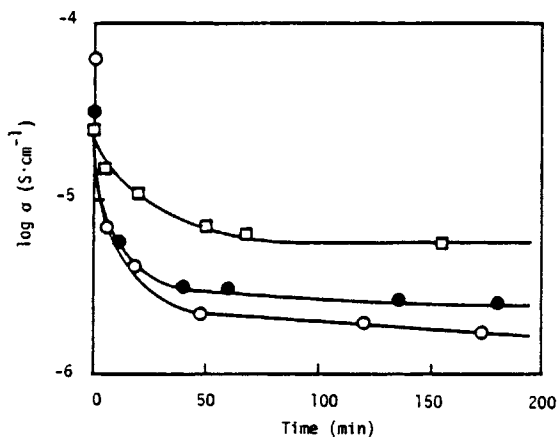


Fig. 3. Time dependence of DC conductivity ( $\sigma$ ) for the cell,  $\text{Li}/\text{sample}/\text{Li}$ , at 3.0 V: ( $\square$ ) E-1; ( $\bullet$ ) P-2; ( $\circ$ ) D-4.

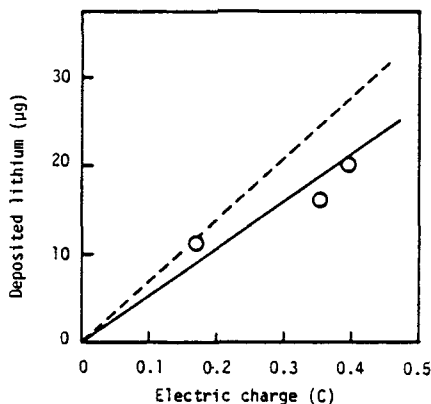


Fig. 4. Relation between electric charge through the cell,  $\oplus$  Li/sample/Pt  $\ominus$ , and deposited lithium onto Pt surface: (O) E-2; (---) theoretical value.

dicates that the substance is lithium. Figure 4 shows the relation between the electric charge through the cell and the amount of the deposited lithium. The broken line represents the theoretical value in which the current efficiency of the electrolysis is assumed to be 100%, i.e., all the electric charge is assumed to be carried by lithium ion. The amount of the deposited lithium increased linearly with the increase in the electric charge. The current efficiency of the cell (4) is found to be 70%, comparing the experimental value with the theoretical value. This result shows that the hybrid films can be utilized for a lithium ionic conductor.

### Battery Application

Figure 5 shows the discharge characteristic of the galvanic cell (5). The initial electromotive force was found to be 3.25 V. For the cell using the hybrid film E-6 with the AC conductivity of about  $10^{-6}$  S·cm<sup>-1</sup>, the electromotive force decreased with time and reached about 1 V at the discharge time of 70 h. If the electromotive force is assumed to be 3.0 V, the discharge current density is estimated to be about 90  $\mu$ A/cm<sup>2</sup>. Since the internal resistance of the hybrid film

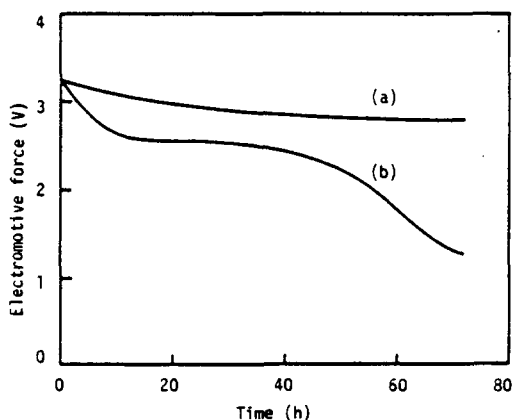


Fig. 5. Discharge characteristic of the galvanic cell, Li/sample/MnO<sub>2</sub>, with discharge resistor of 50 k $\Omega$ : (a) E-3; (b) E-6.

E-6 is high, the IR drop of the cell makes the electromotive force lowered. For the cell using the hybrid film E-3 with the AC conductivity of about  $10^{-5}$  S-cm $^{-1}$ , the stable electromotive force of about 3 V was observed over the time range of 70 h.

In conclusion, these hybrid films offer a polymeric lithium ionic conductor, which is easily processed into thin and flexible films. These films are expected to be used as an electrolyte of lithium batteries.

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