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A Demonstration of Solid-State Cell Based on Poly(Vinylidene Fluoride) System Containing Lithium Perchlorate

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Summary

Flexible film was prepared from poly(vinylidene fluoride) with lithium perchlorate dispersed at molecular level. This film showed lithium ionic conductivity of 10^{-6} S/cm. A solid-state cell was demonstrated by this film with metallic lithium and Manganese dioxide as electrodes. The cell was stable over a week and it showed electromotive force of 3.0 V and current of 50 μA when 50 kΩ of resistance was connected.

Introduction

In recent years, solid electrolytes collected keen interests due to their wide applications for solid-state cells, electrolytic devices, etc. Such solid electrolytes were prepared from inorganic materials such as $RbAg_4I_5$ (HAGENMULLAR and GOOL, 1978), Na-β-Alumina (KUMMER, 1972), Li_3N (ALPEN, 1979), NASICON (GOODENOUGH, et al, 1976), etc. Their high ionic cunductivity was mainly based on the specific crystal structure. Polymeric solid electrolytes are expected as flexible conductive material, because inorganic derivatives are unsuitable for processing. WRIGHT (1975) firstly reported the electrical conductivity in ionic complexes of poly(ethylene oxide) having several kind of alkali metal ions. ARCHER et al. (1980,1981) also studied the lithium ion conduction in poly(ethylene oxide) matrix. These polymeric films showed conductivity of about 10^{-7} S/cm at room temperature. We have already reported the ionic conductivity of several polymer-inorganic salt complexes and high conductivity was observed by using complexes of poly(vinylidene fluoride) and lithium perchlorate (TSUNEMI, et al, 1981, 1982; WATANABE, et al, 1981). This complex showed about 10^{-6} S/cm in lithium ion conductivity at room temperature (WATANABE, et al, 1981). Poly(vinylidene fluoride)-lithium perchlorate complex could be casted from organic additives such as propylene carbonate, ethylene carbonate or γ-butyrolactone. This enable to prepare solid state cell by applying this film as electrolyte.

Experimental

Materials. Poly(vinylidene fluoride)(PVdF) was obtained from Kureha Kagaku Industry Co., Ltd. (m.w.=7.7 x 10^4) and used without further purification. Lithium perchlorate ($LiClO_4$) anhydride was purchased from Wako Pure Chem. Co., Ltd. This was dried in vacuo at 150 °C for 24 h before use. Metallic lithium for electrode was purchased from Alfa Products. Propylene carbonate (PC) was distilled under reduced pressure before use.

Preparation of polymeric films. PC solutions of PVdF and $LiClO_4$ were

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prepared at 120 °C. The concentration of PVdF solution was 10 wt% and that of $LiClO_4$ solution was 25 wt%. Two solutions were mixed with each other at 120 °C. Then the mixed PC solution was poured on the teflon^R seat. PVdF film containing $LiClO_4$ was obtained by heating at 130 °C under reduced pressure for 24 h. PC content in the film was controlled by heating time. Flexible films with thickness of 0.1-0.3 mm were obtained after casting.

Electrical measurement. Metallic lithium was used as reversible electrode for electrical measurements. Alternating current measurements were carried out by a Yokogawa-Hewlett-Packerd 4274A multi frequency LCR meter at the frequency range from 10^2 to 10^5 Hz. Conductivity was calculated from complex impedance plots of measured impedance and phase angle. Direct current measurements were carried out by a Keithley 610C electrometer. Cell constitutions and all the measurements were taken under dry argon atmosphere.

Temperature dependence on conductivity was measured by using thermo-controlled apparatus under argon atmosphere.

Results and discussion

$LiClO_4$ could be dispersed in PVdF matrix at molecular level by mixing them. Then, flexible and transparent or semitransparent polymeric solid electrolyte was prepared by casting method. A typical complex plane impedance plot obtained in this study was shown in Fig. 1. The conductivity of PVdF-$LiClO_4$ films was in the range from 10^{-5} to 10^{-7} S/cm. Their conductivity deeply depended on the amount of containing $LiClO_4$ and PC. Increase of the amount of incorporated $LiClO_4$ contributed to the conductivity due to the increase of Li^+ as carrier. We have already provided that the carrier in polymer matrix was the dissociated Li^+ ions by Tubandt's method and atomic absorption spectrometry (WATANABE, et al, 1981). The contribution of containing amount of PC was also apparent. This effect will be discussed in a latter part. PVdF films having $LiClO_4$ about 20 mol% were mainly used, because this was the upper limit for the preparation of films without impairing their flexibility. The film turned opaque and brittle by adding an excess of $LiClO_4$ in it. Such film had nothing to advantage of using polymeric system.

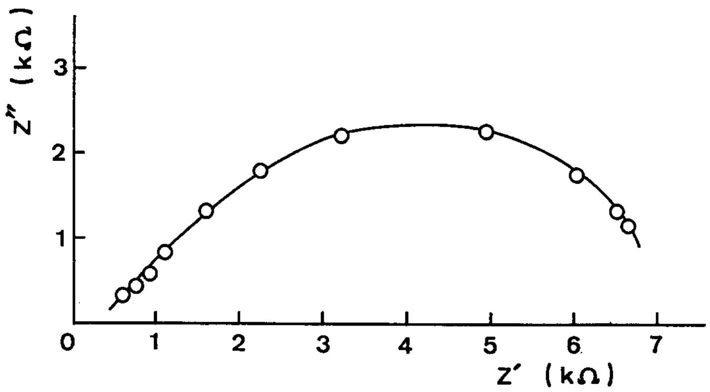

Fig.1 Typical complex plane impedance spectrum of PVdF-$LiClO_4$ film in the frequency range from 10^2 to 10^5 (Hz).

PVdF/$LiClO_4$/PC : 76.6/4.1/19.3 (mol%)

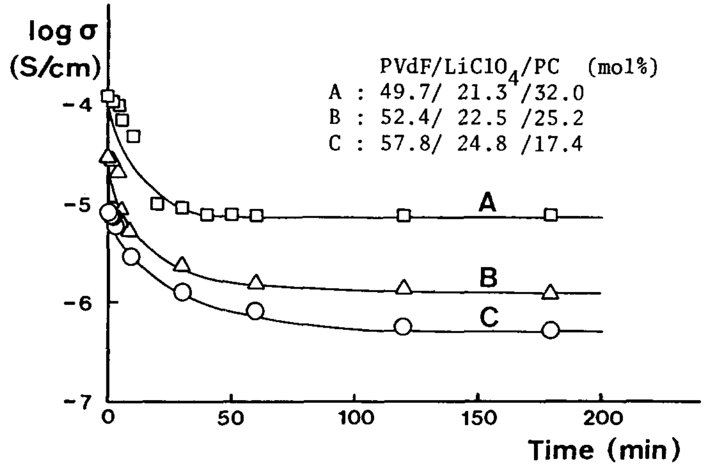

Fig. 2 Time dependence on conductivity of PVdF-$LiClO_4$ films at 3.0 V.

The conductivity was measured by DC method. This film showed initial conductivity of about 10^{-4} S/cm. However, it was decreased with time as shown in Fig. 2. It reached constant (about 1/10 of the initial one) after 60 min. The decrease of conductivity was considered to be due to the formation of concentration gradient of ions in the films by the migration of not only Li^+ cation but also ClO_4^- anion. When this migration reached equilibrium, the films also indicated the constant conductivity.

Time dependence on conductivity was measured with several films containing different amount of PC content. Conductivity of the films containing larger amount of PC reached constant more rapidly. This means that in PC rich film, ions can migrate relatively freely. It was also confirmed that $LiClO_4$ was partially crystallized in the film with 20 mol% LiClO from the X-ray diffraction analysis (TSUNEMI, et al, 1982). Crystal $LiClO_4$ did not dissociate, so that it could not contribute to the conduction. Namely, not all of $LiClO_4$ contained in the film were revealed

TABLE 1

Activation energy of ionic conduction for PVdF-$LiClO_4$-PC films

Sample No.	Composition (mol%)			Ea* (kcal/mol)
	PVdF	$LiClO_4$	PC	
1	65.2	7.2	27.6	9.7
2	76.6	4.1	19.3	11.9
3	80.3	4.3	15.4	12.4
4	72.0	8.0	20.0	13.0
5	49.7	21.3	29.0	12.6
6	52.4	22.5	25.1	14.3
7	57.8	24.8	17.4	17.3

* determined from 0 °C to 60 °C or 100 °C

to participate conduction. It was considered that added PC worked as dissociator of the salt in crystalline state, so number of carrier was increased by this additives such as PC. PC is much less viscous than polymer matrix, carrier came to migrate more freely. Thus, increases of carrier number and mobility deeply depended on the amount of PC.

Activation energy of lithium ionic conduction was calculated from temperature dependence of the conductivity. In the range from 0 to 60 or 100 °C, the relation between 1/T and log σ was seen as good linear line. No phase transition was observed in these films. Activation energy (Ea) of the conduction was summarized in Table 1. Ea of lithium ion conduction in PC solution (1.0 mol/l) was also measured as control. Ea decreased with the increase of PC content. And one can not excel PC solution system in Ea value. This result supported our hypothesis that PC played a part as dissociator and it also contributed to form the molecular path of the ionic conduction.

Solid-state cell was demonstrated by applying film of PVdF/$LiClO_4$/PC complex as electrolyte with metallic lithium and MnO_2 as active material of negative and positive electrodes, respectively. Since the film was

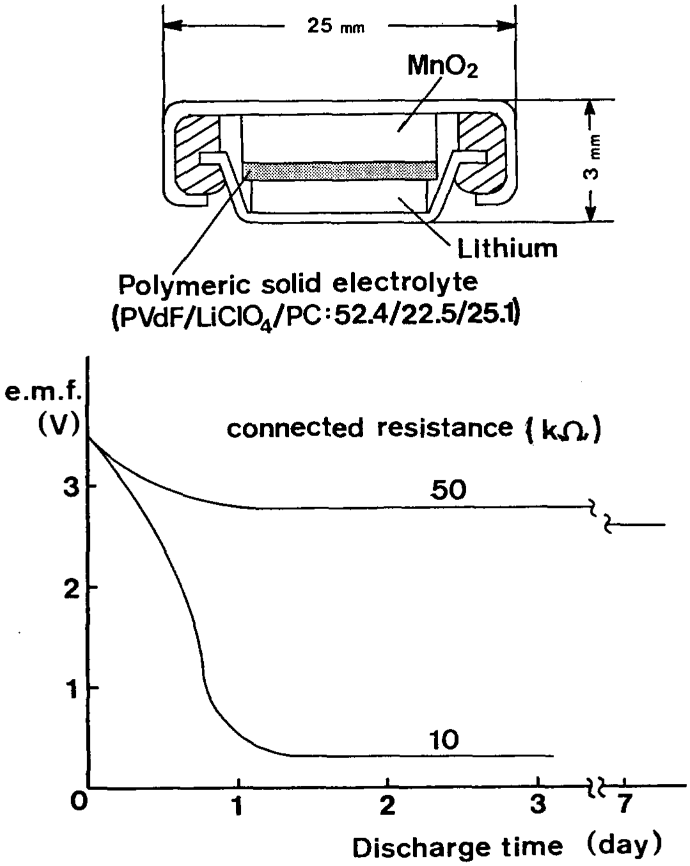

Fig. 3 Discharge curves of solid-state cell composed of Li/PVdF film/MnO_2 system.

lithium-ionic conductor, metallic lithium could supply the lithium ions as carriers. Manganese dioxide was selected because this could transfer electrons to the carrier ions easily. A button type cell of 3 mm thickness and 25 mm diameter (schematic diagram of this cell construction was shown in Fig. 3, upper) was demonstrated. Theoretical electromotive force (e.m.f.) by cell constitution of Li/Electrolyte/MnO_2 was about 3.0 V. And 3.0 V of e.m.f. was obtained stably from our cell. When the discharge resistor of 50 kΩ was connected, about 3.0 V of e.m.f. was recorded stably over a week without decay. However, when the 10 kΩ of resistor was connected, e.m.f. decreased rapidly and it dropped less than 1.0 V within a day. The cells were cleaved after discharge. The electrolyte in the cell connected 50 kΩ resistor remained unaltered.

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